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(54) **Titre :** COMPOSITION D'HUILE LUBRIFIANTE QUI CONTIENT DES BORATES DE METAUX ALCALINS ET PRESENTE DES PROPRIETES DE FROTTEMENT AMELIOREES

(54) **Title:** LUBRICATING OIL COMPOSITION CONTAINING ALKALI METAL BORATES WITH IMPROVED FRICTIONAL PROPERTIES

(57) **Abrégé/Abstract:**

A lubricating oil composition with improved frictional and wear performance, especially when the ratio of polysulfides is controlled, wherein said composition comprises a major amount of an oil of lubricating viscosity, at least one alkali metal borate; at least one dihydrocarbyl polysulfide component comprising a mixture of sulfides and having at least 30% dihydrocarbyl tetrasulfide or higher sulfides; at least one non-acidic phosphorus component comprised of a trihydrocarbyl phosphite; at least one dihydrocarbyl dithiophosphate; and a phosphorus component comprising a dihydrocarbyl phosphite component is disclosed.

ABSTRACT

A lubricating oil composition with improved frictional and wear performance, especially when the ratio of polysulfides is controlled, wherein said composition comprises a major amount of an oil of lubricating viscosity, at least one alkali metal borate; at least one dihydrocarbyl polysulfide component comprising a mixture of sulfides and having at least 30% dihydrocarbyl tetrasulfide or higher sulfides; at least one non-acidic phosphorus component comprised of a trihydrocarbyl phosphite; at least one dihydrocarbyl dithiophosphate; and a phosphorus component comprising a dihydrocarbyl phosphite component is disclosed.

LUBRICATING OIL COMPOSITION CONTAINING ALKALI METAL BORATES WITH IMPROVED FRICTIONAL PROPERTIES

FIELD OF THE INVENTION

The present invention relates to lubricants generally and, more specifically, to lubricants for automotive gears.

BACKGROUND OF THE INVENTION

The use of dispersed alkali metal borates in lubricant formulations is well known. The patent literature has taught the combination of an alkali metal borate with sulfur compounds and particular phosphorus compounds. See for example, U.S. Patent Nos. 4,717,490; 4,472,288; and patents cited therein. These prior art formulations suffered from shortened shelf life compared to other commercially available lubricants which do not use solid dispersions of borate. Published U.S. Patent Application No. US20060252656, filed May 4, 2005, teaches how to overcome this shortcoming by the judicious use of non-acidic phosphorus compounds. Patent Application No. US20060252656 also teaches how to maintain and improve load carrying ability by carefully balancing the ratio of tetrasulfide : trisulfide : disulfide in the lubricating composition.

SUMMARY OF THE INVENTION

The present invention provides a lubricating composition comprising an oil of lubricating viscosity having dispersed therein a minor amount of a mixture of: (a) a hydrated alkali metal borate component; (b) a dihydrocarbyl polysulfide component comprising a mixture including less than 64.5 wt.% dihydrocarbyl trisulfide, greater than 5.5 wt.% dihydrocarbyl disulfide, and at least 30 wt.% dihydrocarbyl tetrasulfide or higher polysulfides; (c) a non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3$ P, where R is a hydrocarbyl of 4 to 24 carbon atoms and (d) a dihydrocarbyl dithiophosphate derivative. Optionally, a dihydrocarbyl hydrogen phosphite component, at least 90 wt.% of which has the formula $(RO)_2$ POH, where R is a hydrocarbyl of 4 to 24 carbon atoms, may also be used in the lubricant composition.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1-5 are graphs of breakaway torque vs. gear shifting cylces of the composition of the present invention and of comparative lubricating oil compositions. Figure 1 is a graph depicting a flat slope and an acceptable break-away torque. Figure 2 is a graph depicting a negative slope with the breakaway torque gradually moving away from an acceptable range. Figure 3 is a graph depicting a flat slope but a break-away torque which is too low. Figure 4 is a graph depicting an undesirable negative slope in which the breakaway torque never quite reaches the desired torque of 2.0 Nm. Figure 5 is a graph depicting a typical commercial oil which also has a negative slope.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a gear oil additive package, a lubricating oil composition, a method of making the gear oil additive package, and a method of making the lubricating oil composition.

The Additive Package

The gear oil additive package of the present invention is an oil-soluble additive composition. The gear oil additive package may be used in a gear lubricating oil. The additive package of the present invention comprises (1) at least one hydrated alkali metal borate component; (2) at least one dihydrocarbyl polysulfide component comprising a mixture including less than about 64.5 wt% dihydrocarbyl trisulfide, greater than about 5.5 wt% dihydrocarbyl disulfide, and at least about 30.0 wt% dihydrocarbyl tetrasulfide or higher polysulfides; (3) at least one non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt% of which has the formula $(RO)_3P$, wherein R is hydrocarbyl group having 4 to 24 carbon atoms; and (4) at least one dihydrocarbyl dithiophosphate. The term “non-acidic” refers to the phosphorus contained in the component and is not meant to limit the acidic or non-acidic hydrocarbyl groups attached to phosphorus. This base mix may be combined with base oil a dialkyl phosphite, foam inhibitors, viscosity modifiers, metal deactivators, and optional detergents, dispersants, and oxidation inhibitors to form a complete lubricant formulation.

Hydrated Alkali-Metal Borates

The first additive component employed in the lubricating oil composition of the present invention is a hydrated particulate alkali metal borate. Hydrated particulate alkali metal borates are well known in the art and are available commercially. Representative patents disclosing suitable borates and methods of manufacture include: U.S. Patent Nos. 3,313,727; 3,819,521; 3,853,772; 3,907,601; 3,997,454; 4,089,790; and 6,534,450.

The hydrated alkali metal borates can be represented by the following formula:

$$M_2O.mB_2O_3.nH_2O$$

where M is an alkali metal of atomic number in the range 11 to 19, e.g., sodium or potassium; m is a number from 2.5 to 4.5 (both whole and fractional); and n is a number from 1.0 to 4.8. Preferred are the hydrated potassium borates, particularly the hydrated potassium triborate microparticles having a potassium-to-boron ratio of about 1:2.75 to 1:3.25. The hydrated borate particles generally have a mean particle size of less than 1 micron.

Dihydrocarbyl Polysulfides

The dihydrocarbyl polysulfide component employed in the present invention comprises a mixture which contains less than about 64.5 wt.%, and preferably no more than about 60.0 wt.% dihydrocarbyl trisulfide, greater than about 5.5 wt.% dihydrocarbyl disulfide, and preferably greater than about 6.0 wt% and at least about 30.0 wt.% and preferably at least 40 wt.% dihydrocarbyl tetrasulfide or higher polysulfides. Preferably, the dihydrocarbyl polysulfide mixture contains predominantly dihydrocarbyl tetrasulfide and higher polysulfides. The term "polysulfide" as used herein may also include minor amounts of dihydrocarbyl monosulfides, also referred to as monosulfide or sulfide. Generally, the monosulfide is present in relatively small amounts of less than about 1 wt.% of the total sulfur-containing compounds present. Typically, monosulfides may be present in amounts ranging from about 0.3 wt.% to about 0.4 wt.%. The monosulfides are preferably less than about 0.4 wt.% and more preferably less than about 0.3 wt.%.

The term "hydrocarbyl" includes hydrocarbon, as well as substantially hydrocarbon groups. "Substantially hydrocarbon" describes groups which contain heteroatom substituents that do not substantially alter the predominantly hydrocarbon nature of the substituent. Non-limiting examples of hydrocarbyl groups include the following: (1) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl) and alicyclic (e.g., cycloalkyl, cycloalkenyl, etc.) substituents, aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents and also includes cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical); (2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which do not substantially alter the predominantly hydrocarbon nature of the substituent and which includes groups such as, e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, and sulfoxy; (3) heteroatom substituents, i.e., substituents which will contain an atom other than carbon in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms include, for example, sulfur, oxygen, nitrogen, and such substituents containing one or more heteroatoms exemplified by pyridyl, furyl, thienyl, and imidazolyl.

In general, no more than about 2, preferably no more than 1, heteroatom substituent will be present for every 10 carbon atoms in the hydrocarbyl group. Typically, there will be no heteroatom substituents in the hydrocarbyl group in which case the hydrocarbyl group is a hydrocarbon. Preferred is an alkyl group; more preferred, the hydrocarbyl group is tertiary butyl.

The organic polysulfides may be prepared as described in U.S. Patent Nos. 6,489,721; 6,642,187; and 6,689,723, which are incorporated by reference herein.

Non-Acidic Phosphorous Components

The lubricating oil composition of the present invention also employs ~~a~~ at least two non-acidic phosphorous component. The at least two non-acidic phosphorus components, according to the present invention, are non-acidic as defined herein and, more preferably, comprise two phosphorus compounds, a trihydrocarbyl phosphite and a phosphoric acid derivative, i.e., a dihyrocarbyl dithiophosphate.

Acidic phosphorus compounds as used herein mean compounds that contain a hydrogen atom bonded directly to a phosphorus atom or a hydrogen atom bonded to a hetero atom which is in turn bonded to a phosphorus atom. Non-acidic phosphorus compounds as used herein means that the trihydrocarbyl phosphite or the dithiophosphate derivative may contain an acid group, such as a carboxylic acid group, but do not contain a hydrogen atom bonded directly to a phosphorus atom or a hydrogen atom bonded to a hetero atom which is in turn bonded to a phosphorus atom. Thus compounds having -P-H, -P-O-H and -P-S-H would be considered to be acidic, whereas the dithiophosphoric acid ester as described in U.S. Patent No. 5,922,657 would be considered non-acidic as used herein even though it has a carboxylic acid functionality.

Acidic phosphoric acid compounds may be based on a phosphorus compound as described in Salentine, U.S. Patent No. 4,575,431, the disclosure of which is incorporated by reference herein. Preferably, if an amino phosphorus compound is employed, then the amino phosphorus compound is an amine dithiophosphate (that is, an amine dithiophosphate salt). Typical dithiophosphates useful in the lubricant of the present invention are well known in the art. These dithiophosphates are those containing two hydrocarbyl groups and one hydrogen functionality, and are therefore acidic and must be neutralized for use in the present composition. The hydrocarbyl groups useful herein are preferably aliphatic alkyl groups of 3 to 8 carbon atoms.

Representative dihydrocarbyl dithiophosphates include di-2-ethyl-1-hexyl hydrogen dithiophosphate, diisoctyl hydrogen dithiophosphate, dipropyl hydrogen dithiophosphate, and di-4-methyl-2-pentyl hydrogen dithiophosphate.

Preferred dithiophosphates are dihexyl hydrogen dithiophosphate, dibutyl hydrogen dithiophosphate, and di-n-hexyl hydrogen dithiophosphate.

For use in the present invention, acidic phosphates are completely neutralized by reaction with alkylamines, as disclosed in Salentine, U.S. Patent No. 4, 575,431. Neutralization must be at least least 80% complete. For best results, neutralization should be in the range of 85% to 100%, wherein 100% neutralization refers to the reaction of one alkylamine with each acid hydrogen atom.

The amine moiety is typically derived from an alkylamine. The amine alkyl group is from 10 to 30 carbon atoms, preferably 12 to 18 carbon atoms in length. Typical amines include pentadecylamine, octadecylamine, cetylamine, and the like. Most preferred is oleylamine. When using a mixture of dithiophosphates and sulfur-free phosphates, the mole ratio of the dithiophosphates to the sulfur-free phosphates should be in the range of 70:30 to 30:70, preferably 55:45 to 45:55, and most preferably 1:1. The mole ratio of the substituted dihydrogen phosphates to the disubstituted hydrogen phosphates should be in the range 30:70 to 55:45, preferably 35:65 to 50:50, and most preferably 45:55.

The preferred non-acidic phosphoric acid derivative is a dithiophosphoric acid ester as described in Camenzind, et al., U.S. Patent No. 5,992,657. Preferably the dihydrocarbyl ester groups are alkyl as exemplified by Irgalube 353 from Ciba Specialty Chemicals.

The phosphorus component of the present invention also includes a trihydrocarbyl phosphite, which is non-acidic. Trihydrocarbyl phosphites useful in the present invention include $(RO)_3$ P wherein R is a hydrocarbyl group of about 4 to 24 carbon atoms, more preferably about 8 to 18 carbon atoms, and most preferably about 10 to 14 carbon atoms. The hydrocarbyl may be saturated or unsaturated. Preferably, the hydrocarbyl group is alkyl. More preferably, the trialkyl phosphite contains at least 90 wt.% of the structure $(RO)_3$ P wherein R is as defined above. Representative trialkyl phosphites include, but are not limited to, tributyl phosphite, trihexyl phosphite, trioctyl phosphite, tridecyl phosphite, trilauryl phosphite and trioleyl phosphite. A particularly preferred trialkyl phosphite is trilauryl phosphite, such as commercially available Duraphos TLP by Rhodia Incorporated Phosphorus and Performance Derivatives or Doverphos 53 by Dover Chemical Corporation. Such trialkyl phosphites may contain small amounts of dialkyl phosphites as impurities, in some cases as much as 5 wt.%. Preferred are mixtures of phosphites containing hydrocarbyl groups having about 10 to 20 carbon atoms. These mixtures are usually derived from animal or natural vegetable sources. Representative hydrocarbyl mixtures are commonly known as coco, tallow, tall oil, and soya.

Optionally, a dihydrocarbyl phosphite may be added to the present invention in addition to the trihydrocarbyl phosphite. Dihydrocarbyl phosphites useful in the present invention include $(RO)_2POH$ where R is as described as above. A particularly preferred dihydrocarbyl phosphite is dialkyl phosphite. More preferred, dialkyl phosphite is dioleyl hydrogen phosphite, such as commercially available Duraphos AP-240L by Rhodia Incorporated Phosphorus and Performance Derivatives. Such dialkyl phosphites may contain small amounts of impurities, in some cases as much as 6 wt.%. Preferred are mixtures of phosphites containing hydrocarbyl groups having about 10 to 20 carbon atoms.

Polyalkylene Co-oligomer

Optionally, a polyalkylene co-oligomer may be employed in the present invention. Preferred polyalkylene co-oligomers are co-oligomers of ethylene and an olefin which have no polar groups. Particularly preferred polyalkylenes are the Lucant® series of synthetic oils which may be purchased from Mitsui Chemicals (U.S.A.) Incorporated, New York, New York, or the SpectraSyn Ultra® series of synthetic oils which may be purchased from ExxonMobil Chemical Company. Typical oils in these series have kinematic viscosities (ASTM D445, @ 100°C) of 10 to 2000 cSt. Preferred oils are those having viscosities between 100 and 2000 cSt.

The Lubricating Oil Composition

The hydrated alkali metal borate, dihydrocarbyl polysulfide and non-acidic phosphorus components are generally added to a base oil that is sufficient to lubricate gears and other components which are present in automotive axles and transmissions, and in stationary industrial gear drives. Typically, the lubricating oil composition of the present invention comprises a major amount of oil of lubricating viscosity and a minor amount of the gear oil additive package.

One embodiment of the present invention comprises the combination of: (1) sodium triborate; (2) tertiary butyl polysulfide; (3) trilauryl phosphite and (4) dialkyl dithiophosphate ester in a major amount of oil of a lubricating viscosity. Optionally a polyalkylene co-oligomer is added to the lubricating oil composition.

The base oil employed may be any of a wide variety of oils of lubricating viscosity. The base oil of lubricating viscosity used in such compositions may be mineral oils or synthetic oils. A base oil having a viscosity of at least 2.5 cSt at 40°C and a pour point below 20°C, preferably at or below 0°C, is desirable. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having the desired viscosity.

Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of ethylene, polyalphaolefin or PAO oils, or oils (i.e., Fischer-Tropsch oils) prepared from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. Examples of Fischer-Tropsch oils used in the present invention include, but are not limited to, those described in U.S. Patent Publication Nos. US20060289337, US20060276355, US20040079078, and U.S. Patent Nos. 6080301, 6090989, 6165949, which are herein incorporated by reference. Other Fischer-Tropsch oils that may be employed in the present process include those oils described in pending U.S. patent applications 11/613,883 and 11/400,570, which are herein incorporated by reference. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_6 to C_{12} alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

Thus, the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. The base oil can also be a mixture of mineral and synthetic oils.

Additionally, other additives well known in lubricating oil compositions may be added to the additive composition of the present invention to complete a finished oil.

The hydrated alkali-metal borate component will generally comprise 0.1 to 20.0 wt.% of the lubricant composition, preferably 0.5 to 15.0 wt.%, and more preferably 1.0 to 9.0 wt.%. The dihydrocarbyl polysulfide component will comprise 0.1 to 10.0 wt.% of the lubricant composition, preferably 0.2 to 4.0 wt.%, and more preferably 0.25 to 3.0 wt.%. The trihydrocarbyl phosphite component will comprise 0.01 to 15.0 wt.% of the lubricant composition, preferably 0.05 to 5.0 wt.%, and more preferably 0.20 to 1.5 wt.%. The dihydrocarbyl dithiophosphate component will comprise 0.03 to 3.0 wt.% of the lubricant composition, preferably 0.07 to 1.5 wt.%, and more preferably 0.15 to 0.9 wt.%. If a dihydrocarbyl phosphite is optionally added to the lubricating oil composition, it will generally comprise 0.01 to 10.0 wt% of the lubricant composition, preferably 0.05 to 5.0 wt%, and more preferably 0.1 to 1.0 wt%.

Optionally, a polyalkylene co-oligomer may be employed in the lubricating oil composition. Preferably, the lubricating oil composition comprises from about 0.1 to 10 wt% of the polyalkene derivative. More preferred, the lubricating oil composition comprises from about 1 to 7 wt% of the polyalkylene derivative. Most preferred, the lubricating oil composition comprises from about 2 to 5 wt% of the polyalkylene derivative.

The lubricating composition described above can be made by addition of an additive package to a lubricating base oil. Generally, the lubricating oil composition will contain 1.0 to 50.0 wt.% of the additive package; preferably, the lubricating oil composition will contain 1 to 10.0 wt% of the additive package; and more preferably, the lubricating oil composition will contain 3.0 to 8.0 wt.% of the additive package.

Other Additives

A variety of other additives can be present in lubricating oils of the present invention. These additives include antioxidants, viscosity index improvers, dispersants, rust inhibitors, foam inhibitors, corrosion inhibitors, other antiwear agents, demulsifiers, friction modifiers, pour point depressants and a variety of other well-known additives. Preferred dispersants include the well known succinimide and ethoxylated alkylphenols and alcohols. Particularly preferred additional additives are the oil-soluble succinimides, oil-soluble alkali or alkaline earth metal sulfonates, and dihydrocarbyl hydrogen phosphites.

The following additive components are examples of some of the components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

1. Metal Detergents

Sulfurized or unsulfurized alkyl or alkenyl phenates, alkyl or alkenyl aromatic sulfonates, borated sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

2. Anti-Oxidants

Anti-oxidants reduce the tendency of mineral oils to deteriorate in service which deterioration is evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by an increase in viscosity. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-5-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-l-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-10-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl-.alpha.-naphthylamine, and alkylated-.alpha.-naphthylamine. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and 15-methylenebis(dibutyldithiocarbamate).

3. Anti-Wear Agents

As their name implies, these agents reduce wear of moving metallic parts. Examples of such agents include, but are not limited to, phosphates, carbamates, esters, and molybdenum complexes.

4. Rust Inhibitors (Anti-Rust Agents)

a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate.

b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

5. Demulsifiers

Addition product of alkylphenol and ethylene oxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

6. Extreme Pressure Anti-Wear Agents (EP/AW Agents)

Zinc dialky-1-dithiophosphate (primary alkyl, secondary alkyl, and aryl type), diphenyl sulfide, methyl trich lorostea rate, chlorinated naphthalene, fluoroalkylpolysiloxane, lead naphthenate, neutralized phosphates, dithiophosphates, and sulfur-free phosphates.

7. Friction Modifiers

Fatty alcohol, fatty acid, amine, borated ester, other esters, phosphates, phosphites and phosphonates.

8. Multifunctional Additives

Sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

9. Viscosity Index Improvers

Polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

10. Pour Point Depressants

Polymethyl methacrylate.

11. Foam Inhibitors

Alkyl methacrylate polymers and dimethyl silicone polymers.

12. Metal Deactivators

Disalicylidene propylenediamine, triazole derivatives, mercaptobenzothiazoles, and mercaptobenzimidazoles.

13. Dispersants

Alkenyl succinimides, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, pentaerythritols, phenate-salicylates and their post-treated analogs, alkali metal or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants.

EXAMPLES

The following Examples are illustrative of the present invention, but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

Automotive Gear Oil Examples

The additive concentrate package shown in Table 1 may be blended by any conventional method. An automotive gear lubricant of typical viscosity (8.0 – 18.0 cSt @ 100°C) grade may be blended by any conventional method with at least one base stock as shown in Table 2 to achieve the desired viscosity range. Specific mixtures of polysulfides were chosen according to the present invention to achieve desired ratios of di-, tri-, tetra- and higher polysulfides. Using mixtures of commercially available polysulfides (such as TBPS 344, TBPS 34, TBPS 454, and dialkyl disulfides available from ChevronPhillips Chemical Company), the ratios of polysulfides (that is, the relative concentrations) can be adjusted according to the present invention to achieve optimum frictional performance while maintaining improved anti-wear performance.

Table 1 - Typical Additive Packages (components in weight %)

Components	**Example 1**	**Example 2**	**Example 3**	**Example 4**
Potassium triborate dispersion	55	62	56	40
Dialkyl polysulfides	5[1]	18		32[2]
Dialkyl dithiophosphate	6.5		8	4
Trialkyl phosphite	13		15	5
Corrosion inhibitors	1.9	1.9	1.9	1.9
Succinate ester dispersant	8	8	9	8
Calcium sulfonate detergent	5	5	5	4
Foam Inhibitor	0.1	0.1	0.1	0.1
Diluent oil	5.5	5	5	5
Total weight %	100.00			100.00

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[1] The dialkylpolysulfide employed in Example 1 contained 7.3 wt% disulfide, 44.4 wt% trisulfide, and 48.3 wt% tetrasulfide or higher.

[2] The dialkylpolysulfide employed in Example 4 contained 2.8 wt% disulfide, 92.4 wt% trisulfide and 4.8 wt% tetrasulfide or higher.

		100.00	100.00	

Table 2 – Typical Gear Lubricant Blend	
Component	**Weight %**
Mineral or Synthetic Base Stocks	80 - 77
Viscosity index improver	9
Package in Table 1	6 - 9
Friction modifier	4
Pour Point Depressant	1
Total weight %	100.00

Although frictional properties of the lubricating oil can be improved by the addition of friction modifiers, the extent of the improvement is limited. Addition of too much friction modifier can lead to detrimental side effects such as loss of oxidation stability. Table 3 shows the effect on oxidation performance of adding too much friction modifier. Oxidation performance is measured by standard method CEC L-48-A-95 which measures the per cent increase in viscosity after heating the lubricant for a specified length of time. Lower per cent viscosity increase is better.

Table 3

		Lube Oil using Example 1	
	Limit	**No FM**	**0.5% FM**
Oxidation Test, CEC L-48-A-95 160°C / 192 hr % increase in viscosity @ 100°C	50% max	45	95

Frictional performance is very important to gear shifting in both manual and automatic transmissions. If the friction is too low, too much pressure must be exerted on the friction plates to achieve synchronization of the gears prior to shifting. If the friction is too high, the friction plates do not release smoothly after the shift is complete, leading to a jerky feel in the transmission.

Friction can be measured by measuring the amount of torque required to cause the friction plates in a transmission to separate after the gear shift is complete. Specifically, this type of torque is called the breakaway torque and is measured in Newton meters of force.

Specifically, breakaway torque is measured by employing a gear cone that is driven at a low rotating speed by an electric engine and gear reduction. A pneumatic cylinder with controlled compressed air pushes the synchronizing collar against the gear cone with a given axial force. Meanwhile the torque is measured. This method enables the determination of the static and dynamic friction coefficients. After release of the applied force, the torque to release the blocked synchronizing collar is determined, which is also known as the breakaway torque.

With any new gear set, there is usually an initial break-in period of about 25 gear shifting cycles before smooth shifting occurs and an average break-away torque can be measured. An ideal break-away torque after 25 cycles (new) is below 10 Nm. In addition to the desired average break-away torque value over 100 shifting cycles being close to 2.0 Nm, it is also important that the break-away torque remain relatively constant after the break-in period. This can be evaluated by looking at the slope of the break-away torque curve over time. It is desired that the curve be flat with a slope close to zero. If the slope is negative, it will lead to lower and lower break-away torque. If the slope is positive, it will lead to higher break-away torque. Neither situation is acceptable because of the changing feel of the automotive transmission to the driver.

The examples of the present invention show how a lubricating oil composition can be achieved, which meets the required frictional criteria mentioned above and produces optimum anti-wear performance, by appropriate balance of components in the lubricating oil additive package. Table 4 shows the average break-away torque after run-in for lubricating oils made as shown in Table 2 using lubricating oil additive packages shown in Table 1.

Table 4

	Target	Oil 1	Oil 2 Comp. Ex.	Oil 3 Comp. Ex.	Oil 4 Comp. Ex.	Commercial Oil
Average Break-Away Torque, Nm	2.0	2.070	1.445	0.712	2.496	1.354
Slope of Curve	flat	flat	negative	flat	negative	negative

Oil 1, prepared using the additive package of Example 1, contains an alkali metal borate, a polysulfide with the specified ratio of tetra-, tri-, and di-sulfides, a dialkyl dithiophosphate ester and a trialkyl phosphite. This particular combination of components meets all frictional requirements and requires only minimal amount of extra friction modifiers to achieve the final desired frictional properties. Oil 2, prepared using the additive package of Example 2, is a similar blend but lacks trialkyl phosphite and dialkyl dithiophosphate ester components. The resultant oil has an unacceptably low break-away torque. Oil 3, prepared using the additive package of Example 3, lacks the polysulfides which are an essential component of the present invention. Not only is the break-away torque extremely low, but the torque keeps changing leading to a negative slope which is also unacceptable. Oil 4, prepared using the additive package of Example 4, has all the basic components of Oil 1 except that the polysulfides in Oil 4 are not of the desired ratio of tetra-, tri-, and di-sulfides as specified in the claims. This leads to an unacceptably high break-away torque.

The effects described above can be seen more explicitly in Figures 1 - 5 which show the actual break-away torque measured at each cycle for Oils 1 – 5. The changes in break-away torque leading to an undesirable negative slope can be readily seen. Figure 1 is a graph depicting a flat slope and an acceptable break-away torque. Figure 2 is a graph depicting a negative slope with the breakaway torque gradually moving away from the acceptable range. Figure 3 is a graph depicting a flat slope but a break-away torque which is too low. Figure 4 is a graph depicting an undesirable negative slope in which the breakaway torque never quite reaches the desired torque of 2.0 Nm. Figure 5 is a graph depicting a typical commercial oil which also has a negative slope.

While frictional performance is important for smooth shifting in a transmission, a lubricating oil must also have acceptable anti-wear performance to protect gears. The preferred lubricating oils described in the present invention also show improved anti-wear performance. This is shown in Table 5. Anti-wear performance can be evaluated using the FZG narrow gear stage test A10/16,6R/120 which measures changes in gear tooth appearance as greater loads (stages) are placed on the gears. Thus a higher load stage result reflects better performance. In Table 5, Oil 1 prepared from additive package 1 which uses trialkyl phosphite and polysulfides with an optimum ratio of tetra-, tri-, and disulfides shows improved anti-wear performance over the other oils which lack the key components of the present invention.

Table 5

	Oil 1	Oil 2	Oil 3	Oil 4	Commercial Oil
FZG Pass Stage	10	9	9	8	9

Although used to prepare an automotive gear oil in the present example, the additive concentrate described in Table 1 may also by used to prepare industrial oils and greases as well.

Industrial Oil Example

Using the lubricating additive concentrates described in Examples 1 - 4, Table 1, industrial gear oils may be blended as shown in Table 6 by any conventional method to achieve any desired ISO viscosity range.

Table 6 – Industrial Gear Lubricant Blend	
Component	**Weight %**
Mineral or Synthetic Base Stocks	97
Packages in Table 1	2.75
Demulsifier	0.25

There are numerous variations on the present invention which are possible in light of the teachings and supporting examples described herein. It is therefore understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described or exemplified herein.

WHAT IS CLAIMED IS:

1. A lubricating oil composition comprising an oil of lubricating viscosity having dispersed therein a minor amount of a mixture of:

   (a) at least one hydrated alkali metal borate component;

   (b) at least one dihydrocarbyl polysulfide component comprising a mixture including less than about 64.5 wt.% dihydrocarbyl trisulfide, greater than about 5.5 wt.% dihydrocarbyl disulfide, and at least about 30.0 wt.% dihydrocarbyl tetrasulfide or higher polysulfides;

   (c) at least one non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3$ P, wherein R is a hydrocarbyl group having 4 to 24 carbon atoms; and

   (d) at least one dihydrocarbyl dithiophosphate.

2. The composition of claim 1 wherein said lubricating oil composition also contains a minor amount of dihydrocarbyl hydrogen phosphite, at least 90 wt.% of which has the formula $(RO)_2$ POH, wherein R is a hydrocarbyl group having 4 to 24 carbon atoms.

3. The composition of claim 1 wherein said lubricating oil composition comprises:

   (a) 0.1 to 20.0 wt.% alkali metal borate;
   (b) 0.1 to 10.0 wt.% the dihydrocarbyl polysulfide component;
   (c) 0.01 to 15.0 wt.% of a non-acidic phosphorus component; and
   (d) 0.03 to 3.0 wt% of the dihydrocarbyl dithiophosphate.

4. The composition of claim 1, wherein said alkali metal borate is a potassium or sodium triborate.

5. The composition of claim 1, wherein said trihydrocarbyl phosphite is a mixture of C_{10} to C_{20} trialkyl phosphites.

6. The composition of claim 1, wherein said dihydrocarbyl dithiophosphate is an amine dithiophosphate salt.

7. A gear oil additive package comprising a mixture of:

(a) a hydrated alkali metal borate component;

(b) a dihydrocarbyl polysulfide component comprising a mixture including less than about 64.5 wt.% dihydrocarbyl trisulfide, greater than about 5.5 wt.% dihydrocarbyl disulfide, and at least about 30.0 wt.% dihydrocarbyl tetrasulfide or higher polysulfides;

(c) a non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3 P$, where R is a hydrocarbyl of 4 to 24 carbon atoms; and

(d) at least one dihydrocarbyl dithiophosphate.

8. A gear oil additive package comprising a mixture of:

(a) a hydrated alkali metal borate component;

(b) a dihydrocarbyl polysulfide component comprising a mixture including less than 70 wt.% dihydrocarbyl trisulfide, more than 5.5 wt.% dihydrocarbyl disulfide, and at least 30 wt.% dihydrocarbyl tetrasulfide or higher polysulfides;

(c) a non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3$ P, where R is a hydrocarbyl group of 4 to 24 carbon atoms;

(d) at least one dihydrocarbyl dithiophosphate; and

(e) a phosphorus component comprising a dihydrocarbyl phosphite component at least 90 wt.% of which has the formula $(RO)_2$ POH, where R is alkyl of 4 to 24 carbon atoms.

9. A lubricating oil composition comprising a major amount of lubricating oil and a minor but effective amount of the gear oil additive package of claim 7 to improve the load carrying and frictional properties of the lubricating composition.

10. A lubricating oil composition comprising a major amount of lubricating oil and a minor but effective amount of the gear oil additive package of claim 8 to improve the load carrying and frictional properties of the lubricating composition

11. A lubricating oil composition wherein the composition contains a major amount of an oil of lubricating viscosity and from about 1.0 to about 10.0 wt.% of said gear oil additive package of claims 7 or 8

12. The gear oil additive package of claims 7 or 8, wherein said borate is a potassium or sodium triborate.

13. The gear oil additive package of claims 7 or 8, wherein said dihydrocarbyl dithiophosphate is an amine dithiophosphate salt.

14. The lubricating oil composition of Claim 1 wherein the major amount of an oil of lubricating viscosity is selected from the group comprising Group I, Group II, Group III, Group IV or Fischer-Tropsch base oils.

15. The lubricating oil composition of Claim 1 comprising a polyalkene co-oligomer.

16. The lubricating oil composition of Claim 15 comprising from about 1-20 wt% of the polyalkene co-oligomer.

17. A method of making a lubricating oil composition comprising mixing a major amount of an oil of lubricating viscosity with

(a) at least one hydrated alkali metal borate component;

(b) at least one dihydrocarbyl polysulfide component comprising a mixture including less than about 64.5 wt.% dihydrocarbyl trisulfide, greater than about 5.5 wt.% dihydrocarbyl disulfide, and at least about 30.0 wt.% dihydrocarbyl tetrasulfide or higher polysulfides;

(c) at least one non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3P$, wherein R is a hydrocarbyl group having 4 to 24 carbon atoms; and

(d) at least one dihydrocarbyl dithiophosphate.

18. A method of making a gear additive package comprising mixing

(a) at least one hydrated alkali metal borate component;

(b) at least one dihydrocarbyl polysulfide component comprising a mixture including less than about 64.5 wt.% dihydrocarbyl trisulfide, greater than about 5.5 wt.% dihydrocarbyl disulfide, and at least about 30.0 wt.% dihydrocarbyl tetrasulfide or higher polysulfides;

(c) at least one non-acidic phosphorus component comprising a trihydrocarbyl phosphite component, at least 90 wt.% of which has the formula $(RO)_3 P$, wherein R is a hydrocarbyl group having 4 to 24 carbon atoms; and

(d) at least one dihydrocarbyl dithiophosphate.

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