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

(11) Publication number: **0 277 729 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **88300500.1**

(22) Date of filing: **21.01.88**

(51) Int. Cl.4: **C10M 163/00** , //(C10M163/00, 133:52,137:10,159:16,159:22, 159:24),C10N10:04,C10N30:06, C10N40:00,C10N60:14

(30) Priority: **21.01.87 US 6004**

(43) Date of publication of application: **10.08.88 Bulletin 88/32**

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

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(54) Lubricant compositions providing wear protection at reduced phosphorus levels.

(57) An additive composition suitable for blending passenger car and heavy duty oils comprising (a) zinc dialkyldithiophosphate having both primary and secondary character such the primary to seconary ratio is about 1:1 to about 5:1, said zinc dialkyldithiophosphate being present in an amount such that a lubricating oil containing an effective amount of the additive composition will have a phosphorus level not greater than about 0.1 wt%; (b) a succinimide dispersant; and (c) a total base number such that a lubricating oil containing an effective amount of the additive composition will have a TBN of at least 8.

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LUBRICANT COMPOSITIONS PROVIDING WEAR PROTECTION AT REDUCED PHOSPHORUS LEVELS

Background of the Invention

Field of the Invention

The present invention is directed to a novel composition that is useful as a lubricant additive. In particular, the present invention relates to a lubricant additive composition that is characterized by antiwear and friction retention properties while providing reduced phosphorus levels. More particularly, the invention relates to formulation of a so-called universal or mixed fleet lubricant oil additive composition (i.e. one that will result in a lubricant meeting the requirements of both heavy duty and passenger car engine tests) which has reduced phosphorus and which comprises zinc dialkyldithiophosphate having both primary and secondary character in combination with a succinimide dispersant.

Description of the Prior Art

Internal combustion engines, both gasoline and diesel, have many moving metal parts wherein metal slides against metal, resulting in metal wear. Since wear is a continuing problem that is associated with moving parts that contact one another, lubricants are used to provide a reduction in such wear. However, high rates of wear are found in internal combustion engines in crankcase bearings and on piston ring and cylinder wall surfaces of internal combustion engines. Relatively high rates of wear can take place in heavy duty engines, such as marine diesel engines, and engines employed in military vehicles.

Lubricating oils, particularly mineral oils, deteriorate under heavy loads and as a result of oxidation during their use in internal combustion engines to form products, some of which are corrosive and some of which agglomerate to form sludge-like deposits and varnish-like deposits. Such sludge-like material occurs when the crankcase lubricant is subjected to alternate hot and cold environments, which are present in ordinary stop-and-go driving. Sludge is a complex mixture of fuel combustion products, unburned fuel, carbon, lead anti-knock residues, and water and, if not maintained in fine suspension in the lubricating oil, will deposit on engine parts. Such deposits are deleterious to engine performance.

Various additives and additive formulations have been added to lubricating oils to minimize deterioration and to enhance performance. Such materials, as neutral and over-based metal long chain alkyl substituted sulfonates, phenates, salicylates, and phosphonates and thiophosphonates have been added as detergents and/or detergent-dispersants. Materials, such as polymers and/or copolymers containing a carboxylate ester function and one or more polar functions, N-substituted long chain alkenyl succinimides, high-molecular weight amides and polyamides, high-molecular weight esters and polyesters, and amine salts of high-molecular weight organic acids, have been added as ashless dispersants to disperse the cold sludge formed under stop-and-go driving conditions. Materials, such as metal dithiophosphates, metal dithiocarbamates, sulfurized terpenes, and phosphosulfurized terpenes, have been added as corrosion inhibitors. In addition, one or more additives are incorporated often into the lubricant composition to furnish or to enhance antiwear and friction retention properties of that composition. Examples of art describing such lubricating oil compositions are discussed hereinbelow.

In U.S. Patent 3,532,626, Rowe discloses lubricating oil compositions that contain a small amount of a mixture of a metal salt of an O,O-diorgano-phosphorodithioate and a boroaryl compound in synergistic proportions. An example of such mixture is a mixture of zinc, O,O-diisopropylphosphorodithioate and 9-hydroxy-9,10 boroxarophenanthrene. The amount of the mixture is sufficient to improve antiwear properties of the compositions.

In U.S. Patent 3,533,945, Vogel discloses the improvement of the lubricating properties of a lubricating oil by incorporating therein a boron-containing ester that is a combined boron esteralkenyl succinic acid ester of a polyhydric alcohol that is prepared by the process comprising the reaction of a polyhydroxy compound with a succinic acid-producing compound and a boron reactant. Vogel discloses that such boron-containing esters are useful, inter alia, as corrosion-inhibiting agents, extreme pressure agents, antiwear agents, and detergents.

In U.S. Patent 3,544,465, Braid discloses lubricant compositions containing esters of O,O-diorgano-S-(2-hydroxyalkyl) phosphorodithioates, which are antioxidants and corrosion inhibitors.

In U.S. Patent 4,557,844, Horodysky discloses the use of certain boron-, phosphorus-, and nitrogen-containing reaction products as antioxidants and antifriction agents in lubricants and fuels.

In U.S. Patent 4,534,873, Clark discloses a friction-reducing additive for use in lubricating oils. The additive comprises a hydrocarbon oil of lubricating viscosity, an extreme pressure antiwear agent, an alkaline material, such as an overbased calcium sulfonate, a viscosity index improving agent, and optionally an antifoam agent and an antioxidant agent. Clark teaches that the antiwear agent comprises a mixture of an oil dispersion of solid, inorganic film-forming potassium borate, antimony dialkylphosphorodithioate, and a liquid chlorinated paraffin.

In U.S. Patent 4,431,552, Salentine discloses a lubricating oil composition having improved wear properties, which composition comprises an oil of lubricating viscosity having dispersed therein a hydrated alkali-metal borate extreme-pressure agent and an effective amount of a mixture of a non-sulfur-containing phosphate, a monothiophosphate, and a dithiophosphate, the mixture of phosphate, monothiophosphate, and dithiophosphate being in the ratio of 0.90-10:0.90-1.10:0.47-0.67.

In U.S. Patent 4,368,129, Hyrodysky, et al., disclose a lubricating oil conposition comprising an oil of lubricating viscosity and a minor amount of a multifunctional additive consisting of the metal salt of a partially borated, partially phosphosulfurized hydroxyl-containing ester derived from a polyol, e.g., a zinc salt of borated, partially phosphosulfurized glycerol monooleate. The additive is an effective friction-reducing, antioxidant, and copper strip passivating additive in lubricants.

Occasionally, certain additives will deleteriously affect the ability of certain other additives to perform their normal function. For example, overbased Group II metal hydrocarbyl sulfonates are effective detergents or dispersants and normal metal salts of dihydrocarbyldithiophosphoric acids are suitable antiwear additives. However, when these two additives appear in the same lubricating oil, the presence of an overbased Group II hydrocarbyl sulfonate will tend to deleteriously affect the effectiveness of the normal metal salts of the dihydrocarbyldithiophosphoric acids to provide sufficient wear protection in the internal combustion engine which employs that particular lubricating oil as its lubricant. In U.S. Patent 4,483,775, Yamaguchi discusses this problem and suggests that the detrimental effect of the overbased calcium hydrocarbyl sulfonates on the wear of metal parts in the internal combustion engine can be overcome by adding to the lubricating oil containing these materials an effective amount of a complex prepared by reacting an insoluble metal salt of a diisopropyl dithiophosphoric acid with an oil-soluble alkenyl or alkyl mono-or bis-succinimide in specific amounts.

In U.S. Patent 4,483,775, Yamaguchi also points out that there is another problem that is associated with the use of phosphorus-containing additives in lubricating oils. The phosphorus can have a deleterious effect upon the catalysts that are employed in the emissions control systems of internal combustion engines of automobiles. Hence, if the overbased metal hydrocarbyl sulfonates tend to offset the effectiveness of the metal dihydrocarbyldithiophosphates, additional amounts of the metal dihydrocarbyldithiophosphates must be employed and such increased amounts of these additives will introduce additional amounts of phosphorus into the lubricating oil. While the effectiveness of the metal dihydrocarbyldithiophosphates relative to its antiwear performance is improved, the side result will be a reduced life for the catalytic converter system of the automobile. Consequently, the automobile manufacturers are interested in finding ways of minimizing the amount of the metal dihydrocarbyldithiophosphates in the lubricating oils without deleteriously affecting the antiwear performance provided by the lubricating oil.

It is generally desirable to formulate an additive composition which is suitable for use in so-called universal or mixed fleet oils. Such an oil, by definition, is one which is capable of passing a rigorous battery of engine tests which measure the performance of the oil for both passenger car and heavy duty (i.e. diesel) applications. However, given the harmful effect on passenger car catalytic converters of phosphorus (which is typically introduced into the oil via the anti-wear agent zinc dialkyldithiophosphate) it would be particularly advantageous if an additive composition suitable for a universal oil could be formulated with reduced levels of phosphorus.

Prior to the present invention, efforts to formulate a low phosphorus universal oil were unsuccessful primarily because of the difficulty encountered in balancing the often conflicting passing requirements of the various engine tests which the industry has established for passenger car and heavy duty oils. For example, heavy duty oils require a TBN of greater than about 8. However, because the detergent additives typically employed to impart TBN (i.e. overbased Group II metal hydrocarbyl sulfonates) tend to reduce the effectiveness of zinc dialkyldithiophosphates (ZDDP) wear inhibiting agents, a higher level of ZDDP--and thus a higher level of phosphorus--is required to pass the wear tests for passenger and heavy duty oils. To complicate matters, heavy duty oils must pass certain friction tests which measure the degree to which the oil impairs friction retention in the clutch, but as the phosphorus level (i.e. as the zinc dialkyldithiphosphate) is increased to accomcdate wear performance, passing these friction tests becomes increasingly difficult. Our work prior to the present invention determined that the minimum phosphorus level in a universal oil that would accommodate the industry's TBN, wear and friction requirements for a universal oil is about 0.1 wt %. Reducing the phosphorus level to below about 0.1 wt % (i.e. by reducing ZDDP wear inhibitor) resulted in failing engine wear tests.

In light of the preceeding discussion, a general object of the invention is to provide an additive composition which affords passing wear protection for a universal oil at reduced phosphorus levels. Other objects will appear hereinafter.

Summary of the Invention

We have now found that the objects of the present invention are provided for in an additive composition for addition to a oil of lubricating viscosity suitable for use in both passenger cars and heavy duty vehicles, comprising: (a) zinc dialkyldithiophosphate having both primary and secondary character such that the primary to secondary ratio is about 1:1 to about 5:1, said mixed primary/secondary zinc dialkyldithiophosphate being present in an amount such that a lubricating oil containing an effective amount of the additive composition has a phosphorus content of not greater than about .1 wt. %; (b) a succinimide dispersant; and (c) a total base number (TBN) such that a lubricating oil containing an effective amount of said additive composition has a TBN of at least 8. Preferably, the molar ratio of primary to seconary alkyl groups in the zinc dialkyldithiophosphate (hereafter occasionaly referred to as "ZDDP") is within the range of about 1.7:1 to about 3.5:1 and preferably about 1.7:1 to about 4.5:1. The preferred amount of succinimide dispersant in the additive composition is such that will provide at least .5 wt % of the succinimide in the finished oil and most preferably about .5 to about 3.5 wt. %. The preferred phosphorus level in the additive composition is such as will provide a phosphorus level of about .06 wt.% to about .09 wt %. The preferred TBN of the additive is such as will provide a TBN in the finished oil within the range of about 8-12 and preferably about 9-11. It should be noted that all dispersant amounts are expressed in temrs of active dispersant absent any diluent, except, however, in the examples where dispersant amounts are expressed in terms of a 40% active material containing added diluent.

In a preferred embodiment, the additive composition of the present invention has a boron content sufficient to provide a boron level in the finished oil of within the range of about 100 ppm(wt) to about 600 ppm and preferably in the range of 150 ppm to 450 ppm.

Among the advantages of the invention is the ability to reduce the level of phosphorus required in an additive composition for a mixed fleet oil despite the requirement of high TBN in such oils, which is necessary for passing heavy duty engine cleanliness tests, while at the same time obtaining passing wear performance. Reducing the phosphorus in the oil composition benefits the catalytic converter in passenger cars. Unexpectedly, the succinimide dispersant required in the present invention is critical in accomplishing the reduction in phosphorus for the following reasons: In accordance with the present invention, increasing the secondary character of the ZDDP makes it possible to reduce the overall amount of ZDDP (and thus the total phosphorus required in the additive and resulting oil) without giving up passing wear performance. However, in an additive composition having sufficient TBN to provide TBN of at least 8 in the finished oil and having a total phosphorus (as provided by primary ZDDP) to provide at least about .1 percent phosphorus in the finished oil, the combined effect of lowering the total phosphorus and simultaneously increasing the secondary character of the ZDDP, while acceptable from the standpoint of retaining engine wear performance, results in failing performance on the friction requirements applicable to heavy duty oils (i.e. the Allison C-3 and Caterpiller TO2 tests). This probelm was not entirely unexpected insofar as it is known that increasing the amount of secondary ZDDP will result in a debit in terms of frictional characteristics of the oil. Thus, reduction in the total amount of ZDDP coupled with an increase in the secondary character of the ZDDP, was not by itself an acceptable route to reduced phosphorus in an additive suitable for a universal oil, given the resulting debit in friction peformance in the heavy duty tests. Surprisingly, in accordance with the present invention, it is only with addition of the succinimide dispersant that friction tests were passed. At the present time, the mechanism for this phenomenon is not well understood, however, without limitation, it is believed that the succinimide interacts in some manner with the secondary ZDDP so as to counteract the deleterious effects of the secondary ZDDP on the frictional performance of the additive composition.

Detailed Description and Preferred Embodiments

The additive composition of the present invention must comprise (a) zinc dialkyldithiophosphate having both primary and secondary character such that the primary to secondary ratio (expressed in moles) is within the range of from about 1:1 to about 5:1, and (b) succinimide dispersant. Also, the total amount of phosphorus in the additive, as provided by the ZDDP, must be such that the amount of phosphorus present in a lubricating oil containing an effective amount of the additive is not greater than about .1% by weight of the lubricating oil, and the TBN of the additive composition must be such that a lubricating oil containing an effective amount of the additive composition will have a TBN of at least 8. An effective amount of the additive composition of the present invention means a treat level in the lubricant which will allow the oil to pass both heavy duty and passenger car tests.

Of course, other components optionally may be present in the additive composition. For example, there may also be present rust inhibitors, oxidation inhibitors, and one or more detergents, such as normal or overbased sulfurized metal phenates or metal sulfonates.

The required zinc dialkyldithiophosphate having both primary and secondary character for use in the present invention functions as a corrosion and wear inhibitor. Typically, zinc dialkyldithiophosphate is prepared by forming a dithiophosphoric acid via a reaction of a phenol or an alcohol with phosphorus pentasulfide and subsequently neutralizing the dithiophosphoric acid with a zinc compound, such as zinc oxide. Such preparation is well known in the art and is presented, for example, in U.S. Patent 2,261,047 and U.S. Patent 4,483,775. This type of dialkyldithiophosphate can be identified by the alcohol that is employed in its preparation. If a primary alcohol is employed, the product is referred to as a primary zinc dialkyldithiophosphate. On the other hand, if the alcohol is a secondary alcohol, the zinc dialkyldithiophosphate is identified as a secondary zinc dialkyldithiophosphate. Suitable primary alcohols for use in the preparation of the primary zinc dialkyldithiophosphate are n-butyl alcohol, n-octyl alcohol, isoamyl alcohol, isooctyl alcohol, and isobutyl alcohol. Suitable secondary alcohols are isopropyl alcohol, methyl isobutyl carbinol, 2-amyl alcohol, and 2-butyl alcohol. If a mixture of primary and secondary alcohols is used, the resulting ZDDP is a hydrid having both primary and secondary character. In the present invention the term "zinc dialkyldithiophosphate having both primary and secondary character" includes any of the following: (a) a zinc dialkyldithiophosphate preparation obtained by mixing a desired amount of primary zinc dialkyldithiophosphate with a desired amount of secondary zinc dialkyldithiophosphate; (b) a zinc dialkyldithiophosphate which results from employing a mixture of primary and secondary alcohols in the preparation of the zinc dialkyldithiophosphate; and (c) a zinc dialkyldithiophosphate obtained by mixing a primary or a secondary zinc dialkyldithiophosphate with a zinc dialkyldithiophosphate meeting the definition of (b). Also, in the present invention the terminology "ratio of primary to secondary," or "primary to secondary ratio," means the molar ratio of primary alkyl groups to secondary alkyl groups in the zinc dialkyldithiophosphate.

In the case of the additive composition of the present invention, the primary to secondary ratio in the zinc dialkyldithiophosphate is within the range of about 1:1 to about 5:1, preferably, within the range of about 1.7:1 to about 3.5:1, and more preferably, within the range of about 1.7:1 to about 2.5:1.

The total amount of the mixed primary/secondary dialkyldithiophosphates should be an amount that will provide a phosphorus content in the lubricating oil composition not greater than 0.1 wt%, based upon the weight of the lubricating oil composition. Preferably, the zinc dialkyldithiophosphate should be present in a total amount that will provide a phosphorus content in the lubricating oil composition that falls within the range of about 0.06 wt% to about 0.09 wt%, and most preferably within the range of about 0.06 wt% to about 0.08 wt%, based upon the weight of the lubricating oil composition.

The prescribed 1°:2° molar ratio in the ZDDP used in the present invention is important when one considers the object of maintaining the phosphorus content in the additive composition at such a level that a finished oil containing an effective amount of the composition has a phosphorus content of not greater than about .1 wt % of the finished oil. If the total phosphorus is decreased, then in accordance with the present invention, passing wear can be maintained by increasing the 2° character of the ZDDP. Such an adjustment appears practicable where the phosphorus (in terms of the finished oil) is between about .06 and about 0.1 wt percent. Other things being equal, as the total phosphorus decreases, increasing the secondary character of the ZDDP provides less and less of an effect in terms of counteracting the loss in wear protection brought about by the reduction in phosphorus. The prescribed ratios of 1° to 2°character are based upon this fact, and the desirability of using the minimum amount of 2° character in the ZDDP to maintain wear protection (given the deleterious effect of the the 2° ZDDP on friction performance). Within the prescribed ratio of 1°:2° character in the ZDDP (i.e. about 1:1 to about 5:1) the ratio will increase as the total phosphorus (in terms of the oil) approaches about .1 wt%, and will decrease as the phosphorus level approaches about .06 wt.%. At a 1°:2° ratio of greater than about 5:1, the presence of 2° character affords little if any ability to decrease the total phosphorus below about .1 wt percent of the finished oil. At the lower limit of 1°:2° of about 1:1, it becomes increasingly difficult to further reduce the total phosphorus, and still pass wear tests regardless how much 2° character is present in the ZDDP.

A second required component of the additive composition of the present invention is a succinimide dispersant. Such succinimide is an N-substituted long chain-alkenyl succinimide. Typically, the alkenyl radical is derived from liquid polyisobutenes containing from 50 to 200 carbon atoms. Such a succinimide is an oil-soluble nitrogen containing composition. The preparation of succinimide dispersants is known in the art. Among such art are U.S. Patents 3,172,892; 3,272,746; and 3,219,666. The disclosures of these patents are incorporated herein by reference. For example, an acylated nitrogen intermediate compound is formed by reacting a substantially aliphatic olefin polymer-substituted succinic-acid producing compound having at least about 50 aliphatic carbon atoms in the polymer substituent with at least about one half equivalent of an amine for each equivalent of acid-producing compound used, said reaction being carried out at a temperature within the range of about 80°C to about 250°C. The amine is selected from a group consisting of alkylene amines, hydroxysubstituted alkylene amines, and polyalkylene polyamines.

The polymer substituent of the succinic acid-producing compound is derived conveniently from a polymer of isobutene. Typically, the polyisobutene has an average molecular weight that is within the range of about 700 to about 5,000. Suitable amines are alkylene amines, alkylene diamines having the structure NH_2-R-NH_2, wherein R is an alkylene group having from 2 to 24 carbon atoms, and the so-called polyalkyleneamines, sometimes referred to as alkylene polyamines or polyalkylene polyamines, which generally have the structure H_2N--(R--NH)$_n$H, where R is an aliphatic hydrocarbon group containing about 2 to about 4 carbon atoms and n is an integer from 1 to 10. Representative amines include methylene amines, ethylene amines, butylene amines, propylene amines, pentalene amines, ethylene diamine, triethylene tetraamine, propylene diamine, decamethylene diamine, octamethylene diamine, di-(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamene, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, etc. A preferred polyalkylene polyamine is tetraethylene pentamine (TEPA).

Preferably the succinimide dispersant is present in the additive composition of the present invention in an amount sufficient to provide a lubricating oil containing an effective amount of the additive composition at least about .5 wt, % by weight of the lubricating oil. While a preferred range is about .5 to about 3.5 the maximum amount of succinimide is an economic consideration and is not critical in the present invention. However the requirement of at least .5 wt% is critical insofar as lesser amounts fail to provide the desired advantage of passing frictional tests, in particular the Allison C-3, when phosphorus levels of less than .1 by weight of the lube oil, in combination with the 1°/2° ratios discussed above, are employed.

In addition to the requirements stated above, the additive composition of the present invention comprises sufficient TBN such that a universal oil comprising an effective treat level of said additive composition is provided with a TBN of at least 8, preferably, within the range of about 9 to about 11, and more preferably, about 10.

Examples of components that are suitable for providing the required TBN in the additive composition of the present invention are overbased metal sulfonates and over based phenates. The sulfonates are normal or basic metal salts of petroleum ("mahogany") sulfonic acids and long chain alkyl substitued benzene sulfonic acids. The phenates are normal or basic salts of alkylphenols, alkylphenol sulfisides, and alkylphenol-aldehyde condensation products. A normal metal salt of an acid is a salt which contains the stoichiometric amount of metal required for the neutralization of the acidic group or groups present in the acid. A basic salt or overbased salt is a salt which contains more metal than is required to stoichiometrically neutralize the acidic group or groups present. While both normal and overbased sulfonates and phenates provide detergent properties for lubricating oil compositions, the overbased or superbasic or hyperbasic salts provide unusually high detergent power and, consequently, have a much greater capacity to neutralize acidic contaminants than do the normal sulfonates and phenates. Typically an overbased sulfonate is prepared by mixing a promoter, catalyst or solvent with a normal sulfonate and a larger excess of metallic base, followed by heating, carbonation and filtration. Carbonation of the reaction mass is accomplished conveniently with carbon dioxide and is employed to increase the amount of metal base colloidally dispersed as metal carbonate in the filtered product. Phenols, trioacids, of phosphorus, alcoholates, alcohols, ketones, and alkanolamines can be used as promoters for catalysts. Typical metallic bases are basic compounds of alkaline earth metals, such as calcium, barium, or magnesium. Overbased metal sulfonates are discussed thoroughly in the prior art. Examples of such art are: United Kingdom Patent Application GB 2,082,619A and U.S. Patents 2,865,956; 2,956,018; 2,671,430; 3,779,920; 3,907,691; 4,137,184; 4,261,840; and 4,326,972.

The overbased metal phenates are presented in the prior art. Typical examples of the prior art are U.S. Patents 2,680,096; 3,036,917; 3,178,368; 3,194,761; 3,437,595; 3,464,910; 3,779,920; and 4,518,807.

In a preferred embodiment of the present invention the reduced-phosphorus additive composition further comprises boron sufficient to provide within the range of from about 100 to about 600 ppm(wt.) boron in the finished oil containing the additive composition of the invention. Optionally, the additive composition may contain an additional dispersant comprising at least on member of the group consisting of Mannich and succinate ester-amide (SEA) dispersant in an amount sufficient to provide preferably up to about 5 wt% of the second dispersant in the finished oil.

The succinate ester-amide dispersant can be prepared in accordance with techniques which have been disclosed in the art (See for example U.S. Patent No. 4,426,305) by reacting an aliphatic hydrocarbon substituted succinic acid anhydride with an oxyalkylated amine.

The long chain aliphatic hydrocarbon-substituted succinic acid compound that is used in the preparation of the second dispersant can be obtained by reacting an ethylenically unsaturated dicarboxylic acid compound (acid or anhydride), such as maleic acid, maleic anhydride, or fumeric acid, with a suitable olefin or halogenated olefin at a temperature within the range of about 100°C to 300°C. An alkenyl or alkyl substituted succinic acid or anhydride is produced. The unsaturated groups in the alkenyl group can be removed by standard hydrogenated techniques. The olefins or halosubstitued olefins contain from about 8 to about 500 carbon atoms, or more, and can include homopolymers and copolymers of monoolefins, such as ethylene, propylene, 1-butene, isobutene, and the like. However, any of the techniques known in the art can be employed to produce this long chain succinic acid compound.

The oxyalkylated amine suitable for reaction with the above described long chain aliphatic hydrocarbon succinic acid compound can be prepared in accordance with known methods by reacting an alkylene oxide with an amine having primary or secondary amine groups. Suitable amines are alkylene diamines having the structure NH_2-R-NH_2, wherein R is an alkylene group having from 2 to 24 carbon atoms, such as ethylene, 1, 2-propylene, trimethylene, hexamethylene, dodecamethylene, tetracosene, etc. Also suitable are the so-called polyalkyleneamines, sometimes referred to as alkylene polyamines or polyalkylene polyamines. These generally have the structure H_2N--$(R\text{-}NH)_nH$, where R is an aliphatic hydrocarbon group containing about 2 to about 4 carbon atoms and n is an integer from 1 to 6. Representative examples include ethylenediamine, 1,2-propylenediamine, 1,2-butylenediamine, 1,3-propanediamine, diethylenetriamine, triethylenetetramine, tetraethylene pentamine (TEPA), etc.

Suitable hydroxyalkylating reactants include halohydrins and vicinal epoxies (olefin oxides) having from 2 to 4 carbon atoms in the alkylating agent, such as ethylene oxide, 1, 2-propylene oxide, 1, 2-butylene oxide, 2-chloro-1, ethanol, 2-chloro-1-propanol, 3-bromo-1-prophanol, and 4-chloro-butanol. The hydroxyalkylating agents can be used in a concentration of about 2.0 to 6 moles per mole of amine, and hydroxyalkylation can be carried out under conventional conditions, i.e., by reaction at 50°C to 300°C for a period of time within the range of 1 to 10 hours.

Subsequently, the long chain aliphatic succinic acid compound is reacted with the N-substituted hydroxy alkyl diamine under conditions that are normally employed in the art and at a temperature within the range of about 0°C to about 250°C. A solvent, such as benzene, toluene, naphtha, lube oil, xylene, and normal hexane, can be used to facilitate the control reaction.

As stated above, the optional second dispersant may also be a Mannich dispersant. Mannich dispersants made from hydrocarbon substituted phenols, formaldehyde and amines are well known in the patent literature. See U.S. Patent Nos. 3,413,347; 3,725,277; 3,368,972; 3,798,165; 3,697,574, and 4,426,305. These patents are incorporated by reference.

The optional second dispersant (Mannich or SEA) can be present in the lubricating oil composition in an amount within the range of about 0 wt % to about 5 wt%, preferably, within the range of about 0 wt% to about 3 wt%.

As stated above, the additive composition of the present invention preferably contains boron in an amount such that a lubricating oil containing an effective amount of the additive composition, will have a boron content within the range of about 100 ppm(wt) to about 600 ppm(wt) boron. The preferred boron level is about 150 to about 450 ppm(wt) in the finished oil. The presence of boron is preferred for the protection of fluorinated elastomer hydrocarbon seals, and also enhances the anti-wear properties of the additive composition, especially where TBN is supplied by high-based calcium sulfonate. The latter is known to deleteriously effect the wear protection afforded by zinc dialkyldithiophosphate. Provided a sufficiently low ratio of calcium to magnesium high base sulfonate is present in the additive formulation of the present invention, the presence of boron may not be required. However in the additive formulation of the present invention, boron is preferably present in an amount sufficient to provide about 150 ppm(wt) to about 450 ppm(wt) in the finished oil.

Boron may be introduced into the additive composition in accordance with conventional techniques. For example, A boron compound, such as boron oxide, boron dihalides (boron trifluoride, boron tribromide, boron tricholoride), boron acids, such as tetraboric acid and metaboric acid, and simple esters of the boron acids, can be reacted with the succinimide, SEA or Mannich dispersants discussed above at a temperature within the range of about 50°C to about 250°C, preferably from about 100°C to about 170°C, with a sufficient concentration of boron compound to yield a boronated dispersant product containing at least 0.15% by weight boron (excluding lube oil). The boron compound can be reacted in a ratio within the range of about 0.1 to 10 moles of boron compound for equivalent of dispersant compound. The reaction can be carried out in the presence of diluent or solvent. Alternatively, a portion of the succinimide, Mannich or SEA dispersant intended for the additive composition of the invention may be segregated and heated with a boronating agent to introduce a higher level of boron than would be desired in the final dispersant. This overboronated product can then be blended back into the unboronated dispersant to achieve the desired level of boron.

The additive composition of the present invention may contain other additive components, such as viscosity index improvers, pour point depressants, and antioxidants.

The additive composition of the present invention comprises a mixture of several additive components, some of which are mandatory and some of which are optional. This blend or mixture is prepared easily by introducing one or more of the components into another component. It is not critical that a particular component be added to another particular component, i.e., there is no particular sequence which must be used when adding the various components in preparing the blend. As noted hereinabove, the blend is a composition that will provide antiwear and friction retention properties to the lubricating oil to which it is added while minimizing the phosphorus level in that particular lubricating oil composition.

The additive composition of the present invention can be added to a petroleum oil or synethetic oil of lubricating viscosity to provide antiwear and friction retention properties while minimizing the amount of phosphorus in the resulting lubricating oil composition. The additive composition of the present invention is quite suitable for addition to a lubricant that is being employed in heavy duty vehicles, such as those used in military operations. Lubricating oil compositions containing the additive composition of the present invention provide suitable anti-wear and friction retention properties. In addition, they contain only a limited amount of phosphorus and, consequently, minimize the phosphorus content in the engine and thus extend the life of the catalyst in the catalytic converter of the automobile. Typically, the additive composition of the present invention will be present in the lubricating oil composition in an amount that is within the range of about 9 wt% to about 12 wt%, based upon the weight of the lubricating oil composition. More particularly, the additive composition is present in the lubricating oil composition in an amount that is within the range of about 10% to about 11 wt%, based upon the weight of the lubricating oil composition.

The scope of the present invention includes concentrates of the additive composition. Such concentrates are made up of about 90 wt% to about 10 wt% of an oil having lubricating viscosity. The concentrates contain the additive composition plus a suitable diluent. Typical diluents are inert diluents, preferably an oil of lubricating viscosity, so that the concentrate may be mixed conveniently with the lubricating oil that will make up the desired lubricating oil composition. Lubricating oils that are suitable as diluents typically will have viscosities that are within the range of about 35 Saybolt Universal Seconds (SUS) at 100°F (38°C) to about 1,000 SUS at 100°F (38°C). While any oil of lubricating viscosity can be used as the diluent for the concentrate of the present invention, suitably, the oil of lubricating viscosity in the lubricating oil composition can be employed as the diluent in the concentrate.

Lubricating oils that are suitable for use in the lubricating oil compositions and concentrates of the present invention are oils of lubricating viscosity and are either petroleum oils or synthetic oils. The petroleum oils can be paraffinic, naphthenic, or even halogen-substituted hydrocarbons. Typical synthetic oils are those comprising synthetic esters, diester, ethers, polyolefins, or combinations thereof. These oils of lubricating viscosity will have viscosities that fall in the range of about 50 SUS to about 5,000 SUS at 100°F (38°C), preferably viscosities in the range of about 50 SUS to about 2,000 SUS at 100°F (38°C), and more preferably, viscosities in the range of about 80 SUS to about 1,000 SUS at 100°F (38°C).

Thus, in accordance with the present invention, there is also provided a lubricating oil composition, which lubricating oil composition comprises a major portion of an oil having lubricating viscosity in combination with a minor portion of an additive composition as described above.

The following examples are being presented for the purpose of illustration only and are not intended to limit the scope of the present invention.

Example I

A preferred embodiment of the lubricating oil additive composition of the present invention was prepared. This embodiment had the composition presented hereinbelow in Table I. This additive was then introduced into a Mid-East base stock. The resulting lubricating oil composition had an SAE grade of 15W-40. The additive composition made up 10.3 wt% of the lubricating oil composition, which had a TBN of about 10. The lubricating oil composition also contained 4.1 wt% Viscoplex 2-50 viscosity index improver obtained from Rohm-Darmstadt. The concentration of each of the components of the additive composition in the lubricating oil composition is also provided in Table I. The additive composition contained 1,700 ppm-(wt) boron, while the SAE 15W-40 oil, identified hereinafter as Sample No. 1, contained 180 ppm(wt) boron. Furthermore, Sample No. 1 contained 784 ppm(wt) phosphorus. The molar ratio of primary to secondary in the zinc dialkyldithiophosphate was 4.4

TABLE I

PREFERRED ADDITIVE COMPOSITION

Additive Component	Concentration (wt%) In Additive	Concentration (wt%) In Sample No. 1
Boron (ppm,wt.)	1700	180
Succinimide Dispersant	56.80	5.85
Zinc Dialkyldithio-phosphate Wear Inhibitor ($1^{o}:2^{o}$ molar ratio=4.4)	9.71	1.00
High-Base Magnesium Sulfonate Rust Inhibitor	10.68	1.10
High-Base Calcium Sulfonate Rust Inhibitor	6.79	0.70
High-Base Sulfurized Calcium Phenate Inhibitor/Detergent	11.46	1.18
Alkyl Diarylamine Oxidation Inhibitor	3.40	0.35
100N Base Oil	1.16	0.12
	100.00	10.30

The SAE 15W-40 oil, Sample No. 1, was subjected to various standard tests, which included the Sequence IID Test to evaluate antitrust properties; the Sequence IIID Test to evaluate oxidation inhibition, oil consumption, and wear; the Sequence V-D Test to evaluate engine cleanliness and wear; the CRC L-38 Test to evaluate non-ferrous bearing corrosion and shear stability; the Caterpillar 1G2 Test to evaluate diesel piston cleanliness; the Caterpillar TO-2 Test to evaluate power shift transmission friction retention; the Detroit Diesel 6V-53T Test to evaluate piston deposits and wear; the Detroit Diesel Allison C-3/Friction Test to evaluate transmission friction retention; and the Detroit Diesel Allison C-3/Seals Test to evaluate seal compatibility. The results of these tests are presented hereinbelow in Table II.

TABLE II

TEST RESULTS FOR SAE 15W-40 OIL SAMPLE NO. 1

Test	Evaluation	Results
CRC L-38	non-Fe corrosion	pass
Bearing wt loss (40 mg max)		5.6
Sequence IID	rust	pass
Avg rust (8.5 min)		8.57
Sequence IIID	oxidation/wear	pass
Viscosity increase (375% max)		144
Avg sludge (9.2 min)		9.68
Piston varnish (9.2 min)		9.42
Ring land face varnish (2.8 min)		7.58
Oil cons (6.38 qt max)		3.47
Wear		
Max (0.0080 in)		0.0014
Avg (0.0040 in)		0.0007
Sequence V-D	cleanliness/wear	pass
Avg sludge (9.4 min)		9.52
Piston varnish (6.7 min)		8.20
Avg varnish (6.6 min)		8.67
Wear		
Max (2.5 mil)		0.4
Avg (1.0 mil)		0.3

Test	Evaluation	Results
Caterpillar 1G2	diesel cleanliness	pass
Top groove fill (80% max)		62
Weighted total demerits (300 max)		271
Caterpillar TO-2	power transmission	pass
Stopping time increase (15% max)		13.4, 12.8
DD6V-53T	scuffing	pass
Piston demerits (400 max)		259
No. 2 & 3 ring demerits (13.0 max)		3.3
Liner scuffing (12% max)		3.9
DDA C-3/Seals	seal compatibility	pass
Buna		OK
Polyacrylate		OK
Silicone		OK
DDA C-3/Friction	transmission	pass
Time (0.86 sec max)		0.81
Torque (75 lb-ft min)		78
Delta Torque (30 max)		13

SAE 15W-40 Oil Sample No. 1, which contained a preferred embodiment of the additive composition of the present invention, met all performance criteria of the tests. It is particularly noteworthy that acceptable wear protection was provided in the Sequence IIID and V-D Tests while acceptable performance was provided in the Caterpillar TO-2 and Allison C-3 Tests. Sample No. 1 is a preferred embodiment of the lubricating oil composition of the present invention.

Example II

Two other SAE 15W-40 oil formulations, which contained similar additive compositions, except for different amounts of the high-base magnesium sulfate rust inhibitor, were tested in a Sequence IID Test for rust inhibition response. These two oil formulations are identified hereinafter as Sample No. 2 and Sample No. 3. The results of these tests are presented hereinafter in Table III.

TABLE III

RUST INHIBITION RESPONSE FOR HIGH-BASE MAGNESIUM SULFONATE RUST INHIBITOR

SAE 15W-40 Sample No.	Inhibitor Conc, wt%	Sequence IID, Avg Rust (1)
1	1.10	8.57
2	1.00	8.43
3	0.92	8.30

(1) 8.5 min is passing.

These results demonstrate that a concentration of 1.10 wt% of this high-base magnesium sulfonate rust inhibitor was needed in the lubricating oil composition to provide acceptable Sequence IID performance.

Example III

Three SAE 15W-40 oil formulations were compared for their oxidation inhibition responses when subjected to the Sequence IIID Test. Sample No. 1 was the formulation presented in Table I hereinabove. Sample No. 4 had a similar composition, but the alkyl diarylamine oxidation inhibitor was replaced by a sulfurized oxidation inhibitor. In Sample No. 5, a North Sea base stock (less stable than the Mid-East stock) was employed. The results are presented hereinbelow in Table IV.

TABLE IV

OXIDATION INHIBITION RESPONSE

Sample No.	1	4	5
Alkyl diarylamine, wt%	0.35	--	0.35
Sulfurized oxidation inhibitor,wt.%	--	0.80	--
Mid-East base oil	X	X	--
North Sea base oil	--	--	X
Sequence IIID Results	pass	fail	fail
Viscosity increase (375% max)	144	738	17,166
Avg sludge (9.2 min)	9.68	9.64	9.56
Piston varnish (9.2 min)	9.42	9.44	9.23
Ring land face varnish (4.8 min)	7.82	7.65	7.03
Wear			
Max (0.0080 in)	0.0014	0.0080	0.0034
Avg (0.0040 in)	0.0007	0.0018	0.0012

Neither Sample No. 4 nor Sample No. 5 provided acceptable Sequence IIID oxidation inhibition. Additional oxidation inhibitors would be required to obtain acceptable performance.

In each sample, the mixture of primary zinc dialkyldithiophosphate and secondary zinc dialkyldithiophosphate provided acceptable wear protection.

Example IV

The amount of borated succinimide dispersant was varied in additive compositions similar to that which was used in the Sample No. 1. Each of the oil compositions containing one of these additive compositions was subjected to a Sequence V-D Test to obtain the gasoline engine cleanliness response for that formulation. The results are presented hereinbelow in Table V.

TABLE V

GASOLINE ENGINE CLEANLINESS RESPONSE

Sample No.	1	6	7	8
Succinimide, wt%	5.85	5.85	5.53	5.35
Sequence V-D	pass	pass	fail	borderline
Avg sludge (9.4 min)	9.52	9.48	9.36	9.40
Piston varnish (6.7 min)	8.20	7.81	7.82	7.91
Avg varnish (6.6 min)	8.67	8.27	8.20	8.94
Wear				
Max (2.5 mil)	0.4	0.5	0.5	0.5
Avg (1.0 mil)	0.3	0.5	0.3	0.4

When the amount of the dispersant was reduced, poorer Sequence V-D sludge protection resulted. However, acceptable wear protection was obtained in each test.

Example V

In this example, the preferred embodiments of the lubricating oil composition of the present invention, Sample No. 1 and Sample No. 6, were compared for diesel cleanliness to Sample No. 9, a similar additive composition but with a different detergent, and Sample No. 4, a similar additive composition but with a different oxidation inhibitor. The different detergent was a low base calcium sulfonate. The different oxidation inhibitor was a sulfurized oxidation inhibitor. The test method employed was the Caterpillar 1G2 Test. The results are presented hereinbelow in Table VI.

TABLE VI

DIESEL MACHINE CLEANLINESS RESPONSE

Additive Composition	Sample No.	Caterpiller 1G2 Top Groove Fill	Caterpiller 1G2 Weighted Total Demerits
Specification		80% max	300 max
Invention	1	62	271
Invention	6	54	373
Option with different Oxidation Inhibitor	4	62	258
Option with different Detergent	9	78	198

Samples Nos. 1 and 6, embodiments of the lubricating oil composition of the present invention, passed the specification for top groove fill; however, Sample No. 6 did not provide an acceptable value for weighted total demerits. On the other hand, the latter sample provided a small top groove fill. Each of the other two samples furnished acceptable diesel engine cleanliness response.

Example VI

This example demonstrates the applicability of the additive composition of the present invention to a single-grade lubricant. Sample No. 10 employed an SAE 30 weight lubricating oil derived from the Mid-East base stock obtained from the British Petroleum Company. An Acryloid 150 pour point depressant obtained from Rohm & Haas was also a component of Sample No. 10. This sample was subjected to a Sequence V-D Test. The results are presented hereinbelow in Table VII. Also shown in Table VII are the results obtained with Sample No. 1, which is a multigrade oil containing a preferred embodiment of the additive composition of the present invention.

TABLE VII

APPLICATION TO SINGLE-GRADE LUBRICANT

Component	Sample No. 1 (SAE 15W-40)	Sample No. 10 (SAE 30)
Invention Additive Composition	10.30	10.30
Viscoplex 2-50	4.10	0.00
Acryloid 150	0.00	0.20
Mid-East base stock	85.60	89.70
Results from Seqiemce V-D Test	pass	pass
Avg sludge (9.4 min)	9.52	9.63
Piston varnish (6.7 min)	8.20	8.10
Avg varnish (6.6 min)	8.67	8.64
Wear		
Max (2.5 mil)	0.4	0.6
Avg (1.0 mil)	0.3	0.4

These results shown an acceptable Sequence V-D performance for the single grade lubricating oil.

Example VII

Another embodiment of a lubricating oil composition of the present invention, Sample No. 11, was prepared and subjected to a Sequence V-D Test and a Caterpiller 1G2 Test. Results of these tests are presented hereinbelow in Table VIII. Sample No. 11 contained 795 ppm(wt) phosphorus and 190 ppm(wt) boron. The results obtained with Sample No. 1 are also provided in Table VIII. Each of these samples was a 15W-40 lubricating oil composition and each contained an embodiment of the additive composition of the present invention. Sample No. 1 contained Viscoplex 2-50, obtained from Rohm Darmstadt. Viscoplex 1-50 is a dispersant polymethacrylate viscosity index improver. Sample No. 11 contained ECA 6911, obtained from Paramins, a division of Exxon Corporation, as a viscosity index improver.

TABLE VIII

MULTI-GRADE LUBRICANT PERFORMANCE

Composition, wt.%	Sample No. 1	Sample No. 11
Additive Composition	10.30	11.00
Viscoplex 2-50	4.10	0.00
ECA-6911	0.00	7.75
Mid-East base stock	85.60	81.25
Test Results		
Sequence V-D	pass	pass
Avg sludge (9.4 min)	9.52	9.64
Piston varnish (6.7 min)	8.20	7.65
Avg varnish (6.6 min)	8.67	8.39
Wear		
Max (2.5 mil)	0.4	0.7
Avg (1.0 mil)	0.3	0.5
Caterpillar 1G2	pass	pass
Top groove fill (80% max)	62	55
Weighted total demerits (200 max)	271	282

Each of these embodiments of the lubricating oil composition of the present invention provided acceptable Sequence V-D test performance and Caterpillar 1G2 test performance.

Example VIII

Two additive compositions were prepared and were added to a Mid-East base stock to provide 15W-40 grade lubricating oil compositions. One additive composition was an embodiment of the present invention and, when added to the base oil, resulted in lubricating oil Sample No. 12. The other was a prior art additive composition and resulted in lubricating oil Sample No. 13. The primary to secondary molar ratio in the zinc dialkyldithiophosphate for Sample No. 12 was 1.7. Samples 13, 14 and 15 contained only primary zinc dialkyldithiophosphate.

Each lubricating oil composition was evaluated in Sequence 1IID, Sequence V-D, and Kombi Tests for wear performance and in Caterpillar TO-2 and Detroit Diesel Allison C-3 (15-1 plates) Tests for friction performance. The results of these tests are presented hereinafter in Table IX.

TABLE IX

COMPARISON OF FRICTION AND WEAR PERFORMANCE OF NEW AND PRIOR ART OILS

	Sample No. 12	Sample No. 13
Composition		
Phosphorus, wt%	0.08	0.11
Boron, ppm(wt)	320	200
ZDDP $1^{o}:2^{o}$ molar ratio	1.7	all 1^{o}
SEA dispersant	3	0
Succinimide dispersant	3	0
TBN	10	10
Wear Performance		
Sequence V-D	pass	pass
Max (2.5 mil)	0.5	0.9
Avg (1.0 mil)	0.4	0.8
Sequence IIID	pass	pass
Max (0.0080 in)	0.003	0.006
Avg (0.0040 in)	0.002	0.004
Kombi	pass	pass
Cam wear max (<3.0)	1.1	2.0
avg (<1.5)	0.6	1.3
Liner wear max (<1.2)	0.6	1.0
avg (<0.5)	0.2	0.2
Friction Performance		
Caterpillier TO-2	pass	pass
Stopping Time Inc (15% max)	11, 13	10, 13, 15
Detroit Diesel Allison C-3		
(15-1 plates)	pass	fail
Sliptime (0.75 max)	0.72	0.88
Torque (80 min)	89	60
Delta Torque (30 max)	13	23

TABLE IX
(Cont'd)

	Sample No. 14	Sample No. 15
Composition		
Phosphorus, wt%	0.11	0.11
Boron, ppm(wt)	200	350
ZDDP $1^\circ:2^\circ$ molar ration	all 1°	all 1°
SEA dispersant	5	5
Succinimide dispersant	0	0
TBN	10	10
Wear Performance		
Sequence V-D	Fail	--
Max (2.5 mil)	3.0	--
Avg (1.0 mil)	1.3	--
Sequence IIID	--	--
Max (0.0080 in)	--	--
Avg (0.0040 in)	--	--
Kombi	Fail	Fail
Cam wear max (<3.0)	2.8	2.4
avg (<1.5)	1.8	1.6
Liner wear max (<1.2)	0.7	0.5
avg (<0.5)	0.2	0.1
Friction Performance		
Caterpiller TO-2	--	--
Stopping Time Inc (15% max)	--	--
Detroit Diesel Allison C-3 (15-1 plates)	--	--
Sliptime (0.75 max)	--	--
Torque (80 min)	--	--
Delta Torque (30 max)	--	--

The SEA dispersant was prepared from propoxylated hexamethylenediamine and Indopol H-1500 polybutenes obtained from Amoco Chemicals Corporation. The succinimide dispersant was also prepared using Indopol H-1500 polybutenes.

These results demonstrate the superior wear performance and friction performance provided by the lubricating oil composition containing the embodiment of the additive composition of the present invention, i.e., Sample No. 12. When compared to Sample No. 13, its wear performance was equivalent to that of Sample No. 13 in the Sequence 1IID Test and better than that of Sample No. 13 in the Sequence V-D Test and the Kombi Test. Furthermore, the friction performance of Sample No. 12 was equal to that of Sample No. 13 in the Caterpillar TO-2 Test and better than that of Sample No. 13 in the Detroit Diesel Allison C-3 Test.

While the embodiment of the additive composition employed in Sample No. 12 contained both polyisobutenyl succinimide dispersant and the succinate ester-amide dispersant, use of the latter is optional in the additive composition of the present invention.

Example IX

Additional lubricating oil formulations were prepared and tested for their friction performances in the Detroit Diesel Allison C-3 Test. The lubricating oil was a 15W-40 grade material derived from a high-sulfur Mid-East base stock. The results are presented hereinbelow in Table X.

TABLE X

ADDITIONAL FRICTION PERFORMANCE

Sample No.	14	15	16	17
Component				
Viscosity index improver	8.0	8.0	8.0	8.0
Succinate ester amide	2.90	---	6.58	---
Succinimide	3.68	6.58	---	---
Mannich	---	---	---	6.58
Zinc dialkyldithiophosphate ($1^\circ:2^\circ$ molar ratio=1.7)	1.06	1.06	1.06	1.06
High-base sulfurized calcium phenate	1.30	1.30	1.30	1.30
Low-base calcium sulfonate	0.40	0.40	0.40	0.40
High-base magnesium sulfonate	1.00	1.00	1.00	1.00
High-base calcium sulfonate	0.70	0.70	0.70	0.70
Alkyl diarylamine	0.40	0.40	0.40	0.40
Diluent, SX-5W oil	0.1	0.1	0.1	0.1
Boron, ppm(wt)	226	226	226	226
DDA C-3 Test Results	pass	pass	fail	fail
Slip Time (<0.85)	0.78	0.78	0.85	0.91
Torque (>75 lb-ft)	86	84	70.5	60
Delta Torque (<30)	16	12	3.5	49
Plate batch	17	17	17	17

Sample No.	18	19	20
Component			
Viscosity Index Improver	8.0	8.0	8.0
Succinate ester amide	---	6.58	---
Succinimide	6.58	---	---
Mannich	---	---	6.58
Zinc dialkyldithiophosphate (1°:2° molar ratio=1.7)	1.06	1.06	1.06
High-base sulfurized calcium phenate	1.30	1.30	1.30
Low-base calcium sulfonate	0.40	0.40	0.40
High-base magnesium sulfonate	1.00	1.00	1.00
High-base calcium sulfonate	0.70	0.70	0.70
Alkyl diarylamine	0.40	0.40	0.40
Diluent, SX-5W oil	0.1	0.1	0.1
Boron, ppm(wt)	226	226	226
DDA C-3 Test Results	fail	fail	fail
Slip Time (<0.85)	0.82	0.81	0.92
Torque (>75 lb-ft)	66	59	49
Delta Torque (<30)	6	19	19
Plate batch	16	16	16

Samples Nos. 14, 15 and 17 contained the additive composition of the present invention. Of these, only Sample No. 17 provided unacceptable friction performance.

Example X

Additional lubricating oil formulations containing embodiments of the additive composition of the present invention were prepared and tested for wear performance in the Sequence IIID and Sequence V-D Tests and for friction performance in the Detroit Diesel Allison C-3 Friction Test. The results of these tests are presented hereinbelow in Table XI. The molar ratio of 1°:2° in the zinc dialkyldithiophosphate to phosphorus from secondary zinc dialkyldithiophosphate is about 3.9.

TABLE XI

ADDITIONAL EMBODIMENTS OF LUBRICANTS OF PRESENT INVENTION

Sample No.	19	20	21	22
Component, wt%				
Succinate ester amide	2.3	0	0	0
Succinimide	2.7	5.4	5.4	5.5
Zinc dialkyldithiphoshpate (1°:2° molar ratio=3.9)	0.9	0.9	0.9	0.9
Alkyl diarylamine	0.8	0	0	0.4
High-base sulfurized calcium phenate	1.2	1.2	1.2	1.2
Low-base calcium sulfonate	0.4	0.4	0.4	4
Sample No.	19	20	21	22
High-base calcium sulfonate	0.6	0.6	0.6	0.7
High-base magnesium sulfonate	0.9	0.9	0.9	0.9
Diluent, SX-5W oil	0.1	0.1	0.1	0.1
Sulfurized oxidation inhibitor	0	0.6	0.5	0
TBN	10	10	10	10
Phosphorus, ppm(wt)	700	690	710	670
Boron, ppm(wt)	180	160	165	160
Wear Performance				
Sequence V-D	pass	pass	pass	pass
Max (<2.5)	0.6	0.5	0.5	0.5
Avg (<1.0)	0.5	0.4	0.4	0.3
Sequence IIID	---	pass	---	pass
Max (<0.0080)	---	0.007	---	0.0014
Avg (<0.0040)	---	0.003	---	0.0007
Friction Performance				
DDA C-3 Friction	---	---	pass	---

The results of these tests show that the additive composition of the present invention provides acceptable wear performance and friction performance at substantially lower phosphorus levels and boron levels. In these tests, the Sequence V-D Test wear passes consistently. The Sequence IIID Test wear was obtained for two of the lubricating oil compositions and acceptable in each case. The Detroit Diesel Allison C-3 friction performance was obtained for Sample No. 21 and was found acceptable.

The results of the above examples indicate that the additive compositions of the present invention are effective in wear control while simultaneously accommodating friction response. The lubricating oils containing them, i.e., the lubricating oils of the present invention, provide acceptable wear performance and friction performance while minimizing the amount of phosphorus in the engine emission system.

As used herein 1° denotes primary and 2° denotes secondary.

Claims

1. An additive composition for addition to an oil of lubricating viscosity suitable for passenger car and heavy duty use comprising: (a) zinc dialkyldithiophosphate having both primary and secondary character such that the primary to secondary ratio is about 1:1 about 5:1, said mixed primary/secondary zinc dialkyldithiophosphate being present in the additive composition in amount such that a lubricating oil containing an effective amount of said additive composition has a phosphorus content of not greater than 0.1 wt %; (b) a succinimide dispersant; and (c) a total base number (TBN) such that a lubricating oil containing an effective amount of said additive composition has a TBN of at least 8.

2. An additive composition according to Claim 1, wherein the succinimide is present in the additive composition in such amount that a lubricating oil containing an effective amount of said additive composition will comprise at least about 0.5 wt % succinimide.

3. An additive composition according to Claim 1 or Claim 2, wherein said mixed primary/secondary zinc dialkyldithiophosphate is present in the additive composition in amount such that a lubricating oil containing an effective amount of said additive composition has a phosphorus content within the range of about 0.06 to about 0.09%.

4. An additive composition according to Claim 3 wherein said mixed primary/secondary zinc dialkyldithiophosphate is present in the additive composition in amount such that a lubricating oil containing an effective amount of said additive composition has a phosphorus content within the range of about 0.07 to about 0.08%.

5. An additive composition according to any preceding claim having a boron content such that a lubricating oil containing an effective amount of said additive composition has a boron content within the range of about 100 to about 600 ppm by weight of the oil.

6. An additive composition according to Claim 5 wherein the boron content is within the range of about 150 to about 350 ppm.

7. An additive composition according to any preceding claim further comprising a dispersant which comprises at least one member selected from succinate ester amide dispersants and Mannich dispersants.

8. An additive composition according to any preceding claim which comprises one or more basic compounds selected from overbased Group I and Group II metal phenates and overbased Group I and Group II metal sulfonates.

9. An additive composition according to any preceding claim having a TBN such that a lubricating oil containing an effective amount of said additive composition has a TBN which is within the range of from about 9 to about 12.

10. An additive composition according to any preceding claim wherein said succinimide is the reaction product of a polyalkylene polyamine and a long chain alkyl substituted succinic acid or anhydride.

11. An additive composition according to Claim 10 wherein the polyalkylene polyamine is TEPA.

12. An additive composition according to Claim 1 having a TBN, phosphorus and boron content such that a lubricating oil containing an effective amount of the additive composition has a TBN of about 9-11, a phosphorus content of about 0.06 to about 0.09 wt %, and a boron content of about 150 to 450 ppm (wt), said additive further comprising a succinate ester amide dispersant.

13. An additive composition for addition to a lubricating oil, comprising (a) at least one zinc dialkyldithiophosphate and (b) a succinimide dispersant wherein the total base number (TBN) of the composition is of a value such that a lubricating oil containing an effective amount of said additive composition has a TBN of at least 8, characterised in that component (a) has both primary and secondary character such that

the primary/secondary ratio is about 1:1 to about 5:1 and is present in an amount such that a lubricating oil containing an effective amount of said additive composition has a phosphorus content of not greater than 0.1 wt %.

14. A lubricating oil composition comprising a major portion of a base oil of lubricating viscosity in combination with a minor portion of an additive composition as claimed in any of Claims 1 to 13.

15. A lubricating oil composition having a major portion of a base oil of lubricating viscosity in combination with a minor portion of an additive composition, the latter comprising (a) zinc dialkyldithiophosphate having both primary and secondary character such that the primary to secondary ratio is about 1:1 to about 5:1, said zinc dialkyldithiophosphate being present in the additive composition in and amount such that a lubricating oil containing an effective amount of the additive composition has a phosphorus content of not greater than about 0.1 wt %; (b) a succinimide dispersant; and (c) a total base number (TBN) such that a lubricating oil containing an effective amount of said additive composition has a TBN of at least 8.

16. A lubricating oil composition according to Claim 15 wherein said succinimide is present in said additive composition in an amount sufficient to provide at least 0.5 wt % succinimide in said lubricating oil composition.

17. A lubricating oil composition according to Claim 15 or Claim 16 comprising a boron content of about 100 to about 600 ppm (wt).

18. A lubricating oil composition according to Claim 17 comprising a boron content within the range of about 150 ppm (wt) to about 400 ppm (wt).

19. A lubricating oil composition according to any of Claims 15 to 18 wherein said additive composition further comprises a succinate ester amide dispersant, a Mannich Dispersant or mixture thereof.

20. A lubricating oil composition comprising a base oil of lubricating viscosity, an effective amount of (a) at least one zinc dialkyldithiophosphate and (b) a succinimide dispersant and having a TBN of at least 8, characterised in that component (a) has both primary and secondary character such that the primary/secondary ratio is about 1:1 to about 1:5 and is present in an amount providing a phosphorus content not greater than 0.1 wt %.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 0500

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.4)
X	EP-A-0 131 400 (LUBRIZOL CORP.) * Page 4, line 5 - page 7, line 8; page 19, line 4 - page 22, line 30; pages 25,26; claims 1,2,5 * ---	1-20	C 10 M 163/00 // (C 10 M 163/00 C 10 M 133:52 C 10 M 137:10 C 10 M 159:16 C 10 M 159:22 C 10 M 159:24) (C 10 N 10/04 C 10 N 30:06 C 10 N 40:25 C 10 N 60:14)
X	US-A-3 190 833 (A. RHODES) * Column 1, line 15 - column 2, line 52; column 3, line 47 - column 4, line 41; examples 6,I,J; claims 1-3 * ---	1-4,8-11,13-16,20	
X	EP-A-0 113 045 (HONDA MOTOR) * Page 2; page 6, line 7 - page 9, line 29; page 12, line 5 - page 13, line 7; page 14, examples; claims 1,9,10,13-15 * ---	1-20	
A	EP-A-0 167 295 (EXXON RESEARCH AND ENGINEERING CO.) * Page 3, line 1 - page 7, line 15; page 9, lines 1-5; page 12, line 23 - page 13, line 2; page 13, line 20 - page 14, line 16; page 18; claims 1,4,5 * -----	5,6,12,17,18	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)** C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-04-1988	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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