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(57) Abstract

An additive mixture for grease compositions and gear lubricants has been developed. The additive mixture comprises at least one metal-containing composition and at least one sulfurized organic compound. This mixture has been found to impart an unexpected improvement in extreme pressure properties to grease compositions and gear lubricants.

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GREASE AND GEAR LUBRICANT COMPOSITIONS COMPRISING AT LEAST ONE METAL-CONTAINING COMPOSITION AND AT LEAST ONE SULFURIZED ORGANIC COMPOUND

BACKGROUND OF THE INVENTION

Field of Invention

This invention relates to grease and gear lubricant compositions and particularly to additives for improving extreme pressure properties of grease and gear lubricant compositions. More specifically, the invention relates to these lubricant compositions comprising at least one metal-containing composition and at least one sulfurized organic compound. It is the combination of the two components making up the additive mixture that imparts the improved load bearing characteristics of the grease or gear lubricant composition.

State of the Art

Additives of the type of the present invention have found use in lubricants formulated for a very specific utility, specifically in metal working processes. Such utility is disclosed in U.S. Patent No. 4,505,830 and in one of the applicant's co-pending application, U. S. Serial No. 777,475 filed September 18, 1985.

A similar type of additive comprising a mixture of zirconium salt of a carboxylic acid or mixture of carboxylic acids and at least one oil-soluble sulfur-containing extreme pressure agent which additive mixture is useful for lubricants is disclosed in U.S. Patent No. 4,171,268.

Halogenated disulfide compounds which are useful as extreme pressure additives for lubricating oils are disclosed in U.S. Patent No. 4,228,021.

In U.S. Patent No. 4,283,294, an additive mixture of Group II A, metal overbased salts and Group I A, metal overbased salts, which may also further comprise an organo sulfur antioxidant compound, is disclosed. It is disclosed in this patent that the lubricating oil compositions containing such additive mixtures are useful in marine diesel engines.

It is disclosed in U.S. Patent Nos. 4,394,276 and 4,394,277 that various sulfur-containing alkane diols may be formulated with lubricating oils to effectively reduce fuel consumption in an internal combustion engine.

U.S. Patent No. 3,384,586 discloses various non-Newtonian colloidal disperse systems and materials which are useful in lubricating oils for imparting improved rheological properties of the oil.

It is pointed out that none of the foregoing disclosures teach the additive mixture of the present invention to be useful in grease or gear lubricant formulations and more particularly, that they impart unexpectedly high weld points when evaluated for extreme pressure properties.

SUMMARY OF THE INVENTION

In accordance with the present invention, grease compositions exhibiting improved extreme pressure properties have been developed.

Further, in accordance with the present invention, it has been discovered that an additive mixture of a metal-containing composition, preferably a basic alkaline earth or alkali metal salt material, and at least one sulfurized organic compound have been found to unexpectedly improve the extreme pressure properties of grease compositions.

Still further, in accordance with the present invention, it has been discovered that the additive mixture of the present invention may also be useful in gear lubricant compositions.

Still further in accordance with the present invention, a method for improving the load bearing characteristics of grease and gear lubricant compositions is provided.

These and other aspects of the invention will become clear to those skilled in the art upon the reading and understanding of the specification.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that the load bearing characteristics of a grease composition and a gear lubricant may be unexpectedly improved by formulating these compositions with a specific additive mixture. Specifically, the additive mixture comprises:

(A) a metal-containing composition; and

(B) at least one sulfurized organic compound.

The (A) component of the additive mixture may be a Newtonian material or a non-Newtonian colloidal disperse system which comprises solid metal-containing colloidal particles predispersed in a disperse medium of at least one inert, organic liquid and a third component selected from the class consisting of organic compounds which are substantially soluble in the disperse medium. The molecules of the organic compound, i.e., the third component, are characterized by containing polar substituents and hydrophobic portions in the molecule. Such systems are disclosed and described in U.S. Patent No. 3,384,586, discussed above, which disclosure relating to such systems is incorporated herein by reference solely for such disclosure. The metal-containing composition of the present invention are preferably salts of alkaline earth metals or alkali metals and at least one acidic organic compound. These salt materials are among those art recognized metal-containing compositions that may be also described by such terms of the art as "overbased", "superbased" and "hyperbased" salts, which terms are recognized as being generic to the materials of the present invention as well as other classes of metal containing materials that have been employed as detergents and/or dispersants in lubricating oil compositions. The method for their preparation is commonly referred to as "overbasing". The term "metal ratio" is also used to define the quantity of metal in these salts or complexes relative to the quantity or organic anion, and is defined as a ratio of the number of equivalents of metal to the number of equivalents thereof which would be present in a normal salt based upon the usual stoichiometry of the compounds involved. For the purposes of the present invention, a metal ratio of 5 or higher is preferred. Such metal-containing compositions are also disclosed in U.S. Patent Nos. 4,505,830, discussed above, and 4,230,586, which disclosures relating solely to such metal-containing compositions are incorporated herein by reference.

The particular metal cation which makes up the metal-containing composition is not particularly critical to the present invention. It is, however, intended to exclude such zinc salts as zinc dialkyldithiophosphate and zinc dialkyldithiocarbamates and similar zinc salts from the scope of this invention. Otherwise, practically any other metal salt is useful for the preparation of component (A) of the additive mixture. More specifically, useful metal compounds in preparing the overbased materials of the additive mixture of the present invention are normally the basic salts of metals in Group I-A and Group II-A of the Periodic Table as well as the transition metals with the exception of zinc within the Group-B elements of the Periodic Table. Such metals include Na, K, Mg, Ca, Ba, Ti, Cr, Fe, Mo, Cu and the like. Also, Group IV-A and Group V-A metals such as Pb, Sn and Sb may be useful within the scope of the present invention.

The alkaline earth metals are preferred for the purposes of the present invention as basic alkaline earth metal salts and include principally calcium, magnesium, barium and strontium, with calcium salts being the most preferred because of their availability and relatively low cost. The most useful acidic organic compounds are carboxylic acids, sulfonic acids, organic phosphorus acids and phenols.

The sulfonic acids are preferred for use in the preparation of component A. They include those represented by the formulas $R^1(SO_3H)_r$ and $(R^2)_xT(SO_3H)_y$. In these formulas, R^1 is an aliphatic or aliphatic-substituted cycloaliphatic hydrocarbon or essentially hydrocarbon radical free from acetylenic unsaturation and containing up to about 60 carbon atoms. When R^1 is aliphatic, it usually contains at least about 15 carbon atoms; when it is an aliphatic-substituted cycloaliphatic radical, the aliphatic substituents usually contain a total of at least about 12 carbon atoms. Examples of R^1 are alkyl, alkenyl and alkoxyalkyl radicals, and aliphatic substituents are alkyl, alkenyl, alkoxy, alkoxyalkyl, carboxyalkyl and the like. Generally, the cycloaliphatic nucleus is derived from a cycloalkane or a cycloalkene such as cyclopentane, cyclohexane, cyclohexene or cyclopentene. Specific examples of R^1 are cetylcyclohexyl, laurylcyclohexyl, cetyloxyethyl, octadecenyl, and radicals derived from petroleum, saturated and unsaturated paraffin wax, and olefin polymers including polymerized monoolefins and diolefins containing about 2-8 carbon atoms per olefinic monomer unit. R^1 can also contain other substituents such as phenyl, cycloalkyl, hydroxy, mercapto, halo, nitro, amino, nitroso, lower alkoxy, lower alkylmercapto, carboxy, carbalkoxy, oxo or thio, or interrupting groups such as -NH-, -O- or -S-, as long as the essentially hydrocarbon character thereof is not destroyed.

R^2 is generally a hydrocarbon or essentially hydrocarbon radical free from acetylenic unsaturation and containing from about 4 to about 60 aliphatic carbon atoms, preferably an aliphatic hydrocarbon radical such as alkyl or alkenyl. It may also, however, contain substituents or interrupting groups such as those enumerated above provided the essentially hydrocarbon character thereof is retained. In general, any non-carbon atoms present in R^1 or R^2 do not account for more than 10% of the total weight thereof.

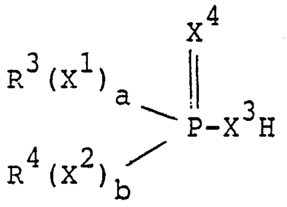
The radical T is a cyclic nucleus which may be derived from an aromatic hydrocarbon such as benzene, naphthalene, anthracene or biphenyl, or from a heterocyclic compound such as pyridine, indole or isoindole. Ordinarily, T is an aromatic hydrocarbon nucleus, especially a benzene or naphthalene nucleus.

The subscript x is at least 1 and is generally 1-3. The subscripts r and y have an average value of about 1-4 per molecule and are generally also 1.

Illustrative sulfonic acids useful in the preparation of component A are mahogany sulfonic acids, pertolatum, sulfonic acids, mono- and polywax-substituted naphthalene sulfonic acids, cetylchlorobenzene sulfonic acids, cetylphenol sulfonic acids, cetylphenol disulfide sulfonic acids, cetoxycapryl benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta-naphthol sulfonic acids, dicapryl nitronaphthalene sulfonic acids, saturated paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy-substitued paraffin wax sulfonic acids, tetraisobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso-substituted paraffin wax sulfonic acids, petroleum naphthene sulfonic acids, cetylcyclopentyl sulfonic acids, lauryl cyclohexyl sulfonic acids, mono- and polywax-substituted cyclohexyl sulfonic acids, postdodecylbenzene sulfonic acids, "dimer alkylate" sulfonic acids, and the like. These sulfonic acids are well-known in the art and require no further discussion herein.

Suitable carboxylic acids include aliphatic, cycloaliphatic and aromatic mono- and polybasic carboxylic acids free from acetylenic unsaturation, including naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids, and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally contain from about 8 to about 50, and preferably from about 12 to about 25, carbon atoms, The cycloaliphatic and aliphatic carboxylic acids are preferred, and they can be saturated or unsaturated. Specific examples include 2-ethylhexanoic acid, linolenic acid, propylene tetramer-substituted maleic acid, behenic acid, isostearic acid, pelargonic acid, capric acid, palmitoleic acid, linoleic acid, lauric acid, oleic acid, ricinoleic acid, undecyclic acid, dioctylcyclopentanecarboxylic acid, myristic acid, dilauryldechydronaphthalenecarboxylic acid, stearyl-octahydroindenecarboxylic acid, palmitic acid, alkyl- and alkenylsuccinic acids, acids formed by oxidation of petrolatum or of hydrocarbon waxes, and commercially available mixtures of two or more carboxylic acids, such as tall oil acids, rosin acids, and the like.

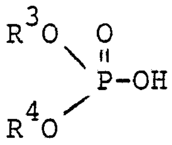
The pentavalent phosphorus acids useful in the preparation of component A may be represented by the formula



$$\left.\begin{matrix} R^3(X^1)_a \\ R^4(X^2)_b \end{matrix}\right\rangle \overset{X^4}{\overset{\|}{P}}-X^3H$$

wherein each of R^3 and R^4 is hydrogen or a hydrocarbon or essentially hydrocarbon radical preferably having from about 4 to about 25 carbon atoms, at least one of R^3 and R^4 being hydrocarbon or essentially hydrocarbon; each of X^1, X^2, X^3 and X^4 is oxygen or sulfur; and each of a and b is 0 or 1. Thus, it will be appreciated that the phosphorus acid may be an organophosphoric, phosphonic or phosphinic acid, or a thio analog of any of these.

Usually, the phosphorus acids are those of the formula:



wherein R^3 is a phenyl radical or (preferably) an alkyl radical having up to 18 carbon atoms, and R^4 is hydrogen or a similar phenyl or alkyl radical. Mixtures of such phosphorus acids are often preferred because of their ease of preparation.

Component A may also be prepared from phenols; that is, compounds containing a hydroxy radical bound directly to an aromatic ring. The term "phenol" as used herein includes compounds having more than one hydroxy group bound to an aromatic ring, such as catechol, resorcinol and hydroquinone. It also includes alkylphenols such as the cresols and ethylphenols, and alkenylphenols. Preferred are phenols containing at least one alkyl substituent containing about 3-100 and especially about 6-50 carbon atoms, such as heptylphenol, octylphenol, dodecylphenol, tetrapropenealkylated phenol, octadecylphenol and polybutenylphenols. Phenols containing more than one alkyl substituent may also be used, but the monoalkylphenols are preferred because of their availability and ease of production.

Also useful are condensation products of the above-described phenols with at least one lower aldehyde, the term "lower" denoting aldehydes containing not more than 7 carbon atoms. Suitable aldehydes include formaldehyde, acetaldehyde, propionaldehyde, the butyraldehydes, the valeraldehydes and benzaldehyde. Also suitable are aldehyde-yielding reagents such as paraformaldehyde, trioxane, methylol, Methyl Formcel and paraldehyde. Formaldehyde and the formaldehyde-yielding reagents are especially preferred.

The equivalent weight of the acidic organic compound is its molecular weight divided by the number of acidic groups (i.e., sulfonic acid, carboxy or acidic hydroxy groups) present per molecule.

Especially preferred for use as component A are basic alkaline earth metal salts having metal ratios from about 4 to about 40, preferably from about 6 to about 30 and especially from about 8 to about 25, and prepared by intimately contacting for a period of time sufficient to form a stable dispersion, at a temperature between the solidification temperature of the reaction mixture and its decomposition temperature:

(A-1) at least one acidic gaseous material selected from the group consisting of carbon dioxide, hydrogen sulfide and sulfur dioxide, with

(A-2) a reaction mixture comprising

(A-2-a) at least one oil-soluble sulfonic acid, or derivative thereof susceptible to overbasing;

(A-2-b) at least one alkaline earth metal or basic alkeline earth metal compound;

(A-2-c) at least one lower aliphatic alcohol; and

(A-2-d) at least one oil-soluble carboxylic acid or functional derivative thereof.

Reagent A-1 is at least one acidic gaseous material which may be carbon dioxide, hydrogen sulfide or sulfur dioxide; mixtures of these gases are also useful. Carbon dioxide is preferred because of its relatively low cost, availability, ease of use and performance.

Reagent A-2 is a mixture containing at least four components of which component A-2-a is at least one oil-soluble sulfonic acid as previously defined, or a derivative thereof susceptible to overbasing. Mixtures of sulfonic acids and/or their derivatives may also be used. Sulfonic acid derivatives susceptible to overbasing include their metal salts, especially the alkaline earth, copper, managanese, iron and lead salts; ammonium salts and amine salts (e.g., the ethylamine, butylamine and ethylene polyamine salts); and esters such as butylamine and ethylene polyamine salts); and esters such as the ethyl, butyl and glycerol esters.

Component A-2-b is at least one alkaline earth metal or a basic compound thereof. Illustrative of basic alkaline earth metal compounds are the hydroxides, alkoxides (typically those in which the alkoxy group contains up to 10 and preferably up to 7 carbon atoms), hydrides and amides. Thus, useful basic alkaline earth metal compounds include calcium hydroxide, magnesium hydroxide, barium hydroxide, stratium hydroxide, calcium oxide, magnesium oxide, barium oxide, strontium oxide, calcium hydride, magnesium hydride, barium hydride, stratium hydride, calcium ethoxide, calcium butoxide and calcium amide. Especially preferred are calcium oxide and calcium hydroxide and the calcium lower alkoxides (i.e., those containing up to 7 carbon atoms). The equivalent weight of component A-2-b for the purpose of this invention is equal to twice its molecular weight, since the alkaline earth metals are divalent.

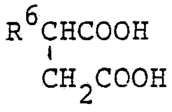
Component A-2-c is at least one lower aliphatic alcohol, preferably a monohydric or dihydric alcohol. Illustrative alcohols are methanol, ethanol, 1-propanol, 1-hexanol, isopropanol, isobutanol, 2-pentanol, 2,2-dimethyl-1-propanol, ethylene glycol, 1-3-propanediol and 1,5-pentanediol. Of these, the preferred alcohols are methanol, ethanol and propanol, with methanol being especially preferred. The equivalent weight of component B-2-c is its molecular weight divided by the number of hydroxy groups per molecule.

Component A-2-d is at least one oil-soluble carboxylic acid as previously described, or functional derivative thereof. Especially suitable carboxylic acids are those of the formula $R^5(COOH)_n$, wherein n is an integer from 1 to 6 and is preferably 1 or 2 and R^5 is a saturated or substantially saturated aliphatic radical (preferably a hydrocarbon radical) having at least 8 aliphatic carbon atoms. Depending upon the value of n, R^5 will be a monovalent to hexavalent radical.

R^5 may contain non-hydrocarbon substituents provided they do not alter substantially its hydrocarbon character. Such substituents are preferably present in amounts of not more than about 10% by weight. Exemplary substituents include the non-hydrocarbon substituents enumerated hereinabove with reference to component A-2-a. R^5 may also contain olefinic unsaturation up to a maximum of about 5% and preferably not more than 2% olefinic linkages based upon the total number of carbon-to-carbon covalent linkages present. The number of carbon atoms in R^5 is usually about 8-700 depending upon the source of R^5. As discussed below, a preferred series of carboxylic acids and derivatives is prepared by reacting an olefin polymer or halogenated olefin polymer with an alpha, beta-unsaturated acid or its anhydride such as acrylic, methacrylic, maleic or fumaric acid or maleic anhydride to form the corresponding substituted acid or derivative thereof. The R^5 groups in these products have a number average molecular weight from about 150 to about 10,000 and usually from about 700 to about 5000, as determined, for example, by gel permeation chromatography.

The monocarboxylic acids useful as component A-2-d have the formula R^5COOH. Examples of such acids are caprylic, capric, palmitic, stearic, isostearic, linoleic and behenic acids. A particularly preferred group of mono-carboxylic acids is prepared by the reaction of a halogenated olefin polymer, such as a chlorinated polybutene, with acrylic acid or methacrylic acid.

Suitable dicarboxylic acids include the substituted succinic acids having the formula



$$\begin{array}{l} R^6CHCOOH \\ \quad | \\ \quad CH_2COOH \end{array}$$

wherein R^6 is the same as R^5 as defined above. R^6 may be an olefin polymer-derived group formed by polymerization of such monomers as ethylene, propylene, 1-butene, isobutene, 1-pentene, 2-pentene, 1-hexene and 3-hexene. R^6 may also be derived from a high molecular weight substantially saturated petroleum fraction. The hydrocarbon-substituted succinic acids and their derivatives constitute the most preferred class of carboxylic acids for use as component A-2-d.

The above-described classes of carboxylic acids derived from olefin polymers, and their derivatives, are well known in the art, and methods for their preparation as well as representative examples of the types useful in the present invention are described in detail in a number of U.S. patents, e.g., U. S. Patent No., 4,119,549.

Functional derivatives of the above-discussed acids useful as component A-2-d includes the anhydrides, esters, amides, imides, amidines and metal salts. The reaction products of olefin polymer-substituted succinic acids and mono- or polyamines, particularly polyalkylene polyamines, having up to about ten amino nitrogens are especially suitable. These reaction products generally comprise mixtures of one or more of amides, imides and amidines. The reaction products of polyethylene amines containing up to about 10 nitrogen atoms and polybutene-substituted succinic anhydride wherein the polybutene radical comprises principally isobutene units are particularly useful. Included in this group of functional derivatives are the compositions prepared by post-treating the amine-anhydride reaction product with carbon disulfide, boron compounds, nitriles, urea, thiourea, guanidine, alkylene oxides or the like. The half-amide, half-metal salt and half-ester, half-metal salt derivatives of such substituted succinic acids are also useful.

Also useful are the esters prepared by the reaction of the substituted acids or anhydrides with a mono- or polyhydroxy compound, such as an aliphatic alcohol or a phenol. Preferred are the esters of olefin polymer-substituted succinic acids or anhydrides and polyhydric aliphatic alcohols containing 2-10 hydroxy groups and up to about 40 aliphatic carbon atoms. This class of alcohols includes ethylene glycol, glycerol, sorbitol, pentaerythritol, polyethylene glycol, diethanolamine, triethanolamine, N,N-di(hydroxyethyl)-ethylene diamine and the like. When the alcohol contains reactive amino groups, the reaction product may comprise products resulting from the reaction of the acid group with both the hydroxy and amino functions. Thus, this reaction mixture can include half-esters, half-amides, esters, amides, and imides.

In summary, the non-metal portion or anion is selected from the group consisting of acetates, formates, carbonates, hydrogen carbonates, sulfides, hydrogen sulfides, sulfites, hydrogen sulfites, chlorides or mixtures thereof.

The ratios of equivalents of the constituents of reagent A-2 may vary widely. In general, the ratio of component A-2-b to A-2-a is at least about 4:1 and usually not more than about 40:1, preferably between 61 and 30:1 and most preferably between 8:1 and 25:1. While this ratio may sometimes exceed 40:1, such an excess normally will serve no useful purpose.

The ratio of equivalents of component A-2-c to component A-2-a is between about 1:1 and 80:1, and preferably between about 2:1 and 50:1; and the ratio of equivalents of component A-2-d to component A-2-a is from about 1:1 to about 1:20 and preferably from about 1:2 to about 1:10.

Reagents A-1 and A-2 are generally contacted until there is no further reaction between the two or until the reaction substantially ceases. While it is usually preferred that the reaction be continued until no further overbased product is formed, useful dispersions can be prepared when contact between reagents A-1 and A-2 is maintained for a period of time sufficient for about 70% of reagent A-1, relative to the amount required if the reaction were permitted to proceed to its completion or "end point", to react.

The point at which the reaction is completed or substantially ceases may be ascertained by any of a number of conventional methods. One such method is measurement of the amount of gas (reagent A-1) entering and leaving the mixture; the reaction may be considered substantially complete when the amount leaving is about 90-100% of the amount entering. These amounts are readily determined by the use of metered inlet and outlet valves.

The reaction temperature is not critical. Generally, it will be between the solidification temperature of the reaction mixture and its decomposition temperature (i.e., the lowest decomposition temperature of any component thereof). Usually, the temperature will be from about 25° to about 200°C. and preferably from about 150°C. Reagents A-1 and A-2 are conveniently contacted at the reflux temperature of the mixture. This temperature will obviously depend upon the boiling points of the various components; thus, when methanol is used as component A-2-c, the contact temperature will be about the reflux temperature of methanol.

The reaction is ordinarily conducted at atmospheric pressure, although superatmospheric pressure often expedites the reaction and promotes optimum utilization of reagent A-1. The process can also be carried out at reduced pressure but, for obvious practical reasons, this is rarely done.

The reaction is usually conducted in the presence of a substantially inert, normally liquid organic diluent, which functions as both the dispersing and reaction medium. This diluent will comprise at least about 10% of the total weight of the reaction mixture. Ordinarily it will not exceed about 80% by weight, and it is preferably about 30-70% thereof.

Although a wide variety of diluents are useful, it is preferred to use a diluent which is soluble in lubricating oil. The diluent usually itself comprises a low viscosity lubricating oil.

Other organic diluents can be employed either alone or in combination with lubricating oil. Preferred diluents for this purpose include the aromatic hydrocarbons such as bezene, toluene and xylene; halogenated derivatives thereof such as chlorobenzene; lower boiling petroleum distillates such as petroleum ether and the various naphthas; normally liquid aliphatic and cycloaliphatic hydrocarbons such as hexane, heptane, hexene, cyclohexene, cyclopentane, cyclohexane and ethylcyclohexane, and their halogenated derivatives. Dialkyl ketones such as dipropyl ketone and ethyl butyl ketone, and the alkyl aryl ketones such as acetophenone, are likewise useful, as are ethers such as n-propyl ether, n-butyl ether, n-butyl methyl ether and isoamyl ether.

When a combination of oil and other diluent is used, the weight ratio of oil to the other diluent is generally from about 1:20 to about 20:1. It is usually desirable for a mineral lubricating oil to comprise at least about 50% by weight of the diluent, especially if the product is to be used as a lubricant additive. The total amount of diluent present is not particularly critical since it is inactive. However, the diluent will ordinarily comprise about 10-80% and preferably about 30-70% by weight of the reaction mixture.

The reaction is preferably conducted in the absence of water, although small amounts may be present (e.g., because of the use of technical grade reagents). Water may be present in amounts up to about 10% by weight of the reaction mixture without having harmful effects.

Upon completion of the reaction, any solids in the mixture are preferably removed by filtration or other conventional means. Optionally, readily removable diluents, the alcoholic promoters, and water formed during the reaction can be removed by conventional techniques such as distillation. It is usually desirable to remove substantially all water from the reaction mixture since the presence of water may lead to difficulties in filtration and to the formation of undesirable emulsions in fuels and lubricants. Any such water present is readily removed by heating at atmospheric or reduced pressure or by azeotropic distillation.

The chemical structure of component A is not known with certainty. The basic salts or complexes may be solutions or, more likely, stable dispersions. Alternatively, they may be regarded as "polymeric salts" formed by the reaction of the acidic material, the oil-soluble acid being overbased, and the metal compound. In view of the above, these compositions are most conveniently defined by reference to the method by which they are formed. Representative of such useful compositions are illustrated by the following examples.

<u>Example 1</u>

A calcium mahogany sulfonate is prepared by double decomposition of a 60% oil solution of 750 parts of sodium mahogany sulfonate with the solution of 750 parts of sodium mahogany sulfonate with the solution of 67 parts of calcium chloride and 63 parts of water. The reaction mass is heated for 4 hours at 90-100°C. to effect the conversion of the sodium mahogany sulfonate to calcium mahogany sulfonate. Then, 54 parts of 91% calcium hydroxide solution is added and the material is heated to 150°C. over a period of five hours. When the material has cooled to 40°C., 98 parts of methanol is added and 152 parts of carbon dioxide is introduced over a period of 2 hours at 42-43°C. Water and alcohol are then removed by heating the mass to 150°C. The residue in the reaction vessel is diluted with 100 parts of mineral oil. The filtered oil solution and the desired carbonated calcium sulfonate overbased material shows the following analysis: sulfate ash content, 16.4%; a neutralization number, as measured against phenopthalein of 0.6(acidic); and a metal ratio of 2.5.

Example 2

A mixture comprising 2890 parts of the overbased material of Example 1 (2.79 equivalents based on sulfonic acid anion), 217 parts of the calcium phenate prepared as indicated below (0.25 equivalents), 939 parts of mineral oil, 494 parts methanol, 201 parts isobutyl alcohol, 128 parts of mixed isomeric primary amyl alcohols (containing about 65% normal amyl, 3% isoamyl and 32% 2-methyl-1-butyl alcohols), 4.7 parts calcium chloride dissolved in 5.8 parts water, and 428 parts of 91% calcium hydroxide (10.6 equivalents) is stirred vigorously at 40°C and 146 parts of carbon dioxide is introduced over a period of 1.2 hours at 40-55°C. Thereafter, five additional portions of calcium hydroxide amounting to 173 parts each are added and each such addition is followed by the introduction of carbon dioxide as previously illustrated. After the sixth calcium hydroxide addition and the carbonation step is completed, the reaction mass is carbonated for an additional one hour at 40-55°C to reduce the neutralization number of the mass to 55 (basic). The carbonated reaction mixture is then heated to 150°C under a nitrogen atmosphere to remove alcohol and any by-product water. 908 parts of oil are added and the contents of the reaction vessel is then filtered. The filtrate, an oil solution of the desired carbonated calcium sulfonate overbased material of high metal ratio shows the following analysis: sulfate ash content 52.7; neutralization number 50.9 (basic); total base number 420 (basic); and a metal ratio of 20.25.

The calcium phenate used above is prepared by adding 2550 parts of mineral oil, 960 parts (5 moles) of heptyl phenol, and 50 parts of water into a reaction vessel and stirring at 25°C. The mixture is heated to 40°C and 7 parts of calcium hydroxide and 231 parts (7 moles) of 91% commerical paraformaldehyde is added over a period of one hour. The contents are heated to 80°C and 200 additional parts of calcium hydroxide (making a total of 207 parts or 5 moles) is added over a period of one hour at 80-90°C. The contents are heated to 150°C and maintained at that temperature for 12 hours while nitrogen is blown through the mixture to assist in the removal of water. If foaming is encountered, a few drops of polymerized dimethylsilicone foam inhibitor may be added to control the foaming. The reaction mass is then filtered. The filtrate, a 33.6% oil solution of the desired calcium phenate of heptyl phenol-formaldehyde condensation product is found to contain 7.56% sulfate ash. Borated complexes of this type may be prepared by heating the basic alkaline earth metal salt with boric acid at about 50-100°C., the number of equivalents of boric acid being roughly equal to half the number of equivalents of alkaline earth metal in the salt. U.S. Patent 3,929,650 is incorporated by reference herein for its disclosure of borated complexes.

Example 3

(a) To a mixture of 1,145 grams of a mineral oil solubtion of a 40% solution of barium mahogany sulfonates (1.0 equivalent) and 200 grams of methyl alcohol at 55°C, there is added 220 grams of barium oxide while the mixture is being blown with carbon dioxide at a rate of 2 to 3 cubic feet per hour. To this mixture there is added an additional 78 grams of methyl alcohol and then 460 grams of barium oxide while the mixture is blown with carbon dioxide. The carbonated product is heated to 150°C for 1 hour and filtered. The filtrate is found to have a barium sulfate ash content of 53.8% and a metal ratio of 8.9.

(b) A carbonated basic metal salt is prepared in accordance with the procedure of (a) except that a total of 16 equivalents of barium oxide is used per equivalent of the barium mahogany sulfonate. The product possess a metal ratio of 13.4.

Example 4

A mixture of 520 parts (by weight) of a mineral oil, 480 parts of a sodium petroleum sulfonate (molecular weight of 480) and 84 parts of water is heated at 100°C for 4 hours. The mixture is then heated with 86 partsof a 76% aqueous solution of calcium chloride and 72 parts of lime (90% purity) at 100°C for 2 hours, dehydrated by hearing to a water content of less than 0.5%, cooled to 50°C, mixed with 130 parts of methyl alcohol, and then blown with carbon dioxide at 50°C until substantially neutral. The mixture is then heated to 150°C to remove the methyl alcohol and water and the resulting oil solution of the basic calcium sulfonate filtered. The filtrate is found to have a calcium sulfate ash content of 16% and a metal ratio of 2.5.

A mixture of 1,305 grams of the above carbonated calcium sulfonate, 930 grams of mineral oil, 220 grams of methyl alcohol, 72 grams of isobutyl alcohol, and 38 grams of pirmary amyl alcohol is prepared, heated to 35°C, and subjected to the following operating cycle 4 times; mixing with 143 grams of 90% calcium hydroxice and treating the mixture with carbon dioxide until it has a base number of 32-39. The resulting product is then heated to 155°C during a period of 9 hours to remove the alcohols and filtered through a siliceous filter aid at this temperature. The filtrate has a calcium sulfate ash content of 39.5% and a metal ratio of 12.2.

Example 5

A mixture of 880 grams (0.968 moles) of a 57.5% oil solution of the calcium sulfonate of tridecylbenzene bottoms (the bottoms constitute a mixture of mono-, di-, and tri-decylbenzene), 15=49 grams of methanol, and 59 grams (1.58 equivalents) of calcium hydroxice are introduced into a reaction vessel and stirred vigorously. The whole is heated to 40-45°C and carbon dioxide is introduced for 0.5 hour at the rate of 2 cubic feet per hour. The carbonated reaction mixture is then heated to 150°C to remove alcohol and any water present, and the residue is filtered for purposes of purification. The product, a 61% oil solution of the desired overbased carbonated calcium sulfonate material shows the following anaylsis: ash content, 16.8%, neutralization number, 7.0 (acidic); and metal ratio, 2.42. By further carbonation in the presence of an alkali or alkaline earth metal oxice, hydroxice, or alkoxide, the metal ratio can readily be increased to 3.5 or greater.

Like component (A) of the additive mixture, the particular species of component (B), i.e., the sulfurized organic compound, is not particularly critical to the present invention. However, it is preferred that the sulfur be incorporated in the organic compound as the sulfide moiety, i.e., in its divalent oxidation state and that it is oil-soluble. Component (B) may be the product of an aliphatic, arylaliphatic or alicyclic hydrocarbon. Olefinic hydrocarbons containing from about 3 to about 30 carbon atoms are preferred for the purposes of the present invention.

The olefinic hydrocarbons which may be sulfurized to form component B are diverse in nature. They contain at least one olefinic double bond, which is defined as a non-aromatic double bond; that is, one connecting two aliphatic carbon atoms. In its broadest sense, the olefinic hydrocarbon may be defined by the formula $R^7R^8C=CR^9R^{10}$, wherein each of R^7, R^8, R^9 and R^{10}

is hydrogen or a hydrocarbon (especially alkyl or alkenyl) radical. Any two of R^7, R^8, R^9 and R^{10} may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

Monoolefinic and diolefinic compounds, particularly the former, are preferred in the preparation of component B, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^9 and R^{10} are hydrogen and R^7 and R^8 are alkyl (that is, the olefin is aliphatic). Olefinic compounds having about 3-30 and especially about 3-20 carbon atoms are particularly desirable.

Propylene, isobutene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutene and diisobutene are particularly desirable because of their availability and the particularly high sulfur-containing compositions which can be prepared therefrom.

The sulfurizing reagent used from the preparation of component B may be, for example, sulfur, a sulfur halide such as sulfur monochloride or sulfur dichloride, a mixture of hydrogen sulfide and sulfur or sulfur dioxide, or the like. Sulfur-hydrogen sulfide mixtures are often preferred and are frequently referred to hereinafter; however, it will be understood that other sulfurization agents may, when appropriate, by substituted therefor.

The amounts of sulfur and hydrogen sulfide per mole of olefinic compound are, respectively, usually about 0.3-3.0 gram-atoms and about 0.1-1.5 moles. The preferred ranges are about 0.5-2.0 gram-atoms and about 0.4-1.25 moles respectively, and the most desirable ranges are about 1.2-1.8 gram-atoms and about 0.4-0.8 mole respectively.

The temperature range in which the sulfurization reaction is carried out is generally about 50-350°C. The preferred range is about 100-200°C., with about 125-180°C. being especially suitable. The reaction is often preferably conducted under superatmospheric pressure; this may be and usually is autogenous pressure (i.e., the pressure which naturally develops during the course of the reaction) but may also be externally applied pressure. The exact pressure developed during the reaction is dependent upon such factors as the design and operation of the system, the reaction temperature, and the vapor pressure of the reactants and products and it may vary during the course of the reaction.

It is frequently advantageous to incorporate materials useful as sulfurization catalysts in the reaction mixture. These materials may be acidic, basic or neutral, but are preferably basic materials, especially nitrogen bases including ammonia and amines, most often alkylamines. The amount of catalyst used is generally about 0.05-2.0% of the weight of the olefinic compound. In the case of the preferred ammonia and amine catalysts, about 0.0005-0.5 mole per mole of olefin is preferred, and about 0.001-0.1 mole is especially desirable.

Following the preparation of the sulfurized mixture, it is preferred to remove substantially all low boiling materials, typically by venting the reaction vessel or by distillation at atmospheric pressure, vacuum distillation or stripping, or passage of an inert gas such as nitrogen through the mixture at a suitable temperature and pressure.

A further optional step in the preparation of component B is the treatment of the sulfurized product, obtained as described hereinabove, to reduce active sulfur. An illustrative method is treatment with an alkali metal sulfide. Other optional treatments may be employed to remove insoluble byproducts and improve such qualities as the odor, color and staining characteristics of the sulfurized compositions.

U.S. Patent 4,119,549 is incorporated by reference herein for its disclosure of suitable sulfurization products useful as component B. Several specific sulfurized compositions are described in the working examples thereof. The following examples illustrate the preparation of two such compositions.

EXAMPLE A

Sulfur (629 parts, 19.6 moles) is charged to a jacketed high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 6 torr and cooling, 1100 parts (19.6 moles) of isobutene, 334 parts (9.8 moles) of hydrogen sulfide and 7 parts of n-butylamine are charged to the reactor. The reactor is heated, using steam in the external jacket, to a temperature of about 171°C. over about 1.5 hours. A maximum pressure of 720 psig. is reached at about 138°C. during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 4.75 hours at about 171°C., the unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized product is recovered as a liquid.

EXAMPLE B

Following substantially the procedure of Example 3, 773 parts of diisobutene is reacted with 428.6 parts of sulfur and 143.6 parts of hydrogen sulfide in the presence of 2.6 parts of n-butylamine, under autogenous pressure at a temperature of about 150-155°C. Volatile materials are removed and the sulfurized product is recovered as a liquid.

The amount of the (A) component combined with the (B) component to make up the additive mixture of the present invention may vary over a wide range. For example, the weight ratio of (A):(B) may range from about 50:1 to about 1:1. However, as a preferred range, the weight ratio of (A):(B) is from about 20:1 to about 10:1.

The (A) component and (B) component of the additive mixture may be added separately or as a mixture to a base grease stock to obtain the grease composition of the present invention or to a base stock for a gear lubricant.

Grease compositions or base grease stocks are derived from both mineral and synthetic oils. The synthetic oils include polyolefin oils (e.g., polybutene oil, decene oligimer, and the like), synthetic esters (e.g., dinonyl sebacate, trioctanoic acid ester of trimethylolpropane, and the like), polyglycol oils, and the like. The grease composition is then made from these oils by adding a thickening agent such as a sodium, calcium, lithium, or aluminum salts of fatty acids such as stearic acid. To this base grease stock, then may be blended the components of the additive mixture of the present invention as well as other known or conventional additives. The grease composition of the present invention may contain from about 1 weight percent to about 50 weight percent of component A and from 0.1 percent to about 5 weight percent of component B of the additive of the present invention. As a preferred embodiment, the effective amount of component A in the grease composition will range from about 5 weight percent to about 25 weight percent and the effective amount of component B will range from about 0.5 weight percent to about 2 weight percent.

Other additives which may optionally be present in the grease compositions and gear lubricants for use in this invention include:

Antioxidants, typically hindered phenols.

Surfactants, usually non-ionic surfactants such as oxyalkylated phenols and the like.

Corrosion, wear and rust inhibiting agents.

Friction modifying agents, of which the following are illustrative: alkyl or alkenyl phosphates or phosphites in which the alkyl or alkenyl group contains from about 10 to about 40 carbon atoms, and metal salts thereof, especially zinc salts; C_{10}-$_{20}$ fatty acid amides; C_{10}-$_{20}$

alkyl amines, especially tallow amines and ethoxylated derivatives thereof; salts of such amines with acids such as boric acid or phosphoric acid which have been partially esterified as noted above; C_{10}-$_{20}$ alkyl-substituted imidazolines and similar nitrogen heterocycles.

Various grease formulations for comparative purposes were tested according to the 4-Ball extreme pressure test, i.e., ASTM D-2783, and according to the roller bearing rust test, i.e., ASTM D-1748. The results for these various grease compositions which were evaluated in side by side tests are set out in Tables I and II.

TABLE I

[1]Lithium Base Grease +	No Additive	10 wgt. % of Component A	1 wgt. % of Component B	10 wgt. % of A + 1wgt. % of B	20 wgt. % of Component A	20 wgt. % of A + 1 wgt. % of B
4 Ball EP (ASTM D-2783) Weld (Kg)	126	250	250	500	315	620
Load Wear Index (Kg)	25.73	29.7	28.0	65.0	44.6	98.1

1-NLGI #1

TABLE II

Lithium Base Grease	No Additive	10 wgt. % of Component A	10 wgt. % Component A + 1 wgt. % of Component B
Roller Bearing Rust Test (ASTM D-1748)	heavy rust	No rust	No rust

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As has been demonstrated by the results set out in the above Tables, particularly Table I, the additive mixture, i.e., the combination of the metal-containing composition with a sulfurized organic compound gives unexpectedly and synergistically high results for the weld points and the load wear index in the 4-Ball EP test. It should be noted that the weld point obtained for grease compositions containing only component A or only component B are each 250(Kg). However, the weld point obtained for a grease composition containing both of these components (i.e., A and B) is 500(Kg). It is further pointed out that the addition of the sulfurized organic compound does not affect the rust or oxidative properties in the grease formulation.

As previously pointed out, the additive mixture of the present invention may be also used in gear lubricant compositions which are prepared and formulated for use in differentials, axles, some manual transmissions and the like. These oils, likewise, may be prepared from mineral or synthetic oils as described above, however, are generally of higher viscosity than typical crankcase or motor oil. Furthermore, these types of lubricants must hold up under extreme pressure conditions, and thus, require the inclusion of extreme pressure agents in their formulation. It has been discovered that the additive mixture of the present invention is the same concentration range and is particularly useful in formulating such gear lubricants.

While the invention has been described and illustrated with reference to certain preferred embodiments thereof, those skilled in the art will appreciate the various changes, modifications and substitutions that can be made therein without departing from the spirit of the invention. For example, different ratios or amounts of the A and B components of the additive mixture, other than preferred ranges set out hereinabove, may be applicable as a consequence of the variations in the particular grease base stock or gear lubricant base stock or in the type of engine or particular end use or the like. It is intended, therefore, that the invention be limited only by the scope of the claims which follow:

WHAT IS CLAIMED IS:

1. A grease composition comprising an extreme pressure effective amount of the mixture comprising:

(A) at least one metal-containing composition; and

(B) at least one sulfurized organic compound.

2. The composition according to claim 1, wherein said component (A) is combined with component (B) in the weight ratio of (A):(B) of about 50:1 to about 1:1.

3. The composition according to claim 2, wherein the weight ratio of (A):(B) is about 20:1 to about 10:1.

4. The composition according to claim 1, wherein the metal ratio of component (A) is at least 5.0.

5. The composition according to claim 1, wherein the metal of said metal-containing composition of component (A) is selected from the group consisting of alkali metals, alkaline earth metals, transition metals, Group IV-A metals, Group V-A metals or mixtures thereof, with the proviso that the transition metal is not zinc.

6. The composition according to claim 5, wherein said metal of said metal-containing composition of component (A) is calcium or sodium.

7. The composition according to claim 5, wherein the non-metal portion of said metal-containing composition is selected from the group consisting of acetates, formates, carbonates, hydrogen carbonates, sulfides, hydrogen sulfides, sulfites, hydrogen sulfites, chlorides or mixtures thereof.

8. The composition according to claim 7, wherein the non-metal portion of said metal-containing composition is a carbonate or hydrogen carbonate.

9. The composition according to claim 1, wherein the sulfurized organic compound is an aromatic, alkyl or alkenyl sulfide or polysulfide, a sulfurized olefin, a sulfurized carboxylic acid ester, a sulfurized ester olefin, a sulfurized oil or mixtures thereof.

10. The composition according to claim 9, wherein the sulfurized organic compound is a sulfurized olefin of about 3 to about 30 carbon atoms.

11. A method for improving the load bearing characteristics of grease compositions and gear lubricants comprising formulating said grease composition or gear lubricants with an extreme pressure effective amount of the mixture comprising:

(A) at least one metal-containing composition; and

(B) at least one sulfurized organic compound.

12. The method according to claim 11, wherein said component (A) is combined with component (B) in the weight ratio of (A):(B) of about 50:1 to about 1:1.

13. The method according to claim 12, wherein the weight ratio of component (A):(B) is about 20:1 to about 10:1.

14. The method according to claim 11, wherein the metal ratio of component (A) is at least 5.0.

15. The method according to claim 11, wherein the metal of said metal-containing composition of component (A) is selected from the group consisting of Group IV-A metals, Group V-A metals, alkali metals, alkaline earth metals, transition metals, or mixtures thereof with the proviso that the transition metal is not zinc.

16. The method according to claim 15, wherein said metal of said metal-containing composition of component (A) is calcium or sodium.

17. The method according to claim 15, wherein the non-metal portion of said metal-containing composition is selected from the group consisting of acetates, formates, carbonates, hydrogen carbonates, sulfides, hydrogen sulfides, sulfites, hydrogen sulfites, chlorides or mixtures thereof.

18. The method according to claim 17, wherein the non-metal portion of said metal-containing composition is a carbonate or hydrogen carbonate.

19. The method according to claim 11, wherein the sulfurized organic compound is an aromatic, alkyl or alkenyl sulfide or polysulfide, a sulfurized olefin, a sulfurized carboxylic acid ester, a sulfurized ester olefin, a sulfurized oil or mixtures thereof.

20. The method according to claim 19, wherein the sulfurized organic compound is a sulfurized olefin of 3 to about 30 carbon atoms.

21. A gear lubricant composition comprising an extreme pressure effective amount of the mixture comprising:

(A) at least one metal-containing composition; and

(B) at least one sulfurized organic compound.

22. The composition according to claim 21, wherein said component (A) is combined with component (B) in the weight ratio of (A):(B) of about 50:1 to about 1:1.

23. The composition according to claim 22, wherein the weight ratio of (A):(B) is about 20:1 to about 10:1.

24. The composition according to claim 21, wherein the metal ratio of component (A) is at least 5.0.

25. The composition according to claim 21, wherein the metal of said metal-containing composition of component (A) is selected from the group consisting of alkali metals, alkaline earth metals, transition metals, Group IV-A, Group V-A metals or mixtures thereof with the proviso that the transition metal is not zinc.

26. The composition according to claim 21, wherein said metal of said metal-containing composition of component (A) is calcium or sodium.

27. The composition according to claim 25, wherein the non-metal portion of said metal-containing composition is selected from the group consisting of acetates, formates, carbonates, hydrogen carbonates, sulfides, hydrogen sulfides, sulfites, hydrogen sulfites, chlorides or mixtures thereof.

28. The composition according to claim 27, wherein the non-metal portion of said metal-containing composition is a carbonate or hydrogen carbonate.

29. The composition according to claim 21, wherein the sulfurized organic compound is an aromatic, alkyl or alkenyl sulfide or polysulfide, a sulfurized olefin, a sulfurized carboxylic acid ester, a sulfurized ester olefin, a sulfurized oil or mixtures thereof.

30. The composition according to claim 29, wherein the sulfurized organic compound is a sulfurized olefin of about 3 to about 30 carbon atoms.