

Description

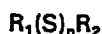
This invention relates to lubricating oil compositions containing sulfur-containing oil-soluble compositions, the lubricating oil compositions containing little or no phosphorus. More particularly, the present invention relates to lubricants containing little or no phosphorus and a composition comprising at least one metal dithiocarbamate, at least one sulfurized organic compound and at least one auxiliary corrosion-inhibitor.

Various compositions prepared by the sulfurization of organic compounds and more particularly olefins and olefin-containing compounds are known in the art, as are lubricants containing these products. Typical sulfurized compositions prepared by reacting olefins such as isobutene, diisobutene, and triisobutene with sulfur under various conditions are described in, for example, *Chemical Reviews*, 65, 237 (1965). Other references describe the reaction of such olefins with hydrogen sulfide and elemental sulfur to form predominantly mercaptans with sulfides, disulfides and higher polysulfides also being formed as by-products. Reference is made to *J. Am. Chem. Soc.*, 60, 2452 (1938), and U.S. Patents 3,221,056, 3,419,614 and 4,191,659. U.S. Patent 3,419,614 describes a process for increasing the yield of mercaptan by carrying out the reaction of olefin with hydrogen sulfide and sulfur at a high temperature in the presence of various basic materials. U.S. Patent 4,191,659 describes the preparation of sulfurized compositions by reaction at superatmospheric pressure of olefins with a mixture of sulfur and hydrogen sulfide in the presence of a catalyst followed by treatment with an alkali metal sulfide. The use of sulfurized natural and synthetic oils as additives in lubricating compositions has been suggested in the art such as in, for example, U.S. Patents 2,299,813 and 4,360,438.

It also has been known that Diels-Alder adducts can be sulfurized to form sulfur-containing compositions which are particularly useful as extreme pressure and anti-wear additives in various lubricating oils. U.S. Patents 3,632,566 and Reissue 27,331 describe such sulfurized Diels-Alder adducts and lubricants containing said adducts. In these patents, the ratio of sulfur to Diels-Alder adduct is described as being a molar ratio of from about 0.5:1.0 to 10.0:1.0. The patents indicate that it is normally desirable to incorporate as much stable sulfur into the compound as possible, and therefore, a molar excess of sulfur normally is employed. The disclosed lubricating compositions may contain other additives normally used to improve the properties of lubricating compositions such as dispersants, detergents, extreme pressure agents, and additional oxidation and corrosion-inhibiting agents, etc. For some lubricant applications, however, the above-described sulfur-containing compositions have not been entirely adequate as multi-purpose additives.

Organophosphorus and metal organophosphorus compounds are used extensively in lubricating oils as extreme pressure agents and anti-wear agents. Examples of such compounds include: phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine; phosphorus esters including dihydrocarbon and trihydrocarbon phosphites; and metal phosphorodithioates such as zinc dialkylphosphorodithioates. Because of the toxicological problems associated with the use of organophosphorus compounds, and particularly with the metal dialkylphosphorodithioates, there is a need to develop lubricant compositions containing low levels of phosphorus yet characterized as having acceptable oxidation inhibition and anti-wear properties. Lubricants containing low levels of phosphorus also are desirable in view of the tendency of phosphorus to poison catalytic converters used to control emissions from gasoline engines.

Polyvalent metal salts of dithiocarbamic acids are known and have been described as being useful oil additives because they serve the dual function of sequestering undesirable metal components of the oil and because they function as anti-oxidants. Lubricating oil compositions have been described comprising combinations of various polyvalent metal dithiocarbamates with other chemical additives exhibiting desirable property-improving characteristics when added to the lubricating oil in combination with the dithiocarbamates. For example, U.S. Patent 2,999,813 describes a lubricating composition comprising a sulfurized mineral oil and a polyvalent metal dithiocarbamate. Preferably, the composition also includes a lead soap of a naphthenic fatty acid. The preparation of lubricating compositions comprising mineral oil, metal salts of dithiocarbamic acids and coupling agents such as alcohols, esters, ketones and other stable oxygen-containing materials is described in U.S. Patent 2,265,851. U.S. Patent 2,394,536 describes lubricating oil compositions containing the combination of organic sulfides and salts of dithiocarbamic acids. Organic sulfides generally are represented by the formula



wherein R_1 and R_2 are aliphatic groups and n is 1, 2 or 3.

U.S. Patent 2,805,996 describes the use of amine-dithiocarbamate complexes in lubricating oil compositions, and U.S. Patent 2,947,695 describes the advantages of utilizing mixtures of polyvalent metal dithiocarbamates in preparing oil-soluble additive compositions useful in the preparation of lubricating oils.

In accordance with the present invention there is provided a lubricating oil composition comprising: a major amount of an oil of lubricating viscosity and, a minor, property improving, amount of an oil-soluble composition comprising:

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(A) at least one metal salt of at least one dithiocarbamic acid of the formula



5 wherein R_1 and R_2 are each independently hydrocarbyl groups containing a total number of carbon atoms so as to render the metal salt oil-soluble; and

(B) at least one oil-soluble sulfurized organic compound comprising the reaction product of sulphur and a Diels-Alder adduct in a molar ratio of less than about 1.7:1, wherein the weight ratio of (A) to (B) is in the range of from about 1:10 to about 50:1; and

10 (C) at least one auxiliary corrosion-inhibitor in the form of an oil-soluble derivative of a dimercaptiothiadiazole wherein the weight ratio of (C) to the mixture of (A) and (B) is from about 0.001:1 to about 0.5:1; and wherein the lubricating oil composition contains less than about 0.1% by weight of phosphorus.

Particular examples of the auxiliary corrosion-inhibitor are the oil-soluble derivatives of dimercaptiothiadiazoles. The compositions of the invention also may contain at least one oil-soluble dispersant or detergent.

Preferred embodiments and features of the invention are described below.

Component (A) of the compositions of the invention is at least one metal salt of at least one dithiocarbamic acid of the formula



wherein R_1 and R_2 are each independently hydrocarbyl groups in which the total number of carbons in R_1 and R_2 is sufficient to render the metal salt oil-soluble. The hydrocarbyl groups R_1 and R_2 may be alkyl groups, cycloalkyl groups, aryl groups, alkaryl groups or aralkyl groups. R_1 and R_2 , taken together, may represent the group consisting of polymethylene and alkyl-substituted polymethylene groups thereby forming a cyclic compound with the nitrogen. Generally, the alkyl group will contain at least two carbon atoms. The metal of the metal salt may be a monovalent metal or a polyvalent metal, although polyvalent metals are preferred since it is generally difficult to prepare oil solutions containing the desired quantities of the alkali metal salts. Suitable polyvalent metals include, for example, the alkaline earth metals, zinc, cadmium, magnesium, tin, molybdenum, iron, copper, nickel, cobalt, chromium, lead, etc. The Group II metals are preferred.

In selecting a metal salt of a dithiocarbamic acid to be used in the compositions of the invention, R_1 , R_2 , and the metal may be varied so long as the metal salt is adequately oil-soluble. The nature and type of the mineral base stock, and the type of service contemplated for the treated lubricating oil are important modifying influences in the choice of metal salt.

Mixtures of metal salts of dithiocarbamic acids also are contemplated as being useful in the present invention. Such mixtures can be prepared by first preparing mixtures of dithiocarbamic acids and thereafter converting said acid mixtures to metal salts, or alternatively, metal salts of various dithiocarbamic acids can be prepared and thereafter mixed to give the desired product. Thus, the mixtures which can be incorporated in the compositions of the invention may be merely the physical mixture of the different metallic dithiocarbamic compounds or different dithiocarbamate groupings attached to the same polyvalent metal atom.

Examples of alkyl groups are ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, pentadecyl and hexadecyl groups including isomeric forms thereof. Examples of cycloalkyl groups include cyclohexyl and cycloheptyl groups, and examples of aralkyl groups include benzyl and phenylethyl. Examples of polymethylene groups include penta- and hexamethylene groups, and examples of alkyl-substituted polymethylene groups include methyl pentamethylene, dimethyl pentamethylene, etc.

Specific examples of the metal dithiocarbamates useful as component (A) in the compositions of this invention include zinc dibutyldithiocarbamate, zinc diamyldithiocarbamate, zinc di(2-ethylhexyl)dithiocarbamate, cadmium dibutyldithiocarbamate, cadmium dioctyldithiocarbamate, cadmium octyl-butyldithiocarbamate, magnesium dibutyldithiocarbamate, magnesium dioctyldithiocarbamate, cadmium dicetyldithiocarbamate, sodium diamyldithiocarbamate, sodium diisopropyldithiocarbamate, etc.

The various metal salts of dithiocarbamic acids utilized in the compositions of this invention are well known in the art and can be prepared by known techniques.

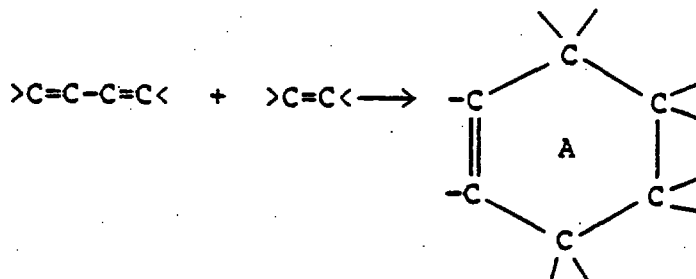
The sulfurized organic compound (component (B)) is derived from a particular type of cyclic or bicyclic olefin which is a Diels-Alder adduct of at least one dienophile with at least one aliphatic conjugated diene. The sulfurized Diels-Alder adducts can be prepared by reacting various sulfurizing agents with the Diels-Alder adducts as described more fully below. Preferably, the sulfurizing agent is sulfur.

The Diels-Alder adducts are a well-known, art-recognized class of compounds prepared by the diene synthesis or Diels-Alder reaction. A summary of the prior art relating to this class of compounds is found in the Russian monograph, *Dienovyi Sintez*, Izdatelstvo Akademii Nauk SSSR, 1963 by A. S. Onischenko. (Translated into the English language by L. Mandel as A. S. Onischenko, *Diene Synthesis*, N.Y., Daniel Davey and Co., Inc., 1964).

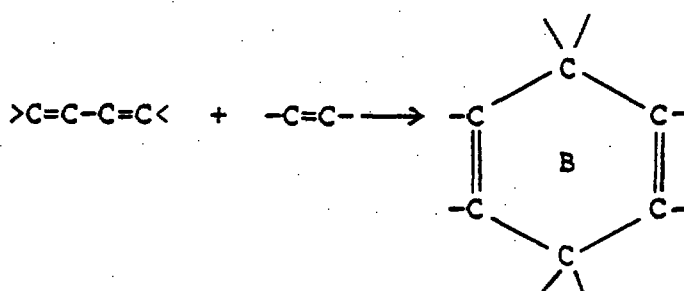
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Basically, the diene synthesis (Diels-Alder reaction) involves the reaction of at least one conjugated diene, $>C=C-C=C<$, with at least one ethylenically or acetylenically unsaturated compound, $>C=C<$ or $-C\equiv C-$, these latter compounds being known as dienophiles. The reaction can be represented as follows:

Reaction 1:

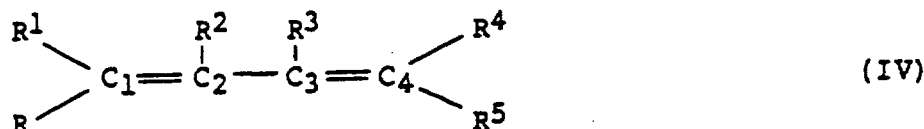


Reaction 2:



The products, A and B are commonly referred to as Diels-Alder adducts. It is these adducts which are used as starting materials for the preparation of the sulfurized Diels-Alder adducts utilized in the invention.

Representative examples of the 1,3-dienes include aliphatic and alicyclic conjugated diolefins or dienes of the formula



wherein R through R^5 are each independently selected from halogen, alkyl, halo, alkoxy, alkenyl, alkenyloxy, carboxy, cyano, amino, alkylamino, dialkylamino, phenyl, and phenyl-substituted with 1 to 3 substituents corresponding to R through R^5 with the proviso that a pair of R's on adjacent carbons do not form an additional double bond in the diene, or R , R^2 , R^3 and R^5 are as defined and R^1 and R^4 are alkylene groups joined together to form a ring including the nitrogen atom. Preferably not more than three of the R variables are other than hydrogen and at least one is hydrogen. Normally the total carbon content of the diene will not exceed 20. In one preferred aspect of the invention, adducts are used where R^2 and R^3 are both hydrogen and at least one of the remaining R variables is also hydrogen. Preferably, the carbon content of these R variables when other than hydrogen is 7 or less. In this most preferred class, those dienes where R, R^1 , R^4 , and R^5 are hydrogen, chloro, or lower alkyl are especially useful. Specific examples of the R variables include the following groups: methyl, ethyl, phenyl, $HOOC-$, $N=C-$, CH_3O- , CH_3COO- , CH_3CH_2O- , $CH_3C(O)-$, $HC(O)-$, Cl, Br, tert-butyl, CF_3 , tolyl, etc. Piperylene, isoprene, methylisoprene, chloroprene, and 1,3-butadiene are among the preferred dienes for use in preparing the Diels-Alder adducts.

In addition to these linear 1,3-conjugated dienes, cyclic dienes are also useful as reactants in the formation of the Diels-Alder adducts. Examples of these cyclic dienes are the cyclopentadienes, fulvenes, 1,3-cyclohexadienes, 1,3-cycloheptadienes, 1,3,5-cycloheptatrienes, cyclooctatetraene, and 1,3,5-cyclononatrienes. Various substituted derivatives of these compounds enter into the diene synthesis.

The dienophiles suitable for reacting with the above dienes to form the adducts used as reactants can be represented by the formula



wherein the K variables are the same as the R variables in Formula IV above with the proviso that a pair of K's may form an additional carbon-to-carbon bond, i.e., $K-C\equiv C-K_2$, but do not necessarily do so.

A preferred class of dienophiles are those wherein at least one of the K variables is selected from electron-accepting groups such as formyl, cyano, nitro, carboxy, carbohydrocarbyloxy, hydrocarbylcarbonyl, hydrocarbylsulfonyl, carbamyl, acylcarbamyl, N-acyl-N-hydrocarbylcarbamyl, N-hydrocarbylcarbamyl, and N,N-dihydrocarbylcarbamyl. Those K variables which are not electron-accepting groups are hydrogen, hydrocarbyl, or substituted-hydrocarbyl groups. Usually the hydrocarbyl and substituted hydrocarbyl groups will not contain more than 10 carbon atoms each.

The hydrocarbyl groups present as N-hydrocarbyl substituted are preferably alkyl of 1 to 30 carbons and especially 1 to 10 carbons. Representative of this class of dienophiles are the following: nitroalkenes, e.g., 1-nitrobutene-1, 1-nitropentene-1, 3-methyl-1-nitrobutene-1, 1-nitroheptene-1, 1-nitrooctene-1, 4-ethoxy-1-nitrobutene-1; alpha, beta-ethylenically unsaturated aliphatic carboxylic acid esters, e.g., alkylacrylates and alpha-methyl alkylacrylates (i.e., alkyl methacrylates) such as butylacrylates and butylmethacrylate, decyl acrylate and decylmethacrylate, di-(n-butyl)-maleate, di-(t-butyl)-maleate; acrylonitrile, methacrylonitrile, beta-nitrostyrene, methylvinylsulfone, acrolein, acrylic acid; alpha, beta-ethylenically unsaturated aliphatic carboxylic acid amides, e.g., acrylamide, N,N-dibutylacrylamide, methacrylamide, N-dodecylmethacrylamide, N-pentylcrotonamide; crotonaldehyde, crotonic acid, beta, beta-dimethyldivinylketone, methyl-vinylketone, N-vinyl pyrrolidone, alkenyl halides, and the like.

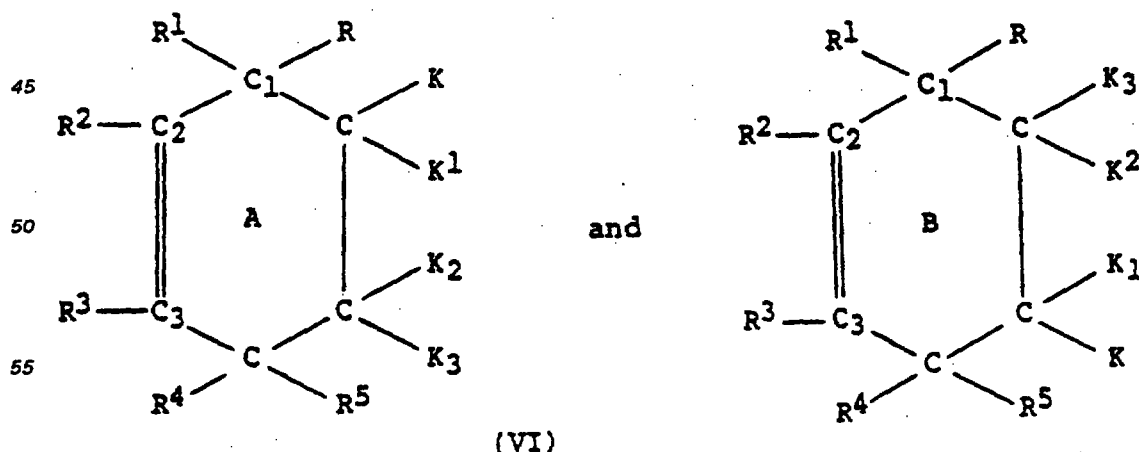
One preferred class of dienophiles are those wherein at least one, but not more than two of K variables is $-C(O)O-R_0$ where R_0 is the residue of a saturated aliphatic alcohol of up to about 40 carbon atoms; e.g., for example at least one K is carbohydrocarbyloxy such as carboethoxy, carbobutoxy, etc., the aliphatic alcohol from which $-R_0$ is derived can be a mono or polyhydric alcohol such as alkylenglycols, alkanols, aminoalkanols, alkoxy-substituted alkanols, ethanol, ethoxy, ethanol, propanol, beta-diethylaminoethanol, dodecyl alcohol, diethylene glycol, tripropylene glycol, tetrabutylene glycol, hexanol, octanol, iso-octyl alcohol, and the like. In this especially preferred class of dienophiles, not more than two K variables will be $-C(O)O-R_0$ groups and the remaining K variables will be hydrogen or lower alkyl, e.g., methyl, ethyl, propyl, isopropyl, and the like.

Specific examples of dienophiles of the type discussed above are those wherein at least one of the K variables is one of the following groups: hydrogen, methyl, ethyl, phenyl, $HOOC-$, $HC(O)-$, $CH_2=CH-$, $H\equiv C-$, $CH_3C(O)O-$, $ClCH_2-$, $HOCH_2-$, alpha-pyridyl, $-NO_2$, Cl, Br, propyl, iso-butyl, etc.

In addition to the ethylenically unsaturated dienophiles, there are many useful acetylenically unsaturated dienophiles such as propiolaldehyde, methylethynylketone, propylethynylketone, propenylethynylketone, propiolic acid, propiolic acid nitrile, ethylpropiolate, tetrolic acid, propargylaldehyde, acetylenedicarboxylic acid, the dimethyl ester of acetylenedicarboxylic acid, dibenzoylacetylene, and the like.

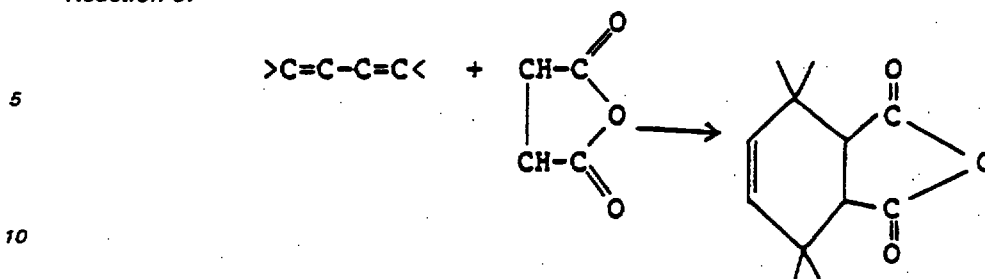
Cyclic dienophiles include cyclopentenedione, coumarin, 3-cyanocoumarin, dimethyl maleic anhydride, 3,6-endomethylene-cyclohexenedicarboxylic acid, etc. With the exception of the unsaturated dicarboxylic anhydrides derived from linear dicarboxylic acids (e.g., maleic anhydride, methylmaleic anhydride, chloromaleic anhydride), this class of cyclic dienophiles are limited in commercial usefulness due to their limited availability and other economic considerations.

The reaction products of these dienes and dienophiles correspond to the general formulae

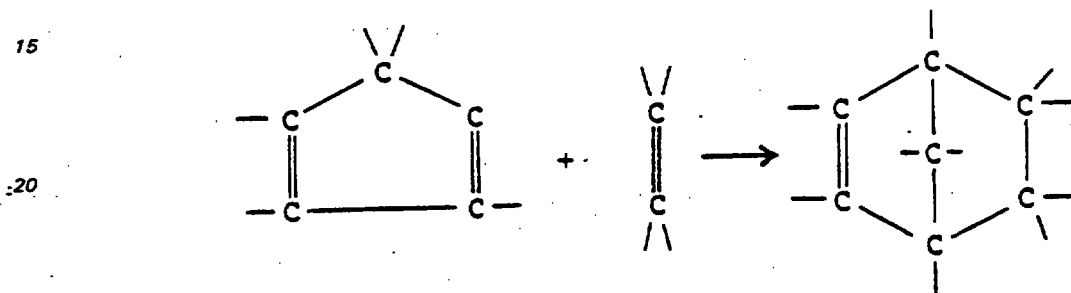


wherein R through R^5 and K through K_3 are as defined hereinbefore. If the dienophile moiety entering into the reaction is acetylenic rather than ethylenic, two of the K variables, one from each carbon, form another carbon-to-carbon double bond. Where the diene and/or the dienophile is itself cyclic, the adduct obviously will be bicyclic, tricyclic, fused, etc., as exemplified below:

Reaction 3:



Reaction 4:



25 Normally, the adducts involve the reaction of equimolar amounts of diene and dienophile. However, if the dienophile has more than one ethylenic linkage, it is possible for additional diene to react if present in the reaction mixture.

The adducts and processes of preparing the adducts are further exemplified by the following examples.

30 Unless otherwise indicated in these and the other examples to follow, and in other parts of the specification and claims, all parts and percentages are by weight.

Example A

35 A mixture comprising 400 parts of toluene and 66.7 parts of aluminum chloride is charged to a two-liter flask fitted with a stirrer, nitrogen inlet tube, and a solid carbon dioxide-cooled reflux condenser. A second mixture comprising 640 parts (equivalent to 5 moles) of butyl acrylate and 240.8 parts of toluene is added to the $AlCl_3$ slurry while maintaining the temperature within the range of 37—58°C over a 0.25 hour period. Thereafter, 313 parts (equivalent to 5.8 moles) of butadiene is added to the slurry over a 2.75 hour period while maintaining the temperature of the reaction mass at 50—61°C by means of external cooling. The reaction mass is blown with nitrogen for about 0.33 hour and then transferred to a four-liter separatory funnel and washed with a solution of 150 parts of concentrated hydrochloric acid in 1100 parts of water. Thereafter, the product is subjected to two additional water washings using 1000 parts of water for each wash. The washed reaction product is subsequently distilled to remove unreacted butyl acrylate and toluene. The residue of this first distillation step is subjected to further distillation at a pressure of 9—10 millimeters of mercury (1.2—1.3 kPa) whereupon 785 parts of the desired product is collected over the temperature of 105—115°C.

Example B

50 The adduct of isoprene and acrylonitrile is prepared by mixing 136 parts of isoprene, 106 parts of acrylonitrile, and 0.5 parts of hydroquinone (polymerization inhibitor) in a rocking autoclave and thereafter heating for 16 hours at a temperature within the range of 130—140°C. The autoclave is vented and the contents decanted thereby producing 240 parts of a light yellow liquid. This liquid is stripped at a temperature of 90°C and a pressure of 10 millimeters of mercury (1.3 kPa) thereby yielding the desired liquid product as the residue.

Example C

60 Using the procedure of Example B, 136 parts of isoprene, 172 parts of methyl acrylate, and 0.9 part of hydroquinone are converted to the isoprenemethyl acrylate adduct.

Example D

65 Following the procedure of Example B, 104 parts of liquified butadiene, 166 parts of methyl acrylate, and 1 part of hydroquinone are charged to the rocking autoclave and heated to 130—135°C for 14 hours. The product is subsequently decanted and stripped yielding 237 parts of the adduct.

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Example E

The adduct of isoprene and methyl methacrylate is prepared by reacting 745 parts of isoprene with 1095 parts of methyl methacrylate in the presence of 5.4 parts of hydroquinone in the rocking autoclave following the procedure of Example B above. 1490 parts of the adduct is recovered.

Example F

The adduct of butadiene and dibutyl maleate (810 parts) is prepared by reacting 915 parts of dibutyl maleate, 216 parts of liquified butadiene, and 3.4 parts of hydroquinone in the rocking autoclave according to the technique of Example B.

Example G

A reaction mixture comprising 378 parts of butadiene, 778 parts of N-vinylpyrrolidone, and 3.5 parts of hydroquinone is added to a rocking autoclave previously chilled to -35°C . The autoclave is then heated to a temperature of $130-140^{\circ}\text{C}$ for about 15 hours. After venting, decanting, and stripping the reaction mass, 75 parts of the desired adduct are obtained.

Example H

Following the technique of Example B, 270 parts of liquified butadiene, 1060 parts of isodecyl acrylate, and 4 parts of hydroquinone are reacted in the rocking autoclave at a temperature of $130-140^{\circ}\text{C}$ for about 11 hours. After decanting and stripping, 1136 parts of the adduct are recovered.

Example I

Following the same general procedure of Example A, 132 parts (equivalent to 2 moles) of cyclopentadiene, 256 parts (equivalent to 2 moles) of butyl acrylate, and 12.8 parts of aluminum chloride are reacted to produce the desired adduct. The butyl acrylate and the aluminum chloride are first added to a two-liter flask fitted with stirrer and reflux condenser. While heating the reaction mass to a temperature within the range of $59-52^{\circ}\text{C}$, the cyclopentadiene is added to the flask over a 0.5 hour period. Thereafter the reaction mass is heated for about 7.5 hours at a temperature of $95-100^{\circ}\text{C}$. The product is washed with a solution containing 400 parts of water and 100 parts of concentrated hydrochloric acid and the aqueous layer is discarded. Thereafter, 1500 parts of benzene are added to the reaction mass and the benzene solution is washed with 300 parts of water and the aqueous phase removed. The benzene is removed by distillation and the residue stripped at 0.2 mm of mercury (27 Pa) to recover the adduct as a distillate.

Example J

Following the technique of Example B, the adduct of butadiene and allylchloride is prepared using two moles of each reactant.

Example K

One-hundred thirty-nine parts (equivalent to 1 mole) of the adduct of butadiene and methyl acrylate is transesterified with 158 parts (equivalent to 1 mole) of decyl alcohol. The reactants are added to a reaction flask and 3 parts of sodium methoxide are added. Thereafter, the reaction mixture is heated at a temperature of $190-200^{\circ}\text{C}$ for a period of 7 hours. The reaction mass is washed with a 10% sodium hydroxide solution and then 250 parts of naphtha is added. The naphtha solution is washed with water. At the completion of the washing, 150 parts of toluene are added and the reaction mass is stripped at 150°C under pressure of 28 mm of mercury (3.7 kPa). A dark-brown fluid product (225 parts) is recovered. This product is fractionated under reduced pressure resulting in the recovery of 178 parts of the product boiling in the range of $130-133^{\circ}\text{C}$ at a pressure of 0.45 to 0.6 mm of mercury (60 to 80 Pa).

Example L

The general procedure of Example A is repeated except that only 270 parts (equivalent to 5 moles) of butadiene is included in the reaction mixture.

The sulfur-containing compounds are readily prepared by heating a mixture of a sulfurizing agent such as sulfur, and at least one of the Diels-Alder adducts of the types discussed hereinabove at a temperature within the range of from about 110°C to just below the decomposition temperature of the Diels-Alder adducts. Temperatures within the range of about 110°C to about 200°C will normally be used. This reaction results in a mixture of products, some of which have been identified. In the compounds of known structure, the sulfur reacts with the substituted unsaturated cycloaliphatic reactants at a double bond in the nucleus of the unsaturated reactant.

The molar ratio of sulfur to Diels-Alder adduct used in the preparation of the sulfur-containing composition is less than about 1.7:1 and preferably less than about 1:1.

The sulfurizing reaction can be conducted in the presence of suitable inert organic solvents such as mineral oils, alkanes of 7 to 18 carbons, etc., although no solvent is generally necessary. After completion of the reaction, the reaction mass can be filtered and/or subjected to other conventional purification techniques. There is no need to separate the various sulfur-containing products as they can be employed in the form of a reaction mixture comprising the compounds of known and unknown structure.

As hydrogen sulfide is an undesirable contaminant, it is advantageous to employ standard procedures for assisting in the removal of the H_2S from the products. Blowing the steam, alcohols, air, or nitrogen gas assists in the removal of H_2S as does heating at reduced pressures with or without the blowing.

It is sometimes advantageous to incorporate materials useful as sulfurization catalysts in the reaction mixture. These materials may be acidic, basic or neutral. Useful neutral and acidic materials include acidified clays such as "Super Filtrol", p-toluenesulfonic acid, dialkylphosphordithioic acids, phosphorus sulfides such as phosphorus pentasulfide and phosphites such as triaryl phosphites (e.g., triphenyl phosphite).

The basic materials may be inorganic oxides and salts such as sodium hydroxide, calcium oxide and sodium sulfide. The most desirable basic catalysts, however, are nitrogen bases including ammonia and amines. The amines include primary, secondary and tertiary hydrocarbyl amines wherein the hydrocarbyl radicals are alkyl, aryl, aralkyl, alkaryl or the like and contain about 1—20 carbon atoms. Suitable amines include aniline, benzylamine, dibenzylamine, dodecylamine, naphthylamine, tallow amines, N-ethylpropylamine, N-phenylbenzylamine, N,N-diethylbutylamine, m-toluidine and 2,3-xylidine. Also useful are heterocyclic amines such as pyrrolidine, N-methyl-pyrrolidine, piperidine, pyridine and quinoline.

The preferred basic catalysts include ammonia and primary, secondary, or tertiary alkylamines having about 1—8 carbon atoms in the alkyl radicals. Representative amines of this type are methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, di-n-butylamine, tri-n-butylamine, tri-sec-hexylamine and tri-n-octylamine. Mixtures of these amines can be used, as well as mixtures of ammonia and amines.

When a catalyst is used, the amount is generally about 0.05—2.0% of the weight of the adduct.

The following examples illustrate the preparation of the sulfur-containing compounds derived from Diels-Alder adducts.

25

Example I

To 255 parts (equivalent of 1.65 moles) of the isoprenemethacrylate adduct of Example C heated to a temperature of 110—120°C, there are added 53 parts (equivalent to 1.65 moles) of sulfur flowers over a 45 minute period. The heating is continued for 4.5 hours at a temperature in the range of 130—160°C. After cooling to room temperature, the reaction mixture is filtered through a medium sintered glass funnel. The filtrate consists of 301 parts of the desired sulfur-containing products.

30

Example II

A reaction mixture comprising 1175 parts (equivalent to 8 moles) of the Diels-Alder adduct of butyl acrylate and isoprene and 192 parts (equivalent to 6 moles) of sulfur flowers is heated for 0.5 hour at 108—110°C and then to 155—165°C for 6 hours while bubbling nitrogen gas through the reaction mixture at 0.25 to 0.5 standard cubic feet (7×10^{-3} to 14×10^{-3} m³) per hour. At the end of the heating period, the reaction mixture is allowed to cool and filtered at room temperature. Thereafter, the product is permitted to stand for 24 hours and refiltered. The filtrate is the desired product.

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Example III

Sulfur (4.5 moles) and the adduct of isoprene-methyl methacrylate (4.5 moles) are mixed at room temperature and heated for one hour at 110°C while blowing nitrogen through the reaction mass at 0.25—0.5 standard cubic feet (7×10^{-3} to 14×10^{-3} m³) per hour. Subsequently the reaction mixture is raised to a temperature of 150—155°C for 6 hours while maintaining the nitrogen blowing. After heating, the reaction mass is permitted to stand for several hours while cooling to room temperature and is thereafter filtered. The filtrate consists of 842 parts of the desired sulfur-containing product.

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Example IV

A one-liter flask fitted with a stirrer, reflux, condenser, and nitrogen inlet line is charged with 256 parts (equivalent to 1 mole) of the adduct of butadiene and isodecyl acrylate, and 51 grams (equivalent to 1.6 moles) of sulfur flowers and then heated for 12 hours at a temperature, stand for 21 hours, and filtered at room temperature to produce the desired product as the filtrate.

50

Example V

A mixture of 1703 parts (equivalent to 9.4 moles) of a butyl acrylate-butadiene adduct prepared as in Example L, 280 parts (equivalent to 8.8 moles) of sulfur and 17 parts of triphenyl phosphite is prepared in a reaction vessel and heated gradually over 2 hours to a temperature of about 185°C while stirring and sweeping with nitrogen. The reaction is exothermic near 160—170°C, and the mixture is maintained at about 185°C for 3 hours. The mixture is cooled to 90°C over a period of 2 hours and filtered using a filter aid. The filtrate is the desired product containing 14.0% sulfur.

60

Example VI

The procedure of Example V is repeated except that the triphenyl phosphite is omitted from the reaction mixture.

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Example VII

The procedure of Example V is repeated except that the triphenyl phosphite is replaced by 2.0 parts of triamyl amine as a sulfurization catalyst.

Example VIII

A mixture of 547 parts of a butyl acrylate-butadiene adduct prepared as in Example L and 5.5 parts of triphenyl phosphite is prepared in a reaction vessel and heated with stirring to a temperature of about 50°C whereupon 94 parts of sulfur are added over a period of 30 minutes. The mixture is heated to 150°C in 3 hours while sweeping with nitrogen. The mixture then is heated to about 185°C in approximately one hour. The reaction is exothermic and the temperature is maintained at about 185°C by using a cold water jacket for a period of about 5 hours. At this time, the contents of the reaction vessel are cooled to 85°C and 33 parts of mineral oil are added. The mixture is filtered at this temperature, and the filtrate is the desired product wherein the sulfur to adduct ratio is 0.98/1.

Example IX

The general procedure of Example VIII with the exception that the triphenyl phosphite is not included in the reaction mixture.

Example X

A mixture of 500 parts (equivalent to 2.7 moles) of a butyl acrylate-butadiene adduct prepared as in Example L and 109 parts (equivalent to 3.43 moles) of sulfur is prepared and heated to 180°C and maintained at a temperature of about 180–190°C for about 6.5 hours. The mixture is cooled while sweeping with a nitrogen gas to remove hydrogen sulfide odor. The reaction mixture is filtered and the filtrate is the desired product containing 15.8% sulfur.

Example XI

A mixture of 728 parts (equivalent to 4.0 moles) of a butyl acrylate-butadiene adduct prepared as in Example L, 218 parts (equivalent to 6.8 moles) of sulfur, and 7 parts of triphenyl phosphite is prepared and heated with stirring to a temperature of about 181°C over a period of 1.3 hours. The mixture is maintained under a nitrogen purge at a temperature of 181–187°C for 3 hours. After allowing the material to cool to about 85°C over a period of 1.4 hours, the mixture is filtered using a filter aid, and the filtrate is the desired product containing 23.1% sulfur.

Example XII

A mixture of 910 parts (equivalent to 5 moles) of a butyl acrylate-butadiene adduct prepared as in Example L, 208 parts (equivalent to 6.5 moles) of sulfur and 9 parts of triphenyl phosphite is prepared and heated with stirring and nitrogen sweeping to a temperature of about 140°C over 1.3 hours. The heating is continued to raise the temperature to 187°C over 1.5 hours, and the material is held at 183–187°C for 3.2 hours. After cooling the mixture to 89°C, the mixture is filtered with a filter aid, and the filtrate is the desired product containing 18.2% sulfur.

Example XIII

A mixture of 910 parts (equivalent to 5 moles) of a butyl acrylate-butadiene adduct prepared as in Example L, 128 parts (equivalent to 4 moles) of sulfur and 9 parts of triphenyl phosphite is prepared and heated with stirring while sweeping with nitrogen to a temperature of 142°C over a period of about one hour. The heating is continued to raise the temperature to 185–186°C over about 2 hours and the mixture is maintained at 185–187°C for 3.2 hours. After allowing the reaction mixture to cool to 96°C, the mixture is filtered with filter aid, and the filtrate is the desired product containing 12.0% sulfur.

Example XIV

The general procedure of Example XIII repeated except that the mixture contain 259 parts (equivalent to 8.09 moles) of sulfur. The product obtained in this manner contains 21.7% sulfur.

It has been found that, if these sulfur-containing products are treated with an aqueous solution of sodium sulfide containing from about 5% to about 75% by weight Na_2S , the treated product may exhibit less of a tendency to darken freshly polished copper metal.

Treatment involves the mixing together of the sulfurized reaction product and the sodium sulfide solution for a period of time sufficient for any unreacted sulfur to be scavenged, usually a period of a few minutes to several hours depending on the amount of unreacted sulfur, the quantity and the concentration of the sodium sulfide solution. The temperature is not critical but normally will be in the range of about 20°C to about 100°C. After the treatment, the resulting aqueous phase is separated from the organic phase by conventional techniques, i.e., decantation, etc. Other alkali metal sulfides, M_2S_x where M is an alkali metal and x is 1, 2, or 3 may be used to scavenge unreacted sulfur but those where x is greater than 1 are not nearly as effective. Sodium sulfide solutions are preferred for reasons of economy and effectiveness. This procedure is described in more detail in U.S. Patent 3,498,915.

It has also been determined that treatment of the reaction products with solid, insoluble acidic

materials such as acidified clays or acidic resins and thereafter filtering the sulfurized reaction mass improves the product with respect to its color and solubility characteristics. Such treatment comprises thoroughly mixing the reaction mixture with from about 0.1% to about 10% by weight of the solid acidic material at a temperature of about 25—150°C and subsequently filtering the product.

5 As previously mentioned, there is no need to separate the sulfur-containing products which are produced in the above reactions. The reaction product is a mixture which comprises the compounds whose structures have been ascertained but which also comprises compounds whose structures are unknown. Since it is economically unfeasible to separate the components of the reaction mixture, they are employed in combination as a mixture of sulfur-containing compounds.

10 In order to remove the last traces of impurities from the reaction mixture, particularly when the adduct employed was prepared using a Lewis acid catalyst, (e.g., AlCl_3) it is sometimes desirable to add an organic inert solvent to the liquid reaction product and, after thorough mixing, to refilter the material. Subsequently the solvent is stripped from the product. Suitable solvents include solvents of the type mentioned hereinabove such as benzene, toluene, the higher alkanes, etc. A particularly useful class of solvents are the
15 textile spirits.

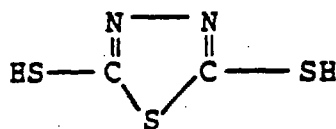
In addition, other conventional purification techniques can be advantageously employed in purifying sulfurized products used in this invention. For example, commercial filter aids can be added to the materials prior to filtration to increase the efficiency of the filtration. Filtering through diatomaceous earth is particularly useful where the use contemplated requires the removal of substantially all solid materials.
20 However, such expedients are well known to those skilled in the art and require no elaborate discussion herein.

The weight ratio of metal salt (A) to sulfurized adduct (B) in composition of the invention is within the range of from about 1:10 to about 50:1. The precise amounts of the two components to be included in the compositions of the invention can be readily determined by one skilled in the art.

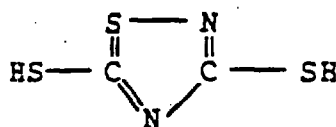
25 The compositions of the present invention also contain at least one auxiliary corrosion-inhibiting material (component (C)). In one embodiment, corrosion-inhibiting component (C) is at least one dimercaptothiadiazoole or oil-soluble derivative thereof. Such materials provide corrosion-inhibiting properties, and particularly, such compositions are useful in inhibiting copper activity such as copper staining.

30 The dimercaptothiadiazoles which can be utilized in the present invention starting materials for the preparation of oil-soluble derivatives containing the dimercaptothiadiazoole nucleus have the following structural formulae and names.

35 2,5-Dimercapto-1,3,4-thiadiazole



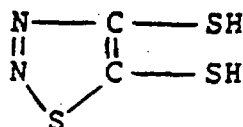
40 3,5-Dimercapto-1,2,4-thiadiazole



45 3,4-Dimercapto-1,2,5-thiadiazole



50 4,5-Dimercapto-1,2,3-thiadiazole



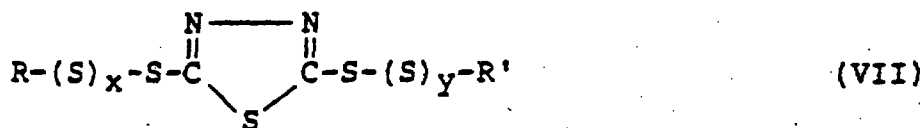
60 Of these the most readily available, and the one preferred for the purposes of this invention, is 2,5-dimercapto-1,3,4-thiadiazole. This compound will sometimes be referred to hereinafter as DMTD. However,

it is to be understood that any of the other dimercaptothiadiazoles may be substituted for all or a portion of the DMTD.

DMTD is conveniently prepared by the reaction of one mole of hydrazine, or a hydrazine salt, with two moles of carbon disulfide in an alkaline medium, followed by acidification.

The compositions of the present invention are lubricating oils, and component (C) is generally DMTD or derivatives of DMTD. Derivatives of DMTD have been described in the art, and any such compounds can be included in the compositions of the present invention. The preparation of some derivatives of DMTD is described in E. K. Fields "Industrial and Engineering Chemistry", 49, p. 1361-4 (September 1957). For the preparation of the oil-soluble derivatives of DMTD, it is possible to utilize already prepared DMTD or to prepare the DMTD in situ and subsequently adding the material to be reacted with DMTD.

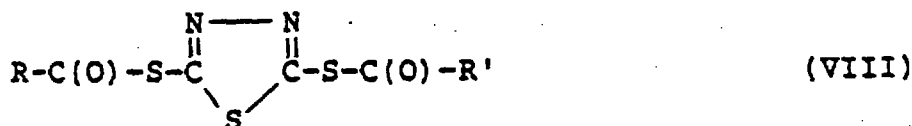
U.S. Patents 2,719,125; 2,719,126; and 3,087,937 describe the preparations of various 2,5-bis(hydrocarbon dithio)-1,3,4-thiadiazoles. The hydrocarbon group may be aliphatic or aromatic, including cyclic, alicyclic, aralkyl, aryl and alkaryl. Such compositions are effective corrosion-inhibitors for silver, silver alloys and similar metals. Such polysulfides which can be represented by the following general formula



wherein R and R' may be the same or different hydrocarbon groups, and x and y be integers from 0 to about 8, and the sum of x and y being at least 1. A process for preparing such derivatives is described in U.S. Patent 2,191,125 as comprising the reaction of DMTD with a suitable sulphenyl chloride or by reacting the dimercapto diathiazole with chlorine and reacting the resulting disulphenyl chloride with a primary or tertiary mercaptan. Suitable sulphenyl chlorides useful in the first procedure can be obtained by chlorinating a mercaptan (RSH or R'SH) with chlorine in carbon tetrachloride. In a second procedure, DMTD is chlorinated to form the desired bisulphenyl chloride which is then reacted with at least one mercaptan (RSH and/or R'SH).

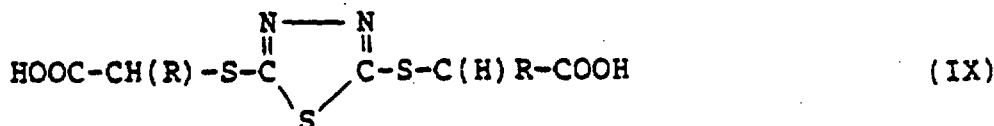
U.S. Patent 3,087,932 describes a one-step process for preparing 2,5-bis(hydrocarblydithio)-1,3,4-thiadiazole. The procedure involves the reaction of either DMTD or its alkali metal or ammonium salt and a mercaptan in the presence of hydrogen peroxide and a solvent. Oil-soluble or oil-dispersible reaction products of DMTD can be prepared also by the reaction of the DMTD with a mercaptan and formic acid. Compositions prepared in this manner are described in U.S. Patent 2,749,311. Any mercaptan can be employed in the reaction although aliphatic and aromatic mono- or poly-mercaptan containing from 1 to 30 carbon atoms are preferred.

Carboxylic esters of DMTD having the general formula



wherein R and R' are hydrocarbon groups such as aliphatic, aryl and alkaryl groups containing from about 2 to about 30 or more carbon atoms are described in U.S. Patent 2,760,933. These esters are prepared by reacting DMTD with an organic acid halide (chloride) and a molar ratio of 1:2 at a temperature of from about 25 to about 130°C. Suitable solvents such as benzene or dioxane can be utilized to facilitate the reaction. The reaction product is washed with dilute aqueous alkali to remove hydrogen chloride and any unreacted carboxylic acid.

Condensation products of alpha-halogenated aliphatic monocarboxylic acids having at least 10 carbon atoms with DMTD are described in U.S. Patent 2,836,564. These condensation products generally are characterized by the following formula



wherein R is an alkyl group of at least 10 carbon atoms. Examples of alpha-halogenated aliphatic fatty acids which can be used include alpha-bromo-lauric acid, alpha-chloro-lauric acid, alpha-chloro-stearic acid, etc.

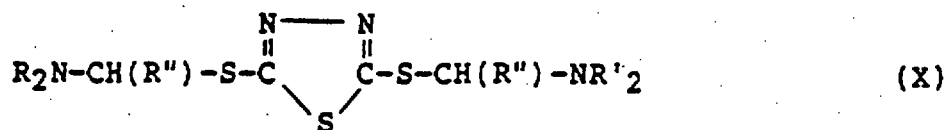
Oil-soluble reaction products of unsaturated cyclic hydrocarbons and unsaturated ketones are described in U.S. Patents 2,764,547 and 2,799,652, respectively.

Examples of unsaturated cyclic hydrocarbons described in the '547 patent include styrene, alpha-methyl styrene, pinene, dipentene, cyclopentadiene, etc. The unsaturated ketones described in U.S. Patent 2,799,652 include aliphatic, aromatic or heterocyclic unsaturated ketones containing from about 4 to 40

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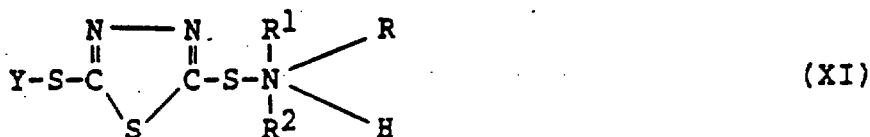
carbon atoms and from 1 to 6 double bonds. Examples include mesityl oxide, phorone, isophorone, benzalacetophenone, furfural acetone, difurfuryl acetone, etc.

U.S. Patent 2,765,289 describes products obtained by reacting DMTD with an aldehyde and a diaryl amine in molar proportions of from about 1:1:1 to about 1:4:4. The resulting products are suggested as having the general formula

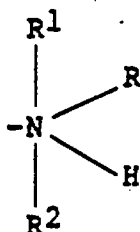


wherein R and R' are the same or different aromatic groups, and R'' is hydrogen, an alkyl group, or an aromatic group. The aldehydes useful in the preparation of such products as represented by Formula X include aliphatic or aromatic aldehydes containing from 1 to 24 carbon atoms, and specific examples of such aldehydes include formaldehyde, acetaldehyde, benzaldehyde, 2-ethylhexyl aldehyde, etc.

Component (C) in the compositions of the present invention also may be amine salts of DMTD such as those having the following formula

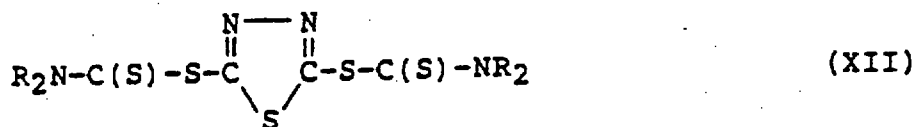


in which Y is hydrogen or the amino group



in which R is an aliphatic, aromatic or heterocyclic group, and R¹ and R² are independently aliphatic, aromatic or heterocyclic groups containing from about 6 to about 60 carbon atoms. The amine used in the preparation of the amine salts can be aliphatic or aromatic mono- or polyamines, and the amines may be primary, secondary or tertiary amines. Specific examples of suitable amines include hexylamine, dibutylamine, dodecylamine, ethylenediamine, propylenediamine, tetraethylenepentamine, and mixtures thereof. U.S. Patent 2,910,439 lists suitable amine salts.

Dithiocarbamate derivatives of DMTD are described in U.S. Patents 2,690,999 and 2,719,827. Such compositions can be represented by the following formulae



and



wherein the R groups are straight-chain or branch-chain saturated or unsaturated hydrocarbon groups selected from the group consisting of alkyl, aralkyl and alkaryl groups.

U.S. Patent 2,850,453 describes products which are obtained by reacting DMTD, and aldehyde and an alcohol or an aromatic hydroxy compound in a molar ratio of from 1:2:1 to 1:6:5. The aldehyde employed can be an aliphatic aldehyde containing from 1 to 20 carbon atoms or an aromatic or heterocyclic aldehyde containing from about 5 to about 30 carbon atoms. Examples of suitable aldehydes include formaldehyde, acetaldehyde, benzaldehyde. The reaction can be conducted in the presence or absence of suitable solvents by (a) mixing all of the reactants together and heating, (b) by first reacting an aldehyde with the alcohol or the aromatic hydroxy compound, and then reacting the resultant intermediate with the thiadiazole, or (c) by reacting the aldehyde with thiadiazole first and the resulting intermediate with the hydroxy compound.

U.S. Patent 2,703,784 describes products obtained by reacting DMTD with an aldehyde and a mercaptan. The aldehydes are similar to those disclosed in U.S. Patent 2,850,453, and the mercaptans may be aliphatic or aromatic mono- or poly-mercaptans containing from about 1 to 30 carbon atoms. Examples of suitable mercaptans include ethyl mercaptan, butyl mercaptan, octyl mercaptan, thiophenol, etc.

The preparation of 2-hydrocarbyldithio-5-mercapto-1,3,4-thiadiazoles having the formula



wherein R' is a hydrocarbyl substituent is described in U.S. Patent 3,663,561. The compositions are prepared by the oxidative coupling of equimolecular portions of a hydrocarbyl mercaptan and DMTD or its alkali metal mercaptide. The compositions are reported to be excellent sulfur scavengers and are useful in preventing copper corrosion by active sulfur. The mono-mercaptans used in the preparation of the compounds are represented by the formula



wherein R' is a hydrocarbyl group containing from 1 to about 280 carbon atoms. A peroxy compound, hypohalide or air, or mixtures thereof can be utilized to promote the oxidative coupling. Specific examples of the mono-mercaptan include methyl mercaptan, isopropyl mercaptan, hexyl mercaptan, decyl mercaptan, and long chain alkyl mercaptans, for example, mercaptans derived from propene polymers and isobutylene polymers especially polyisobutylenes, having 3 to about 70 propene or isobutylene units per molecule.

Another material useful as component (C) in the compositions of the present invention is obtained by reacting a thiadiazole, preferably DMTD with an oil-soluble dispersant, preferably a substantially neutral or acidic carboxylic dispersant in a diluent by heating the mixture above about 100°C. This procedure, and the derivatives produced thereby are described in U.S. Patent 4,136,043. The oil-soluble dispersants which are utilized in the reaction with the thiadiazoles are often identified as "ashless dispersants". Various types of suitable ashless dispersants useful in the reaction are described in the '043 patent.

Another material useful as component (C) in the compositions of the invention is obtained by reacting a thiadiazole, preferably DMTD, with a peroxide, preferably hydrogen peroxide. The resulting nitrogen- and sulfur-containing composition is then reacted with a polysulfide, mercaptan or amino compound (especially oil-soluble, nitrogen-containing dispersants). This procedure and the derivatives produced thereby are described in U.S. Patent 4,246,126.

U.S. Patent 4,140,643 describes nitrogen and sulfur-containing compositions which are oil-soluble and which are prepared by reacting a carboxylic acid or anhydride containing up to about 10 carbon atoms and having at least one olefinic bond with compositions of the type described in U.S. Patent 4,136,043. The preferred carboxylic acid or anhydride is maleic anhydride.

U.S. Patent 4,097,387 described DMTD derivatives prepared by reacting a sulfur halide with an olefin to form an intermediate which is then reacted with an alkali metal salt of DMTD. More recently, U.S. Patent 4,487,706 describes a DMTD derivative prepared by reacting an olefin, sulfur dichloride and DMTD in a one-step reaction. The olefins generally contain from about 6 to 30 carbon atoms.

The amount of the auxiliary corrosion-inhibitor such as the oil-soluble derivatives of dimercaptothiadiazole (component (C)) included in the compositions of the present invention may vary over a wide range depending upon the intended end use of the composition. In the lubricating oil compositions of the present invention, the amount of the thiadiazole derivative included in the composition should be an amount sufficient to provide the desired corrosion-inhibiting properties to the final lubricating oil. Thus, the weight ratio of the auxiliary corrosion-inhibitor (C) to the mixture of components (A) and (B) is from about 0.001:1 to about 0.5:1.

The compositions of the present invention also may contain other materials which are useful in providing additional desirable properties to the composition. Materials which have desirable properties which may be included in the compositions of the invention include, for example, detergents and dispersants of the ash-producing or ashless-type, extreme pressure agents, anti-wear agents, color stabilizers, anti-foam agents, etc.

In one embodiment of the present invention, the compositions of the present invention will contain, in addition to components (A), (B) and (C), at least one oil-soluble dispersant/detergent (component (D)). The dispersant/detergents may be of the ash-producing or the ashless type.

The ash-producing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids or carboxylic acids. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid group. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing

agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of about 50°C and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60–200°C.

Ashless detergents and dispersants are so called despite the fact that, depending on its constitution, the dispersant may upon combustion yield a non-volatile material such as boric oxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricant compositions of this invention.

The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. patents including the following:

3,163,603	3,351,552	3,541,012
3,215,707	3,399,141	3,542,680
3,271,310	3,433,744	3,574,101
3,281,357	3,488,048	3,630,904
3,311,558	3,451,933	3,632,511
3,340,281	3,467,668	3,725,441
3,346,493	3,522,179	Re 26,433

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably olyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. patents:

3,275,544	3,454,555
3,438,757	3,565,804

(3) Reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. patents are illustrative:

2,459,112	3,442,808	3,591,598
2,984,550	3,454,497	3,634,515
3,166,516	3,461,172	3,697,574
3,355,270	3,539,633	3,725,480
3,413,347	3,586,629	3,980,569

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, or the like. Exemplary materials of this type are described in the following U.S. patents:

3,036,003	3,282,955	3,493,520	3,639,242
3,200,107	3,366,569	3,513,093	3,649,659
3,254,025	3,373,111	3,539,633	3,697,574
3,278,550	3,442,808	3,579,450	3,703,536
3,281,428	3,455,832	3,600,372	3,708,422

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. patents:

3,329,658	3,666,730
3,449,250	3,687,849
3,519,565	3,702,300

When the detergent/dispersant (component (D)) is included in the composition of the invention, the weight ratio of component (D) to the combined weight of (A) and (B) will be in the range of from about 1:0.5 to about 1:5.

Oil-soluble compositions comprising components (A), (B) and (C) and/or (D) can be added directly to a lubricant to form a composition in accordance with the invention. Preferably, however, the oil-soluble compositions are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from about 20% to about 90% by weight of the oil-soluble compositions and may contain, in addition, one or more other additives known in the art and described below. The remainder of the concentrate is the substantially inert normally liquid diluent.

The combination of components (A), (B), (C) and/or (D) is useful particularly for improving the properties of lubricants containing little or no phosphorus, that is lubricants containing less than 0.1% and more generally less than about 0.08% phosphorus. In some instances, the lubricating compositions may contain no phosphorus. Generally, any phosphorus which is present within the lubricating oil compositions of the present invention is in the form of a phosphorodithioate, and more particularly, as Group II metal phosphorodithioates, organic phosphites such as trialkyl phosphites, etc. Lubricating oil compositions containing less than about 0.1% by weight of phosphorus, and more preferably generally less than about 0.08% by weight of phosphorus generally are known in the art as "low phosphorus lubricating oils". In such low phosphorus or no phosphorus lubricants, it is preferred to use a sulfurized Diels-Alder adduct (component (B)) prepared by reacting sulfur with an adduct in a mole ratio of less than 1:1.

The lubricating oil compositions of the present invention comprise a major amount of oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers, chlorinated polybutylenes, etc.); poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃₋₈ fatty acid esters, of the C₁₃Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

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

Silicon-based oils such as the polyalkylpolyaryl-, polyalkoxy, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-hexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexyl-(4-methyl-2-pentoxyl)disiloxane, poly(methyl)siloxanes, poly(methylphenyl)siloxanes, etc.). Other synthetic lubricating oils include polymeric tetrahydrofurans and the like.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many

such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

The oil-soluble compositions containing components (A), (B), (C) and/or (D) will be employed in the lubricating composition of the invention in an amount sufficient to provide the desired improvement in properties such as improved oxidation-corrosion-inhibition, anti-wear and/or extreme pressure properties. More generally, this amount will be from about 0.001% to about 20% by weight of the particular oil in which they are utilized. The optimum amount to be used in a given lubricant obviously would depend on the other contents of the particular oil in which they are utilized. The optimum amount to be used in a given lubricant obviously would depend on the other contents of the particular lubricating composition, the operating conditions to which it is to be subjected, and the particular additives employed. In lubricating compositions operated under extremely adverse conditions, such as lubricating compositions for marine diesel engines, the compositions may be present in the lubricant in amounts of up to about 30% by weight, or more, of the total weight of the lubricating composition.

In one preferred embodiment, the lubricating oil compositions will comprise an oil of lubricating viscosity and components (A), (B) and (C) as described above. Generally, however, component (D) also will be included in the lubricants. The invention also contemplates the use of other additives in the lubricant compositions of this invention. Such additives include, for example, oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers and anti-foam agents.

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl)disulfide, dibutyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene. Group II metal phosphorodithioates include zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)phosphorodithioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol. When it is desired to formulate lubricating oils containing especially low amounts of phosphorus, such phosphorodithioates should be avoided when possible.

Many of the above-mentioned auxiliary extreme pressure agents and corrosion-oxidation inhibitors also serve as anti-wear agents. Zinc dialkylphosphorodithioates are well known examples.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See, for example, page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. publishers, Cleveland, Ohio, 1967).

Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their use are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,877; 2,721,878; and 3,250,715.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

The following are illustrative examples of the lubricant compositions of the present invention (as well as examples of oil-soluble compositions comprising components (A), (B), (C) and/or (D), and additive concentrates). All parts and percentages are by weight of the total composition unless otherwise indicated.

Example 1

	Parts by Weight
Molybdenum di(2-ethylhexyl)dithiocarbamate	5
Product of Example XIII	0.5
DMTD derivatives of Formula VII where x = 0 and R and R ¹ are hexyl groups	0.2

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Example 2

Parts by Weight

5	Zinc dibutyldithiocarbamate	5
	Product of XIII	0.5
10	DMTD derivatives of Formula VII where x = 0 and R and R ¹ are hexyl groups	0.2

Example 3

	Zinc diamyldithiocarbamate	10
15	Product of Example IV	10
20	Reaction product of DMTD, formaldehyde and tertiary octyl mercaptan prepared as in Example I of U.S. Patent 2,703,784	0.1

Example 4

	Zinc diamyldithiocarbamate	10
25	Product of Example IV	10
30	2-ethyldithia-5-mercapto-1, 3,4-thiadiazole prepared with the procedure of Example I of U.S. Patent 3,663,561	0.1

Example 5

	Mineral oil	70
35	Composition of Example 3	30

Example 6

40	Mineral oil	94
	Composition of Example 4	3

Example 7

45	Mineral oil	93.5
	Zinc diamyldithiocarbamate	3.90
	Product of Example IV	2.0
50	Reaction product of DMTD, formaldehyde and tertiary octyl mercaptan prepared as in Example I of U.S. Patent 2,702,784	0.1
55	Reaction product of alkylene polyamine with polybutenyl (molecular weight of about 1700) succinic anhydride	1.4
	Silicon anti-foam agent	0.01

Example 8

Parts by Weight

60	Mineral oil	89.5
65	Zinc diamyldithiocarbamate	2.0

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Example 8 — contd.

		Parts by Weight
	Product of Example III	2.0
5	Reaction product of ethylenepolyamine with polyisobutenyl (molecular weight of about 1000) succinic anhydride	4.1
	Basic magnesium petroleum sulfonate	1.5
10	Reaction product of DMTD, formaldehyde and t-octyl mercaptan prepared as in Example I of U.S. Patent 2,703,784	0.2
	Alkylated arylamine	0.7
15	Silicon anti-foam agent	0.007

Example 9

20	Mineral oil	90.3
	Zinc diamylthiocarbamate	2.0
	Product of Example III	2.0
25	Reaction product of ethylenepolyamine with polyisobutenyl (molecular weight of about 1000) succinic anhydride	4.1
	Basic magnesium petroleum sulfonate	1.5
30	1,3,4-thiadiazolyl-2,5-bis-(diethyl dithiocarbamate)	0.1
	Silicon anti-foam agent	0.007

35 Lubricating oil compositions containing the compositions of the invention as illustrated above exhibit improved corrosion-inhibiting, anti-oxidant, anti-wear and extreme pressure properties. When the lubricating oil composition of this invention contain substantially no phosphorus and a sulfurized Diels-Alder adduct having a molar ratio of sulfur to adduct of less than 1:1, good nitrile seal compatability is obtained.

40 Claims

1. A lubricating oil composition comprising:
a major amount of an oil of lubricating viscosity and, a minor, property improving, amount of an oil-
45 soluble composition comprising:
(A) at least one metal salt of at least one dithiocarbamic acid of the formula



50 wherein R_1 and R_2 are each independently hydrocarbyl groups containing a total number of carbon atoms so as to render the metal salt oil-soluble; and

(B) at least one oil-soluble sulfurized organic compound comprising the reaction product of sulphur and a Diels-Alder adduct in a molar ratio of less than about 1.7:1, wherein the weight ratio of (A) to (B) is in the range of from about 1:10 to about 50:1; and

55 (C) at least one auxiliary corrosion-inhibitor in the form of an oil-soluble derivative of a dimercaptiothiadiazole wherein the weight ratio of (C) to the mixture of (A) and (B) is from about 0.001:1 to about 0.5:1; and wherein the lubricating oil composition contains less than about 0.1% by weight of phosphorus.

2. A lubricating oil composition according to claim 1 wherein R_1 and R_2 are alkyl groups containing at least 2 carbon atoms and wherein the metal of the metal salt (A) is a polyvalent metal.

60 3. A lubricating oil composition according to either of claims 1 and 2 wherein (B) is a sulfurized Diels-Alder adduct of at least one dienophile with at least one aliphatic conjugated diene and the dienophile comprises an alpha, beta-ethylenically unsaturated aliphatic carboxylic acid ester, carboxylic acid amide, halide, nitrile, aldehyde, ketone, or mixture thereof.

65

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Example 8 — contd.

		Parts by Weight
5	Product of Example III	2.0
	Reaction product of ethylenepolyamine with polyisobutenyl (molecular weight of about 1000) succinic anhydride	4.1
	Basic magnesium petroleum sulfonate	1.5
10	Reaction product of DMTD, formaldehyde and t-octyl mercaptan prepared as in Example I of U.S. Patent 2,703,784	0.2
	Alkylated arylamine	0.7
15	Silicon anti-foam agent	0.007

Example 9

20	Mineral oil	90.3
	Zinc diamyldithiocarbamate	2.0
	Product of Example III	2.0
25	Reaction product of ethylenepolyamine with polyisobutenyl (molecular weight of about 1000) succinic anhydride	4.1
	Basic magnesium petroleum sulfonate	1.5
30	1,3,4-thiadiazolyl-2,5-bis-(diethyl dithiocarbamate)	0.1
	Silicon anti-foam agent	0.007

35 Lubricating oil compositions containing the compositions of the invention as illustrated above exhibit improved corrosion-inhibiting, anti-oxidant, anti-wear and extreme pressure properties. When the lubricating oil composition of this invention contain substantially no phosphorus and a sulfurized Diels-Alder adduct having a molar ratio of sulfur to adduct of less than 1:1, good nitrile seal compatability is obtained.

40 Claims

1. A lubricating oil composition comprising:
a major amount of an oil of lubricating viscosity and, a minor, property improving, amount of an oil-
soluble composition comprising:
45 (A) at least one metal salt of at least one dithiocarbamic acid of the formula



50 wherein R_1 and R_2 are each independently hydrocarbyl groups containing a total number of carbon atoms so as to render the metal salt oil-soluble; and

(B) at least one oil-soluble sulfurized organic compound comprising the reaction product of sulphur and a Diels-Alder adduct in a molar ratio of less than about 1.7:1, wherein the weight ratio of (A) to (B) is in the range of from about 1:10 to about 50:1; and

55 (C) at least one auxiliary corrosion-inhibitor in the form of an oil-soluble derivative of a dimercaptiothiadiazole wherein the weight ratio of (C) to the mixture of (A) and (B) is from about 0.001:1 to about 0.5:1; and wherein the lubricating oil composition contains less than about 0.1% by weight of phosphorus.

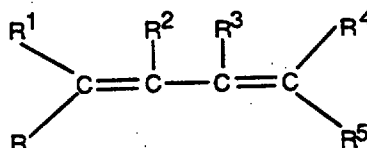
2. A lubricating oil composition according to claim 1 wherein R_1 and R_2 are alkyl groups containing at least 2 carbon atoms and wherein the metal of the metal salt (A) is a polyvalent metal.

60 3. A lubricating oil composition according to either of claims 1 and 2 wherein (B) is a sulfurized Diels-Alder adduct of at least one dienophile with at least one aliphatic conjugated diene and the dienophile comprises an alpha, beta-ethylenically unsaturated aliphatic carboxylic acid ester, carboxylic acid amide, halide, nitrile, aldehyde, ketone, or mixture thereof.

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4. A lubricating oil composition according to claim 3 wherein the aliphatic conjugated diene corresponds to the formula



wherein R and R¹ to R⁵ are each independently selected from hydrogen, alkyl, halo, alkoxy, alkenyl, alkenyloxy, carboxyl, cyano, amino, alkylamino, dialkylamino, phenyl, and phenyl substituted with one to three substituents corresponding to R and R¹ to R⁵; or R, R², R³ and R⁵ are as described above and R¹ and R⁴ are alkylene groups joined together to form a cyclic diene.

5. A lubricating oil composition according to claim 4 wherein the diene is 1,3-butadiene.

6. A lubricating oil composition according to any one of claims 3 to 5 wherein the dienophile contains at least one, but not more than two, —C(O)OR₀ groups wherein R₀ is a residue of a saturated aliphatic alcohol of up to about 40 carbon atoms.

7. A lubricating oil composition according to any one of claims 3 to 5 wherein the dienophile is an ester of acrylic acid or methacrylic acid.

8. A lubricating oil composition according to any preceding claim, further comprising (D) an oil-soluble dispersant/detergent wherein the weight ratio of (D) to the combined weight of (A) and (B) is in the range of from about 1:0.5 to about 1.5.

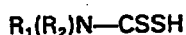
9. A lubricating oil composition according to any preceding claim wherein any phosphorus present is present in the form of a phosphorodithioate.

10. A lubricating oil composition according to any one of claims 1 to 8 wherein the lubricating oil composition contains substantially no phosphorus.

11. A lubricating oil composition according to any one of claims 1 to 10 wherein (B) is a reaction product of sulphur and a Diels-Alder adduct in a molar ratio of less than about 1:1.

12. A process for preparing a lubricating oil composition comprising adding to a major amount of an oil of lubricating viscosity, a minor, property improving amount of an oil-soluble composition comprising:

(A) at least one metal salt of at least one dithiocarbamic acid of the formula



(I)

wherein R₁ and R₂ are each independently hydrocarbyl groups containing a total number of carbon atoms so as to render the metal salt oil-soluble; and

(B) at least one oil-soluble sulfurized organic compound comprising the reaction product of sulphur and a Diels-Alder adduct in a molar ratio of less than about 1.7:1, wherein the weight ratio of (A) to (B) is in the range of from about 1:10 to about 50:1; and

(C) at least one auxiliary corrosion-inhibitor in the form of an oil-soluble derivative of a dimercaptiothiadiazole wherein the weight ratio of (C) to the mixture of (A) and (B) is from about 0.001:1 to about 0.5:1; and wherein the lubricating oil composition contains less than about 0.1% by weight of phosphorus.

Patentansprüche

1. Schmierölzusammensetzung, umfassend: eine größere Menge eines öls mit Schmierviskosität und eine kleinere, die Eigenschaften verbessernde Menge einer öllöslichen Zusammensetzung, umfassend: (A) mindestens ein Metallsalz mindestens einer Dithiocarbaminsäure der Formel



(II)

in der R₁ und R₂ jeweils unabhängig Kohlenwasserstoffreste mit einer derartigen Gesamtkohlenstoffatomzahl bedeuten, daß das Metallsalz öllöslich wird und

(B) mindestens eine öllösliche, geschwefelte organische Verbindung, die das Reaktionsprodukt von Schwefel und einem Diels-Alder-Addukt in einem molaren Verhältnis von weniger als etwa 1,7:1 umfaßt, wobei das Gewichtsverhältnis von (A) zu (B) im Bereich von etwa 1:10 bis 50:1 liegt; und

(C) mindestens einen Korrosions-Inhibitor-Zusatz in Form eines öllöslichen Derivats eines Dimercaptiothiadiazols, wobei das Gewichtsverhältnis von (C) zu dem Gemisch von (A) und (B) etwa 0,001:1 bis etwa 0,5:1 beträgt; und wobei die Schmierölzusammensetzung weniger als etwa 0,1 Gew.-% an Phosphor enthält.

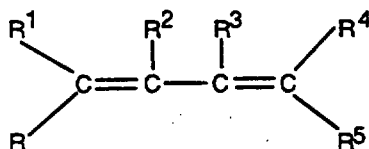
2. Schmierölzusammensetzung nach Anspruch 1, wobei R₁ und R₂ Alkylreste mit mindestens zwei Kohlenstoffatomen bedeuten und wobei das Metall des Metallsalzes (A) ein mehrwertiges Metall bedeutet.

3. Schmierölzusammensetzung nach einem der Ansprüche 1 und 2, wobei (B) ein geschwefeltes Diels-Alder-Addukt von mindestens einem Dienophil mit mindestens einem aliphatisch konjugierten Dien ist und das Dienophil ein Carbonsäureester, ein Carbonsäureamid, ein Halogenid, ein Nitril, ein Aldehyd, ein



Keton, welche aliphatisch und α -, β -ethylenisch ungesättigt sind, oder ein Gemisch davon umfaßt.

4. Schmierölzusammensetzung nach Anspruch 3, wobei das aliphatisch konjugierte Dien der Formel



entspricht, in der R und R¹ bis R⁵ jeweils unabhängig Wasserstoffatome, Halogenatome, Alkylreste, Alkoxyreste, Alkenylreste, Alkenyloxyreste, Carboxylgruppen, Cyanogruppen, Aminogruppen, Alkylaminoreste, Dialkylaminoreste oder Phenylgruppen oder mit 1 bis 3 Substituenten entsprechend R und R¹ bis R⁵ substituierte Phenylgruppen bedeuten; oder R, R², R³ und R⁵ die vorstehende Bedeutung haben und R¹ und R⁴ Alkylengruppen sind, die miteinander verbunden ein cyclisches Dien bilden.

5. Schmierölzusammensetzung nach Anspruch 4, wobei das Dien 1,3-Butadien ist.

6. Schmierölzusammensetzung nach einem der Ansprüche 3 bis 5, wobei das Dienophil mindestens eine, aber nicht mehr als zwei —C(O)OR₆-Gruppen enthält, wobei R₆ der Rest eines gesättigten aliphatischen Alkohols mit bis zu 40 Kohlenstoffatomen bedeutet.

7. Schmierölzusammensetzung nach einem der Ansprüche 3 bis 5, wobei das Dienophil ein Ester einer Acryl- oder Methacrylsäure ist.

8. Schmierölzusammensetzung nach einem der vorhergehenden Ansprüche umfassend weiterhin (D) ein öllösliches Dispersant/Detergent, wobei das Gewichtsverhältnis von (D) zum Gesamtgewicht von (A) und (B) im Bereich von etwa 1:0,5 bis etwa 1,5 liegt.

9. Schmierölzusammensetzung nach einem der vorhergehenden Ansprüche, wobei jeglich vorhandener Phosphor in Form eines Phosphordithioates vorliegt.

10. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 8, wobei die Schmierölzusammensetzung im wesentlichen keinen Phosphor enthält.

11. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 10, wobei (B) ein Umsetzungsprodukt von Schwefel mit einem Diels-Alder-Addukt in einem molaren Verhältnis von weniger als etwa 1:1 ist.

12. Verfahren zur Herstellung einer Schmierölzusammensetzung, umfassend: die Zugabe einer größeren Menge eines öls mit Schmierviskosität und eine kleineren, die Eigenschaften verbessernde Menge einer öllöslichen Zusammensetzung, umfassend:

(A) mindestens ein Metallsalz mindestens einer Dithiocarbamidsäure der Formel



in der R₁ und R₂ jeweils unabhängig Kohlenwasserstoffreste mit einer derartigen Gesamtkohlenstoffatomzahl bedeuten, daß das Metallsalz öllöslich wird und

(B) mindestens eine öllösliche, geschwefelte organische Verbindung, die das Reaktionsprodukt von Schwefel und einem Diels-Alder-Addukt in einem molaren Verhältnis von weniger als etwa 1,7:1 umfaßt, wobei das Gewichtsverhältnis von (A) zu (B) im Bereich von etwa 1:10 bis 50:1 liegt; und

(C) mindestens einen Korrosions-Inhibitor-Zusatz in Form eines öllöslichen Derivats eines Dimercaptiothiadiazols, wobei das Gewichtsverhältnis von (C) zu dem Gemisch von (A) und (B) etwa 0,001:1 bis etwa 0,5:1 beträgt; und wobei die Schmierölzusammensetzung weniger als etwa 0,1 Gew.-% an Phosphor enthält.

Revendications

1. Composition d'huile lubrifiante qui comprend: une importante quantité d'une huile de viscosité lubrifiante et une petite quantité, améliorant les propriétés, d'une composition soluble dans l'huile comprenant:

(A) au moins un sel de métal d'au moins un acide dithiocarbamique de formule



dans laquelle R₁ et R₂ sont chacun indépendamment des groupes hydrocarbonés contenant un nombre d'atomes de carbone capable de rendre le sel de métal soluble dans l'huile; et

(B) au moins un composé organique sulfuré soluble dans l'huile comprenant le produit de la réaction du soufre et d'un composé d'addition de Diels-Alder dans un rapport molaire inférieur à environ 1,7:1, le rapport pondéral de (A) à (B) étant compris dans l'intervalle allant d'environ 1:10 à environ 50:1; et

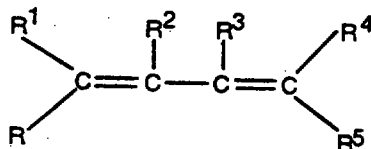
(C) au moins un inhibiteur auxiliaire de corrosion sous la forme d'un dérivé soluble dans l'huile d'un dimercaptiothiadiazole, le rapport pondéral de (C) au mélange de (A) et (B) étant compris entre environ 0,001:1 et environ 0,5:1; et où la composition de l'huile lubrifiante contient moins d'environ 0,1% en poids de phosphore.



2. Composition d'huile lubrifiante selon la revendication 1, dans laquelle R_1 et R_2 sont des groupes alkyle contenant au moins 2 atomes de carbone et le métal du sel des métaux (A) est un métal polyvalent.

3. Composition d'huile lubrifiante selon la revendication 1 ou 2, dans laquelle B est un composé d'addition sulfuré de Diels-Alder d'au moins un diénophile avec au moins un diène aliphatique conjugué, le diénophile comprenant une cétone, un aldéhyde, un nitrile, un halogénure, un amide d'acide carboxylique, un ester d'acide carboxylique aliphatique à insaturation alpha-, bêta-éthylénique, ou leurs mélange.

4. Composition d'huile lubrifiante selon la revendication 3, dans laquelle le diène aliphatique conjugué correspond à la formule



dans laquelle R et R^1 à R^5 sont chacun choisis indépendamment parmi un atome d'hydrogène, d'halogène, un groupe alkyle, alcoxy, alcényle, alcényloxy, carboxyle, cyano, amino, alkylamino, dialkylamino, phényle et phényle substitué avec un à trois substituants correspondants à R et R^1 à R^5 ; ou R, R^2 , R^3 et R^5 sont tels que décrits ci-dessus et R^1 et R^4 sont des groupes alkylène liés conjointement pour former un diène cyclique.

5. Composition d'huile lubrifiante selon la revendication 4, dans laquelle le diène et le 1,3-butadiène.

6. Composition d'huile lubrifiante selon l'une quelconque des revendications 3 à 5, dans laquelle le diénophile contient au moins un, mais pas plus de deux, groupes $-C(O)OR_0$ où R_0 est un résidu d'un alcool aliphatique saturé contenant jusqu'à environ 40 atomes de carbone.

7. Composition d'huile lubrifiante selon l'une quelconque des revendications 3 à 5, dans laquelle le diénophile est un ester de l'acide acrylique ou de l'acide méthacrylique.

8. Composition d'huile lubrifiante selon l'une quelconque des revendications précédentes, qui comprend en outre (D) un dispersant/détergent soluble dans l'huile, le rapport pondéral de (D) au poids combiné de (A) et (B) étant compris dans l'intervalle allant d'environ 1:0,5 à environ 1:5.

9. Composition d'huile lubrifiante selon l'une quelconque des revendications précédentes, dans laquelle tout phosphore présent est présent sous la forme d'un phosphorodithioate.

10. Composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 8, dans laquelle la composition d'huile lubrifiante ne contient pratiquement pas de phosphore.

11. Composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 10, dans laquelle (B) est un produit de la réaction du soufre et d'un composé d'addition de Diels-Alder dans un rapport molaire inférieur à environ 1:1.

12. Procédé de préparation d'une composition d'huile lubrifiante qui comprend l'addition à une quantité importante d'une huile de viscosité lubrifiante, d'une petite quantité, améliorant les propriétés, d'une composition soluble dans l'huile comprenant:

(A) au moins un sel de métal d'au moins un acide dithiocarbamique de formule



dans laquelle R_1 et R_2 sont chacun indépendamment des groupes hydrocarbonés contenant un nombre d'atomes de carbone capable de rendre le sel de métal soluble dans l'huile; et

(B) au moins un composé organique sulfuré soluble dans l'huile comprenant le produit de la réaction du soufre et d'un composé d'addition de Diels-Alder dans un rapport molaire inférieur à environ 1,7:1, le rapport pondéral de (A) à (B) étant compris dans l'intervalle allant d'environ 1:10 à environ 50:1; et

(C) au moins un inhibiteur auxiliaire de corrosion sous la forme d'un dérivé soluble dans l'huile d'un dimercaptothiadiazole, le rapport pondéral de (C) au mélange de (A) et (B) étant compris entre environ 0,001:1 et environ 0,5:1; et où la composition de l'huile lubrifiante contient moins d'environ 0,1% en poids de phosphore.

