(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 903 093 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.03.2008 Bulletin 2008/13

(21) Application number: **07113742.6**

(22) Date of filing: **02.08.2007**

(51) Int Cl.:
C10M 159/22 *(2006.01)*
C10N 30/04 *(2006.01)*
C10N 40/25 *(2006.01)*
C10N 70/00 *(2006.01)*

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **19.09.2006 EP 06120924**

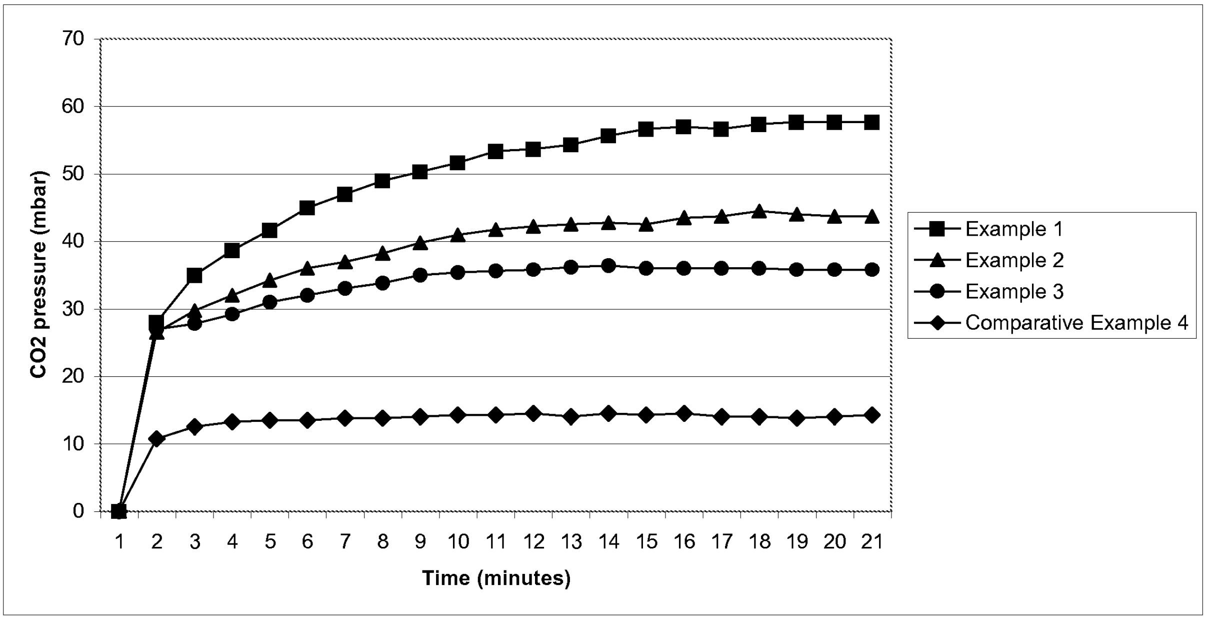
(71) Applicant: **Infineum International Limited**
Abingdon
Oxfordshire OX13 6BB (GB)

(72) Inventors:
- **Arrowsmith, Stephen,**
  c/o Infineum UK Ltd
  Abingdon, Oxfordshire OX13 6BB (GB)
- **Kosidowski, Laura,**
  c/o Infineum UK Ltd
  Abingdon, Oxfordshire OX13 6BB (GB)
- **Spencer, Jeremy,**
  c/o Infineum UK Ltd
  Abingdon, Oxfordshire OX13 6BB (GB)
- **Watts, Peter,**
  c/o Infineum UK Ltd
  Abingdon, Oxfordshire OX13 6BB (GB)

(74) Representative: **Lewis, Pauline Therese et al**
Infineum UK Limited,
P.O. Box 1,
Milton Hill
Abingdon,
Oxfordshire OX13 6BB (GB)

(54) A lubricating oil composition

(57) A lubricating oil composition including at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent. The detergent includes less than 6.0% by combined mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt. The lubricating oil composition exhibits an improved rate of acid neutralization.



EP 1 903 093 A1

Description

[0001] The present invention is concerned with a lubricating oil composition suitable for use as a marine diesel cylinder lubricant. In particular, the present invention is concerned with a marine diesel cylinder lubricant that exhibits an increased rate of acid neutralization.

[0002] Fuels used in marine diesel engines generally include a high sulphur content, such as, for example, 2-3%. The exhaust gases therefore include sulphur oxides which react with moisture to form sulphuric acid which corrodes and wears components in the diesel engine, such as cylinder liners and piston rings. Therefore, any acid must be neutralized as quickly as possible.

[0003] EP 0 839 894A discloses a marine diesel cylinder lubricant that exhibits a rapid neutralization rate. The lubricant includes (A) at least one compound selected from the group consisting of overbased sulphonates, phenates or salicylates of alkaline earth metals, and (B) a bis-type succinic imide compound having an absorption ratio, α/β, of absorption peaks in an IR spectrum of not more than 0.005, wherein α is the intensity of an absorption peak at 1550 ± 10 cm^{-1} and β is the intensity of absorption peak at $1700\pm cm^{-1}$.

[0004] EP 1 051 467B also discloses a marine diesel cylinder lubricant that exhibits a rapid neutralization rate. The lubricant includes 0.5 to 2.5 % by weight of a succinimide dispersant, 3.5 to 10 % by weight of an overbased sulphonate detergent and 11 to 24.5 % by weight of an overbased phenate detergent.

[0005] The aim of the present invention is to provide a lubricant composition that exhibits an increased rate of acid neutralization.

[0006] In accordance with the present invention there is provided a lubricating oil composition including at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the detergent including less than 6.0% by combined mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

[0007] The lubricating oil composition preferably has a total base number ('TBN') of more than 30, preferably more than 35, mgKOH/g, as determined by ASTM D2896. The lubricating oil composition preferably has a TBN of less than 100 mgKOH/g, as determined by ASTM D2896.

[0008] In accordance with the present invention there is also provided use to increase the rate of acid neutralization of a lubricating oil composition of at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the sulphurized overbased metal phenate detergent including less than 6.0% by mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

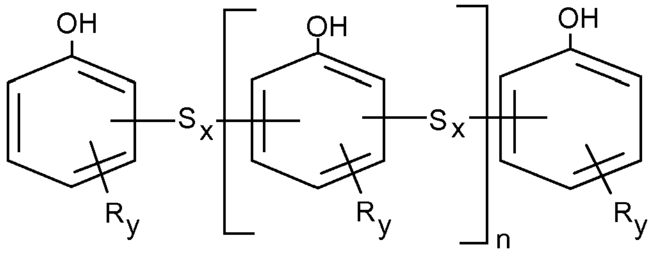
[0009] In accordance with the present invention there is also provided a method of increasing the rate of acid neutralization of a lubricating oil composition, the method including the step of adding to the lubricating oil composition at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the sulphurized overbased metal phenate detergent including less than 6.0% by mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

[0010] By 'alkyl phenol' we mean phenol having a linear or branched alkyl group attached thereto.

[0011] The metal is preferably calcium.

[0012] The overbased phenate detergent is prepared from mono-, di- and polysulphides of C_9-C_{15} alkyl phenols. The C_9-C_{15} alkyl substituted phenols may contain one or more C_9-C_{15} alkyl groups per aromatic ring. Preferably, the overbased phenate detergent is prepared from mono-, di- and polysulphides of C_{10}-C_{13} alkyl phenols.

[0013] The sulphurized C_9-C_{15} alkyl phenols may be represented by the general formula I:



I

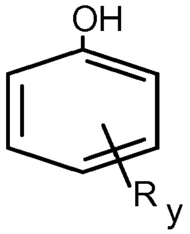
wherein R represents a C_9-C_{15} alkyl radical, n is an integer of 0 to 20, y is an integer of 0 to 4 and may be different for each aromatic nucleus and x is an integer of from 1 to 7, typically 1 to 4. The individual groups represented by R may be the same or different and may contain from 9 to 15, preferably 10 to 13, carbon atoms. Preferably n is 0 to 4, y is 1 or 2 and may be different for each aromatic nucleus and x is 1 to 4.

[0014] The sulphurized C_9-C_{15} alkyl substituted phenols may be mixtures of the above general formula and may include un-sulphurized phenolic material. It is preferred that the level of un-sulphurized phenolic material is kept to a minimum. The sulphurized C_9-C_{15} alkyl substituted phenols may contain up to 15%, preferably up to 9%, by weight of un-sulphurized phenolic material. One preferred group of sulphurized C_9-C_{15} alkyl substituted phenols are those with a sulphur content of between 4 and 16 mass %, preferably 4 to 14%, and most preferably 6 to 12 mass %.

[0015] The sulphurized phenols, which will normally comprise a mixture of different compounds, typically contain at least some sulphur which is either free, or is only loosely bonded; the sulphur thus being available to attack nitrile elastomeric seals and is referred to as active sulphur. This active sulphur may be present in the form of polysulphides, for example when x is three or greater in formula I ; in this form the active sulphur may be present at levels which are typically up to 2 wt % or more.

[0016] The sulphurized C_9-C_{15} alkyl phenols are prepared by the reaction of C_9-C_{15} alkyl phenols in the presence of a sulphurizing agent; the sulphurizing agent being an agent which introduces S_x bridging groups between phenols where x is 1 to 7. Thus the reaction may be conducted with elemental sulphur or a halide thereof such as sulphur monochloride or sulphur dichloride. Preferably, sulphur monochloride is used.

[0017] The C_9-C_{15} alkyl substituted phenols may be any phenol of general formula II



II

wherein R and y are as defined above. Mixtures of phenols of general formula II may be used.

[0018] It is preferred that the oil soluble sulphurized phenol is derived from sulphur monochloride and has low levels of chlorine such as less than 1000 ppm of chlorine. Preferably the chlorine content is 900 ppm or less e.g. 800 or less and most preferably 500 ppm or less.

[0019] It is preferred that the phenol is a mixture of phenols and as such has an average molecular weight of between 210 and 310, preferably between 230 and 290, and most preferably between 250 and 270. Most preferred mixtures are mixtures of para-substituted monoalkylphenols. It is preferred that the phenols of general formula II are not hindered phenols although they may be mixtures of phenols which comprise a minor proportion, such as less than 25 wt %, e.g. less than 10 wt %, of hindered phenol. By 'hindered phenols' is meant phenols in which all the ortho and para reactive sites are substituted, or sterically hindered phenols in which, either both ortho positions are substituted or only one ortho position and the para position are substituted and, in either case, the substituent is a tertiary alkyl group, e.g. t-butyl. It is preferred that for a given mixture of mono and di-alkyl substituted phenols, e.g. dodecyl substituted, that the mono-substituted phenol is present in at least 80 wt % and preferably in the range 90 to 95 wt %. It is preferred that the mole ratio of phenol to sulphur monochloride is 2 or greater and most preferably is 2.2 or greater.

[0020] The level of sulphur, the required conversion of phenolic material to keep the un-sulphurized material to a minimum and the chlorine levels are linked. It is difficult to keep chlorine levels low whilst increasing sulphur content and achieving the desired conversion, because more chlorine containing starting material, i.e. S_2Cl_2, is usually required to achieve these targets; the task is to be able to achieve low chlorine whilst at the same time not having a detrimental effect on the other two factors. It is preferred that the reaction is carried out in the temperature range of -15 or -10 to 150°C, e.g. 20 to 150°C and preferably 60 to 150°C. It is most preferred that the reaction is carried out at less than 110°C; the use of reaction temperatures below 110°C with certain phenols results in lower levels of chlorine. Typically the reaction temperature is between 60 and 90°C. Preferably the sulphur monochloride is added to the reaction mixture at a rate of 4×10^{-4} to 15^{-4} $cm^3min^{-1}g^{-1}$ phenol. If the reaction mixture is not adequately mixed during this addition the chlorine content may increase. The resultant product preferably has a sulphur content of at least 4%, e.g. between 4 and 16%, more preferably 4 to 14 % and most preferably at least 6%, e.g. 7 to 12%. The process has the advantage of not requiring complicated post reaction purification steps in order to reduce the levels of chlorine in the intermediate product.

[0021] Olefins and acetylenic compounds may be used to remove active sulphur from the sulphurized C_9-C_{15} alkyl substituted phenols.

[0022] Suitable olefins include mono-olefins, di-olefins, tri-olefins or higher homologues. By suitable is meant olefins which are capable of reacting with active sulphur and whose properties are such that the excess of such olefins used may be removed from the reaction mixture without resulting in significant decomposition of the sulphurized phenol. Preferred olefins are those with a boiling point of up to 200°C and most preferably have a boiling point in the range of 150°C to 200°C.

[0023] The mono-olefins may be unsubstituted aliphatic mono-olefins meaning that they contain only carbon and hydrogen atoms, or they may be substituted with one or more heteroatoms and/or heteroatom containing groups e.g. hydroxyl, amino, cyano. An example of a suitable cyano substituted mono-olefin is fumaronitrile. The mono-olefins may also be substituted with aromatic functionality as, for example, in styrene. The mono-olefins may contain for example ester, amide, carboxylic acid, carboxylate, alkaryl, amidine, sulphinyl, sulphonyl or other such groups. It is preferred that the mono-olefins are aliphatic and are not substituted with heteroatoms and/or heteroatom containing groups other than hydroxyl or carboxylate groups. The mono-olefins may be branched or non-branched.

[0024] The mono-olefin preferably has from 4 to 36 carbon atoms and most preferably 8 to 20 carbon atoms. The mono-olefin may, for example, be an α-olefin. Examples of α-olefins which may be used include: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1 tetracosene, 1-pentacosene, 1-hexacosene, 1-octacosene, and 1-nonacosene. The α-olefin may be a mixture of α-olefins such as the following commercially available mixtures: C_{15}-C_{18}, C_{12}-C_{16}, C_{14}-C_{16}, C_{14}-C_{18}, C_{16}-C_{20}, C_{22}-C_{28}, and C_{30+} (Gulftene available from the Gulf Oil Company).

[0025] Another class of mono-olefins are those containing a saturated alicyclic ring and one double bond, e.g. an exocyclic double bond. The alicyclic ring preferably contains at least six carbon atoms, and, advantageously, the alicyclic ring is substituted by a methylene bridging group that forms a four-membered ring with three of the ring carbon atoms. The methylene carbon atom in such a bridging group may be substituted, preferably by two methyl groups, e.g. as in β-pinene. Other examples of mono-olefins include α-pinene, methylene cyclohexane, camphene, and methylene cyclopentane etc. and unsaturated compounds such as the various derivatives of acrylic acid such as acrylate, methacrylate and acrylamide derivatives.

[0026] An example of a suitable mono-olefin is the C_{12} tetramer of propylene. Other suitable mono-olefins include oligomers of, for example, ethylene. Typically oligomeric olefins are mixtures; therefore mixtures of oligomeric mono-olefins may be used such as mixtures of propylene oligomers.

[0027] The di-olefins, tri-olefins and higher homologues may be any such olefins which meet the above identified performance requirement for the olefin. Preferred di-olefins, tri-olefins and higher homologues are those selected from:

(a) an acyclic olefin having at least two double bonds, adjacent double bonds being separated by two saturated carbon atoms; or

(b) an olefin comprising an alicyclic ring, which ring comprises at least eight carbon atoms and at least two double bonds, each double bond being separated from the closest adjacent double bond(s) by two saturated carbon atoms.

[0028] The preferred olefins of group (a) are unsubstituted or substituted linear terpenes. Unsubstituted linear terpenes for use in accordance with the invention may be represented by the formula $(C_5H_8)_n$ wherein n is at least 2, that is, a terpene containing carbon and hydrogen atoms only. An example of an unsubstituted linear terpene is squalene (in which n in the above formula is 6). Possible substituents for linear terpenes to be used are, for example, hydroxyl groups. Suitable substituted terpenes include farnasol and geraniol with geraniol being preferred. Other examples of suitable di-olefins include dicyclopentadiene, dipentene, 1,3-cyclohexadiene, 1,5,-cyclooctadiene, methylcyclopentadiene, limonene and 1,4-cyclohexadiene and polybutadiene etc.

[0029] If desired, the group (b) olefins may contain at least three double bonds, each end of each double bond being separated from each adjacent double bond by two saturated carbon atoms. An example of a suitable group (b) olefin having three double bonds is 1,5,9-cyclododecatriene. An example of another tri-olefin is cycloheptatriene.

[0030] The acetylenic compounds are compounds which are capable of reacting with active sulphur and whose properties are such that the excess of such compounds may be removed from the reaction mixture without resulting in significant decomposition of the sulphurized phenol. An example of a suitable acetylene material is phenyl acetylene.

[0031] Olefins are preferred to acetylenic compounds.

[0032] More than one olefin may of course be used if desired. Where two or more olefins are used, these need not be compounds from the same group. Thus, for example, mixtures of mono and diolefins may be used although this is not preferred.

[0033] The olefin or acetylenic compound and active sulphur-containing sulphurized phenol may be added in any order. Thus, for example, the olefin or acetylenic compound may be introduced into a vessel already containing the sulphurized phenol, or vice versa, or the two materials may be introduced simultaneously into the vessel. This process may be carried out in a suitable solvent for the reactants and/or products. This is a solvent which does not cause problems in removal which effect stability of the product. An example of a suitable solvent which may be used is SN150 basestock. In some instances the olefin when used in a sufficient amount may act as a solvent for the reaction.

[0034] The mass ratio of sulphurized phenol to olefin or acetylenic compound is such that the olefin or acetylenic compound is always in excess of that required to react with the active sulphur present in the intermediate. The exact levels will depend on the nature of the olefin or acetylenic compound, i.e. whether or not, for example, it is a mono, di or tri olefin, its molecular weight and the molecular weight of the sulphurized phenol used, its level of sulphur and level of active sulphur. For example, when the olefin is C_{12} propylene tetramer the ratio is preferably in the range 1.3:1 to 9:1.

[0035] It is preferred that the reaction between the sulphurized phenol and the olefin or acetylenic compound is carried out at an elevated temperature of greater that 120°C and, most preferably between 120°C to 250°C, and for 0.5 to 60 hours.

[0036] Substantially all of the unreacted olefin or acetylenic compound should be removed preferably by means of vacuum distillation, post reaction, or other separation methods. The exact method used will depend on the nature of the olefin or acetylenic compound used. In some circumstances the unreacted olefin or acetylenic compound may be removed by simply applying a vacuum to the reaction vessel or may require the use of applied heating to elevate the temperature of the reaction mixture. Preferably the unreacted material is removed by means of vacuum distillation and where necessary with the use of heating. Other material, such as volatile material when vacuum distillation is used, may be removed at the same time as the unreacted olefin or acetylenic compound. By 'substantially all the unreacted olefin or acetylenic compound' is meant that proportion which may be removed by the use of such techniques as, for example, vacuum distillation. Typically there will be less than 3 wt % of unreacted olefin or acetylenic compound remaining in the product and preferably between 0 to 3 wt % and most preferably 0.5 wt % or less. This residual material may comprise as a major proportion the higher molecular weight fractions present in the original olefin composition or mixture used. For example, in the case of the olefin being a propylene tetramer, which is typically a mixture of olefins, residual material after removal of excess olefin may comprise a high proportion of, for example, pentamer and higher homologues of propylene.

[0037] It has been found that removal of substantially all the unreacted olefin or acetylenic compound is required so that lubricating oil compositions comprising olefin or acetylenic compound reacted additives achieve acceptable performance in the Panel Coker test. This is an industry standard bench test which is used to screen additives in lubricating oil formulations to evaluate their efficacy as, for example, antioxidants and/or their ability to prevent deposition of carbonaceous deposits by maintaining such deposits in a dispersed form in the oil. If the excess olefin or acetylenic compound is not removed inferior Panel Coker performance of the oil is observed. This is a particular problem with di-olefins.

[0038] On completion of the reaction between sulphur monochloride and the phenol, the temperature of the reaction mixture is increased to the olefin or acetylenic compound reaction temperature and the reaction carried out. This increase in temperature may be achieved by means of a ramped temperature increase to the reaction temperature. The olefin or acetylenic compound may be added to the intermediate reaction mixture before, during or after the temperature increase.

[0039] A catalyst may be used for the reaction between the olefin or acetylenic compound and the sulphurized phenol. Suitable catalysts include sulphurisation catalysts and nitrogen bases. The preferred catalysts are nitrogen bases. Suitable nitrogen bases include nitrogen-containing ashless dispersants which are commercially available materials such as Mannich bases and the reaction products of hydrocarbyl acylating agents with amines, in particular polyisobutenyl succinimides may be used; these may be prepared by any of the conventional routes. It is preferred to use a polyisobutenyl succinimide in which the polyisobutenyl succinic anhydride is prepared using the so-called thermal process in which polyisobutene is reacted directly with maleic anhydride, without the use of chlorine, before reaction with the amine to produce the final dispersant. Other suitable nitrogen bases include simple amines such as, for example, mono-, di-, and tri-butylamines, polyamines such as, for example, diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA), cyclic amines for example morpholines and aromatic amines such as commercial diphenylamines. A particularly suitable amine is n-octylamine. It has also surprisingly been found that nitrile seal compatibility improves with the use of increasing levels of catalyst to prepare the additives of the present invention.

[0040] The reaction with olefin or acetylenic compound has the benefit of reducing the level of chlorine in sulphurized compounds.

[0041] The sulphurized C_9-C_{15} alkyl substituted phenols are used to prepare the overbased metal phenates by reaction with alkali or alkaline earth metal salts or compounds. The overbased metal phenates may also have low levels of chlorine e.g. less than 1000 ppm. The overbased metal phenates comprise neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased metal phenates may have a TBN (total base number as determined by ASTM D 2896) of 50 or greater, preferably 100 or greater, more preferably 150 or greater, and typically of from 250 to 450 or more. The metals are in particular the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium and mixtures of calcium and/or magnesium with sodium.

[0042] The overbased phenates may include at least one further surfactant such as, for example, a sulphonic acid or an aliphatic carboxylic acid such as, for example, stearic acid.

[0043] Sulphonic acids are typically obtained by sulphonation of hydrocarbyl-substituted, especially alkyl-substituted, aromatic hydrocarbons, for example, those obtained from the fractionation of petroleum by distillation and/or extraction, or by the alkylation of aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, biphenyl or their halogen derivatives, for example, chlorobenzene, chlorotoluene or chloronaphthalene. Alkylation of aromatic hydrocarbons may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 100 carbon atoms, such as, for example, haloparaffins, olefins that may be obtained by dehydrogenation of paraffins, and polyolefins, for example, polymers of ethylene, propylene, and/or butene. The alkylaryl sulphonic acids usually contain from about 7 to about 100 or more carbon atoms. They preferably contain from about 16 to about 80 carbon atoms, or 12 to 40 carbon atoms, per alkyl-substituted aromatic moiety, depending on the source from which they are obtained.

[0044] Another type of sulphonic acid which may be used comprises alkyl phenol sulphonic acids. Such sulphonic acids can be sulphurized. Whether sulphurized or non-sulphurized these sulphonic acids are believed to have surfactant properties comparable to those of sulphonic acids, rather than surfactant properties comparable to those of phenols.

[0045] Sulphonic acids suitable for use also include alkyl sulphonic acids. In such compounds the alkyl group suitably contains 9 to 100 carbon atoms, advantageously 12 to 80 carbon atoms, especially 16 to 60 carbon atoms.

[0046] Carboxylic acids which may be used include mono- and dicarboxylic acids. Preferred monocarboxylic acids are those containing 1 to 30 carbon atoms, especially 8 to 24 carbon atoms. Examples of monocarboxylic acids are iso-octanoic acid, stearic acid, oleic acid, palmitic acid and behenic acid. Iso-octanoic acid may, if desired, be used in the form of the mixture of C_8 acid isomers sold by Exxon Chemical under the trade name "Cekanoic". Other suitable acids are those with tertiary substitution at the α-carbon atom and dicarboxylic acids with more than 2 carbon atoms separating the carboxylic groups. Further, dicarboxylic acids with more than 35 carbon atoms, for example, 36 to 100 carbon atoms, are also suitable. Unsaturated carboxylic acids can be sulphurized.

[0047] In another aspect of the invention, the carboxylic acid/derivative, if used, has 8 to 11 carbon atoms in the carboxylic-containing moiety.

[0048] In a further aspect of the invention, where a carboxylic acid/derivative is used, this is not a monocarboxylic acid/derivative with more than 11 carbon atoms in the carboxylic-containing moiety. In another aspect, the carboxylic acid/derivative is not a dicarboxylic acid/derivative with more than 11 carbon atoms in the carboxylic-containing moiety. In a further aspect, the carboxylic acid/derivative is not a polycarboxylic acid/derivative with more than 11 carbon atoms in the carboxylic-containing moiety. In another aspect, a carboxylic acid surfactant is not a hydrocarbyl-substituted succinic acid or a derivative thereof.

[0049] Examples of other surfactants which may be used include the following compounds, and derivatives thereof: naphthenic acids, especially naphthenic acids containing one or more alkyl groups, dialkylphosphonic acids, dialkylthiophosphonic acids, and dialkyldithiophosphoric acids, high molecular weight (preferably ethoxylated) alcohols, dithiocarbamic acids, thiophosphines, and dispersants. Surfactants of these types are well known to those skilled in the art.

[0050] Metal salts of sulphurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art.

[0051] Examples of suitable overbasing agents are carbon dioxide, a source of boron, for example, boric acid, sulphur dioxide, hydrogen sulphide, and ammonia. Preferred overbasing agents are carbon dioxide or boric acid, or a mixture of the two. The most preferred overbasing agent is carbon dioxide and, for convenience, the treatment with an overbasing agent will in general be referred to as "carbonation". Unless the context clearly requires otherwise, it will be understood that references herein to carbonation include references to treatment with other overbasing agents.

[0052] Advantageously, on completion of the carbonation step, part of the basic calcium compound remains uncarbonated. Advantageously, up to 15 mass % of the basic calcium compound remains uncarbonated, especially up to 11 mass %.

[0053] Carbonation is effected at less than 100°C. Typically the carbonation is effected at at least 15°C, preferably at least 25°C. Advantageously, carbonation is carried out at less than 80°C, more advantageously less than 60°C, preferably at most 50°C, more preferably at most 40°C, and especially at most 35°C. Advantageously, the temperature is maintained substantially constant during the or each carbonation step, with only minor fluctuations. Where there is more than one carbonation step, both or all carbonation steps are preferably carried out at substantially the same temperature, although different temperatures may be used, if desired, provided that each step is carried out at less than 100°C.

[0054] Carbonation may be effected at atmospheric, super-atmospheric or subatmospheric pressures. Preferably, carbonation is carried out at atmospheric pressure.

[0055] Advantageously, there is a first carbonation step that is followed by a "heat-soaking" step in which the mixture is maintained, without addition of any further chemical reagents, in a selected temperature range (or at a selected temperature), which is normally higher than the temperature at which carbonation is effected, for a period before any further processing steps are carried out. The mixture is normally stirred during heat-soaking. Typically, heat-soaking may be carried out for a period of at least 30 minutes, advantageously at least 45 minutes, preferably at least 60 minutes, especially at least 90 minutes. Temperatures at which heat-soaking may be carried out are typically in the range of from 15°C to just below the reflux temperature of the reaction mixture, preferably 25°C to 60°C: the temperature should be such that substantially no materials (for example, solvents) are removed from the system during the heat-soaking step. We have found that heat-soaking has the effect of assisting product stabilization, dissolution of solids, and filtrability.

[0056] Preferably, following the first carbonation step (and the heat-soaking step, if used), a further quantity of basic calcium compound is added to the mixture and the mixture is again carbonated, the second carbonation step advantageously being followed by a heat-soaking step.

[0057] Basic calcium compounds for use in manufacture of the overbased detergents include calcium oxide, hydroxide, alkoxides, and carboxylates. Calcium oxide and, more especially, hydroxide are preferably used. A mixture of basic compounds may be used, if desired.

[0058] The mixture to be overbased by the overbasing agents should normally contain water, and may also contain one or more solvents, promoters or other substances commonly used in overbasing processes.

[0059] Examples of suitable solvents are aromatic solvents, for example, benzene, alkyl-substituted benzenes, for example, toluene or xylene, halogen-substituted benzenes, and lower alcohols (with up to 8 carbon atoms). Preferred solvents are toluene and methanol. The amount of toluene used is advantageously such that the percentage by mass of toluene, based on the calcium overbased detergent (excluding oil) is at least 1.5, preferably at least 15, more preferably at least 45, especially at least 60, more especially at least 90. For practical/economic reasons, the said percentage of toluene is typically at most 1200, advantageously at most 600, preferably at most 500, especially at most 150. The amount of methanol used is advantageously such that the percentage by mass of methanol, based on the calcium detergent (excluding oil) is at least 1.5, preferably at least 15, more preferably at least 30, especially at least 45, more especially at least 50. For practical/economic reasons, the said percentage of methanol (as solvent) is typically at most 800, advantageously at most 400, preferably at most 200, especially at most 100. The above percentages apply whether the toluene and methanol are used together or separately.

[0060] Examples of suitable promoters are lower alcohols (with up to 8 carbon atoms) and water. Preferred promoters for use in accordance with the invention are methanol and water. The amount of methanol used is advantageously such that the percentage by mass of methanol, based on the initial charge of basic calcium compound, for example, calcium hydroxide (that is, excluding any basic calcium compound added in a second or subsequent step) is at least 6, preferably at least 60, more preferably at least 120, especially at least 180, more especially at least 210. For practical/economic reasons, the said percentage of methanol (as promoter) is typically at most 3200, advantageously at most 1600, preferably at most 800, especially at most 400. The amount of water in the initial reaction mixture (prior to treatment with the overbasing agent) is advantageously such that the percentage by mass of water, based on the initial charge of basic calcium compound(s), for example, calcium hydroxide, (that is, excluding any basic calcium compound(s) added in a second or subsequent step) is at least 0.1, preferably at least 1, more preferably at least 3, especially at least 6, more especially at least 12, particularly at least 20. For practical/economic reasons, the said percentage of water is typically at most 320, advantageously at most 160, preferably at most 80, especially at most 40. If reactants used are not anhydrous, the proportion of water in the reaction mixture should take account of any water in the components and also water formed by neutralization of the surfactants. In particular, allowance must be made for any water present in the surfactants themselves.

[0061] Advantageously, the reaction medium comprises methanol, water (at least part of which may be generated during salt formation), and toluene.

[0062] If desired, low molecular weight carboxylic acids (with 1 to about 7 carbon atoms), for example, formic acid, inorganic halides, or ammonium compounds may be used to facilitate carbonation, to improve filtrability, or as viscosity agents for overbased detergents. The process does not, however, require the use of an inorganic halide or ammonium salt catalyst, for example, ammonium salts of lower carboxylic acids or of alcohols, and the overbased detergents produced are thus preferably free from groups derived from such a halide or ammonium catalyst. (Where an inorganic halide or ammonium salt is used in an overbasing process the catalyst will normally be present in the final overbased detergent.)

[0063] Oil-soluble, dissolvable, or stably dispersible as that terminology is used herein does not necessarily indicate that the additives or intermediates are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does 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 or intermediate, if desired.

[0064] The overbased phenates can be incorporated into base oil in any convenient way. Thus, they can be added directly to the oil by dispersing or by dissolving them in the oil at the desired level of concentration, optionally with the aid of a suitable solvent such as, for example, toluene, cyclohexane, or tetrahydrofuran. In some cases blending may be effected at room temperature: in other cases elevated temperatures are advantageous such as up to 100°C.

[0065] Base oils include those suitable for use in marine diesel engines.

[0066] Synthetic base oils include alkyl esters of dicarboxylic acids, polyglycols and alcohols: poly-α-olefins, polybutenes, alkyl benzenes, organic esters of phosphoric acids and polysilicone oils.

[0067] Natural base oils include mineral lubricating oils which may vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, mixed, or paraffinic-naphthenic, as well as to the method used in their production, for example, distillation range, straight run or cracked, hydrorefined, solvent extracted and the like.

[0068] More specifically, natural lubricating oil base stocks which can be used may be straight mineral lubricating oil or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crude oils. Alternatively, if desired, various blended oils may be employed as well as residual oils, particularly those from which asphaltic constituents have been removed. The oils may be refined by any suitable method, for example, using acid, alkali, and/or clay or other agents such, for example, as aluminium chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents, for example, phenol, sulphur dioxide, furfural, dichlorodiethylether, nitrobenzene, or crotonaldehyde.

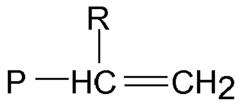
[0069] The lubricating oil base stock conveniently has a viscosity of about 2.5 to about 12 cSt or mm^2/sec and preferably about 3.5 to about 9 cSt or mm^2/sec at 100°C.

[0070] Additional additives may be incorporated into the lubricating oil composition to enable it to meet particular requirements. Examples of additives which may be included in lubricating oil compositions are further detergents, dispersants, anti-wear agents and pour point depressants.

[0071] The ashless dispersants 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.

[0072] 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 C_2 to C_{18} olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C_2 to 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 α,ω-diene, such as a C_3 to 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 oligomer typically having $\overline{M}_n$ of from 700 to 5000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

[0073] One preferred class of olefin polymers is polybutenes and specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a 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. That is, the polymer has the following structure:



$$P-\overset{\substack{R\\|}}{HC}=CH_2$$

wherein P is the polymer chain and R is a C_1-C_{18} alkyl group, typically methyl or ethyl. Preferably the polymers will have at least 50% of the polymer chains with terminal vinylidene unsaturation. EAO copolymers of this type preferably contain 1 to 50 wt% ethylene, and more preferably 5 to 48 wt% ethylene. Such polymers may contain more than one alpha-olefin and may contain one or more C_3 to C_{22} diolefins. Also usable are mixtures of EAO's of varying ethylene content. Different polymer types, e.g. EAO and PIB, may also be mixed or blended, as well as polymers differing in $\overline{M}_n$; components derived from these also may be mixed or blended.

[0074] Suitable olefin polymers and copolymers may be prepared by various catalytic polymerization processes. In one method, hydrocarbon feed streams, typically C_3 - C_5 monomers, are cationically polymerized in the presence of a Lewis acid catalyst and, optionally, a catalytic promoter, e.g., an organoaluminum catalyst such as ethylaluminum dichloride and an optional promoter such as HCl. Most commonly, polyisobutylene polymers are derived from Raffinate I refinery feedstreams. Various reactor configurations can be utilized, e.g. tubular or stirred tank reactors, as well as fixed bed catalyst systems in addition to homogeneous catalysts. Such polymerization processes and catalysts are described, e.g., in US-A 4,935,576; 4,952,739; 4,982,045; and UK-A 2,001,662.

[0075] Conventional Ziegler-Natta polymerization processes may also be employed to provide olefin polymers suitable for use in preparing dispersants and other additives. However, preferred polymers may be prepared by polymerising the appropriate monomers in the presence of a particular type of Ziegler-Natta catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and, preferably, a cocatalyst or an activator, e.g., an alumoxane compound or an ionising ionic activator such as tri (n-butyl) ammonium tetra (pentafluorophenyl) boron.

[0076] Metallocene catalysts are, for example, bulky ligand transition metal compounds of the formula:

$$[L]_mM[A]_n$$

where L is a bulky ligand; A is a leaving group, M is a transition metal and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a 1^+ valency state. The ligands L and A may be bridged to each other, and if two ligands A and/or L are present, they may be bridged. The metallocene compound may be a full sandwich compound having two or more ligands L which may be cyclopentadienyl ligands or cyclopentadienyl derived ligands, or they may be half sandwich compounds having one such ligand L. The ligand may be mono- or polynuclear or any other ligand capable of η-5 bonding to the transition metal.

[0077] One or more of the ligands may π-bond to the transition metal atom, which may be a Group 4, 5 or 6 transition metal and/or a lanthanide or actinide transition metal, with zirconium, titanium and hafnium being particularly preferred.

[0078] The ligands may be substituted or unsubstituted, and mono-, di-, tri, tetra- and penta-substitution of the cyclopentadienyl ring is possible. Optionally the substituent(s) may act as one or more bridge between the ligands and/or leaving groups and/or transition metal. Such bridges typically comprise one or more of a carbon, germanium, silicon, phosphorus or nitrogen atom-containing radical, and preferably the bridge places a one atom link between the entities being bridged, although that atom may and often does carry other substituents.

[0079] The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens.

[0080] Such polymerizations, catalysts, and cocatalysts or activators are described, for example, in US 4,530,914; 4,665,208; 4,808,561; 4,871,705; 4,897,455; 4,937,299; 4,952,716; 5,017,714; 5,055,438; 5,057,475; 5,064,802; 5,096,867; 5,120,867; 5,124,418; 5,153,157; 5,198,401; 5,227,440; 5,241,025; EP-A-129,368; 277,003; 277,004; 420436; 520,732; WO91/04257; 92/00333; 93/08199 and 93/08221; and 94/07928.

[0081] The oil soluble polymeric hydrocarbon backbone will usually have a number average molecular weight ($\overline{M}_n$) within the range of from 300 to 20,000. The $\overline{M}_n$ of the polymer backbone is preferably within the range of 500 to 10,000, more preferably 700 to 5,000, where its use is to prepare a component having the primary function of dispersancy. Polymers of both relatively low molecular weight (e.g. $\overline{M}_n$ = 500 to 1500) and relatively high molecular weight (e.g. $\overline{M}_n$ = 1500 to 5,000 or greater) are useful to make dispersants.

[0082] Particularly useful olefin polymers for use in dispersants have $\overline{M}_n$ within the range of from 1500 to 3000. Where the oil additive component is also intended to have a viscosity modifying effect, it is desirable to use a polymer of higher molecular weight, typically with $\overline{M}_n$ of from 2,000 to 20,000; and if the component is intended to function primarily as a viscosity modifier then the molecular weight may be even higher, e.g., $\overline{M}_n$ of from 20,000 up to 500,000 or greater. Furthermore, the olefin polymers used to prepare dispersants preferably have approximately one double bond per polymer chain, preferably as a terminal double bond.

[0083] Polymer molecular weight, specifically $\overline{M}_n$, can be determined by various known techniques. One convenient method is gel permeation chromatography (GPC), which additionally provides molecular weight distribution information (see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979). Another useful method, particularly for lower molecular weight polymers, is vapour pressure osmometry (see, e.g., ASTM D3592). The oil soluble polymeric hydrocarbon backbone may be functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, halogen, or boron. It can be attached to a saturated hydrocarbon part of the oil soluble polymeric hydrocarbon backbone via substitution reactions or to an olefinic portion via addition or cycloaddition reactions. Alternatively, the functional group can be incorporated into the polymer in conjunction with oxidation or cleavage of the polymer chain end (e.g. as in ozonolysis).

[0084] Useful functionalization reactions include: halogenation of the polymer at an olefinic bond and subsequent reaction of the halogenated polymer with an ethylenically unsaturated functional compound (e.g. maleation where the polymer is reacted with maleic acid or anhydride); reaction of the polymer with an unsaturated functional compound by the "ene" reaction absent halogenation; reaction of the polymer with at least one phenol group (this permits derivatization in a Mannich base-type condensation); reaction of the polymer at a point of unsaturation with carbon monoxide using a Koch-type reaction to introduce a carbonyl group in an iso or neo position; reaction of the polymer with the functionalizing compound by free radical addition using a free radical catalyst; reaction with a thiocarboxylic acid derivative; and reaction of the polymer by air oxidation methods, epoxidation, chloroamination, or ozonolysis. It is preferred that the polymer is not halogenated.

[0085] The functionalized oil soluble polymeric hydrocarbon backbone is then further derivatized with a nucleophilic reactant such as an amine, amino-alcohol, alcohol, metal compound or mixture thereof to form a corresponding derivative.

[0086] Useful amine compounds for derivatizing functionalized polymers comprise at least one amine and can comprise one or more additional amine or other reactive or polar groups. These amines may be hydrocarbyl amines or may be predominantly hydrocarbyl amines in which the hydrocarbyl group includes other groups, e.g. hydroxyl groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Particularly useful amine compounds include mono- and polyamines, e.g. polyalkylene and polyoxyalklene polyamines of about 2 to 60, conveniently 2 to 40 (e.g., 3 to 20), total carbon atoms and about 1 to 12, conveniently 3 to 12, and preferably 3 to 9 nitrogen atoms in the molecule. Mixtures of amine compounds may advantageously be used such as those prepared by reaction of alkylene dihalide with ammonia. Preferred amines are aliphatic saturated amines, including, e.g., 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; and polypropyleneamines such as 1,2-propylene diamine; and di-(1,2-propylene)triamine.

[0087] Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines. A particularly useful class of amines are the polyamido and related amido-amines as disclosed in US 4,857,217; 4,956,107; 4,963,275; and 5,229,022. Also usable is tris(hydroxymethyl)amino methane (THAM) as described in US 4,102,798; 4,113,639; 4,116,876; and UK 989,409. Dendrimers, star-like amines, and comb-structure amines may also be used. Similarly, one may use the condensed amines disclosed in US 5,053,152. The functionalized polymer is reacted with the amine compound according to conventional techniques as described in EP-A 208,560; US 4,234,435 and US 5,229,022 .

[0088] The functionalized oil soluble polymeric hydrocarbon backbones also may be derivatized with hydroxy compounds such as monohydric and polyhydric alcohols or with aromatic compounds such as phenols and naphthols. Polyhydric alcohols are preferred, e.g. alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof. An ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding ashless dispersants comprise the ether-alcohols and including, for example, the oxy-alkylene, oxy-arylene. They are exemplified by ether-alcohols having up to 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms. The ester dispersants may be di-esters of succinic acids or acidic esters, i.e. partially esterified succinic acids; as well as partially esterified polyhydric alcohols or phenols, i.e. esters having free alcohols or phenolic hydroxyl radicals. An ester dispersant may be prepared by one of several known methods as illustrated, for example, in US 3,381,022.

[0089] A preferred group of ashless dispersants includes those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines (e.g. tetraethylene pentamine, pentaethylene (di)pentamine, polyoxypropylene diamine) aminoalcohols such as trismethylolaminomethane and optionally additional reactants such as alcohols and reactive metals, e.g. pentaerythritol, and combinations thereof). Also useful are dispersants wherein a polyamine is attached directly to the long chain aliphatic hydrocarbon as shown in US 3,275,554 and 3,565,804 where a halogen group on a halogenated hydrocarbon is displaced with various alkylene polyamines.

[0090] Another class of ashless dispersants comprises Mannich base condensation products. Generally, these are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compounds (e.g. formaldehyde and paraformaldehyde) and about 0.5 to 2 moles polyalkylene polyamine as disclosed, for example, in US 3,442,808. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon (e.g. $\overline{M}_n$ of 1,500 or greater) on the benzene group or may be reacted with a compound containing such a hydrocarbon, for example, polyalkenyl succinic anhydride, as shown in US 3,442,808.

[0091] Examples of functionalized and/or derivatized olefin polymers based on polymers synthesized using metallocene catalyst systems are described in US 5,128,056; 5,151,204; 5,200,103; 5,225,092; 5,266,223; EP-A-440,506; 513,157; 513,211. The functionalization and/or derivatizations and/or post treatments described in the following patents may also be adapted to functionalize and/or derivatize the preferred polymers described above: US 3,087,936; 3,254,025; 3,275,554; 3,442,808, and 3,565,804.

[0092] The dispersant can be further post-treated by a variety of conventional post treatments such as boration, as generally taught in US 3,087,936 and 3,254,025. This is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from the group consisting of boron oxide, boron halides, boron acids and esters of boron acids, in an amount to provide from about 0.1 atomic proportion of boron for each mole of the acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of the acylated nitrogen composition. Usefully the dispersants contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. %, boron based on the total weight of the borated acyl nitrogen compound. The boron, which appears be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g. the metaborate salt of the diimide. Boration is readily carried out by adding from about 0.05 to 4, e.g. 1 to 3, wt. % (based on the weight of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from 135° to 190° C, e.g. 140°-170° C, for from 1 to 5 hours followed by nitrogen stripping. Alternatively, the boron treatment can be carried out by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine while removing water.

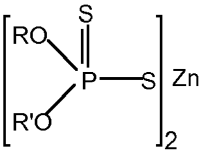
[0093] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralisers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 450 or more.

[0094] Detergents that may be used include oil-soluble neutral and overbased sulphonates, phenates, sulphurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulphonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulphurized phenates having TBN of from 50 to 450.

[0095] Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralising the formed DDPA with a zinc compound. The zinc dihydrocarbyl dithiophosphates can be made from mixed DDPA which in turn may be made from mixed alcohols. Alternatively, multiple zinc dihydrocarbyl dithiophosphates can be made and subsequently mixed.

[0096] Thus the dithiophosphoric acid containing secondary hydrocarbyl groups used in this invention may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralisation reaction.

[0097] The preferred zinc dihydrocarbyl dithiophosphates useful in the present invention are oil soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R and R' may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R' groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R') in the dithiophosphoric acid will generally be about 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. At least 50 (mole) % of the alcohols used to introduce hydrocarbyl groups into the dithiophosphoric acids are secondary alcohols.

[0098] Additional additives are typically incorporated into the compositions of the present invention. Examples of such additives are antioxidants, anti-wear agents, friction modifiers, rust inhibitors, anti-foaming agents, demulsifiers, and pour point depressants.

[0099] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C_8 to C_{18} dialkyl fumarate/vinyl aceteate copolymers and polyalkylmethacrylates.

[0100] Foam control can be provided by many compounds including antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0101] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount which enables the additive to provide its desired function. Representative effective amounts of such additives, when used in a marine diesel lubricant are as follows:

Additive	Mass % a.i.* (Broad)	Mass % a.i.* (Preferred)
Detergent(s)	1-18	3-12
Dispersant(s)	0.5-5	1-3
Anti-wear agent(s)	0.1-1.5	0.5-1.3
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.		

[0102] The components may be incorporated into a base oil in any convenient way. Thus, each of the components can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0103] Preferably all the additives except for the pour point depressant are blended into a concentrate or additive package, that is subsequently blended into basestock to make finished lubricant. Use of such concentrates is conventional. The concentrate will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of base lubricant.

[0104] Preferably the concentrate is made in accordance with the method described in US 4,938,880. That patent describes making a premix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 100°C. Thereafter the pre-mix is cooled to at least 85°C and the additional components are added.

[0105] The final formulations may employ from 2 to 30 mass % and preferably 10 to 25 mass %, typically about 15 to 23 mass % of the concentrate or additive package with the remainder being base oil.

[0106] The invention will now be described by way of illustration only with reference to the following examples. In the examples, unless otherwise noted, all treat rates of all additives are reported as mass percent active ingredient.

Synthesis of Sulphurized Dodecylphenol

Charges:

[0107] Charge weights (g) to make approx. 1 kg of sulphurized dodecylphenol:

Reactor	Charge (g)
Dodecylphenol	1102
Measuring cylinder	
Sulphur monochloride	275
Caustic trap	
Sodium hydroxide (50% aqueous)	800
Water	800
Reactor addition	
Dec-1-ene	202

Heating Profile

Day 1:

[0108]

Start Temp. (°C)	Target Temp. (°C)	Ramp Time (min.)	Dwell Time (min.)
Ambient	60	10	2
60	80	120	90
80	85	30	2
85	110	30	180

Days 2 and 3:

[0109]

Start Temp. (°C)	Target Temp. (°C)	Ramp Time (min.)	Dwell Time (min.)
Ambient	110	40	2
110	175	50	Hold

Method

Day 1

[0110] Sulphur monochloride (SMC) is corrosive and toxic, and therefore the following method of charging was used to minimize the risk of exposure. A charge of SMC, close to the proposed weight, was first poured into a 150 ml beaker and from there to a 100 ml measuring cylinder which had been placed on a balance. The exact weight was recorded from which the dodecylphenol (DDP) charge was calculated. The caustic trap was set up at this stage by charging a 3 litre beaker with sodium hydroxide solution.

[0111] The DDP was then weighed into a 1 litre baffled flask. The flask was set up for reflux and heated to 60°C under a nitrogen blanket using the above profile. At 60°C the sulphur monochloride addition was started via a peristaltic pump over 4 hours using two 16 gauge flat ended stainless steel needles joined by viton tubing. The weight loss over time was noted varying the addition rate as necessary. During this time, while the temperature was allowed to follow the programmed ramp given above, the stirrer was adjusted to keep the mixture stirring briskly. The mixture thickened during addition; stirring was started at approx. 270 rpm and had been increased to 500 rpm by the end of addition.

[0112] At the end of addition the stainless needle and septum were removed, a nitrogen sparge was placed in the vessel and nitrogen bubbled through the mixture at 200 ml min^{-1}. The temperature was ramped to 110°C following the profile and then the mixture was held at 110°C for 3 hours. The stirrer was turned down to 240 rpm at 110°C because the mixture became much thinner.

[0113] Finally the heating was stopped, the funnel to the trap raised out of the solution, the mixture air-cooled to below 60°C (raising the sparge out of the solution at 85 °C) and the nitrogen flow stopped. It was left standing overnight.

Day 2:

[0114] Nitrogen sparge and stirring were restarted as before. The viscous mixture was heated gently until mechanical stirring could be switched on. The prep was then heated to 110°C in 40 minutes. At 110°C decene was added (17% of estimated sulphurized DDP) and the mixture was heated to 175°C in a further 50 minutes.

[0115] The prep was held at 175°C for up to 6 hours until the required UV ratio (see below) was reached and then the heating was switched off but stirring and nitrogen were continued until the prep had cooled below 60°C. The prep was then switched off.

[0116] UV ratio: The UV ratio of absorbances at 291:325 nm was measured on sulphurized DDP samples to determine the extent of polysulphide breakdown from the initial reaction. The peak at 325 nm was expected to diminish during a successful desulphurization to produce a final ratio exceeding 3.0.

Day 3:

[0117] The caustic trap was removed and the flask set up for distillation. Nitrogen blanket and stirring were started and the prep heated to 175°C using the same profile as in Day 2. The mixture was much thinner that on day 2 due to the decene addition and stirring could be started immediately. At 175°C high vacuum was applied and held for 2 hours. At the end of 2 hours the heating was switched off and the prep cooled to below 60°C under vacuum with stirring and nitrogen still on. Once below 60°C the prep was switched off. In the case of A (see Table below) the sulphurized DDP was then used as such. In the case of B (see Table below) the product obtained was blended with SN 150 oil (14%) at 60°C for 1 hr.

Synthesis of Overbased Phenates

Examples A (Phenate / Stearate) and B (Phenate / Sulphonate / Stearate)

Charges:

[0118]

	Mass (g)	
Reactor	**Example A**	**Example B**
Toluene	695	632
Methanol	397	361
Water	26	24
Oil, SN 150	30	30
Sulphurized dodecylphenol	622	
Sulphurized dodecylphenol		457
Alkylbenzene sulphonic acid (Mol. Wt. approx. 660, active matter 83%)	0	39
Reactor Additions		
Calcium hydroxide	212	195
Carbon dioxide	65	66
Oil, SN 150 (second oil charge)	144	178
Stearic Acid	93	84
Centrifuge addition		
Toluene (further toluene charge)	1072	431

Heating Profile:

[0119]

Start Temp	**Final Temp**	**Ramp Time**	**Dwell Time**
(°C)	(°C)	(min.)	(min.)
Ambient	40	10	2
40	28	10	2
28	60	60	2

(continued)

Start Temp	Final Temp	Ramp Time	Dwell Time
(°C)	(°C)	(min.)	(min.)
60	65	15	-
65	70	90	-
70	75	15	-
75	110	50	-
110	120	15	Hold

Method:

[0120] The toluene, methanol, water and initial oil were weighed into a 2 litre reaction vessel. The vessel was set up for reflux and heated to 40°C using the above heating profile. The mixture was stirred at 200 rpm. Calcium hydroxide was added at 33°C. At 40°C stirring was increased to 400 rpm and the sulphurized dodecylphenol (and alkylbenzene sulphonic acid, if required) were run in over a period of approx. 25 minutes. The prep was then cooled back to 28°C.

[0121] At 28°C carbonation was started at a rate of approx. 150 ml min-1. Carbonation time was 180 minutes.

[0122] Heat soak: after carbonation the mixture was ramped from 28°C to 60°C using the above profile. The stearic acid was added at 60°C at the end of the heat soak. After adding the stearic acid the reaction vessel was rearranged for distillation and a blanket of nitrogen was applied. The mixture was stripped according to the above profile. The second oil charge was added at 120°C.

[0123] Centrifugation: The product was decanted into a 3 litre beaker and weighed. A further toluene charge was added to the beaker and stirred. The mixture was transferred into centrifuge cans and spun in a centrifuge at 2500 rpm for 30 min. After spinning the mixtures were decanted to be stripped on a rotary evaporator.

[0124] Rotary Evaporator Strip: The oil bath was pre-heated to 160°C and was maintained at this temperature ± 10°C. An empty 2 litre pear shaped flask was placed on the rotovap, spun briskly and a vacuum of approx. 400 mbar was applied. The supernatant liquid was then bled in slowly over approx. 40 min. and the solvent allowed to flash off. After all the mixture had been added the vacuum was increased to full vacuum and maintained for 1 hour. After 1 hour the vacuum was released and the product was cooled.

[0125] The overbased detergent produced had the following characteristics:

	Example A	Example B	Comparative Example-OLOA 219*
TBN	258	258	250
Unsulphurized alkyl phenol and its unsulphurized calcium salt, mass%	5.58	3.84	6.15
* OLOA 219 is a commercially available 250 BN calcium phenate.			

[0126] The detergents in the table above were tested for their rates of neutralization using the following test method:

Acid Neutralisation Rig Method

[0127] A 100ml two neck round bottom flask was fitted with a digital manometer (Digitron model 2083) and an injection port consisting of a glass tap and quick fit adapter. The flask was charged with 30 g of sample (to 0.1 mg) and a magnetic stirrer added. The flask was placed in an oil bath at 40°C ± 1 °C and the sample was allowed to reach equilibrium. 0.182 g of 18M sulphuric acid was charged to a syringe and injected into the flask via the injection port and the pressure of the CO_2 gas evolved was recorded as a function of time. The results are shown in the table below and also in the attached graph.

[0128] The amount of dodecyl phenol (DDP) and its calcium salt was measured as follows:

Method for Analysis of (Ca) DDP content

[0129] The determination of dodecyl phenol (DDP) and its calcium salt content was done by reverse phase HPLC using a u.v. detector. Alkylphenol species were differently eluted within ten minutes. The remaining sample impurities were washed out from the column with pure methanol. A series of four calibration standards were prepared by dissolving known amounts of reference DDP in the mobile phase (84% methanol-16% water), concentrations were selected according to the most appropriate range of detector response factor and linearity. Analyses of test specimens were carried out within the calibration range of response. About 0.3g of sample solution was dissolved in about 3g of dichloromethane (AR grade). The solution was gently agitated. A 20ml volumetric flask was half filled with the mobile phase and into this, about 2.6g of the dichloromethane solution was directly weighed (to nearest 0.1 mg). The sample was homogenised by agitation or by sonication in a water bath for 2 minutes. The flask was diluted to volume with mobile phase and then, by means of a 5 mL plastic syringe and a 0.45 μm disposable cellulose acetate filter, the sample was filtered directly into the HPLC vial. The sample and calibration solutions were chromotographed using the HPLC conditions below. Integration of the peaks was carried out between 4 and 9 minutes, the baseline being flat (the slope being less than 5%) with no drift of the u.v. detector. The reference point for the baseline was taken at 9 minutes. A linear calibration curve was generated by plotting the integrated areas of the standards against the amount of DDP used to prepare the standards. This calibration curve was used to determine the content of DDP and its calcium salt by combined mass% in the sample.

[0130] The HPLC was run with the following conditions:
Column: C8(2) 150 mm X 4,6 mm, 5 μm particles size (Luna 100A Phenomex column or equivalent);
Flow rate: 1.2 mL/min;
Mobile phase: methanol 84% and water 16%;
Typical injection volume: 5 μl;
Total run time: 38 min;

0- 10 min	84% methanol - 16% water;
10.10 - 20.00 min	100% methanol (column wash);
20.10 - 38.00 min	84% methanol - 16% water;

Temperature of the column compartment: 40°C;
UV detector settings: Wavelength: 230 nm (reference at 360 nm for DAD systems).

	Example 1	**Example 2**	**Example 3**	**Comparative Example 4**
Example A	8.00		16.00	
Example B		16.00		
OLOA 219				16.00
425 BN Calcium Sulphonate, Infineum M7117	7.10	7.10	7.10	7.10
ExxonMobil SN600	64.90	56.90	56.90	56.90
ExxonMobil BS 2500	20.00	20.00	20.00	20.00
TBN	50	70	70	70
VK @ 40°C	180.2	196.6	211.8	209.7

Acid Neutralization Testing, CO_2 pressure changes				
Time, minutes	**Example 1**	**Example 2**	**Example 3**	**Comparative Example 4**
0	0	0	0	0
1	28.0	26.5	27.0	10.8
2	35.0	29.8	27.8	12.5
3	38.7	32.0	29.2	13.3
4	41.7	34.3	31.0	13.5
5	45.0	36.0	32.0	13.5

(continued)

Acid Neutralization Testing, CO_2 pressure changes				
Time, minutes	**Example 1**	**Example 2**	**Example 3**	**Comparative Example 4**
6	47.0	37.0	33.0	13.8
7	49.0	38.3	33.8	13.8
8	50.3	39.8	35.0	14.0
9	51.7	41.0	35.4	14.3
10	53.2	41.8	35.6	14.3
11	53.7	42.3	35.8	14.5
12	54.3	42.5	36.2	14.0
13	55.7	42.8	36.4	14.5
14	56.7	42.5	36.0	14.3
15	57.0	43.5	36.0	14.5
16	56.7	43.8	36.0	14.0
17	57.3	44.5	36.0	14.0
18	57.7	44.0	35.8	13.8
19	57.7	43.8	35.8	14.0
20	57.7	43.8	35.8	14.3

[0131] The results above show that the use of an overbased sulphurized metal phenate including less than 6.0% by mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt unexpectedly produces a higher rate of acid neutralization than the use of an overbased sulphurized metal phenate including more than 6.0% by mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

Claims

1. A lubricating oil composition including at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the detergent including less than 6.0% by combined mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

2. The composition as claimed in any one of the preceding claims, wherein the sulphurized overbased metal phenate detergent is prepared from a C_{10}-C_{13} alkyl phenol.

3. The composition as claimed in any one of the preceding claims, wherein the sulphurized overbased metal phenate detergent also includes at least one further surfactant selected from a sulphonic acid or a carboxylic acid.

4. The composition as claimed in claim 3, wherein the sulphurized overbased metal phenate detergent also includes stearic acid as a further surfactant.

5. The composition as claimed in any one of the preceding claims, wherein the sulphurizing agent is sulphur monochloride.

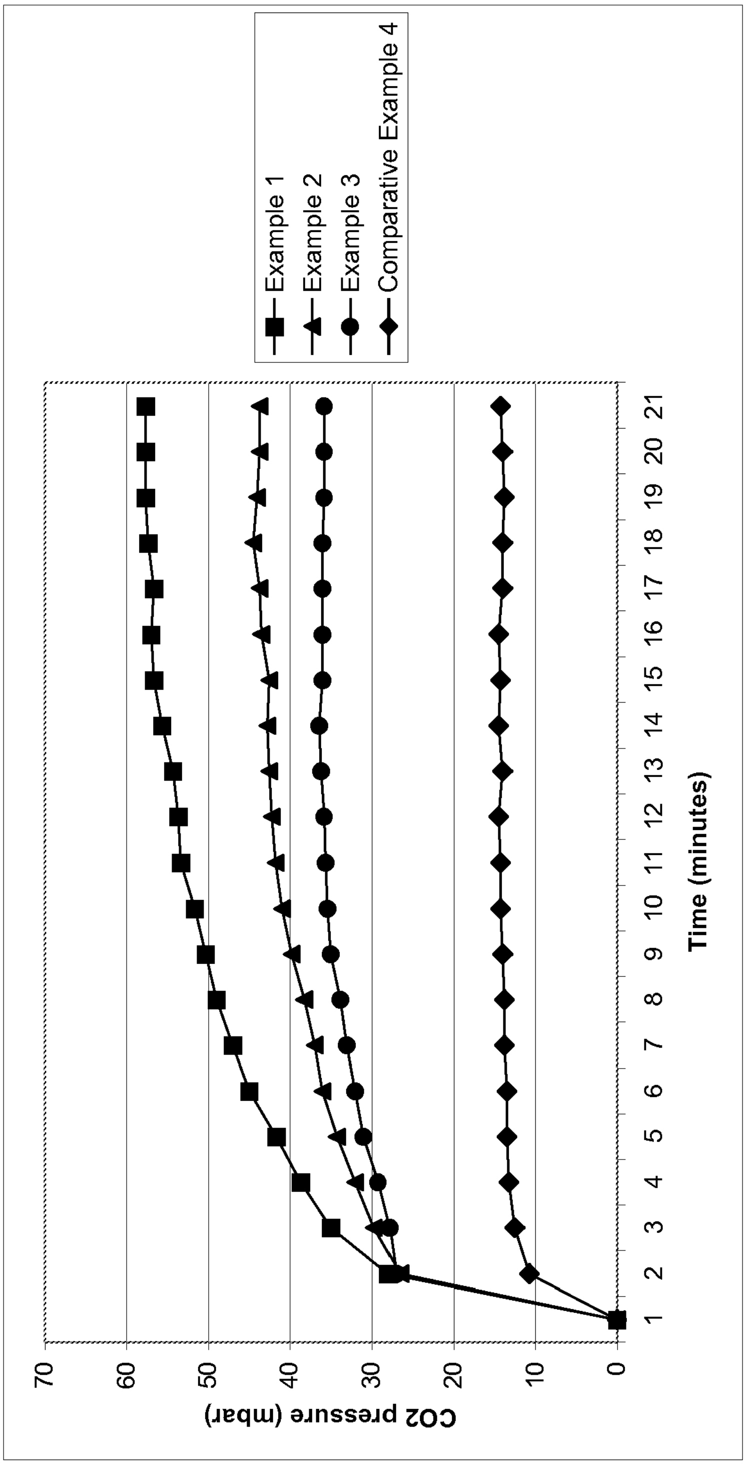
6. The composition as claimed in any one of the preceding claims, wherein the metal is calcium.

7. The composition as claimed in any one of the preceding claims, wherein the overbased metal phenate detergent has been prepared using a carbonation temperature of less than 100°C, preferably less than 80°C.

8. The composition as claimed in any one of the preceding claims, wherein the overbasing agent is carbon dioxide.

9. Use to increase the rate of acid neutralization of a lubricating oil composition of at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the sulphurized overbased metal phenate detergent including less than 6.0% by combined mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.

10. A method of increasing the rate of acid neutralization of a lubricating oil composition, the method including the step of adding to the lubricating oil composition at least one sulphurized overbased metal phenate detergent prepared from a C_9-C_{15} alkyl phenol, at least one sulphurizing agent, at least one metal and at least one overbasing agent; the sulphurized overbased metal phenate detergent including less than 6.0% by combined mass of unsulphurized C_9-C_{15} alkyl phenol and its unsulphurized metal salt.


CO2 pressure (mbar)
70
60
50
40
30
20
10
0
Time (minutes)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
Example 1
Example 2
Example 3
Comparative Example 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 11 3742

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 5 024 773 A (LISTON THOMAS V [US]) 18 June 1991 (1991-06-18) * column 3, line 43 - column 4, line 12 * * column 4, line 30 - column 5, line 22; examples; tables IV,VII * -----	1-3,5-10	INV. C10M159/22 ADD. C10N30/04 C10N40/25 C10N70/00
X	EP 0 989 178 A1 (COSMO SOGO KENKYUSHO KK [JP]; COSMO OIL CO LTD [JP]) 29 March 2000 (2000-03-29) * paragraphs [0004], [0016], [0026]; examples * -----	1-4,6-10	
X	US 4 123 371 A (HORI TAKASHI ET AL) 31 October 1978 (1978-10-31) * column 3, lines 19-50; examples * * column 4, line 32; claims * -----	1,2,6-10	
A	EP 0 094 814 A2 (EXXON RESEARCH ENGINEERING CO [US]) 23 November 1983 (1983-11-23) * page 1, lines 2-17; claims; examples * * page 5, line 16 - page 8, line 3 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	17 January 2008	Kazemi, Pirjo

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

2

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 07 11 3742

17-01-2008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5024773 A	18-06-1991	NONE	
EP 0989178 A1	29-03-2000	WO 9850500 A1	12-11-1998
US 4123371 A	31-10-1978	FR 2376159 A1	28-07-1978
		GB 1599310 A	30-09-1981
		JP 1303226 C	28-02-1986
		JP 54041829 A	03-04-1979
		JP 60028878 B	06-07-1985
		SU 888816 A3	07-12-1981
EP 0094814 A2	23-11-1983	BR 8302526 A	17-01-1984
		CA 1207313 A1	08-07-1986
		DE 3379663 D1	24-05-1989
		JP 7103390 B	08-11-1995
		JP 58225197 A	27-12-1983
		JP 5194977 A	03-08-1993
		JP 7021152 B	08-03-1995
		US 5069804 A	03-12-1991

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0839894 A **[0003]**
- EP 1051467 B **[0004]**
- EP 490454 A **[0072]**
- US 4935576 A **[0074]**
- US 4952739 A **[0074]**
- US 4982045 A **[0074]**
- GB 2001662 A **[0074]**
- US 4530914 A **[0080]**
- US 4665208 A **[0080]**
- US 4808561 A **[0080]**
- US 4871705 A **[0080]**
- US 4897455 A **[0080]**
- US 4937299 A **[0080]**
- US 4952716 A **[0080]**
- US 5017714 A **[0080]**
- US 5055438 A **[0080]**
- US 5057475 A **[0080]**
- US 5064802 A **[0080]**
- US 5096867 A **[0080]**
- US 5120867 A **[0080]**
- US 5124418 A **[0080]**
- US 5153157 A **[0080]**
- US 5198401 A **[0080]**
- US 5227440 A **[0080]**
- US 5241025 A **[0080]**
- EP 129368 A **[0080]**
- EP 277003 A **[0080]**
- EP 277004 A **[0080]**
- EP 420436 A **[0080]**
- EP 520732 A **[0080]**
- WO 9104257 A **[0080]**
- WO 9200333 A **[0080]**
- WO 9308199 A **[0080]**
- WO 9308221 A **[0080]**
- WO 9407928 A **[0080]**
- US 4857217 A **[0087]**
- US 4956107 A **[0087]**
- US 4963275 A **[0087]**
- US 5229022 A **[0087] [0087]**
- US 4102798 A **[0087]**
- US 4113639 A **[0087]**
- US 4116876 A **[0087]**
- GB 989409 A **[0087]**
- US 5053152 A **[0087]**
- EP 208560 A **[0087]**
- US 4234435 A **[0087]**
- US 3381022 A **[0088]**
- US 3275554 A **[0089] [0091]**
- US 3565804 A **[0089] [0091]**
- US 3442808 A **[0090] [0090] [0091]**
- US 5128056 A **[0091]**
- US 5151204 A **[0091]**
- US 5200103 A **[0091]**
- US 5225092 A **[0091]**
- US 5266223 A **[0091]**
- EP 440506 A **[0091]**
- EP 513157 A **[0091]**
- EP 513211 A **[0091]**
- US 3087936 A **[0091] [0092]**
- US 3254025 A **[0091] [0092]**
- US 4938880 A **[0104]**

Non-patent literature cited in the description

- **W. W. YAU ; J. J. KIRKLAND ; D. D. BLY.** Modern Size Exclusion Liquid Chromatography. John Wiley and Sons, 1979 **[0083]**