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(54) **LUBRICATING COMPOSITIONS CONTAINING SULPHONATES AND PHENATES**

SULFONATE UND PHENATE ENTHALTENDE SCHMIERMITTELZUSAMMENSETZUNGEN

COMPOSITIONS LUBRIFIANTES CONTENANT DES SULFONATES ET DES PHENATES

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EP 1 680 491 B1

Description

FIELD OF INTENTION

[0001] The present invention relates to a method of lubricating a two-stroke marine diesel engine comprising supplying thereto a detergent composition containing (a) at least 3 weight percent of an overbased sulphonate detergent with a metal ratio of 12.5:1 to 40: 1; (b) at least 1.5 weight percent of a sulphur containing phenate detergent with a metal ratio of not more than 3; and (c) an oil of lubricating viscosity, wherein the sulphur containing phenate contains oligomers of hydrocarbyl phenol with at least 50 wt % of said oligomers in the form of the tetramer or higher oligomers. The detergent compositions are used in marine diesel cylinder lubricants.

BACKGROUND OF THE INVENTION

[0002] It is known to add various additives to an oil of lubricating viscosity for diesel or gasoline engines to reduce wear and improve cleanliness. In diesel engines an oil of lubricating viscosity is used particularly to reduce wear of cylinder liners and piston rings. Often engine operating temperatures and pressures are sufficient to breakdown the film of the oil of lubricating viscosity on the internal walls of the cylinder. As a consequence of this the cylinder excessively wearing and decreased engine cleanliness due to deposits.

[0003] US Patent 6,277,794, Dunn, discloses the use of a marine diesel engine lubricant composition containing (a) an overbased metal detergent having a TBN of at least 300 and/or (b) a metal detergent other than component (a), provided that if detergent (b) is present the composition does not contain a minor amount of an extreme pressure additive; and (c) ashless antiwear additives; and (d) an oil of lubricating viscosity.

[0004] US Patent 6,339,051, Carey et al., discloses diesel cylinder oils with improved cleanliness and load carrying capabilities by using an additive package containing at least one detergent, an antioxidant, an antiwear agent and a dispersant. The detergent component contains at least one of an overbased phenate, phenylate, salicylate or sulphonate.

[0005] US Patent 6,376,434, Katafuchi, discloses lubricating oil compositions for diesel engines containing at least one of (a) overbased sulphonate, overbased phenates and overbased salicylates; and (b) a bis-type succinic imide compound.

[0006] US Patent 6,551,965, Nagamatsu, discloses a marine diesel lubricating oil composition containing an overbased alkyl sulphonate detergent and an overbased sulphurised alkylphenate detergent. The overbased sulphurised alkylphenate has a TBN of 110 or more.

[0007] British Patent application GB 2,328,217A discloses marine diesel lubricating oil compositions containing a polyalkylene succinimide compound for improving anti-wear. The lubricating oil composition can further include up to 6% of at least one highly overbased detergent selected from alkyl or alkenyl phenates, alkyl or alkenyl phenate-carboxylates, alkyl or alkenyl aromatic sulphonates; and mixtures thereof.

[0008] European Patent application EP 1,086,960 discloses a lubricating oil composition containing novel succinimide compounds and at least one detergent selected from overbased sulphonates, phenates and salicylates of alkaline earth metals.

[0009] East German Patent DD298519 discloses marine diesel engines employing an anticorrosion detergent-dispersant additive combination containing (a) weakly basic or neutral alkaline earth sulphonates; and (b) medium or highly basic alkaline earth sulphonates, phenolates or phenolate sulphides in which the ratio of sulphonate groups to phenolic groups is 1:3.6 to 4.4; and (c) a succinimide ash free detergent.

US Patent 4,952,328 discloses a lubricating oil composition comprising a sulfonate having a metal ratio of 14.7, a Ca sulfurised phenate having a metal ratio of 2.3 and/or 1.1, GMO and further additives. The compositions have good high temperature oxidation stability, low wear and low deposit formation.

JP 09-227503 discloses a process for the production of a sulfurised phenol tetramer which is useful as an intermediate for lubricant additives.

EP-A-0 765 931 discloses a composition comprising an overbased sulfurised metal alkyl phenate having a TBN of 250 and a ratio of metal to phenate of 1.9 and a metal alkylaryl sulfonate having a base number of 400 and a ratio of metal to sulfonate of 15.

[0010] It would be desirable to use compositions with cleanliness properties. The invention provides methods using compositions with cleanliness properties.

[0011] It would be desirable to use compositions capable of decreasing cylinder wear and reducing deposits. The invention provides methods using compositions capable of decreasing cylinder wear and reducing deposits.

SUMMARY OF THE INVENTION

[0012] The present invention provides a

method of lubricating a 2-stroke marine diesel engine comprising supplying thereto a composition comprising:

(a). at least 3 weight percent of an overbased sulphonate detergent with a metal ratio of 12.5:1 to 40:1;
(b). at least 1.5 weight percent of a sulphur containing phenate detergent with a metal ratio of not more than 3; and
(c). an oil of lubricating viscosity,

wherein the sulphur containing phenate contains oligomers of hydrocarbyl phenol with at least 50 wt % of said oligomers in the form of the tetramer or higher oligomers.
Preferred embodiments of the invention are apparent from the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

[0013] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:
[0014] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
[0015] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
[0016] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.
[0017] The composition used in the method of the invention comprises:

(a) at least 3 weight percent of an overbased sulphonate detergent with a metal ratio of 12.5:1 to 40:1;
(b) at least 1.5 weight percent of a sulphur containing phenate detergent with a metal ratio of not more than 3; and
(c) an oil of lubricating viscosity,

wherein the sulphur containing phenate contains oligomers of hydrocarbyl phenol with at least 50 wt % of said oligomers in the form of the tetramer or higher oligomers.
[0018] The total amount of (a) and (b) can be in the range from 4.5 wt % to 35 wt %, preferably 6.5 wt % to 32 wt %, more preferably 9 wt % to 30 wt % and even more preferably 12 wt % to 28 wt % of the lubricating oil composition. The specific amount of component (a) and component (b) preferably are present such that component (a) can deliver at least 50%, preferably at least 55%, more preferably at least 60, even more preferably at least 65 and even more preferably at least 70% of the total amount of base number (TBN) supplied by the detergents (a) and (b). In one embodiment the weight percent of component (a) is 94.7 wt% and component (b) is 5.3 wt %. In one embodiment the amount of component (a) is 75 wt% and component (b) is 25 wt %.
[0019] In one embodiment weight percent ratio of overbased sulphonate to sulphur containing phenate detergent can be 30:1 to 0.85:1, preferably 25:1 to 0.9:1 and even more preferably 20:1 to 0.95:1.

Overbased Sulphonate Detergent

[0020] The sulphonate detergent of the composition can be represented by the formula:

$$(R^1)_k\text{-A-}SO_3M \qquad (I)$$

[0021] wherein, each R^1 is independently an alkyl, cycloalkyl, aryl, acyl, or other hydrocarbyl group with a 6 to 40, preferably 8 to 25 and even more preferably 9 to 20 carbon atoms; A can be independently a cyclic or acyclic hydrocarbon group; M is hydrogen, a valence of a metal ion, an ammonium ion and mixtures thereof; and k is an integer between 0 and 5, for example 0, 1, 2, 3, 4, 5 or mixtures thereof. Preferably k is between 1 and 3, more preferably 1 or 2 and even more preferably 1. Preferably hydrogen is less than 30%, preferably less than 20%, even more preferably less than 10% and even more preferably less than 5% of the available M entities.
[0022] In one embodiment k is 1 and R^1 is a branched alkyl group with 6 to 40 carbon atoms. In one embodiment k is 1 and R^1 is a linear alkyl group with 6 to 40 carbon atoms.

[0023] The most preferred sulphonate components are calcium polypropene benzenesulphonate and calcium monoalkyl and dialkyl benzenesulphonates wherein the alkyl groups contain at least 10 carbons, for example 11, 12, 13, 14, or 15 carbon atoms.

[0024] When M is a valence of a metal ion, the metal can be monovalent, divalent, trivalent or mixtures of such metals. When monovalent, the metal M can be an alkali metal, preferably lithium, sodium, or potassium; and more preferably potassium, which can be used alone or in combination with other metals. When divalent, the metal M can be an alkaline earth metal, preferably magnesium, calcium, barium or mixtures of such metals, more preferably calcium, which can be used alone or in combination with other metals. When trivalent, the metal M can be aluminium, which can be used alone or in combination with other metals. In one embodiment the metal is an alkaline earth metal. In one embodiment the metal is calcium.

[0025] When A is cyclic hydrocarbon group, suitable groups include phenyl or fused bicyclic groups such as naphthalene, indenyl, indanyl, bicyclopentadienyl and mixtures thereof. Although A can be a fused bicyclic ring, benzene rings are preferred.

[0026] When A is an acyclic hydrocarbon group, the carbon chain can be linear or branched, although linear is preferred. Suitable groups include derivatives of carboxylic acids containing 7 to 30, preferably 7 to 20, more preferably 8 to 20 and even more preferably 8 to 15 carbon atoms. Further the chain can be saturated or unsaturated, although saturated is preferred.

[0027] Typically the overbased sulphonate detergent has a TBN (total base number) of at least 400, preferably at least 425, more preferably at least 450 and even more preferably at least 475. In one embodiment the overbased sulphonate detergent has a TBN of 500.

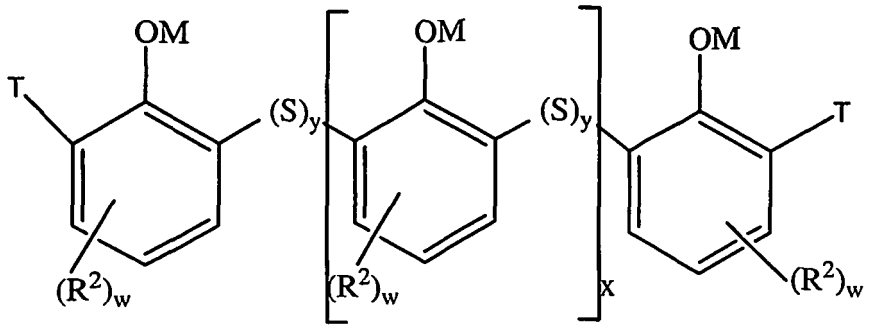
Overbasing the Sulphonate Detergent

[0028] The sulphonate detergent is overbased. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterised by a metal content in excess of that which would be present for neutralisation according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one organic solvent and promoter such as phenol or a mixture of alcohols. A mixture of alcohols typically contains methanol and at least one alcohol with 2 to 7 carbon atoms, and can contain 50-60 mole percent methanol. The acidic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term " metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the substrate. An overbased sulphonate detergent typically has a metal ratio of 12.5:1 to 40:1, preferably 13.5:1 to 40:1, more preferably 14.5:1 to 40:1, even more preferably 15.5:1 to 40:1 and even more preferably 16.5:1 to 40:1. Furthermore the overbased detergent preferably has a low in-process viscosity and a low final viscosity.

[0029] A sulphonate detergent with 500 TBN and its preparation are disclosed in U.S. Patent 5,792,732. In Example 2 thereof, a 500 TBN all-linear alkylbenzene sulphonate is prepared by reacting an alkyl benzene sulphonate from Witco Corp. with $Ca(OH)_2$ and CaO in n-heptane and methanol and bubbling with CO_2. It is also reported in the aforementioned patent (col. 5) that a 500 TBN overbased sulphonate containing highly branched alkylbenzene sulphonate is available from Witco Corp. as Petronate ® C-500. Another method for preparing an overbased sulfonate detergent of high metal ratio is disclosed in U.S. Patent 6,444,625 (see, for instance, column 3, bottom). The latter process includes providing a sulfonic acid to a reactor, adding a lime reactant for neutralization and overbasing, adding a lower aliphatic C_1 to C_4 alcohol and a hydrocarbon solvent, and carbonating the process mixture with carbon dioxide during which process the exotherm of the reaction is maintained between 27° and 57°C. Alternatively, a high metal-ratio detergent can be prepared by using a mixture of short chain alcohols, with or without a hydrocarbon solvent, conducting the addition of lime reactants and carbon dioxide in multiple iterations, and, if desired the process of adding lime and carbon dioxide and of removal of volatile materials can be repeated. The overbased sulphonate detergent in the present invention may be used alone or with other, overbased sulphonates.

Sulphur Containing Phenate Detergent

[0030] The sulphur containing phenate detergent of the composition can be represented by the formula:



(II)

wherein the number of sulphur atoms y can be in the range from 1 to 8, preferably 1 to 6 and even more preferably 1 to 4; R^2 can be hydrogen or hydrocarbyl groups; T is hydrogen or an (S)y linkage terminating in hydrogen, an ion or a non-phenolic hydrocarbyl group; and M is as described above.

[0031] The monomeric units of structure (II) combine in such a way with itself x number of times to form oligomers of hydrocarbyl phenol. Oligomers are described as dimers, trimers, tetramers, pentamers and hexamers when x is equal to 0. 1. 2, 3, and 4. Typically the number of oligomers represented by x can be in the range from 0 to 10, preferably 1 to 9, more preferably 1 to 8, even more even more preferably 2 to 6 and even more preferably 2 to 5. Typically an oligomer is present in significant quantities if concentrations are above 0.1 wt %, preferably above 1 wt % and even more preferably above 2 wt %. Typically an oligomer is present in trace amounts if concentrations are less than 0.1 wt %, for example, oligomers with 11 or more repeat units may be present. Generally in at least 50% of the molecules, x is 2 or higher. The overall sulfur-containing phenate detergent will preferably contain less than 20 wt% dimeric structures.

[0032] The sulphur containing phenate detergent contains oligomers of hydrocarbyl phenol with at least 50 wt % in the form of the tetramer or higher oligomers. Preferably the tetramer or higher oligomers are present in amounts of at least 52 wt %, more preferably at least 54 wt %, even more preferably at least 56 wt % and even more preferably at least 58 wt %.

[0033] The sulphur containing phenate detergent preferably contains less than 20 wt %, preferably less than 18 wt %, more preferably less than 16 wt % and even more preferably less than 14 wt % of hydrocarbyl phenol dimers.

[0034] The sulphur containing phenate detergent contains a substrate level excluding M and any carbonate of M in the range 45 wt % to 95 wt %, preferably 50 wt % to 85 wt % and even more preferably 55 wt % to 75 wt % of the sulphur containing phenate detergent. The "substrate" means the anionic portion of Structure II or similar structures. The substrate level is calculated excluding any contribution of diluent oil to the detergent.

[0035] In Structure II, each R^2 can be hydrogen or a hydrocarbyl group containing 4 to 80, preferably 6 to 45, more preferably 8 to 20 and even more preferably 9 to 14 carbon atoms. The number of R^2 substituents (w) other than hydrogen on each aromatic ring can be in the range from 0 to 4, more preferably 1 to 3 and even more preferably 1 to 2. Where two or more hydrocarbyl groups are present they may be the same or different; and the minimum total number of carbon atoms present in the hydrocarbyl substituents on all the rings, to ensure oil solubility, can be 8 or preferably 9. The preferred components include 4-alkylated phenols containing alkyl groups with the number of carbon atoms between 9 and 14, for example 9, 10, 11, 12, 13, 14 and mixtures thereof. The 4-alkylated phenols typically contain sulphur at position 2.

[0036] Typically the sulphur containing phenate detergent has a TBN in the range of 30 to 220, preferably 40 to 205, more preferably 50 to 190 and even more preferably 70 to 175. In one embodiment the sulphur containing phenate detergent has a TBN of 150. The sulphur containing phenate detergent may be used alone or with other sulphur containing phenate detergents.

[0037] The sulphur containing phenate detergent typically has a metal ratio of not more than 3, preferably not more than 2.7, more preferably not more than 2.5, even more preferably not more than 2.3 and even more preferably not more than 2.1.

[0038] The sulphur containing phenate further contains oligomers of hydrocarbyl phenol with at least 50 wt % of such oligomers being in the form of the tetramer or higher oligomers. A suitable example of calcium alkyl phenol sulphide detergent is commercially available from The Lubrizol Corporation.

Oils of Lubricating Viscosity

[0039] The invention further includes oil of lubricating viscosity. The oil includes natural and synthetic oils, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0040] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0041] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0042] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0043] Natural oils useful in making the lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[0044] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly (1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0045] Other synthetic lubricating oils include but are not limited to liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

[0046] Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index 80-120); Group III (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil and mixtures thereof. Preferably the oil of lubricating viscosity an API Group I, Group II, Group III, Group IV oil and mixtures thereof. More preferably the oil of lubricating viscosity an API Group I, Group II, Group III oil and mixtures thereof.

[0047] The oil of lubricating viscosity is typically present at 55 to 99.9, preferably 61 to 98.9, and more preferably 65 to 96.8 and even more preferably 67 to 94 weight percent of the lubricating oil composition.

Other Performance Additives

[0048] Optionally the lubricating oil composition can include at least one performance additive other than components (a)-(c) selected from the group consisting of metal deactivators, detergents, dispersants, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0049] The total combined amount of the other performance additives present can be 0 to 10, preferably 0.1 to 7, more preferably 0.2 to 5 and even more preferably 1 to 5 weight percent of the lubricating oil composition.

Metal Deactivators

[0050] Metal deactivators can be used to neutralise the catalytic effect of metal for promoting oxidation in lubricating oil. Examples of metal deactivators include derivatives of benzotriazole, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N-dialkyldithio-carbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, and 2-alkyldithio-5-mercapto thiadiazoles.

[0051] Preferably the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds can contain one or more hydrocarbyl substituents at one or more of the following ring positions 1- or 2- or 4-or 5- or 6- or 7-. The hydrocarbyl groups contain 1 to 30, preferably 1 to 15, preferably 1 to 7 carbon atoms. Preferably the metal deactivator is 5-methylbenzotriazole (tolyltriazole). The metal deactivator can be used alone or in combination with other metal deactivators.

Dispersants

[0052] Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant and polymeric dispersants. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number

average molecular weight in the range 350 to 5000, preferably 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 4,234,435.

[0053] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene succinimide with number average molecular weight in the range 350 to 5000, preferably 500 to 3000. The polyisobutylene succinimide can be used alone or in combination with other dispersants.

[0054] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc can be used alone or in combination.

[0055] Another class of ashless dispersant is Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0056] Dispersants can also be post-treated conventional method by a reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, boron compounds, and phosphorus compounds.

Detergents

[0057] Detergents, in addition to those described above as components (a) and (b), are known and can include neutral or overbased, Newtonian or non-Newtonian, basic salts of alkali, alkaline earth and transition metals with one or more hydrocarbyl sulphonic acid, carboxylic acid, phosphorus acid, mono- and/or di- thiophosphoric acid, alkyl phenol, sulphur coupled alkyl phenol compounds, salixarates, saligenins or mixtures thereof. Commonly used metals include sodium, potassium, calcium, magnesium lithium or mixtures thereof. Most commonly used metals include sodium, magnesium, calcium or mixtures thereof. Detergents and in particular overbased detergents and their preparation are disclosed in US Patent 3,629,109.

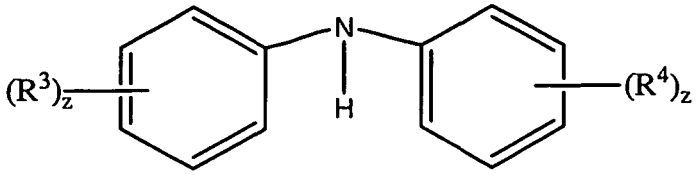
Antiwear Agents

[0058] The lubricating oil composition may additionally contain an antiwear agent. Useful antiwear agents include zinc hydrocarbyl dithiophosphates, phosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides or mixtures thereof. Examples of suitable zinc hydrocarbyl dithiophosphates compounds can include zinc isopropyl methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl)-dithiophosphate, zinc di(cyclohexyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, zinc isopropyl n-butyl dithiophosphate, isobutyl primary amyl dithiophosphate, methylamyl dithiophosphate, isopropyl 2-ethylhexyl dithiophosphate, and mixtures thereof.

Antioxidants

[0059] Antioxidants are known antioxidants and include diphenylamines, hindered phenols, molybdenum dithiocarbamates, sulphurised olefins and mixtures thereof.

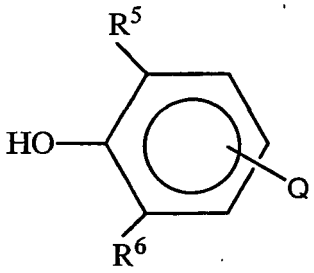
[0060] Diphenylamine antioxidants can be represented by the formula:



(III)

wherein R^3 and R^4 hydrocarbyl groups, preferably arylalkyl or alkyl groups. The arylalkyl groups can contain 6 to 20, preferably 6 to 10 carbons atoms. The alkyl groups can be linear or branched, preferably linear; the alkyl groups can contain 1 to 24, preferably 2 to 18 and even more preferably 4 to 12 carbon atoms; and z is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains a hydrocarbyl group. Preferred alkylated diphenylamines include octyl diphenylamine, nonyl diphenylamine, bis-octyl diphenylamine and bis-nonyl diphenylamine.

[0061] Sterically hindered phenols can be represented by the formula:

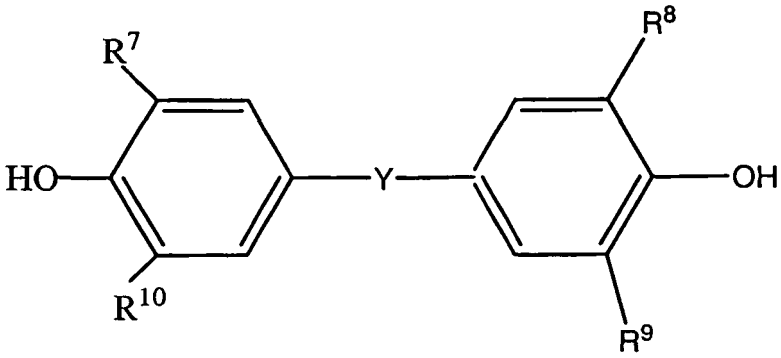


(IV)

wherein R^5 and R^6 are independently branched or linear alkyl groups containing 1 to 24, preferably 4 to 18, and even more preferably 4 to 12 carbon atoms; and Q is hydrogen, a hydrocarbyl group or a bridging group linking to a second aromatic group.

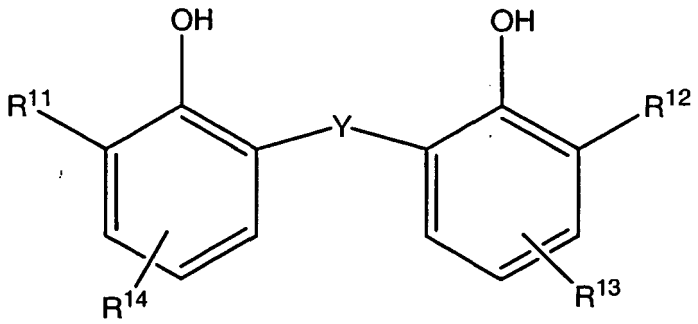
[0062] R^5 and R^6 can be either straight or branched chain; branched is preferred. Preferably the phenol is butyl substituted containing two t-butyl groups. Examples of suitable hydrocarbyl groups include 2-ethylhexyl, n-butyl and dodecyl groups. Examples of suitable bridging groups include $-CH_2-$(methylene bridge) and $-CH_2OCH_2-$ (ether bridge).

[0063] When present, the sterically hindered bridged phenols can be represented by the formulae:



(V)

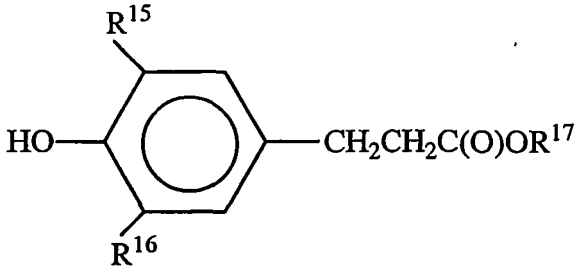
or



(VI)

wherein R^7, R^8, R^9, R^{10}, R^{11}, R^{12} are either straight or branched chain and contain 4 to 18, preferably 4 to 12 carbon atoms. Preferably the phenol is butyl substituted. R^{13} and R^{14} are independently hydrogen or hydrocarbyl; preferably R^{13} and R^{14} are arylalkyl or alkyl groups. The alkyl groups of R^{13} and R^{14} can be linear or branched, linear being preferred. R^{13} and R^{14} are preferably in the para position. The arylalkyl or alkyl groups typically contain 1 to 15, preferably 1 to 10, and more preferably 1 to 5 carbon atoms. The bridging group Y can include $-CH_2-$ (methylene bridge) or $-CH_2OCH_2-$ (ether bridge).

[0064] Examples of methylene-bridged sterically hindered phenols include 4,4 -methylene-bis-(6-tert-butyl-o-cresol), 4,4 -methylene-bis-(2-tert-amyl-o-cresol), 2,2-methylene-bis-(4-methyl-6-tert-butylphenol), and 4,4 -methylene-bis-(2,6-di-tertbutylphenol). In one embodiment, the sterically hindered phenol antioxidant can be a hindered ester represented by the formula:



(VII)

wherein R^{15} and R^{16} are straight or branched alkyl groups that can be substituted or unsubstituted, containing 3 to 22, preferably 3 to 18, more preferably 4 to 12 carbon atoms. Specific examples include of alkyl groups di-secondary butyl and tri-tertiary butyl. R^{17} can be hydrocarbyl. Suitable examples of R^{17} include 2-ethylhexyl or n-butyl, dodecyl, $-CH_2CH_2COOH$ and mixtures thereof.

[0065] Suitable examples of molybdenum dithiocarboamates which can be used as antioxidants include commercial materials sold under the trade names such as Vanlube 822™ and Molyvan™ A from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 and S-600 from Asahi Denka Kogyo K. K and mixtures thereof.

[0066] Examples of suitable olefins that can be sulphurised to form antioxidants include propylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially preferred olefins. Alternatively, the olefin can be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester such as butyl(meth)acrylate.

[0067] Another class of sulphurised olefins include fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil; and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and mixed with olefins.

Corrosion Inhibitors

[0068] Corrosion inhibitors can include amine salts of carboxylic acids such as octylamine octanoate (octylamine salt of octanoic acid), condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine, e.g. a polyalkylene polyamine such as triethylenetetramine, and half esters of alkenyl succinic acids in which the alkenyl radical contains 8 to 24 carbon atoms with alcohols such as polyglycols.

Antiscuffing Agents

[0069] The lubricant may also contain an antiscuffing agent. Antiscuffing agents that decrease adhesive wear are often sulphur containing compounds. Typically the sulphur containing compounds include organic sulphides and polysulphides, such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, di-tertiary butyl polysulphide, sulphurised sperm oil, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, sulphurised Diels-Alder adducts, alkyl sulphenyl N'N-dialkyl dithiocarbamates, the reaction product of polyamines with polybasic acid esters, chlorobutyl esters of 2,3-dibromopropoxyisobutyric acid, acetoxymethyl esters of dialkyl dithiocarbamic acid and acyloxyalkyl ethers of xanthogenic acids and mixtures thereof.

Extreme Pressure Agents

[0070] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulphides and polysulphides such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised sperm oil, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, *e.g.,* dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; the zinc salts of a phosphorodithioic acid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithi-

ophosphoric acid with propylene oxide; and mixtures thereof.

Foam Inhibitors

[0071] Foam inhibitors are known and can include organic silicones such as polyacetates, dimethyl silicone, polysiloxanes, polyacrylates or mixtures thereof. Examples of foam inhibitors include poly ethyl acrylate, poly 2-ethylhexylacrylate, poly vinyl acetate and mixtures thereof.

Demulsifiers

[0072] Demulsifiers are known and include derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof.

Pour Point Depressants

[0073] Pour point depressants are known and include esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

Friction Modifiers

[0074] Friction modifiers are known and can include fatty amines, esters, especially glycerol esters such as glycerol monooleate, borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxylated fatty amines, metal salts of fatty acids, sulfurized olefins, fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines and amine salts of alkylphosphoric acids.

Viscosity Modifiers

[0075] Viscosity modifiers are known and are typically polymeric materials including styrene-butadiene rubbers, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated radical isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates, esters of maleic anhydride-styrene copolymers and mixtures thereof.

Process

[0076] The invention also includes a process to prepare the composition of the present invention, comprising mixing:

(a) at least 3 weight percent of an overbased sulphonate detergent with a metal ratio of about 12.5:1 to about 40:1;
(b) at least 1.5 weight percent of a sulphur containing phenate detergent with a metal ratio of not more than 3; and
(c) an oil of lubricating viscosity,

wherein the sulphur containing phenate contains oligomers of hydrocarbyl phenol with at least 50 wt % of said oligomers in the form of the tetramer or higher oligomers.

[0077] The mixing conditions are typically 15°C to 130°C, preferably 20°C to 120°C and even more preferably 25°C to 110°C; and for a period of time in the range 30 seconds to 48 hours, preferably 2 minutes to 24 hours, and even more preferably 5 minutes to 16 hours; and at pressures in the range 86.4 kPa to 266 kPa (650 mm Hg to 2000 mm Hg), preferably 91.8 kPa to 200 kPa (690 mm Hg to 1500 mm Hg), and even more preferably 95.1 kPa to 133 kPa (715 mm Hg to 1000 mm Hg).

[0078] The process optionally includes mixing other performance additives as described above. The optional performance additives can be added sequentially, separately or as a concentrate.

[0079] If the present invention is in the form of a concentrate (which can be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of each of the above-mentioned dispersant, as well as other components, to diluent oil is typically in the range of 80:20 to 10:90 by weight.

Industrial Application

[0080] The compositions of the present invention are useful as detergents in an internal combustion engines, for example diesel fuelled engines, gasoline fuelled engines, natural gas fuelled engines or a mixed gasoline/alcohol fuelled engines.

[0081] The invention provides a method for lubricating a 2-stroke marine diesel engine comprising supplying thereto a lubricant comprising the composition as described herein. The use of the lubricating oil composition can impart one or more of improved cleanliness decreased cylinder wear, reduced deposits and mixtures thereof.

[0082] The following examples provide an illustration of the invention.

EXAMPLES

[0083] A sample of a 500 TBN sulphonate detergent is prepared using a flange vessel with flange and clip, overhead stirrer with paddle and polytetrafluoroethylene (PTFE) stirrer gland, Dean Stark trap and double surface condenser, a mantle/thermocouple temperature controller system, the equipment from just above the mantle to just below the condenser being covered with glass wool. The vessel is charged with 35.1 parts by weight of C_{16}-C_{24} alkylbenzene sulphonic acid and 31.8 parts by weight of mineral oil (SN 150) and heated to 30°C. The reactor is charged through a port with alcohols containing methanol and a mixture of iso-butanol/amyl alcohol present at 11.6 parts by weight. The weight ratio of methanol to the mixture of iso-butanol/amyl alcohol is 1.31. The reactor is charged with 14.9. parts by weight of calcium hydroxide and the mixture is heated to 54°C where carbon dioxide is added to form a carbonated product. The carbonated product is further treated three more times with similar (or equal) portions of calcium hydroxide and carbon dioxide. Water is removed by stripping before repeating the addition of alcohol, calcium hydroxide and carbon dioxide 2 times. The product is stripped and filtered.

Reference Examples R1-R7

Reference Example 1 (R1)

[0084] An oil of lubricating viscosity is prepared by blending 80wt % of Exxon™ 600N oil with 11.9 mm^2s^{-1} (cSt) at 100°C with 20 wt % of Exxon™ 150BS oil with 31.7 mm^2s^{-1} (cSt) at 100°C. A commercially available conventional sulphur containing phenate detergent ("type 1") and a sulphonate detergent with a total base number of 500 are added to the oil of lubricating viscosity at 4.6 wt % and 12.9 wt % respectively. The "sulphur containing phenate detergent ('type 1')" has a metal ratio of 8.6:1. The alkylphenol of the sulphur containing phenate oligomer has about 22 wt % in the form of the dimer, about 23 wt % in the form of the trimer and about 46 wt % in the form of the tetramer or higher oligomers.

Reference Example 2 (R2)

[0085] The experimental procedure is identical to the process of Reference Example 1, except the phenate detergent is commercially available conventional sulphur containing phenate detergent ("type 2"). The "sulphur containing phenate detergent type 2" has a metal ratio of 7.7:1. The alkylphenol of the sulphur containing phenate oligomer has about 22 wt % in the form of the dimer, about 23 wt % in the form of the trimer and about 46 wt % in the form of the tetramer or higher oligomers.

Reference Example 3 (R3)

[0086] The experimental procedure is identical to the process of Reference Example 1, except the phenate detergent is added at 3.08 wt % and the sulphonate is added at 13.33 wt %.

Reference Example 4 (R4)

[0087] The experimental procedure is identical to the process of Reference Example 2, except the phenate detergent is added at 3.08 wt % and the sulphonate is added at 13.33 wt %.

Reference Example 5 (R5)

[0088] The experimental procedure is identical to the process of Reference Example 1, except a detergent package of a sulphonate with a total base number of 400 is added at 7.5 wt %; and a commercially available phenate detergent with a total base number of 250 is added at 16 wt %. Furthermore the oil of lubricating viscosity contains a polyisobutylene

succinimide dispersant at 1.2 wt %.

Reference Example 6 (R6)

[0089] The experimental procedure is identical to the process of Reference Example 1, except sulphonate with a total base number of 400 is added at 1.93 wt %; and a commercially available phenate detergent with a total base number of 250 is added at 3.0 wt %.

Reference Example 7 (R7)

[0090] The experimental procedure is identical to the process of Reference Example 1, except sulphonate with a total base number of 400 is added at 3.2 wt %; and a commercially available phenate detergent with a total base number of 250 is added at 1.3 wt %.

Example 1 (Ex1)

[0091] The experimental procedure is identical to the process of Reference Example 1, except the phenate detergent is a commercially product available from The Lubrizol Corporation with a total base number of 150. The phenate detergent has a metal ratio of 1:1. The alkylphenol of the sulphur containing phenate is oligomerised with about 13 wt % in the form of the dimer, about 21 wt % in the form of the trimer and about 60 wt % in the form of the tetramer or higher oligomers.

Example 2 (Ex2)

[0092] The experimental procedure is identical to the process of Reference Example 3, except the phenate detergent is a commercially product available from The Lubrizol Corporation with a total base number of 150.

Example 3 (Ex3)

[0093] The experimental procedure is identical to the process of Reference Example 1, except a detergent package of a sulphonate with a total base number of 500 is added at 10.67 wt %; and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 5.56 wt %. Furthermore the oil of lubricating viscosity contains a polyisobutylene succinimide dispersant in an amount of 1.2 wt %.

Example 4 (Ex4)

[0094] The experimental procedure is identical to the process of Reference Example 3, except the sulphonate with a total base number of 500 is added at 9.52 wt % and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 14.93 wt %. Furthermore the oil of lubricating viscosity contains a polyisobutylene succinimide dispersant at 0.6 wt %.

Example 5 (Ex5)

[0095] The experimental procedure is identical to the process of Reference Example 3, except the sulphonate with a total base number of 500 is added at 12.66 wt % and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 4.62 wt %. Furthermore the oil of lubricating viscosity contains a zinc oxide-polyisobutylene succinimide dispersant at 0.81 wt %.

Example 6 (Ex6)

[0096] The experimental procedure is identical to the process of Reference Example 5, except the sulphonate with a total base number of 500 is added at 12.88 wt % and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 3.85 wt %.

Example 7 (Ex7)

[0097] The experimental procedure is identical to the process of Reference Example 5, except the sulphonate with a total base number of 500 is added at 12.33 wt % and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 2.31 wt %.

Example 8 (Ex8)

[0098] The experimental procedure is identical to the process of Reference Example 5, except the sulphonate with a total base number of 500 is added at 13.77 wt % and the phenate detergent commercially available from The Lubrizol Corporation has a total base number of 150 is added at 0.77 wt %.

Test 1: Pressurised Differential Scanning Calorimetry (PDSC)

[0099] Approximately 2.50mg ±0.25mg of sample is placed in a "TA DSC 2920™ Calorimeter," heated to 215°C at 40°C min^{-1} and held at 690 kPa. The oxidation induction time for an oil of lubricating viscosity is determined by calculating the length of time a heated sample takes to oxidise. The results obtained by testing the lubricants of the indicated Examples are as shown:

Example	PDSC Oxidation Induction Time (mins)
R1	35.1
R2	29.5
Ex1	50
R3	27.1
R4	16.1
Ex2	43

Test 2: Panel Coker

[0100] Approximately 233g of sample is placed in a 250ml Panel Coker apparatus and heated to 325°C. The sample is splashed against a metal plate for 15 seconds and then baked for 45 seconds. The splashing and baking cycle is continued for approximately 3 hours. The sample is cooled to room temperature and the amount of deposits left on the metal plate is weighed. The results obtained by testing the lubricants of the indicated Examples are as shown:

Example	Deposits (mg)
R1	140
R2	297
Ex1	110
R3	264
R4	353
Ex2	217
R5	88.3
Ex3	24.9
Ex4	15.4
R6	88.9
Ex5	19.2
Ex6	53.4
R7	334.4
Ex7	112.5
Ex8	183.2

[0101] The analysis of the experimental data obtained for the following combinations of reference examples and invention examples R1, R2 with Ex3; R1, R4 with Ex2; R5 with Ex3 and Ex4; R6 with Ex5 and Ex6; and R7 with Ex7 and Ex8 shows that overbased sulphonate detergents used in combination with the sulphur containing phenate detergents of the invention, have improved oil oxidation properties and less deposit formation than combinations of overbased sulphonate detergents and other commercially available sulphur containing phenate detergents.

[0102] Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless

otherwise indicated.

Claims

1. A method of lubricating a 2-stroke marine diesel engine comprising supplying thereto a composition comprising:

   (a). at least 3 weight percent of an overbased sulphonate detergent with a metal ratio of 12.5:1 to 40:1;
   (b). at least 1.5 weight percent of a sulphur containing phenate detergent with a metal ratio of not more than 3; and
   (c). an oil of lubricating viscosity,

   wherein the sulphur containing phenate contains oligomers of hydrocarbyl phenol with at least 50 wt % of said oligomers in the form of the tetramer or higher oligomers.

2. The method of claim 1, wherein the sulphonate detergent has a total base number of at least 400.

3. The method of claim 1, wherein the sulphonate detergent has a total base number of at least 450.

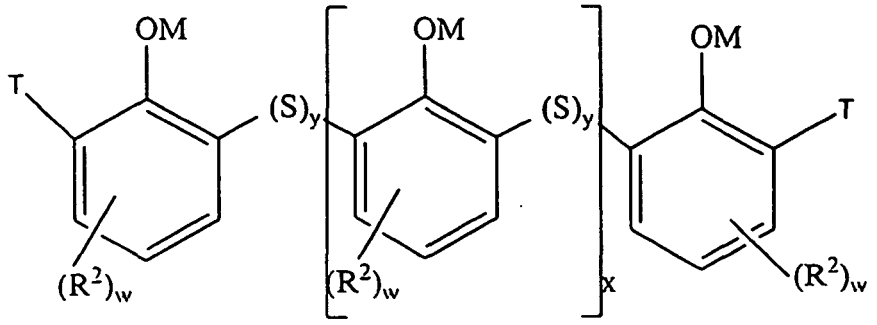
4. The method of claim 1, wherein the substrate of the sulphonate detergent is represented by the formula:

   $$(R1)_k\text{-}A\text{-}SO_3M \qquad (I)$$

   wherein, each R^1 is independently a hydrocarbyl group with a about 6 to about 40 carbon atoms; A is a cyclic or acyclic hydrocarbon group; M is a valence of metal ion, hydrogen, ammonium ion, or mixtures thereof; and k is 1 to about 5.

5. The method of claim 1, wherein the sulphonate detergent incorporates a metal ion selected from the group consisting of alkali metals, alkaline earth metals and mixtures thereof.

6. The method of claim 1, wherein the sulphur containing phenate detergent is represented by the formula:



(II)

   wherein the number of sulphur atoms y is 1 to 8; T is hydrogen or an (S)y linkage terminating in hydrogen, an ion or a non-phenolic hydrocarbyl group; M is hydrogen, a valence of a metal ion, an ammonium ion and mixtures thereof, provided hydrogen is present on less than 30% of the M entities; and R^2 is hydrogen or hydrocarbyl groups containing 4 to 80 carbon atoms; x is 0 to 10, provided that at least 50 % of x is 2 or higher; w, is in the range from 0 to 3, provided that at least one aromatic ring contains an R^2 substituent and the total number of carbon atoms in the R^2 groups is at least 8.

7. The method of claim 1, wherein the sulphur containing phenate detergent contains less than 20 wt % dimeric structures.

8. The method of claim 1, wherein the sulphur containing phenate detergent contains a substrate level excluding metal M and any carbonate of M in the range about 45 to about 95 wt % of the sulphur containing phenate detergent.

9. The method of claim 1, wherein the sulphur containing phenate detergent has a total base number between about 30 to about 220.

10. The method of claim 1, wherein the oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV oil or mixtures thereof.

11. The method of claim 1 further comprising at least one optional performance additive selected from the group consisting of metal deactivators, detergents, dispersants, antioxidants, antiwear agents, corrosion inhibitors, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, friction modifiers, viscosity modifiers, pour point depressants and mixtures thereof.

Patentansprüche

1. Verfahren zum Schmieren eines Zweitakt-Schiffsdieselmotors, umfassend das Zuführen einer Zusammensetzung, die

(a) wenigstens 3 Gew.-% eines überbasischen Sulfonat-Tensids mit einem Metallverhältnis von 12,5:1 bis 40: 1;
(b) wenigstens 1,5 Gew.-% eines schwefelhaltigen Phenat-Tensids mit einem Metallverhältnis von nicht mehr als 3; und
(c) ein Öl mit Schmierviskosität

umfasst, wobei das schwefelhaltige Phenat Oligomere von Hydrocarbylphenol mit wenigstens 50 Gew.-% der Oligomere in Form des Tetramers oder höherer Oligomere enthält.

2. Verfahren gemäß Anspruch 1, wobei das Sulfonat-Tensid eine Gesamtbasenzahl von wenigstens 400 aufweist.

3. Verfahren gemäß Anspruch 1, wobei das Sulfonat-Tensid eine Gesamtbasenzahl von wenigstens 450 aufweist.

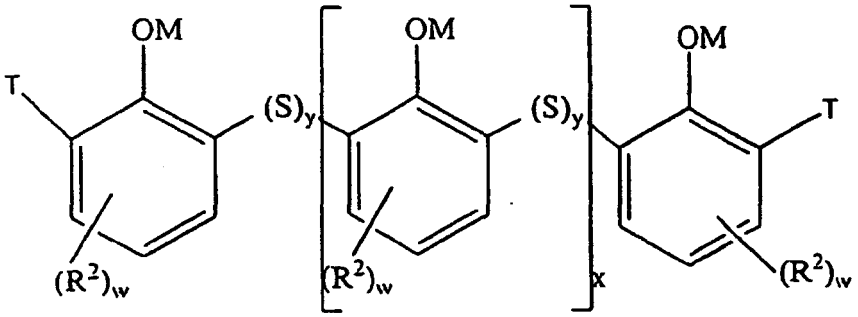
4. Verfahren gemäß Anspruch 1, wobei das Substrat des Sulfonat-Tensids durch die Formel

$$(R^1)_k\text{-A-}SO_3M \qquad (I)$$

dargestellt wird, wobei jedes R^1 unabhängig für eine Hydrocarbylgruppe mit etwa 6 bis etwa 40 Kohlenstoffatomen steht, A eine cyclische oder acyclische Kohlenwasserstoffgruppe ist, M ein Metallion, Wasserstoff, ein Ammoniumion oder Gemische davon ist und k = 1 bis etwa 5 ist.

5. Verfahren gemäß Anspruch 1, wobei das Sulfonat-Tensid ein Metallion enthält, das aus der Gruppe ausgewählt ist, die aus Alkalimetallen, Erdalkalimetallen und Gemischen davon besteht.

6. Verfahren gemäß Anspruch 1, wobei das schwefelhaltige Phenat-Tensid durch die Formel



(II)

dargestellt wird, wobei die Zahl der Schwefelatome y = 1 bis 8 beträgt, T Wasserstoff oder eine mit Wasserstoff, einem Ion oder einer nichtphenolischen Hydrocarbylgruppe endende $(S)_y$-Verknüpfung ist, M Wasserstoff, ein Metallion, ein Ammoniumion oder Gemische davon ist, mit der Maßgabe, dass Wasserstoff an weniger als 30% der M-Exemplare vorhanden ist, und es sich bei R^2 um Wasserstoff oder Hydrocarbylgruppen, die 4 bis 80 Kohlenstoffatome enthalten, handelt, x = 0 bis 10 ist, mit der Maßgabe, dass wenigstens 50% von x = 2 oder höher ist, w im Bereich von 0 bis 3 liegt, mit der Maßgabe, dass wenigstens ein aromatischer Ring einen R^2-Substituenten enthält und die Gesamtzahl der Kohlenstoffatome in den R^2-Gruppen wenigstens 8 beträgt.

7. Verfahren gemäß Anspruch 1, wobei das schwefelhaltige Phenat-Tensid weniger als 20 Gew.-% dimere Strukturen enthält.

8. Verfahren gemäß Anspruch 1, wobei das schwefelhaltige Phenat-Tensid einen Substratanteil ohne das Metall M und gegebenenfalls Carbonat von M im Bereich von etwa 45 bis etwa 95 Gew.-% des schwefelhaltigen Phenat-Tensids enthält.

9. Verfahren gemäß Anspruch 1, wobei das schwefelhaltige Phenat-Tensid eine Gesamtbasenzahl zwischen etwa 30 und etwa 220 aufweist.

10. Verfahren gemäß Anspruch 1, wobei das Öl mit Schmierviskosität ein Öl der API-Gruppe I, Gruppe II, Gruppe III, Gruppe IV oder Gemische davon umfasst.

11. Verfahren gemäß Anspruch 1, das weiterhin wenigstens ein optionales Performance-Additiv umfasst, das aus der Gruppe ausgewählt ist, die aus Metalldesaktivatoren, Tensiden, Dispergiermitteln, Antioxidantien, Antiverschleißmitteln, Korrosionsinhibitoren, Antikratzmitteln, Extremdruckmitteln, Schauminhibitoren, Demulgatoren, Reibungsmodifikatoren, Viskositätsmodifikatoren, Gießpunkterniedrigern und Gemischen davon besteht.

Revendications

1. Procédé de lubrification d'un moteur diesel marin à 2 temps comprenant la fourniture à celui-ci d'une composition comprenant :

   (a) au moins 3 % en poids d'un détergent sulfonate surbasique présentant un rapport métallique de 12,5:1 à 40:1 ;
   (b) au moins 1,5 % en poids d'un détergent phénate contenant du soufre présentant un rapport métallique non supérieur à 3 ; et
   (c) une huile de viscosité lubrifiante,

   dans lequel le phénate contenant du soufre contient des oligomères d'hydrocarbylphénol, au moins 50 % en poids desdits oligomères se présentant sous la forme d'un tétramère ou d'oligomères supérieurs.

2. Procédé selon la revendication 1, dans lequel le détergent sulfonate a un nombre total de base d'au moins 400.

3. Procédé selon la revendication 1, dans lequel le détergent sulfonate a un nombre total de base d'au moins 450.

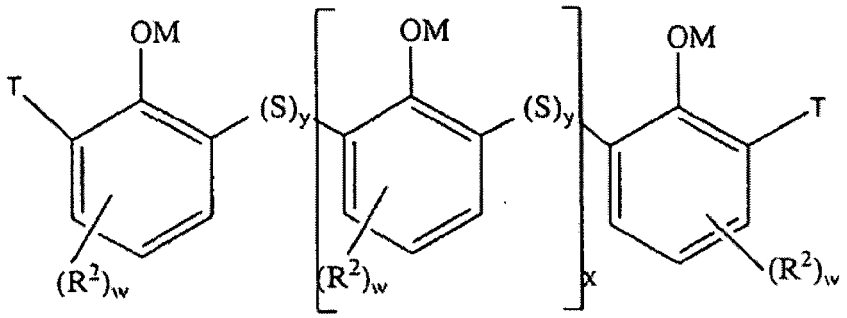
4. Procédé selon la revendication 1, dans lequel le substrat du détergent sulfonate est représenté par la formule :

$$(R^1)_k\text{-A-}SO_3M \qquad (I)$$

   où,
   chaque R^1 est indépendamment, un groupe hydrocarbyle ayant environ 6 à environ 40 atomes de carbone ; A est un groupe hydrocarbure cyclique ou acyclique ; M est une valence d'ion métallique, un atome d'hydrogène, un ion ammonium ou un mélange de ceux-ci ; et k est 1 à environ 5.

5. Procédé selon la revendication 1, dans lequel le détergent sulfonate incorpore un ion métallique choisi dans le groupe constitué par les métaux alcalins, les métaux alcalino-terreux et leurs mélanges.

6. Procédé selon la revendication 1, dans lequel le détergent phénate contenant du soufre est représenté par la formule :



(II)

où le nombre d'atomes de soufre y est de 1 à 8 ; T est un atome d'hydrogène ou une liaison (S)y se terminant par un atome d'hydrogène, un ion ou un groupe hydrocarbyle non phénolique ; M est un atome d'hydrogène, une valence d'un ion métallique, un ion ammonium et leurs mélanges, à condition que l'hydrogène soit présent sur moins de 30 % des entités M ; et R^2 est un atome d'hydrogène ou des groupes hydrocarbyle contenant 4 à 80 atomes de carbone ; x est 0 à 10, à condition qu'au moins 50 % de x soit 2 ou plus ; w est une valeur allant de 0 à 3, à condition qu'au moins un cycle aromatique contienne un substituant R^2 et le nombre total d'atomes de carbone dans les groupes R^2 est d'au moins 8.

7. Procédé selon la revendication 1, dans lequel le détergent phénate contenant du soufre contient moins de 20 % en poids de structures dimères.

8. Procédé selon la revendication 1, dans lequel le détergent phénate contenant du soufre contient un taux de substrat, à l'exclusion de M métallique et de tout carbonate de M, allant d'environ 45 à environ 95 % en poids du détergent phénate contenant du soufre.

9. Procédé selon la revendication 1, dans lequel le détergent phénate contenant du soufre a un nombre de base total entre environ 30 et environ 220.

10. Procédé selon la revendication 1, dans lequel l'huile de viscosité lubrifiante comprend une huile API du Groupe I, du Groupe II, du Groupe III, du Groupe IV ou leurs mélanges.

11. Procédé selon la revendication 1, comprenant en outre au moins un additif de performance optionnel choisi dans le groupe constitué par les désactivateurs de métaux, les détergents, les dispersants, les antioxydants, les agents anti-usure, les inhibiteurs de corrosion, les agents anti-rayage, les agents de pression extrême, les inhibiteurs de mousse, les agents désémulsionnants, les modificateurs de frottement, les modificateurs de viscosité, les agents abaissant le point d'écoulement et leurs mélanges.

REFERENCES CITED IN THE DESCRIPTION

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