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3,480,548

ALKALINE EARTH METAL POLYBORATE CARBONATE OVERBASED ALKALINE EARTH METAL SULFONATE LUBE OIL COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A lubricating oil composition comprising hydrocarbon lubricating oil and an amount sufficient to impart detergent properties thereto of an additive consisting of an oil soluble normal alkaline earth metal hydrocarbon sulfonate and an alkaline earth metal polyborate alkaline earth metal carbonate in colloidal-like dispersion in said composition. The lubricating oil composition is prepared by reacting a lubricating oil dispersion of an alkaline earth metal carbonate and alkaline earth metal hydrocarbon sulfonate with a boron compound selected from the group consisting of boric acids, boron oxides and aqueous alkyl esters of boric acids.

BACKGROUND OF INVENTION

Field of invention

This invention is in the field of art relating to fluent compositions specialized and designed for use between two relatively moving surfaces in contact therewith for reducing friction therebetween and preserving the surface. The lubricant compositions of the invention contain an organic acid salt and an inorganic compound other than water and those of a kind which can react with any organic acid radical of any compound present containing such radical so as to form an organic acid salt and other than inorganic compounds or free elements in plants or animal matter.

PRIOR ART

Normal oil soluble alkaline earth metal sulfonate-oil dispersed alkaline earth metal carbonate combinations, that is, alkaline earth metal carbonate overbased (as hyperbasic) alkaline earth metal sulfonates have been employed in lubricating oil detergent compositions because of their ability to reduce formation of sludge or varnish deposits and their effectiveness to counteract the harmful effects of the acidic products of oil degradation. Further, if sludge is formed these overbased sulfonates function to maintain it in a dispersed state throughout the lubricating oil medium. An undesirable characteristic of the carbonated overbased sulfonate is that under severe conditions it tends to accelerate oxidation of the oil and thereby undesirably cause a material change in the viscosity of the lubricant composition as well as corrosion of the metal surface being lubricated. Examples of lubricating oil compositions containing the alkaline earth metal carbonate overbased alkaline earth metal sulfonate are found in U.S. 3,057,896 and 3,312,618.

Hereinbefore and hereinafter the term "overbased" denotes excess equivalents of alkaline earth metal moiety over the number of equivalents of sulfonic moiety, said excess contributed by the inorganic salt components of the additive. Further, the term "normal" refers to an alkaline earth metal ratio of 1 and "alkaline earth metal ratio" is the ratio of the number of equivalents of alkaline

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earth metal moiety to the number of equivalents of sulfonic acid moiety.

SUMMARY OF INVENTION

We have discovered, and this constitutes our invention, lubricating oil compositions containing a novel additive which not only functions as an effective detergent but has substantially improved oxidation stability and anti-corrosive properties, particularly in the field of reducing rust especially of ferrous metals. More particularly, our invention is directed to a lubricating oil composition comprising between about 10 and 99.9 wt. percent of a lubricating oil and between about 0.1 and 90 wt. percent of an additive consisting of oil soluble alkaline earth metal hydrocarbon sulfonate and a colloidal-like dispersion of an alkaline earth metal polyborate coated alkaline earth metal carbonate hereafter known as "boronated overbased alkaline earth metal sulfonate," said additive having an alkaline earth metal ratio of between about 1.5:1 and 40:1 and a boron to alkaline earth metal mole ratio of between about 1:10 and 4:1, a boron to alkaline earth metal carbonate mole ratio of between about .05:1 and 10:1, and said sulfonate derived from an oil soluble hydrocarbon sulfonic acid of an average molecular weight between about 300 and 2000. The boronated overbased alkaline earth metal sulfonate is prepared by contacting in a hydrocarbon lubricating oil medium an alkaline earth metal carbonated overbased sulfonate, hereafter known as "overbased alkaline earth metal sulfonate" with a boron compound selected from the group consisting of boron oxide, boron acid and aqueous boron acid ester at a temperature of between about 50 and 250° C., in reactant quantities sufficient to result in a boron to alkaline earth metal mole ratio of between about 0.1:1 and 4:1 and a boron to carbonate mole ratio of between about .05:1 and 10:1.

DETAILED DESCRIPTION OF THE INVENTION

The structural arrangement of the compositions of the invention is a hydrocarbon lubricating oil medium containing alkaline earth metal sulfonate (alkaline earth metal ratio of 1) and colloidal-like particles of alkaline earth metal polyborate coated alkaline earth metal carbonate; the normal sulfonate functions to disperse ordinarily oil insoluble particles of boronated alkaline earth metal carbonate in to a colloidal dispersion in a lubricating oil medium. In the preparation of the composition of the invention when the colloidal dispersion of alkaline earth metal sulfonate and alkaline earth metal carbonate is boronated within the context of the invention, a portion, e.g., between about 1 and 90 wt. percent of the alkaline earth metal carbonate is converted into alkaline earth metal polyborate which forms a coating on the outside of the remaining individual colloidal alkaline earth metal carbonate particles. The polyborate in combination with the carbonate appears to function to enhance the oxidation stability and anti-corrosion property of the overall additive combination. It is further theorized the anti-corrosive properties are enhanced by the fact that the polyborate alkaline earth metal carbonate particles due to the polyborate coating releases acid neutralizing alkaline earth metal carbonate more slowly in the lubricating oil systems thereby rendering a more even and thereby a more effective release of the acid neutralizing carbonate.

The alkaline earth metal polyborate formed in the composition of the invention is of the empirical formula $MB_xO_{1.5x+y+1}H_{2y}$ where M is an alkaline earth metal moiety such as Ca^{++} , Ba^{++} and Mg^{++} , x is an average integer from 1 to 20 or higher usually from 3 to 8, 2x is greater than y and y is an average integer equal to or greater than zero. The integers, x and y, are defined as average since in the preparation of the composition of the

invention a complex mixture of alkaline earth metal polyborates are normally formed such as alkaline earth metal (e.g. calcium) type metaborates, diborates, tetraborates, hexaborates and etc. The polyborates may be described as metal salts of polyboric acid, the polyboric acids being described as condensed acids formed by the removal of at least some water from a condensation of two or more moles of orthoboric acid. Polyborates and polyboric acids are further described in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," volume 5, pgs. 1-149, 47 (1929),

As heretofore stated, the lubricating oil compositions of the invention consist of hydrocarbon lubricating oil comprising about 10 and 99.9 wt. percent of the composition and between about 0.1 and 90 wt. percent of the boronated overbased alkaline earth metal sulfonate, said boronated overbased alkaline earth metal sulfonate in the compositions of the invention having a boron to alkaline earth metal mole ratio of between about 1:10 and 4:1, and alkaline earth metal ratio of at least 1.5 and up to 40 and higher, a boron to alkaline earth metal carbonate mole ratio of between about .05:1 and 10:1, said sulfonate derived from a hydrocarbon sulfonic acid of a molecular weight between about 300 and 2000. These values normally result in an additive consisting of a normal alkaline earth metal sulfonate content of 10-98 wt. percent and alkaline earth metal polyborate content between about 1 and 70 wt. percent and an alkaline earth metal carbonate content of between about 1 and 70 wt. percent.

The higher additive concentration lubricating oil compositions of the invention, e.g., those containing between about 25 and 90 wt. percent of boronated overbased alkaline earth metal sulfonate are generally the direct product in the manufacture of the lubricant composition and are referred to in the art as concentrates. The compositions of the invention are prepared as a concentrate primarily to facilitate interaction between reactants and for obvious storage and handling reasons as well as versatility in making up diluted lubricant compositions most suitable for use under automotive conditions. In automotive lubricating oil compositions the boronated overbased alkaline earth sulfonate normally constitutes between about 0.1 and 10 wt. percent, preferably between 0.1 and 5 wt. percent, of the composition and are prepared by diluting the concentrate with additional hydrocarbon lubricating oil and adding other lube oil additives, if desired. In any event, whether the lubricant compositions of the invention be in their concentrate or dilute form, they will have at least some lubricating ability with improved detergent, anti-oxidant and anti-corrosive properties.

In the finished lubricating oil composition other additives may be included. These other additives can be any of the standard suitable pour depressors, additional sludge dispersant, antioxidants, silver corrosion inhibitors, viscosity index improvers and friction modifiers. Exactly what other additives are included in the finish oil and the particular amount thereof will of course depend on the particular use and conditions desired for the finished oil products.

The lubricant compositions are prepared by contacting in a hydrocarbon lubricating oil medium an overbased alkaline earth metal sulfonate having an alkaline earth metal ratio of at least about 1.5:1 and up to 40:1 and higher with a boron compound selected from the group consisting of boron oxide, boron acids and aqueous boron acid esters at a temperature between about 80 and 200° C., preferably between about 100 and 175° C. in sufficient reactant quantities to form a reactant mole ratio of boron to alkaline earth metal of between about 0.1:1 and 4:1, a boron to alkaline earth metal carbonate mole ratio of between about 10:1 and 0.05, and said contacting normally conducted for a period between about 1 and 7 hours. Advantageously, in the reaction the hydrocarbon lubricating oil medium normally constitutes between about 25 and 75 wt. percent which results in a concentrate product hav-

ing a lube oil content of between 20 and 80 wt. percent and a boronated overbased alkaline earth metal sulfonate content of between about 80 and 20 wt. percent. If desired, the final product may be purified by standard means such as filtration through diatomaceous earth to remove non-colloidal solid bodies and subjecting the filtrate to vacuum distillation to remove volatile impurities and by-products.

In a preferred procedure, the reaction is conducted in an inert gas (e.g. nitrogen) atmosphere and during the reaction volatile by-product materials are preferably substantially removed such as water and carbon dioxide. Further, an inert azeotroping agent can be included in the reaction system, e.g., in an amount between about 5 and 50 wt. percent, in order to facilitate the removal of the water by-product. Examples of such azeotroping agents are any of the inert liquid agents which form an azeotrope with water having an azeotrope distillation point within the reaction temperature range. Specific examples of suitable azeotroping agents are toluene, xylene, isooctane, and decane. To further facilitate the removal of the volatile by-products of the reaction inert gas (e.g. nitrogen) may be blown through the reaction mixture, e.g. at a rate of between about 0.05 and 50 s.c.f.h./lb. mixture.

The alkaline earth metal carbonate overbased alkaline earth metal sulfonate reactant in the manufacture of the compositions of the invention are derived from oil soluble hydrocarbon sulfonic acids, having an average molecular weight of between about 300 and 2000. The oil soluble sulfonic acids are in turn derived from natural (e.g. petroleum) or synthetically manufactured hydrocarbons and mixtures thereof. Typical oil soluble sulfonic acids contemplated herein include petroleum sulfonic acids such as the mahogany sulfonic acids, alkylated aromatic sulfonic acids, petrolatum sulfonic acids, paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, polyalkylene (e.g. polyisobutylene) sulfonic acids, mono- and polywax or other alkyl substituted benzene sulfonic acids, mono- and polywax or other alkyl substituted naphthelene sulfonic acids, mono- and polywax or other alkyl substituted cycloalkyl (e.g. cyclohexyl) sulfonic acids and mixtures of the foregoing. Preferably, the sulfonic acids employed will have been derived from the sulfonation of a petroleum fraction or a synthetic hydrocarbon or mixtures thereof. It will be a monosulfonic acid having a molecular weight between about 450 and 550, most preferably about 500 but the molecular weight of the sulfonic acid can be as low as about 300 or as high as about 2000 for making sufficiently oil soluble sulfonates. By oil soluble we mean soluble in a conventional mineral lubricating oil fraction to the extent of at least about 5 wt. percent.

In ordinary instances, the oil soluble sulfonic acid employed in the preparation of the alkaline earth metal carbonate overbased alkaline earth metal sulfonate reactant is supplied from sulfonation of petroleum or synthetic hydrocarbon oil stocks and is diluted by an oily water immiscible organic medium which for most cases will be a petroleum hydrocarbon or synthetic hydrocarbon lubricating oil fraction, a gas oil fraction or even a lighter cut such as benzene or a solvent naphtha in order to facilitate its handling and interaction with reactants.

The aforescribed oil soluble sulfonic acid precursor is converted into the alkaline earth metal carbonate overbased alkaline earth metal sulfonate reactant by any standard procedures known in the art. For example, one procedure calls for first forming the normal alkaline earth metal sulfonate. This can be accomplished by first reacting the sulfonic acid with an alkali metal base such as alkali metal hydroxide to form alkali metal sulfonate, and then reacting the formed alkali metal sulfonate with an aqueous alkaline earth metal salt solution, e.g. alkaline earth metal chloride to form the normal alkaline earth metal sulfonate. Another way to form the normal alkaline earth metal sulfonate precursor is to directly neutralize

the oil soluble sulfonic acid with an alkaline earth metal hydroxide, oxide or hydrated oxide. The resultant salt is a normal alkaline earth metal sulfonate. The thus formed normal alkaline earth metal sulfonate can then be overbased by the addition of alkaline earth metal hydroxide, oxide or hydrated oxide and the resultant mixture is blown with carbon dioxide to convert the additionally added inorganic alkaline earth metal compound to alkaline earth metal carbonate.

Alternatively to the foregoing procedure, the overbased alkaline earth metal sulfonate reactant component may be prepared by combining in a lubricating oil medium sulfonic acid and an alkaline earth metal hydroxide, oxide or hydrated oxide in excess of what is required to neutralize the sulfonic acid and blowing the resultant mixture with carbon dioxide at a temperature to form the overbased alkaline earth metal sulfonate.

Methods of preparing the alkaline earth metal carbonate overbased alkaline earth metal sulfonate reactants contemplated herein are further described in U.S. 3,057,896, 3,027,325, 3,105,049, 3,152,991, 3,155,616, 3,223,630, 3,325,494, 3,256,186, 3,262,880 and 3,312,618.

Specific examples of the overbased alkaline earth metal sulfonate reactants contemplated herein are calcium carbonate overbased calcium sulfonates having a calcium metal ratio of 1.5, 12 and 18, barium carbonate overbased barium sulfonate having a barium metal ratio of 1.1, magnesium carbonate overbased magnesium sulfonate having a magnesium metal ratio of 12, said sulfonates derived from oil soluble petroleum and synthetic hydrocarbon alkylate sulfonic acid mixture of a molecular weight of about 500.

The boron reactants useful in the preparation of the boronated overbased alkaline earth metal sulfonate component of the lubricant compositions of the invention are illustrated by boric acid, tetraboric acid, metaboric acid, boron oxide, boron oxide hydrate, boronic acids (i.e., alkyl-BOH₂) and aryl-B(OH)₂ and esters of such boron acids. Specific examples of boronic acids include methyl boronic acids, phenyl boronic acids, cyclohexyl boronic acids, p-heptylphenyl boronic acid, dodecyl boronic acid, and octadecyl boronic acid. The boron acid esters include especially mono-, di-, and triorganic esters of boric acid or a boronic acid with alcohols or phenols such as, e.g., methanol, ethanol, isopropanol, cyclohexanol, cyclopentanol, 1-octanol, 2-octanol, dodecanol, behenyl alcohol, oleyl alcohol, stearyl alcohol, benzyl alcohol, 2-butylcyclohexanol, ethylene glycol, propylene glycol, trimethyl-ene glycol, 1,3-butanediol, 2,4-hexanediol, 1,2-cyclohexanediol, 1,3-octanediol, glycerol, pentaerythritol, diethylene glycol, carbitol, 2-methoxyethanol, diethylene glycol, tripropylene glycol, phenol, naphthol, p-butylphenol, o,p-diheptylphenol, p-cyclohexylphenol, 2,2-bis(p-hydroxyphenyl)propane, polyisobutene (W.M. 1500) substituted phenol or chlorophenol-m-nitrophenol, 6-bromooctanol, and 7-ketodecanol. Lower alcohols, 1,2-glycols and 1,3-glycols, i.e., those having less than about 8 carbon atoms are especially useful for preparing boron acid esters for the purpose of this invention. Methods of preparing boron esters are known and disclosed in the art (such as Chemical Reviews, pp. 959-1064, vol. 56). One method involves the reaction of boron trichloride with 3 moles of alcohol or a phenol to yield a tri-organic borate. Another method involves the reaction of boric oxide with alcohol or a phenol. Still another method involves the direct esterification of tetraboric acid with an alcohol or a phenol. Another method involves the direct esterification of boric acid with a glycol to form, e.g., a cyclic alkylene borate.

Hereinafter and hereinbefore by the term "aqueous" modifying "boron esters" we mean sufficient water present to hydrolyze the boron esters, e.g., a mole ratio of water to boron ester of between about 1.5:1 and 100:1.

Suitable base oils useful in the composition of the invention as well as diluent in the manufacture of said compositions and the alkaline earth metal carbonate over-

based alkaline earth metal sulfonate reactant component include a wide variety of hydrocarbon lubricating oils such as naphthenic base, paraffinic base and mixed base mineral oils. In addition, hydrocarbon lubricating oils derived from coal products and synthetic hydrocarbon oils, e.g., alkylene polymers such as polypropylene and polyisobutylene of a molecular weight of between about 250 and 2500 are also contemplated. Advantageously, hydrocarbon lubricating base oils having an SUS viscosity at 100° F. between about 50 and 2000 are employed.

Specific examples of the boronated overbased alkaline earth metal sulfonates contemplated herein are a calcium polyborate coated calcium carbonate calcium sulfonate having a boron/calcium mole ratio of 1:1, a B/carbonate ratio of 3:1 and a calcium metal ratio of 18; barium polyborate-barium carbonate overbased barium sulfonate having a barium metal ratio of 1.1, a B/Ba ratio of 1.2:1 and a B/CO₃ ratio of ~10:1; and a magnesium polyborate-magnesium carbonate having a magnesium metal ratio of 10, a B/Mg ratio of 1.2:1 and a B/carbonate ratio of 6:1, the sulfonates being derived from an oil soluble petroleum sulfonic acid of a molecular weight of 475±25.

The following examples further illustrate the invention but are not to be considered as limitations thereof.

EXAMPLE I

This example illustrates the preparation of the compositions of the invention.

To a 3 liter reactor fitted with a variable speed stirrer, means for heating, means for collecting volatile overhead and purging with gases, there was charged 1431 grams of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate derived from an oil soluble hydrocarbon sulfonic acid of an M.W. of about 475 having an analysis as follows:

Test:	Result
Ca, total, percent wt.	13.2
Ca, basic, percent wt.	12.5
Sulfur, percent wt.	1.1
Total base number (HClO ₄)	351
Visc. SUS at 210° F.	118
Sp. grav. 60/60° F.	1.14
Ca metal ratio	18
Diluent oil, percent weight	~50
Carbonate, wt. percent	16.6

The foregoing charge lubricating oil dispersion was heated to 150° C. under a nitrogen atmosphere whereupon a slurry of 333 grams (5.4 moles) of powdered boric acid, 236 grams paraffinic lube oil (100 SUS at 100° F.), and an additional 236 grams of the aforescribed charge lubricating oil dispersion was introduced into the reaction flask over a 1.5 hour period keeping the reaction temperature at 150° C., the rate of addition being controlled in a manner to avoid foaming over. During this addition, both carbon dioxide and H₂O were continuously vented from the reactor. After the boric acid slurry addition the reactor temperature was raised to 175° C. for a 2-hour period with nitrogen blowing to remove any water by-products.

To the reaction mixture 79 grams of diatomaceous earth were added and the resultant mixture was held for 10 minutes at 175° C. with agitation. Through a 32 gram filter cake of diatomaceous earth said resultant mixture was filtered under a nitrogen atmosphere at 175° C. and 1559 grams of filtrate were obtained. The remaining filter cake was washed with 1000 mls. of isooctane and the isooctane was stripped by aspirator at 100° C. to give an additional 333 grams of filtrate which equals a combined filtrate product of 1892 grams. The filtrate product was analyzed and determined to be a lubricating oil composition containing ~50 wt. percent

boronated calcium carbonate overbased calcium sulfonate giving the following specific analysis:

Test:	Result
Ca, total, wt. percent -----	10.4
Ca, basic (HClO ₄), wt. percent -----	9.6
Boron, wt. percent -----	2.25
CO ₂ , wt. percent -----	7.3
Ca metal ratio -----	18
B/Ca mole ratio -----	0.8:1
B/CO ₂ mole ratio -----	1.14:1
TBN (HClO ₄) -----	269
Sp. grav. 60/60° F. -----	1.1259
Kin. visc., 210° F., cs. -----	14.22

EXAMPLE II

To a 2 liter reactor fitted with a mechanical stirrer, means for heating and purging with gases, there was charged 500 g. of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate derived from an oil soluble hydrocarbon sulfonic acid as described in Example I along with 50 g. of powdered boric acid. The reaction mixture was heated to 150° C. under an atmosphere of nitrogen and held at this temperature for 1 hour while allowing both CO₂ and H₂O off gases to escape from the system. The reaction mixture was then filtered at 150° C. through a filter cake of diatomaceous earth to afford 485 g. of additive concentrate containing 53 wt. percent of a calcium polyborate coated calcium carbonate overbased calcium sulfonate of the following analysis:

Test:	Result
Calcium, total, wt. percent -----	13.1
Calcium, basic, wt. percent -----	11.0
Boron, wt. percent -----	1.59
TBN (HClO ₄) -----	308
CO ₂ , wt. percent -----	9.5
B/Ca mole ratio -----	0.45:1
B/CO ₂ mole ratio -----	0.68:1

EXAMPLE III

To a 5 liter three necked flask equipped with mechanical stirrer, heater, gas inlet tube and vent to the atmosphere, there was charged 800 g. of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate described in Example I and 80 g. of powdered boric acid. The mixture was slowly heated to 150° C. under a nitrogen atmosphere to avoid excessive foaming and held at this temperature for two hours. An additional 80 g. of powdered boric acid was then charged to the hot reactor, and the reaction held at 150° C. for 3 additional hours. Filtration through a filter cake of diatomaceous earth gave 668 g. of a clear oil additive concentrate containing 56 wt. percent calcium polyborate coated calcium carbonate overbased calcium sulfonate of the following analysis:

Test:	Result
Ca, total, wt. percent -----	11.6
Ca, alkaline, wt. percent -----	10.7
S, wt. percent -----	0.77
CO ₂ , wt. percent -----	7.6
Boron, wt. percent -----	2.6

EXAMPLE IV

To a 2 liter three necked flask equipped with stirrer, gas inlet tube, thermocouple and vent to the atmosphere, there was added 500 g. of a hydrocarbon lubricating oil solution containing 50 wt. percent of a calcium carbonate overbased calcium sulfonate previously described in Example I and 75 g. of powdered boric acid. The temperature was brought to 150° C. over a three hour period under a blanket of nitrogen to avoid foaming. After heating at 150° C. for two hours an additional 50 g. powdered boric acid was added and heating continued two more hours. A third and final addition of 50 g. powdered boric acid was

made, and the reactor held at 150° C. for two hours with a vigorous nitrogen gas purge to remove volatile by-products. Filtration yielded 434 g. product directly, and an additional 97 g. were obtained by solvent washing of the filter cake as in Example I. The product was an oil additive concentrate containing 60 wt. percent of a calcium polyborate coated carbonate overbased calcium sulfonate with the following analysis:

Tests:	Result
Ca, total, wt. percent -----	10.5
Ca, basic, wt. percent -----	9.1
Boron, wt. percent -----	5.5
CO ₂ , wt. percent -----	5.7

EXAMPLE V

This example illustrates the preparation of a calcium polyborate coated carbonate overbased sulfonate, a composition of this invention, which specifically contains calcium carbonate in its crystalline vaterite state in the product.

To a 1 liter reactor fitted with stirrer, heater, and gas inlet tube, there was charged 200 g. of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate (vaterite) overbased calcium sulfonate derived from an oil soluble hydrocarbon sulfonic acid of a M.W. of about 500 and having the following analysis:

Tests:	Result
Calcium, total, wt. percent -----	12.2
TBN (HClO ₄) -----	266
Sulfur, wt. percent -----	2.1
CO ₂ , wt. percent -----	2.1
Ca metal ratio -----	~11
Diluent oil, wt. percent -----	~50

To the charged reactor 80 g. of a paraffinic lubricating oil of 45 SUS viscosity at 210° F. were added along with 30 g. of powdered boric acid and this was heated at 150° C. for 1.5 hours under a nitrogen atmosphere. Additional boric acid, 25 g., was added and the mixture heated at 150° C. for 1.5 hours. A third boric acid charge of 25 g. was made and after 2 hours heating with a nitrogen purge the material was filtered to yield 226 g. of an oil solution containing 46% of a calcium polyborate coated carbonate overbased calcium sulfonate of the following analysis:

Tests:	Result
Calcium, total, wt. percent -----	7.9
Calcium, basic, wt. percent -----	7.1
Boron, wt. percent -----	2.87
CO ₂ , wt. percent -----	5.6
SUS, 210° F. -----	82

Infrared spectroscopy and X-ray diffraction analyses of the product indicated the CaCO₃ remained in the crystalline form. A combination of X-ray line broadening techniques and electron microscopy revealed that the average CaCO₃ crystallite size had decreased by about 10% but that the average core particle size had increased about 25% indicating only the outer layer of the CaCO₃ had reacted to give a calcium polyborate shell.

EXAMPLE VI

This example illustrates the preparation of a product containing a high B/CO₂ mole ratio.

To a 3 liter reactor equipped as previously described there was charged 1500 g. of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate of the following analysis:

Tests:	Result
Ca, total, wt. percent -----	4.75
Ca, basic, wt. percent -----	2.79
TBN -----	76.7
CO ₂ , wt. percent -----	4.4

Boric acid, 166 g., was charged to the reactor and the temperature brought to 150° C. After heating at 150° C.

with nitrogen gas purge to aid in water and by-product removal, 16 grams of diatomaceous earth were added and the product filtered. The product, 1384 g., was identified as a lubricating oil containing calcium polyborate coated calcium carbonate calcium sulfonate of the following analysis:

Tests:	Result
Ca, total, wt. percent -----	4.6
Ca, basic (HClO ₄), wt. percent -----	2.67
Boron, wt. percent -----	2.15
CO ₂ , wt. percent -----	0.3
B/CO ₂ mole ratio -----	29.2:1
B/Ca mole ratio -----	1.73:1
Ca metal ratio -----	1.5

EXAMPLE VII

This demonstrates the use of hydrocarbon solvent to assist in the preparation of materials designated by this invention.

To a 2 liter flask equipped with mechanical stirrer, thermocouple, gas inlet tube and Dean-Stark trap, there was charged 200 grams of a lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate described in Example I, 40 grams of powdered boric acid and 150 ml. of toluene. The reactants were heated at reflux for three hours during which time 12 ml. of water were azeotropically removed. This represents essentially 1 mole of water lost for each mole of boric acid charged. The mixture was stripped of solvent and volatiles at a temperature of 150° C. under water aspirator vacuum. Filtration yielded 166 g. of a 57 wt. percent calcium polyborate coated calcium carbonate overbased calcium sulfonate solution in lubricating oil of the following analysis:

Tests:	Result
Ca, total, wt. percent -----	11.9
Ca, basic (HClO ₄), wt. percent -----	11.9
Boron, wt. percent -----	3.14
CO ₂ , wt. percent -----	7.8
Kin. vis. 210° F., cs. -----	21.8
B/CO ₂ mole ratio -----	1.5:1
B/Ca mole ratio -----	0.97:1

EXAMPLE VIII

This example demonstrates the use of a polar protonic solvent to aid in the preparation of compositions expressed in this invention.

To a 1 liter reactor equipped as in Example VII, there was added 200 grams of an oil solution containing 50 wt. percent of the calcium carbonate overbased calcium sulfonate described in Example I along with 40 grams of powdered boric acid, 150 ml. toluene and 150 ml. of 2-methoxyethanol. The reactants were heated at reflux for 1 hour, volatile components and by-products were removed by stripping under a nitrogen gas purge at 175° C., and then filtered to give 165 g. of a lubricating oil containing calcium polyborate coated calcium carbonate overbased calcium sulfonate of the following analysis:

Tests:	Result
Ca, total, wt. percent -----	10.8
Ca, basic, wt. percent -----	10.0
Boron, wt. percent -----	2.78
CO ₂ , wt. percent -----	7.4

EXAMPLE IX

This example demonstrates the use of metaboric acid (HBO₂) as a reactant in preparing a composition of this invention.

To a 2 liter reactor equipped with stirrer, gas inlet tube and vent to atmosphere, there was charged 1000 grams of the calcium carbonate overbased calcium sulfonate solution in oil described under Example I along with 142 grams of metaboric acid. The reaction mixture was heated for 2 hours at 150° C. with nitrogen gas purge to assist in removal of volatile products. Ten grams of diatomaceous

earth were admixed and the sample filtered hot to afford 929 grams of a lubricating oil composition containing calcium polyborate coated calcium carbonate overbased calcium sulfonate of the following analysis:

Tests:	Results
Ca, total, wt. percent -----	12.0
Ca, basic, wt. percent -----	11.4
Boron, wt. percent -----	2.89
CO ₂ , wt. percent -----	9.2
Kin. vis. 210° F., cs. -----	58.6

EXAMPLE X

This example demonstrates the use of an ester of boric acid to prepare a composition of this invention.

To a 1 liter reactor equipped with stirrer, gas inlet tube, thermocouple and condenser, there was charged 200 grams of a hydrocarbon lubricating oil solution containing 50 wt. percent calcium carbonate overbased calcium sulfonate described in Example I, 200 ml. of isooctane, 67 grams of tri-n-propylborate and 12.8 grams of water. The mixture was heated at total reflux for two hours and stripped of volatiles to 160° C. with vigorous nitrogen blowing. The reaction mixture was filtered to give 74 grams of product. The remainder along with the filter cake was washed with approximately 500 ml. of isooctane, filtered through a bed of diatomaceous earth and stripped free of solvent to give 98 grams of additional product. The product was identified as a lubricating oil containing calcium polyborate coated calcium carbonate overbased calcium sulfonate of the following analysis:

Tests:	Result
Ca, basic, wt. percent -----	11.0
Boron, wt. percent -----	1.8
CO ₂ , wt. percent -----	9.5

EXAMPLE XI

This example demonstrates the preparation of a lubricating oil composition containing magnesium polyborate coated magnesium carbonate overbased magnesium sulfonate.

To a 12 liter reactor fitted with a stirrer, means for heating, means for purging with gases and measuring temperature, there was charged 4292 grams of a hydrocarbon lubricating oil solution containing 50 wt. percent magnesium carbonate overbased magnesium sulfonate derived from an oil soluble hydrocarbon sulfonic acid of a M.W. of about 500 having an analysis as follows:

Tests:	Result
Mg, total, wt. percent -----	6.6
Mg, basic (HClO ₄ titration) wt. percent -----	6.4
S, wt. percent -----	1.1
CO ₂ , wt. percent -----	7.6
TBN -----	281
Mg metal ratio -----	12

The foregoing charge lubricating oil dispersion was heated to 150° C. under a nitrogen atmosphere whereupon a slurry of 1000 grams (16 moles) of powdered boric acid, 708 grams paraffinic lube oil (100 SUS at 100° F.) and an additional 708 grams of the aforescribed charge lubricating oil dispersion was introduced into the reaction flask over a 3.25 hour period keeping the reaction temperature at 150° C., the rate of addition being controlled in a manner to avoid foaming over. During this addition both CO₂ and H₂O were continuously vented from the reactor. After the boric acid slurry addition the reactor temperature was raised to 175° C. for a 2-hour period with nitrogen blowing to remove any water and volatile by-products.

To the reaction mixture 63 grams of diatomaceous earth were added and the resultant mixture was held about 10 minutes at 175° C. with stirring. The resultant mixture as filtered through a 97 gram filter cake of diatomaceous earth and 5730 grams of filtrate obtained. The filtrate was analyzed and determined to be a lubricat-

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ing oil composition containing ~50 wt. percent magnesium polyborate coated magnesium carbonate overbased magnesium sulfonate giving the following specific analysis:

Tests:	Result
Mg, total, wt. percent -----	5.9
Mg, basic, wt. percent -----	5.1
CO ₂ , wt. percent -----	4.4
S, wt. percent -----	0.90
Boron, wt. percent -----	2.01
B/Mg mole ratio -----	0.77
B/CO ₃ mole ratio -----	1.8

EXAMPLE XII

This example demonstrates the preparation of a barium polyborate coated barium carbonate overbased barium sulfonate.

To a 1 liter reactor equipped with stirrer, gas inlet tube, vent to atmosphere and means for heating, there was charged 180 grams of a hydrocarbon lubricating oil solution containing 50 wt. percent barium carbonate overbased barium sulfonate derived from an oil soluble hydrocarbon sulfonic acid of a M.W. of about 450 having an analysis as follows:

Tests:	Result
Barium, wt. percent -----	14.6
CO ₂ , wt. percent -----	1.5
Barium metal ratio -----	1.1
Kin. vis., 210° F., cs. -----	61.4
Diluent oil, wt. percent -----	~50

To the foregoing charge there was added 20.0 grams of powdered boric acid and the reactor was then heated to 150° C. for about two hours under a slow purge of nitrogen gas to remove volatile by-products. The mixture was then filtered through a cake of diatomaceous earth to give 150 grams of a hydrocarbon lubricating oil product containing about 54 wt. percent of a barium polyborate coated barium carbonate overbased barium sulfonate. The product gave the following analysis:

Tests:	Result
Barium, total, wt. percent -----	12.4
Boron, wt. percent -----	1.18
S, wt. percent -----	1.2
B/Ba mole ratio -----	1.2

EXAMPLE XIII

This example illustrates the detergent effect and superiority of the lubricant oil compositions of the invention.

An example of the composition of the invention and a comparative composition were tested in the well known Caterpillar 1-H engine test (Caterpillar Tractor Co.) which is described in FTMS 79a-346 BT and Caterpillar Information Letter No. 46. Performance of the test lubricant is judged by examination of the piston for percent coverage by lacquer and percent of the groove filled with coke. The higher the percentage the less effective the lubricating oil compositions from a detergent aspect.

The comparative composition employed is a standard SAE 30 type formulation comprising 92.3 wt. percent paraffinic lubricating oil, 6 wt. percent of an additive combination of 6 parts ethoxylated polyisobutane thiophosphonic acid, 2 parts calcium carbonate overbased calcium sulfonate (derived from an about 500 M.W. hydrocarbon sulfonic acid) of a total base number of 300+2 parts lube oil diluent, 0.4 wt. percent zinc isopropyl 1,3-dimethylbutyl dithiophosphate, 1.1 wt. percent butylmethacrylate - stearylmetacrylate copolymer, 0.2 wt. percent octadecylmethacrylate - stearylmetacrylate copolymer and 100 p.p.m. silicon antifoam concentrate. The base composition had an SUS viscosity at 100° F. of 540 and at 210° F. of 68.

The composition representative of the composition of

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the invention was the duplicate of the comparative composition except for the calcium carbonate overbased calcium sulfonate there was substituted the boronated version thereof, i.e., calcium polyborate coated calcium carbonate overbased calcium sulfonate wherein the B/Ca mole ratio was 1:1 and the B/CO₃ mole ratio was 3:1.

The lacquer and cake buildup on the engine found in the engine using the comparative composition after 120 hours running time was not equaled in the engine using the representative composition of the invention until after 480 hours of running time.

EXAMPLE XIV

This example illustrates the superior anti-corrosion properties of the compositions of the invention.

Three lubricating compositions were tested in the Ford Rust Test.

The Ford Rust Test comprises lubricating a 1964 Ford 289 CID V-8 engine. The engine is run under the following test conditions:

Description:	Value
Duration, hours -----	45
Speed, r.p.m. -----	1500
Load, BHP -----	28
Fuel pressure, p.s.i. -----	4.5
Fuel/air ratio -----	0.085
Crankcase ventilation -----	1
Temperature, °F.:	
Jacket out -----	90
Oil gallery -----	110
Rocker arm covers -----	60
Intake air -----	110

¹ Vented to atmosphere.

At the end of the 45 hour period the various engine parts are inspected, namely, the external and internal area valve lifters and push rods. A rating of between 0 and 10 is assigned. A rating of 10 represents no rusting and a rating of 0 indicates heavy rusting of the entire surface.

Two of the test compositions (A and B) were representative of the composition of the invention and the third was a comparative composition (C). Both the representative and comparative compositions were essentially identical except the compositions of the invention contained a calcium polyborate coated calcium carbonate overbased calcium sulfonate, whereas the comparative composition C contained calcium carbonate overbased calcium sulfonate. Analysis of the test compositions is found below in Table I:

TABLE I

Test Composition	A	B	C
Percent wt. Ca, total.	0.0175	0.0175	0.0175
Percent wt. Ca, basic.	0.0170	0.0170	0.0170
TBN (HClO ₄)	4.5	4.5	4.5
Ca Metal Ratio	18	18	18
Percent wt. B	0.023	0.093	0
B/Ca mole ratio	0.5:1	2.6:1	-----
B/CO ₃ mole ratio	0.68:1	3.9:1	-----

The Ford Rust Test results are reported below in Table II:

TABLE II

Composition:	Rust Rating		
	External	Internal	Push Rod
A	9.6	7.4	7.2
B	9.7	9.5	9.0
C	9.4	4.4	5.3

As can be seen from the foregoing, the compositions of the invention have substantially greater rust preventing properties than lubricating oil compositions containing the unboronated overbased alkaline earth metal sulfonate.

EXAMPLE XV

This example illustrates the superior antioxidant properties of the compositions of the invention.

Three test compositions were subjected to oxidative conditions. Compositions AA and BB are representative of compositions of the invention consisting of lubricating oil containing calcium polyborate coated calcium carbonate overbased calcium sulfonate. Composition CC represents a comparative composition. Composition CC is a lube oil containing calcium carbonate overbased calcium sulfonate. In all compositions the calcium sulfonate was derived from a hydrocarbon sulfonic acid of a molecular weight of about 475. These compositions are described as follows:

TABLE III

Tests	AA	BB	CC
Paraffin Lube oil, wt. percent	97.41	95.0	97.72
Percent wt. Additive Concentrate*	2.59	5.0	2.28
Percent wt. Ca, Total	0.30	0.30	0.30
Percent wt. Ca, Basic	0.28	0.28	0.28
Percent wt. S	0.025	0.025	0.025
Percent wt. B	0.077	0.13	0
Ca Metal Ratio	18	18	18
TBN (HClO ₄)	7.8	7.8	7.8
Visc. SUS at 100° F	353	342	349
B/CA mole ratio	0.95:1	1.6:1	0

*About 50 wt. percent lube oil.

Eight hundred ccs. of each of the above test compositions were heated in an oil bath to 300° F. and oxygen at a rate of 3 liters per hour were introduced there-through while stirring the compositions at 300 r.p.m. At the end of 216 hours the heated air-blown products were analyzed for viscosity increase. The greater the viscosity increase the greater the degree of oxidation of the composition in question. The test results are reported below in Table IV:

TABLE IV

Composition:	Percent viscosity increase
AA -----	82
BB -----	32
CC -----	113

As can be seen from the foregoing the boronated carbonated overbased sulfonate compositions AA and BB are substantially more resistant to oxidation than the non-boronated composition CC.

We claim:

1. A method of producing lubricant composition comprising between about 10 and 99.9 wt. percent hydrocarbon oil of a lubricating viscosity and between about 0.1 and 90 wt. percent of a boronated alkaline earth metal carbonate overbased alkaline earth metal sulfonate prepared by the process consisting essentially of contacting a hydrocarbon lubricating oil medium, an alkaline earth metal carbonate overbased alkaline earth metal sulfonate having an alkaline earth metal ratio between about 1.5 and 40 with a boron compound selected from the class consisting of boron oxide, boron acids and aqueous boron acid esters at a temperature between about 80 and 200° C. utilizing a boron to alkaline earth metal reactant mole ratio of between about 0.1:1 and 4:1 and boron to alkaline earth metal carbonate reactant mole

ratio of between about .05:1 and 10:1, said sulfonate derived from an oil soluble hydrocarbon sulfonic acid of a molecular weight between about 300 and 2000, said hydrocarbon lubricating oil, said alkaline earth metal carbonate overbased alkaline earth metal sulfonate and said boron compound being present in sufficient quantities to form said lubricant composition.

2. A method in accordance with claim 1 wherein said alkaline earth metal is calcium and said hydrocarbon sulfonic acid has an average molecular weight between about 450 and 550 and said boron compound is boric acid.

3. A method in accordance with claim 1 wherein said contacting is conducted under an inert gas atmosphere and wherein volatile reaction by-products are substantially removed as formed.

4. A method in accordance with claim 1 wherein said alkaline earth is calcium, said boron compound is boric acid, said sulfonic acid is of a molecular weight between about 450 and 550, said contacting conducted in an inert gas atmosphere while substantially removing volatile by-products as formed therein by blowing said reaction mixture with inert gas.

5. A method in accordance with claim 1 wherein said alkaline earth is magnesium, and said boron compound is boric acid, and said sulfonic acid has a molecular weight between about 450 and 550.

6. A method in accordance with claim 1 wherein said alkaline earth metal is barium, said boron compound is boric acid and said sulfonic acid is of a molecular weight between about 450 and 550.

7. The lubricant composition produced by the method of claim 1.

8. The lubricant composition produced by the method of claim 2.

9. The lubricant composition produced by the method of claim 3.

10. The lubricant composition produced by the method of claim 4.

11. The lubricant composition produced by the method of claim 5.

12. The lubricant composition produced by the method of claim 6.

13. A lubricant composition produced by the method of claim 1 wherein said alkaline earth metal carbonate overbased alkaline earth metal sulfonate and said boron compound are present in a quantity sufficient to produce said composition containing between about 0.1 and 10 wt. percent of said boronated alkaline earth metal carbonate overbased alkaline earth metal sulfonate.

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