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(54) Dispersants for lubricating oil.

(57) Novel dispersant compositions for lubricating oil are described. They exhibit little fluoroelastomer antagonism and are effective in controlling sludge, varnish and wear. The dispersants comprise two components. One is formed by reacting aminoguanidine with a long chain succinic acylating agent. The product may be borated if desired. The other component is formed by reacting (i) a succinic acylating agent and (ii) an alkylene polyamine, and then heating the resultant succinimide concurrently or in any sequence with (iii) a dicarboxylic acylating agent having less than 20 carbon atoms, and (iv) a boron compound to form a product having (1) a total base number of about 33-45 milligrams of KOH per gram of product, excluding weight of any solvent or diluent, and (2) a boron level of about 1.0-1.4 wt% excluding weight of any solvent or diluent.

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This invention relates to new and highly useful dispersants for use as additives to natural and synthetic lubricating oils. More particularly this invention relates to novel dispersant compositions that have reduced reactivity toward fluoroelastomers coupled with effective dispersancy, especially for engine oils for either spark-ignition passenger car service or heavy duty diesel engine service.

A continuing problem in the art of lubrication is to provide lubricant compositions which satisfy the demands imposed upon them by the original equipment manufacturers. One such requirement is that the lubricant satisfy one or more tests for fluoroelastomer degradation under specified laboratory test conditions. The commercial reality is that if the lubricant is unable to pass the applicable test or tests, it is unlikely to meet acceptance in the market-place. Standard test methods for evaluating fluoroelastomer compatibility of lubricant compositions include the Volkswagen PV 3334 Seal Test and the CCMC Viton Seal Test (CEC L-39-T-87 Oil/Elastomer Compatibility Test).

More recently, a new, even more severe fluoroelastomer test procedure has been developed, namely the Volkswagen PV 3344 Seal Test. This test is so severe that a variety of commercially-available premium motor oils from various manufacturers have been found to fail this test.

Thus, a need has arisen for a dispersant that exhibits reduced antagonism toward fluoroelastomers in at least one of the above standard test procedures. At the same time it is important for the product to have sufficient effectiveness as a dispersant to satisfy various requirements of sludge, varnish and wear control.

This invention is deemed to fulfill the foregoing need in an effective and efficient manner. The dispersant compositions of this invention are deemed to fulfill these requirements as they exhibit little antagonism toward fluoroelastomers and most if not all are capable of achieving passing results in one or more of the foregoing test procedures. Moreover, the dispersants make possible highly effective control of sludge, varnish and wear under various types of engine service.

In accordance with this invention, there is provided an oil-soluble dispersant composition which comprises:

a) an oil-soluble product formed by reacting aminoguanidine with a long chain alkyl or alkenyl succinic acylating agent in a mole ratio of about 0.4 to about 1.3 moles (and preferably about 0.8 to about 1.3 moles) of aminoguanidine and/or basic salt thereof per mole of said acylating agent; and

b) an oil-soluble product formed by reacting (i) an acyclic hydrocarbyl succinic acylating agent and (ii) an alkylene polyamine having an average of about 3 to about 6 nitrogen atoms (and preferably an average of about 4 to about 5 nitrogen atoms) per molecule in a mole ratio of about 1.6 to 2 (and preferably about 1.8 to 2) moles of (i) per mole of (ii) to form a succinimide and heating the succinimide so formed concurrently or in any sequence and at a temperature in the range of about 150 to about 180°C with (iii) at least one dicarboxylic acylating agent having less than 20 carbon atoms in the molecule, and (iv) at least one boron compound to form a product having (1) a total base number in the range of about 33 to about 45 milligrams of KOH per gram of said product (as active ingredient, i.e., excluding the weight of solvent or diluent, if any, that may be associated with said product), and (2) a boron content in the range of about 1.0 to about 1.4 wt% (again excluding the weight of any solvent and/or diluent that may be associated with said product);

wherein a) and b) are proportioned such that for every 0.7 to 1.8 part by weight of nitrogen (and preferably for every 0.8 to 1.7 part by weight of nitrogen) from a), there is about 0.3 to about 1.5 part by weight of nitrogen (and preferably about 0.4 to about 1.4 part by weight of nitrogen) from b).

Another embodiment of this invention is a composition which comprises from 1 to 99 wt% of at least one oil of lubricating viscosity and from 99 to 1 wt% of a combination of the above components a) and b), proportioned as above.

Still another embodiment is an additive concentrate formulated for use as a crankcase lubricating oil additive (also known as a DI-pack) which comprises the above components a) and b), proportioned as above; c) at least one oil-soluble metal dihydrocarbyl dithiophosphate (preferably one or more zinc dialkyl dithiophosphate antiwear/extreme pressure agents); d) at least one alkali or alkaline earth metal-containing detergent (e.g., an alkali or alkaline earth metal sulfonate, carboxylate, salicylate, or sulfurized alkylphenate, or combination of two or more of such detergents); and e) one or more inhibitors selected from oxidation inhibitor(s), foam inhibitor(s), rust inhibitor(s), corrosion inhibitor(s) and friction inhibitor(s); wherein components a), b), c), d) and e) are proportioned in the additive concentrate such that blending a minor amount of the additive concentrate in a base oil (e.g., at a concentration in the range of 3.2 to 16.1 wt% on an active ingredient basis) provides an oil blend that contains a dispersant amount of a) plus b) proportioned as above, a wear-inhibiting amount of c), a detergent amount of d), and an inhibiting amount of each said inhibitor selected. On an active ingredient basis, a minor dispersing amount of a) plus b) in the finished lubricating oil is typically in the range of about 2 to about 5.5 wt% with the proviso that the level of nitrogen from b) in the finished lubricating oil does not exceed 0.042 wt%. Similarly, a minor wear-inhibiting amount of c) in the finished lubricating oil is typically in the range of about 0.5 to about 1.25 wt%, and when the wear inhibitor is in the form of a phosphorus-containing product, a minor wear-inhibiting amount is typically equivalent to a phosphorus content in the finished lubricating oil in the range of about 0.04 to about 0.12 wt% of phosphorus. Likewise, a minor detergent amount of d) in the finished lubricating oil is typically in the range of about 0.5 to about 3.5 wt%, a minor oxidation inhibiting amount of oxidation inhibitor in the finished lubricating oil is typically in the range of about 0.2 to about 3 wt%, a minor foam inhibiting amount of foam inhibitor in the finished lubricating oil is typically in the range of about 0.0002 to about 0.001 wt%, a minor rust inhibiting amount of rust inhibitor in the finished lubricating oil is typically in the range of about 0.01 to about 0.4 wt%, a minor corrosion inhibiting amount of corrosion inhibitor in the finished lubricating oil is typically in the range of about 0.01 to about 0.4 wt%, and a minor friction inhibiting amount of friction inhibitor in the finished lubricating oil is typically in the range of about 0.02 to about 2 wt%. In each instance, the respective components a), b), c), and d), and each of the selected components of e) can be a single component or it can be a mixture of two or more of the specified type of components.

A further embodiment provides a finished lubricating oil composition which comprises a major amount of at least one oil of lubricating viscosity; a minor dispersant amount of a) plus b) proportioned as above; a minor wear-inhibiting amount of c); a minor detergent amount of d); and at least one inhibitor of e), e.g., optionally, but preferably, a minor oxidation inhibiting amount of at least one oxidation inhibitor; optionally, but preferably, a minor foam inhibiting amount of foam inhibitor; optionally, a minor friction inhibiting amount of friction inhibitor; optionally, a minor rust inhibiting amount of rust inhibitor; and optionally, a minor corrosion inhibiting amount of corrosion inhibitor. The finished lubricating oil composition preferably additionally contains a minor viscosity improving amount of at least one viscosity index improver. Accordingly, this invention provides lubricant compositions comprising oil of lubricating viscosity and one or more, and preferably all, of the following components: viscosity index improver, metal (most preferably zinc) dialkyl dithiophosphate, alkali or alkaline earth metal detergent (preferably sulfonate, sulfurized phenate and/or salicylate), antioxidant (preferably phenolic, aromatic amine, sulfurized olefin or copper-based), and antifoam agent (preferably silicone-based). Other typical additive components can also be present. For further details, see for example U.S. Pat. No. 5,137,980.

Still another embodiment involves the use of components a) and b), proportioned as above, in minor amount in oil of lubricating viscosity to provide dispersancy and to minimize degradation of fluoroelastomers that are in contact with the oil either during additive qualification tests or during use under actual service conditions.

In each and every one of the above described embodiments, it is preferred, though not required, that component a) thereof be a borated component, i.e., the product thereof is heated with a boron compound or other suitable boron source at a temperature high enough to form a product having a boron content in the range of up to about 1 wt%, excluding the weight of solvent and/or diluent, if any, that may be associated with said product.

These and other embodiments of this invention will be still further apparent from the ensuing description and appended claims.

Base Oils.

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 type and viscosity suitable for use in forming a passenger car engine oil, a heavy duty diesel engine oil, or a drivetrain lubricant.

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 80 to about 200°C, and preferably in the range of 140 to 200°C, with temperatures in the range 160 to 170°C being most preferred. The reaction can be conducted in the presence or absence of a solvent or reaction diluent. When using alkenyl succinic acylating agents in which the alkenyl substituent is derived from a polyolefin of lower molecular weight (e.g., a GPC number average molecular weight of 1300), it is preferred to conduct the acylation reaction in the absence of a reaction diluent, and to add a diluent, such as a mineral oil to the reaction product after it has been produced. On the other hand, with alkenyl succinic acylating agents in which the alkenyl substituent is derived from a polyolefin of somewhat higher molecular weight (e.g., a GPC number average molecular weight of 2100), it is desirable to conduct the reaction in a suitable diluent such as process oil or the like. 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 (excluding the weight of any diluent or solvent that may be associated with the product). 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 very 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 an infrared peak in the region of 1590 cm^{-1}. Additionally, the spectrum may exhibit a peak in the region of 1690 cm^{-1}, but AG dispersants can be used that do not exhibit this latter peak. When made at mole 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 structures of the products of this invention are 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. Such acylating agents have been extensively described and discussed in the literature, for example U.S. Pat. Nos. 3,215,707; 3,219,666; 3,231,587; 3,254,025; 3,282,955; 3,361,673; 3,401,118; 3,912,764; 4,110,349; 4,234,435; 4,908,145; 5,071,919; 5,080,815; and 5,137,978. In fact, suitable acylating agents of this type are manufactured in large quantities and are in widespread use in the manufacture of dispersants. Preferred acylating agents for use in forming component a) are derived from a polyalkene having a number average molecular weight as determined by GPC in the range of 900 to 5000. Most preferably they have a number average molecular weight in the range of 1200 to 2500. While homopolymers and copolymers of a variety of 1-olefins can be used for preparing the acylating agents, commercial grades of polyisobutene are the preferred materials.

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

EXAMPLE A-1

Into a reaction vessel are charged 1665 g (0.48 mole) of 60% active polyisobutenyl succinic anhydride (PIBSA) (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 PIBSA 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 A-2

The procedure of Example A-1 is repeated using a chemically equivalent amount of PIBSA produced using a polyisobutylene having a number average molecular weight of about 1290 in lieu of the higher molecular weight PIBSA of Example A-1.

EXAMPLE A-3

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

EXAMPLE A-4

Example A-3 is repeated except that the PIBSA of Example A-2 is employed.

EXAMPLE A-5

Product formed as in Example A-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 A-6

Example A-5 is repeated, but using 2000 g of product formed as in Example A-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 A-7

Product formed as in Example A-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 A-8

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

EXAMPLES A-9 to A-15

The procedure of Example A-1 is repeated seven times in the same manner except that the proportions of AGB and PIBSA are varied such that the respective AGB:PIBSA mole ratios are 0.4:1, 0.5:1. 0.6:1, 0.7:1, 0.8:1, 0.9:1 and 1:1.

EXAMPLES A-16 to A-22

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

EXAMPLES A-23 to A-36

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

EXAMPLE A-37

Example A-1 is repeated except that 1.0 mole of AGB is reacted with 0.8 mole of PIBSA. Boration to a boron level of 0.2% is carried out at a suitable temperature between 145 and 165°C using boric acid. Water is stripped off at approximately 155°C and 40 mm Hg on completion of the boration.

Component b).

This oil-soluble ashless dispersant is obtained by reacting (i) an acyclic hydrocarbyl succinic acylating agent and (ii) an alkylene polyamine having an average of about 3 to about 6 nitrogen atoms (and preferably an average of about 4 to about 5 nitrogen atoms) per molecule in a mole ratio of about 1.6 to 2 (and preferably about 1.8 to 2) moles of (i) per mole of (ii) to form a succinimide and heating the succinimide so formed concurrently or in any sequence and at a temperature in the range of about 150 to about 180°C with (iii) at least one dicarboxylic acylating agent having less than 20 carbon atoms in the molecule, and (iv) at least one boron material to form a product having (1) a total base number in the range of about 33 to about 45 milligrams of KOH per gram of said product (excluding the weight of any solvent and/or diluent that may be associated with said product), and (2) a boron content in the range of about 1.0 to about 1.4 wt% (again excluding the weight of any solvent and/or diluent that may be associated with said product).

Aliphatic hydrocarbyl-substituted succinic acid derivatives (acid, anhydride, lower alkyl ester, or acyl halide), such as alkenyl succinic anhydrides, that are used as reactant (i) above are of the same general types as used in forming component a). Thus for further details one should refer to the description given hereinabove. It is to be understood and appreciated however that the acylating agents used in forming components a) and b) need not be identical to each other. For example, the number average molecular weights of polyolefins used in forming these respective succinic acylating agents can be the same, or they can differ from each other whereby the number average molecular weight of either one of the polyolefins can be higher than that of the other. Likewise the succinic acylating agents used in forming components a) and b) can (and preferably are) both anhydrides, although it is possible to use different kinds of functionalized succinic acylating agents in forming these respective components (e.g., using an anhydride for forming one of the components, and a free acid for forming the other).

Alkylene polyamines having an average of from about 3 to about 6 nitrogen atoms per molecule used as reactants (ii) in forming component b) are generally referred to in the art as dialkylene triamines, trialkylene tetramines, tetraalkylene pentamines and pentaalkylene hexamines. The alkylene groups of these materials can have from 2 to 4 or more carbon atoms each. Preferred for use are the polyethylene polyamines, i.e., the polyalkylene polyamines in which the alkylene groups are ethylene (i.e., dimethylene) groups. The alkylene polyamines used in the synthesis of component b) can be substantially pure compounds of the specified structure (e.g., substantially pure tetraethylene pentamine of the formula:

$$H_2N\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH_2)$$

or they can be technical grade materials such as are available on the open market from a number of suppliers. These technical grade products are often referred to for example as diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine even though they typically comprise linear, branched and cyclic species.

The dicarboxylic acylating agent having less than 20 carbon atoms in the molecule used as reactant (iii) in post-treating the succinimide is preferably selected from (a) acyclic dicarboxylic acids having up to 6 carbon atoms in the molecule and wherein the carboxyl groups are attached to adjacent carbon atoms, (b) anhydrides of the said dicarboxylic acids, (c) acyl halides of the said dicarboxylic acids, and (d) acyclic mono- and/or dihydrocarbyl esters of the said dicarboxylic acids having no more than 7 carbon atoms per hydrocarbyl group. Examples of these acylating agents include maleic acid, maleic anhydride, α-ethylmaleic acid, malic acid, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, succinic acid, succinic anhydride, α-methylsuccinicacid, α,α-dimethylsuccinic acid, α,β-dimethylsuccinic acid, α-ethylsuccinic acid, thiomalic acid, tartaric acid, the monoalkyl esters of the foregoing acids wherein the alkyl group has from 1 to 7 carbon atoms, the dialkyl esters of the foregoing acids wherein each alkyl group has from 1 to 7 carbon atoms, the monoalkenyl esters of the foregoing acids wherein the alkenyl group has from 2 to 7 carbon atoms, the dialkenyl esters of the foregoing acids wherein each alkenyl group has from 2 to 7 carbon atoms, the acyl chlorides of the foregoing acids, and the like. The most preferred post-treating agent for use in the practice of this invention is maleic anhydride.

Reactant (iv) is a boron-containing material of the same general type as can be used in borating component a) in accordance with preferred embodiment thereof. Likewise the temperature and other boration conditions used can be the same or similar to those applicable for use in forming a borated version of component a). Thus for further details reference should be had to the applicable discussion hereinabove. It is to be understood and appreciated however that the borating agents and boration conditions used in forming component b) and in forming a borated version of component a) need not be identical to each other. Thus, for example the borating agents can both be the same boron acid, boron ester, boron halide, boron oxide, ammonium borate, organoborane, or superborated ashless dispersant, or conversely, the borating agent used in forming one of the components can differ from that used in borating the other. Likewise the times, temperatures and proportions of ingredients used in the respective borations can be the same or different from each other -- one component can be borated to a higher level than the other.

Suitable procedures for producing component b) are illustrated in the following examples.

EXAMPLE B-1

In a first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene having a GPC number average molecular weight of about 1300 and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 are reacted at 165-170°C for 4 hours. In a second stage reaction, maleic anhydride (MA) is added to the first stage reaction product in amount equivalent to 0.35 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1.5 hours after which oil is added. In a third stage reaction, boric acid is added to the second stage reaction mixture at a temperature of 150-155°C in an amount corresponding to 4.0 moles per mole of TEPA initially employed. The mixture is heated at 150°C for one hour and then water formed in the third stage reaction is removed by applying a vacuum of 40 mm for one hour. The resulting succinimide is both acylated and boronated and has a nitrogen content of 1.74%, and a boron content of 1.20%.

EXAMPLE B-2

The procedure of Example B-1 is repeated except that the amount of boric acid is reduced to 3.0 moles per mole of TEPA initially used. The final product, diluted to 1.70% nitrogen content with 100 solvent neutral mineral oil contains 0.82% boron.

EXAMPLE B-3

Repetition of Example B-1 wherein the amount of boric acid is still further reduced to 2.0 moles per mole of TEPA initially used yields a concentrate (diluted as in Example B-1) having a boron content of 0.62%.

EXAMPLE B-4

Example B-1 is repeated but using 3.25 moles of boric acid per mole of TEPA initially used. The product concentrate (diluted as in Example B-1) contains 0.88% boron.

EXAMPLE B-5

The procedure of Example B-1 is repeated except that the reaction with boric acid is conducted before the reaction with maleic anhydride and the amount of boric acid used corresponds to 3.0 moles per mole of TEPA used in the first stage reaction. The final product (diluted as in Example B-1) contains 0.9% boron.

EXAMPLE B-6

Example 5 is repeated except that the maleic anhydride and the boric acid are concurrently reacted with the succinimide formed in the first stage reaction. One such product on dilution with 100 solvent neutral mineral oil contained 1.66% nitrogen and 0.87% boron.

EXAMPLE B-7

In the first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene with a GPC number average molecular weight of about 1300 and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 are reacted at 165-170°C for 4 hours and then mineral oil added. In a second stage reaction, maleic anhydride (MA) is added to the first stage reaction product in an amount equivalent to 0.3 moles per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1-1/2 hours. In a third stage reaction, boric acid (BA) is added to the second stage reaction product in an amount equivalent to 3.0 moles per mole of TEPA used in the first stage and the resultant mixture is heated at 150-155°C for 2-1/2 hours. The additive concentrate has a nitrogen content of 1.8% and a boron content of 0.9%.

EXAMPLE B-8

The procedure of Example B-7 is repeated except that in the first stage the PIBSA and TEPA are reacted in a molar ratio of 1.7:1. In the second stage the MA is used in amount equivalent to a mole ratio of 0.4:1 relative to the TEPA used in the first stage. In the third stage, the boric acid (3.0 moles per mole of TEPA used in the first stage reaction) is added in an oil slurry. The product on dilution has a nitrogen content of 1.95% and a boron content of 0.64%.

EXAMPLE B-9

In the first stage reaction, polyisobutenylsuccinic anhydride having a GPC number average molecular weight of about 1200 and TEPA are reacted in a mole ratio of 1.8:1. In a second stage, maleic anhydride is added to the first stage reaction product in an amount equivalent to 0.35 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1-1/2 hours after which mineral oil is added.

In a third stage reaction, boric acid is added to the second stage reaction product in an amount equivalent to 0.4 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 150 to 155°C for 3 hours. The product has a nitrogen content of 1.85% and a boron content of 0.15%.

Component c).

Metal hydrocarbyl dithiophosphates are usually prepared by reacting phosphorus pentasulfide with one or more alcohols or phenolic compounds or diols to produce a hydrocarbyl dithiophosphoric acid which is then neutralized with one or more metal-containing bases. When a monohydric alcohol or phenol is used in this reaction, the final product is a zinc dihydrocarbyl dithiophosphate. On the other hand, when a suitable diol (e.g., 2,4-pentanediol) is used in this reaction, the final product is a zinc salt of a cyclic hydrocarbyl dithiophosphoric acid. See, for example, U.S. Pat. No. 3,089,850. These cyclic derivatives function in essentially the same way as the dihydrocarbyl analogs.

Suitable oil-soluble metal dihydrocarbyl dithiophosphates include molybdenum dihydrocarbyl dithiophosphates, nickel dihydrocarbyl dithiophosphates, copper dihydrocarbyl dithiophosphates, cadmium dihydrocarbyl dithiophosphates, cobalt dihydrocarbyl dithiophosphates, and similar materials. The hydrocarbyl groups include cyclic and acyclic groups, both saturated and unsaturated, such as alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, cycloalkylalkyl, aralkyl, and the like. It will be understood that the hydrocarbyl groups may contain elements other than carbon and hydrogen provided such other elements do not detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group. Thus the hydrocarbyl groups may contain ether oxygen atoms, thioether sulfur atoms, secondary or tertiary amino nitrogen atoms, and/or inert functional groups such as esterified carboxylic groups, keto groups, thioketo groups, and the like. The preferred materials are the oil-soluble zinc dihydrocarbyl dithiophosphates, especially the oil-soluble zinc dialkyl dithiophosphates, and most especially oil-soluble zinc dialkyl dithiophosphates in which the alkyl groups are a mixture of primary and secondary alkyl groups. Such primary and secondary alkyl group mixtures can be formed by forming a mixture of two or more zinc dialkyldithiophosphates that results in a mixture or combination of zinc dialkyl dithiophosphates having the desired types and proportions of primary and secondary alkyl groups. Alternatively, the primary and secondary alkyl group mixtures can be formed by reacting phosphorus pentasulfide with a mixture or combination of primary and secondary alcohols that yields a zinc dialkyl dithiophosphate product having the desired types and proportions of primary and secondary alkyl groups.

The phosphorodithioic acids from which the metal salts are formed can be prepared by the reaction of about 4 moles of one or more alcohols (cyclic or acyclic) or one or more phenols or mixture of one or more alcohols and one or more phenols (or about 2 moles of one or more diols) per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from about 50 to about 200°C. The reaction generally is completed in about 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

The alcohols used in forming the phosphorodithioic acids by the above method are preferably primary alcohols, or secondary alcohols. Mixtures thereof are also suitable. The primary alcohols include propanol, butanol, isobutyl alcohol, pentanol, 2-ethyl-1-hexanol, isooctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, octadecanol, eicosanol, and the like. The primary alcohols may contain various substituent groups such as halogen atoms, nitro groups, etc., which do not interfere with the desired reaction. Among suitable secondary alcohols are included 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, 4-methyl-2-pentanol, 5-methyl-2-hexanol, and the like. In some cases, it is preferable to utilize mixtures of various alcohols, such as mixtures of 2-propanol with one or more higher molecular weight primary alcohols, especially primary alcohols having from 4 to about 13 carbon atoms in the molecule. Such mixtures preferably contain at least 10 mole percent of 2-propanol, and usually will contain from about 20 to about 90 mole percent of 2-propanol. In one specific embodiment, the alcohol comprises about 30 to 50 mole percent of 2-propanol, about 30 to 50 mole percent isobutyl alcohol and about 10 to 30 mole percent of 2-ethyl-1-hexanol.

Other suitable mixtures of alcohols include 2-propanol/butanol; 2-propanol/2-butanol; 2-propanol/2-ethyl-1-hexanol; butanol/2-ethyl-1-hexanol; isobutyl alcohol/2-ethyl-1-hexanol; and 2-propanol/tridecanol.

Cycloaliphatic alcohols suitable for use in the production of the phosphorodithioic acids include cyclopentanol, cyclohexanol, methylcyclohexanol, cyclooctanol, borneol and the like. Preferably, such alcohols are used in combination with one or more primary alkanols such as butanol, isobutyl alcohol, or the like.

Illustrative phenols which can be employed in forming the phosphorodithioic acids include phenol, o-cresol, m-cresol, p-cresol, 4-ethylphenol, 2,4-xylenol, and the like. It is desirable to employ phenolic compounds in combination with primary alkanols such propanol, butanol, hexanol, or the like.

Other alcohols which can be employed include benzyl alcohol, cyclohexenol, and their ring-alkylated analogs.

It will be appreciated that when mixtures of two or more alcohols and/or phenols are employed in forming the phosphorodithioic acid, the resultant product will normally comprise a mixture of three or more different dihydrocarbyl phosphorodithioic acids, usually in the form of a statistical distribution in relation to the number and proportions of alcohols and/or phenols used.

Illustrative diols which can be used in forming the phosphorodithioic acids include 2,4-pentanediol, 2,4-hexanediol, 3,5-heptanediol, 7-methyl-2,4-octanediol, neopentyl glycol, 2-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, and the like.

The preparation of the zinc salts of the dihydrocarbyl dithiophosphoric acids or the cyclic hydrocarbyl dithiophosphoric acids is usually effected by reacting the acid product with a suitable zinc compound such as zinc oxide, zinc carbonate, zinc hydroxide, zinc alkoxide, or other appropriate zinc salt. 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. 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 the zinc oxide or hydroxide with one equivalent of the acid. Basic zinc salts are prepared by adding an excess (i.e., more than one equivalent) of the zinc oxide or hydroxide with one equivalent of the dihydrocarbyl phosphorodithioic acid or cyclic hydrocarbyl phosphorodithioic acid.

In some cases, incorporation of certain ingredients such as small amounts of zinc 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 dihydrocarbyl dithiophosphates.

Examples of useful zinc salts of dihydrocarbyl dithiophosphoric acids, and methods for preparing such salts are found in the prior art such as for example, U.S. Pat. Nos. 4,263,150; 4,289,635; 4,308,154; 4,322,479; 4,417,990; and 4,466,895.

The preferred zinc salts of dialkyl dithiophosphoric acids generally contain alkyl groups having at least three carbon atoms each, and preferably the alkyl groups contain up to 10 carbon atoms although as noted above, even higher molecular weight alkyl groups are entirely feasible. A few illustrative zinc dialkyl dithiophosphates include zinc diisopropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc diisobutyl dithiophosphate, zinc di-sec-butyl dithiophosphate, the zinc dipentyl dithiophosphates, the zinc dihexyl dithiophosphates, the zinc diheptyl dithiophosphates, the zinc dioctyl dithiophosphates, the zinc dinonyl dithiophosphates, the zinc didecyl dithiophosphates, and the higher homologs thereof. Mixtures of two or more such zinc compounds are often preferred for use, such as zinc salts of dithiophosphoric acids formed from mixtures of isopropyl alcohol and secondary butyl alcohol; isopropyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol; isopropyl alcohol, butyl alcohol, and pentyl alcohol; isobutyl alcohol and octyl alcohol; and the like.

The metal dihydrocarbyldithiophosphates may be products that have been post-treated with such compounds as carboxylic acids or epoxides.

Component d).

In general, the metal-containing detergents which can be employed are oil-soluble or oil-dispersible basic salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The salts can be low-base materials or overbased materials or combinations thereof. Preferably at least a portion of component d) is an over-based metal detergent with a total base number (TBN) of at least 200, and more preferably in the range of about 250 to about 500. In this connection, TBN is determined in accordance with ASTM D-2896-88.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The usual methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of at least about 50°C, and filtering the resulting mass. Use in the neutralization step of a "promoter" to aid the incorporation of a large excess of metal likewise is desirable. 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, 2-propanol, octyl alcohol, 2-ethoxyethanol, 2-ethoxy(2-ethoxyethanol), ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60° to 200°C.

Examples of suitable metal-containing detergents include, but are not limited to, the basic or overbased salts of such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the lithium, sodium, potassium, calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; and other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of basic or overbased salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, basic or overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates) can also be used.

As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the terms "oil-soluble" and "oil-dispersible" are applied to these metal-containing detergents so as to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much the same way as if they were fully and totally dissolved in the oil.

Collectively, the various basic or overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic alkali metal or alkaline earth metal-containing organic acid salts.

Methods for the production of oil-soluble basic and overbased alkali and alkaline earth metal-containing detergents are known and are extensively reported in the patent literature. See for example, the disclosures of U.S. Pat. Nos. 2,451,345; 2,451,346; 2,485,861; 2,501,731; 2,501,732; 2,585,520; 2,671,758; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 3,178,368; 3,367,867; 3,496,105; 3,629,109; 3,865,737; 3,907,691; 4,100,085; 4,129,589; 4,137,184; 4,148,740; 4,212,752; 4,617,135; 4,647,387; and 4,880,550.

Component e).

The inhibitors which can be used in the practice of this invention include one or more oxidation inhibitors, foam inhibitors, rust inhibitors, corrosion inhibitors and friction inhibitors.

Oxidation inhibitors suitable for use in the compositions of this invention include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, sulfurized olefin antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like. Mixtures of two or more of these respective types of antioxidants can be used.

Illustrative sterically hindered phenolic antioxidants include ortho-alkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol,4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such phenolic compounds are also suitable.

Also useful are methylene-bridged alkylphenols, and these can be used singly or alternatively, in combinations with each other, or in combinations with sterically-hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tert-butylphenol), and similar compounds. Preferred mixtures of methylene-bridged alkylphenols are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used. Although aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, ring-alkylated diphenylamines containing 1 or more alkyl ring-substituents each having up to about 16 carbon atoms, phenyl-α-naphthylamine, phenyl-β-naphthylamine, alkyl- or aralkyl-substituted phenyl-α-naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl-β-naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine wherein one or both rings are substituted by an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, and more preferably 8 or 9 carbon atoms. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominately a 4,4'-dinonyldiphenylamine wherein the nonyl groups are branched.

Another useful type of oxidation inhibitor for inclusion in the compositions of this invention is one or more oil-soluble sulfurized phenolic compounds. Oil-soluble sulfurized linear alpha-olefins are also highly satisfactory oxidation inhibitors. Copper compounds when used in small controlled concentrations, all as described in U.S. Pat. No. 4,867,890, are also suitable.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one ring-alkylated di(phenyl)amine wherein each alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

Suitable foam inhibitors are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176). Typical foam inhibitors include silicones and organic polymers such as acrylate polymers. 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). Also useful are the metal salts of styrene-maleic anhydride copolymers (U.S. Pat. No. 3,296,131).

Rust inhibitors that can be used 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. 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, dimer and trimer acids. 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; and the like.

Among the suitable corrosion inhibitors are the thiazoles, triazoles and thiadiazoles. Examples 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 products 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 corrosion inhibitors include ether amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like.

Friction inhibitors which can be used include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat.

4,105,571, oleamide, sulfurized linear olefins, and the like. Glycerol oleates such as glycerol monooleate, glycerol dioleate and pentaerythritol monooleate are further examples of suitable friction inhibitors which can be used to control friction and improve fuel economy.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

Still other suitable additives can be included if desired.

The practice and advantages of this invention will become still further apparent from the following illustrative examples. It is to be understood that these examples do not constitute, are not intended to constitute, and should not be construed as constituting, limitations on the generic aspects of this invention. In these examples, all percentages are by weight, and are on an active ingredient basis.

EXAMPLE I

A 10W-40 finished lubricant of this invention is formed from the following components:

Component	Percentage
a)	3.17
b)	1.09
c)	1.06
d)	2.67
e)	1.40
Base oil, VI Improver, Diluent Oils	Balance to 100%

Component a) is formed as in Example A-5 and component b) as in Example B-4. Component c) is a mixture of zinc dialkyldithiophosphates of which 50% are C_3 and C_6 secondary alkyl groups and 50% are C_3, C_4 and C_8 primary and secondary alkyl groups. Component d) is a mixture of 1.32% overbased calcium sulfonate, 0.7% low-base calcium sulfonate, and 0.65% sulfurized alkylphenate. Component e) is a mixture of 0.8% tertiary butylated phenolic antioxidant, 0.2% aromatic amine antioxidant, 0.4% sulfurized olefin oxidation inhibitor, and less than 0.001% of silicone type foam inhibitor. Commercial materials used in forming this component mixture include HITEC® 611, 1656, 4733, 7169, and 7304 additives (Ethyl Petroleum Additives, Ltd.; Ethyl Petroleum Additives, Inc.); OLOA 216C additive (Chevron Chemical Company); and Naugalube 438L additive (Uniroyal Chemical Company). The viscosity index improver is of the OCP type (Paratone 8000; Exxon Chemical Company). The finished lubricant has a total base number (TBN) of 10 mg of KOH per gram using the ASTM D2896 procedure, a zinc content of 0.12%, a phosphorus content of 0.11% a calcium content of 0.35% and a boron content of 0.02%.

EXAMPLE II

A 10W-40 lubricant of this invention is formed from the following components:

Component	Percentage
a)	3.11
b)	1.10
c)	0.94
d)	2.36
e)	1.50
Base oil, VI Improver, Diluent Oils	Balance to 100%

Component a) is formed as in Example A-37 and component b) as in Example B-4. Component c) is a mixture of C_3 and C_6 zinc dialkyldithiophosphates. Component d) is a mixture of 1.18% overbased calcium sulfonate, 0.85% low-base calcium sulfonate, and 0.33% sulfurized alkylphenate. Component e) is a mixture of 1.0% tertiary butylated phenolic antioxidant, 0.5% aromatic amine antioxidant, and less than 0.001% of silicone type foam inhibitor.

EXAMPLE III

A finished lubricant of this invention is produced from the same components as in Example I but using the following proportions:

Component	Percentage
a)	2.97
b)	1.37
c)	1.06
d)	2.67
e)	1.40
Base oil, VI Improver, Diluent Oils	Balance to 100%

EXAMPLE IV

A lubricating oil composition of this invention is produced using components a) and b) as in Example II, a 400 TBN overbased magnesium alkylbenzene sulfonate as component d), and components c) and e) as in Example I in the proportions given in the following table:

Component	Percentage
a)	3.11
b)	1.10
c)	1.06
d)	2.28
e)	1.40
Base oil, VI Improver, Diluent Oils	Balance to 100%

The performance of the compositions of this invention is illustrated by the results of the MWM KD 12E engine test which measures performance of heavy duty diesel engine lubricants under controlled conditions. Performance is expressed in terms of a numerical scale in which the higher the numerical value, the better the performance. In two such tests a lubricant of this invention and a comparable lubricant not of this invention were used. Both contained in addition to dispersant, a mixture of primary and secondary alkyl zinc dialkyl dithiophosphates, a mixture of high-base and low-base calcium sulfonates and a calcium sulfurized alkyl phenate in substantially the same relative proportions. The principal difference between these two lubricants is that the dispersant of the lubricant not of this invention consisted solely of a higher dosage level of component a). Both lubricants were formulated to 10W-40 specification grade and had a TBN of 10 mg of KOH per gram and an ash level of 1.42%. The lubricant of this invention gave a rating of 80.6 as compared to a rating of 70.9 for the lubricant not of this invention.

In tests conducted in similar fashion using the Volkswagen Intercooled (PV 1431) Test, a typical composition of this invention formed as in Example II was found to give significantly better piston cleanliness than a comparable lubricant composition not of this invention. In both cases the diesel engine was operated on a diesel fuel with a sulfur content of 0.3%.

In the standard OM 364A test, a 10W-40 lubricant of this invention exhibited excellent dispersancy and varnish control performance, as well as good wear performance.

The excellent fluoroelastomer seal performance made possible by this invention is illustrated by the results of tests conducted using the stringent Volkswagen PV 3344 test procedure. In one set of tests VITON AK6 fluoroelastomer and the SAE 10W-40 heavy duty crankcase lubricant of Example I were used. Table I summarizes the results.

Table I -

Fluoroelastomer Compatibility Test Results		
Property	Results	Test Specifications
Tensile strength	9.5 MPa	8.0 Minimum
Elongation	188%	160% Minimum
Hardness	72	Report only
Cracking	No cracking	No cracking

A duplicate set of tests was carried out using the same test procedure and fluoroelastomer, but using a composition formed as in Example III. The results are summarized in Tables II and III.

Table II -

Fluoroelastomer Compatibility Test Results		
Property	Results	Test Specifications
Tensile strength	9.5 MPa	8.0 Minimum
Elongation	188%	160% Minimum
Hardness	72	Report only
Cracking	No cracking	No cracking

Table III -

Fluoroelastomer Compatibility Test Results		
Property	Results	Test Specifications
Tensile strength	8.5 MPa	8.0 Minimum
Elongation	181%	160% Minimum
Hardness	70	Report only
Cracking	No cracking	No cracking

It will be seen from Tables I, II and III that in these tests the lubricant compositions of this invention passed all requirements of the severe Volkswagen PV 3344 test procedure and in so doing, gave excellent results. Similar excellent results have been achieved with other compositions of this invention.

As used herein, the term "oil-soluble" means that the product under discussion can be dissolved or stably dispersed in a 100 Solvent Neutral mineral oil to a concentration of at least 1% by weight at 25°C.

At various places throughout this disclosure patents and other publications have been referred to. The contents of all such documents are incorporated by reference herein in toto as if fully set forth in this specification.

Claims

1. An oil-soluble dispersant composition which comprises:

a) an oil-soluble product formed by reacting aminoguanidine with a long chain alkyl or alkenyl succinic acylating agent in a mole ratio of about 0.4 to about 1.3 moles of aminoguanidine and/or basic salt thereof per mole of said acylating agent; and

b) an oil-soluble product formed by reacting (i) an acyclic-hydrocarbyl succinic acylating agent and (ii) an alkylene polyamine having an average of about 3 to about 6 nitrogen atoms per molecule in a mole ratio of about 1.6 to 2 moles of (i) per mole of (ii) to form a succinimide and heating the succinimide so formed concurrently or in any sequence and at a temperature in the range of about 150 to about 180°C with (iii) at least one dicarboxylic acylating agent having less than 20 carbon atoms in the molecule, and (iv) at least one boron compound to form a product having (1) a total base number in the range of about 33 to about 45 milligrams of KOH per gram of said product excluding the weight of solvent or diluent, if any, that may be associated with said product, and (2) a boron content in the range of about 1.0 to about 1.4 wt% excluding the weight of any solvent and/or diluent that may be associated with said product;

wherein a) and b) are proportioned such that for every 0.7 to 1.8 part by weight of nitrogen from a) there is about 0.3 to about 1.5 part by weight of nitrogen from b).

2. A composition according to Claim 1 wherein said mole ratio in a) is about 0.8 to about 1.3 moles of aminoguanidine and/or basic salt thereof per mole of said acylating agent; wherein said alkylene polyamine of b) has an average of about 4 to about 5 nitrogen atoms per molecule; wherein said mole ratio of (i) per mole of (ii) in b) is about 1.8 to 2 moles of (i) per mole of (ii); and wherein for every 0.8 to 1.7 part by weight of nitrogen from a), there is about 0.4 to about 1.4 part by weight of nitrogen from b).

3. A composition according to Claim 2 wherein said component a) is borated such that it has a boron content of up to about 1 wt%, excluding the weight of solvent and/or diluent, if any, associated with said product.

4. A composition which comprises from 1 to 99 wt% of at least one oil of lubricating viscosity and from 99 to 1 wt% of a composition according to Claim 1.

5. A composition which comprises from 1 to 99 wt% of at least one oil of lubricating viscosity and from 99 to 1 wt% of a composition according to Claim 3.

6. An additive concentrate which comprises:

a) an oil-soluble product formed by reacting aminoguanidine with a long chain alkyl or alkenyl succinic acylating agent in a mole ratio of about 0.4 to about 1.3 moles of aminoguanidine and/or basic salt thereof per mole of said acylating agent;

b) an oil-soluble product formed by reacting (i) an acyclic hydrocarbyl succinic acylating agent and (ii) an alkylene polyamine having an average of about 3 to about 6 nitrogen atoms per molecule in a mole ratio of about 1.6 to 2 moles of (i) per mole of (ii) to form a succinimide and heating the succinimide so formed concurrently or in any sequence and at a temperature in the range of about 150 to about 180°C with (iii) at least one dicarboxylic acylating agent having less than 20 carbon atoms in the molecule, and (iv) at least one boron compound to form a product having (1) a total base number in the range of about 33 to about 45 milligrams of KOH per gram of said product excluding the weight of solvent or diluent, if any, that may be associated with said product, and (2) a boron content in the range of about 1.0 to about 1.4 wt% excluding the weight of any solvent and/or diluent that may be associated with said product;

c) at least one oil-soluble metal dihydrocarbyl dithiophosphate;

d) at least one alkali or alkaline earth metal-containing detergent; and

e) one or more inhibitors selected from at least one oxidation inhibitor, at least one foam inhibitor, at least one rust inhibitor, at least one corrosion inhibitor, and at least one friction inhibitor;

said components a) and b) being proportioned such that for every 0.7 to 1.8 part by weight of nitrogen from a) there is about 0.3 to about 1.5 part by weight of nitrogen from b), and components a), b), c), d) and e) being proportioned in the additive concentrate such that blending a minor proportion of the additive concentrate in a base oil provides an oil blend that contains a dispersant amount of a) plus b) proportioned as above, a wear-inhibiting amount of c), a detergent amount of d), and an inhibiting amount of each said inhibitor selected.

7. A composition according to Claim 6 wherein said metal dihydrocarbyl dithiophosphate is at least one zinc dialkyl dithiophosphate antiwear/extreme pressure agent.

8. A composition according to Claim 7 wherein the alkyl groups of said zinc dialkyl dithiophosphate are a mixture of primary alkyl groups and secondary alkyl groups.

9. A composition according to Claim 6 wherein said component a) is borated such that it has a boron content of up to about 1 wt%, excluding the weight of solvent and/or diluent, if any, associated with said product.

10. A composition according to Claim 9 wherein said metal dihydrocarbyl dithiophosphate is at least one zinc dialkyl dithiophosphate antiwear/extreme pressure agent.

11. A composition according to Claim 10 wherein the alkyl groups of said zinc dialkyl dithiophosphate are a mixture of primary alkyl groups and secondary alkyl groups.

12. A lubricating oil composition which comprises a major amount of at least one oil of lubricating viscosity and

a) a minor dispersant amount of an oil-soluble product formed by reacting aminoguanidine with a long chain alkyl or alkenyl succinic acylating agent in a mole ratio of about 0.4 to about 1.3 moles of aminoguanidine and/or basic salt thereof per mole of said acylating agent;

b) a minor dispersant amount of an oil-soluble product formed by reacting (i) an acyclic hydrocarbyl succinic acylating agent and (ii) an alkylene polyamine having an average of about 3 to about 6 nitrogen atoms per molecule in a mole ratio of about 1.6 to 2 moles of (i) per mole of (ii) to form a succinimide and heating the succinimide so formed concurrently or in any sequence and at a temperature in the range of about 150 to about 180°C with (iii) at least one dicarboxylic acylating agent having less than 20 carbon atoms in the molecule, and (iv) at least one boron compound to form a product having (1) a total base number in the range of about 33 to about 45 milligrams of KOH per gram of said product excluding the weight of solvent or diluent, if any, that may be associated with said product, and (2) a boron content in the range of about 1.0 to about 1.4 wt% excluding the weight of any solvent and/or diluent that may be associated with said product;

c) a minor wear-inhibiting amount of at least one oil-soluble metal dihydrocarbyl dithiophosphate;

d) a minor detergent amount of at least one alkali or alkaline earth metal-containing detergent; and

e) a minor inhibitor amount of one or more inhibitors selected from at least one oxidation inhibitor, at least one foam inhibitor, at least one rust inhibitor, at least one corrosion inhibitor, and at least one friction inhibitor;

said components a) and b) being proportioned such that for every 0.7 to 1.8 part by weight of nitrogen from a) there is about 0.3 to about 1.5 part by weight of nitrogen from b), with the proviso that said lubricating oil composition does not contain more than 0.042 wt% of nitrogen from b).

13. A composition according to Claim 12 further comprising a viscosity index improving amount of a viscosity index improver.

14. A composition according to Claim 12 wherein said metal dihydrocarbyl dithiophosphate is at least one zinc dialkyl dithiophosphate antiwear/extreme pressure agent.

15. A composition according to Claim 14 wherein the alkyl groups of said zinc dialkyl dithiophosphate are a mixture of primary alkyl groups and secondary alkyl groups.

16. A composition according to Claim 12 wherein said composition further comprises a viscosity index improving amount of a viscosity index improver and wherein said metal dihydrocarbyl dithiophosphate is at least one zinc dialkyl dithiophosphate antiwear/extreme pressure agent.

17. A composition according to Claim 12 wherein e) comprises a minor oxidation inhibiting amount of at least one oxidation inhibitor; a minor foam inhibiting amount of foam inhibitor; and a minor friction inhibiting amount of friction inhibitor.

18. A composition according to Claim 12 wherein said component a) is borated such that it has a boron content of up to about 1 wt%, excluding the weight of solvent and/or diluent, if any, associated with said product.

19. A composition according to Claim 18 wherein said composition further comprises a viscosity index improving amount of a viscosity index improver and wherein said metal dihydrocarbyl dithiophosphate is at least one zinc dialkyl dithiophosphate antiwear/extreme pressure agent.

20. A composition according to Claim 19 wherein the alkyl groups of said zinc dialkyl dithiophosphate are a mixture of primary alkyl groups and secondary alkyl groups; and wherein e) comprises a minor oxidation inhibiting amount of at least one oxidation inhibitor, a minor foam inhibiting amount of foam inhibitor, and a minor friction inhibiting amount of friction inhibitor.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 0225

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 460 309 (ETHYL PETROLEUM ADDITIVES) * page 13, line 38 - line 42 * * page 13; example 1 * * page 16, line 57 - page 17, line 31 * ---	1,2,4,6,7,12-14,16,17	C10M133/56 C10M163/00 C10M167/00 //(C10M133/56, 133:56), (C10M163/00, 133:56,133:56, 137:10, 159:20), C10N10:04, C10N30:00, C10N30:04, C10N60:00, C10N60:14
P,A	WO-A-95 00607 (ETHYL CORPORATION) * page 2, line 21 - line 36 * * page 8, line 5 - line 25 * ---	1-7,9,10,12-14,16-20	
A	EP-A-0 310 365 (AMOCO CORPORATION) * page 7, line 6 - line 20; claims 15,17 * * page 9, line 64 - page 10, line 8 * ---	1,3-7,9,10,12-14,16-20	
A	EP-A-0 516 461 (ETHYL PETROLEUM ADDITIVES) * page 2, line 20 - line 22 * * page 2, line 48 - line 54 * * page 7, line 9 - line 14 * * page 35; example I * * page 36, line 20 - line 25 * * page 37, line 5 - line 10 * --- -/--	7,8,10,11,14,15,20	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 May 1995	Hilgenga, K

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	GB-A-1 121 681 (THE LUBRIZOL CORPORATION) * page 2, line 29 - line 37 * * page 6; examples 6,12,14 * * page 7, line 95 - line 97 * * page 8, line 42 - line 49 * * page 10, line 54 - line 61 * ---	1,2,4, 6-8, 12-17	
A	GB-A-998 869 (MONSANTO COMPANY) * page 10, line 10 - line 20; claims 1,4 * -----	1,2,4,6, 7,12-14, 16,17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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