(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 638 632 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **94305974.1**

(22) Date of filing : **12.08.94**

(51) Int. Cl.^{6} : **C10M 163/00,** C10M 167/00, // (C10M163/00, 133:52, 137:10, 159:20, 159:22, 159:24), (C10N10/02, 40:25)

(30) Priority : **13.08.93 GB 9316985**

(43) Date of publication of application :
15.02.95 Bulletin 95/07

(84) Designated Contracting States :
BE DE ES FR GB IT

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(54) Motor oil compositions, additive concentrates for producing such motor oils, and the use thereof.

(57) Lubricants and additive concentrates comprising : (a) a dispersant made by reacting aminoguanidine and/or a basic salt thereof with an acyclic hydrocarbyl succinic acylating agent in a mole ratio of 0.4 :1 to 1.3 :1, respectively ; (b) a zinc dihydrocarbyl dithiophosphate in which at least 35 mol percent of the hydrocarbyl groups are secondary hydrocarbyl groups ; and (c) a basic calcium detergent additive complement exhibit excellent performance characteristics.

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This invention relates to lubricant compositions, and more particularly to lubricants and additive concentrates of enhanced performance characteristics.

Over the years the demand for performance improvements in lubricating oils and functional fluids has persisted and, if anything, progressively increased. For example, lubricating oils for use in internal combustion engines, and in particular, in spark-ignition and diesel engines, are constantly being modified and improved to provide improved performance. Various organizations around the world as well as the automotive manufacturers continually seek to improve the performance of lubricating oils. Various standards have been established and modified over the years through the efforts of these organizations. As engines have increased in power output and complexity, and in many cases decreased in size, the performance requirements have been increased to provide lubricating oils that will exhibit a reduced tendency to deteriorate under conditions of use and thereby to reduce wear and the formation of such undesirable deposits as varnish, sludge, carbonaceous materials and resinous materials which tend to adhere to various engine parts and reduce the operational efficiency of the engine.

An objective therefore is to provide novel compositions capable of effectively controlling wear and formation of undesirable quantities of such varnish, sludge, and carbonaceous deposits.

Flexible engine seals are used in assembling internal combustion engines and drivetrains to prevent leakage of lubricants at locations where moving parts, such as crank-case shafts, extend outside the engine block. Accordingly, qualification tests have been established whereby the effect of a lubricant composition on a given seal-type material is measured under a particular set of controlled laboratory bench test conditions. The commercial reality is that the lubricant needs to exhibit good performance in a variety of elastomer compatibility tests to achieve acceptance in the marketplace. Thus another objective is to provide compositions capable of passing such seal compatibility tests.

U.S. Pat. No. 5,080,815 to Fenoglio et al describes dispersants having improved compatibility toward a particular fluoroelastomer. Those dispersants are formed by reacting a hydrocarbyl-substituted dicarboxylic acid compound such as a hydrocarbyl-substituted dicarboxylic acid anhydride with aminoguanidine or a basic salt thereof in a ratio of about 1.5 to about 2.2 moles of aminoguanidine or basic salt thereof per mole of hydrocarbyl-substituted dicarboxylic acid compound.

U.S. Pat. No. 4,908,145 to Fenoglio describes dispersants for lubricating oils that are also compatible with that fluorohydrocarbon elastomer. These dispersants are enriched in alkyl-bis-3-amino-1,2,4-triazole (e.g., polybutenyl-bis-3-amino-1,3,4-triazoles) and are formed by reacting an alkyl-substituted dicarboxylic acid compound, such as a polyisobutenyl succinic acid compound, with a basic salt of aminoguanidine at a ratio of from about 1.6 to about 2 moles of aminoguanidine compound per mole of the alkyl-substituted dicarboxylic acid compound.

Both of the foregoing patents show in Table II thereof that dispersants made in accordance with their teachings exhibited good compatibility with VITON fluoroelastomer in the Caterpillar VITON Compatibility Test. These patents also show results of spot dispersancy bench tests which indicate that a product prepared by reacting one mole of aminoguanidine bicarbonate per mole of polyisobutenyl succinic anhydride was relatively ineffective as a dispersant.

In one of its embodiments, this invention provides a lubricant composition which comprises a major amount of oil of lubricating viscosity containing at least the following components:

a) 0.03 to 0.15 wt% of nitrogen as an oil-soluble product formed by reacting aminoguanidine and/or a basic salt thereof with an acyclic hydrocarbyl succinic acylating agent in a mol ratio in the range of 0.4 to 1.3 mols of aminoguanidine and/or basic salt thereof per mol of said acylating agent;

b) 0.08 to 0.14 wt% of zinc as oil-soluble zinc dihydrocarbyl dithiophosphate in which at least 35 mol % of the hydrocarbyl groups present are secondary hydrocarbyl groups; and

c) 0.15 to 0.40 wt% of calcium as a basic calcium detergent additive complement in which at least 60 mol %, preferably at least 75 mol %, of the calcium is derived from overbased calcium detergent having a total base number (TBN) of at least 200 mg of KOH per gram.

Preferably, the lubricant composition further comprises up to 0.1 wt% of magnesium as an overbased magnesium detergent additive complement having a TBN of at least 300 mg of KOH per gram.

Additionally, the lubricant composition further comprises at least one oil-soluble antioxidant and at least one foam inhibitor, and/or at least one viscosity index improver.

Preferably, the lubricant compositions have a TBN in the range of 6 to 15 mg of KOH per gram.

Preferred zinc dihydrocarbyl dithiophosphates are mixtures of zinc dialkyl dithiophosphates containing primary and secondary alkyl groups and in which at least 35 mol % of the alkyl groups are secondary alkyl groups.

Preferably, the basic calcium detergent additive complement in the compositions of this invention is comprised of a mixture of (i) and (ii), or (i) and (iii), or (i), (ii) and (iii), wherein (i) is an overbased calcium sulfonate detergent composition having a TBN of at least 280 mg of KOH per gram thereof, and is present in amount such that at least 40 wt% of the calcium is derived therefrom; (ii) is an overbased calcium sulfurized phenate detergent composition having a TBN of at least 100 mg, preferably at least 200 mg, of KOH per gram thereof, and if present is present in amount such that up to 50 wt% of the calcium is derived therefrom; and (iii) is a low base calcium sulfonate detergent having a TBN of up to 40 mg of KOH per gram thereof, and if present is present in amount such that up to 25 wt% of the calcium is derived therefrom.

Preferably, at least 50 wt% of the magnesium of the overbased magnesium detergent additive complement is comprised of an overbased magnesium sulfonate detergent composition having a TBN of at least 300 mg of KOH per gram thereof.

Preferred oil-soluble dispersant products used pursuant to this invention are formed by reacting aminoguanidine and/ or a basic salt thereof with an alkenyl succinic acylating agent in a mol ratio in the range of 0.8 to 1.2 mols of aminoguanidine and/or basic salt thereof per mole of the acylating agent. In addition, the alkenyl group of the acylating agent is derived from a polyolefin having a GPC number average molecular weight in the range of 900 to 2500.

Also provided by this invention are additive concentrates which comprise at least the following components:

a) 0.3 to 0.8 wt% of nitrogen as an oil-soluble product formed by reacting aminoguanidine and/or a basic salt thereof with an acyclic hydrocarbyl succinic acylating agent in a mol ratio in the range of 0.4 to 1.3 mols of aminoguanidine and/or basic salt thereof per mol of said acylating agent;

b) 0.5 to 1.2 wt% of zinc as oil-soluble zinc dihydrocarbyl dithiophosphate in which at least 35 mol % of the hydrocarbyl groups present are secondary hydrocarbyl groups; and

c) 1.0 to 4.0 wt% of calcium as a basic calcium detergent additive complement in which at least 60 mol %, preferably at least 75 mol %, of the calcium is derived from overbased calcium detergent having a TBN of at least 100 mg, preferably at least 200 mg, of KOH per gram.

Preferably, such additive concentrates further comprise up to 0.8 wt% of magnesium as an overbased magnesium detergent additive complement having a TBN of at least 300 mg of KOH per gram, and optionally but preferably, 0.5 to 20 wt% of at least one oil-soluble antioxidant; and optionally but preferably, 0.001 to 0.05 wt% of at least one foam inhibitor.

Preferably these additive concentrates have a TBN in the range of 50 to 120 mg KOH per gram.

In accordance with this invention, it has been found that additive components such as described above can be used in formulating motor oil compositions that can pass at least the following tests:

- the Test Sequence VE engine test as described in ASTM Specification D4485-91 for the Performance of Automotive Engine Oils (hereinafter "Sequence VE engine test");
- the Volkswagen P-VW 5106 cam and tappet wear test (hereinafter "P-VW 5106 test");
- the Test L-38 engine test as described in ASTM Specification D4485-91 for the Performance of Automotive Engine Oils (hereinafter "L-38 engine test");
- the CEC L-35-U-92 test for motor oil evaluation in a turbocharged passenger-car diesel engine using a Volkswagen 1.6 liter diesel engine P-VW 1431 (hereinafter "P-VW 1431 engine test");
- the Volkswagen specification for elastomer compatibility tests for motor oils P-VW 3344 (hereinafter "P-VW 3344 seal test); and
- the DKA 06/79 high temperature piston deposit engine test using a Volkswagen 1.6 liter gasoline engine VW 1302 (hereinafter "VW 1302 engine test").

Further, it has been found that the additive components such as described above can be used in formulating motor oil compositions that can pass at least the following tests:

- the CEC L-38-T-87 gasoline engine valve train scuffing test using the PSA TU3 engine (hereinafter "Peugeot TU3 test");
- the Mercedes-Benz VDA 521-01 elastomer compatibility tests for SRE NBR-34 nitrile butadiene rubber (hereinafter "M-B NBR-34 seal test") and for FPM AK-6 fluoroelastomer (hereinafter "M-B AK-6 seal test"); and
- the MAN QC 13-017 elastomer compatibility tests for SRE NBR-28 nitrile butadiene rubber (hereinafter "MAN NBR-28 seal test") and for FPM AK-6 fluoroelastomer (hereinafter "MAN AK-6 seal test").

Other embodiments of this invention will be apparent from the ensuing description and appended claims.

The base oils used in forming the lubricant compositions of this invention can be natural or synthetic oils of lubricating viscosity, or suitable blends thereof. Thus the base oils can be hydrocarbon oils derived from petroleum (or tar sands, coal, shale, etc.). Likewise, the base oils can be or include natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly-α-olefins (e.g., hydrogenated or unhydrogenated α-olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; and the like. Mixtures of mineral, natural and/or synthetic oils in any suitable proportions are also useable.

In most cases the base oil is preferably a petroleum-derived mineral oil of the types conventionally used in forming passenger car, heavy duty diesel engine oils, or drivetrain lubricants.

Component a).

For convenience, the term "AG dispersant" is used to designate a product made by reacting aminoguanidine or a basic salt thereof with a hydrocarbyl-substituted succinic acid or anhydride in a mole ratio of from about 0.4 to 1.3 moles of the aminoguanidine or basic salt thereof per mole of the succinic acid or anhydride compound. Likewise, the term "borated AG dispersant" is used to designate a product made in two stages, namely, (i) reacting aminoguanidine or a basic salt thereof with a hydrocarbyl-substituted succinic acid or anhydride in a mole ratio of from about 0.4 to 1.3 moles of the aminoguanidine or basic salt thereof per mole of the succinic acid or anhydride compound; and (ii) borating the product so produced.

To prepare the AG dispersant, a suitably proportioned mixture of an aliphatic hydrocarbyl-substituted succinic acid derivative (acid, anhydride, lower alkyl ester, or acyl halide) and aminoguanidine or a basic salt thereof is heated, preferably under an inert atmosphere, at a temperature in the range of about 120 to about 200°C. Preferably the reaction is conducted in an inert diluent such as a light mineral oil. Reaction times are typically in the range of from 1 to 4 hours. Suitable inert atmospheres include nitrogen, argon, krypton, neon, etc. As noted above, it is required pursuant to this invention, to employ a product made using from about 0.4 to 1.3 moles of aminoguanidine or basic salt thereof per mole of the aliphatic hydrocarbyl-substituted succinic acid derivative. In order to prepare borated AG dispersant, AG dispersant formed as above is heated in combination with a suitable boron-containing material such that the resultant product contains up to about 1% by weight of boron. Temperatures in the range of about 80 to about 200°C are generally satisfactory for use in the boration reaction. Suitable methods for conducting boration are well known to those skilled in the art. See in the connection, U.S. Pat. Nos. 3,087,936; 3,254,025; 3,322,670; 3,344,069; 4,080,303; 4,426,305; 4,925,983 and 5,114,602.

AG dispersants are characterized by having a peak in the region of 1590 cm^{-1}. Additionally, the spectrum may exhibit a peak in the range of 1690 cm^{-1}, but AG dispersants can be used that do not exhibit this latter peak. When made at mol ratios of about 1:1 or lower, a peak at 1725 cm^{-1} appears. The 1590 cm^{-1} peak is nearly absent in the Examples of U.S. Pat. No. 5,080,815. The chemical structure of the products of this invention is unknown, but on the basis of their infrared spectra, they do not appear to have any significant content of triazole moieties, as is shown by the absence of the 1640 cm^{-1} IR peak present in the Examples of U.S. Pat. No. 5,080,815.

Methods are known for producing suitable aliphatic hydrocarbyl-substituted succinic acid derivatives (acid, anhydride, lower alkyl ester, or acyl halide), such as alkenyl succinic anhydrides, to be used in reaction with aminoguanidine or basic salts thereof. Reference may be had, for example, to U.S. Pat. Nos. 4,234,435; 4,908,145; 5,080,815; 5,071,919 and 5,137,978.

The synthesis of typical AG dispersants and borated AG dispersants are set forth in the following examples.

EXAMPLE 1

Into a reaction vessel are charged 1665 g (0.47 mole) of 60% active polyisobutenyl succinic anhydride (PSA) (formed from polyisobutylene having a number average molecular weight of about 2060), 76.8 g (0.56 mole) of 98.5% aminoguanidine bicarbonate (AGB), and 600 g of a 100 neutral base oil. The mole ratio of AGB to PSA is 1.2:1. The mixture is heated at 170°C under a nitrogen sweep for 2 hours with stirring. The product is filtered while hot and allowed to cool.

EXAMPLE 2

The procedure of Example 1 is repeated using a chemically equivalent amount of PSA formed from polyisobutylene having a number average molecular weight of about 1290 in lieu of the higher molecular weight

PSA of Example 1.

EXAMPLE 3

The procedure of Example 1 is repeated except that the AGB:PSA mole ratio is 1.1:1.

EXAMPLE 4

Example 3 is repeated except that the PSA of Example 2 is employed.

EXAMPLE 5

Product formed as in Example 3 is borated by heating 2290 g of the 44% active product so formed with 212.5 g of a superborated polyisobutenyl succinic ester-amide containing approximately 2.5% of boron at 160°C for 2 hours. The resultant product is diluted with 154 g oil to give a product containing 0.2% boron.

EXAMPLE 6

Example 5 is repeated, but using 2000 g of product formed as in Example 4 and 185.6 g of the superborated ester-amide. The boron content of the borated product is 0.2% on dilution with 134 g oil.

EXAMPLE 7

Product formed as in Example 1 (2290 g) is borated by heating with 572.5 g of the superborated ester-amide and diluted with oil to give a product with 0.5% boron.

EXAMPLE 8

Example 7 is repeated with the exception that 2000 g of active product formed as in Example 2 is used instead of the higher molecular weight product of Example 1.

EXAMPLES 9-15

The procedure of Example 1 is repeated seven times in the same manner except that the proportions of AGB and PSA are varied such that the respective AGB:PSA mole ratios are 0.4:1, 0.5:1. 0.6:1, 0.7:1, 1.0:1, 0.9:1 and 1:1.

EXAMPLES 16-22

Examples 9-15 are repeated, but using product formed as in Example 2 in place of the product formed as in Example 1.

EXAMPLES 23-36

The respective products formed as in Examples 9-22 are borated to boron levels of 0.2% using the boration procedure of Example 5.

EXAMPLE 37

Example 1 is repeated except that 1.0 mole of AGB is reacted with 1.0 mole of PSA. Boration is carried out as described in Example 5 to provide a preferred product of this invention.

Component b).

It is important to use an oil-soluble zinc dihydrocarbyl dithiophosphate in which at least 35 mol % of the hydrocarbyl groups present are secondary hydrocarbyl groups, such as isopropyl, sec-butyl, and/or 4-methyl-2-pentyl groups. Usually, a mixture of zinc dihydrocarbyl dithiophosphates is employed. One way of achieving such mixtures is to combine appropriate proportions of an all-primary zinc dialkyl dithiophosphate with an all-secondary zinc dialkyl dithiophosphate. Alternatively, a suitably proportioned mixture of primary and secondary alcohols can be used in forming the dialkyl dithiophosphoric acid intermediate used in the production of the zinc dialkyl dithiophosphate. Regardless of which of these approaches is followed, the dithiophosphoric acids from which the zinc salts are formed can be prepared by the reaction of about 4 moles of one or more alcohols per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from about 50 to about 120°C. The reaction generally is completed in about 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

Primary alcohols which may be used in forming the dialkyl dithiophosphoric acid intermediate include propanol, butanol, isobutyl alcohol, pentanol, neopentanol, hexanol, heptanol, 2-ethyl-1-hexanol, isooctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, octadecanol, eicosanol, and the like. Among suitable secondary alcohols are included 2-propanol, 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, 4-methyl-2-pentanol, 5-methyl-2-hexanol, and the like. Thus each alkyl group in the dithiophosphoric acid intermediate (and thus in the zinc dithiophosphate salt as well) typically contains in the range of 3 to about 20 carbon atoms, preferably in the range of 3 to about 12, and most preferably in the range of 3 to about 8 carbon atoms.

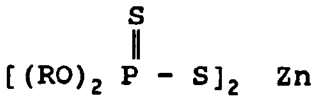
The preparation of the zinc salts of the dialkyl dithiophosphoric acid intermediates is usually effected by reacting the acid product with a suitable zinc compound such as zinc oxide or zinc hydroxide. Simply mixing and heating such reactants is normally sufficient to cause the reaction to occur, and the resulting product is usually of sufficient purity for use without further purification. Typically the salts are formed in the presence of a diluent such as an alcohol, water or a light mineral oil. Neutral salts are prepared by reacting one equivalent of zinc oxide or hydroxide with one equivalent of the acid. Basic metal salts are prepared by adding an excess (i.e., more than one equivalent) of the metal oxide or hydroxide with one equivalent of the dialkyl dithiophosphoric acid. Typical procedures for producing zinc dialkyl dithiophosphates are given in U.S. Pat. Nos. 4,085,053; 4,104,291; 4,215,067; and 4,634,541.

In some cases, incorporation of certain ingredients such as small amounts of metal acetate or acetic acid in conjunction with the zinc reactant will facilitate the reaction and provide an improved product. For example, use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide tends to facilitate the formation of zinc dialkyl dithiophosphates.

If desired, one or more of the zinc dialkyl dithiophosphates may be treated with an epoxide (e.g., an alkylene oxide having up to about 8 carbon atoms in the molecule) to form an adduct. Procedures for preparing epoxide adducts are reported, for example, in U. S. Pat. No. 3,390,082.

Mixed-acid zinc salts such as described in U. S. Pat. Nos. 4,308,154 and 4,417,970 can be used provided of course that the proportion of secondary alkyl groups in the product is in the range required pursuant to this invention.

One preferred group of zinc salts is a mixture of dialkyl dithiophosphates wherein the zinc salts contain from about 4.8 to about 6.6% by weight of isobutyl groups, from about 4.8 to about 6.7% by weight of 2-ethyl-1-hexyl groups, from about 14.0 to about 14.5% by weight of isopropyl groups, and from about 16.7 to about 20.1% by weight of 4-methyl-2-pentyl groups. Another particularly preferred mixture of zinc dialkyl dithiophosphates is a mixture which contains from about 4.6 to about 6.4% by weight of isobutyl groups, from about 2.2 to about 3.1% by weight of primary amyl groups, from about 1.4 to about 2.0% by weight of primary octyl groups, from about 11.6 to about 12.7% by weight of isopropyl groups, and from about 21.4 to about 23.4% by weight of 4-methyl-2-pentyl groups. The weight percentages of the respective alkyl groups as set forth in this paragraph are based on the total weight of the zinc salts which, for the purposes of calculation only, are assumed to have the general formula:



$$[(\mathrm{RO})_2\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}-\mathrm{S}]_2\ \mathrm{Zn}$$

where each R is one of the designated alkyl groups. In other words, in calculating the weight percentages of the respective alkyl groups, the amount of any solvent or diluent that may be present in the mixture of zinc dialkyl dithiophosphates is omitted, and the assumption is made -- solely for the purposes of the calculations -- that the zinc dialkyl dithiophosphates are not overbased, or treated with an epoxide or zinc carboxylate, although in fact they may be overbased and/or treated in such manner.

One way of forming a typical mixture of zinc salts characterized by having on a weight basis about 4.8 to about 6.6% by weight of isobutyl groups, from about 4.8 to about 6.7% by weight of 2-ethyl-1-hexyl groups, from about 14.0 to about 14.5% by weight of isopropyl groups, and from about 16.7 to about 20.1% by weight of 4-methyl-2-pentyl groups is to mix LUBRIZOL® 1060 zinc dialkyldithiophosphate and HiTEC® 685 zinc dialkyldithiophosphate in a weight ratio (using both additives on an as received basis) of 1.79:1, respectively. Similarly, one way of forming a typical mixture of zinc salts having on a weight basis from about 4.6 to about 6.4% by weight of isobutyl groups, from about 2.2 to about 3.1% by weight of primary amyl groups, from about 1.4 to about 2.0% by weight of primary octyl groups, from about 11.6 to about 12.7% by weight of isopropyl groups, and from about 21.4 to about 23.4% by weight of 4-methyl-2-pentyl groups is to mix HiTEC® 7169 zinc dialkyldithiophosphate and either HiTEC® 7198 or 7197 zinc dialkyldithiophosphate in a weight ratio (again, both additives being weighed on an as received basis) of 3.29:1, respectively. LUBRIZOL is a trademark of The Lubrizol Corporation and HiTEC is a trademark of Ethyl Petroleum Additives, Ltd.,and Ethyl Petroleum Additives, Inc.

Component c).

This component comprises one or more calcium salts of at least one acidic organic compound. These include low-based and overbased calcium sulfonates, low-base and overbased calcium phenates, low-base and overbased calcium sulfurized phenates, and low-base and overbased calcium carboxylates. The term "overbased" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. Thus this term is inclusive of those material which have been referred to in the art as overbased, superbased, hyperbased, etc. The actual stoichiometric excess of metal in the overbased salt can vary considerably, for example, from about 0.1 equivalent to about 50 or more equivalents depending on the materials used, the reactions utilized, and the process conditions employed. Generally speaking, the overbased calcium salts useful in this invention contain from about 1.1 to about 40 or more equivalents of calcium, more preferably from about 1.5 to about 30 and most preferably from about 2 to about 25 equivalents of calcium for each equivalent of material which is overbased.

Generally, overbased materials are prepared by treating with an acidic material, a reaction mixture comprising the organic material to be overbased, a reaction medium consisting essentially of at least one inert, organic solvent for the organic material to be overbased, a stoichiometric excess of a metal base, and a promoter. The most commonly employed methods involve use of a mineral oil as the reaction medium and a stoichiometric excess of metal oxide, hydroxide, alkoxide, carbonate, bicarbonate, or sulfide as the metal base. Suitable acidic materials used in producing the overbased salts include such acids as formic acid, acetic acid, oleic acid, palmitic acid, nitric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, boric acid, SO_2, SO_3, CO_2, H_2S, N_2O_3, and the like. The most preferred acid material for use in forming the overbased calcium salts is carbon dioxide. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, ethanol. 2-propanol, octyl alcohol, Cellosolve alcohol, Carbitol alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, and dodecylamine. Typically, the reaction mass is filtered on completion of the overbasing operation. For a comprehensive discussion of suitable promoters, see U.S. Pat. Nos. 2,616,904; 2,695,910 and 2,777,874. A particularly effective method for preparing the overbased calcium salts comprises mixing an acid with an excess of a basic calcium neutralizing agent such as calcium oxide or hydroxide and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60° to 300°C, and preferably about 100 to about 200°C.

The overbased calcium salts can also be formed by overbasing a preformed low base or non-overbased calcium salt.

The overbased calcium sulfonates can be derived from suitable aliphatic, cycloaliphatic, aromatic or heterocyclic sulfonic acids and/or the salts thereof. In general such acids can be represented by the formulas $R(SO_3H)_n$ and $(R')_xT(SO_3H)_y$ where R is an aliphatic or aliphatic-substituted cycloaliphatic group free from acetylenic unsaturation and having up to about 60 carbon atoms; n is at least one, and is generally in the range of 1 to 3; R' is an aliphatic group free from acetylenic unsaturation (typically alkyl or alkenyl) and having about 4 to about 60 carbon atoms; T is a cyclic nucleus which may be derived from an aromatic hydrocarbon such as benzene, toluene, xylene, naphthalene, anthracene, biphenyl, etc., or from a heterocyclic compound such as pyridine, indole, isoindole, etc. Ordinarily T is an aromatic hydrocarbon nucleus such as benzene or naphthalene; and x and y have an average value of about 1 to 4 per molecule, most often an average of about 1. Examples of such acids are petroleum sulfonic acids, paraffin wax sulfonic acids, wax-substituted cyclohexyl sulfonic acids, cetylcyclopentyl sulfonic acids, wax-substituted aromatic sulfonic acids, mahogany sulfonic acids, tetraisobutylene sulfonic acids, tetraamylene sulfonic acids, and the like. Most preferably, the overbased calcium salts are formed from alkylaryl sulfonic acids, such as alkylbenzene sulfonic acids. The alkyl group or groups present on the aromatic ring typically each contain from about 8 to about 40 carbon atoms. Suitable overbased calcium sulfonates having total base numbers of at least about 150 milligrams of KOH per gram of the overbased composition are available as articles of commerce from a number of well known suppliers. One such material is HiTEC® 611 additive (Ethyl Petroleum Additives, Inc.) which has a nominal TBN of about 300.

Overbased calcium phenates are typically formed by overbasing calcium alkylphenates and/or calcium alkenylphenates where the aromatic ring is substituted with one or more alkyl or alkenyl groups (usually 1 to 2) that render the finished product soluble or at least stably dispersible in oil. The alkyl or alkenyl substituents on the aromatic ring typically contain at least about 6 carbon atoms and may contain as many as 500 or more carbon atoms. Preferred substituents are derived from alpha-olefins such as are formed by wax cracking or chain growth of ethylene on aluminum alkyls such as triethyl aluminum, or from olefin oligomers such as olefin dimers, trimers, tetramers and/or pentamers. However higher polymers such as polypropenes, polyisobutenes, polyamylenes, and copolymers such as copolymers of ethylene and propylene, etc., are also useful as source materials for forming the substituted phenols from which the calcium phenate is produced. In most cases the phenate will have an alkyl or alkenyl substituent having in the range of about 6 to about 50 carbon atoms. The phenolic ring may also additionally contain short chain substituents such as methyl, ethyl, isopropyl, butyl, etc. substituents. Likewise, the phenate may be a derivative of a polyhydroxy aromatic compound, such as catechol, resorcinol, or hydroquinone.

The overbased sulfurized calcium phenates can be formed from the substituted phenols described above by reacting the substituted phenol with sulfur monochloride, sulfur dichloride or elemental sulfur. The phenol:sulfur compound molar ratio is usually in the range of about 1:0.5 to about 1:1.5 or more. Reaction temperatures in the range of about 60 to about 200°C are usually employed. Generally the phenol:sulfur group molar ratio in the sulfurized phenate is in the range of about 2:1 to about 1:2. The overall process for producing the overbased sulfurized calcium phenate can be conducted in multiple stages as by forming the sulfurized phenol and then conducting the overbasing process which itself can be operated in stages with multiple introduction of additional reactants, promoters, etc. during the course of the overbasing operation. Alternatively, the sulfurization and overbasing can be conducted concurrently by charging the reactants such that the sulfurized phenol or phenate is formed in situ and is overbased as the reaction proceeds. All such process details are well known and reported in the literature.

Suitable overbased carboxylic acids which can be used in this invention include overbased aliphatic carboxylic acids, overbased cycloaliphatic carboxylic acids, overbased aromatic carboxylic acids, and overbased heterocyclic carboxylic acids. Such acids can be monocarboxylic or polycarboxylic acids, and the principal requirement is that the acid have sufficient chain length to be soluble or at least stably dispersible in lubricating oil. Thus the acids generally contain from about 8 to about 50, and preferably from about 12 to about 30, carbon atoms, although certain acids such as alkyl- or alkenyl-substituted succinic acids can have an average of up to 500 or more carbon atoms per molecule. The acids are usually free of acetylenic unsaturation. Examples include linolenic acid, capric acid, linoleic acid, oleic acid, stearic acid, lauric acid, ricinoleic acid, undecylic acid, palmitoleic acid, 2-ethylhexanoic acid, myristic acid, isostearic acid, behenic acid, pelargonic acid, propylene tetramer-substituted succinic acid, isobutene trimer-substituted succinic acid, octylcyclopentane carboxylic acid, stearyl-octahydroindenecarboxylic acid, tall oil acids, rosin acids, polybutenyl succinic acids derived from polybutene having a GPC number average molecular weight in the range of 200 to 1500, acids formed by oxidation of wax, and like acids.

The preferred overbased carboxylic acids are the overbased aromatic carboxylic acids in which the aromatic nucleus is substituted by at least one carboxyl group (usually 1 to 4, preferably 1 to 2) and by at least one aliphatic hydrocarbyl group (usually 1 to 2, preferably one), preferably derived from a polyalkene, and most preferably having an average in the range of about 40 to about 400 carbon atoms. Optionally, but most preferably, the aromatic nucleus is also substituted by at least one hydroxyl group (usually 1 to 2, preferably one). Examples of such substituted aromatic carboxylic acids include substituted benzoic, phthalic, and salicylic acids. Most preferred of the aromatic carboxylic acids are the overbased calcium salts of aliphatic-substituted salicylic acids wherein the substituent is derived from polyalkenes, particularly polymerized lower 1-monoolefins, such as polyethylene, polypropylene, polyisobutylene, ethylene-propylene copolymers, etc., having average carbon contents of about 50 to about 400 carbon atoms.

Overbased calcium calixerates such as described in U.S. Pat. No. 5,114,601 are also suitable.

Suitable low base calcium alkylbenzene sulfonate detergent compositions, most preferably low base calcium propylene-derived alkylaryl sulfonates are formed by preparing an alkali or alkaline earth metal salt of an alkylbenzene sulfonic acid and if desired, subjecting the salt in the presence of a small excess of an alkali or alkaline earth metal base such as an oxide, hydroxide or alcoholate to the action of an acidic material such as carbon dioxide so that a small amount of overbasing occurs. This controlled overbasing can be conducted using the same materials in much the same way as the overbasing described above, except of course the amount of metal base is such that the desired total base number of the resultant composition is achieved. Suitable low base materials of the foregoing types are available as articles of commerce. HiTEC® 614 additive (Ethyl Petroleum Additives, Inc.) is a good example of a commercially-available calcium alkylbenzene sulfonate. Low-base calcium sulfurized alkylphenates are also suitable components in the compositions of this invention.

Component d).

The overbased magnesium salts utilized pursuant to this invention are generally similar in character to the overbased calcium salts. In other words, the overbased magnesium salts are overbased magnesium salts of at least one acidic organic compound, and thus include overbased magnesium sulfonates, overbased magnesium phenates, overbased magnesium sulfurized phenates, overbased magnesium carboxylates, and overbased magnesium calixerates. In addition, the processes by which overbased magnesium salts are produced are in many respects similar to the processes used in forming the overbased calcium salts. However, despite these similarities it is desirable pursuant to this invention to utilize a combination of at least one overbased calcium salt and at least one overbased magnesium salt.

Accordingly, except for neutralizing and overbasing the acidic material with a magnesium base such as magnesium oxide, magnesium hydroxide or a magnesium alcoholate, instead of using a calcium base, the process approaches outlined above for preparing the overbased calcium salts can be utilized for producing the overbased magnesium salts. Desirable processes for producing overbased magnesium sulfonates are described for example in U.S. Pat. Nos. 4,137,186; 4,201,682; and 4,474,710. Other suitable overbased magnesium salts and/or other methods for producing suitable overbased magnesium salts are described for example in U.S. Pat. Nos. 4,647,387; 4,775,490; 4,957,642; 5,032,299; 5,089,155; and 5,173,203. Synthesis of overbased magnesium calixerates is described in U.S. Pat. No. 5,114,601. A variety of suitable overbased magnesium salts are available as articles of commerce from a number of different suppliers.

The preferred overbased magnesium salts are overbased magnesium alkylbenzene sulfonate detergent compositions having a total base number of at least about 300 milligrams of KOH per gram thereof, and most preferably a total base number in the range of about 350 to about 500 milligrams of KOH per gram thereof. Since such compositions are formed in an inert diluent, usually a mineral oil diluent, the total base number reflects the basicity of the overall composition including diluent, and any other materials (e.g., promoter, etc.) that may be contained in the detergent composition.

Representative patents describing, inter alia, overbased calcium and/or magnesium sulfonates, phenates, sulfurized phenates, and/or carboxylates, and their preparation include U.S. Pat. Nos. 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; 3,595,791; 4,259,193; 4,608,184; 4,664,824; 4,710,308; 4,780,224; 4,865,754; 4,873,007; 4,954,272; 4,971,710; 4,973,411; 4,995,993; 4,810,396; 4,810,398; 4,822,502; 4,865,754; 4,869,837; 4,879,053; 4,880,550; 4,910,334; 4,929,373; 4,997,584; 5,011,618; 5,013,463; 5,021,174; 5,024,773; 5,030,687; 5,035,816; 5,041,231; 5,069,804; 5,089,158; 5,102,566; 5,108,630; 5,108,631; 5,112,506; 5,132,033; 5,137,648; 5,162,085; and 5,169,545.

Other Components.

Various other additives can be used in the compositions of this invention. These include alkali metal detergents, oxidation inhibitors, friction modifiers, rust inhibitors, foam inhibitors, copper corrosion inhibitors, demulsifying agents, and the like. Alkali metal detergents include sodium, potassium and lithium alkylbenzene sulfonates and sulfurized alkyl phenates. Oxidation inhibitors include phenolic antioxidants, amine antioxidants, organic copper compounds, organo borates, organo phosphites, organo phosphates, organo thio- or dithiophosphates, and the like. Examples of phenolic antioxidants include alkylated monophenols, alkylated hydroquinones, sulfur-bridged alkylphenols, methylene-bridged alkylphenols, and hydroxybenzyl-substituted aromatic compounds. Amine antioxidants include phenylene diamines, amino diphenylamines, phenyl-substituted naphthalenes, alkyl-substituted aromatic secondary amines, aminophenols, and the like. U.S. Pat. Nos. 4,122,033; 4,486,326; 4,664,822; 4,767,551; 4,770,799; 4,820,430; 4,867,890 and 5,102,566 describe, inter alia, suitable organic copper antioxidants. Mixtures of copper and molybdenum salts as described in U.S. Pat. No. 4,705,641 can also be used as antioxidants.

Friction modifiers comprise such substances as phosphoric acid esters, phosphorous acid esters, amine salts of phosphoric acid esters, amine salts of phosphorous esters, sorbitan fatty acid esters, pentaerythritol fatty acid esters, glycerine fatty acid esters, trimethylolpropane fatty acid esters, glycol fatty acid esters, carboxylic acids, carboxylic esters, carboxylic acid amides, metal salts of carboxylic acids, fats and oils, higher alcohols, and sulfur-containing compounds, all of which are described for example in U.S. Pat. No. 5,064,546. Further types and/or illustrations of suitable friction modifiers are given in U.S. Pat. Nos. 3.778,375; 3,779,928; 3,879,306; 3,932,290; 3,933,659; 4,028,258; 4,176,074; 4,105,571; 4,280,916; 4,344,853; 4,455,243; 4,495,088; 4,921,624; and 4,959,168. Preferred friction modifiers include glycerol monooleate and sulfurized long-chain (e.g., C_{12}-C_{20}) monoolefins.

Rust inhibitors suitable for use in the compositions of this invention may be a single compound or a mixture of compounds having the property of inhibiting corrosion of ferrous metal surfaces. Such materials include oil-soluble monocarboxylic acids such as 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, behenic acid, cerotic acid, etc., and oil-soluble polycarboxylic acids including dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Amine salts of such acids are also useful. Other suitable corrosion inhibitors include alkenylsuccinic acids in which the alkenyl group contains 10 or more carbon atoms such as, for example, tetrapropenylsuccinic acid, tetradecenylsuccinic acid, hexadecenylsuccinic acid, and the like; long-chain α,ω-dicarboxylic acids in the molecular weight range of 600 to 3000; and other similar materials. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of acidic corrosion inhibitors are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. The corresponding half amides of such alkenyl succinic acids are also useful. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are known to those skilled in the art and a number of such materials are available as articles of commerce.

Foam inhibitors which can be used include silicones and organic polymers such as acrylate polymers. Various antifoam agents are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176). Mixtures of silicone-type antifoam agents such as the liquid dialkyl silicone polymers with various other substances are also effective. Typical of such mixtures are silicones mixed with an acrylate polymer, silicones mixed with one or more amines, and silicones mixed with one or more amine carboxylates. Other such mixtures include combinations of a dimethyl silicone oil with (i) a partial fatty acid ester of a polyhydric alcohol (U.S. Pat. No. 3,235,498); (ii) an alkoxylated partial fatty acid ester of a polyhydric alcohol (U.S. Pat. No. 3,235,499); (iii) a polyalkoxylated aliphatic amine (U.S. Pat. No. 3,235,501); and (iv) an alkoxylated aliphatic acid (U.S. Pat. No. 3,235,502). Use of a silicone-type foam inhibitor is preferred.

Copper corrosion inhibitors which can be used include thiazole, triazole and thiadiazole derivatives. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles,2,5-bis(hydrocarbylthio)-1,3-4-thiadiazoles, and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, especially the 2-hydrocarbyldithio-5-mercapto-1,3,4-dithiadiazoles and the 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,749,311; 2,760,933; 2,765,289; 2,850,453; 2,910,439; 3,663,561; 3,862,798; 3,840,549; and 4,097,387. Other suitable inhibitors of copper corrosion include ether amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like.

Typical additives which may be employed as demulsifiers include alkyl benzene sulfonates, polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, salts and esters or oil soluble acids, and the like. Thus, for example use can be made of oxyalkylated trimethylol alkanes with molecular weights in the range of 1,000 to 10,000, and preferably in the range of 3,000 to 8,000. Preferably, the oxyalkylated trimethylol alkane is an oxyalkylated trimethylol ethane or propane, especially where the oxyalkylene groups are composed of a mixture of propyleneoxy and ethylenoxy groups and where these groups are so disposed as to form relatively hydrophobic blocks adjacent the trimethylol group and relatively hydrophilic blocks remote the trimethylol group. Typical oxyalkylated trimethylol propane demulsifiers are described in U.S. Pat. No. 3,101,374. Commercially available products of this type are available from BASF Corporation under the Pluradot trademark. They are available in various molecular weights. Pluradot HA-510 has an average molecular weight of 4,600 and Pluradot HA-530 has an average molecular weight of about 5,300. Pluradot additives are propoxylated and ethoxylated trimethylol propanes.

Another type of suitable demulsifers are oxyalkylated alkyl phenol-formaldehyde condensation products. Typically, 4,000 to about 6,000 and are comprised of lower alkyl substituted phenol moieties joined together by methylene groups and in which the hydroxyl groups of the phenolic moieties have been ethoxylated. One such commercial product is marketed by Ceca S.A. of Paris, France under the "Prochinor GR77" trade name. The product is supplied as a concentrate in an aromatic solvent and the active ingredient is believed to be an ethoxylated nonylphenol-formaldehyde condensate of molecular weight 4,200 (by gel permeation chromatography calibrated with polystyrene).

Another suitable type of demulsifier is comprised of the tetra-polyoxyalkylene derivatives of ethylene diamine, especially the tetra-poly(oxyethylene)-poly(oxypropylene) derivatives of ethylene diamine. Materials of this type are available commercially from BASF Corporation under the "Tetronics" trademark. Materials of this general type are described in U.S. Pat. No. 2,979,528.

Mixtures of alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Petrolite Corporation under the TOLAD trademark, are also suitable.

Other demulsifying agents which can be used include esters such as disclosed in U.S. Pat. Nos. 2,674,619 and 3,098,827.

Preferred demulsifiers are proprietary materials available from BASF Corporation under the Pluronic trademark. These are block copolymers of propylene oxide and ethylene oxide.

Depending upon the viscosity grade required, the lubricant compositions can contain one or more viscosity index improvers (polymeric materials which are often supplied in the form of a solution in a solvent or carrier fluid). Viscosity index improvers can and often do, but need not, contain substituent groups to confer additional properties such as dispersancy and/or antioxidancy. Among the numerous types of materials known for use as viscosity index improvers are hydrocarbon polymers grafted with, for example, nitrogen-containing monomers or polymers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate; post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine; styrene-maleic anhydride polymers post-treated with alcohols and/or amines, and the like. Such materials are suitable for use in the finished lubricants of this invention. U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; 4,519,929; 5,035,819; 5,035,820; 5,035,821; and 5,035,822 are among many patents that describe dispersant-viscosity index improvers. Such products combine the activity of dispersants and viscosity index improvers, and are suitable for use in the lubricants of this invention.

The finished lubricants of the invention may contain pour point depressants, materials which are used in oil-base compositions to improve low temperature properties. See, for example, the books Lubricant Additives by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967); Gear and Transmission Lubricants by C. T. Boner (Reinhold Publishing Corp., New York, 1964); and Lubricant Additives by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973) for discussions of this subject. Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715.

The compositions of this invention can contain supplemental ashless dispersants such as alkaryl succinimides made from polyamines, succinic ester-amides, Mannich base dispersants, and the like. Methods for the manufacture of such dispersants are known and a number of suitable materials are commercially available. Such dispersants can be post-treated, such as by boration, or the like.

Still other types of additives can be used in the practice of this invention as long as they are compatible with the remainder of the composition and do not materially interfere with the performance of the composition.

Proportions.

The essential components of this invention are employed in the proportions specified hereinabove.

The ancillary components utilized in the finished lubricants of this invention are typically employed in the following weight percentages based on the weight of the finished lubricant composition:

Ancillary Components	General Range	Preferred Range
Oxidation Inhibitor	0 - 4	0.05 - 2
Friction Modifier	0 - 3	0 - 1
Rust Inhibitor	0 - 3	0.02 - 1
Foam Inhibitor	0 - 0.3	0.0002 - 0.1
Copper Corrosion Inhibitor	0 - 0.3	0 - 0.1
Demulsifying Agent	0 - 0.1	0 - 0.02
Viscosity Index Improver	0 - 15	0 - 12
Pour Point Depressant	0 - 5	0 - 2
Supplemental ashless dispersant	0 - 5	0 - 10

Any other additives employed in the finished lubricants of this invention will be used in their customary proportions such as are recommended by the suppliers thereof.

The additive concentrates of this invention will contain the various ingredients in amounts proportioned to yield finished lubricants having the proportions of the respective ingredients as set forth above. In general, the additive concentrates will contain less than 50 weight %, e.g., a total of from 2 to 45 weight %, of diluents or solvents such as light mineral oil with the balance of the composition being composed of the respective additives being utilized.

The following examples illustrate the practice of this invention. These examples are not intended to constitute, do not constitute, and should not be construed as constituting, limitations upon the scope of this invention. In these examples all percentages are by weight unless otherwise specified.

EXAMPLE I

The following additive components are blended into a base oil blend of 150 and 600 solvent neutral mineral oils: 7.0% of AG dispersant, 1.0% of zinc di-(secondary alkyl)dithiophosphate wherein the alkyl groups are isopropyl and 4-methyl-2-pentyl groups (HiTEC® 7169 additive; Ethyl Petroleum Additives Ltd.; Ethyl Petroleum Additives, Inc.), 0.3% of mixed primary and secondary alkyl zinc dialkyl dithiophosphate (HiTEC® 1656 additive), 1.3% of overbased calcium alkylbenzene sulfonate having a nominal TBN of 300 (HiTEC® 611 additive), 0.9% of low-base calcium alkylbenzene sulfonate having a nominal TBN of 20 (HiTEC® 7304 additive), 1.5% of overbased calcium sulphurized alkylphenate having a nominal TBN of 255, 0.4% of overbased magnesium alkylbenzene sulfonate having a nominal TBN of 400, 0.5% of bis(alkylphenyl) amine antioxidant (Naugalube 438L; Uniroyal Chemical Co.) and 0.003% of a 20% solution of methyl silicone antifoam agent. The AG dispersant is formed from aminoguanidine bicarbonate and polyisobutenyl succinic anhydride derived from polyisobutene having a GPC number average molecular weight of about 2100. These are reacted in a mol ratio of approximately 1:1, and the product is post-borated to a level of 0.2% boron. The lubricant is formulated to 15W40 grade using TLA 347E viscosity index improver (Texaco Chemical Co.). Motor oil formulated in this manner and having a TBN of 11.0 was subjected to the following qualification test procedures:

- Sequence VE engine test;
- P-VW 5106 test;
- L-38 engine test;
- P-VW 1431 engine test;
- P-VW 3344 seal test; and
- P-VW 1302 engine test.

Passing results were achieved in all instances.

EXAMPLE II

A finished 15W40 engine oil is produced as in Example I except that the antioxidant system used is composed of 0.6% of methylene-bridged alkyl phenol antioxidant (HiTEC® 4782 additive), 0.2% of tertiary butyl phenol antioxidant (HiTEC® 4733 additive), and 0.25% of the Naugalube 438L antioxidant. Lubricant formulated in this matter having a TBN of 10.8 was subjected to the P-VW 3344 seal test and was found to yield passing results.

EXAMPLE III

The procedure of Example II is repeated except that AG dispersant is derived from polyisobutene having a GPC number average molecular weight of approximately 1300. The AG dispersant is borated to a level of 0.4% boron. Motor oil formulated in this manner (TBN = 12.7) was subjected to the Sequence VE engine test and gave passing results.

EXAMPLE IV

Example I is repeated with the following changes:

a) The base oil is a blend of 100 and 300 Solvent neutral mineral oils formulated to 15W40 grade with Shellvis 251 viscosity index improver.

b) The detergent system is 2.0% of the overbased calcium sulfonate, 1.4% of the low-base calcium sulfonate and 0.5% of low base calcium sulphurized alkylphenate (OLOA 216C; Chevron Chemical Co.; a product having a nominal TBN of about 150).

c) No magnesium detergent is used.

d) The three-component antioxidant system of Example 2 is used but at the level of 1.0%, 0.5% and 0.25%, respectively. Lubricant formulated in this manner having a TBN of 8.5 was found to give passing results in each of the following tests:

- Peugeot TU3 test;
- P-VW 3344 seal test;
- M-B NBR-34 seal test;
- M-B AK-6 seal test;
- MAN NBR-28 seal test; and
- MAN AK-6 seal test.

EXAMPLE V

A lubricant is formulated as in Example IV with the exception that the AG dispersant is formed from a polyisobutenyl succinic anhydride in which the polyisobutenyl substituent is derived from the polyisobutene referred to in Example III. Engine oil with a TBN of 9.1 formed in this manner gave passing results in the Peugeot TU3 test.

EXAMPLE VI

A finished crankcase lubricant is formulated to contain:

- 74.0% of 150 solvent neutral oil
- 5.0% of 500 solvent neutral oil
- 7.0% of AG dispersant of Example I
- 1.21% of zinc di-(secondary alkyl) dithiophosphate of Example I
- 0.8% of overbased calcium alkylbenzene sulfonate (46% oil)
- 0.6% of overbased magnesium alkylbenzene sulfonate of Example I

- 1.26% of overbased calcium alkylphenate of Example I
- 0.1% of alkylated diphenylamine antioxidant
- 0.3% of sulphurized α-olefin antioxidant
- 0.03% of additional separately added process oil diluent
- 9.7% of olefin copolymer viscosity index improver (ECA 6911; Exxon Chemical Co.) supplied with 89% oil carrier

Lubricant formulated in this manner gave passing results in the P-VW 3344 seal test.

EXAMPLE VII

Example VI is repeated with the following changes: The finished lubricant contains 1.31% of the mixed primary and secondary alkyl zinc dialkyl dithiophosphate of Example I in lieu of the zinc di-(secondary alkyl) dithiophosphate. The detergent system in this finished lubricant is 2.60% of HiTEC® 611 additive and 0.64% of low-base calcium alkylbenzene sulfonate (HiTEC® 614 additive). The antioxidant system in this finished lubricant is 0.80% of the methylene-bridged phenolic antioxidant of Example II and 0.25% of the bis (alkylphenyl) amine antioxidant of Example I. Lastly, the finished lubricant contains 0.004% of the methyl silicone foam inhibitor of Example 1 and 0.29% of additional separately added process oil diluent. Lubricant formulated as in this example passed the P-VW 3344 seal test.

EXAMPLE VIII

A lubricant is formed as in Example VII but substituting 7.0% of the AG dispersant of Example 3 for the AG dispersant of Example VII. Here again, lubricant formulated in this manner was found to give passing results in the P-VW 3344 seal test.

All additive components used pursuant to this invention are "oil-soluble" which means that the material can be dissolved in or be stably dispersed in the base oil used to at least the minimum concentration required for use as described herein. Preferably, the material has a solubility or dispersibility in the base oil well in excess of such minimum concentration. However the term "oil-soluble" does not signify that the material must dissolve or be dispersible in all proportions in the base oil.

In all cases, numerical ranges given herein, if not qualified, are susceptible to latitude as if qualified by the term "about" or "approximately". Thus this disclosure and the ensuing claims are to be interpreted with this caveat in mind.

Some additive components are supplied in the form of solutions of the active ingredient(s) in an inert diluent or solvent, such as a diluent oil. For example, ashless dispersants and metal detergents are usually provided in the form of such solutions. Unless expressly stated to the contrary, the amounts and concentrations of each additive component are expressed on an "as received" basis -- i.e., the amount of solvent or diluent that may be associated with such component as received is included.

Total base numbers referred to herein are typically determined in accordance with ASTM test procedure D2896.

Claims

1. A lubricant composition which comprises a major amount of oil of lubricating viscosity comprising:
    a) 0.03 to 0.15 wt% of nitrogen as an oil-soluble product formed by reacting aminoguanidine and/or a basic salt thereof with an acyclic hydrocarbyl succinic acylating agent in a mol ratio in the range of 0.4 to 1.3 mols of aminoguanidine and/or basic salt thereof per mol of said acylating agent;
    b) 0.08 to 0.14 wt% of zinc as oil-soluble zinc dihydrocarbyl dithiophosphate in which at least 35 mol % of the hydrocarbyl groups present are secondary hydrocarbyl groups; and
    c) 0.15 to 0.40 wt% of calcium as a basic calcium detergent additive complement in which at least 60 mol % of the calcium is derived from overbased calcium detergent having a TBN of at least 200 mg of KOH per gram.

2. A lubricant composition in accordance with Claim 1 further comprising up to 0.1 wt% of magnesium as

an overbased magnesium detergent additive complement having a TBN of at least 300 mg of KOH per gram.

3. A lubricant composition in accordance with Claim 1 or Claim 2 in which the TBN of said composition is in the range of 6 to 15 mg of KOH per gram.

4. A lubricant composition in accordance with any of the preceding claims further comprising at least one oil-soluble antioxidant and at least one foam inhibitor.

5. A lubricant composition in accordance with any of the preceding claims further comprising at least one viscosity index improver.

6. A lubricant composition in accordance with any of the preceding claims wherein said zinc dihydrocarbyl dithiophosphate is a mixture of zinc dialkyl dithiophosphates wherein primary and secondary alkyl groups are present, and wherein at least 35 mol % of the alkyl groups are secondary alkyl groups.

7. A lubricant composition in accordance with any of the preceding claims wherein said basic calcium detergent additive complement is comprised of an overbased calcium sulfonate detergent composition having a TBN of at least 280 mg of KOH per gram thereof.

8. A lubricant composition in accordance with any of the preceding claims wherein said basic calcium detergent additive complement is comprised of a mixture of i) and ii), or i) and iii), or i), ii) and iii), wherein:
   i) is an overbased calcium sulfonate detergent composition having a TBN of at least 280 mg of KOH per gram thereof, and is present in amount such that at least 40 wt% of the calcium is derived therefrom;
   ii) is an overbased calcium sulfurized phenate detergent composition having a TBN of at least 100 mg of KOH per gram thereof, and if present is present in amount such that up to 50 wt% of the calcium is derived therefrom; and
   iii) is a low base calcium sulfonate detergent having a TBN of up to 40 mg of KOH per gram thereof, and if present is present in amount such that up to 25 wt% of the calcium is derived therefrom.

9. A lubricant composition in accordance with any of the preceding claims wherein said oil-soluble product is formed by reacting aminoguanidine and/or a basic salt thereof with an alkenyl succinic acylating agent in a mol ratio in the range of 0.8 to 1.2 mols of aminoguanidine and/or basic salt thereof per mole of said acylating agent, and wherein the alkenyl group of said acylating agent is derived from a polyolefin having a GPC number average molecular weight in the range of 900 to 2500.

10. An additive concentrate which comprises:
   a) 0.3 to 0.8 wt% of nitrogen as an oil-soluble product formed by reacting aminoguanidine and/or a basic salt thereof with an acyclic hydrocarbyl succinic acylating agent in a mol ratio in the range of 0.4 to 1.3 mols of aminoguanidine and/or basic salt thereof per mol of said acylating agent;
   b) 0.5 to 1.2 wt% of zinc as oil-soluble zinc dihydrocarbyl dithiophosphate in which at least 35 mol % of the hydrocarbyl groups present are secondary hydrocarbyl groups; and
   c) 1.0 to 4.0 wt% of calcium as a basic calcium detergent additive complement in which at least 60 mol % of the calcium is derived from overbased calcium detergent having a TBN of at least 200 mg of KOH per gram.

11. An additive concentrate in accordance with Claim 10 further comprising up to 0.8 wt% of magnesium as an overbased magnesium detergent additive complement having a TBN of at least 300 mg of KOH per gram, and optionally, 0.5 to 20 wt% of at least one oil-soluble antioxidant; and optionally, 0.001 to 0.05 wt% of at least one foam inhibitor.

12. An additive concentrate in accordance with Claim 10 or Claim 11 in which the TBN of said concentrate is in the range of 50 to 120 mg of KOH per gram.

13. An additive concentrate in accordance with any of Claims 10-12 wherein said zinc dihydrocarbyl dithiophosphate is a mixture of zinc dialkyl dithiophosphates wherein primary and secondary alkyl groups are present, and wherein at least 35 mol % of the alkyl groups are secondary alkyl groups.

14. An additive concentrate in accordance with any of Claims 10-13 wherein said basic calcium detergent additive complement is comprised of an overbased calcium sulfonate detergent composition having a TBN

of at least 280 mg of KOH per gram thereof.

15. An additive concentrate in accordance with any of Claims 10-14 wherein said basic calcium detergent additive complement is comprised of a mixture of i) and ii), or i) and iii), or i), ii) and iii), wherein:
i) is an overbased calcium sulfonate detergent composition having a TBN of at least 280 mg of KOH per gram thereof, and is present in amount such that at least 40 wt% of the calcium is derived therefrom;
ii) is an overbased calcium sulfurized phenate detergent composition having a TBN of at least 100 mg of KOH per gram thereof, and if present is present in amount such that up to 50 wt% of the calcium is derived therefrom; and
iii) is a low base calcium sulfonate detergent having a TBN of up to 40 mg of KOH per gram thereof, and if present is present in amount such that up to 25 wt% of the calcium is derived therefrom.

16. An additive concentrate in accordance with any of Claims 10-15 wherein said oil-soluble product is formed by reacting aminoguanidine and/or a basic salt thereof with an alkenyl succinic acylating agent in a mol ratio in the range of 0.8 to 1.2 mols of aminoguanidine and/or basic salt thereof per mole of said acylating agent, and wherein the alkenyl group of said acylating agent is derived from a polyolefin having a GPC number average molecular weight in the range of 900 to 2500.

17. The use of a lubricant composition as defined in any one of claims 1 to 9 or an additive concentrate according to any one of claims 10 to 16 in formulating a motor oil composition that can pass at least the Sequence VE engine test, the P-VW 5106 test, the L-38 engine test, the P-VW 1431 engine test, the P-VW 3344 seal test, and the P-VW 1302 engine test.

18. The use of a lubricant composition as defined in any one of claims 1 to 9 or an additive concentrate as defined in any one of claims 10 to 16 in formulating a motor oil composition that can pass at least the Peugeot TU3 test, the P-VW 3344 seal test, the M-B NBR-34 seal test, the M-B AK-6 seal test, the MAN NBR-28 seal test, and the MAN AK-6 seal test.