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(54) **Lubricating oil composition**

(57) The use, in a lubricating oil composition comprising base oil, of one or more magnesium detergents, for the reduction of clogging in a diesel particulate filter.

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Description

[0001] The present invention relates to a lubricating oil composition, in particular to a lubricating oil composition which is suitable for lubricating internal combustion engines.

[0002] In view of the adverse affects that the sulphated ash, sulphur and phosphorus concentrations of lubricating oil compositions may have on vehicle exhaust after-treatment devices such as diesel particulate filters (DPF), there is a trend towards lubricating oil compositions having reduced sulphated ash, sulphur and/or phosphorus concentrations therein (i.e. so-called low-SAPS lubricating oil compositions).

[0003] Phosphorus concentrations may be generally reduced by reducing the amount of zinc dithiophosphates which are present as anti-wear additives in lubricating oil compositions.

[0004] Sulphur levels in lubricating oil compositions may be reduced by employing low sulphur level base oils and reducing the amount of sulphur-containing additives employed therein.

[0005] Sulphated ash is the total weight percent of residue remaining after a lubricating oil composition has been carbonised, and the residue subsequently treated with sulphuric acid and heated to constant weight. The sulphated ash content in a lubricating oil composition is related to the total metal content therein. Sulphated ash may be conveniently measured according to ASTM D874.

[0006] The major sources of sulphated ash in a lubricating oil composition are generally any metal detergent additives and zinc dithiophosphate anti-wear additives that are employed therein.

[0007] Sulphated ash deposits can clog the diesel particulate filter (DPF) of vehicles, thereby reducing filter life, raising back pressure in the vehicle engine and causing increased fuel consumption.

[0008] The tendency of diesel particulate filters to become clogged can be measured by tests such as the Volkswagen (VW) diesel particulate filter (DPF) test. This severe diesel particulate filter test forms part of the VW factory fill specification 52195.

[0009] In order to minimise problems in the diesel particulate filters of vehicles, in current low-SAPS lubricating oil compositions, sulphated ash levels, and consequently detergent levels, are low.

[0010] However, reducing the amount of detergents present in a lubricating oil composition in order to reduce the sulphated ash content thereof can have an adverse effect on the basicity of the lubricating oil composition.

[0011] Total Base Number (TBN) is a measure of how well a lubricating oil composition can neutralise acidic by-products of combustion/oxidation and is defined as the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize all basic constituents present in 1 gram of a sample of the lubricating oil composition (test methods include, for example, ISO 3771, ASTM D-2896 and ASTM D-4739).

[0012] A high TBN is desirable in lubricating oil compositions in order to control corrosive engine wear from the acidic by-products of combustion/oxidation. Detergent additives in a lubricating oil composition are the primary source of basicity (TBN) and help to control, for example, top-ring deposits and bore polish.

[0013] Hence, metal detergents are the primary source of TBN in crankcase lubricating oil compositions.

[0014] Consequently, the starting TBN (i.e. of fresh unused lubricating oil compositions) of low-SAPS lubricating oil compositions tends to be lower than in lubricating oil compositions having higher sulphated ash, sulphur and/or phosphorus concentrations therein.

[0015] It is therefore highly desirable to be able to reduce the adverse clogging effect of sulphated ash on the diesel particulate filter unit without having to compromise on the basicity of the lubricating oil composition.

[0016] EP-A-1362905 describes fuel oil and lubricating oil compositions for diesel engines having a diesel particulate filter. Said compositions comprise a small amount of a molybdenum compound to improve the combustion property of particulate matter trapped in a diesel particulate filter.

[0017] Whilst said compositions may comprise additional known additives for their conventional purposes, it should be noted that EP-A-1362905 is in no way concerned with using specific additives to try to reduce clogging in a diesel particulate filter from the outset.

[0018] In this regard, the bench tests in EP-A-1362905 are designed merely to show how the afore-mentioned molybdenum compound might be suitable for use in improving burn-off of calcium and magnesium deposits. However, there is no disclosure, and indeed no comparison, in EP-A-1362905 of the degree of clogging of a real diesel particulate filter from a lubricating oil composition comprising a calcium or magnesium based detergent.

[0019] US-A-6114288 discloses lubricating oil compositions for internal combustion engines having a sulphated ash content in the range of from 0.8 to 1.8 mass % according to JIS K2272, which compositions comprise base oil, specific zinc dialkyl dithiophosphates and metallic detergent chosen from i) calcium alkylsalicylate and ii) a mixture of calcium alkylsalicylate and magnesium alkylsalicylate.

[0020] Whilst the Examples in US-A-6114288 test the wear performance of lubricating oil compositions comprising various alkaline earth metal detergents such as calcium sulphonate, magnesium sulphonate, calcium salicylate and magnesium salicylate, it is of note that US-A-6114288 is in no way concerned with the performance of said lubricating oil compositions in diesel particulate filter tests, and in particular in the VW diesel particulate filter test.

[0021] US 2002/0019320 A1 describes lubricating oil compositions having a low sulphated ash content, a low phosphorus content, and a low sulphur content. Said lubricating oil compositions are said to have good detergency at high temperatures.

[0022] Detergents used in the lubricating oil compositions of US 2002/0019320 A1 are those containing an organic acid metal salt which is selected from the group consisting of a non-sulphurised alkali metal or alkaline earth metal salt of an alkylsalicylic acid having a TBN of 10 to 350 mg.KOH/g and a non-sulphurised alkali metal or alkaline earth metal salt of an alkylphenol derivative having a Mannich base structure, in an amount of 0.1 to 1 wt. % in terms of sulphated ash.

[0023] Whilst various alkaline earth detergents are used in the Examples of US 2002/0019320 A1, it is of note that the preferred alkaline earth metal is calcium and that none of the lubricating oil compositions of US 2002/0019320 A1 are actually tested in a diesel particulate filter test, and in particular in the VW diesel particulate filter test.

[0024] US 2004/0127371 A1 seeks means to reduce the amount of metal-containing compounds in lubricating oil compositions in order that said compositions are more suitable for use in engines provided with particulate filters.

[0025] US 2004/0127371 A1 indicates that the amount of detergent needed to neutralise mineral acids generated during the combustion and ameliorate engine corrosion can be reduced in engines operated by low sulphur fuels.

[0026] Accordingly, US 2004/0127371 A1 describes a lubricating oil composition for use in a compression ignited (diesel) internal combustion engine operated with diesel fuel having a sulphur content of less than 50 ppm, said lubricating oil composition comprising a major amount of oil of lubricating viscosity, and at least one metal-containing detergent, wherein said lubricating oil composition has a total ash content of less than 1.0 wt. %, based on the total weight of the lubricating oil composition.

[0027] It will be appreciated that the approach used in US 2004/0127371 A1 reduces the TBN demand placed on a lubricating oil composition in the first place by reducing generation of acidic species.

[0028] However, US 2004/0127371 A1 does not provide any teaching on how to reduce the adverse clogging effect of sulphated ash on the diesel particulate filter units without having to compromise on the basicity of the lubricating oil composition.

[0029] US 2004/0176260 A1 discusses accumulation of ash in exhaust gas after-treatment devices from metal detergents and zinc dialkyl dithiophosphate additives and the resulting deterioration in detergency and anti-wear properties if this problem is addressed by reducing the content of said additives in a lubricating oil composition.

[0030] US 2004/0176260 A1 discloses means to compensate for this deterioration by blending specific ashless dispersants and phosphorus-containing ashless anti-wear additives, alternatively with a fatty acid amide in specific amounts whilst decreasing the amounts of zinc dialkyl dithiophosphate and metallic detergents.

[0031] However, it has been surprisingly found in the present invention that for a given sulphated ash content, the use of magnesium detergents in lubricating oil compositions give improved performance in diesel particulate filter tests, that is to say, reduced filter clogging, as compared to the use of calcium detergents therein.

[0032] Accordingly, for a given performance in diesel particulate filter tests, it is now surprisingly possible to use greater amounts of magnesium detergent in a lubricating oil composition vis-à-vis a lubricating oil composition comprising calcium detergent and/or to use a magnesium detergent having a higher TBN than a calcium detergent in order to meet the basicity requirements of a lubricating oil composition.

[0033] Thus, the disadvantages associated with trying to achieve a balance of the basicity properties of a lubricating oil composition and reducing diesel particulate clogging in a diesel particulate filter may therefore be overcome by the use of magnesium detergents.

[0034] The present invention provides the use, in a lubricating oil composition comprising base oil, of one or more magnesium detergents, for the reduction of clogging in a diesel particulate filter.

[0035] In particular, the present invention provides the use, in a lubricating oil composition comprising base oil, of one or more magnesium detergents, for improving the reduction of clogging in a diesel particulate filter, especially as compared to the use of calcium detergents therein.

[0036] Clogging of the diesel particulate filter is preferably measured using the VW diesel particulate filter test.

[0037] The one or more magnesium detergents used in the present invention are preferably selected from magnesium salicylate detergents, magnesium phenate detergents and magnesium sulphonate detergents. Magnesium salicylate and magnesium phenate detergents are particularly preferred.

[0038] In order to maintain the total sulphated ash content of the lubricating oil composition preferably at a level of not greater than 1.0 wt. %, more preferably at a level of not greater than 0.9 wt. % and most preferably at a level of not greater than 0.8 wt. %, based on the total weight of the lubricating oil composition, said one or more magnesium detergents are preferably used in a total amount of not greater than 0.2 wt. % in terms of magnesium content, more preferably in a total amount of not greater than 0.17 wt. % in terms of magnesium content and most preferably in a total amount of not greater than 0.15 wt. % in terms of magnesium content, based on the total weight of the lubricating oil composition.

[0039] The magnesium detergents used in the present invention can be either neutral or overbased. The expression "overbased" is equivalent to "basic", "superbased", "hyperbased" and "high-metal containing salts". These magnesium detergents contain an excess metal content compared to the amount of metal which would be present according to the

stoichiometry of the metal and the acidic organic compound reacted with the metal. Processes for making such neutral and basic metal salts are well known in the art. Neutral salts can be made by heating a mineral oil solution of an acidic organic compound with a stoichiometric equivalent amount of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature above 50 °C and filtering the resulting mass. Basic salts are made similarly with the exception that a stoichiometric excess of the metal is used. Preferably, overbased magnesium detergents are used.

[0040] Detergents can be characterized by their total base number (TBN). Preferably, the total base numbers of the one or more magnesium detergents are each, independently, in the range of from 30 to 600 mg.KOH/g, more preferably in the range of from 30 to 450 mg.KOH/g and most preferably in the range of from 30 to 350 mg.KOH/g, as measured by ISO 3771.

[0041] Magnesium salicylates that may be conveniently used may be either substituted or unsubstituted. Suitable substituents include aliphatic groups containing from 1 to 40 carbon atoms and optionally containing one or more oxygen and/or nitrogen atoms, and hydroxy groups. Preferred substituents are alkyl groups containing in the range of from 6 to 30 carbon atoms, preferably in the range of from 12 to 20 carbon atoms. Preferably, the substituents are linear. The magnesium salicylates may contain in the range of from 1 to 4 substituents, preferably in the range of from 1 to 3, most preferably 1 or 2 substituents. Most preferably, the magnesium salicylates may be substituted by 1 linear alkyl group containing in the range of from 14 to 18 carbon atoms.

[0042] Generally, mono-alkyl salicylic acids are prepared by alkylation of phenol and subsequent carboxylation. Therefore, a small amount (generally at most 20 %mol) of dialkyl salicylate and unsubstituted salicylate can be present in the mono-alkyl salicylate.

[0043] Magnesium salicylates which may be used in the present invention are commercially available. For example, a commercial magnesium salicylate is that available under the trade designation "Infineum C9012" from Infineum.

[0044] A process by which magnesium salicylates can be prepared, has been described in US-A-4627928.

[0045] EP-A-1195427 describes magnesium phenates and methods of making such detergents.

[0046] EP-A-1195427, WO-A-97/14774 and US-A-5534168 describe magnesium sulphonate and methods of making overbased magnesium sulphonates.

[0047] Magnesium phenates and magnesium sulphonates which may be used in the present invention are commercially available. For example, a commercial magnesium sulphonate is that available under the trade designation "Infineum C9340" from Infineum.

[0048] The starting TBN value of the lubricating oil composition used in the present invention is preferably in the range of from 4.0 to 12.0 mg.KOH/g, more preferably in the range of from 6.0 to 11.0 mg.KOH/g, even more preferably in the range of from 6.0 to 10.0 mg.KOH/g and most preferably in the range of 6.0 to 9.5 mg.KOH/g, as measured by ISO 3771.

[0049] The lubricating oil composition preferably has a sulphated ash content of not greater than 1.0 wt. %, more preferably not greater than 0.9 wt. % and most preferably not greater than 0.8 wt. %, based on the total weight of the lubricating oil composition.

[0050] The lubricating oil composition preferably has a sulphur content of not greater than 1.2 wt. %, more preferably not greater than 0.8 wt. % and most preferably not greater than 0.3 wt. %, based on the total weight of the lubricating oil composition.

[0051] In the present invention, preferred lubricating oil compositions have one or more of the following features:

(i) greater than 0.04 wt. % of phosphorus;
(ii) greater than 0.045 wt. % of phosphorus;
(iii) at least 0.04 wt. % of phosphorus;
(iv) less than 0.09 wt. % of phosphorus;
(v) not greater than 0.10 wt. % of phosphorus;
(vi) at most 0.085 wt. % of phosphorus;
(vii) not greater than 1.0 wt. % of sulphated ash;
(viii) not greater than 0.9 wt. % of sulphated ash;
(ix) not greater than 0.8 wt. % of sulphated ash;
(x) not greater than 1.2 wt. % of sulphur;
(xi) not greater than 0.8 wt. % of sulphur; and
(xii) not greater than 0.3 wt. % of sulphur, based on the total weight of the lubricating oil composition.

[0052] In the present invention, particularly preferred lubricating oil compositions have one or more of the following features:

(A): those having features (i) and (iv); those having features (i) and (v); those having features (i) and (vi); those having features (ii) and (iv); those having features (ii) and (v); those having features (ii) and (vi); those having features

(iii) and (iv); those having features (iii) and (v); and those having features (iii) and (vi);
(B): those having features (i), (iv) and (vii); those having features (i), (iv) and (viii); those having features (i), (iv) and (ix); those having features (i), (v) and (vii); those having features (i), (v) and (viii); those having features (i), (v) and (ix); those having features (i), (vi) and (vii); those having features (i), (vi) and (viii); those having features (i), (vi) and (ix); those having features (ii), (iv) and (vii); those having features (ii), (iv) and (viii); those having features (ii), (iv) and (ix); those having features (ii), (v) and (vii); those having features (ii), (v) and (viii); those having features (ii), (v) and (ix); those having features (ii), (vi) and (vii); those having features (ii), (vi) and (viii); those having features (ii), (vi) and (ix); those having features (iii), (iv) and (vii); those having features (iii), (iv) and (viii); those having features (iii), (iv) and (ix); those having features (iii), (v) and (vii) ; those having features (iii), (v) and (viii); those having features (iii), (v) and (ix); those having features (iii), (vi) and (vii); those having features (iii), (vi) and (viii); and those having features (iii), (vi) and (ix) ;
(C): those having features (i), (iv) and (x); those having features (i), (iv) and (xi); those having features (i), (iv) and (xii) ; those having features (i), (v) and (x); those having features (i), (v) and (xi) ; those having features (i), (v) and (xii); those having features (i), (vi) and (x); those having features (i), (vi) and (xi) ; those having features (i), (vi) and (xii); those having features (ii), (iv) and (x); those having features (ii), (iv) and (xi); those having features (ii), (iv) and (xii) ; those having features (ii), (v) and (x) ; those having features (ii), (v) and (xi); those having features (ii), (v) and (xii); those having features (ii), (vi) and (x); those having features (ii), (vi) and (xi) ; those having features (ii), (vi) and (xii); those having features (iii), (iv) and (x); those having features (iii), (iv) and (xi); those having features (iii), (iv) and (xii); those having features (iii), (v) and (x); those having features (iii), (v) and (xi); those having features (iii), (v) and (xii); those having features (iii), (vi) and (x); those having features (iii), (vi) and (xi); and those having features (iii), (vi) and (xii); and
(D): those having features (i), (iv), (vii) and (x); those having features (i), (iv), (viii) and (x); those having features (i), (iv), (ix) and (x); those having features (i), (v), (vii) and (x); those having features (i), (v), (viii) and (x); those having features (i), (v), (ix) and (x); those having features (i), (vi), (vii) and (x); those having features (i), (vi), (viii) and (x); those having features (i), (vi), (ix) and (x); those having features (ii), (iv), (vii) and (x); those having features (ii), (iv), (viii) and (x); those having features (ii), (iv), (ix) and (x); those having features (ii), (v), (vii) and (x); those having features (ii), (v), (viii) and (x); those having features (ii), (v), (ix) and (x); those having features (ii), (vi), (vii) and (x); those having features (ii), (vi), (viii) and (x); those having features (ii), (vi), (ix) and (x); those having features (iii), (iv), (vii) and (x); those having features (iii), (iv), (viii) and (x); those having features (iii), (iv), (ix) and (x); those having features (iii), (v), (vii) and (x); those having features (iii), (v), (viii) and (x); those having features (iii), (v), (ix) and (x); those having features (iii), (vi), (vii) and (x); those having features (iii), (vi), (viii) and (x); those having features (iii), (vi), (ix) and (x); those having features (i), (iv), (vii) and (xi); those having features (i), (iv), (viii) and (xi); those having features (i), (iv), (ix) and (xi); those having features (i), (v), (vii) and (xi); those having features (i), (v), (viii) and (xi); those having features (i), (v), (ix) and (xi); those having features (i), (vi), (vii) and (xi); those having features (i), (vi), (viii) and (xi); those having features (i), (vi), (ix) and (xi); those having features (ii), (iv), (vii) and (xi); those having features (ii), (iv), (viii) and (xi); those having features (ii), (iv), (ix) and (xi); those having features (ii), (v), (vii) and (xi); those having features (ii), (v), (viii) and (xi); those having features (ii), (v), (ix) and (xi); those having features (ii), (vi), (vii) and (xi); those having features (ii), (vi), (viii) and (xi); those having features (ii), (vi), (ix) and (xi) ; those having features (iii), (iv), (vii) and (xi); those having features (iii), (iv), (viii) and (xi); those having features (iii), (iv), (ix) and (xi); those having features (iii), (v), (vii) and (xi); those having features (iii), (v), (viii) and (xi); those having features (iii), (v), (ix) and (xi); those having features (iii), (vi), (vii) and (xi); those having features (iii), (vi), (viii) and (xi); those having features (iii), (vi), (ix) and (xi); those having features (i), (iv), (vii) and (xii); those having features (i), (iv), (viii) and (xii); those having features (i), (iv), (ix) and (xii); those having features (i), (v), (vii) and (xii); those having features (i), (v), (viii) and (xii); those having features (i), (v), (ix) and (xii); those having features (i), (vi), (vii) and (xii); those having features (i), (vi), (viii) and (xii); those having features (i), (vi), (ix) and (xii); those having features (ii), (iv), (vii) and (xii) ; those having features (ii), (iv), (viii) and (xii); those having features (ii), (iv), (ix) and (xii); those having features (ii), (v), (vii) and (xii); those having features (ii), (v), (viii) and (xii); those having features (ii), (v), (ix) and (xii); those having features (ii), (vi), (vii) and (xii); those having features (ii), (vi), (viii) and (xii); those having features (ii), (vi), (ix) and (xii); those having features (iii), (iv), (vii) and (xii); those having features (iii), (iv), (viii) and (xii); those having features (iii), (iv), (ix) and (xii); those having features (iii), (v), (vii) and (xii); those having features (iii), (v), (viii) and (xii); those having features (iii), (v), (ix) and (xii); those having features (iii), (vi), (vii) and (xii); those having features (iii), (vi), (viii) and (xii); and those having features (iii), (vi), (ix) and (xii).

[0053] The amount of base oil incorporated in the lubricating oil composition is preferably present in an amount in the range of from 60 to 92 wt. %, more preferably in an amount in the range of from 75 to 90 wt. % and most preferably in an amount in the range of from 75 to 88 wt. %, with respect to the total weight of the lubricating oil composition.

[0054] There are no particular limitations regarding the base oil used in the present invention, and various conventional known mineral oils and synthetic lubricating oils may be conveniently used.

[0055] Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

[0056] Naphthenic base oils have low viscosity index (VI) (generally 40-80) and a low pour point. Such base oils are produced from feedstocks rich in naphthenes and low in wax content and are used mainly for lubricants in which colour and colour stability are important, and VI and oxidation stability are of secondary importance.

[0057] Paraffinic base oils have higher VI (generally >95) and a high pour point. Said base oils are produced from feedstocks rich in paraffins, and are used for lubricants in which VI and oxidation stability are important.

[0058] Fischer-Tropsch derived base oils may be conveniently used as the base oil in the lubricating oil composition of the present invention, for example, the Fischer-Tropsch derived base oils disclosed in EP-A-776959, EP-A-668342, WO-A-97/21788, WO-00/15736, WO-00/14188, WO-00/14187, WO-00/14183, WO-00/14179, WO-00/08115, WO-99/41332, EP-1029029, WO-01/18156 and WO-01/57166.

[0059] Synthetic processes enable molecules to be built from simpler substances or to have their structures modified to give the precise properties required.

[0060] Synthetic base oils include hydrocarbon oils such as olefin oligomers (PAOs), dibasic acids esters, polyol esters, and dewaxed waxy raffinate. Synthetic hydrocarbon base oils sold by the Shell group under the designation "XHVI" (trade mark) may be conveniently used.

[0061] Preferably, the base oil is constituted from mineral oils and/or synthetic base oils which contain more than 80% wt of saturates, preferably more than 90 % wt., as measured according to ASTM D2007.

[0062] It is further preferred that the base oil contains less than 1.0 wt. %, preferably less than 0.1 wt. % of sulphur, calculated as elemental sulphur and measured according to ASTM D2622, ASTM D4294, ASTM D4927 or ASTM D3120.

[0063] Preferably, the viscosity index of the base oil is more than 80, more preferably more than 120, as measured according to ASTM D2270.

[0064] Preferably, the lubricating oil composition has a kinematic viscosity in the range of from 2 to 80 mm^2/s at 100 °C, more preferably of from 3 to 70 mm^2/s, most preferably of from 4 to 50 mm^2/s.

[0065] In the present invention, the lubricating oil composition may optionally further comprise one or more additional additives such as anti-oxidants, anti-wear additives, supplementary detergents, dispersants, friction modifiers, viscosity index improvers, pour point depressants, corrosion inhibitors, defoaming agents and seal fix or seal compatibility agents.

[0066] In one embodiment of the present invention, the lubricating oil composition may comprise one or more aminic and/or phenolic antioxidants.

[0067] Examples of aminic antioxidants which may be conveniently used include alkylated diphenylamines, phenyl-α-naphthylamines, phenyl-β-naphthylamines and alkylated α-naphthylamines.

[0068] Preferred aminic antioxidants include dialkyldiphenylamines such as p,p'-dioctyl-diphenylamine, p,p'-di-α-methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyldiphenylamine and mono-octyldiphenylamine, bis(dialkylphenyl)amines such as di-(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and n-t-dodecyl-phenyl-1-naphthylamine, 1-naphthylamine, arylnaphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthyl-amine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine and 3,7-dioctylphenothiazine.

[0069] Preferred aminic antioxidants include those available under the following trade designations: "Sonoflex OD-3" (ex. Seiko Kagaku Co.), "Irganox L-57" (ex. Ciba Specialty Chemicals Co.) and phenothiazine (ex. Hodogaya Kagaku Co.).

[0070] Examples of phenolic antioxidants which may be conveniently used include C7-C9 branched alkyl esters of 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-benzenepropanoic acid, 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctylacetate, alkyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, n-butyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,6-d-t-butyl-a-dimethylamino-p-cresol, 2,2'-methylene-bis(4-alkyl-6-t-butylphenol) such as 2,2'-methylenebis(4-methyl-6-t-butylphenol, and 2,2-methylenebis(4-ethyl-6-t-butylphenol), bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol, 4,4'-methylenebis(2,6-di-t-butyl-phenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane, 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethyleneglycol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycolbis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate], 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 2,2'-thiobis(4,6-di-t-butylresorcinol), polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]methane, 1,1,3-tris(2-methyl-4-hydroxy-5-t-

butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, bis-[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl) methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol, and p-t-butylphenol - formaldehyde condensates and p-t-butylphenol - acetaldehyde condensates.

[0071] Preferred phenolic antioxidants include those available under the following trade designations: "Irganox L-135" (ex. Ciba Specialty Chemicals Co.), "Anteeji DBH" (ex. Kawaguchi Kagaku Co.,), "Yoshinox SS" (ex. Yoshitomi Seiyaku Co.), "Antage W-400" (ex. Kawaguchi Kagaku Co.), "Antage W-500" (ex. Kawaguchi Kagaku Co.), "Antage W-300" (ex. Kawaguchi Kagaku Co.), "Ionox 220AH" (ex. Shell Japan Co.), bisphenol A, produced by the Shell Japan Co., "Irganox L109" (ex. Ciba Specialty Chemicals Co.), "Tominox 917" (ex. Yoshitomi Seiyaku Co.), "Irganox L115" (ex. Ciba Specialty Chemicals Co.), "Sumilizer GA80" (ex. Sumitomo Kagaku), "Antage RC" (ex. Kawaguchi Kagaku Co.), "Irganox L101" (ex. Ciba Speciality Chemicals Co.), "Yoshinox 930" (ex. Yoshitomi Seiyaku Co.), "Ionox 330" (ex. Shell Japan Co.).

[0072] The lubricating oil composition may comprise mixtures of one or more phenolic antioxidants with one or more aminic antioxidants.

[0073] In a preferred embodiment of the present invention, the lubricating oil composition may comprise one or more anti-wear additives.

[0074] Anti-wear additives that may be conveniently used include molybdenum-containing compounds, boron-containing compounds and zinc-containing compounds.

[0075] Examples of such molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO-A-98/26030, sulphides of molybdenum and molybdenum dithiophosphate.

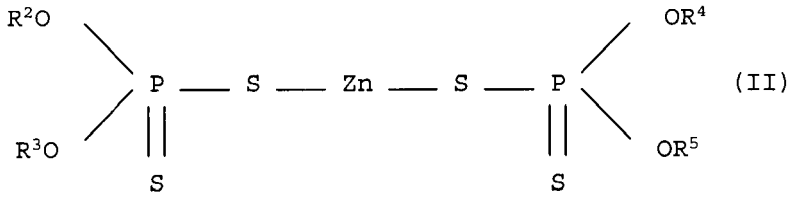
[0076] Said molybdenum-containing anti-wear additives may be conveniently added to the lubricating oil composition in an amount in the range of from 0.1 to 3.0 wt. %, based on the total weight of lubricating oil composition.

[0077] Boron-containing compounds that may be conveniently used include borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

[0078] Said boron-containing anti-wear additives may be conveniently added to the lubricating oil composition in an amount in the range of from 0.1 to 3.0 wt. %, based on the total weight of lubricating oil composition.

[0079] Preferred zinc-containing anti-wear additives are one or more zinc dithiophosphates selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates.

[0080] Zinc dithiophosphate is a well known additive in the art and may be conveniently represented by general formula II;



wherein R^2 to R^5 may be the same or different and are each a primary alkyl group containing from 1 to 20 carbon atoms preferably from 3 to 12 carbon atoms, a secondary alkyl group containing from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms, an aryl group or an aryl group substituted with an alkyl group, said alkyl substituent containing from 1 to 20 carbon atoms preferably 3 to 18 carbon atoms.

[0081] Zinc dithiophosphate compounds in which R^2 to R^5 are all different from each other can be used alone or in admixture with zinc dithiophosphate compounds in which R^2 to R^5 are all the same.

[0082] Preferably, the or each zinc dithiophosphate used in the present invention is a zinc dialkyl dithiophosphate.

[0083] Examples of suitable zinc dithiophosphates which are commercially available include those available ex. Lubrizol Corporation under the trade designations "Lz 1097" and "Lz 1395", those available ex. Chevron Oronite under the trade designations "OLOA 267" and "OLOA 269R", and that available ex. Ethyl under the trade designation "HITEC 7197"; zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 677A", "Lz 1095" and "Lz 1371", that available ex. Chevron Oronite under the trade designation "OLOA 262" and that available ex. Ethyl under the trade designation "HITEC 7169"; and zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1370" and "Lz 1373" and that available ex. Chevron Oronite under the trade designation "OLOA 260".

[0084] The lubricating oil composition may preferably comprise in the range of from 0.4 to 1.0 wt. % of zinc dithio-

phosphate, more preferably in the range of from 0.4 to 0.9 wt. % and most preferably in the range of from 0.45 to 0.8 wt. %, based on total weight of the lubricating oil composition.

[0085] The total amount of phosphorus in the lubricating oil composition is preferably in the range of from 0.04 to 0.1 wt. %, more preferably in the range of from 0.04 to 0.09 wt. % and most preferably in the range of from 0.045 to 0.085 wt. %, based on total weight of the lubricating oil composition.

[0086] Supplementary detergents that may be conveniently used in the lubricating oil composition include one or more calcium detergents selected from calcium salicylates, calcium phenates and calcium sulphonates.

[0087] The calcium detergents can be either neutral or overbased. Preferably, the total base number of said calcium detergents is in the range of from 30 to 600 mg.KOH/g, more preferably in the range of from 30 to 450 mg.KOH/g, most preferably in the range of from 30 to 350 mg.KOH/g, as measured by ISO 3771.

[0088] Examples of commercial calcium detergents include the calcium salicylates which are available from Infineum under the trade designations "Infineum M7101", "Infineum M7102" and "Infineum M 7105".

[0089] In order that said calcium detergents do not adversely affect the diesel particulate filters of internal combustion engines, it is preferred that said one or more calcium detergents are used in a total amount of no greater than 0.12 wt. % in terms of calcium content, more preferably in a total amount of no greater than 0.08 wt. % in terms of calcium content and most preferably in a total amount of no greater than 0.05 wt. % in terms of calcium content, based on the total weight of the lubricating oil composition.

[0090] The lubricating oil composition may comprise an ash-free dispersant which is preferably admixed in an amount in the range of from 5 to 15 wt. %, based on the total weight of the lubricating oil composition.

[0091] Examples of dispersants which may be used include the polyalkenyl succinimides and polyalkenyl succininic acid esters disclosed in Japanese Patent Nos. 1367796, 1667140, 1302811 and 1743435. Preferred dispersants include borated succinimides.

[0092] Preferred friction modifiers that may be conveniently used include fatty acid esters and fatty acid amides.

[0093] The total amount of friction modifiers added to the lubricating oil composition in conveniently in the range of from 0.05 to 2.0 wt. %, based on the total weight of the lubricating oil composition.

[0094] Examples of viscosity index improvers which may conveniently used in the lubricating oil composition include the styrene-butadiene copolymers, styrene-isoprene stellate copolymers and the polymethacrylate-based and ethylene-propylene copolymers and the like disclosed in Japanese Patent Nos. 954077, 1031507, 1468752, 1764494 and 1751082. Such viscosity index improvers may be conveniently employed in an amount in the range of from 1 to 20 wt. %, based on the total weight of the lubricating oil composition. Similarly, dispersing-type viscosity index improvers comprising copolymerized polar monomer containing nitrogen atoms and oxygen atoms in the molecule may also be used therein.

[0095] Polymethacrylates such as those as disclosed in Japanese Patent Nos. 1195542 and 1264056 may be conveniently employed in the lubricating oil compositions of the present invention as effective pour point depressants.

[0096] Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating oil composition as corrosion inhibitors.

[0097] Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating oil composition as defoaming agents.

[0098] Compounds which may be conveniently used in the lubricating oil composition as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

[0099] The lubricating oil composition as herein before described may be conveniently prepared by admixing the one or more magnesium detergents, and, optionally, one or more additional additives, for example as herein before described, with base oil.

[0100] In the present invention, lubricating oil compositions comprising one or more magnesium detergents and base oil have been surprisingly found to give advantageous performance in diesel particulate filter tests, in particular in the VW diesel particulate filter test.

[0101] In a preferred embodiment of the present invention, the use of said lubricating oil compositions gives a result of less than 50 % weight increase of a diesel particulate filter, as measured by the VW diesel particulate filter test.

[0102] In another embodiment of the present invention, there is provided a method of improving performance in a diesel particulate filter test, in particular in the VW diesel particulate filter test, said method comprising lubricating an internal combustion engine with a lubricating oil composition as hereinbefore described comprising one or more magnesium detergents and base oil.

[0103] The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the invention in any way.

EXAMPLES

Formulations

[0104] Table 1 indicates the formulations that were tested.

[0105] The formulations in Table 1 comprised conventional antioxidants, anti-foams, dispersants, friction modifiers, seals fix additives, pour point depressants, viscosity index modifiers and zinc dithiophosphate additives.

[0106] The magnesium detergent used was that available under the trade designation "Infineum C9012" (TBN 345 mg.KOH/g) from Infineum.

[0107] The calcium detergents used were those available under the trade designations "Infineum M7101" (TBN 168 mg.KOH/g), "Infineum M7102" (TBN 64 mg.KOH/g) and "Infineum M7105" (TBN 280 mg.KOH/g) from Infineum.

[0108] The base oils used in said formulations were Group III base oils available from the Shell group under the trade designations "XHVI-5.2" and "XHVI-8.2".

[0109] All formulations described in Table 1 were SAE 5W30 viscosity grade oils.

TABLE 1

Additive (wt. %)	**Ex. 1**	**Ex. 2**	**Comp. Ex. 1**	**Comp. Ex. 2**
Anti-foam	30ppm	30ppm	30ppm	30ppm
Calcium salicylate[1]	-	-	0.80	1.20
Calcium salicylate[2]	-	1.00	-	-
Calcium saliylate[3]	-	-	1.60	1.00
Magnesium salicylate[4]	2.20	1.20	-	-
Phenolic antioxidant[5]	4.00	4.00	4.00	4.00
PIB succinimide dispersant	8.00	8.00	8.00	8.00
Zinc dithiophosphates	0.50	0.80	0.50	0.60
Viscosity modifiers	11.50	8.70	12.00	12.00
Other additives[6]	-	0.70	-	2.50
Base Oil[7]	73.80	75.60	73.10	70.70
TOTAL	100	100	100	100

[1] TBN 168 mg.KOH/g. Available from Infineum under the trade designation "Infineum M7101".
[2] TBN 64 mg.KOH/g. Available from Infineum under the trade designation "Infineum M7102".
[3] TBN 280 mg.KOH/g. Available from Infineum under the trade designation "Infineum M7105".
[4] TBN 345 mg.KOH/g. Available from Infineum under the trade designation "Infineum C9012".
[5] Antioxidant available under the trade designation "IRGANOX L-135" from Ciba Specialty Chemicals.
[6] Mixture of conventional additives selected from pour point depressant, friction modifier, corrosion inhibitor and seal fix additives.
[7] Group III base oil mixtures of XHVI-5.2 and XHVI-8.2 except for Comp. Ex. 2 which used only XHVI-5.2.

VW Diesel Particulate Filter (DPF) Test

[0110] The VW diesel particulate filter (DPF) test forms part of the VW factory fill specification 52195.

[0111] The experimental methodology used to obtain the results of Table 2 was in accordance with the publicly available test that is carried out on a commercial basis by an independent lubricant test laboratory, ISP.

[0112] The VW diesel particulate filter test measures the percentage weight increase of a diesel particulate filter after a 450 hour engine test.

[0113] The publicly available test quotes results with respect to a percentage weight increase against the weight increase of the diesel particulate filter using a standard test reference oil.

[0114] The test limit for a VW pass is set at < 50 % weight increase against this reference oil.

Results and Discussion

[0115] The formulations described in Table 1 were tested using the afore-mentioned test and the results obtained thereon are included in Table 2.

[0116] It is apparent from Table 2 that for a given sulphated ash level, the use of magnesium detergent vis-à-vis calcium detergents surprisingly gives improved performance in the VW diesel particulate filter test to the extent that the lubricating oil composition of Example 1 is much lower than the VW test limit whereas the comparable lubricating oil composition of Comparative Example 1 exceeds the VW test limit.

[0117] Example 2 demonstrates that the use of magnesium detergent in combination with calcium detergent gives rise to a lubricating oil composition which is lower than the VW test limit.

TABLE 2

Results	Ex. 1	Ex. 2	Comp. Ex. 1	Comp. Ex. 2
Soap (mmol/kg)	9.0	9.0	9.0	9.1
Starting Total Base Number (TBN) (mg.KOH/g)	9.50	6.40	7.70	6.70
Total Sulphated ash (wt. %)(ASTM D874)	0.80	0.61	0.80	0.70
Total Sulphur (wt. %)(ASTM D2622)	<0.3	0.21	<0.3	<0.3
Total Phosphorus (wt. %) (ICP-OES method)	0.049	0.083	0.047	0.059
Ca (wt. %) (ICP-OES method)	-	0.025	0.207	0.167
Mg (wt.%) (ICP-OES method)	0.163	0.083	-	-
Starting Kinematic Viscosity (100 °C) (mm^2/s)	12.09	12.21	12.10	12.20
Starting Kinematic Viscosity (40 °C) (mm^2/s)	69.50	70.05	69.45	68.16
Cold Cranking Shear (CCS)Viscosity (-30 °C) (P)(Pa.s)	64.03	62.58	63.78	59.25
% Weight Increase of Diesel Particulate Filter (VW Diesel Particulate Test)	40.00	42.19	63.96	57.80

Claims

1. The use, in a lubricating oil composition comprising base oil, of one or more magnesium detergents, for the reduction of clogging in a diesel particulate filter.

2. Use according to Claim 1, wherein the clogging is measured by the VW diesel particulate filter test.

3. Use according to Claim 1 or 2, wherein the lubricating oil composition has a sulphated ash content of not greater than 1.0 wt. %, based on the total weight of the lubricating oil composition.

4. Use according to any one of Claims 1 to 3, wherein the one or more magnesium detergents are selected from magnesium salicylate detergents, magnesium phenate detergents and magnesium sulphonate detergents.

5. Use according to Claim 4, wherein the one or more magnesium detergents each, independently, have a TBN (total base number) value in the range of from 30 to 600 mg.KOH/g, as measured by ISO 3771.

6. Use according to any one of Claims 1 to 5, wherein the base oil is selected from mineral oil and/or synthetic oil.

7. Use according to any one of Claims 1 to 6, wherein the one or more magnesium detergents are present in a total amount of not greater than 0.2 wt. % in terms of magnesium content, based on the total weight of the lubricating oil composition.

8. Use according to any one of Claims 1 to 7, wherein the lubricating oil composition has a phosphorus content in the range of from 0.04 to 0.1 wt. %, based on the total weight of the lubricating oil composition.

9. Use according to any one of Claims 1 to 8, wherein the lubricating oil composition further comprises one or more additives selected from anti-oxidants, anti-wear additives, supplementary detergents, dispersants, friction modifiers, viscosity index improvers, pour point depressants, corrosion inhibitors, defoaming agents and seal fix or seal compatibility agents.

10. Method of improving performance in a diesel particulate filter test, comprising lubricating an internal combustion engine with a lubricating oil composition as described in any one of Claims 1 to 9.

11. Use of a lubricating oil composition as described in any one of Claims 1 to 9 in order to obtain a result of less than 50 % weight increase of a diesel particulate filter, as measured by the VW diesel particulate filter test.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 12 4257

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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	20 February 2007	Bertrand, Samuel

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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