#### EP 2 607 462 A1 (11)

(12)

# **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

26.06.2013 Bulletin 2013/26

(21) Application number: 12196639.4

(22) Date of filing: 12.12.2012

(51) Int Cl.:

C10M 143/06 (2006.01) C10N 20/04 (2006.01) C10N 40/25 (2006.01)

C10N 20/02 (2006.01) C10N 30/04 (2006.01)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

**Designated Extension States:** 

**BA ME** 

(30) Priority: 20.12.2011 EP 11194522

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

(72) Inventors:

Doan, Minh Abingdon, Oxfordshire OX13 6BB (GB)

**Garner, Terence** Abingdon, OXfordshire OX13 6BB (GB)

(74) Representative: Lewis, Pauline Therese et al

PO Box 1 Milton Hill **Abingdon** 

Oxfordshire OX13 6BB (GB)

(54)Marine engine lubrication

(57)Polyisobutylene of 400 - 8,000 molecular weight and 50 - 50,000 mm<sup>2</sup>/sec kinematic viscosity at 100°C, when used as an additive at 1 - 25 mass % in a trunk piston diesel engine lubricant composition, reduces de-

posit formation in a centrifuge of a trunk piston diesel engine when the composition lubricates the engine during operation.

EP 2 607 462 A1

#### Description

10

15

20

30

40

45

50

55

#### **FIELD OF THE INVENTION**

<sup>5</sup> **[0001]** This invention concerns reducing deposit formation in a centrifuge system in a trunk piston diesel engine.

#### **BACKGROUND OF THE INVENTION**

**[0002]** Trunk piston diesel engines are used in marine, power generation and rail traction applications and may have a rated speed of between 300 and 1000 rpm. In trunk piston diesel engines, a single lubricant composition is used for crankcase and cylinder lubrication. All major moving parts of the engine, i.e. the main and big end bearings, camshaft and valve gear, are lubricated by a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation system which finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin.

[0003] Trunk piston diesel engines use a centrifuge system to remove contaminants such as, for example, soot or water, from the lubricant composition. The centrifuge system relies on the use of a sealing medium that is heavier than the lubricant. The sealing medium is generally water. When the lubricant composition passes through the centrifuge system, it comes into contact with the water. The lubricant therefore needs to be capable of shedding the water and remaining stable in the presence of water. If the lubricant is unable to shed the water, the water builds up in the lubricant forming an emulsion, which leads to deposits building up in the centrifuge system and prevents the centrifuge system from working properly. The centrifuge system normally operates at temperatures of less than 100°C, such as less than 95°C, e.g. around 90°C.

**[0004]** Traditional trunk piston diesel engine lubricant compositions have a total base number of 30-40. However, the recent development of trunk piston diesel engines having very low oil consumption has resulted in lubricant formulators increasing the total base number up to, for example, 50-60. Unfortunately, this increase in total base number affects the ability of the lubricant composition to shed any contamination with the sealing medium used in the centrifuge systems, resulting in deposits building up in the centrifuge system.

[0005] The aim of the present invention is to provide for the reduction of deposit formation in a centrifuge system in a trunk piston diesel engine.

**[0006]** US-A-2008/0287329 Al ("'329") describes a lubricant oil for a marine four-stroke engine that includes 1 to 20 % by weight of at least one polyisobutylene. '329 states that the increase of viscosity of such lubricant oils is slowed down. However, '329 makes no mention of the above-mentioned deposit formation problem in the centrifuge of trunk piston engines.

# 35 SUMMARY OF THE INVENTION

[0007] It is now found that a polyisobutylene additive in a trunk piston engine oil lubricant enables the above deposit formation to be overcome.

**[0008]** Thus, the present invention provides the use of a polyisobutylene of number-average molecular weight in the range of 400 to 8000, such as 1,300 to 2,225, and having a kinematic viscosity at 100°C in the range of 50 to 50,000, such as 630 to 2,500, mm<sup>2</sup>/sec, as an additive constituting 1-25 mass % of a trunk piston diesel engine lubricant composition to reduce deposit formation in a centrifuge in a trunk piston diesel engine when the composition is lubricating the engine during its operation.

**[0009]** Preferably, the trunk piston diesel engine lubricant composition contains little or no brightstock. Preferably, the trunk piston diesel engine lubricant composition is substantially free of brightstock. Even more preferably, the trunk piston diesel engine lubricant composition contains no brightstock.

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

"active ingredients" or "(a.i.)" refers to additive material that is not diluent or solvent;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof; the expressions "consists of" or "consists essentially of" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

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

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

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

5 **[0011]** Furthermore in this specification, if and when used:

"calcium content" is as measured by ASTM 4951;

"phosphorus content" is as measured by ASTM D5185;

"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;

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

**[0012]** Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0013] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

# **DETAILED DESCRIPTION OF THE INVENTION**

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

#### **OIL OF LUBRICATING VISCOSITY**

10

15

20

25

30

35

40

45

50

55

**[0015]** The lubricant of composition contains a major proportion of an oil of lubricating viscosity. Such lubricating oils may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40, such as 3 to 15, mm²/sec, as measured at 100°C, and a viscosity index of 80 to 100, such as 90 to 95. The lubricating oil may comprise greater than 60, typically greater than 70. mass % of the composition.

**[0016]** The oil may include 'brightstock' which refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at 100°C of from 28 to 36 mm<sup>2</sup>s<sup>-1</sup>. It is, however, preferred that little or no brightstock is included, for example less than 5, 4, 3, 2 or 1 mass %, based on the mass of the composition. Brightstock may be completely or substantially absent.

**[0017]** Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

**[0018]** Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkybenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivative, analogues and homologues thereof.

**[0019]** Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters and C<sub>13</sub> oxo acid diester of tetraethylene glycol.

[0020] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with

two moles oftetraethylene glycol and two moles of 2-ethylhexanoic acid.

**[0021]** Esters useful as synthetic oils also include those made from  $C_5$  to  $C_{12}$  monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0022] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

**[0023]** Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment are unrefined oils.

#### POLYISOBUTYLENE

15

30

40

45

50

**[0024]** The polyisobutylene additive may be present in the following proportions: 1 to 20, or 1 to 15, such as 1-10, such as 1-6, such as 1-5, such as 1-4 mass percent.

**[0025]** As mentioned above, the polyisobutylene has a number-average weight in the range of 400 to 8,000, such as 1,300 to 2,225. Among other ranges that may be used, the following may be mentioned: 900 - 3,000, 1,000 - 8,000, 1,500 - 6,000 and 2,000 - 5,000, and also a lower limit of 500.

**[0026]** Also, the polyisobutylene has a kinematic viscosity at 100°C in the range of 50 to 50,000, such as 630 to 2,500, mm²/sec. Among other ranges that may be used, the following may be mentioned: 2,000 - 6,000, 2,000 - 5,000, and 3,000 - 4,500, mm²/stc. Polyisobutylene also embraces mixtures of several polyisobutylenes, synthesised separately and possibly having molecular weights outside the ranges of values indicated above, provided that the mixture of the various polyisobutylenes has a molecular weight lying within said ranges.

[0027] Polyisobutylene is commercially available.

#### **CO-ADDITIVES**

[0028] One or more of the following may also be indicated in the composition.

# **Detergents**

[0029] A detergent is an additive that reduces formation of deposits, for example, high-temperature varnish and lacquer deposits, in engines; it has acid-neutralising properties and is capable of keeping finely divided solids in suspension. It is based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

**[0030]** A detergent comprises a polar head with a long hydrophobic tail. Large amounts of a metal base are included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle.

[0031] The detergent is preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a surfactant selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing is provided by an oil-insoluble salt of the metal, e.g. carbonate, basic carbonate, acetate, formate, hydroxide or oxalate, which is stabilised by the oil-soluble salt of the surfactant. The metal of the oil-soluble surfactant salt may be the same or different from that of the metal of the oil-insoluble salt. Preferably the metal, whether the metal of the oil-soluble or oil-insoluble salt, is calcium.

**[0032]** The TBN of the detergent may be low, i.e. less than 50 mg KOH/g, medium, i.e. 50-150 mg KOH/g, or high, i.e. over 150 mg KOH/g, as determined by ASTM D2896. Preferably the TBN is medium or high, i.e. more than 50 TBN. More preferably, the TBN is at least 60, more preferably at least 100, more preferably at least 150, and up to 500, such as up to 350 mg KOH/g, as determined by ASTM D2896.

[0033] Surfactants for the surfactant system of the overbased detergent preferably contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impart

the desired oil-so lubility.

10

15

20

25

30

35

40

45

50

55

**[0034]** Phenols, for use in preparing the detergents may be non-sulphurized or, preferably, sulphurized. Further, the term "phenol" as used herein includes phenols containing more than one hydroxyl group (for example, alkyl catechols) or fused aromatic rings (for example, alkyl naphthols) and phenols which have been modified by chemical reaction, for example, alkylene-bridged phenols and Mannich base-condensed phenols; and saligenin-type phenols (produced by the reaction of a phenol and an aldehyde under basic conditions).

[0035] Preferred phenols may be derived from the formula

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

[0036] The phenols are frequently used in sulphurized form. Sulphurized hydrocarbyl phenols may typically be represented by the formula:

$$S_x$$
  $OH$   $OH$   $R_y$   $R_y$ 

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

**[0037]** In the above formulae, hydrocarbyl groups represented by R are advantageously alkyl groups, which advantageously contain 5 to 100, preferably 5 to 40, especially 9 to 12, carbon atoms, the average number of carbon atoms in all of the R groups being at least 9 in order to ensure adequate solubility in oil. Preferred alkyl groups are nonyl (tripropylene) groups.

[0038] In the following discussion, hydrocarbyl-substituted phenols will for convenience be referred to as alkyl phenols. [0039] A sulphurizing agent for use in preparing a sulphurized phenol or phenate may be any compound or element which introduces  $-(S)_{x}$ - bridging groups between the alkyl phenol monomer groups, wherein x is generally from 1 to about 4. Thus, the reaction may be conducted with elemental sulphur or a halide thereof, for example, sulphur dichloride or, more preferably, sulphur monochloride. If elemental sulphur is used, the sulphurization reaction may be effected by heating the alkyl phenol compound at from 50 to 250, preferably at least 100, °C. The use of elemental sulphur will typically yield a mixture of bridging groups  $-(S)_{x}$ - as described above. If a sulphur halide is used, the sulphurization reaction may be effected by treating the alkyl phenol at from -10 to 120, preferably at least 60, °C. The reaction may be conducted in the presence of a suitable diluent. The diluent advantageously comprises a substantially inert organic diluent, for example mineral oil or an alkane. In any event, the reaction is conducted for a period of time sufficient to effect substantial reaction. It is generally preferred to employ from 0.1 to 5 moles of the alkyl phenol material per equivalent of sulphurizing agent.

**[0040]** Where elemental sulphur is used as the sulphurizing agent, it may be desirable to use a basic catalyst, for example, sodium hydroxide or an organic amine, preferably a heterocyclic amine (e.g., morpholine).

[0041] Details of sulphurization processes are well known to those skilled in the art.

**[0042]** Regardless of the manner in which they are prepared, sulphurized alkyl phenols useful in preparing overbased detergents generally comprise diluent and unreacted alkyl phenols and generally contain from 2 to 20 mass %, preferably 4 to 14 mass %, and most preferably 6 to 12 mass%, sulphur based on the mass of the sulphurized alkyl phenol.

**[0043]** As indicated above, the term "phenol" as used herein includes phenols that have been modified by chemical reaction with, for example, an aldehyde, and Mannich base-condensed phenols.

**[0044]** Aldehydes with which phenols may be modified include, for example, formaldehyde, propionaldehyde and butyraldehyde. The preferred aldehyde is formaldehyde. Aldehyde-modified phenols suitable for use are described in,

for example, US-A-5 259 967.

10

20

30

35

40

45

50

55

[0045] Mannich base-condensed phenols are prepared by the reaction of a phenol, an aldehyde and an amine. Examples of suitable Mannich base-condensed phenols are described in GB-A-2 121 432.

[0046] In general, the phenols may include substituents other than those mentioned above provided that such substituents do not detract significantly from the surfactant properties of the phenols. Examples of such substituents are methoxy groups and halogen atoms.

[0047] Salicylic acids used in accordance with the invention may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents, for example, as discussed above for phenols. Processes similar to those described above may also be used for sulphurizing a hydrocarbyl-substituted salicylic acid, and are well known to those skilled in the art. Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. [0048] Preferred substituents in oil-soluble salicylic acids from which overbased detergents in accordance with the invention may be derived are the substituents represented by R in the above discussion of phenols. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms. [0049] Sulphonic acids used in accordance with the invention 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 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 7 to 100 or more carbon atoms. They preferably contain from 16 to 80, or 12 to 40, carbon atoms per alkyl-substituted aromatic moiety, depending on the source from which they are obtained.

[0050] When neutralizing these alkylaryl sulphonic acids to provide sulphonates, hydrocarbon solvents and/or diluent oils may also be included in the reaction mixture, as well as promoters and viscosity control agents.

[0051] Another type of sulphonic acid that may be used in accordance with the invention 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.

[0052] Sulphonic acids suitable for use in accordance with the invention also include alkyl sulphonic acids, such as alkenyl sulphonic acids. In such compounds the alkyl group suitably contains 9 to 100, advantageously 12 to 80, especially 16 to 60, carbon atoms.

[0053] Carboxylic acids that may be used in accordance with the invention include mono- and dicarboxylic acids. Preferred monocarboxylic acids are those containing 1 to 30, especially 8 to 24, carbon atoms. (Where this specification indicates the number of carbon atoms in a carboxylic acid, the carbon atom(s) in the carboxylic group(s) is/are included in that number.) 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 Chemicals under the trade name "Cekanoic". Other suitable acids are those with tertiary substitution at the  $\alpha$ -carbon atom and dicarboxylic acids with more than 2 carbon atoms separating the carboxylic groups. Further, dicarboxylic acids with more than 35, for example, 36 to 100, carbon atoms are also suitable. Unsaturated carboxylic acids can be sulphurized. Although salicylic acids contain a carboxylic group, for the purposes of the present invention they are considered to be a separate group of surfactants, and are not considered to be carboxylic acid surfactants. (Nor, although they contain a hydroxyl group, are they considered to be phenol surfactants.)

[0054] Examples of other surfactants which may be used in accordance with the invention 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. Surfactants of the hydrocarbyl-substituted carboxylalkylene-linked phenol type, or dihydrocarbyl esters of alkylene dicarboxylic acids, the alkylene group being substituted with a hydroxy group and an additional carboxylic acid group, or alkylene-linked polyaromatic molecules, the aromatic moieties whereof comprise at least one hydrocarbyl-substituted phenol and at least one carboxy phenol, may also be suitable for use in the present invention; such surfactants are described in EP-A-708 171.

[0055] Further examples of detergents useful in the present invention are optionally sulphurized alkaline earth metal hydrocarbyl phenates that have been modified by carboxylic acids such as stearic acid, for examples as described in EP-A- 271 262 (LZ-Adibis); and phenolates as described in EP-A- 750 659 (Chevron).

[0056] Also suitable for use in the present invention are overbased metal compounds, preferably overbased calcium detergents, that contain at least two surfactant groups, such as phenol, sulphonic acid, carboxylic acid, salicylic acid

and naphthenic acid, that may be obtained by manufacture of a hybrid material in which two or more different surfactant groups are incorporated during the overbasing process.

**[0057]** Examples of hybrid materials are an overbased calcium salt of surfactants phenol and sulphonic acid; an overbased calcium salt of surfactants phenol and carboxylic acid; an overbased calcium salt of surfactants phenol, sulphonic acid and salicylic acid; and an overbased calcium salt of surfactants phenol and salicylic acid.

**[0058]** In the instance where at least two overbased metal compounds are present, any suitable proportions by mass may be used, preferably the mass to mass proportion of any one overbased metal compound to any other metal overbased compound is in the range of from 5:95 to 95:5; such as from 90:10 to 10:90; more preferably from 20:80 to 80:20; especially from 70:30 to 30:70; advantageously from 60:40 to 40:60.

**[0059]** The hybrid detergent preferably includes at least 5 mass% of salicylate, more preferably at least 10 mass% of salicylate. The hybrid detergent preferably includes at least 5 mass% of phenate. The amount of salicylate and phenate in the hybrid detergent can be determined using techniques such as chromatography, spectroscopy and/or titration, well known to persons skilled in the art. The hybrid detergent may also include other surfactants such as sulphonate, sulphurized phenate, thiophosphate, naphthenate, or oil-soluble carboxylate. The hybrid detergent may include at least 5 mass% of sulphonate. The surfactant groups are incorporated during the overbasing process.

[0060] Particular examples of hybrid materials include, for example, those described in WO-A- 97/46643; WO-A-97/46644; WO-A- 97/46645; WO-A- 97/46646; and WO-A- 97/46647.

**[0061]** By an "overbased calcium salt of surfactants" is meant an overbased detergent in which the metal cations of the oil-insoluble metal salt are essentially calcium cations. Small amounts of other cations may be present in the oil-insoluble metal salt, but typically at least 80, more typically at least 90, for example at least 95, mole %, of the cations in the oil-insoluble metal salt, are calcium ions. Cations other than calcium may be derived, for example, from the use in the manufacture of the overbased detergent of a surfactant salt in which the cation is a metal other than calcium. Preferably, the metal salt of the surfactant is also calcium.

**[0062]** Preferably, the TBN of the hybrid detergent is at least 300 mg KOH/g, such as at least 330 mg KOH/g, more preferably at least 350 mg KOH/g, more preferably at least 400 mg KOH/g, most preferably in the range of from 400 to 600 mg KOH/g, such as up to 500 mg KOH/g, as determined by ASTM D2896.

**[0063]** Preferably, the amount of overbased metal detergent in the lubricant is at least 0.5, preferably in the range of from 5 to 50, more preferably from 10 to 50, mass % based on the total amount of the lubricant composition.

**[0064]** The overbased metal detergents may or may not be borated, and typically the boron contributing compound, e.g the metal borate, is considered to form part of the overbasing. The detergent may include both a non-borated detergent and a borated detergent.

**[0065]** The overbased metal detergents preferably have a sulphated ash content (as determined by ASTM D874) of at least 0.85%, more preferably at least 1.0% and even more preferably at least 1.2%.

**[0066]** The detergent or detergents may include phenol as an unreacted component and, if so, the amount of phenol contributes to the total phenol content present in the trunk piston diesel engine lubricant composition. All of the phenol present in the trunk piston diesel engine lubricant composition may come from the detergent or detergents.

[0067] The trunk piston engine oil preferably also includes at least one dispersant, anti-wear additive or anti-oxidant.

### **Dispersants**

10

15

20

30

35

40

45

50

55

**[0068]** The trunk piston diesel engine lubricant composition may include at least one dispersant. A dispersant is an additive for a lubricating composition whose primary function is to improve engine cleanliness.

**[0069]** A noteworthy class of dispersants are "ashless", meaning a non-metallic organic material that forms substantially no ash on combustion, in contrast to metal-containing, hence ash-forming, materials. Ashless dispersants comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g. an O, P or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed.

**[0070]** Examples of ashless dispersants are succinimides, e.g. polyisobutene succinic anhydride; and polyamine condensation products that may be borated or unborated.

**[0071]** If present, the dispersant is preferably present in an amount from 0.5 to 5 mass %, based on the total amount of the lubricant composition.

# Anti-wear Additive

**[0072]** The trunk piston diesel engine lubricant composition may include at least one anti-wear additive. The anti-wear additive may be metallic or non-metallic, preferably the former.

[0073] Dihydrocarbyl dithiophosphate metal salts are examples of the anti-wear additives. The metal in the dihydro-

carbyl dithiophosphate may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. Zinc salts are preferred, preferably in the range of 0.1 to 1.5, preferably 0.5 to 1.3, mass %, based upon the total mass of the lubricating oil composition. They may be prepared in accordance with known techniques by firstly forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with  $P_2S_5$  and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared comprising both hydrocarbyl groups that are entirely secondary and hydrocarbyl groups that are entirely primary. To make the zinc salt, any basic or neutral zinc compound may 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.

**[0074]** The preferred zinc dihydrocarbyl dithiophosphates are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:

 $[(RO) (R^1O) P(S)S]_2 Zn$ 

where R and  $R^1$  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  $R^1$  groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, l-propyl, n-butyl, l-butyl, sec-butyl, amyl, n-hexyl, l-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylehexyl, phenyl, butyl-phenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil-solubility, the total number of carbon atoms (i.e. in R and  $R^1$ ) in the dithiophoshoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

**[0075]** If present, the anti-wear additive is preferably present in an amount from 0.10 to 3.0 mass %, based on the total amount of the lubricant composition.

#### Anti-oxidants

10

15

25

30

35

40

45

50

55

**[0076]** The trunk piston diesel engine lubricant composition may include at least one anti-oxidant. The anti-oxidant may be aminic or phenolic. As examples of amines there may be mentioned secondary aromatic amines such as diarylamines, for example diphenylamines wherein each phenyl group is alkyl-substituted with an alkyl group having 4 to 9 carbon atoms. As examples of anti-oxidants there may be mentioned hindered phenols, including mono-phenols and bis-phenols.

**[0077]** Preferably, the anti-oxidant, if present, is provided in the composition in an amount of up to 3 mass %, based on the total amount of the lubricant composition.

**[0078]** Other additives such as pour point depressants, anti-foamants, metal rust inhibitors, pour point depressants and/or demulsifiers may be provided, if necessary.

**[0079]** The terms 'oil-soluble' or 'oil-dispersable' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

**[0080]** The lubricant compositions of this invention comprise defined individual (i.e. separate) components that may or may not remain the same chemically before and after mixing.

[0081] It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby the additives can be added simultaneously to the oil of lubricating viscosity to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function in the final formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant.

**[0082]** Thus, the additives may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing active ingredients in an amount, based on the additive package, of, for example, from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass % of additives in the appropriate proportions, the remainder being base oil.

[0083] The final formulations may typically contain about 5 to 40 mass % of the additive packages(s), the remainder being base oil.

# **EXAMPLES**

[0084] The present invention is illustrated by, but in no way limited to, the following examples.

## 5 Examples

[0085] The following examples use a centrifuge water shedding test which evaluates the ability of an oil to shed water from a prepared test mixture of oil and water. The test uses an Alfa Laval MAB103B 2.0 centrifuge coupled to a Watson Marlow peristaltic pump. The centrifuge is sealed with 2 litres of water. A measurement is made of the amount of deposits formed in the centrifuge during the test. The test is carried out at 87°C. Pre-measured amounts of water and the test oil are mixed together and then passed through the centrifuge at a rate of 2 litres/min. The test is run for an hour and a half, allowing the mixture to pass through the centrifuge about 10 times. The centrifuge is weighed before and after the test. A poor trunk piston diesel engine lubricant composition will produce a larger amount of deposits in the centrifuge system.

**[0086]** Trunk piston engine oils ('TPEOs') were prepared having TBNs of about 40. The TPEOs were subjected to the centrifuge water shedding test. Details of the TPEOs and the test results are shown below in Table 1.

TABLE 1

	_		
"	U		
٠,	•		

10

15

25

30

35

40

45

55

Reference 1 2 Example Co-Additives (mass %) 16 16 16 Lubricating Oil (mass %) 75.5 82.3 80.94 Brightstock (mass %) 8.5 PIB 2225 (mass %) 1.7 PIB 450 (mass %) 3.06 41.17 40.63 **TBN** 40.46 ۷I 104 105 104 Deposits (g) **Bowl** 4 3 0 0 Hood **Top Disc** 1 0 **Distributor & Disc** 37 4 28 Total Deposits (g) 45 12 33 PIB = Polyisobutylene (number-average molecular weight

**[0087]** The results show that Examples 1 and 2, containing PIB and no brightstock, performed better in the water-shedding test than the Reference Example that contained brightstock, but no PIB.

aiven).

### 50 Claims

- 1. The use of a polyisobutylene of number-average molecular weight in the range of 400 to 8000, such as 1,300 to 2,225, and having a kinematic viscosity at 100°C in the range of 50 to 50,000, such as 630 to 2,500, mm<sup>2</sup>/sec, as an additive constituting 1-25 mass % of a trunk piston diesel engine lubricant composition to reduce deposit formation in a centrifuge in a trunk piston diesel engine when the composition is lubricating the engine during its operation.
- 2. The use as claimed in claim 1 wherein the composition includes less than 0.5 mass% of brightstock, preferably less than 0.1 mass% of brightstock.

3. The use as claimed in claim 1, wherein the composition is substantially free of brightstock.
4. The use as claimed in claim 1 wherein the composition contains no brightstock.

- 5. The use as claimed in claim 1, 2, 3 or 4, wherein the number-average molecular weight of the polyisobutylene is in the range of 900 8,000; or 1000 to 6,000 such as 1,500 5,000, such as 2,000 5,000.
  - **6.** The use as claimed in any of claims 1 5, wherein the kinematic viscosity at 100°C of the polyisobutylene is in the range of 200 6,000; such as 2,000 6,000, such as 2,000 5,000, such as 3,000 4,500, mm<sup>2</sup>/sec.
  - 7. The use as claimed in any of claims 1 5, wherein the TBN of the composition is 30 or greater, such as 35 or greater, such as 45 or greater, such as 50 or greater, such as at most 60 or 70, for example 50 60.



# **EUROPEAN SEARCH REPORT**

Application Number

EP 12 19 6639

	DOCUMENTS CONSIDERE	D TO BE RELEVANT		
Category	Citation of document with indication of relevant passages	on, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Υ	US 2005/119140 A1 (CHAM ET AL) 2 June 2005 (200 * the whole document *		7	INV. C10M143/06
Υ	US 2008/287329 A1 (LANC AL) 20 November 2008 (2 * the whole document *	ON DENIS [FR] ET 1	7	ADD. C10N20/02 C10N20/04 C10N30/04 C10N40/25
A	EP 2 090 642 A1 (INFINE 19 August 2009 (2009-08 * example 1 *		7	C10N40/25
A	EP 1 889 896 A2 (INFINE 20 February 2008 (2008-* claim 13; example 1 *	02-20)	7	
				TECHNICAL EIELDS
				TECHNICAL FIELDS SEARCHED (IPC)
				C10M
	The present search report has been d	·		- Francisco
	Place of search  Munich	Date of completion of the search  14 January 2013	Gre	Examiner B, Tobias
-		<u>*</u>		
X : part Y : part docu	ATEGORY OF CITED DOCUMENTS  cularly relevant if taken alone cularly relevant if combined with another ment of the same category nological background	T : theory or principle ur E : earlier patent docum after the filing date D : document cited in th L : document cited for o	ent, but publis e application ther reasons	
	-written disclosure rmediate document	& : member of the same		

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

EP 12 19 6639

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-01-2013

	document earch report		Publication date		Patent family member(s)		Publicatio date
US 200	5119140	A1	02-06-2005	AU CA CN JP SG US	2004231172 2486328 1624091 2005133098 111278 2005119140	A1 A A A1	19-05-2 30-04-2 08-06-2 26-05-2 30-05-2 02-06-2
US 200	8287329	A1	20-11-2008	CN EP FR JP KR US WO ZA	101115824 1828360 2879621 2008524367 20070091336 2008287329 2006064138 200705089	A1 A A A A1 A1	30-01-2 05-09-2 23-06-2 10-07-2 10-09-2 20-11-2 22-06-2 26-08-2
EP 209	0642	A1	19-08-2009	AT AU CA CN EP ES JP SG US	552326 2009200452 2653107 101503646 2090642 2380884 2009185293 155131 2009203559	A1 A A1 T3 A A1	15-04-2 27-08-2 08-08-2 12-08-2 19-08-2 21-05-2 20-08-2 30-09-2 13-08-2
EP 188	9896	A2	20-02-2008	AU CA EP JP SG	2007203663 2596211 1889896 2008056933 139726	A1 A2 A	28-02-2 08-02-2 20-02-2 13-03-2 29-02-2

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

### Patent documents cited in the description

- US 20080287329AL A **[0006]**
- US 5259967 A [0044]
- GB 2121432 A [0045]
- EP 708171 A **[0054]**
- EP 271262 A [0055]
- EP 750659 A [0055]

- WO 9746643 A [0060]
- WO 9746644 A [0060]
- WO 9746645 A [0060]
- WO 9746646 A [0060]
- WO 9746647 A [0060]