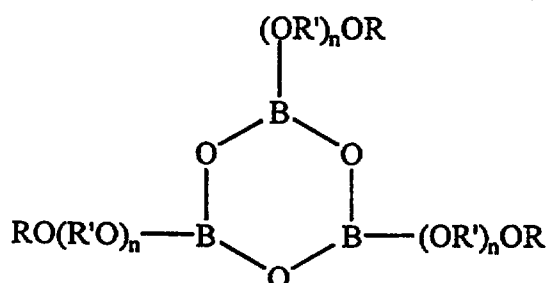


ANTIWEAR AGENTS FOR LUBRICATING COMPOSITIONS

The invention relates generally to compounds useful as antiwear additives for oleaginous compositions. In particular, the present invention relates to acyclic borate thioester and cyclic metaborate thioalkylester compounds suitable for use as antiwear additives for lubricating and power transmitting oils or fluids.

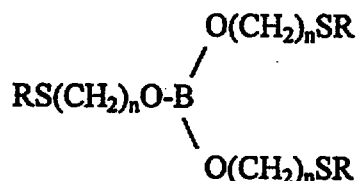
Boron-containing compounds, particularly borate esters, are known to act as antiwear agents when added to lubricating oils. EP-A-0216909 discloses antiwear agents that are esters of metaboric acid, and have the following formula:



wherein each R is independently hydrogen or a hydrocarbyl group containing from 1 to 18 carbon atoms and each R' is independently an alkylene group containing from 2 to 4 carbon atoms.

It is further well-known that sulfur-containing compounds act as anti-oxidants in lubricating compositions and can further enhance the effect of boron-based antiwear agents. The above-described European Patent Specification discloses the use of the defined metaboric acid ester in combination with an oil-soluble sulfurized organic compound in relative amounts sufficient to provide a weight ratio of sulfur to boron of from 0.5:1 to 20:1.

Antiwear agents providing both boron and sulfur are disclosed in, for example, US-A-3303130, which describes an organo thioalkyl borate antiwear agent of the general formula:

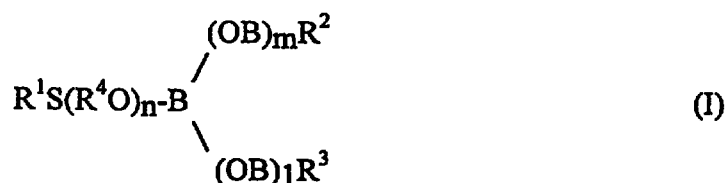


wherein R is selected from the group consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals containing 1 to 16 carbon atoms and n is an integer of 2 to 16, inclusive. These compounds are formed by reacting a thioalcohol with boric acid in a molar ratio of at least 3:1, and provide an antiwear additive having a weight ratio of sulfur to boron of 3.33:1. Similar compounds formed by reacting an alcohol, a hydroxysulfide and a boron compound, and the use thereof as a friction reducer in lubricating oil compositions are disclosed in US-A- 4492640.

Because of increased demand for lubricating oil additives and fierce competition between manufacturers, there has been a continued need for improved antiwear additives. The present invention provides an improved antiwear additive for lubricating oils which comprises a single compound that provides a relatively high weight ratio of boron to sulfur, while simultaneously providing antioxidant and friction modifier properties.

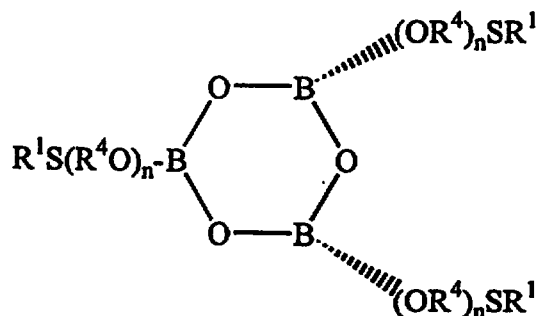
In a first aspect, the present invention provides a sulfur-containing boroester compound comprising:

an acyclic thioalkyl borate ester having the general formula (I):



wherein R^1 represents a hydrocarbyl radical having from 4 to 12 carbon atoms, R^2 and R^3 independently represent $-(\text{OR}^4)_n\text{SR}^1$ or $-(\text{OR}^4)_n\text{SR}^1\text{OH}$; R^4 represents a hydrocarbyl radical having from 1 to 6 carbon atoms; n is an integer of from between about 1 to 4; and 1 and m are independently 0, 1 or 2; or

a thioalkyl-substituted cyclic metaborate ester having the general formula (II):



wherein n , R^1 and R^4 , are defined as in formula (I); or a mixture of the acyclic thioalkyl borate ester of formula (I) and the thioalkyl-substituted cyclic metaborate ester of formula (II).

In a second aspect, the invention provides an oleaginous composition comprising, or made by admixing, a major amount of an oil of lubricating viscosity or of a power transmitting oil and a minor amount of a sulfur-containing boroester as defined in the first aspect of the invention.

In a third aspect, the invention provides a method of making an oleaginous composition comprising blending a major amount of an oil of lubricating viscosity or of a power transmitting oil and a minor amount of a sulfur-containing boroester as defined in the first aspect of the invention.

In a fourth aspect, the invention provides an additive concentrate comprising a sulfur-containing boroester compound as defined in the first aspect of the invention and an oleaginous carrier therefor.

In a fifth aspect, the invention provides a process for forming a sulfur-containing compound, such as a sulfur-containing boroester compound as defined in the first aspect of the invention, which comprises reacting at least an equivalent molar amount of boric acid with an alkoxyalkyl sulfide.

In a sixth aspect, the invention provides the use of a sulfur-containing boroester compound for improving the antiwear properties of lubricating or power transmitting oils or fluids.

The invention will now be discussed in more detail as follows.

In the sulfur-containing boroester compound of the invention, whether the acyclic or cyclic, it is preferred that R^1 represents a hydrocarbyl radical having from between 6 to 9 carbon atoms; R^4 represents a hydrocarbyl radical having from between 2 to 4 carbon atoms; and l , m and n are all 1. More preferably R^1 represents a hydrocarbyl radical having 6 carbon atoms; and R^4 represents a hydrocarbyl radical having 2 carbon atoms.

The acyclic borate thioester and cyclic metaborate thioester antiwear additives of the present invention may be the product of a condensation reaction of an alkoxyalkyl sulfide and boric acid in a molar ratio of at least about 1:1. Suitable

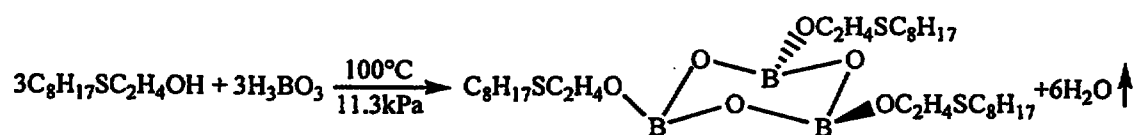
alkoxyalkyl sulfides are compounds of formula (III):



wherein R^1 and R^4 are defined as above. Preferable compounds of formula III include hydroxyethyldodecyl sulfide, 1-hydroxy-2-methyl-3-thio-decane and hydroxyethyloctyl sulfide (HEOS). The alkoxyalkyl sulfide can comprise a single compound or a mixture thereof.

When reacted with boric acid, the alkoxyalkyl sulfide may form a reaction product that can include both the acyclic compound of formula I and the cyclic compound of formula II. The reaction strongly favours formation of the cyclic metaborate thioester and the reaction product may, in fact, contain only insignificant amounts, or essentially no, acyclic borate thioester. The boric acid and hydroxalkyl sulfide may be reacted in a molar ratio of about 1: 1 or can be reacted in the presence of a slight molar excess of alkoxyalkyl sulfide (no greater than about 2: 1). The reaction may be conducted at a temperature of from 0 to 150, preferably from 60 to 120, °C and at a pressure from -100 to 0, preferably from -70 to -30, kPa.

The boric acid and hydroxalkyl sulfide may be reacted either neat or in an inert or non-participating polar solvent. Using hydroxyethyloctyl sulfide (HEOS) and boric acid reactants as examples, the reaction is believed to proceed as follows:



Lubricating oils and power transmitting oils to which the antiwear additives of the invention can be advantageously added are derived from natural oils, synthetic oils or mixtures of natural oils and synthetic oils. Suitable oils include base stocks obtained by isomerization of synthetic wax and slack wax, as well as base stocks produced by hydrocracking the aromatic and polar components of the crude.

Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene, isobutylene copolymers, chlorinated polyactenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzene);

polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); and alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as derivatives, analogues and homologues thereof.

Synthetic oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof where the terminal hydroxyl groups have been modified by (for example) esterification or etherification. This class of synthetic oils can be exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; as well as the alkyl or aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having a number average molecular weight of 1000 and diphenyl ether of polypropylene glycol having a number average molecular weight of 1000 to 1500), and mono- and poly-carboxylic esters thereof (e.g., acetic acid esters, mixed C₃ to C₈ fatty acid esters and C₁₂ oxo diester of tetraethylene glycol).

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids and alkenylmalonic acids) with an alcohol (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl isophthalate, didecyl phthalate, dielcosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic oils. These oils include tetra-ethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tertbutylphenyl) silicate, hexa-(4-methyl-2-pentoxo)-disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and diethyl ester of decylphosphonic acid), polymeric tetra-hydrofurans and poly- α -olefins.

Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. Mineral oils to which the antiwear additives of the invention can be added include all common mineral oil base stocks. This includes oils that are naphthenic or paraffinic in chemical structure. The oils may be refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural or dichlorodiethyl ether. They may also be hydrotreated or hydrorefined, dewaxed by chilling or by catalytic processing, or hydrocracked. The mineral oil may also be produced from natural crude sources or be composed of isomerized wax materials or residues of other refined processes.

The lubricating or power transmitting oils may be derived from unrefined oils, highly refined oils, re-refined oils or mixtures thereof. Unrefined oils are obtained directly from natural sources or synthetic sources (e.g., shale or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is used without further treatment. Refined oils are similar to unrefined oils except that the refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration and percolation, all of which are known to those of ordinary skill in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oil breakdown products.

The compounds of the invention can be incorporated into lubricating oils and power transmitting oils as antiwear additives in an amount from 0.001 to 5, preferably from 0.001 to 1.5, most preferably from 0.2 to 1.0, mass %. The oleaginous materials may be formulated to contain other additives such as viscosity modifiers, auxiliary antioxidants, friction modifiers, dispersants, antifoaming agents, auxiliary antiwear agents, pour point depressants, detergents, and rust inhibitors.

It will be understood that the various components of the composition, essential as well as optimal and customary, may react under the conditions of formulation, storage, or use,

and that the invention also provides the product obtainable or obtained as a result of any such reaction.

Compositions containing the above additives are typically blended into base oils in amounts sufficient to provide their normal attendant function. Representative examples of amounts in which these additives are conventionally blended to lubricating oils are as follows:

Additive	wt.% (broad)*	Wt.%(preferred)
Viscosity Modifier	.01-12	.01-4
Corrosion Inhibitor	.01-5	.01-1.5
Oxidation Inhibitor	.01-5	.01-1.5
Dispersant	.1-20	.1-8
Pour Point Depressant	.01-5	.01-1.5
Anti-Foaming Agents	.001-3	.001-0.15
Anti-Wear Agents	.001-5	.001-1.5
Friction Modifiers	.01-5	.01-3
Detergents/Rust inhibitors	.01-10	.01-3
Base Oil	Balance	Balance

*active ingredient

The additives can be incorporated into the lubricating oil in any convenient manner. Thus, they can be added directly to the oil by dispersing or dissolving same in the oil. Such blending can be performed at room temperature or at elevated temperatures. Alternatively, the additives may be first formed into concentrates comprising the additives in an oleaginous carrier therefor, which are subsequently blended with the oil. The final formulations may typically contain from 2 to 20 mass % of additives.

Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, amides of aromatic acids and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Mixtures of such dispersants can also be employed. The dispersants may optionally be post-treated with conventional reagents known in the art (see, e.g., U-S- Patent Nos. 3,254,025; 3,505,677; and 4,857,214).

The preferred dispersant for use in combination with the sulfur boron

antiwear additives of the present invention are alkenyl succinimides. These acyclic hydrocarbyl-substituted succinimides are formed with various amines, polyamines and amine derivatives, and are well known to those of ordinary skill in the art. An example of a particularly suitable dispersant is the polyisobutenyl succinimide reaction product of polyisobutylene succinic anhydride, wherein the polyisobutene moiety preferably has a number average molecular weight in the range from 500 to 5000, preferably from 800 to 2500, and an alkylene polyamine such as triethylene tetramine or tetraethylene pentamine or mixtures of polyamines containing 3 to 12 nitrogen atoms per molecule, known in the art as PAM. The use of alkenyl succinimides that have been treated with an inorganic acid of phosphorus (or an anhydride thereof) and a boronating agent are also suitable for use in combination with the compounds of the invention and are more compatible with elastomeric seals made from such substances as fluoroelastomers and silicon-containing elastomers.

Suitable antioxidants for use in combination with the additives of the present invention include amine-type and phenolic antioxidants. Examples of amine-type antioxidants include phenyl alpha naphthylamine, phenyl beta naphthylamine and bis-alkylated diphenyl amines (e.g., p,p'-bis(alkylphenyl)-amines wherein the alkyl groups each contain from 8 to 12 carbon atoms). Phenolic antioxidants include sterically hindered phenols (e.g., 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol) and bis-phenols (e.g., 4,4"-methylenebis(2,6-di-tert-butylphenol)). Phosphorus compounds, such as ZDDP, or phosphates are also commonly added to automatic transmission fluids (ATF) and passenger car motor oils (PCMO) as antioxidants. In addition to providing antiwear properties, the compounds of the present invention provide antioxidant credits to lubricating compositions, allowing for the formulation of lubricating compositions with a reduced amount, or no amount, of dedicated antioxidant additive.

Suitable friction modifiers are molecules having a polar head group and an oleophilic tail group. The polar head groups cause the molecule to be adsorbed onto the friction surface. These groups can be, but are not limited to, amines, mono- and diethoxylated amines, carboxylic acids, amides, imides, alcohols, phenols, thiols, sulfonic acids, phosphates, phosphates, esters and combinations thereof. The oleophilic groups are typically alkyl groups, normally linear alkyl groups. These alkyl groups range in carbon number from between C₈ to C₃₀, preferably from C₁₂ to C₂₀. They may be saturated or unsaturated, and may contain hetero atoms such as nitrogen or sulfur providing that the hetero atoms do not adversely affect the ability of the molecule to function as a friction modifier.

Examples of friction modifiers suitable for use with the antiwear additives of the invention include oleamide; tallow amine; diethoxylated tallow amine; N,N-bis(2-hydroxyethyl)-octadecyl amine; N,N-bis(2-hydroxyethyl)-stearyloxypropylamine; oleic acid; N,N-hydroxyethyl,N-(N',N'-bis(2-hydroxyethyl)ethylamine)-stearylamine; and the diamide produced from isostearic acid and tetraethylene pentamine.

Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil soluble viscosity modifying polymers generally have weight average molecular weights from 10,000 to 1,000,000, preferably from 20,000 to 500,000, as determined by gel permeation chromatography or light scattering methods.

Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of unsaturated dicarboxylic acid and vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene and isoprene/butadiene, as well as partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

Lubricating oils and power transmission oils incorporating the antiwear additives of the invention may also contain rust inhibitors such as nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols and anionic alkyl sulfonic acids, as well as corrosion inhibitors, such as thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof; derivatives of 1,3,4-thiadiazoles; and thio and polythio sulfenamides of thiadiazoles. Such oils may also contain an antifoamant, including polyacrylate-type antifoamants, polysiloxane-type antifoamants and fluorosilicone-type antifoamants, and detergents, such as overbased and neutral calcium sulfonate, calcium phenate, magnesium sulfonate and magnesium phenate.

The invention will now be illustrated by the following examples.

EXAMPLE 1 (SYNTHESIS)

In a 5 liter, three neck flask, 2280 grams of hydroxyethyloctyl sulfide (12 mol) and 744 grams of boric acid powder (12 mol) were combined. The flask was equipped with a stirrer, a thermometer and a condenser connected to vacuum. The flask was heated to 110 °C, and pressure within the flask reduced to -70kPa. After a few minutes water began to

evolve. The temperature in the flask was allowed to fall to 100°C at which point heating was terminated and the exothermic reaction proceeded unassisted until 2 molar equivalents of water evolved and were collected. Heat was then applied until one additional molar equivalent of water evolved and was collected.

The product was characterized by a combination of analytical techniques. HPLC separation analysis showed that one primary species was formed. ^{13}C NMR Spectroscopy indicated that the material had a characteristic sharp single resonance associated with a borated alkoxy methylene carbon at 62.8(1C) ppm relative to TMS. ^{11}B NMR Spectroscopy showed only one boro-oxygen ester signal at -3 ppm relative to H_3BO_3 . The simplicity of the carbon and boron NMR spectral result was indicative of a highly symmetric meta-boroester structure. Characteristic carbon signals associated with the incorporation of hydroxyethyloctyl sulfide were found at 33(1C), 31.8(1C), 31.2(1C), 29.6(1C), 28.8(1C), 28.6(1C), 22.4(1C) and 13.6(1C).

EXAMPLE 2

To demonstrate the ability of the compounds of the present invention to provide antiwear and antioxidant activity in lubricating oils, Additive Packages (Adpacks) A to G were formulated as shown below and added to a viscosity modified base oil at a 7 mass % treat rate to form formulated oils. The formulated oils were then subjected to LMOT testing (described below) to determine antioxidancy improvements, and FZG testing (Four Square Gear Test, ASTM D-5182) to determine antiwear activity.

Each Adpack (A to G) contained:

- 0.45% diphenylamine (antioxidant);
- 0.15% friction modifiers;
- 0.001% fluorinated silicone antifoamant;
- 3.5% of a borated PIBSA-PAM (dispersant); and
- a base stock oil.

They differed in respect of the molecular weight of the PIB in the dispersant, the presence and amount of HEOS-metaborate ester of Example 1, the presence or otherwise of 0.50% tolyl triazole (corrosion inhibitor) and the amount of base stock oil, as shown in the table below.

ADPACK	Mw of PIB	HEOS-metaborate (amount)	Corrosion Inhibitor	Basestock (amount)
A	950	0.46	-	2.439
B	950	0.46	✓	1.939
C	2200	0.46	-	2.439
D	2200	0.46	✓	1.939
E	950	-	-	2.899
F	950	0.92	-	2.899
G	2200	0.92	✓	1.479

✓ represents presence and - represent absence

All percentages and amounts are mass %

In the Adpacks, all percentages and amounts represent mass %.

The Laboratory Multiple Oxidation Test (LMOT) is used to measure the ability of lubricant compositions to resist heat and air oxidation. In the LMOT, 50cc of a test lubricant, 2.2g of iron filings, and 0.5g of a 1% copper solution (Nuodex® Copper 82 copper naphthenate in mineral spirits made into a 1% solution by dissolution of Nuodex 8% copper in I00NLP oil (Exxon Chemical)). At a temperature of $150^{\circ}\text{C} \pm 2^{\circ}\text{C}$, air is passed through the sample ($25\text{cc} \pm 2\text{cc}/\text{min.}$). One drop per day of the sample lubricant is placed on a blotter until sludge appears. The results of the LMOT are presented in terms of days until sludge is observed (days to failure).

Table 1 below summarises the results.

TABLE 1

	A	B	C	D	E	F	G
Viscosity at 100°C (mm ² s ⁻¹)	8.2	8.2	8.8	8.9	8.0	8.6	10
LMOT at 320°F (160°C) (days to failure)	8.5	9	11	10	7	11	11
FZG (failure stage)	---	---	---	10	8	11	12

As shown by the data of Table 1, the addition of adpack D, containing 0.46 mass % HEOS metaborate ester, to the base stock oil improved the FZG by two load stages compared with an oil formulated without the borate ester (Adpack E). The use of additional HEOS metaborate ester (Adpacks F and G) led to further improvement in antiwear properties. The results of the LMOT testing display the ability of the HEOS metaborate ester to simultaneously function as an antioxidant. Specifically, the data regarding Adpacks A to D, containing 0.46 HEOS metaborate ester, demonstrate an increased LMOT of 1.5 to 3 days compared with the oil formulated without the additive of the invention (Adpack E). The addition of Adpack F or G, which contained 0.92 mass % of the HEOS metaborate ester, provided a four day increase in the LMOT result compared with the composition formulated with Adpack E.

EXAMPLE 3

To demonstrate the results achieved when the additives of the invention are co-formulated with commonly used phosphorus-based additives, three oil compositions were formulated to contain 0.31 mass % HEOS metaborate ester and either 0.30 mass % triphenylphosphate (TPP) (Adpack H); 0.16 mass % of mixed phosphites (Adpack I); or 0.19 mass % dibutyl phosphite (DBP) (Adpack

J). The three formulated oils were subjected to FZG and LMOT testing. The results are shown below:

TABLE 2

	H	I	J
Viscosity At 100°C (mm ² s ⁻¹)	8.03	7.99	7.99
LMOT At 320°F (160°C) (days to failure)	10.5	9	10.5
FZG (failure stage)	9	10	12

The data of Table 2 demonstrate that an adpack containing HEOS metaborate ester (0.31 mass %), co-formulated with phosphorus-based friction modifiers, simultaneously provide antiwear and antioxidant properties in formulated oils.

EXAMPLE 4

The antiwear properties of HEOS metaborate (0.31 wt.%) dispersant combinations (PIBSA PAM (950 Mw polyisobutylene)) (3.5 wt.%), in which the HEOS-metaborate ester in an automatic transmission fluid (K) were compared with a fully formulated reference ATF (L) (containing no phosphorus-based, or other antiwear additives) in the industry standard Ford MERCON Vickers Pump Test (Ford Motor Company, MERCON Automatic Transmission Fluid Specification for Service, March 5, 1987). The strong antiwear performance of the borate ester-dispersant combination, shown below in Table 3, was surprising given that the ATF contained no other antiwear additives. The data of Table 4 compare the measured Vickers Pump wear for the additized oil with the industry standards.

TABLE 3

<u>Additive Combination</u>	<u>FZG Failing Load Stage</u>
K	13
L	8

TABLE 4

<u>ATF Fluid Wear Result</u>	<u>GM Dextron 111* Pass/Fail Limit</u>
12 mg Total Wear	15 mg maximum Total Wear

* Hydra-matic Division, General Motors Corp.

EXAMPLE 5

To demonstrate the antiwear performance of the HEOS metaborate ester and dispersant combination in passenger car motor oils (PCMO), a PCMO containing 3.5 wt.% of a standard PIBSA-PAM dispersant (M) was compared with a PCMO containing the same dispersant and 0.28 wt.% HEOS-metaborate ester (N).

Corrosive wear with the two samples was compared using the industry standard L38 Wear Test (ASTM D-5119), the results being provided below in Table 5. As the data of Table 5 demonstrate, the addition of only 0.28 wt.% of the antiwear additive of the invention provided an approximately 50% improvement in the antiwear results.

TABLE 5

<u>Additive</u>	<u>L38 Wear Results (mg)</u>
M	56.7
N	25.8

EXAMPLE 6

Lubricating oils are typically required to meet industry standards for oxidation performance. Antioxidants are normally added into these oils to prevent the

oxidative degradation that normally occurs during usage. In PCMO and ATF lubricants, phosphorus compounds, such as ZDDP or phosphates, are often used for this purpose. The following tests demonstrate that the antioxidant effect of the HEOS metaborate ester antiwear additive of the present invention is sufficiently high to allow the formulation of an oil without an additional ZDDP or phosphite antioxidant.

An ATF-containing Adpack N (described in Example 5) was subjected to a Ford MERCON Aluminum Beaker Oxidation Test (ABOT) (Ford MERCON method BJ110-4). The results achieved are compared with the industry standard limits in Table 6

TABLE 6

ABOT	Result with Adpack N	Industry Limit
Δ total acid no. (TAN)	1.28	<4.0
% viscosity increase @ 250hrs.	8.89	<40%
Diff IR @ 250hrs.	22.2%	<40%
% pentane insol @ 250hrs.	0.53	<1.0
Cu Strip @ 300hrs.	3b	3b max

EXAMPLE 7

The frictional properties of lubricating oils play a significant role towards improving fuel economy in automobiles. Use of friction reducers allows formulators to adjust the coefficient of friction to meet these needs. A combination of a HEOS metaborate ester and dispersant was found to provide excellent friction reducing characteristics. To demonstrate these friction-reducing effects, a reference oil fully formulated with dispersant (5.5 wt.%), antifoamant, detergent, phosphorus-based antiwear/antioxidant and demulsifier additives, but containing no friction reducer, was compared with the same oil further formulated with 2.11 wt.% HEOS metaborate ester and 7.69 wt.% dispersant (Adpack O) using a High Frequency Reciprocal Rig(HFRR) test.

In the HFRR test, a metal disc is affixed to a platen within a bath. Opposite the platen, there is provided a vibrator arm to which a mass of 400g is attached. A metal ball is affixed to the end of the vibrator arm. A sample of a lubricating oil is pipetted into the bath, immersing the disc, and the vibrator arm is lowered so that the ball contacts the disc. The vibrator arm is then vibrated at a frequency of 20Hz, with a stroke of 1000 microns. After each five minute period the temperature of the oil sample is increased 20°C (6 steps from 40°C to 140°C).

The disc is then removed from the platen, and the wear scar caused by contact with the ball is measured (diameters X and Y) using an optical microscope provided with a calibrated graticule.

The results are shown below.

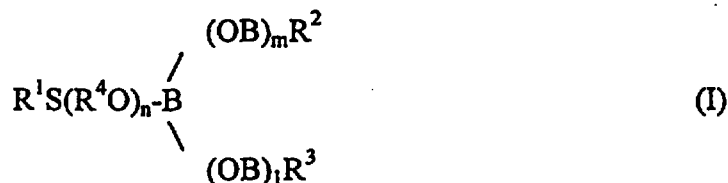
TABLE 7

<u>Temperature (°C)</u>	<u>Ref. Oil</u>	<u>Ref. Oil + Adpack 0</u>
40	0.12	0.099
60	0.126	0.111
80	0.133	0.115
100	0.133	0.115
120	0.134	0.116
140	0.135	0.119



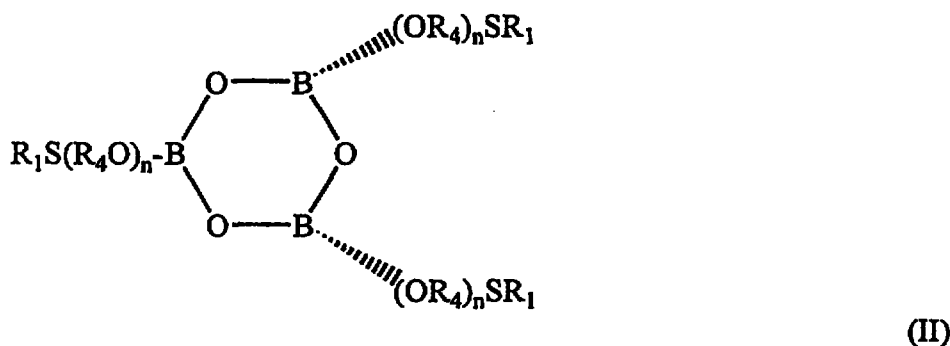
Claims

1. A sulfur-containing boroester compound comprising:
an acyclic thioalkyl borate ester having the general formula (I):



wherein R^1 represents a hydrocarbyl radical having from 4 to 12 carbon atoms, R^2 and R^3 independently represent $-(\text{OR}^4)_n\text{SR}^1$ or $-(\text{OR}^4)_n\text{SR}^1\text{OH}$; R^4 represents a hydrocarbyl radical having from 1 to 6 carbon atoms; n is an integer of from 1 to 4; and l and m are independently 0, 1 or 2; or

a thioalkyl-substituted cyclic metaborate ester having the general formula (II):



wherein n , R^1 and R^4 , are defined as in formula (I); or

a mixture of the acyclic thioalkyl borate ester of formula (I) and the thioalkyl-substituted cyclic metaborate ester of formula (II).

2. The sulfur-containing boroester compound as claimed in claim 1 wherein R^1 represents a hydrocarbyl radical having from 6 to 9 carbon atoms; R^4 represents a hydrocarbyl radical having from 2 to 4 carbon atoms; and l , m and n are all 1.

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3. The sulfur-containing boroester compound as claimed in either of the preceding claims wherein R^1 represents a hydrocarbyl radical having 6 carbon atoms; and R^4 represents a hydrocarbyl radical having 2 carbon atoms.
4. An oleaginous composition comprising, or made by admixing, a major amount of an oil of lubricating viscosity or of a power transmitting oil, and a minor amount of a sulfur-containing boroester compound as claimed in any of claims 1 to 3.
5. A method of making an oleaginous composition comprising blending a major amount of an oil of lubricating viscosity or of a power transmitting oil and a minor amount of a sulfur-containing boroester compound as claimed in any of claims 1 to 3.
6. The oleaginous composition or method as claimed in claims 4 or claim 5 wherein the sulfur-containing boroester compound comprises from between 0.001 to 5, such as 0.02 to 1, mass % of the composition.
7. The oleaginous composition or method as claimed in any of claims 4 to 6, wherein R^1 represents a hydrocarbyl radical having from 6 to 9 carbon atoms; R^4 represents a hydrocarbyl radical having from 2 to 4 carbon atoms; and l , m and n are 1.
8. The oleaginous composition or method as claimed in claim 7 wherein R^1 represents a hydrocarbyl radical having 6 carbon atoms; and R^4 represents a hydrocarbyl radical having 2 carbon atoms.
9. The oleaginous composition or method as claimed in any of claims 4 to 8 wherein the oil is a synthetic oil or a natural oil.
10. The oleaginous composition or method as claimed in any of claims 4 to 9 further comprising one or more dispersants, viscosity modifiers, corrosion inhibitors, pour point depressants, anti-foaming agents, anti-wear agents, friction modifiers, detergents and rust inhibitors.

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11. The oleaginous composition or method as claimed in claim 10 wherein the dispersant is a reaction product of polyisobutylene succinic anhydride and a hydrocarbyl polyamine.
12. An additive concentrate comprising a sulfur-containing boroeaster compound as claimed in any of claims 1 to 3 and an oleaginous carrier therefor.
13. A process for forming a sulfur-containing boroeaster compound which comprises reacting at least an equivalent molar amount of boric acid with an alkoxyalkyl sulfide.
14. The process as claimed in claim 13, wherein the said boric acid and alkoxyalkyl sulfide are reacted at a temperature within the range between 0 to 150, such as 60 to 120, °C and at a pressure within the range of -100 to 0, such as -70 to -30, kPa.
15. The process as claimed in claim 13 or claim 14 wherein the boric acid and the alkoxyalkyl sulfide are reacted in the absence of a solvent.
16. The process as claimed in any of claims 13 to 15 wherein the alkoxyalkyl sulfide is hydroxyethyloctyl sulfide, hydroxyethyldodecyl sulfide, or 1-hydroxy-2-methyl-3-thio-decane.
17. The process as claimed in any of claims 13 to 16 wherein the sulfur-containing boroeaster compound is as claimed in any of claims 1 to 3.
18. The product formed by the process as claimed in any of claims 13 to 17.

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