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CA 2841048 A1 2013/01/10

(21) **2 841 048**

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) **A1**

(86) **Date de dépôt PCT/PCT Filing Date:** 2012/06/26
(87) **Date publication PCT/PCT Publication Date:** 2013/01/10
(85) **Entrée phase nationale/National Entry:** 2014/01/06
(86) **N° demande PCT/PCT Application No.:** US 2012/044118
(87) **N° publication PCT/PCT Publication No.:** 2013/006303
(30) **Priorité/Priority:** 2011/07/07 (US61/505,172)

(51) **Cl.Int./Int.Cl.** *C10M 141/06* (2006.01)
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(54) Titre : LUBRIFIANT FOURNISSANT UNE PROPRETE AMELIOREE POUR DES MOTEURS A DEUX TEMPS
(54) Title: LUBRICANT PROVIDING IMPROVED CLEANLINESS FOR TWO-STROKE CYCLE ENGINES

(57) **Abrégé/Abstract:**
A lubricant composition comprising an oil of lubricating viscosity, 0.1 to 2 percent by weight of a Mannich dispersant, and 0.1 to 2 percent by weight of a succinimide dispersant, wherein the succinimide dispersant provides at least about 40 parts per million by weight of nitrogen atoms to the lubricant composition, provides cleanliness to a two-stroke cycle engine.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 January 2013 (10.01.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/006303 A1

(51) International Patent Classification:
C10M 141/06 (2006.01) *C10N 40/26* (2006.01)
C10N 10/04 (2006.01) *C10N 30/04* (2006.01)

(21) International Application Number:
PCT/US2012/044118

(22) International Filing Date:
26 June 2012 (26.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/505,172 7 July 2011 (07.07.2011) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2013/006303 A1

(54) **Title**: LUBRICANT PROVIDING IMPROVED CLEANLINESS FOR TWO-STROKE CYCLE ENGINES

(57) **Abstract**: A lubricant composition comprising an oil of lubricating viscosity, 0.1 to 2 percent by weight of a Mannich dispersant, and 0.1 to 2 percent by weight of a succinimide dispersant, wherein the succinimide dispersant provides at least about 40 parts per million by weight of nitrogen atoms to the lubricant composition, provides cleanliness to a two-stroke cycle engine.

TITLE

Lubricant Providing Improved Cleanliness for Two-Stroke Cycle Engines

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to an engine lubricant, particularly for two-stroke cycle engines.

[0002] Two-stroke cycle engines are widely used for portable power equipment and also represent an important portion of the engines used in transportation, particularly in the developing regions of the world. The lubricants required for the operation of two-stroke cycle engines are, in some designs, mixed with the liquid fuel, and this fuel-lubricant mixture is typically passed through the crankcase and, ultimately, to the combustion chambers, where the entire fuel-lubricant composition is burned. It is important, in such engines, to provide a lubricant composition which maintains suitable properties of lubricity and cleanliness. Problems with cleanliness can be observed as deposit or varnish formation within the engine in such areas as the piston skirt, the ring area of the piston, or the crankcase. It is desired to find an economical lubricant additive package that provides good cleanliness to a two-stroke cycle engine.

[0003] U.S. Publication 2011-0030637, Dohner et al., February 10, 2011 (previously published as WO2009/126381, October 15, 2009), discloses a lubricant comprising, among other components, about 3 to about 30 percent by weight of a nitrogen-containing dispersant bearing a hydrocarbyl group of at least 26 carbon atoms and having a nitrogen content of at least 3 percent by weight, wherein the nitrogen content of the lubricant is at least about 0.2 percent by weight. The dispersant may be a succinimide dispersant. The lubricant may further comprise about 1.1 to about 15 percent by weight of a Mannich dispersant.

[0004] U.S. Patent 7,900,590, Cleveland et al., March 8, 2011 (previously published as US 2005/0139174, June 30, 2005) discloses methods and lubricant and fuel compositions for two-stroke engine containing power valves. A lubricant composition comprises, among other components, (A) an oil of lubricating viscosity and (B) an additive composition that comprises (1) a reaction product of a fatty hydrocarbyl-substituted monocarboxylic acylating and a (select) reactive nitrogen-containing compound; and (2) a member selected from the group consisting of (a) a hydrocarbyl-substituted aminophenol; (b) a Mannich reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine; (c) a reaction product of a hydrocarbyl-substituted polycarboxylic acylating agent and a polyamine; and

(d) a mixture thereof. The hydrocarbyl-substituted polycarboxylic acylating agent can be a polyisobutenylsuccinic anhydride.

[0005] U.S. Patent 7,795,192, Petric et al., September 14, 2010 (previously published as US 2005-013856, June 16, 2005), discloses a lubricant composition suitable for lubricating a direct fuel injection two-stroke engine, comprising, among other components, a condensation product of a fatty hydrocarbyl monocarboxylic acid with a polyethylene polyamine, and a Mannich dispersant, being the reaction product of a polybutene-substituted phenol, formaldehyde, and ethylenediamine or dimethylamine. The lubricant may further comprise an additional dispersant which may be, among others, a mono-succinimide dispersant.

[0006] U.S. Publication 2008-0009428, Svarcas et al., January10, 2008, discloses a lubricant composition suitable for lubricating a two stroke engine comprising an oil of lubricating viscosity, a synthetic ester, a normally liquid solvent, a Mannich dispersant, and a condensation product of a fatty acid having about 12 to about 24 carbon atoms with a polyamine. In a comparative example, a commercial two-cycle oil comprises, among other components, a fatty acid imidazole dispersant, and a succinimide dispersant.

SUMMARY OF THE INVENTION

[0007] The disclosed technology provides a lubricant composition comprising: (a) an oil of lubricating viscosity; (b) 0.1 to 2 percent by weight of a Mannich dispersant; and (c) 0.2 to 2 percent by weight of a succinimide dispersant; wherein the succinimide dispersant provides at least about 40 parts per million by weight of nitrogen atoms to the lubricant composition. In one embodiment, the lubricant composition further comprises (d) a metal-containing detergent.

[0008] The disclosed technology also provides a method of lubricating an internal combustion engine, such as a two-stroke cycle engine, comprising supplying thereto the lubricant composition.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0010] One component of the disclosed technology is an oil of lubricating viscosity, also referred to as a base oil. The base oil may be selected from any of the base oils in Groups I-V of the American Petroleum Institute (API) Base Oil Interchangeability Guidelines, namely

Base Oil Category	Sulfur (%)		Saturates(%)	Viscosity Index
Group I	>0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	>120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III or IV			

Groups I, II and III are mineral oil base stocks. The oil of lubricating viscosity can include natural or synthetic oils and mixtures thereof. Mixture of mineral oil and synthetic oils, e.g., polyalphaolefin oils and/or polyester oils, may be used. In some embodiments of the present invention, the oil will be a mineral oil, that is, Group I, II, or III, and in some embodiments it will be a Group II oil or a Group III oil.

[0011] Natural oils include animal oils and vegetable oils (e.g. vegetable acid esters) as well as 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. Hydrotreated or hydrocracked oils are also useful oils of lubricating viscosity. Oils of lubricating viscosity derived from coal or shale are also useful.

[0012] Synthetic oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, alkylated diphenyl ethers, and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, e.g., esterification or etherification, are other classes of synthetic lubricating oils. Other suitable synthetic lubricating oils comprise esters of dicarboxylic acids and those made from C_5 to C_{12} monocarboxylic acids and polyols or polyol ethers. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as poly-alkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

[0013] Other synthetic oils include those produced by Fischer-Tropsch reactions, typically hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0014] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures thereof) of the types disclosed hereinabove can be used. Unrefined 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 to improve one or more properties. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Rerefined oils often are additionally processed to remove spent additives and oil breakdown products.

[0015] Another components that may be considered a part of the oil of lubricating viscosity includes bright stock (a high viscosity mineral oil fraction), which may be typically present, if desired, in amounts of 1 to 5 or 1.5 to 3 percent by weight.

[0016] The amount of oil of lubricating viscosity in a fully formulated lubricant of the disclosed technology (including the diluent or carrier oils present in the additional components) will typically be 20 to 60 percent by weight, or 25 to 55 percent, or 30 to 50 percent by weight.

[0017] The lubricant will also include a Mannich dispersant and a succinimide dispersant. Dispersants in general are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain.

[0018] One component of the present technology is a Mannich dispersant, sometimes referred to as a Mannich base dispersant. A Mannich dispersant is a reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine or ammonia. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 10 to 400 carbon atoms, in another instance 30 to 180 carbon atoms, and in a further instance 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefin. Useful olefins include alpha-olefins, such as 1-decene, which are commercially available.

[0019] The polyolefins which can form the hydrocarbyl substituent can be prepared, for instance, by polymerizing olefin monomers by well-known polymerization methods and are also commercially available. The olefin monomers include monoolefins, including monoolefins having 2 to 10 carbon atoms such as ethylene, propylene, 1-butene, isobutylene, and 1-decene. An especially useful monoolefin source is a C4 refinery stream having a 35 to 75 weight percent butene content and a 30 to 60 weight percent isobutene content. Useful olefin monomers also include diolefins such as isoprene and 1,3-butadiene. Olefin monomers can also include mixtures of two or more monoolefins, of two or more diolefins, or of one or more monoolefins and one or more diolefins. Useful polyolefins include polyisobutylenes having a number average molecular weight of 140 to 5000, in another instance of 400 to 2500, and in a further instance of 140 or 500 to 1500. The polyisobutylene can have a vinylidene double bond content of 5 to 69%, in a second instance of 50 to 69%, and in a third instance of 50 to 95%. The polyolefin can be a homopolymer prepared from a single olefin monomer or a copolymer prepared from a mixture of two or more olefin monomers. Also possible as the hydrocarbyl substituent source are mixtures of two or more homopolymers, two or more copolymers, or one or more homopolymers and one or more copolymers. The foregoing description of suitable hydrocarbyl groups or polyolefin groups is also applicable to the hydrocarbyl substituent of the succinimide dispersant, described in detail below.

[0020] The hydrocarbyl-substituted phenol which is used to prepare the Mannich dispersant can be prepared by alkylating phenol with an olefin or polyolefin described above, such as a polyisobutylene or polypropylene, using well-known alkylation methods.

[0021] The aldehyde used to form the Mannich dispersant can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde.

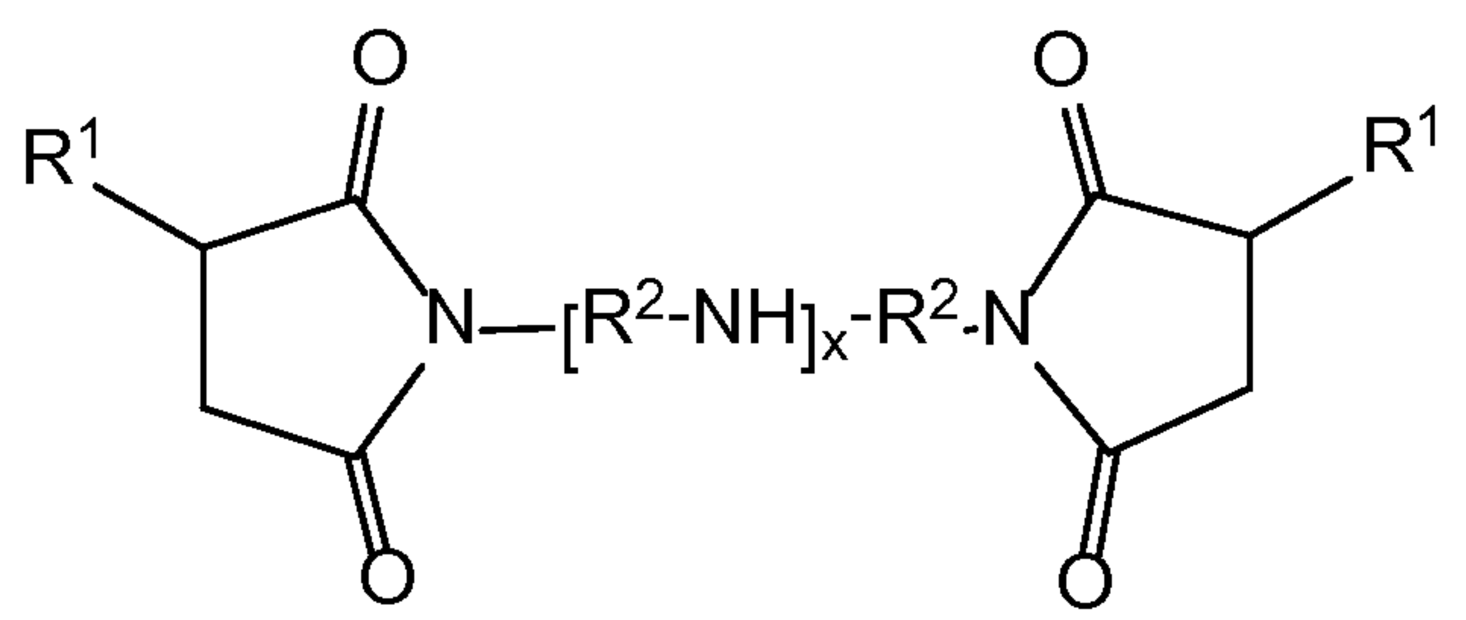
[0022] The amine used to form the Mannich dispersant can be a monoamine or a polyamine, including those materials described above for the succinimide dispersants, including alkanolamines having one or more hydroxyl groups. Useful amines include ethanolamine, diethanolamine, methylamine, dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine and 2-(2-aminoethylamino)ethanol. The Mannich dispersant can be prepared by reacting a hydrocarbyl-substituted phenol, an aldehyde, and an amine as described in U.S. Patent No. 5,697,988. In one embodiment, the Mannich reaction product is prepared from an alkylphenol derived from a polyisobutylene, formaldehyde, and an amine that is a primary monoamine, a secondary monoamine, or an alkylenediamine, in particular, ethylenediamine or dimethylamine. In one embodiment, the alkylphenol may be prepared from a high-vinylidene polyisobutene, having, e.g., greater than 50, greater than 70 or greater than 75 percent terminal vinylidene groups (i.e., such percentage of polyisobutylene molecules having vinylidene end groups; that is, mole percentage of polyisobutylene molecules having a terminal vinylidene group.) The foregoing description of the amine is also applicable to the description of the amine used in preparing the succinimide dispersant, described below.

[0023] In one embodiment the Mannich dispersant comprises the reaction product of a hydrocarbyl-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and a primary or secondary amine. In one embodiment the Mannich dispersant comprises the reaction product of a polyisobutene-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and dimethylamine.

[0024] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is found in paragraphs [0137] to [0141] of published application US 2010-0197536.

[0025] The amount of the Mannich dispersant will typically be 0.1 to 2 percent by weight of the lubricant composition. In other embodiments it may be present at 0.15 to 1.5 percent, or 0.2 to 1.05 percent, or 0.2 to 1 percent, or 0.3 to 0.6 percent by weight.

[0026] A second type of dispersant that will be present in the disclosed compositions is a succinimide dispersant. In one embodiment, the succinimide dispersant is a condensation product of hydrocarbyl-substituted succinic anhydride or a reactive equivalent thereof (e.g., an anhydride, ester, or acid halide), with a polyethylene polyamine. Succinimide dispersants may generally be viewed as comprising a variety of chemical structures including typically



where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight (M_n) of 500-5000 based on the polyisobutylene precursor, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. In the above structure, the amine portion is shown as an alkylene polyamine, although other aliphatic and aromatic mono- and polyamines may also be used. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892 and in EP 0355895.

[0027] Succinimide dispersants may also be described as being prepared from hydrocarbyl-substituted succinic acylating agent which are, in turn, prepared by the so-called "chlorine" route or by the so-called "thermal" or "direct alkylation" route. These routes are described in detail in published application US 2005-0202981, paragraphs 0014 through 0017. A direct alkylation or low-chlorine route is also described in U.S. Patent 6,077,909; refer to column 6 line 13 through col. 7 line 62 and column 9 lines 10 through col. 10 line 11. Illustrative thermal or direct alkylation processes involve heating a polyolefin, typically at 180 to 250 °C, with maleic anhydride under an inert atmosphere. Either reactant may be in excess. If the maleic anhydride is present in excess, the excess may be removed after reaction by distillation. These reactions may employ, as the polyolefin, high vinylidene polyisobutylene, that is, having greater than 50, 70, or 75% terminal vinylidene groups (α and β isomers). In certain embodiments, the succinimide dispersant may be prepared by the direct alkylation route. In other embodiments it may comprise a mixture of direct alkylation and chlorine-route dispersants.

[0028] The succinimide dispersant will be one which is capable of providing a relatively large quantity of nitrogen to the lubricant. The nitrogen will be nitrogen atoms that are a part of the amine component or the condensed amide or imide groups of the dispersant. That is, it will impart at least 40 parts per million by weight of nitrogen to the lubricant, and in some embodiments at least 70 or 100 or 130 or 150 parts per million, and up to, for example, 1000 or 900 or 800 or 600 parts per million. These amounts will be determined by both the amount of the succinimide dispersant in the lubricant formulation and the amount of nitrogen within the given dispersant. Thus, certain of the succinimide dispersants of the present technology are comparatively high in nitrogen content, i.e., at least 3 percent or at least 4 percent or at least 4.4 percent by weight, and up to 6 or 5.5 or 5 percent.

[0029] Such high nitrogen dispersants are, in certain embodiments, characterized as having a high TBN, total base number (ASTM D 974), due to the presence of basic amine functionality. The present succinimide dispersant may thus have a TBN of at least 90 or 100 or 110 and up to, for instance, 160 or 140 or 120. Other suitable TBN ranges may be 60 to 160 or 70 to 140 or 80 to 120. Such values are to be calculated on the basis of an oil-free dispersant, as will be evident to the skilled person. In certain applications, the succinimide dispersant may be borated.

[0030] The amount of the succinimide dispersant will typically be 0.1 to 2 percent by weight of the lubricant composition. In other embodiments it may be present at 0.15 to 1.5 percent, or 0.2 to 1 percent, or 0.3 to 0.6 percent by weight. The relative amounts of the Mannich dispersant and the succinimide dispersant, expressed as a weight ratio, may be 80:20 to 20:80 or alternatively 70:30 to 30:70 or 65:35 to 45:55. The total amount of the Mannich dispersant and the succinimide dispersant, and optionally any other nitrogen-containing dispersants that may be present, may be 0.2 to 4 percent by weight, or 0.3 to 3 percent, or 0.4 to 2 percent.

[0031] Other dispersants may also be present, if desired. They may be lower nitrogen-content dispersants than the above-described succinimide dispersant, or they may have shorter or longer hydrocarbyl chains, or they may have other functional groups. One such dispersant may be a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent, such as a fatty acid, with an amine. The fatty acid may contain 10 to 26 carbon atoms (e.g., 12 to 24 or 14 to 20 or 16 to 18). An example is isostearic acid. The amine may be a polyethylene polyamine as described above. The condensation product may be an amide or an imidazoline. Other dispersants include high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Other dispersants include polymeric dispersant additives, also referred to as dispersant viscosity modifiers, which are generally hydrocarbon-based polymers containing polar functionality to impart dispersancy characteristics to the polymer.

[0032] Either one or both or all of the dispersants may be post-treated with any of a variety of agents to impart desirable properties thereto, while retaining, in some embodiments, a relatively high TBN for the succinimide dispersant. Such post-treatment includes reaction with urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds such as boric acid, phosphorus compounds, or mixtures thereof. References detailing such treatment are listed in U.S. Patent 4,654,403.

[0033] Other materials may also be present in the lubricants described herein, and in particular those materials which are desirable to provide a lubricant for a two-stroke cycle engine. One such material is a solvent, which may be used to aid in the solubility of the additives in the lubricant or in the fuel with which it is conventionally to be mixed or to adjust the viscosity parameters of the lubricant. Typically such a material is a combustible solvent (other than oil of lubricating viscosity, described above), having a flash point of less than about 105°C, in which the remaining components of the lubricant are soluble. The solvent is typically a hydrocarbonaceous solvent, that is, one which exhibits principally hydrocarbon character, even though relatively small numbers of heteroatoms may be present in the molecule. The solvent may be a hydrocarbon and may have predominantly non-aromatic (e.g., alkane) character. The solvent may thus comprises less than 20 percent by weight aromatic components and may be substantially free from polynuclear aromatic components. A particularly suitable solvent is kerosene, which is a non-aromatic petroleum distillate having a boiling range of 180-300°C. Another useful solvent is Stoddard solvent, which has a boiling range of 154-202°C.

[0034] The solvent is characterized by a kinematic viscosity of less than 5 mm^2s^{-1} (cSt) at 100°C, such as less than 2.0 or 1.5 or 1.0 mm2s-1. Thus, solvents are of lower viscosity than the oils of lubricating viscosity, which, accordingly, may have a kinematic viscosity of at least 1.0 or 1.5 or 2.0 or 5 $mm^{-}s^{-1}$ at 100°C.

[0035] The amount of the solvent, if it is present, may be at least 5 percent by weight of the lubricant, or at least 10 percent, up to 50 or 40 or 30 percent. Suitable ranges may include combinations of the above values, or 15 to 30 percent by weight.

[0036] The lubricant composition may also contain a polymer such as polyisobutene, or, more generally, an olefin polymer. Olefin polymers are well known as additives for two-stroke cycle engines. Generally they are relatively low molecular weight materials, having a molecular weight (number average) of 5000 or less, such as 500 to 3000 or 1000 to 2500. Occasionally, however, higher molecular weight olefin polymers have been used in two-cycle lubricants; see, for example, U.S. patent 5,741,764, Patel et al., April 21, 1991. Such polymers may be hydrogenated to remove most or all of any remaining ethylenic unsaturation. If an olefin copolymer, such as a low molecular weight polyisobutylene is present, it may be present in an amount of up to 50 percent, such as 10 to 50 percent by weight or 15 to 45 percent or 20 to 40 percent or 25 to35 percent by weight.

[0037] Another material which may be present is a hydrocarbyl-substituted phenol. This may be a similar material to that used in the preparation of the Mannich dispersant, above, and its description as recited there will be applicable for this component as well. In one embodiment, the hydrocarbyl-substituted phenol may be a polyisobutylene-substituted phenol, and the polyisobutylene group may have a number average molecular weight of 300 to 3000 or 500 to 2000 or 750 to 1600 or about 1000. It is believed that the presence of a hydrocarbyl-substituted phenol may provide some antioxidant performance to the lubricant. The hydrocarbyl phenol, if it is present, may be present, in an amount of up to 10 percent, such as 1 to 5 percent or 2 to 4 percent or 2.5 to 3.5 percent by weight.

[0038] The lubricant composition may also contain a detergent such as a metal-containing detergent. Detergents are often overbased materials, otherwise referred to as overbased or superbased salts. These are generally single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization 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, a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol.

[0039] The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

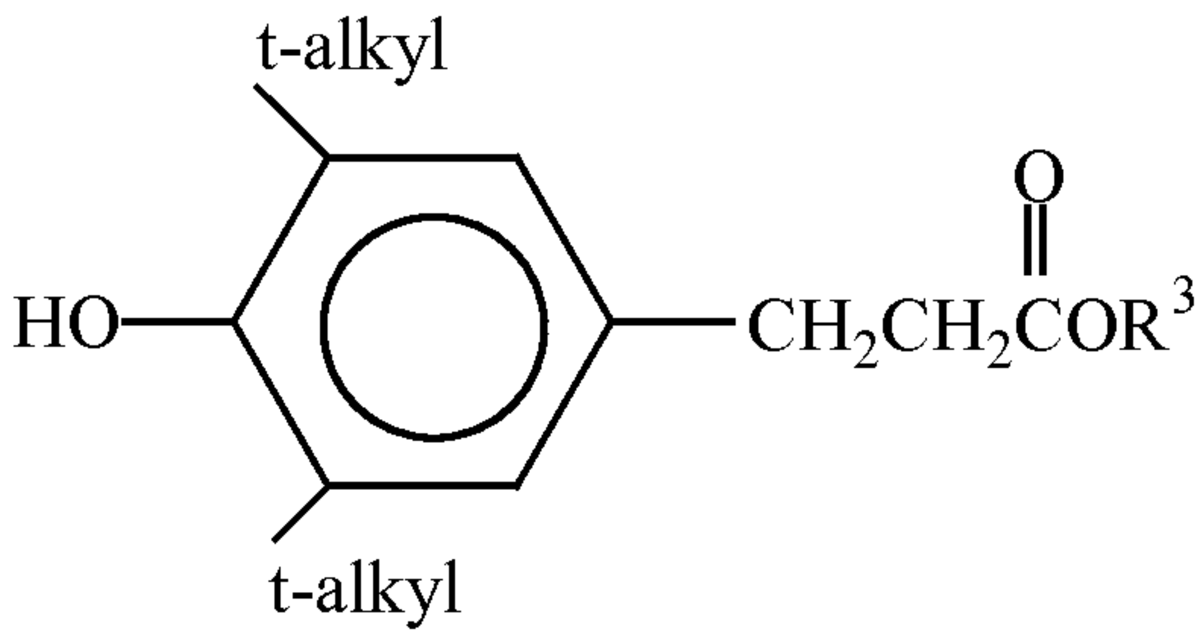
[0040] Such overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of alkylaromatic sulfonic acids, carboxylic acids, phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Yet other detergents are referred to as salixarate detergents. These include overbased materials prepared from salicylic acid (which may be unsubstituted) with a hydrocarbyl-substituted phenol, such entities being linked through –CH2– or other alkylene bridges. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate." Salixarate derivatives and methods of their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968.

[0041] In certain embodiments the detergent may be an overbased sulfonate, phenate, salicylate, or salixarate detergent. In certain embodiments it may comprise an overbased calcium phenate detergent. The phenols useful in making phenate detergents can be represented by $(R^1)_a\text{-Ar-}(OH)_b$, where R^1 is an aliphatic hydrocarbyl group of 4 to 400 or 6 to 80 or 6 to 30 or 8 to 25 or 8 to 15 carbon atoms; Ar is an aromatic group such as benzene, toluene or naphthalene; a and b are each at least one, the sum of a and b being up to the number of displaceable hydrogens on the aromatic nucleus of Ar, such as 1 to 4 or 1 to 2. There is typically an average of at least 8 aliphatic carbon atoms provided by the R^1 groups for each phenol compound. Phenate detergents are also sometimes provided as sulfur-bridged species.

[0042] While the metal salt of the phenate detergent is typically calcium, the metal compounds useful in making the basic metal salts are more generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). Examples include alkali metals such as sodium, potassium, lithium, copper, magnesium, calcium, barium, zinc, and cadmium. In one embodiment the metals are sodium, magnesium, or calcium. The anionic portion of the basic metal compound can be hydroxide, oxide, carbonate, borate, or nitrate.

[0043] In certain embodiments the metal-containing detergent contributes at least about 0.1 total base number, or at least 0.3 or 0.4 or 0.6 TBN to the lubricant composition, and in some embodiments up to 3 or 2 or 1 TBN. The amount of the metal-containing detergent, if present, may in certain embodiments be up to 3 percent, e.g., 0.1 to 3 percent or 0.2 to 2 percent or 0. 25 to 1 percent or 0.3 to 0.6 percent by weight. In other embodiments, the metal-containing detergent may be present in an amount to deliver at least 0.01 percent sulfated ash to the composition. The detergent may be present in an amount to deliver 0.01 to 0.12 percent sulfated ash or, alternatively, 0.05 to 0.1 percent, or even 0.06 to 0.09 percent. In certain embodiments, the present lubricant is not an ash-free lubricant; that is, it may be an ash-containing detergent, containing 0.01 to 0.12 percent sulfated ash or, alternatively, 0.05 to 0.1 percent, or even 0.06 to 0.09 percent, which ash may be provided by the metal-containing detergent or detergents or in whole or in part from other sources such as zinc salts (e.g., zinc dialkyldithiophosphates), molybdenum compounds, or titanium compounds.

[0044] Another material which may be present in the lubricant is an antioxidant. Antioxidants encompass phenolic antioxidants, which may be hindered phenolic antioxidants, one or both ortho positions on a phenolic ring being occupied by bulky groups such as t-butyl. The para position may also be occupied by a hydrocarbyl group or a group bridging two aromatic rings. In certain embodiments the para position is occupied by an ester-containing group, such as, for example, an antioxidant of the formula



wherein R^3 is a hydrocarbyl group such as an alkyl group containing, e.g., 1 to 18 or 2 to 12 or 2 to 8 or 2 to 6 carbon atoms; and t-alkyl can be t-butyl. Such antioxidants are described in greater detail in U.S. Patent 6,559,105.

[0045] Antioxidants also include aromatic amines. In one embodiment, an aromatic amine antioxidant can comprise an alkylated diphenylamine such as nonylated diphenylamine or a mixture of a di-nonylated and a mono-nonylated diphenylamine.

[0046] Antioxidants also include sulfurized olefins such as mono- or disulfides or mixtures thereof. These materials generally have sulfide linkages of 1 to 10 sulfur atoms, e.g., 1 to 4, or 1 or 2. Materials which can be sulfurized to form the sulfurized organic compositions of the present invention include oils, fatty acids and esters, olefins and polyolefins made thereof, terpenes, or Diels-Alder adducts. Details of methods of preparing some such sulfurized materials can be found in U.S. Pat. Nos. 3,471,404 and 4,191,659.

[0047] Molybdenum compounds can also serve as antioxidants, and these materials can also serve in various other functions, such as antiwear agents or friction modifiers. U.S. Pat. No. 4,285,822 discloses lubricating oil compositions containing a molybdenum- and sulfur-containing composition prepared by combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and contacting the complex with carbon disulfide to form the molybdenum- and sulfur-containing composition.

[0048] Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.005 to 5 percent by weight or 0.007 to 1 percent or 0.01 to 0.5 percent of 0.01 to 0.1 percent.

[0049] Yet another material that may optionally be present, or which may be absent, is a metal salt of a phosphorus acid. Metal salts of the formula

$$[(R^8O)(R^9O)P(=S)\text{-}S]_n\text{-}M$$

where R^8 and R^9 are independently hydrocarbyl groups containing 3 to 30 carbon atoms, are readily obtainable by heating phosphorus pentasulfide (P_2S_5) and an alcohol or phenol to form an O,O-dihydrocarbyl phosphorodithioic acid. The alcohol which reacts to provide the R^8 and R^9 groups may be a mixture of alcohols, for instance, a mixture of isopropanol and 4-methyl-2-pentanol, and in some embodiments a mixture of a secondary alcohol and a primary alcohol, such as isopropanol and 2-ethylhexanol. The resulting acid may be reacted with a basic metal compound to form the salt. The metal M, having a valence n, generally is aluminum, tin, manganese, cobalt, nickel, zinc, or copper, and in many cases, zinc, to form zinc dialkyldithiophosphates ("ZDDP"). Such materials are well known and readily available to those skilled in the art of lubricant formulation. Suitable variations to provide good phosphorus retention in an engine are disclosed, for instance, in US published application 2008-0015129, see, e.g., claims. In certain embodiments, the lubricant formulation may be free from ZDDP or may contain only a low amount of one or more ZDDPs, such as to provide 0 to 0.05, or 0.001 to 0.02, or 0.001 to 0.005, or 0.005 to 0.01 weight percent phosphorus to the composition, and in one embodiment the lubricant formulation may contain the aforementioned amounts of phosphorus from all sources, total.

[0050] Other conventional components may also be present, including pour point depressants; friction modifiers such as fatty esters; viscosity index modifiers; metal deactivators; rust inhibitors, corrosion inhibitors, high pressure additives, anti-wear additives, and antifoam agents. Any of these materials can be present or can be eliminated, if desired.

[0051] The components of the present invention can be prepared by mixing the indicated components directly, or by preparing one or more of the components in the form of a concentrate, to which other components (such as oil or solvent) can subsequently be added.

[0052] The present lubricant may be supplied to an engine in any of a variety of ways, depending at least in part on the design of the engine. It may be supplied from a sump, in which case the optional volatile solvents will likely not be present. This arrangement would be more likely used in engines which are not designed to consume the lubricant in the combustion chamber. Many two-stroke cycle engines, however, are not sump-lubricated, and for them, the lubricant may be supplied along with the fuel, either by injection into the fuel stream or by premixing the lubricant into the bulk fuel.

[0053] The fuel into which the lubricant for a two-cycle engine is mixed is commonly, but not necessarily, gasoline. Other possible liquid fuels included gasoline-alcohol mixtures ("gasohol") having 5%, 10%, or a larger percentage of ethanol, including 85% ("E-85"). The lubricant may be blended into the liquid fuel in an amount or ratio of 1:200 to 1:25 by weight, or 1:60 to 1:40, or about 1:50 (e.g., about 2% lubricant).

[0054] The lubricant of the present technology may be profitably employed in a two-stroke cycle engine. Such engines are commonly used in lawn and garden equipment, portable contractor equipment such as pumps and electrical generators, low-cost transportation vehicles, such as mopeds, as well as commercial and recreational vehicles including motorcycles, outboard engines (for boats and marine vehicles), snowmobiles, and personal watercraft vehicles. In some larger recreational applications as in outboard engines, engines with a displacement of 2,000 to 3,000cm^3 generate approximately 150 kW (201 hp). 2-stroke cycle engines can also be found in very small applications, such as in power tools like weed trimmers or chain saws. These smaller engines typically output 1-5 kW and may have a cylinder displacement of 20 to 80cm^3. In some embodiments, therefore, the engines may have a power output of less than 150 kW, such as less than 100 or less than 50 or less than 20 kW; or 0.1 to 15 kW or 0.5 to 10 kW or 1-5 kW, and optionally a cylinder displacement of 10 to 300 cm^3, or 15-100 or 20-80 cm^3.

[0055] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0056] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0057] A series of lubricant compositions is tested in an SRM-265 two-stroke cycle string trimmer engine, 25.4 cm^3 engine displacement. The test is conducted for 50 hours or until engine seizure occurs, running the engine on a gasoline-lubricant mixture. The test consists of two stages, a full throttle portion and an idle portion. The engine is operated at the full throttle condition for 2 minutes and 15 seconds. The engine is operated at the idle condition for 15 seconds. These two cycles are repeated for a total duration of 50 hours without interruption. At the end of the test, the engine is disassembled and inspected for varnish deposits and port blocking. The lubricants and the piston skirt varnish ratings are reported in the table below. ASTM merit scale ratings are used to evaluate engine parts with a rating of 10 representing a clean part and lower numbers representing more severe degrees of varnish down to the most severe which has a merit rating of 1.

Amounts, % by weight	Ex 1*	Ex 2*	Ex 3	Ex 4*
Mineral oil : Balance to = 100%				
Polyisobutene	27.7	27.7	27.7	27.7
Solvent	17.7	17.3	17.3	17.3
Commercial viscosity index improver[a]	0.21	0.21	0.21	0.21
Antioxidant[b]	0.01	0.01	0.01	0.01
Polyolefin-substituted phenol	3.0	3.0	3.0	3.0
Overbased Ca phenate detergent	0.35	0.35	0.35	0.35
Mannich dispersant[c]	—	—	1.00	2.00
Succinimide dispersant[d]	—	1.73	0.86	—
Piston skirt varnish rating	3.8	4.8	7.4	5.2

* A reference or comparative example.

a. Viscoplex™ 1-3003 from Rohmax, as received, including any oil

b. Ethanox™, from Albemarle

c. product of polyisobutylene phenol, formaldehyde, and dimethylamine; includes 10-11% heavy aromatic solvent.

d. 4.7% N content

[0058] The results show markedly improved piston skirt varnish with Example 3 of the present invention, compared with the reference examples having approximately the same total amount of dispersants.

[0059] The formulations below are subjected to a low temperature detergency test. The test lubricant is used to lubricate a Husqvarna HVA 232 E-Tech™ Scrub Cutter engine, a two-stroke cycle engine. After a 15 minute breaking in phase, the carburetor H-needle is set to provide 3% CO at 8400 r.p.m., steady state conditions. The test cycle comprises 2 seconds at full throttle followed by 3 seconds at idle, continuing for 36,000 cycles over 50 hours. The only load is the inertia from the grass cutter. The L-needle is set to give maximum 12,000 (± 500) r.p.m. The lowest speed is normally around 6000 r.p.m. At the end of the test, cleanliness of various parts of the engine is measured. The results are shown in the table below. The maximum (best) rating for total cleanliness is 15.

mounts, % by weight	Ex 5*	Ex 6*	Ex 7*	Ex 8*	Ex 9
Mineral oil : Balance to = 100%					
Polyisobutene	30.6	30.6	30.6	30.6	30.6
Solvent	25.0	25.0	25.0	25.0	25.0
Polyolefin-substituted phenol	3.57	3.57	3.57	3.57	3.57
Overbased Ca phenate detergent	0.42	0.42	0.42	0.42	0.42
Mannich dispersant[c]	—	—	—	1.00	0.43
Succinimide dispersant[d]	—	0.52	1.04	—	0.37
Cleanliness ratings:					
Crankcase	3.00	3.00	3.50	3.00	3.75
Piston skirt	2.50	3.00	3.00	3.00	3.00
Ring area	3.25	3.25	3.50	3.00	3.50
Total	8.75	9.25	10.00	9.00	10.25

* A reference or comparative example.

c. product of polyisobutylene phenol, formaldehyde, and dimethylamine; includes 10-11% heavy aromatic solvent.

d. 4.7% N content

[0060] The results show significantly improved overall cleanliness for the formulation of Example 9, even though the total amount of dispersants is considerably less than in comparative Examples 6-8.

[0061] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

What is claimed is:

1. A lubricant composition comprising:

(a) an oil of lubricating viscosity;

(b) about 0.1 to about 2 percent by weight of a Mannich dispersant;

(c) about 0.1 to about 2 percent by weight of a succinimide dispersant; and

(d) a metal-containing detergent;

wherein the succinimide dispersant provides at least about 40 parts per million by weight of nitrogen atoms to the lubricant composition.

2. The lubricant composition of claim 1 wherein the Mannich dispersant comprises the reaction product of a hydrocarbyl-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and a primary or secondary amine.

3. The lubricant composition of claim 1 or claim 2 wherein the Mannich dispersant comprises the reaction product of a polyisobutene-substituted phenol, formaldehyde or a reactive equivalent of formaldehyde, and dimethylamine.

4. The lubricant composition of any of claims 1 through 3 wherein the amount of the Mannich dispersant is about 0.2 to about 1.05 percent by weight.

5. The lubricant composition of any of claims 1 through 4 wherein the succinimide dispersant is a condensation product of hydrocarbyl-substituted succinic anhydride or a reactive equivalent thereof, with a polyethylene polyamine.

6. The lubricant composition of any of claims 1 through 4 wherein the succinimide dispersant has a total base number of at least about 70 on an oil-free basis.

7. The lubricant composition of any of claims 1 through 6 wherein the succinimide dispersant has a total base number of at least about 90 on an oil-free basis.

8. The lubricant composition of any of claims 1 through 7 wherein the succinimide dispersant has a nitrogen content of at least about 3 percent by weight on an oil-free basis.

9. The lubricant composition of any of claims 1 through 8 wherein the amount of the succinimide dispersant is about 0.2 to about 1 percent by weight.

10. The lubricant composition of any of claims 1 through 9 wherein the total amount of nitrogen-containing dispersants in the composition is about 0.2 to about 4 percent by weight.

11. The lubricant composition of any of claims 1 through 10 wherein the weight ratio of the Mannich dispersant to the succinimide dispersant is about 80:20 to about 20:80.

12. The lubricant composition of any of claims 1 through 11 wherein the metal-containing detergent is an overbased sulfonate, phenate, salicylate, or salixarate detergent.

13. The lubricant composition of any of claims 1 through 12 wherein the metal containing detergent comprises an overbased calcium phenate detergent.

14. The lubricant composition of any of claims 1 through 13 wherein the metal containing detergent contributes at least about 0.1 total base number to the lubricant composition.

15. The lubricant composition of any of claims 1 through 14 wherein the amount of phosphorus contained therein is 0 to 0.05 weight percent.

16. The lubricant composition of claim 15 wherein the amount of phosphorus is provided by one or more zinc dialkyldithiophosphates.

17. A composition prepared by admixing the components of any of claims 1 through 16.

18. A method of lubricating an internal combustion engine, comprising supplying thereto the lubricant composition of any of claims 1 through 17.

19. The method of claim 18 wherein the internal combustion engine is a two-stroke cycle engine.

20. The method of claim 18 or claim 19 wherein the internal combustion engine has a power output of less than 150 kW (201 horsepower).

21. The method of any of claims 18 through 20 wherein the internal combustion engine has a power output of 0.1 to 15 kW.

21. The method of any of claims 18 through 21 wherein the lubricant composition is provided as a mixture with a liquid fuel.