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(54) **USE OF GREASE AND GEAR LUBRICANT COMPOSITIONS COMPRISING AT LEAST ONE METAL-CONTAINING COMPOSITION AND AT LEAST ONE SULFURIZED ORGANIC COMPOUND.**

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US-A- 2 307 183
US-A- 4 119 549
US-A- 4 228 021
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Description

This invention relates to the use of grease and gear lubricant compositions and particularly to the use of additives to improve the extreme pressure properties of grease and gear lubricant compositions. More specifically, the invention relates to the use in such compositions of 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 to the grease or gear lubricant composition.

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 US-A-4 505 830 and in WO-A-8 701 723.

Thus, WO-A-8 701 723 describes lubricants for metal working processes, especially cutting, which contain a basic alkaline earth metal salt or at least one organic acid together with an active sulfur-containing sulfurization product of an olefinic hydrocarbon. The amount of sulfurized product is less than the amount of basic alkaline earth metal salt in all of the examples of WO-A-8 701 723.

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 US-A-4 171 268.

Halogenated disulfide compounds which are useful as extreme pressure additives for lubricating oils are disclosed in US-A-4 228 021. This patent also discloses the use of an overbased material with the halosulfurized additives.

In US-A-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 US-A-4 394 276 and US-A-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.

US-A-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.

GB-A-1 121 713 describes lubricant additive compositions comprising an alkaline earth metal salt of an acidic phosphosulfurized olefin polymer, a fatty acid derivative including sulfurized aliphatic esters, Group II metal phosphorothioate adducts, and a polar-substituted amine.

US-A-4 119 549 describes lubricant additives comprising sulfurized compositions prepared by reacting unsaturated compounds with a mixture of sulfur and hydrogen sulfide under super-atomospheric pressure and in the presence of a catalyst. It is indicated that these additives may be combined with other additives such as ash-containing detergents, for example, basic alkali and alkaline earth metal salts. Example A at column 11 of this patent discloses a lubricating composition suitable for use as a crankcase lubricant comprising inter alia 1.57% of an overbased calcium sulfonate detergent together with 0.27% of a sulfurized isobutene prepared by reacting isobutene, sulfur and hydrogen sulfide in a mole ratio of isobutene: sulfur: hydrogen sulfide of 1:0.8:0.5 at a temperature of 171 °C in the presence of a catalyst comprising n-butylamine in an amount of 0.005 moles per mole isobutene. The use of a composition as specifically disclosed in Example A of US-A-4 119 549 is disclaimed from the scope of the present invention.

US-A-3 899 432 describes lubricating compositions containing a substantially neutral Group II metal salt of a hydrocarbyl sulfonic acid, an overbased Group II metal salt of a hydrocarbyl sulfonic acid, a Group II metal salt of a dihydrocarbyl dithiophosphoric acid, tricresyl phosphate, and a sulfurized mixture of olefins and fatty acid esters.

It is pointed out that none of the foregoing disclosures teach the particular 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.

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 and gear lubricant compositions.

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.

Thus, the invention provides use of a mixture comprising:

(A) at least one overbased metal-containing organic composition wherein the metal of said metal-containing organic composition is selected from alkali metals, alkaline earth metals, Group V-A metals, titanium, chromium and copper, with the proviso that the metal is not zinc; and

(B) at least one sulfurized organic compound; wherein said component (A) is combined with component (B) in the weight ratio of (A):(B) in the range of 50:1 to 1:1, with the proviso that the weight ratio of (A):(B) is not 5.81:1 when component (A) is an overbased calcium sulfonate and component (B) is a sulfurized isobutene prepared by reacting isobutene, sulfur and hydrogen sulfide in a mole ratio of isobutene: sulfur: hydrogen sulfide of 1:0.8:0.5 at a temperature of 171 °C in the presence of a catalyst comprising n-butylamine in an amount of 0.005 moles per mole isobutene;

to enhance the extreme pressure properties of a grease or gear lubricant composition.

The invention also provides 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 overbased metal-containing organic composition wherein the metal of said metal-containing organic composition is selected from alkali metals, alkaline earth metals, Group V-A metals, titanium, chromium and copper, with the proviso that the metal is not zinc; and

(B) at least one sulfurized organic compound; wherein said component (A) is combined with component (B) in the weight ratio of (A):(B) in the range of 50:1 to 1:1, with the proviso that the weight ratio of (A):(B) is not 5.81:1 when component (A) is an overbased calcium sulfonate and component (B) is a sulfurized isobutene prepared by reacting isobutene, sulfur and hydrogen sulfide in a mole ratio of isobutene: sulfur: hydrogen sulfide of 1:0.8:0.5 at a temperature of 171 °C in the presence of a catalyst comprising n-butylamine in an amount of 0.005 moles per mole isobutene.

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 the specific additive mixture indicated above.

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 organic compounds which are substantially soluble in the disperse medium. The molecules of the organic compound, i.e., the third component, are characterised by containing polar substituents and hydrophobic portions of the molecule. Such systems are disclosed and described in US-A-3 384 586, discussed above. The metal-containing compositions 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 recognised metal-containing compositions that may be also described by such terms of the art as "overbased", "superbased" and "hyperbased" salts, which terms are recognised 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 US-A-4 505 830, discussed above, and US-A-4 230 586.

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. More specifically, useful metal compounds in preparing the overbased materials of the additive mixture of the present invention are the basic salts of metals in Group I-A and Group II-A of the Periodic Table, Group V-A metals, titanium, chromium and copper, with the proviso that the metal is not zinc.

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 formulae $R^1(SO_3H)_r$ and $(R^2)_xT\text{-}(SO_3H)_y$. In these formulae, R^1 is an aliphatic or aliphatic-substituted cycloaliphatic hydrocarbon or essentially hydrocarbon radical free from acetylenic unsaturation and containing up to 60 carbon atoms. When R^1 is aliphatic, it usually contains at least 15 carbon atoms; when it is an aliphatic-substituted cycloaliphatic radical, the aliphatic substituents usually contain a total of at least 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 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 4 to 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.

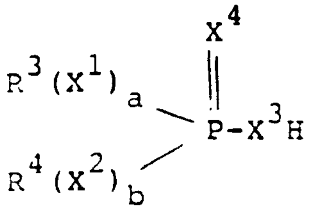
The radical T is a cyclic nucleus which may be derived from an aromatic hydrocarbon such as benzene, naphthalene, anthracene or biphenyl, or from a heterocyclic compound such as pyridine, indole or isoindole. Ordinarily, T is an aromatic hydrocarbon nucleus, especially a benzene or naphthalene nucleus.

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

Illustrative sulfonic acids useful in the preparation of component A are mahogany sulfonic acids, petrolatum, 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, tetraamylene 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.

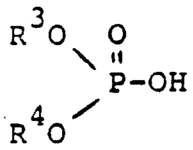
Suitable carboxylic acids include aliphatic, cycloaliphatic and aromatic mono- and polybasic carboxylic acids free from acetylenic unsaturation, including naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids, and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally contain from 8 to 50, and preferably from 12 to 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.

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



wherein each of R^3 and R^4 is hydrogen or a hydrocarbon or essentially hydrocarbon radical preferably having from 4 to 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 3-100 and especially 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 abovedescribed 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, 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 4 to 40, preferably from 6 to 30 and especially from 8 to 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 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 over-basing;

(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, strontium hydroxide, calcium oxide, magnesium oxide, barium oxide, strontium oxide, calcium hydride, magnesium hydride, barium hydride, strontium 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.

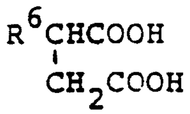
Component A-2-c is at least one lower aliphatic alcohol, preferably a monohydric or dihydric alcohol. Illustrative alcohols are methanol, ethanol, 1-propanol, 1-hexanol, isopropanol, isobutanol, 2-pentanol, 2,2-dimethyl-1-propanol, ethylene glycol, 1-3-propanediol and 1,5-pentanediol. Of these, the preferred 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 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 150 to 10,000 and usually from 700 to 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



$$R^6\underset{\displaystyle CH_2COOH}{\underset{|}{C}}HCOOH$$

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., US-A-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 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 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 amine 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 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 4:1 and usually not more than 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 1:1 and 80:1, and preferably between 2:1 and 50:1; and the ratio of equivalents of component A-2-d to component A-2-a is from 1:1 to 1:20 and preferably from 1:2 to 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 25° to 200°C. and preferably from 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 10% of the total weight of the reaction mixture. Ordinarily it will not exceed 80% by weight, and it is preferably 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 benzene, 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 1:20 to 20:1. It is usually desirable for a mineral lubricating oil to comprise at least 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 10-80% and preferably 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 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.

Example 1

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 phenolphthalin 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 oat 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 discloses 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 5.7 x 10^{-2} to 8.5 x 10^{-2} m^3 (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 possesses 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 parts of 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 primary amyl alcohol is prepared, heated to 35 ° C, and subjected to the following operating cycle 4 times; mixing with 143 grams of 90% calcium hydroxide 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 hydroxide 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 5.7×10^{-2} m^3 (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 analysis: 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 oxide, hydroxide, 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 3-30 and especially 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 0.3-3.0 gram-atoms and 0.1-1.5 moles. The preferred ranges are 0.5-2.0 gram-atoms and 0.4-1.25 moles respectively, and the most desirable ranges are 1.2-1.8 gram-atoms and 0.4-0.8 mole respectively.

The temperature range in which the sulfurization reaction is carried out is generally 50-350 ° C. The preferred range is 100-200 ° C., with 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 0.05-2.0% of the weight of the olefinic compound. In the case of the preferred ammonia and amine catalysts, 0.0005-0.5 mole per mole of olefin is preferred, and 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.

US-A-4,119,549 discloses 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 800 Pa (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 5 MPa (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 A, 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 for use according to the present invention ranges in a weight ratio of (A):(B) of from 50:1 to about 1:1, preferably from 20:1 to 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 or 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 for use in the present invention as well as other known or conventional additives. The grease composition may contain from 1 weight percent to 50 weight percent of component A and from 0.1 percent to 5 weight percent of component B of the additive. As a preferred embodiment, the effective amount of component A in the grease composition will range from 5 weight percent to 25 weight percent and the effective amount of component B will range from 0.5 weight percent to 2 weight percent.

Other additives which may optionally be present in grease compositions and gear lubricants 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 10 to 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.

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 extreme pressure test (ASTM D-2783). It has also been found that the addition of the sulfurized organic compound does not affect the rust or oxidative properties in a grease formulation.

As previously pointed out, the additive mixture for use in 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 in the same concentration range 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 in accordance with the present invention as defined in the appended claims.

Claims

1. Use of a mixture comprising:

(A) at least one overbased metal-containing organic composition wherein the metal of said metal-containing organic composition is selected from alkali metals, alkaline earth metals, Group V-A metals, titanium, chromium and copper, with the proviso that the metal is not zinc; and

(B) at least one sulfurized organic compound; wherein said component (A) is combined with component (B) in a weight ratio of (A):(B) in the range of 50:1 to 1:1, with the proviso that the weight ratio of (A):(B) is not 5.81:1 when component (A) is an overbased calcium sulfonate and component (B) is a sulfurized isobutene prepared by reacting isobutene, sulfur and hydrogen sulfide in a mole ratio of isobutene: sulfur: hydrogen sulfide of 1:0.8:0.5 at a temperature of 171 °C in the presence of a catalyst comprising n-butylamine in an amount of 0.005 moles per mole isobutene;

to enhance the extreme pressure properties of a grease or gear lubricant composition.

2. Use according to claim 1, wherein the metal ratio of component (A) is at least 5.0.

3. Use according to either of claims 1 and 2, wherein said metal of said metal-containing composition of component (A) is calcium or sodium.

4. Use according to any preceding claim, wherein the sulfurized organic compound is an aromatic, alkyl or alkenyl sulfide or polysufide, a sulfurized olefin, a sulfurized carboxylic acid ester, a sulfurized ester olefin, a sulfurized oil or a mixture thereof.

5. Use according to claim 4, wherein the sulfurized organic compound is a sulfurized olefin containing 3 to 30 carbon atoms.

6. Use according to any preceding claim wherein the weight ratio of components (A):(B) is 20:1 to 10:1.

7. 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 overbased metal-containing organic composition wherein the metal of said metal-containing organic composition is selected from alkali metals, alkaline earth metals, Group V-A metals, titanium, chromium and copper, with the proviso that the metal is not zinc; and

(B) at least one sulfurized organic compound; wherein said component (A) is combined with component (B) in a weight ratio of (A):(B) in the range of 50:1 to 1:1, with the proviso that the weight ratio of (A):(B) is not 5.81:1 when component (A) is an overbased calcium sulfonate and component (B) is a sulfurized isobutene prepared by reacting isobutene, sulfur and hydrogen sulfide in a mole ratio of isobutene: sulfur: hydrogen sulfide of 1:0.8:0.5 at a temperature of 171 °C in the presence of a catalyst comprising n-butylamine in an amount of 0.005 moles per mole isobutene.

8. A method according to claim 7, wherein the metal ratio of component (A) is at least 5.0.

9. A method according to either of claims 7 and 8, wherein said metal of said metal-containing composition of component (A) is calcium or sodium.

10. A method according to any one of claims 7 to 9, 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 a mixture thereof.

11. A method according to claim 10, wherein the sulfurized organic compound is a sulfurized olefin containing 3 to 30 carbon atoms.

12. A method according to any one of claims 7 to 11 wherein the weight ratio of components (A)-:(B) is 20:1 to 10:1.

Patentansprüche

1. Verwendung eines Gemisches, umfassend

(A) mindestens eine überalkalisierte, metallhaltige organische Zusammensetzung, wobei das Metall der metallhaltigen, organischen Zusammensetzung ausgewählt ist aus Alkalimetallen, Erdalkalimetallen, Metallen der V. Hauptgruppe, Titan, Chrom, und Kupfer mit der Maßgabe, daß das Metall nicht Zink ist, und

(B) mindestens eine geschwefelte, organische Verbindung, wobei Komponente (A) zusammen mit Komponente (B) in einem Gewichtsverhältnis (A):(B) im Bereich von 50:1 bis 1:1 vorliegt, mit der Maßgabe, daß das Gewichtverhältnis (A):(B) nicht 5.81:1 ist, wenn Komponente (A) ein überalkalisiertes Calciumsulfonat und Komponente (B) ein geschwefeltes Isobuten ist, das durch Umsetzung von Isobuten, Schwefel und Schwefelwasserstoff in einem Molverhältnis Isobuten:Schwefel:Schwefelwasserstoff von 1:0.8:0.5 bei einer Temperatur von 171 °C in Anwesenheit eines Katalysators, der n-Butylamin in einer Menge von 0.005 Mol pro Mol Isobuten umfaßt, hergestellt wurde,

zur Verbesserung der Extremdruck-Eigenschaften einer Schmierfett- oder einer Getriebeschmiermittelzusammensetzung.

2. Verwendung nach Anspruch 1, wobei das Metallverhältnis der Komponente (A) mindestens 5.0 ist.

3. Verwendung nach Anspruch 1 oder 2, wobei das Metall der metallhaltigen Zusammensetzung der Komponente (A) Calcium oder Natrium ist.

4. Verwendung nach einem der vorstehenden Ansprüche, wobei die geschwefelte organische Verbindung ein aromatisches Sulfid oder Polysulfid, ein Alkyl- oder Alkenylsulfid oder -polysulfid, ein geschwefeltes Olefin, ein geschwefelter Carbonsäureester, ein geschwefelter Olefinester, ein geschwefeltes Öl oder deren Gemisch ist.

5. Verwendung nach Anspruch 4, wobei die geschwefelte organische Verbindung ein geschwefeltes Olefin mit 3 bis 30 C-Atomen ist.

6. Verwendung nach einem der vorstehenden Ansprüche, wobei das Gewichtsverhältnis der Komponenten (A):(B) zwischen 20:1 und 10:1 liegt.

7. Verfahren zur Verbesserung der Lastaufnahmecharakteristiken von Schmierfettzusammensetzungen und Getriebeschmiermitteln, umfassend die Herstellung von einer Schmierfettzusammensetzung oder Getriebeschmiermitteln mit einer in bezug auf die Extremdruck-Eigenschaften wirksamen Menge des Gemisches, umfassend

(A) mindestens eine überalkalisierte, metallhaltige organische Zusammensetzung, wobei das Metall der metallhaltigen organischen Zusammensetzung ausgewählt ist aus Alkalimetallen, Erdalkalimetallen, Metallen der V. Hauptgruppe, Titan, Chrom und Kupfer, mit der Maßgabe, daß das Metall nicht Zink ist, und

(B) mindestens eine geschwefelte, organische Verbindung, wobei die Komponente (A) zusammen mit der Komponente (B) in einem Gewichtsverhältnis (A):(B) im Bereich von 50:1 bis 1:1 vorliegt, mit der Maßgabe, daß das Gewichtverhältnis (A):(B) nicht 5.81:1 ist, wenn die Komponente (A) ein überalkalisiertes Calciumsulfonat und Komponente (B) ein geschwefeltes Isobuten ist, das durch Umsetzung von Isobuten, Schwefel und Schwefelwasserstoff in einem Molverhältnis Isobuten:Schwefel:Schwefelwasserstoff von 1:0.8:0.5 bei einer Temperatur von 171 °C in Anwesenheit eines Katalysators, der n-Butylamin in einer Menge von 0.005 Mol pro Mol Isobuten umfaßt, hergestellt wurde.

8. Verfahren nach Anspruch 7, wobei das Metallverhältnis der Komponente (A) mindestens 5.0 ist.

9. Verfahren nach Anspruch 7 oder 8, wobei das Metall der metallhaltigen Zusammensetzung der Komponente (A) Calcium oder Natrium ist.

10. Verfahren nach einem der Ansprüche 7 bis 9, wobei die geschwefelte organische Verbindung ein aromatisches Sulfid oder Polysulfid, ein Alkyl- oder Alkenylsulfid oder -polysulfid, ein geschwefeltes Olefin, ein geschwefelter Carbonsäureester, ein geschwefelter Olefinester, ein geschwefeltes Öl oder deren Gemisch ist.

11. Verfahren nach Anspruch 10, wobei die geschwefelte organische Verbindung ein geschwefeltes Olefin mit 3 bis 30 C-Atomen ist.

12. Verfahren nach einem der Ansprüche 7 bis 11, wobei das Gewichtsverhältnis der Komponenten (A):(B) zwischen 20:1 und 10:1 liegt.

Revendications

1. Utilisation d'un mélange comprenant :

(A) au moins une composition organique contenant un métal sur-basique, dans laquelle le métal de ladite composition organique contenant un métal est choisi parmi les métaux alcalins, les métaux alcalino-terreux, les métaux du groupe VA, le titane, le chrome et le cuivre, à condition que le métal ne soit pas le zinc; et

(B) au moins un composé organique soufré; dans lequel ledit constituant (A) est combiné au constituant (B) dans un rapport pondéral (A)/(B) dans la gamme de 50 : 1 à 1 : 1, à condition que le rapport pondéral (A)/(B) ne soit pas égal à 5,81 : 1 lorsque le constituant (A) est un sulfonate de calcium sur-basique et que le constituant (B) est un isobutène soufré préparé par réaction d'isobutène, de soufre et de sulfure d'hydrogène, dans un rapport molaire isobutène/soufre/sulfure d'hydrogène de 1 : 0,8 : 0,5, à une température de 171 ° C, en présence d'un catalyseur comprenant de la n-butylamine, à raison de 0,005 mole par mole d'isobutène;

pour améliorer les propriétés extrême-pression d'une graisse ou d'une composition lubrifiante pour boîte de vitesse.

2. Utilisation selon la revendication 1, dans laquelle la proportion de métal dans le constituant (A) est d'au moins 5,0.

3. Utilisation selon les revendications 1 et 2, dans laquelle ledit métal de ladite composition contenant un métal du constituant (A) est le calcium ou le sodium.

4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le composé organique soufré est un sulfure ou polysulfure aromatique, d'alkyle ou d'alcényle, une oléfine soufrée, un ester d'acide carboxylique soufré, une oléfine d'ester soufrée, une huile soufrée ou un mélange de ceux-ci

5. Utilisation selon la revendication 4, dans laquelle le composé organique soufré est une oléfine soufrée contenant 3 à 30 atomes de carbone.

6. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le rapport pondéral des constituants (A)/(B) est de 20 : 1 à 10 : 1.

7. Procédé pour améliorer les caractéristiques extrémepression de compositions de graisse et de lubrifiants pour boîte de vitesse, comprenant la formulation de ladite composition de graisse ou dudit lubrifiant pour boîte de vitesse avec une quantité, efficace pour les propriétés extrémepression, du mélange comprenant :

(A) au moins une composition organique contenant un métal sur-basique, dans laquelle le métal de ladite composition organique contenant un métal est choisi parmi les mètaux alcalins, les métaux alcalino-terreux, les métaux du groupe VA, le titane, le chrome et le cuivre, à condition que le métal ne soit pas le zinc; et

(B) au moins un composé organique soufré; dans lequel ledit constituant (A) est combiné au constituant (B) dans un rapport pondéral (A)/(B) dans la gamme de 50 : 1 à 1 : 1, à condition que le rapport pondéral (A)/(B) ne soit pas égal à 5,81 : 1 lorsque le constituant (A) est un sulfonate de çalcium sur-basique et que le constituant (B) est un isobutène soufré préparé par réaction d'isobutène, de soufre et de sulfure d'hydrogène, dans un rapport molaire isobutène/soufre/sulfure d'hydrogène de 1 : 0,8 : 0,5, à une température de 171 ° C, en présence d'un catalyseur comprenant de la n-butylamine, à raison de 0,005 mole par mole d'isobutène.

8. Procédé selon la revendication 7, dans lequel la proportion du métal dans le constituant (A) est d'au moins 5,0.

9. Procédé selon l'une quelconque des revendications 7 et 8, dans lequel le métal de ladite composition contenant un métal du constituant (A) est le calcium ou le sodium.

10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel le composé organique soufré est un sulfure ou polysulfure aromatique, d'alkyle ou d'alcényle, une oléfine soufrée, un ester d'acide carboxylique soufré, une oléfine d'ester soufrée, une huile soufrée ou un mélange de ceux-ci.

11. Procédé selon la revendication 10, dans lequel le composé organique soufré est une oléfine soufrée contenant 3 à 30 atomes de carbone.

12. Procédé selon l'une quelconque des revendications 7 à 11, dans lequel le rapport pondéral des constituants (A)/(B) est de 20 : 1 à 10 : 1.