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(54) A method of reducing deposit formation in a centrifuge system in a trunk piston diesel engine

(57) A method of reducing deposit formation in a centrifuge system in a trunk piston diesel engine. The method includes the step of lubricating the trunk piston diesel engine with a trunk piston diesel engine lubricant composition having a total base number of more than 40 mg KOH/g, as determined by ASTM D2896, and including:

- at least 40 mass % of an oil of lubricating viscosity;
- at least one detergent, preferably at least two detergents; and
- at least 1.5 mass % of phenol, based on the total amount of the lubricant composition;

with the proviso that if the trunk piston diesel engine lubricant composition includes at least one phenate detergent, the trunk piston diesel engine lubricant composition includes more than 1.7 mass %, preferably more than 1.9 mass %, of phenol.

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Description

[0001] This invention concerns a method of reducing deposit formation in a centrifuge system in a trunk piston diesel engine.

[0002] Trunk piston diesel engines are used in marine, power generation and rail traction applications and 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 a method of reducing deposit formation in a centrifuge system in a trunk piston diesel engine.

[0006] In accordance with the present invention there is provided a method of reducing deposit formation in a centrifuge system in a trunk piston diesel engine; the method including the step of lubricating the trunk piston diesel engine with a trunk piston diesel engine lubricant composition having a total base number of more than 40 mg KOH/g, as determined by ASTM D2896, and including:

- at least 40 mass % of an oil of lubricating viscosity;
- at least one detergent, preferably at least two detergents; and
- at least 1.5 mass % of phenol, based on the total amount of the lubricant composition;

with the proviso that if the trunk piston diesel engine lubricant composition includes at least one phenate detergent, the trunk piston diesel engine lubricant composition includes more than 1.7 mass %, preferably more than 1.9 mass %, of phenol.

[0007] The phenol may be added separately to the trunk piston diesel engine lubricant composition and/or it may be added as part of the detergent, for example, as part of the unreacted components present in the detergent. If the phenol is part of the detergent, the amount of phenol present can be detected by persons skilled in the art using processes such as titration and chromatography.

[0008] It is preferred that the trunk piston diesel engine lubricant composition includes a sulphurized or unsulphurized alkyl phenol.

[0009] It is also preferred that the trunk piston diesel engine lubricant composition has a total base number of at least 50 mg KOH/g, and preferably at most 70 mg KOH/g.

[0010] It has surprisingly been found that the trunk piston diesel engine lubricant composition defined above is capable of shedding contamination with sealing mediums used in centrifuge systems in trunk piston diesel engines, even though it has a TBN of more than 40 mg KOH/g. The trunk piston diesel engine lubricant composition therefore exhibits a longer life when compared to trunk piston diesel engine lubricant compositions that are poor at shedding sealing mediums.

[0011] In accordance with the present invention there is also provided use of the trunk piston diesel engine lubricant composition defined above to reduce build-up of deposits in a centrifuge in a trunk piston diesel engine.

Oil of Lubricating Viscosity

[0012] The oil of lubricating viscosity (sometimes referred to as lubricating oil) may be any oil suitable for the lubrication of a trunk piston diesel engine. The lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as a naphthenic base, paraffinic base or mixed base oil.

Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tridecyl adipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutene and poly-alpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60, typically greater than 70, mass % of the composition, and typically have a kinematic viscosity at 100°C of from 2 to 40, for example for 3 to 15, mm^2s^{-1} and a viscosity index of from 80 to 100, for example from 90 to 95.

[0013] Another class of lubricating oils is hydrocracked oils, where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have a kinematic viscosity at 100°C of from 2 to 40, for example from 3 to 15, mm^2s^{-1} and a viscosity index typically in the range of from 100 to 110, for example from 105 to 108.

[0014] 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^2s^{-1} and are typically used in a proportion of less than 40, preferably less than 30, more preferably less than 20, mass %, based on the mass of the composition.

[0015] The trunk piston diesel engine lubricant composition preferably includes at least 50 mass %, more preferably at least 60 mass %, even more preferably at least 70 mass %, of oil of lubricating viscosity, based on the total amount of the lubricant composition.

Detergents

[0016] 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.

[0017] 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.

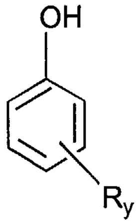
[0018] The detergent is preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a surfactant selected from phenol, sulphonic acid, carboxylic acid, salicylic acid and naphthenic acid, wherein the overbasing 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.

[0019] 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.

[0020] 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-solubility.

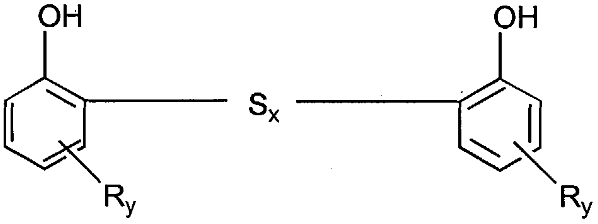
[0021] Phenols, for use in preparing the detergents may be non-sulphurized or, preferably, sulphurized. Further, the term "phenol" as used herein includes phenols containing more than one hydroxyl group (for example, alkyl catechols) or fused aromatic rings (for example, alkyl naphthols) and phenols 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).

[0022] 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.

[0023] The phenols are frequently used in sulphurized form. Sulphurized hydrocarbyl phenols may typically be represented by the formula:



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

[0024] 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.

[0025] In the following discussion, hydrocarbyl-substituted phenols will for convenience be referred to as alkyl phenols.

[0026] 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.

[0027] 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).

[0028] Details of sulphurization processes are well known to those skilled in the art.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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.

[0040] 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 α-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.)

[0041] 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.

[0042] 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).

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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.

[0047] 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.

[0048] 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.

[0049] 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.

[0050] 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.

[0051] 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.

[0052] 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%.

[0053] 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.

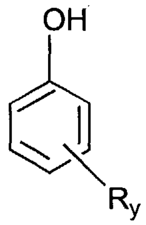
Phenols

[0054] The trunk piston diesel engine lubricant composition includes at least 1.5 mass % of phenol, preferably at least 1.7 mass %, more preferably at least 1.9 mass %, based on the total amount of the lubricant composition. More preferably, the trunk piston diesel engine lubricant composition includes at least 2.0 mass % of phenol, even more preferably at least 2.1 mass %, and most preferably at least 2.2 mass %, based on the total amount of the lubricant composition. If the trunk piston diesel engine lubricant composition includes at least one phenate detergent, the trunk piston diesel engine lubricant composition includes more than 1.7 mass % of phenol, preferably more than 1.9 mass %, even more preferably more than 2.0 mass % of phenol, even more preferably more than 2.2 mass %, and most preferably more than 2.4 mass %, based on the total amount of the lubricant composition.

[0055] The phenol may be added separately to the trunk piston diesel engine lubricant composition and/or it may added as part of the detergent, usually as an unreacted component.

[0056] The phenol may be non-sulphurized or sulphurized. 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).

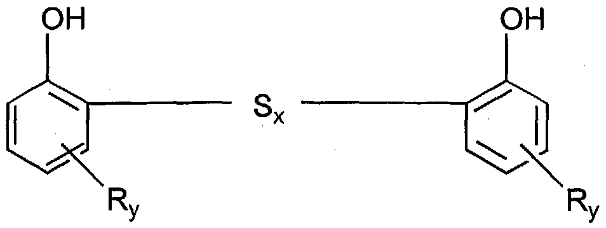
[0057] Preferred phenols may be derived from the formula



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. R preferably includes 2 to 20 carbon atoms.

[0058] The preferred phenols are nonyl-phenol, dodecyl-phenol or a mixture of C_{14}, C_{16} and C_{18}-alkyl phenols.

[0059] The phenols are frequently used in sulphurized form. Sulphurized hydrocarbyl phenols may typically be represented by the formula:



where x is generally from 1 to 4. In some cases, more than two phenol molecules may be linked by S_x bridges. R preferably includes 2 to 20 carbon atoms.

[0060] 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.

[0061] 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.

[0062] 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.

[0063] 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.

[0064] The trunk piston engine oil preferably also includes at least one dispersant, anti-wear additive or anti-oxidant.

Dispersants

[0065] 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.

[0066] 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.

[0067] Examples of ashless dispersants are succinimides, e.g. polyisobutene succinic anhydride; and polyamine condensation products that may be borated or unborated.

[0068] 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

[0069] 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.

[0070] Dihydrocarbyl dithiophosphate metal salts are examples of the anti-wear additives. The metal in the dihydrocarbyl 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.

[0071] 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, I-propyl, n-butyl, I-butyl, sec-butyl, amyl, n-hexyl, I-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylehexyl, phenyl, butylphenyl, 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.

[0072] 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

[0073] 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 antioxidants there may be mentioned hindered phenols, including mono-phenols and bis-phenols.

[0074] 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.

[0075] Other additives such as pour point depressants, anti-foamants, metal rust inhibitors, pour point depressants and/or demulsifiers may be provided, if necessary.

[0076] 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.

[0077] 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.

[0078] 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.

[0079] 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.

[0080] The final formulations may typically contain about 5 to 40 mass % of the additive packages(s), the remainder being base oil.

[0081] The present invention is illustrated by, but in no way limited to, the following examples.

Examples

[0082] 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. Premeasured amounts of water and the test oil are mixed together, heated to 87°C 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.

[0083] Trunk piston engine oils ('TPEOs') were prepared having TBNs ranging from 30 to 50. 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

	Comparative Example 1	**Comparative Example 2**	**Comparative Example 3**	**Example 1**	**Example 2**	**Example 3**
TBN	30	50	50	50	50	50
168 BN Calcium Salicylate	5.29	17.25	17.25	17.25	17.25	17.25
280 BN Calcium Salicylate	7.57	7.50	7.50	7.50	7.50	7.50
Dispersant			1.00	1.00	1.00	1.00
Sulphurised Dodecyl-Phenol				1.00		
Unsulphurized Dodecyl-Phenol					1.00	
Mixture of C_{14}, C_{16} and C_{18}-alkyl phenols						1.00
ZDDP	1.06	0.77	0.77	0.77	0.77	0.77
Anti-foam	0.10	0.10	0.10	0.10	0.10	0.10
Brightstocks	12.00	12.00	12.00	12.00	12.00	12.00
SN600	73.98	62.38	61.38	60.38	60.38	60.38
Alkylphenol content (%)	0.45	0.99	0.99	1.99	1.99	1.99
Shedding Test						
Deposits at End of Test (grams)	53	109	127	27	33	33

[0084] As shown in Table 1, as the TBN of the TPEO increases from 30 to 50 (see Comparatives Examples 1, 2 and

3), the amount of deposits produced also increases. Table 1 also shows that if the amount of alkylphenol is increased (see Examples 1, 2 and 3), the amount of deposits can be reduced.

[0085] In the following examples, the TPEOs include a phenate detergent:

Table 2

	Comparative Example 4	Example 4	Example 5	Example 6	Example 7
TBN	50	50	50	50	50
168 BN Calcium Salicylate	17.25	17.25	17.25	17.25	17.25
250 BN Calcium. Phenate	8.40	8.40	8.40	8.40	8.40
Sulphurised Nonyl-Phenol			1.00		
Sulphurised Dodecyl-Phenol		1.00			
Unsulphurized Dodecyl-Phenol				1.00	
Mixture of C_{14}, C_{16} and C_{18}-alkyl phenols					1.00
ZDDP	0.77	0.77	0.77	0.77	0.77
Anti-foam	0.10	0.10	0.10	0.10	0.10
Brightstocks	12.00	12.00	12.00	12.00	12.00
SN600	61.48	60.48	60.48	60.48	60.48
Alkylphenol content (%)	1.70	2.70	2.70	2.70	2.70
Shedding Test					
Deposits at End of Test (grams)	270	182	82	130	188

[0086] Comparative Example 4, which includes only 1.7% alkylphenol, produces 270g of deposits. Examples 4, 5, 6 and 7 show that if the amount of alkylphenol is increased, the amount of deposits can be reduced.

[0087] In the following examples, the phenol is added to the TPEO as unreacted components of the detergents.

Table 3

	Comparative Example 2	Example 8	Example 9	Example 10
TBN	50	50	45	50
280 BN Calcium Salicylate	17.25			
250 BN Calcium Salicylate	7.50			
168 BN Calcium Salicylate		17.90	17.90	25.00
64 BN Calcium Salicylate		31.25	20.43	12.50
ZDDP	0.77	0.77	0.77	0.77
Anti-foam	0.10	0.10	0.10	0.10
Brightstocks	12.00	10.00	10.00	10.00
SN600	68.03	39.98	50.80	51.63
Alkylphenol content (%)	0.99	2.06	1.62	1.63

Table 3 (continued)

	Comparative Example 2	Example 8	Example 9	Example 10
Shedding Test				
Deposits at End of Test (grams)	109	4	3	4

[0088] Comparative Example 2, which includes only 0.99% alkylphenol, produces 109g of deposits. Examples 8, 9 and 10 show that if the amount of alkylphenol is increased by the selection of detergents including more alkylphenol, the amount of deposits is reduced dramatically.

Claims

1. A method of reducing deposit formation in a centrifuge in a trunk piston diesel engine; the method including the step of lubricating the trunk piston diesel engine with a trunk piston diesel engine lubricant composition having a total base number of more than 40 mg KOH/g, as determined by ASTM D2896, and including:

- at least 40 mass % of an oil of lubricating viscosity;
- at least one detergent, preferably at least two detergents; and
- at least 1.5 mass % of phenol, based on the total amount of the lubricant composition;

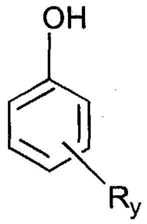
with the proviso that if the trunk piston diesel engine lubricant composition includes at least one phenate detergent, the trunk piston diesel engine lubricant composition includes more than 1.7 mass %, preferably more than 1.9 mass %, of phenol.

2. The method as claimed in claim 1, wherein the phenol in the composition is an unreacted component of the detergent.

3. The method as claimed in claim 1, wherein the phenol in the composition is not an unreacted component of the detergent.

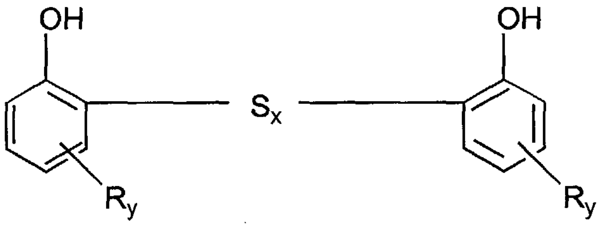
4. The method as claimed in claim 1, wherein part of the phenol in the composition is an unreacted component of the detergent and part of the phenol is not an unreacted component of the detergent.

5. The method as claimed in any one of the preceding claims, wherein the phenol is derived from the formula



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

6. The method as claimed in any one of the preceding claims, wherein the phenol is represented by the formula:



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

7. The method as claimed in any one of the preceding claims, wherein the detergent has a TBN of at least 60 mg KOH/g.

8. The method as claimed in any one of the preceding claims, the composition having a total base number of at least 45, preferably at least 50, preferably at most 70 mg KOH/g.

9. The method as claimed in any one of the preceding claims, further including at least one of the following: a dispersant, an anti-wear agent, an anti-oxidant, a pour point depressant, an anti-foamant and a demulsifier.

10. The method as claimed in any one of the preceding claims, wherein the sealing medium is water.

11. Use of the trunk piston diesel engine lubricant composition defined in any one of the preceding claims, to reduce build-up of deposits in a centrifuge system of a trunk piston diesel engine.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 25 5473

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	1 December 2004	Dötterl, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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