

LUBRICATING OIL WITH ENHANCED PISTON CLEANLINESS CONTROL

[0001] The present invention relates to lubricating oil compositions. More specifically, the present invention relates to lubricating oil compositions that have reduced levels of sulfated ash, phosphorus and sulfur (low "SAPS"), yet provide improved lubricant performance in internal combustion engines.

[0002] Environmental concerns have led to continued efforts to reduce the emissions of carbon monoxide (CO), hydrocarbon and nitrogen oxide (NO_x) from compression-ignited (diesel-fueled) and spark-ignited (gasoline-fueled) internal combustion engines. There have also been continued efforts to reduce the particulate emissions from compression-ignited internal combustion diesel engines. To meet the contemporary emission standards for passenger cars and other vehicles, original equipment manufacturers (OEMs) have been applying exhaust gas after-treatment devices. Such exhaust gas after-treatment devices include, but are not limited to, catalytic converters and/or particulate traps.

[0003] Catalytic converters typically contain one or more oxidation catalysts, NO_x storage catalysts, and/or NH₃ reduction catalysts. The catalysts contained therein generally comprise a combination of catalytic metals such as platinum, and metal oxides. Catalytic converters are installed in the exhaust systems, for example, the exhaust pipes of automobiles, to convert the toxic gases to nontoxic gases. The use of catalytic converters is thought to be essential in bucking global warming trends and combating other environmental detriments. The catalysts, however, can be poisoned and rendered less effective, if not useless, as a result of exposure to certain elements or compounds, especially phosphorus compounds. Among the many ways phosphorus compounds may be introduced into the exhaust gas is the degradation of

phosphorus-containing lubricating oil additives. Examples of phosphorus lubricating oil additives include zinc dialkyldithiophosphates and the like. Zinc dialkyldithiophosphates are among the most effective and conventionally used antioxidants and antiwear agents, from both a performance and cost-effectiveness standpoint, in lubricating oil compositions. While they are effective antioxidants and antiwear agents, the phosphorus, sulfur and ash they introduce into the engine react with the catalysts and may shorten the service life of the catalytic converters. Reduction catalysts are susceptible to damage by sulfur and sulfur compounds in the exhaust gas, which are introduced by the degradations of both the base oil used to blend the lubricants and sulfur-containing lubricant oil additives. Examples of sulfur-containing lubricant oil additives include, but are not limited to, magnesium sulfonate and other sulfated or sulfonated detergents.

[0004] Particulate traps are usually installed in the exhaust system, especially in diesel engines, to prevent the carbon black particles or very fine condensate particles or agglomerates thereof (*i.e.*, “diesel soot”) from being released into the environment. Aside from polluting air, water, and other elements of the environment, diesel soot is a recognized carcinogen. These traps, however, can be blocked by metallic ash, which is the degradation product of metal-containing lubricating oil additives including common ash-producing detergent additives.

[0005] To insure a long service life for the after-treatment devices, it is desirable to identify lubricating oil additives that exert a minimum negative impact on such devices. To this end, OEMs often set various limits for maximum sulfur, phosphorus, and/or sulfated ash levels for “new service fill” and “first fill” lubricants. For instance, when used in light-duty passenger-car internal combustion engines, the sulfur levels are typically required to be at or below 0.30 wt.%, the phosphorus levels

at or below 0.08 wt.%, and the sulfated ash contents at or below 0.8 wt.%. The maximum sulfur, phosphorus and/or sulfated ash levels may differ, however, when the lubricating compositions are used in heavy-duty internal combustion engines. For example, the maximum sulfated ash level may be as high as 1.0 wt.% in those heavy-duty engines. Such lubricating oil compositions are also referred to as “low SAPS” (low sulfated ash, phosphorus, sulfur) lubricating oil compositions for gasoline engines, and/or light duty diesel engines, and “low SAPS” or “LEDL” (low emission diesel lubricant) oil compositions for heavy duty diesel engines. Various tests have been established and standardized to measure the levels of SAPS in any particular lubricating oil compositions. For example, in Europe, a lubricant meeting the ACEA gasoline and diesel engine low SAPS specification must pass, *inter alia*, the “CEC L-78-T-99” test, which measures the cleanliness and extent of piston ring sticking after running a Volkswagen turbocharged direct injection automotive diesel engine for an extended time period, cycling alternatively between idle and full power. Similar specifications and testing standards of varied stringencies can also be found in other countries and regions, such as Japan, Canada, and the United States.

[0006] Meeting the low SAPS environmental standards does not eliminate the need to provide adequate lubricant performance. Automobile spark ignition and diesel engines have valve train systems, including valves, cams and rocker arms, all of which must be lubricated and protected from wear. Further, engine oils must provide sufficient detergency so as to insure engine cleanliness and suppress the production of deposits, which are products of non-combustibles and incomplete combustibles of hydrocarbon fuels and deterioration of engine oils.

[0007] As discussed above, the need to preserve the integrity of catalytic converters has led to the use of less phosphate and phosphorus-containing additives.

However, the use of detergents, which are typically metal sulfonate detergents, is often inevitable because of the sustained needs to neutralize the oxidation-derived acids and suspend polar oxidation residues in the lubricant. These detergents, however, contributes to the production of sulfated ash. Indeed, the amount of ash permitted under most of the current environmental standards can be exceeded by far less metal sulfonate detergent than is necessary to achieve adequate detergency performance. Reducing the levels of detergent overbasing may reduce the level of ash produced, but it also reduces the acid neutralizing capacity of the lubricant composition, potentially leading to acid corrosion of the engine pistons and other parts.

[0008] Therefore, it would be advantageous to identify low SAPS lubricating oil compositions and additives that not only foster cleaner environment by allowing the catalyst converters and particulate traps to effectively reduce pollutants, but also improve fuel economy by, for instance, reducing friction within an engine. A need is thus apparent for compromises or new approaches through which both the environmental standards and the engine lubrication needs can be satisfied.

[0009] Various low SAPS additives and lubricant compositions have been identified as capable of providing piston cleanliness in internal combustion engines. For example, U.S. Patent Application 11/217,674 (published as U.S. 2006/0052254) disclosed a low SAPS lubricant composition that provided good piston cleanliness in an XUD-IIBTE (CEL-L-56-T-98) test. The lubricating oil composition of this application had a sulfur content of up to 0.3 wt.%, a phosphorus content of up to 0.08 wt.%, a sulfated ash content of up to 0.80 wt.%, and contained less than 5 mmoles of salicylate soap per kilogram of lubricating oil composition. A companion application, U.S. Patent Application 11/218,647 (published as U.S. 2006/0058200) disclosed a

low SAPS lubricating oil composition with similar advantages. That composition comprised (a) a major amount of an oil of lubricating viscosity; (b) at least one nitrogen-containing dispersant to provide a nitrogen content of at least 0.075 wt.%, the dispersant having a polyalkenyl backbone of molecular weight of about 900 to about 3000 Daltons; and (c) an oil-soluble or oil-dispersible source of boron to provide a wt.% ratio of nitrogen to boron of about 3:1 to about 5:1; (d) an antioxidant; and (e) a zinc dihydrocarbyldithiophosphate. In U.S. Patent Application 11/226,793 (published as U.S. 2006/0068999), yet another low SAPS lubricating oil composition comprising (1) a major amount of an oil of lubricating viscosity; (2) an overbased magnesium-containing lubricating oil detergent having a TBN of 200 to 500 present in such an amount to provide a TBN of 5.3 to 7.3 to the finished composition; and (3) 2.5 to 4 wt.% of an ashless dispersant, was said to provide enhanced piston merits.

[0010] Low SAPS lubricating oil compositions have also been known to impart certain other desirable properties. For example, an internal combustion engine oil of this kind was reported to retain high total base number (TBN) in U.S. Patent Application 11/176,424 (published as U.S. 2006/0014653). The composition had a sulfated ash content of not greater than 0.9 wt.%, and a phosphorus content from 0.04 to 0.1 wt.%. The composition contained base oil; one or more detergents selected from phenate detergents, salicylate detergents, and sulphonate detergents, wherein said one or more detergents each, independently, had a TBN value of from 30 to 350 mg KOH/g; and at least 3.5 wt.% of one or more antioxidants selected from the group of aminic antioxidants and phenolic antioxidants.

[0011] In another example, U.S. Patent Application 11/288,600 (published as U.S. 2006/0116300) disclosed a low SAPS lubricating oil composition that provided improved lubricant performance, and especially antiwear properties, in compression-

ignited diesel engines according to a Mack T10 screener test. That low SAPS lubricating oil composition comprised (1) a major amount of an oil of lubricating viscosity; (2) a minor amount of a calcium salicylate detergent; (3) a minor amount of an overbased magnesium detergent; and (4) a minor amount of a basic, low molecular weight nitrogen-containing dispersant derived from a polymer having a number average molecular weight of no greater than 1100 Daltons.

[0012] It has now been found that reaction products of polyisobutylenes and monounsaturated acylating agents, when accompanied by at least one ashless dispersant, at least one metal-containing detergent, at least one antiwear additive, and at least one antioxidant, significantly enhance piston cleanliness control in internal combustion engines. The present invention therefore provides a low sulfated ash, low phosphorus and low sulfur lubricant composition, including an additive package or a concentrate, comprising such a reaction product of a polyisobutylene and a monounsaturated acylating agent. The present invention also provides methods of using and making such a lubricating oil composition.

[0013] A reaction product of a polyisobutylene and a monounsaturated acylating agent is typically prepared from its non-carboxylated polyisobutylene precursor. Polyisobutylenes (PIBs) are also known as polyisobutenes to persons skilled in the art. They have also been given the name “butyl rubber,” as they are much used in that capacity. In the lubricant and/or fuel additive field, PIBs have found wide use as dispersants, viscosity improvers, thickeners, and the like. The common uses for PIBs have been summarized, for example, in section 3.3 (page 846) of *Speight*, CHEMISTRY & TECHNOLOGY OF PETROLEUM CHEMICAL INDUSTRIES, v.76, 3d ed. (N.Y. Marcel Dekker, Inc., 1999); and in section 4.1 of *Immel*, ULMANN’S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY (Wiley-VCH Verlag GmbH & Co. KGaA,

2002). Useful PIBs generally contain residual unsaturation in amounts of about one ethylene double bond per polymer chain, positioned anywhere along the chain. Preferably, however, the PIBs are prepared from a pure isobutylene steam or a Raffinate I stream, resulting in a reactive isobutylene polymer with terminal vinylidene olefins. These particular PIBs comprising terminal vinylidene olefins are often referred to as “highly reactive polyisobutylenes (HR-PIBs)” by those skilled in the art. Particularly preferably, a useful HR-PIB would have a terminal vinylidene content of at least about 50%, for example, at least about 55%, or at least about 65%, or at least about 70%, or at least about 80%, or more preferably, at least about 85%. Such HR-PIBs can be prepared according to various art-recognized techniques, such as, for example, those described in U.S. Patent Nos. 4,152,499 and 4,605,808. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures and claims herein, are incorporated by reference. Certain HR-PIBs are commercially available, for example, under the trade name of GLISSOPAL™ (from BASF®).

[0014] Reaction products of PIBs and monounsaturated acylating agents, especially the succinic anhydride derivatives, namely, the polyisobutylene succinic anhydrides (PIBSAs), have been used as precursors in manufacturing ashless dispersants. Examples of such use can be found in U.S. Patent Nos. 5,827,806 and 6,245,725, each disclosing, *inter alia*, the making of a preferred set of nitrogen-containing ashless dispersants from certain PIBSAs, polyethylene amines (*e.g.*, tetraethylene pentamine, polyoxypropylene diamine), and aminoalcohols (*e.g.*, triethylolaminomethane).

[0015] PIBSAs have also been applied directly, *i.e.*, without derivatization, as dispersants. For example, U.S. Patent No. 6,632,781 disclosed using a dispersant

mixture comprising a polyalkylene succinic dispersant selected from the group consisting of: (1) a polyalkylene succinic anhydride, preferably a PIBSA; (2) a non-nitrogen containing derivative of the polyalkylene succinic anhydride; and (3) mixtures of polyalkylene succinic anhydrides; (4) mixtures of non-nitrogen containing derivatives of the polyalkylene succinic anhydride; and (5) mixtures of one or more polyalkylene succinic anhydrides and one or more non-nitrogen containing derivatives of polyalkylene succinic anhydrides. That dispersant was said to impart enhanced water tolerance and lubricant-oil compatibility for alkali metal borates.

[0016] The present invention provides a low sulfated ash, low phosphorus and low sulfur lubricant composition, including an additive package or a concentrate, comprising at least one reaction product of a PIB and a monounsaturated acylating agent. The lubricant additive compositions of the invention provide superior piston cleanliness, but are also compatible for low SAPS applications. The present invention further provides methods of applying and making these compositions.

SUMMARY OF THE INVENTION

[0017] In first aspect, there is provided a lubricant composition suitable for use in an internal combustion engine, which comprises an admixture of: (a) a major amount of an oil of lubricating viscosity; (b) one or more ashless dispersants; (c) one or more metal-containing detergents; and (d) a piston-cleanliness-enhancing amount of at least one reaction product of a polyisobutylene and a monounsaturated acylating agent, wherein the polyisobutylene has a number average molecular weight of about 200 to about 5000 Daltons; wherein said lubricant composition has a sulfur content of at or below about 0.3 wt.%, a phosphorus content of at or below about 0.09 wt.%, and a sulfated ash content of at or below about 1.6 wt.%, based on the total weight of said lubricating oil composition.

[0017a] In a second aspect, there is provided a method of improving piston cleanliness in an internal combustion engine, said method comprising: operating said internal combustion engine with a low phosphorus, low sulfur and low sulfated ash lubricating oil composition as disclosed hereinabove.

[0017b] In a third aspect, there is provided a method of operating an internal combustion engine provided with exhaust gas after-treatment devices, which method comprises lubricating said engine with a lubricating oil composition as disclosed hereinabove.

[0017c] The present disclosure provides lubricating oil compositions that provide high piston cleanliness, especially when the machines housing those compositions operate at elevated temperatures, but which introduce low levels of phosphorous, low levels of sulfur, and low levels of sulfated ash to the internal combustion engines. The levels of phosphorous in the lubricating oil compositions of the present disclosure are typically at or below about 0.09 wt.%, and preferably at or below about 0.08 wt.%, and more preferably at or below about 0.07 wt.%, and particularly preferably at or below about 0.05 wt.%. The levels of sulfur produced by the lubricating oil compositions of the present disclosure are typically at or below about 0.30 wt.%, and preferably at or below about 0.20 wt.%, and particularly

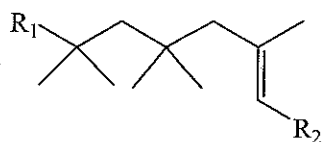
preferably at or below about 0.10 wt.%. The levels of sulfated ash produced by the lubricating oil compositions of the present disclosure are typically at or below about 1.60 wt.%, but preferably at or below about 1.00 wt.%, more preferably at or below about 0.80 wt.%, even more preferably at or below about 0.50 wt.%, and particularly preferably at or below about 0.45 wt.%. In one embodiment of the present, the level of sulfated ash will be from above about 0.50 to about 1.60 wt.%, preferably from above about 0.5 to about 0.8 wt.%.

[0018] Therefore, the present lubricating compositions are more desirable from an environmental standpoint than the conventional internal combustion engine lubricating oils that contain higher phosphorous, sulfur and sulfated ash. The compositions of the present disclosure facilitate longer service lives for the catalytic converters and the particulate traps, while providing the desired piston cleanliness.

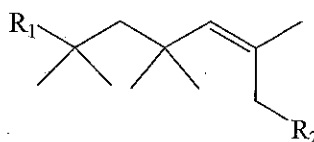
[0019] In a first embodiment, the present lubricating oil composition comprises:

- a major amount of a base oil of lubricating viscosity;
- one or more detergents;
- one or more dispersants; and
- a piston-cleanliness-enhancing amount of at least one reaction product of a polyisobutylene and a monounsaturated acylating agent, wherein the polyisobutylene has a number average molecular weight of about 200 to about 5000 Daltons, preferably from about 500 to about 4500 Daltons; wherein, based on the total weight of the lubricating composition, the phosphorus content is no more than about 0.09 wt.%; the sulfur content is no more than about 0.3 wt.%; and the sulfated ash content is no more than about 1.6 wt.%.

The reaction product of a polyisobutylene and a monounsaturated acylating agent may be one represented by either Formula A or Formula B:



[Formula A]



[Formula B]

wherein R_1 is a polyisobutylene chain of number average molecular weight of about 200 to about 5000 Daltons, preferably from about 500 to about 4500 Daltons; and R_2 is a carboxyl-containing group.

[0020] The lubricating oil composition of this embodiment may optionally further comprise one or more additives selected from: (1) antiwear agents; (2) friction modifiers; (3) antioxidants; (4) corrosion inhibitors; (5) anti-foam additives; (6) seal fixes or seal pacifiers; (7) pour point depressants; (8) viscosity index modifiers; and (9) multifunctional additives.

[0021] In a second embodiment, the disclosure provides an additive package composition or a concentrate comprising at least one reaction product of a PIB and a monounsaturated acylating agent in an organic diluent liquid, for example, base oil. The additive package composition or concentrate of this embodiment preferably further comprises various other additives desired in lubricating oil, such as, for example, ashless dispersants, metal-containing detergents, antiwear additives, antioxidants, friction modifiers, corrosion inhibitors, anti-foam additives, pour point depressants, viscosity index improvers, and seal fixes or seal pacifiers.

[0022] In a third embodiment, the disclosure provides a method of operating an internal combustion engine provided with one or more exhaust gas after-treatment devices, which method comprises lubricating said engine with a lubricating composition of the first embodiment, or with an additive package composition or a concentrate of the second embodiment.

[0023] In a fourth embodiment, the disclosure provides a method of preparing a lubricating oil composition of the first embodiment or an additive package or a concentrate of the second embodiment.

[0024] Persons skilled in the art will understand other and further objects, advantages, and features of the present disclosure by reference to the following description.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Various preferred features and embodiments are described below by way of non-limiting illustrations.

[0026] The present invention provides lubricating oil compositions as described above. The compositions have a total sulfur content of at or below about 0.30 wt.% in typical embodiments, at or below about 0.20 wt.% in some other embodiments, and at or below about 0.10 wt.% in further embodiments. The major source of sulfur in the composition of the invention is often the base stocks and the additives. An exemplary lubricating oil composition of the present invention contains about 0.2 wt.% of sulfur, based on the total weight of the composition.

[0027] The lubricating oil compositions have a total phosphorus content of at or below about 0.09 wt.% in typical embodiments, at or below about 0.08 wt.% in some other embodiments, at or below about 0.07 wt.% in yet other embodiments, and at or below about 0.05 wt.% in further embodiments. An exemplary lubricating oil composition of the present invention contains about 0.07 wt.% of phosphorus, based on the total weight of the composition.

[0028] The lubricating oil compositions have a total sulfated ash content of, as determined by the ASTM D-874, at or below about 1.60 wt.% in typical embodiments, at or below about 1.00 wt.% in some other embodiments, at or below

about 0.80 wt.% in yet other embodiments, at or below about 0.50 wt.% in some other embodiments, and at or below about 0.45 wt.% in further embodiments. An exemplary lubricating oil composition of the present invention has a sulfated ash content of about 0.6 wt.%, based on the weight of the lubricant compositions. Another exemplary lubricating oil composition of the present invention has a sulfated ash content of about 0.8 wt.%, based on the weight of the lubricant composition.

Oil of Lubricating Viscosity

[0029] The low-SAPS lubricating oil composition of the present invention is comprised of one or more base oils, which are present in a major amount (*i.e.*, an amount greater than about 50 wt.%). Generally, the base oil is present in an amount greater than about 60 wt.%, or greater than about 70 wt.%, or greater than about 80 wt.% of the lubricating oil composition. The base oil sulfur content is typically less than about 1.00 wt.%, preferably less than about 0.60 wt.%, more preferably less than about 0.40 wt.%, and particularly preferably less than about 0.30 wt.%.

[0030] The low-SAPS lubricating oil composition may have a viscosity at 100°C of up to about 16.3 mm²/s, and in one embodiment of about 5 to about 16.3 mm²/s (cSt), and in one embodiment of about 6 to about 13 mm²/s (cSt). The low-SAPS lubricating oil composition may have a high-temperature/high-shear viscosity at 150°C as measured by the procedure in ASTM D4683 of up to about 4 mm²/s (cSt), and in one embodiment up to about 3.7 mm²/s (cSt), and in another embodiment about 2 to about 4 mm²/s (cSt), and in yet another embodiment about 2.5 to about 3.7 mm²/s (cSt), and in one further embodiment about 2.6 to about 3.5 mm²/s (cSt).

[0031] The base oil used in the lubricant compositions of the invention may be a natural oil, a synthetic oil, or a mixture thereof, provided that the sulfur content of such an oil does not exceed the above-indicated sulfur concentration limit required to

sustain the low SAPS lubricating oil compositions. The natural oils that are suitable include animal oils and vegetable oils (*e.g.*, castor oil, lard oil). The natural oils may also include mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful.

[0032] Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (*e.g.*, polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); poly(1-hexenes), poly-(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (*e.g.*, dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (*e.g.*, biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers and the derivatives, analogs and homologs thereof, and the like. Synthetic lubricating oils also include oils prepared by a known Fischer-Tropsch gas-to-liquid synthetic procedure.

[0033] Another class of known synthetic lubricating oils includes alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by a process such as esterification or etherification. Examples of these synthetic oils include polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (*e.g.*, methyl-polyiso-propylene glycol ether having a molecular weight of 1000 Daltons or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500 Daltons); and mono- and polycarboxylic esters thereof (*e.g.*, acetic acid esters, mixed C₃-C₈ fatty acid esters, and C₁₃ Oxo acid diester of tetraethylene glycol).

[0034] Another suitable class of synthetic lubricating oils are the esters of dicarboxylic acids (*e.g.*, phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (*e.g.*, butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0035] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

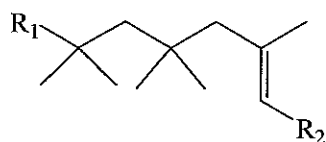
[0036] The synthetic oil can also be a poly-alpha-olefin (PAO). Typically, the PAOs are derived from monomers having from 4 to 30, or from 4 to 20, or from 6 to 16 carbon atoms. Examples of useful PAOs include those derived from octene, decene, mixtures thereof, and the like. These PAOs may have a viscosity from about 2 to about 15, or from about 3 to about 12, or from about 4 to about 8 mm²/s (cSt) at 100°C. Mixtures of mineral oil with one or more of the foregoing PAOs may be used.

[0037] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more) of the types of oils disclosed above can be used in the lubricating compositions of the present invention. Unrefined (or raw) oils are those obtained directly from a natural or synthetic source without further purification

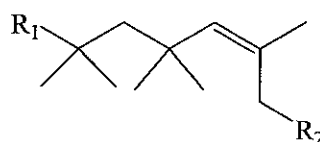
treatment. Refined oils are similar-to the unrefined oils except they have been further treated in one or more purification steps. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Rerefined oils are oils that have been used in service but are subsequently treated so that they may be re-applied in service. Because the used oils almost always contain spent additives and breakdown products, in addition to the standard oil refining steps, steps that would remove the spent additives and breakdown products must be taken. Such rerefined oils are also known as reclaimed or reprocessed oils.

Reaction Products of a PIB & a Monounsaturated Acylating Agent

[0038] It has been found that the incorporation of certain reaction products of polyisobutylenes and monounsaturated acylating agents into base oils provides low SAPS lubricating oils that have the desired levels of piston cleanliness in internal combustion engines. The reaction products of polyisobutylenes and monounsaturated acylating agents of the present invention may be represented by either Formula A or Formula B, as listed below:



[Formula A]



[Formula B]

wherein R_1 is a polyisobutylene (PIB) chain; and R_2 is a carboxyl-containing group. This new approach allows for top tier engine performance with lower than conventional levels of detergents and wear inhibitors.

[0039] The R₁ of Formula A and/or Formula B is a PIB chain. Suitable PIBs that many constitute the chain may be any PIBs that have a number average weight of about 200 to about 5000 Daltons, preferably from about 500 to about 4500 Daltons, particularly preferably from about 1000 to about 3500 Daltons. An exemplary lubricating oil composition of the present invention incorporates a PIB that has a number average molecular weight of about 2300 Daltons.

[0040] The R₂ of Formula A and/or Formula B is a carboxyl-containing group derived from a monocarboxylic acid, dicarboxylic acid, dicarboxylic acid anhydride, anhydride-producing material, or derivatives thereof. Such materials may include, for example, acids, anhydrides, or acid esters. More specifically, such materials may include one or more selected from: (1) monounsaturated C₄ to C₂₀ dicarboxylic acids, wherein (a) the carboxyl groups are vicinyl (*i.e.*, located on adjacent carbon atoms), and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono-unsaturation; (2) derivatives of (1) such as anhydrides and/or C₁ to C₁₀ alcohol-derived monoesters or diesters of (1); (3) monounsaturated C₃ to C₂₀ monocarboxylic acids wherein each of the carbon-carbon double bonds is conjugated with the carboxyl group, *i.e.*, is of the structure: -C=C-CO-; and (4) derivatives of (3) such as C₁ to C₁₀ alcohol-derived monoesters or diesters of (3). In certain embodiments, the R₂ of Formula A and/or Formula B can also be derived from a mixture comprising any proportions of 2 or more of materials (1) to (4). Such materials are also termed “monounsaturated acylating agents” herein. Upon reaction with the PIB backbone, the monounsaturation of each of the monocarboxylic acids, dicarboxylic acids, anhydrides, or derivatives thereof becomes saturated. Thus, for example, maleic anhydride becomes backbone substituted succinic anhydride; acrylic acid becomes back-bone substituted propionic acid. Exemplary monounsaturated carboxylic

reactants include fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower and intermediate alkyl (*e.g.*, C₁ to C₁₀ alkyl) acid esters of the foregoing. Examples of suitable alkyl acid esters include methyl maleate, ethyl fumarate, methyl fumarate, and the like. A particularly preferred monocarboxylic acid-, dicarboxylic acid-, or anhydride-producing material is maleic anhydride. Accordingly, a preferred reaction product of a PIB and a monounsaturated acylating agent is a polyisobutylene succinic anhydride (PIBSA).

[0041] The reaction product of a PIB and a monounsaturated acylating agent of the present invention can be prepared by known procedures. For example, an HR-PIB precursor of Formula A and/or Formula B can be prepared by a cationic polymerization process, at a temperature that is predetermined according to the desired molecular weight for the PIB oligomer. For example, a PIB that has an average molecular weight of about 2300 Daltons can be prepared at a temperature of about 5°F. A catalyst such as BF₃ is often used to advance the polymerization. Following the reaction, the catalyst is typically removed, for example, by extracting the catalyst dissolved in a hot distilled water phase. In another aspect of the polymerization process, the feed into the reactor may include materials such as hexanes and isopropanol. The unreacted residuals of reactive materials, including the unreacted isobutylene monomers, are often removed or purified from the PIB oligomers according to known methods, such as, for example, by flashing in a flash drum and/or using an extraction column. Some HR-PIBs are also commercially available, for example, under the trade name of GLISSOPAL™ (by BASF®).

[0042] Reaction products of such HR-PIBs and monounsaturated acylating agents can be prepared according to known methods. For example, The succinic

anhydride derivative of PIB (*i.e.*, PIBSA) can be prepared in accordance with methods described in U.S. Patent Nos. 6,245,724, 6,933,351, 6,156,850, and others. To the extent they do not conflict with the disclosures and claims herein, the relevant contents of these patents are incorporated by reference. Specifically, a PIBSA can be prepared using a catalyzed “thermal” or “ene” process, wherein the polyisobutylene is reacted with maleic anhydride at an elevated temperature in the presence of sulfonic acid or one or more other strong acid. This process is capable of producing PIBSAs with a range of apparent succinic ratios. Such ratios may be adjusted to attain the desired apparent succinic ratios by modifying reaction parameters such as, for example, the length of time it takes to inject the sulfonic acid or one or more strong acids into the reactor, the maleic anhydride:PIB charge mole ratio, and the reaction hold time. Persons skilled in the art would understand that the apparent succinic ratio is preferably in the range of between about 1 and about 2, preferably between about 1.2 to about 1.6, more preferably between about 1.3 and about 1.4. Various PIBSA products can also be obtained from commercial vendors such as Chevron Oronite Company LLC.

[0043] Suitably, the reaction products of PIBs and monounsaturated acylating agents may be present in the lubricating oil compositions of the present invention in an amount that is sufficient to provide substantially enhanced piston-cleanliness and/or maintain such cleanliness in internal combustion engines. By “substantially enhanced,” it is meant that the pistons are measurably cleaner when assessed against standards of various countries and regions, such as the ACEA standards in Europe and the JASO standards in Japan. Preferably, the amount of one or more reaction products of PIBs and monounsaturated acylating agents is about 0.01 to about 5.00 wt.%, more preferably, about 0.50 to about 4.00 wt.%, particularly preferably, about

1.00 wt.% to 2.50 wt.%. An exemplary lubricating oil composition of the present invention comprised about 2.00 wt.% of a PIBSA, wherein the PIB chain has a number average molecular weight of about 2300 Daltons.

Metal-Containing Detergents

[0044] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound. The composition of the present invention may contain one or more detergents, which are normally salts, and especially overbased salts. Overbased salts, or overbased materials, are single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, in a reaction medium comprising at least one inert, organic solvent (such as mineral oil, naphtha, toluene, xylene) in the presence of a stoichiometric excess of a metal base and a promoter.

[0045] The acidic organic compounds useful in making the overbased compositions of the present invention include carboxylic acids, sulfonic acids, phosphorus-containing acids, phenols or mixtures thereof. Preferably, the acidic organic compounds are carboxylic acids or sulfonic acids with sulfonic or thiosulfonic groups (such as hydrocarbyl-substituted benzenesulfonic acids), and hydrocarbyl-substituted salicylic acids.

[0046] Carboxylate detergents, *e.g.*, salicylates, can be prepared by reacting an aromatic carboxylic acid with an appropriate metal compound such as an oxide or hydroxide. Neutral or overbased products may then be obtained by methods well known in the art. The aromatic moiety of the aromatic carboxylic acid can contain heteroatoms, such as nitrogen and oxygen. Preferably, the moiety contains only carbon atoms. More preferably, the moiety contains six or more carbon atoms, such as a benzene moiety. The aromatic carboxylic acid may contain one or more aromatic moieties, such as one or more benzene rings, fused or otherwise connected *via* alkylene bridges. Examples of aromatic carboxylic acids include salicylic acids and sulfurized derivatives thereof, such as hydrocarbyl substituted salicylic acid and derivatives thereof. Processes for sulfurizing, for example a hydrocarbyl-substituted salicylic acid, are known to those skilled in the art. Salicylic acids are typically prepared by carboxylation, for example, by the Kolbe-Schmitt process, of phenoxides. In that case, salicylic acids are generally obtained in a diluent in admixture with uncarboxylated phenol.

[0047] Sulfonates can be prepared by using sulfonic acid in to sulfonate alkyl-substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or those obtained from alkylation of aromatic hydrocarbons. 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.

[0048] Metal salts of phenols and sulfurized phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide. Neutral or overbased products may be obtained by methods well known in the art. For example, 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 that are mixtures of compounds in which 2 or more phenols are bridged by sulfur-containing bridges.

[0049] The metal compounds useful in making the overbased salts are generally any Group 1 or Group 2 metal compounds in the Periodic Table of the Elements. The Group 1 metals of the metal compound include Group 1a alkali metals (*e.g.*, sodium, potassium, lithium) as well as Group 1b metals such as copper. The Group 1 metals are preferably sodium, potassium, lithium and copper, more preferably sodium or potassium, and particularly preferably sodium. The Group 2 metals of the metal base include the Group 2a alkaline earth metals (*e.g.*, magnesium, calcium, strontium, barium) as well as the Group 2b metals such as zinc or cadmium. Preferably the Group 2 metals are magnesium, calcium, barium, or zinc, more preferably magnesium or calcium, particularly preferably calcium.

[0050] Examples of the overbased detergents include, but are not limited to calcium sulfonates, calcium phenates, calcium salicylates, calcium stearates and mixtures thereof. Overbased detergents suitable for use with the lubricating oils of the present invention may be low overbased (*i.e.*, Total Base Number (TBN) below about 100). The TBN of such a low-overbased detergent may be from about 5 to about 50, or from about 10 to about 30, or from about 15 to about 20. The overbased detergents suitable for use with the lubricating oils of the present invention may alternatively be high overbased (*i.e.*, TBN above about 100). The TBN of such a high-overbased detergent may be from about 150 to about 450, or from about 200 to about 350, or from about 250 to about 280. A low-overbased calcium sulfonate detergent with a TBN of about 17, and a high-overbased calcium sulfurized phenate with a TBN of about 260 are two exemplary overbased detergents in the lubricating oil compositions of the present invention. The lubricating oil compositions of the

present invention may comprise more than one overbased detergents, which may be all low-TBN detergents, all high-TBN detergents, or a mix of the those two types.

[0051] In the lubricant oil compositions of the present invention, the amount of the overbased detergent(s), if present, may be about 0.05 to about 16 mM, or about 3 to about 15 mM, or about 4 to about 14 mM. In an exemplary embodiment of the present invention, about 4 mM of a low-TBN detergent plus about 10 mM of a high-TBN detergent are present in the lubricating oil composition.

[0052] Suitable detergents for the lubricating oil compositions of the present invention also include "hybrid" detergents such as, for example, phenate/salicylates, sulfonate/phenates, sulfonate/salicylates, sulfonates/phenates/salicylates, and the like. Hybrid detergents have been described, for example, in U.S. Patent Nos. 6,153,565, 6,281,179, 6,429,178, and 6,429,179. Relevant disclosures of these patent applications and patents, to the extent they do not conflict with the disclosures and claims herein, are incorporated by reference.

Ashless Dispersants

[0053] Dispersants are generally used to maintain in suspension insoluble materials resulting from oxidation during use, thus preventing sludge flocculation and precipitation or deposition on metal parts. Nitrogen-containing ashless (metal-free) dispersants are basic, and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional sulfated ash. An ashless dispersant generally comprises an oil soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Many types of ashless dispersants are known in the art.

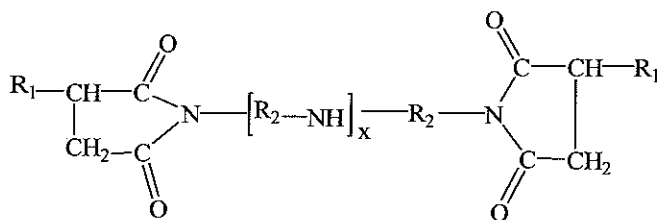
[0054] Typical dispersants include, but are not limited to, amines, alcohols, amides, or ester polar moieties attached to the polymer backbones *via* bridging

groups. The ashless dispersant of the present invention may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons, long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0055] "Carboxylic dispersants" are reaction products of carboxylic acylating agents (acids, anhydrides, esters, etc.) comprising at least 34 and preferably at least 54 carbon atoms with nitrogen containing compounds (such as amines), organic hydroxy compounds (such as aliphatic compounds including monohydric and polyhydric alcohols, or aromatic compounds including phenols and naphthols), and/or basic inorganic materials. These reaction products include imides, amides, and esters.

[0056] Succinimide dispersants are a type of carboxylic dispersants. They are produced by reacting hydrocarbyl-substituted succinic acylating agent with organic hydroxy compounds, or with amines comprising at least one hydrogen atom attached to a nitrogen atom, or with a mixture of the hydroxy compounds and amines. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or a succinic acid-producing compound, the latter encompasses the acid itself. Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0057] Succinic-based dispersants have a wide variety of chemical structures, which may be represented by the formula:



wherein each R_1 is independently a hydrocarbyl group, such as a polyolefin-derived group. Typically the hydrocarbyl group is an alkyl group, such as a polyisobutyl group. Alternatively expressed, the R_1 groups can contain about 40 to about 500 carbon atoms, and these atoms may be present in aliphatic forms. R_2 is an alkylene group, commonly an ethylene (C_2H_4) group. Succinimide dispersants have been more fully described in, for example, U.S. Patent Nos. 4,234,435, 3,172,892 and 6,165,235. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures herein, are incorporated by reference.

[0058] The polyalkenes from which the substituent groups are derived are typically homopolymers and interpolymers of polymerizable olefin monomers of 2 to 16 carbon atoms, and usually 2 to 6 carbon atoms. The amines which are reacted with the succinic acylating agents to form the carboxylic dispersant composition can be monoamines or polyamines.

[0059] Succinimide dispersants are referred to as such since they normally contains nitrogen largely in the form of imide functionality, although the amide functionality may be in the form of amine salts, amides, imidazolines as well as mixtures thereof. To prepare a succinimide dispersant, one or more succinic acid-producing compounds and one or more amines are heated and typically water is removed, optionally in the presence of a normally liquid and substantially inert organic liquid solvent/diluent. The reaction temperature is generally in the range of

about 80°C up to the decomposition temperature of the mixture or the product, which typically falls between about 100°C and about 300°C. Additional details and examples of the procedures for preparing the succinimide dispersants of the present invention have been described in, for example, U.S. Patent Nos. 3,172,892, 3,219,666, 3,272,746, 4,234,435, 6,440,905 and 6,165,235. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures herein, are incorporated by reference.

[0060] Suitable ashless dispersants may also include amine dispersants, which are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples thereof have been described, for example, in U.S. Patent Nos. 3,275,554, 3,438,757, 3,454,555, 3,565,804, and the like. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures herein, are also incorporated by reference.

[0061] Suitable ashless dispersants may further include “Mannich dispersants,” which are reaction products of alkyl phenols in which the alkyl group contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). These dispersants have been described, for example, in U.S. Patent Nos. 3,036,003, 3,586,629, 3,591,598, 3,980,569, and the like. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures and claims herein, are likewise incorporated by reference.

[0062] Suitable ashless dispersants may even include post-treated dispersants, which are obtained by reacting carboxylic, amine or Mannich dispersants with reagents such as dimercaptothiazoles, urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitrile epoxides, boron compounds and the like. Post-treated dispersants have been

described, for example, in U.S. Patent Nos. 3,329,658, 3,449,250, 3,666,730, and the like. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures and claims herein, are further incorporated by reference.

[0063] Suitable ashless dispersants may be polymeric, which are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substitutes. Polymeric dispersants have been described, for example, in U.S. Patent Nos. 3,329,658, 3,449,250, 3,666,730, and the like. Relevant disclosures of these patents, to the extent they do not conflict with the disclosures and claims herein, are similarly incorporated by reference.

[0064] In an exemplary lubricating oil composition of the present invention, a bissuccinimide treated with ethylene carbonate was used as the ashless dispersant. The dispersant(s) of the present invention are preferably non-polymeric (*e.g.*, are mono- or bissuccinimides).

[0065] The ashless dispersant is suitably present in an amount of about 0.5 to about 10.0 wt.%, preferably about 3.0 to about 7.0 wt.%. An exemplary lubricating oil composition of the present invention comprises an ethylene-carbonate treated bissuccinimide dispersant derived from a PIBSA wherein the PIB chain has a number average molecular weight of about 2300 Daltons (PIBSA 2300) in an amount of about 6.5 wt.%. Another lubricating oil composition of the present invention comprises a similar dispersant in an amount of about 6.0 wt.%, in combination with another borated bissuccinimide derived from another PIBSA wherein the PIB chain has a number average molecular weight of about 1300 Daltons (PIBSA 1300). Preferably, the lubricating oil composition comprises from about 0.01 to about 0.35 wt.%,

preferably from about 0.05 to about 0.25 wt.%, particularly preferably from about 0.08 to about 0.12 wt.% of total nitrogen from dispersant.

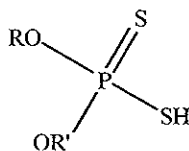
Other Additives

[0066] The lubricating oil compositions of the present invention may optionally comprise various other additives, including, but not limited to, antiwear agents, friction modifiers, antioxidants, corrosion inhibitors, viscosity index improvers, and other additives commonly used to lubricate internal combustion engines.

Antiwear Agents

[0067] Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are the most commonly used in lubricating oil in amounts of about 0.1 to about 10 wt.%, preferably about 0.2 to about 2 wt.%, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then 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 where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most often employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0068] The preferred oil-soluble zinc dialkyldithiophosphates may be produced from dialkyldithiophosphoric acids of the formula:



The hydroxyl alkyl compounds from which the dialkyldithiophosphoric acids are derived can be represented generically by the formula ROH or R'OH, wherein R or R' is alkyl or substituted alkyl, preferably branched or non-branched alkyl containing 3 to 30 carbon atoms. More preferably, R or R' is a branched or non-branched alkyl containing 3 to 8 carbon atoms.

[0069] Mixtures of hydroxyl alkyl compounds may also be used. These hydroxyl alkyl compounds need not be monohydroxy alkyl compounds. The dialkyldithiophosphoric acids may thus be prepared from mono-, di-, tri-, tetra-, and other polyhydroxy alkyl compounds, or mixtures of two or more of the foregoing. Preferably, the zinc dialkyldithiophosphate derived from only primary alkyl alcohols is derived from a single primary alcohol. Preferably, that single primary alcohol is 2-ethylhexanol. Preferably, the zinc dialkyldithiophosphate derived from only secondary alkyl alcohols. Preferably, that mixture of secondary alcohols is a mixture of 2-butanol and 4-methyl-2-pentanol.

[0070] The phosphorus pentasulfide reactant used in the dialkyldithiophosphoric acid formation step may contain minor amounts of any one or more of P₂S₃, P₄S₃, P₄S₇, or P₄S₉. Compositions as such may also contain minor amounts of free sulfur.

[0071] Although the lubricating oil compositions of the present invention are capable of providing excellent antiwear performance in the presence of amounts of

zinc dialkyldithiophosphate providing greater amounts of phosphorus, the improved performance of the inventive lubricating oil compositions are particularly apparent in low SAPS formulations which, by definition, have phosphorus levels of no greater than about 0.08 wt.%. Therefore, lubricating oil compositions of the present invention contain less than about 0.08 wt.% of phosphorus, more preferably from about 0.03 to about 0.075 wt.% of phosphorus. An exemplary lubricating oil composition of the present invention comprises about 11.5 mM zinc dialkyldithiophosphate.

Viscosity Index Modifiers

[0072] The viscosity index of the base stock is increased, or improved, by incorporating therein certain polymeric materials that function as viscosity modifiers (VM) or viscosity index improvers (VII). Generally, polymeric materials useful as viscosity modifiers are those having number average molecular weights (M_n) of from about 5,000 to about 250,000, preferably from about 15,000 to about 200,000, more preferably from about 20,000 to 150,000 Daltons. These viscosity modifiers can optionally be grafted with grafting materials such as, for example, maleic anhydride, and the grafted material can be reacted with, for example, amines, amides, nitrogen-containing heterocyclic compounds or alcohol, to form multifunctional viscosity modifiers (dispersant-viscosity modifiers).

[0073] Exemplary lubricating oil compositions of the present invention employ various polyalkyl methacrylate copolymers, which may or may not be grafted by maleic anhydride. The copolymers may be employed at an amount from about 0.1 to about 10 wt.% of the lubricating oil composition.

Friction Modifiers

[0074] Lubricating oil compositions of the present invention further comprise a sulfur-containing molybdenum compound. Certain sulfur-containing organo-molybdenum compounds are known to function as friction modifiers in lubricating oil compositions, while also providing antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof.

[0075] Oil-soluble or dispersible trinuclear molybdenum compounds can be prepared by reacting in the appropriate liquid(s)/solvent(s) a molybdenum source such as $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13n}(\text{H}_2\text{O})$, where n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetralkylthiuram disulfide. Other oil-soluble or dispersible trinuclear molybdenum compounds can be formed during a reaction in the appropriate solvent(s) of a molybdenum source, such as of $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13.n}(\text{H}_2\text{O})$, a ligand source such as tetralkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur-abstracting agent such as cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[\text{M}']_2[\text{Mo}_3\text{S}_7\text{A}_6]$, where M' is a counter ion, and A is a halogen such as Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate liquid(s)/solvent(s) to form an oil-soluble or dispersible trinuclear molybdenum compound. The appropriate liquid/solvent may be, for example, aqueous or organic.

[0076] The terms "oil-soluble" or "dispersible" 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] An exemplary lubricating oil composition of the present invention employs a molybdenum succinimide complex as friction modifier. Of the lubricating oil composition, the molybdenum complex may constitute from about 0.15 to about 0.55 wt.%, preferably from about 0.28 to about 0.45 wt.% .

Antioxidants

[0078] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons or esters, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in, for example, U.S. Patent No. 4,867,890.

[0079] Aromatic amines having at least two aromatic groups attached directly to the nitrogen constitute another class of compounds that is frequently used for antioxidantancy. Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines may contain more than two aromatic groups. The aromatic rings are often substituted by one or more substituents selected from, for example, alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

[0080] Lubricating oil compositions in accordance with the present invention preferably contain from about 0.05 to about 5.00 wt.%, more preferably from about

0.10 to about 3.00 wt.%, and particularly preferably from about 0.20 to about 0.80 wt.% of phenolic antioxidant, aminic antioxidant, or a combination thereof, based on the total weight of the lubricating oil composition. An exemplary lubricating oil composition of the present invention comprises about 0.40 wt.% of an antioxidant that is di-C₈-diphenylamine. Another exemplary lubricating oil composition of the present invention comprises about 0.30 wt.% of a dinonyl diphenylamine as an antioxidant.

[0081] Additional additives may be incorporated into the compositions of the invention to satisfy the particular performance requirements associated with low SAPS applications in internal combustion engines. Examples of such other additives include, for example, rust inhibitors, anti-foaming agents, and seal fixes or seal pacifiers.

[0082] Rust inhibitor or anticorrosion agents may be a nonionic polyoxyethylene surface active agent. Nonionic polyoxyethylene surface active agents include, but are not limited to, polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate. Rust inhibitors or anticorrosion agents may also be other compounds, which include, for example, stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohols, and phosphoric esters. An exemplary lubricating oil composition of the present invention comprises a calcium stearate salt.

[0083] Foam inhibitors typically include alkyl methacrylate polymers and dimethyl silicone polymers. Exemplary compositions of the present invention contain

silicon-based foam inhibitors in amounts ranging from about 5 to about 40 ppm, preferably from about 8 to about 35 ppm, more preferably from about 10 to about 25 ppm, based on the total weight of the composition.

[0084] Seal fixes are also termed seal swelling agents or seal pacifiers. They are often employed in lubricant or additive compositions to insure proper elastomer sealing, and prevent premature seal failures and leakages. Seal swell agents may be, for example, oil-soluble, saturated, aliphatic, or aromatic hydrocarbon esters such as di-2-ethylhexylphthalate, mineral oils with aliphatic alcohols such as tridecyl alcohol, triphosphite ester in combination with a hydrocarbonyl-substituted phenol, and di-2-ethylhexylsebacate.

[0085] Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant as well as an oxidation inhibitor. These multifunctional additives are well known.

[0086] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base oil in an amount that enables the additive to provide its desired function. It may be desirable, although not essential, to prepare one or more additive concentrates comprising additives (concentrates sometimes being referred to as additive packages) whereby several additives can be added simultaneously to the oil to form the lubricating oil composition. The final composition may employ from about 5 to about 30 wt.%, preferably about 5 to about 25 wt.%, typically about 10 to about 20 wt.% of the concentrate, the remainder being the oil of lubricating viscosity. The components can be blended in any order and can be blended as combinations of components.

[0087] This invention will be further understood by reference to the following examples, which are not to be considered as limitative of its scope.

EXAMPLES

[0088] The following examples are provided to illustrate the present invention without limiting it. While the present invention has been described with reference to specific embodiments, this application is intended to encompass those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Example 1:

[0089] Oil A was prepared and tested for piston cleanliness and tendency to piston ring sticking according to the Volkswagen Turbocharged DI test, a European passenger car diesel engine test (CEL-L-78-T-99), which is part of the ACEA B specification promulgated by the European Automobile Manufacturers Association in 2004. This test was used to simulate repeated cycles of high-speed operation followed by idling. A Volkswagen 1.9 liter, inline, four-cylinder turbocharged direct injection automotive diesel engine (VW TDi) was mounted on an engine dynamometer stand. A 54-hour, 2-phased procedure that cycles between 30 minutes of 40°C oil sump at idle and 150 minutes of 145°C oil sump at full power (4150 rpm) was carried out without interim oil top-ups. After the procedure, the pistons were rated for carbon and lacquer deposits, as well for groove carbon filling. The piston rings were evaluated for ring sticking. The piston cleanliness and ring sticking of VW TDi engine tests were also carried out with Comparative Example Oil B. The results are given in Table 1.

[0090] Oil A shows a distinct and surprising improvement over Comparative Oil B in the VW TDi piston cleanliness and ring sticking test.

[0091] Oil A: A lubricating oil composition was prepared comprising about 1.50 wt.% of a polyisobutylene succinic anhydride derived from a polyisobutylene

having a number average molecular weight of about 2300 Daltons, an ethylene carbonate-treated bissuccinimide dispersant, a low-overbased calcium sulfonate detergent, an overbased sulfurized and carbonated calcium phenate, a zinc dihydrocarbyl dithiophosphate, a moly succinimide, a di-C₈-diphenylamine antioxidant, a silicon-based foam inhibitor, an ethylene polymer, a rust inhibitor, and mineral oil base stocks. Oil A had a sulfated ash content of about 0.78 wt.%, nitrogen content of about 0.092 wt.%, sulfur content of about 0.183 wt.%, and phosphorus content of about 0.071 wt.%.

[0092] Comparative Example Oil B: the formulation of Oil A was duplicated except that Oil B does not contain PIBSA 2300. Oil B had a sulfated ash content of about 0.78 wt.%, nitrogen content of about 0.092 wt.%, sulfur content of 0.183 wt.%, and phosphorus content of 0.071 wt.%.

Table 1: Test type: VWTDI2 SAE: 5W30

Components	Oil A		Oil B	
PIBSA 2300	1.50	wt.%	None	
Bissuccinimide dispersant	6.50	wt.%	6.50	wt.%
Low-TBN calcium sulfonate	4	mM	4	mM
Calcium Stearate	35	mM	35	mM
High-TBN sulfurized & carbonated calcium phenate	10	mM	10	mM
Zinc dialkyldithiophosphate	11.5	mM	11.5	mM
Moly succinimide	0.37	wt.%	0.37	wt.%
Di-C ₈ -diphenylamine	0.40	wt.%	0.40	wt.%
Silicon-based foam inhibitor	25	ppm	25	ppm
Ethylene polymer	0.84	wt.%	0.82	wt.%
Diluent Oil	0.71	wt.%	0.71	wt.%
Length of test	54	hours	54	hours
P-MER AVG:G1-3&L1&2	63		57	
PCInRL206Avg	66		66	
VW Lmt-PCLN Combnd AV	67		67	
AvRStk (8R-4P) ASF (0-10)	0.62		0.93	
MxRStk (1Rg) ASF (0-10)	2.5		5	
Grvs. 1st RStk, AV, ASF	1.25		1.88	
Grvs. 1st RStk, MX, ASF	2.5		5	
Grvs. 2nd RStk, MX, ASF	0		0	
# of Rings with ASF >=2.5	2		3	
Scoring (*)	Pass ACEA B4 or B5		Fail ACEA B4 & B5	

- The pass/fail score according to the ACEA standards B4 and B5 are listed in the following Table 1.1:

Table 1.1

	ACEA B4 limits	ACEA B5 limits
P-MER Avg	63 ($\geq$ RL206 - 3)	66 ($\geq$ RL206)
# Rngs w/ASF ≥ 2.5	≤ 1.2	≤ 1.2
Grvs. 1st RStk, MX. ASF	≤ 2.5	≤ 2.5
Grvs. 2nd Rstk, MX. ASF	≤ 0.0	≤ 0.0

Example 2

[0093] Oil C was prepared and tested for piston cleanliness and tendency to piston ring sticking according to the Volkswagen Turbocharged DI test described above. The Piston cleanliness and ring sticking of VW TDi engine tests were also carried out with Comparative Example Oil D. The results are given in Table 3. The results were scored against the more stringent Japanese piston cleanliness standards (JASO C2 test standards), wherein the P-MER AVG has a minimum value of 65.

[0094] Oil C shows a distinct and surprising improvement over Comparative Oil D in the VW TDi piston cleanliness and ring sticking test.

[0095] Oil C: A lubricating oil composition was prepared comprising about 2.00 wt.% of a succinic anhydride derivative of polyisobutylene having a number average molecular weight of about 2300, an ethylene carbonate-treated bissuccinimide dispersant that is a mixture of one derived from PIBSA 2300 and another derived from PIBSA 1300 (*i.e.*, the polyisobutylene precursor had a number average molecular weight of about 1300 Daltons), a low-overbased calcium sulfonate detergent, an overbased sulfurized and carbonated calcium phenate, a mixture of primary and secondary zinc dihydrocarbyl dithiophosphate, a moly succinimide, a triborate wear inhibitor, a viscosity improver, a di-C₈-diphenylamine antioxidant, a silicon-based foam inhibitor, and mineral oil base stocks. Oil C had a sulfated ash content of about 0.59 wt.%, nitrogen content of about 0.113 wt.%, sulfur content of about 0.213 wt.%, and phosphorus content of 0.074 wt.%.

[0096] Comparative Example Oil D: The formulation of Oil C was duplicated except that Oil F did not contain PIBSA 2300. Oil D has a sulfated ash content of about 0.59 wt.%, nitrogen content of about 0.113 wt.%, sulfur content of 0.213 wt.%, and phosphorus content of 0.074 wt.%.

Table 3: Test: VWTDI2 SAE: 0W30

Components	Oil C		Oil D	
PIBSA 2300	2.00	wt.%	None	
Bissuccinimide dispersant derived from PIBSA 2300	6.00	wt.%	6.00	wt.%
Bissuccinimide dispersant derived from PIBSA 1300	1.80	wt.%	1.80	wt.%
Low-TBN calcium sulfonate	7.5	mM	7.5	mM
High-TBN sulfurized and carbonated calcium phenate	17.5	mM	17.5	mM
1° and 2° Zinc dialkyldithiophosphate mix	12.0	mM	12.0	mM
Moly succinimide	0.30	wt.%	0.30	wt.%
Dinonyl diphenylamine	0.30	wt.%	0.30	wt.%
Silicon-based foam inhibitor	10	ppm	10	ppm
Triborate wear/oxidation inhibitor	0.20	wt.%	0.20	wt.%
Viscosity improver polymer	5.80	wt.%	7.0	wt.%
Diluent Oil	0.71	wt.%	0.71	wt.%
Length of test	54	hours	54	hours
P-MER AVG:G1-3&L1&2	73		65	
PCInRL148Avg	62		62	
PCInRL206Avg	65		65	
VW Lmt-PCLN Combnd AV	66		66	
AvRStk (8R-4P) ASF (0-10)	0		0	
Grvs, 1st RStk, MX, ASF	0		0	
Grvs. 2nd RStk, MX, ASF	0		0	
# of Rings with ASF >=2.5	0		0	
Scoring (**)	Pass JASO C2		Borderline pass JASO C2	

** The pass/fail scores were given according to the JASO piston cleanliness standard

C2

WHAT IS CLAIMED IS:

1. A lubricant composition suitable for use in an internal combustion engine, which comprises an admixture of:

(a) a major amount of an oil of lubricating viscosity;

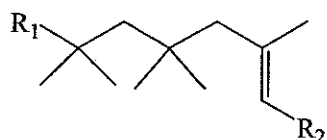
(b) one or more ashless dispersants;

(c) one or more metal-containing detergents; and

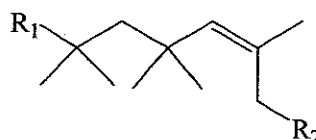
(d) a piston-cleanliness-enhancing amount of at least one reaction product of a polyisobutylene and a monounsaturated acylating agent, wherein the polyisobutylene has a number average molecular weight of about 200 to about 5000 Daltons;

wherein said lubricant composition has a sulfur content of at or below about 0.3 wt.%, a phosphorus content of at or below about 0.09 wt.%, and a sulfated ash content of at or below about 1.6 wt.%, based on the total weight of said lubricating oil composition.

2. The lubricant composition of claim 1, wherein the reaction product of a polyisobutylene and a monounsaturated acylating agent is represented by either of the formulas:



[Formula A]



[Formula B]

wherein R₁ is a polyisobutylene chain with a number average molecular weight of about 200 to about 5000 Daltons; and R₂ is a carboxyl-containing group.

3. The composition of claim 1 or claim 2, further comprising one or more additives selected from: antiwear agents, friction modifiers, antioxidants, corrosion inhibitors, viscosity index improvers, anti-foaming agents, seal fixes, pour point depressants, and other multi-functional additives.
4. The composition of any one of the preceding claims, wherein the sulfur content of the composition is at or below about 0.2 wt.%, based on the total weight of said composition.
5. The composition of claim 4, wherein the sulfur content of the composition is at or below about 0.1 wt.%, based on the total weight of said composition.
6. The composition of any one of the preceding claims, wherein the phosphorus content of the composition is at or below about 0.08 wt.%, based on the total weight of said composition.
7. The composition of claim 6, wherein the phosphorus content of the composition is at or below about 0.07 wt.%, based on the total weight of said composition.
8. The composition of claim 7, wherein the phosphorus content of the composition is at or below about 0.05 wt.%, based on the total weight of said composition.
9. The composition of any one of the preceding claims, wherein the sulfated ash content of the composition is at or below about 1.0 wt.%, based on the total weight of said composition.
10. The composition of claim 9, wherein the sulfated ash content of the composition is at or below about 0.8 wt.%, based on the total weight of said composition.

11. The composition of claim 10, wherein the sulfated ash content of the composition is at or below about 0.5 wt.%, based on the total weight of said composition.
12. The composition of claim 11, wherein the sulfated ash content of the composition is at or below about 0.45 wt.%, based on the total weight of said composition.
13. The composition of any one of the preceding claims, wherein the amount of the at least one reaction product of a PIB and a monounsaturated acylating agent is about 0.01 to about 5.0 wt.%, based on the total weight of the lubricant composition.
14. The composition of claim 13, wherein the amount of the at least one reaction product of a PIB and a monounsaturated acylating agent is about 0.5 to about 4.0 wt.%, based on the total weight of the lubricant composition.
15. The composition of claim 14, wherein the amount of the at least one reaction product of a PIB and a monounsaturated acylating agent is about 1.0 to about 2.5 wt.%, based on the total weight of the lubricant composition.
16. The composition of any one of the preceding claims, wherein the PIB in the at least one reaction product of a PIB and a monounsaturated acylating agent has a number average molecular weight of about 500 to about 4500 Daltons.
17. The composition of claim 16, wherein the PIB has a number average molecular weight of about 1000 to about 3500 Daltons.
18. The composition of claim 17, wherein the PIB has a number average molecular weight of about 2300 Daltons.

19. The composition of claim 17, wherein the PIB has a number average molecular weight of about 1300 Daltons.
20. The composition of any one of the preceding claims, wherein the PIB in the at least one reaction product of a PIB and a monounsaturated acylating agent is a highly reactive PIB.
21. The composition of any one of the preceding claims, wherein the monounsaturated acylating agent is derived from an anhydride or an anhydride-producing material.
22. The composition of claim 21, wherein the monounsaturated acylating agent is derived from maleic anhydride.
23. The composition of any one of the preceding claims, wherein the one or more metal-containing detergents is present in an amount of about 0.05 to about 16 mM.
24. The composition of any one of the preceding claims, wherein the ashless dispersant is a bissuccinimide derived from one or more PIBSAs.
25. The composition of claim 24, wherein the ashless dispersant is a bissuccinimide derived from a PIBSA wherein the PIB chain has a number average molecular weight of about 2300 Daltons.
26. The composition of claim 24, wherein the ashless dispersant is a bissuccinimide derived from a mixture of a first PIBSA wherein the PIB chain has a number average molecular weight of about 2300 Daltons, and a second PIBSA wherein the PIB chain has a number average molecular weight of about 1300 Daltons.
27. The composition of claim 24, wherein the bissuccinimide is present in an amount of about 0.5 wt.% to about 10 wt.%.

28. The composition of claim 3, wherein the antiwear agent is a metal dicarbyldithiophosphate.
29. The composition of claim 28, wherein the metal dicarbyldithiophosphate is zinc dialkylthiophosphate.
30. The composition of claim 29, wherein the amount of zinc dialkylthiophosphate present contributes from about 0.03 to about 0.075 wt.% of phosphorus to the composition.
31. The composition of any one of the preceding claims, wherein the ashless dispersant contributes about 0.08 to about 0.12 wt.% of nitrogen to the composition.
32. The composition of any one of the preceding claims, wherein the metal-containing detergent is a calcium overbased detergent.
33. The composition of claim 32, wherein the calcium overbased detergent is selected from: calcium sulfonates, calcium phenates, calcium salicylates, calcium stearates, and mixtures thereof.
34. The composition of any one of claims 3 to 33, wherein the antioxidant is a diphenylamine.
35. The composition of claim 34, wherein the diphenylamine is present from about 0.05 wt.% to about 5.00 wt.%, based on the total weight of the composition.
36. The composition of any one of claims 3 to 35, wherein the friction modifier is a molybdenum succinimide complex.
37. The composition of claim 36, wherein the molybdenum succinimide complex is present in an amount of from about 0.15 to about 0.55 wt.%, based on the total weight of the composition.

38. The composition of any one of claims 3 to 37, wherein the viscosity index modifier is an ethylene polymer or a polyalkyl methacrylate copolymer.
39. A method of improving piston cleanliness in an internal combustion engine, said method comprising:
operating said internal combustion engine with a low phosphorus, low sulfur and low sulfated ash lubricating oil composition as claimed in any one of claims 1 to 38.
40. A method of operating an internal combustion engine provided with exhaust gas after-treatment devices, which method comprises lubricating said engine with a lubricating oil composition according to any one of claims 1 to 38.
41. The method according to claim 40, wherein said internal combustion engine is selected from: (1) a light duty diesel-fueled internal combustion engine; (2) a heavy duty diesel-fueled internal combustion engine; and (3) a gasoline-fueled internal combustion engine.
42. The method according to claim 40, wherein said exhaust gas after-treatment devices are one or more devices selected from particulate traps and catalytic converters.