

(19)



(11)

EP 2 690 165 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

29.01.2014 Bulletin 2014/05

(51) Int Cl.:

C10M 159/22 (2006.01)

C10M 159/20 (2006.01)

C10N 10/04 (2006.01)

C10N 30/04 (2006.01)

C10N 40/25 (2006.01)

(21) Application number: **12177849.2**

(22) Date of filing: **25.07.2012**

(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

(71) Applicant: **Infineum International Limited**

**Abingdon,
Oxfordshire OX13 6BB (GB)**

(72) Inventor: **Shaw, Robert**

Abingdon, Oxfordshire OX13 6BB (GB)

(74) Representative: **Goddard, Frances Anna et al**

**PO Box 1
Milton Hill
Abingdon, Oxfordshire OX13 6BB (GB)**

(54) **Lubricating oil compositions**

(57) The invention relates to the finding that use of magnesium-based detergent additives in a lubricating oil composition can effect reduced inlet valve deposit formation in direct injection internal combustion engines.

EP 2 690 165 A1

Description

[0001] This invention relates to lubrication of direct injection internal combustion engines with crankcase lubricating oil compositions (or lubricants), more especially to lubrication of gasoline-fuelled direct injection engines and diesel-fuelled direct injection engines, and to use of additives in lubricating oil compositions to reduce inlet valve deposit formation.

[0002] A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally below the crankshaft of the engine and to which circulated oil returns. It is well-known to include additives in crankcase lubricants for several purposes.

[0003] One type of additive that is commonly used in a lubricating oil composition for acid neutralisation is a detergent additive. Many types of detergent additives are known for crankcase lubricating oil composition. Of these, the most commonly used commercially are alkali or alkaline earth metal salts of sulfonate, phenate or salicylate.

[0004] For example, in European Patent Application No. EP1724329A, a lubricant with no more than 0.08 wt% phosphorous comprising a metal detergent system comprising a calcium salicylate detergent and a magnesium salicylate detergent, wherein the mass ratio of magnesium atoms to calcium atoms is greater than 1, is stated to exhibit improved wear performance despite the reduced phosphorous content.

[0005] One problem that arises from use of a direct-injection internal combustion engine is accumulation of carbon deposits around the inlet valves of the engine. This type of deposit is thought to be caused by oil mist, carbon and other particulates picked up in the engine crankcase and re-circulated by the exhaust gas recirculation system into parts of the engine where the lubricant is not intended to reside. It is thought that the oil mist, particulates and fuel constituents deposit a sticky coating on the intake valve, which once formed serves as a base for further deposits. The deposits can cause the valves to open and close more slowly, prevent the valves closing properly or cause the valves to stick. All of these effect a reduction in the engine efficiency. This problem is a feature of a direct-injection engine, in which the inlet valves are not flushed clean by the fuel in use.

[0006] A solution to this problem has been proposed in the form of a catalytic surface applied to the engine valves to counteract the formation of carbon deposits. However, this solution has not been successful commercially.

[0007] The present invention resides in the use of a magnesium salicylate detergent as an additive in a lubricating oil composition to reduced inlet valve deposit formation in a direct-injected internal combustion engine.

[0008] In this specification, the following words and expressions, if and when used, shall have the meanings ascribed below:

"active ingredient" 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 in excess of 50 mass % of a composition;

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

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

[0009] Furthermore in this specification:

"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.

[0010] 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.

[0011] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

[0012] The present invention resides in the use of a lubricating oil composition containing a magnesium salicylate detergent to reduce inlet valve deposits.

[0013] The lubricating oil composition will comprise a lubricating oil base stock, into which a number of additives including the magnesium salicylate additive are blended. The base oil and these additives are described more fully below.

[0014] The oil of lubricating viscosity is sometimes referred to as the base oil or base stock, and provides the primary

liquid constituent of the lubricating oil composition into which additives and possibly other oils are blended.

[0015] A base oil may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil and heavy duty diesel oil. Generally the viscosity of the oil ranges from 2 to 30, especially 5 to 20, mm²s⁻¹ at 100°C.

[0016] Natural oils include animal and vegetable oils (e.g. castor and lard oil), liquid petroleum oils and hydrotreated, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

[0017] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymers of olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly (1-hexenes), poly (1-octenes), poly (1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di (2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivatives, analogues and homologues thereof.

[0018] 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 these esters include 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 of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0019] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0020] Unrefined, refined and re-refined oils can be used in the compositions 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, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

[0021] Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch-synthesised hydrocarbons made from synthesis gas containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

[0022] Base oil may be categorised in Groups 1 to V according to the API EOLCS 1509 definition.

[0023] The oil of lubricating viscosity is provided in a major amount, in combination with a minor amount of the magnesium salicylate additive and, if necessary, one or more co-additives such as described hereinafter, constituting the lubricating oil composition. This preparation may be accomplished by adding the additive directly to the oil or by adding it in the form of a concentrate thereof to disperse or dissolve the additive. Additives may be added to the oil by any method known to those skilled in the art, either prior to, contemporaneously with, or subsequent to, addition of other additives.

[0024] The terms "oil-soluble" or "oil-dispersible", or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. They 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.

[0025] Metal detergents are now used predominantly for their acid-neutralisation properties, and the term 'detergent' is used herein to define a material capable of providing this functions within the lubricating oil composition. They are based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants, and that generally comprise a polar head with a long hydrophobic tail. In use, a metal detergent provides a source of base (such as metal hydroxide or metal carboxylate), which neutralises the acidic combustion by-products such as NO_x and SO_x present in the oil. These acidic combustion by-products cause oxidation and thus degradation of the lubricants as well as corrosion of the engine components.

[0026] The metal salts of acidic organic compounds may contain a substantially stoichiometric amount of the metal

in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 100 or greater, and typically will have a TBN of from 250 to 450 or more.

[0027] In the lubricant used in the present invention, the magnesium salicylate detergent additive may be the sole detergent additive present in the lubricating oil composition. Alternatively, the lubricating oil composition may comprise a combination of two or more alkali or alkaline earth metal-containing detergent additives.

[0028] The metal detergent system comprises magnesium salicylate and optionally comprises other alkali or alkaline earth metal salicylate detergents, such as, calcium salicylate. Conveniently, each salicylate is alkyl-substituted for example with independent alkyl groups having from 8 to 30 carbon atoms and which may be linear, branched or cyclic. As examples of alkyl groups there may be mentioned the following: octyl, nonyl, decyl, dodecyl, pentadecyl, octadecyl, eicosyl, docosyl, tricosyl, hexacosyl, triacontyl, dimethylcyclohexyl, ethylcyclohexyl, methylcyclohexylmethyl and cyclohexylethyl. The lubricating oil composition used in the present invention comprises metal detergents that are neutral or overbased alkali or alkaline earth metal salicylates having a TBN of from 50 to 450, preferably a TBN of 50 to 250, or mixtures thereof.

[0029] The lubricating oil composition of the present invention may comprise other detergents, including oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present in detergents used in a lubricant according to the present invention, and mixtures of calcium and/or magnesium with sodium. Combinations of detergents, whether overbased or neutral or both, may be used.

[0030] In one embodiment of the present invention, the lubricating oil composition includes metal detergents that are chosen from neutral or overbased calcium sulfonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulfurized phenates having TBN of from 50 to 450, and mixtures thereof.

[0031] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples included those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms per alkyl substituted aromatic moiety.

[0032] The oil soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 mass % (preferably at least 125 mass %) of that stoichiometrically required.

[0033] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide and neutral or overbased products may be obtained by methods well known in the art. Sulfurized phenols may be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide or sulfur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulfur containing bridges.

[0034] Preferably, substantially all of the metal detergent present in the lubricating oil composition used in the present invention is either a magnesium-based detergent or a calcium-based detergent. Suitably, detergent present in the lubricating oil composition comprising at least 50 mass%, preferably at least 60 mass% and more preferably at least 70 mass% magnesium-based detergent. In a preferred embodiment, the detergent present in the lubricating oil composition comprises 100 mass% magnesium-based detergent.

[0035] If the lubricating oil composition comprises a combination of two or more detergent additives, the magnesium salicylate detergent additive preferably provides the largest proportion of the detergent additive in the lubricating oil composition.

[0036] The detergent additive present in a lubricating oil composition used for the present invention suitably comprises at least 40 mass%, preferably at least 50 mass%, more preferably at least 60 mass% and advantageously at least 70 mass% magnesium salicylate detergent. The detergent additive present in a lubricating oil composition used for the present invention may comprise no more than 95 mass%, for example, no more than 90 mass%, even no more than 85 mass% magnesium salicylate detergent.

[0037] However, in one preferred embodiment of the present invention, the detergent additive present in a lubricating oil composition used for the present invention comprises 100 mass% magnesium salicylate detergent.

Other Additives

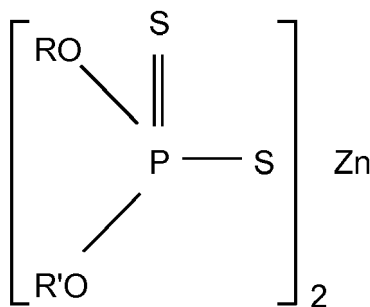
[0038] Other additives, such as the following, may also be present in the lubricating oil composition used for the present invention.

[0039] Ashless dispersants comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersants may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and a polyalkylene polyamine.

[0040] Anti-wear agents may comprise dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc.

[0041] Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first 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 metal compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

[0042] The preferred zinc dihydrocarbyl dithiophosphates (ZDDP) are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



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

[0043] To limit the amount of phosphorus introduced into the lubricating oil composition by ZDDP to no more than 0.08 mass %, the ZDDP should preferably be added to the lubricating oil compositions in amounts no greater than from about 1.1 to 1.3 mass %, based upon the total mass of the lubricating oil composition.

[0044] Viscosity modifiers (VM) function to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional.

[0045] Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/ isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

[0046] Oxidation inhibitors or antioxidants reduce the tendency of base stocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, aromatic amines, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfides, ashless oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorus esters, metal thiocar-

bamates and oil-soluble copper compounds as described in U.S. Patent 4,867,890.

[0047] Friction Modifiers which include boundary lubricant additives that lower friction coefficient and hence improve fuel economy may be used. Examples include ester-based organic friction modifiers such as partial fatty acid esters of polyhydric alcohols, for example, glycerol monooleate; and amine-based organic friction modifiers. Further examples are additives that deposit molybdenum disulphide such as organo-molybdenum compounds where the molybdenum is, for example, in dinuclear or trinuclear form.

[0048] Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

[0049] Copper and lead bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4 thiadiazoles such as those described in U.S. Patent Nos. 2,719,125; 2,719,126; and 3,087,932; are typical. Other similar materials are described in U.S. Patent Nos. 3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in GB Patent Specification No. 1,560,830. Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 mass % active ingredient.

[0050] A small amount of a emulsifying component may be used. A preferred demulsifying component is described in EP 330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reacting a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

[0051] Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which improve the low temperature fluidity of the fluid are C₈ to C₁₈ dialkyl fumarate/vinyl acetate copolymers, polyalkylmethacrylates and the like.

[0052] Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0053] The individual additives may be incorporated into a base stock in any convenient way. Thus, each of the components can be added directly to the base stock or base oil blend by dispersing or dissolving it in the base stock or base oil blend at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

[0054] Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate or additive package described herein as the additive package, which is subsequently blended into base stock to make the finished lubricant. The concentrate will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the concentrate is combined with a predetermined amount of a base lubricant.

[0055] The concentrate is preferably made in accordance with the method described in US 4,938,880.

[0056] The lubricating oil composition used in the present invention may employ from 2 to 20, preferably 4 to 18, and most preferably 5 to 17, mass % of the concentrate or additive package with the remainder being base stock.

[0057] Suitably, the lubricating oil composition used in the present invention has a sulphated ash concentration of not greater than 1.5 mass %, preferably not greater than 1.2 mass% and in some embodiments, not greater than 0.10 mass% or even 0.08 mass%.

[0058] A lubricating oil composition used in the present invention suitably has a sulphur concentration, expressed as atoms of sulphur, of not greater than 0.3, preferably not greater than 0.2, mass %.

[0059] A lubricating oil composition used in the present invention may have a phosphorus content of at least 0.005 mass%, preferably at least 0.01 mass %, more preferably at least 0.04 mass%, based on the mass of the oil composition. A lubricating oil composition according to the present invention may have a phosphorus content of at no more than 0.15 mass%, preferably no more than 0.12 mass% and for some applications no more than 0.09 mass%, based on the mass of the oil composition.

[0060] A lubricating oil composition according to the present invention may have a total base number (TBN) of between 2 and 20, preferably between 4 and 15.

Engines

[0061] The invention is applicable to a range of internal combustion engines such as compression-ignited and spark-ignited, two-or four-stroke reciprocating engines. However, the invention provides particular advantage in use with direct injection compression-ignited or spark-ignited internal combustion engines.

Examples

[0062] The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

Example 1

[0063] Four fully-formulated lubricating oil compositions were blended by methods known in the art. The four lubricants differed only in the detergent additive present in the lubricant. The amount of each detergent additive was chosen to ensure each oil had a sulphated ash content of 0.65 mass%. The type and amount of detergent additive present in each of the four oils is set out in Table 1 below:

Table 1

Detergent/Mass %	Oil 1	Oil 2	Oil 3	Oil 4
Calcium sulfonate	1.30			
Magnesium Salicylate		1.59		
Magnesium Sulfonate			1.33	
Calcium salicylate				1.20

[0064] Each of the four lubricants was tested in the VW FSi test (identified by reference PV1481) to assess inlet valve deposits. The test provides a measure of weight increase resulting from deposit formation on the inlet valves. To run this test, a VW 1.4 litre, 77 KW direct injection FSi gasoline engine is used. Before the test is run, the intake valves are weighed. The test is run with the engine filled with a mass of oil corresponding to a filling volume of 3,200 cm³ at 15 °C, with a 200ml sample of the new oil being retained as a reference sample. The test run consists of 4 stages each at specific engine speed, which are repeated 1333 times, with the total running time of the test being 5998.5 minutes. The full details of the test set up and run procedure are set out in document PV1481:2005-02, the contents of which are incorporated herein by reference. At the end of the test, the oil is collected and weighed to determine the oil consumption. The intake valves are cleaned of residual oil by bathing in petroleum ether (40/60 mixture) for 10 seconds. The cleaned valves are then air dried before being reweighed to determine weight gain as a measure of the amount of deposit formation.

[0065] The weight increase for each of Oils 1-4 is shown below:

Lubricant 1	: 895
Lubricant 2	: 333
Lubricant 3	: 780
Lubricant 4	: 658

[0066] It can be seen from these results that lubricants containing magnesium based detergents such as in Oils 2 and 3 provide significant improvements in performance compared to Oil 1 containing the calcium sulfonate detergent.

[0067] Whilst Oil 4 illustrates that salicylate-type detergents outperform sulfonate-type detergents in this test, it could not have been predicted that magnesium salicylate detergent would perform so much better than any of the other detergent additives tested.

Claims

1. The use of a magnesium salicylate detergent as an additive in a lubricating oil composition to reduced inlet valve deposit formation in a direct injection internal combustion engine.
2. The use according to Claim 1, wherein the lubricating oil composition comprises a combination of two or more alkali or alkaline earth metal-containing detergent additives.
3. The use according to Claim 1 or 2, wherein the detergent present in the lubricating oil composition comprises 100 mass% magnesium-based detergent.

4. The use according to Claim 1, 2 or 3, wherein the magnesium salicylate detergent additive provides the largest proportion of the detergent additive in the lubricating oil composition.
5. The use according to any one of the preceding claims, wherein the magnesium salicylate detergent comprises at least 40, mass%, suitably at least 50 mass%, preferably at least 60 mass% and more preferably at least 70 mass% of the detergent additive.
6. The use according to any one of the preceding claims, wherein the detergent additive present in the lubricating oil composition comprises no more than 95 mass%, for example, no more than 90 mass%, even no more than 85 mass% magnesium salicylate detergent.
7. The use according to any one of Claims 1 to 5, wherein the detergent additive present in a lubricating oil composition used for the present invention comprises 100 mass% magnesium salicylate detergent.



EUROPEAN SEARCH REPORT

Application Number
EP 12 17 7849

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2012/047949 A1 (LUBRIZOL CORP [US]; COOK STEPHEN J [GB]; MAYHEW ALEXANDRA [GB]; DAVIES) 12 April 2012 (2012-04-12) * paragraphs [0042] - [0043]; claim 17 *	1-7	INV. C10M159/22 C10M159/20
A	US 2004/198614 A1 (CALDER RAYMOND M [GB]) 7 October 2004 (2004-10-07) * claim 1 *	1-7	ADD. C10N10/04 C10N30/04 C10N40/25
A	MACKNEY ET AL: "Reducing Deposits in a DISI Engine", POWERTRAIN AND FLUID SYSTEMS CONFERENCE AND EXHIBITION, XX, XX, no. 2002-01-2660, 21 October 2002 (2002-10-21), pages 1-12, XP002286798, * abstract *	1-7	
A	JP 2003 155492 A (NIPPON OIL CORP) 30 May 2003 (2003-05-30) * abstract *	1-7	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 1 October 2012	Examiner Bertrand, Samuel
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
EPO FORM 1503 03.82 (P04C01)

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

EP 12 17 7849

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.

01-10-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012047949 A1	12-04-2012	NONE	

US 2004198614 A1	07-10-2004	EP 1608725 A1	28-12-2005
		JP 2006522204 A	28-09-2006
		US 2004198614 A1	07-10-2004
		WO 2004094573 A1	04-11-2004

JP 2003155492 A	30-05-2003	JP 3933450 B2	20-06-2007
		JP 2003155492 A	30-05-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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

- EP 1724329 A [0004]
- US 4867890 A [0046]
- US 2719125 A [0049]
- US 2719126 A [0049]
- US 3087932 A [0049]
- US 3821236 A [0049]
- US 3904537 A [0049]
- US 4097387 A [0049]
- US 4107059 A [0049]
- US 4136043 A [0049]
- US 4188299 A [0049]
- US 4193882 A [0049]
- GB 1560830 A [0049]
- EP 330522 A [0050]
- US 4938880 A [0055]