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EXTREME PRESSURE LUBRICANTS

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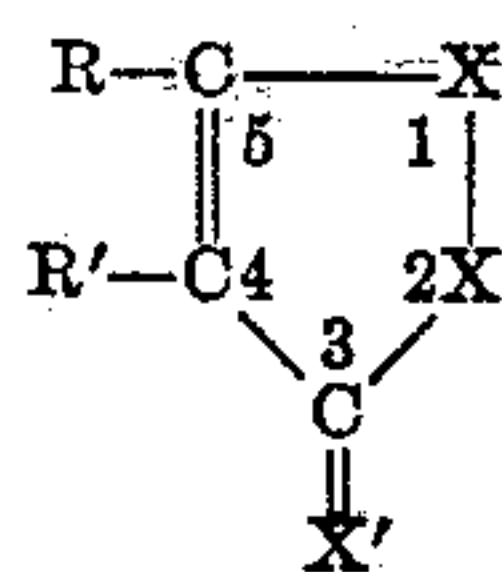
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This invention relates to lubricants, and more particularly to oleaginous base lubricants suitable for use under extreme pressure, high temperature and high speed conditions.

It is well known that the high pressure occurring in certain types of gears and bearings may cause a film of lubricant to rupture with consequent damage to the machinery. It has been shown that base lubricants such as mineral oils, animal and vegetable oils, and synthetic lubricating oils can be improved with regard to their protective effect between rubbing surfaces by the addition of certain substances, so that excessive wear, scuffing and seizure, which normally follow a break in the film of lubricant, can thus be prevented even under the most unfavorable pressure, temperature, and speed conditions. Lubricants possessing this highly desirable property are called extreme pressure lubricants.

It is known that certain elements or compounds of elements of the type of chlorine, phosphorus and lead are capable of imparting extreme pressure properties to lubricants when blended therewith. Among the compounds heretofore used are notable the lead soaps, phosphoric acid esters and certain chlorinated organic compounds.

It has now been found that lubricants of improved extreme pressure and anti-wear properties are provided by incorporating with base oleaginous lubricating media, an organic heterocyclic chalcogenic compound which is representable by the formula, $B \cdot X_3$, wherein B is an unsaturated organic residue, as will be more fully described hereinafter, and the X's are selected independently from the chalcogen atoms, namely, oxygen, sulfur, selenium and tellurium, at least two of which X's in a given molecule are chalcogen atoms of atomic number of at least 16, namely S, Se and Te. The indicated compounds $B \cdot X_3$, are further characterized by properties which indicate that they are representable by the general formula:



(I)

wherein R and R' are the same or different atoms or radicals and are selected from hydrogen, alkyl, alkaryl, aralkyl, cycloalkyl and aryl radicals and fractions of such radicals which together with the two carbon atoms to which they are directly attached in Formula I form a closed ring, including such radicals which are or also contain

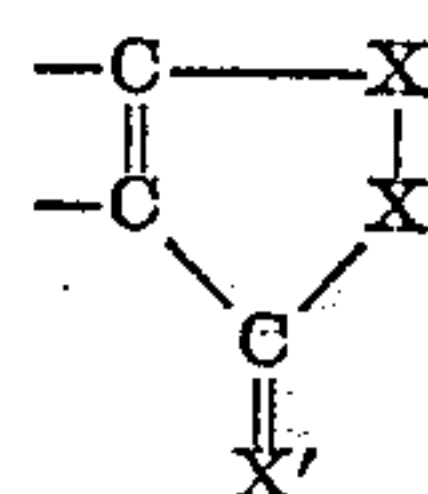
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such substituent atoms or groups as halogen, amino, nitro, hydroxyl, carboxyl, carboxylates such as salt and ester forms of carboxyl, carboxyhydrocarbyl, e. g. carboxymethyl, sulfonic acid, sulfonates, hydrocarbyloxy, e. g. methoxy, ethoxy, phenoxy, benzyloxy, acyl, hydrocarbyl, e. g. methylol, phenylol (hydroxyphenyl), alkyl, e. g. propan-2-yl, acylamino, mercapto and sulfide.

A preferred class of the foregoing-defined compounds, for their utility in the present invention, are those compounds represented by Formula I, and wherein at least one of R and R' is an aryl radical, including substituted aryl radicals, and the other R is hydrogen, another aryl radical or such that together with the other R and the 4- and 5-carbon atoms of the heterocyclic ring, forms an aryl radical, i. e. a 1,2-arylene radical.

According to the general Formula I, the heterocyclic compounds which are utilized in accordance with this invention contain a five-membered heterocyclic ring, the hetero-atoms of which ring, besides the carbon atoms, are two adjacent X atoms (S, Se or Te), and they have a further chalcogen atom (O, S, Se or Te) attached to a ring carbon atom which is attached to a ring heteroatom. The other two ring carbon atoms are joined together through an unsaturated (ethylenic) linkage, which two carbon atoms carry the organic substituents R and R' of the compounds. The compounds represented by Formula I, and wherein each of the three heteroatoms, the X's and X' is a sulfur atom, have been called "trithiones"; they are preferably named 3-thiono-1,2-dithioles or 3-thiono-1, 2-dithia-cyclopentenes, in accordance with the rules for naming ring compounds as set forth in Patterson et al. text on "The Ring Index" Monogram Series No. 84 (Reinhold Publishing Corp.)

In order to simplify further reference to the class of compounds under consideration herein, and in conformity to the use of the name "trithiones" to designate the trithio-compounds, the term "trichalcogenones" will be used hereinafter in the specification and in the claims to designate the generic class of compounds which contains the heterocyclic atomic grouping represented by the following portion of Formula I:



wherein each of the X's and X' is a chalcogen atom. Thus, the trichalcogenones which come

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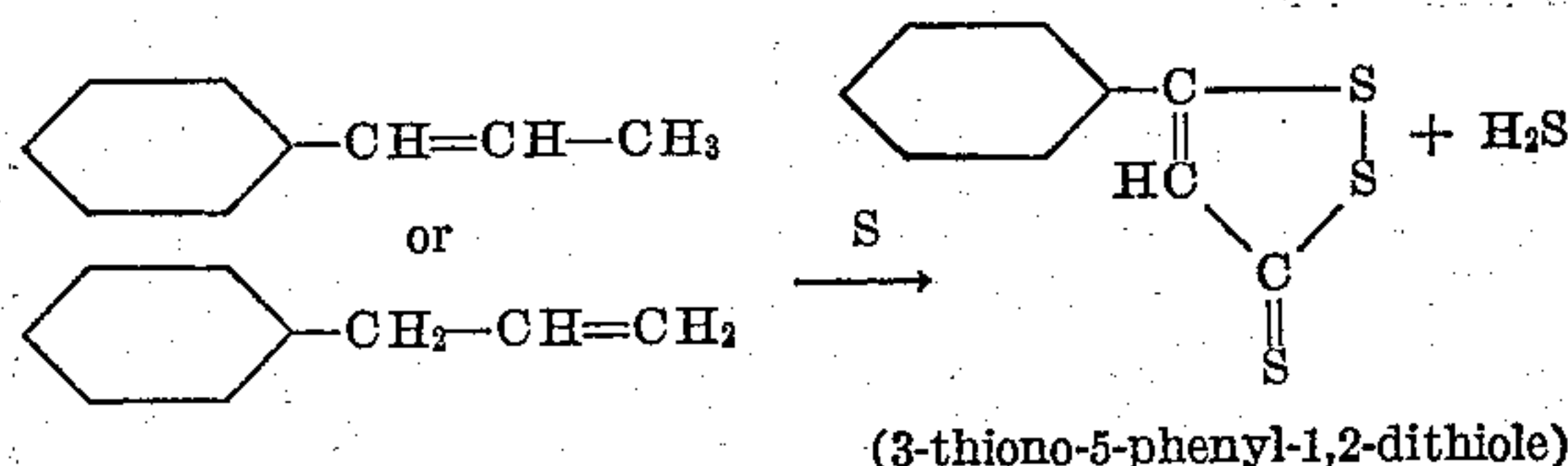
into consideration in the present invention are those in which both of the ring-chalcogen atoms are selected from sulfur, selenium and tellurium.

The trichalcogenones which are to be utilized in the practice of this invention are preparable by a variety of reactions and from a variety of classes of organic compounds, which will be better understood from descriptions of preparations thereof given hereinafter:

A. TREATMENT OF UNSATURATED HYDROCARBONS WITH SULFUR

1. Phenyl-substituted alkenes

a. Both allylbenzene and propenyl benzene react with sulfur at about 175°–250° F., in a ratio of 1 mol proportion of unsaturated hydrocarbon to 5 gram atom proportions of sulfur to yield the same trithione and H₂S.



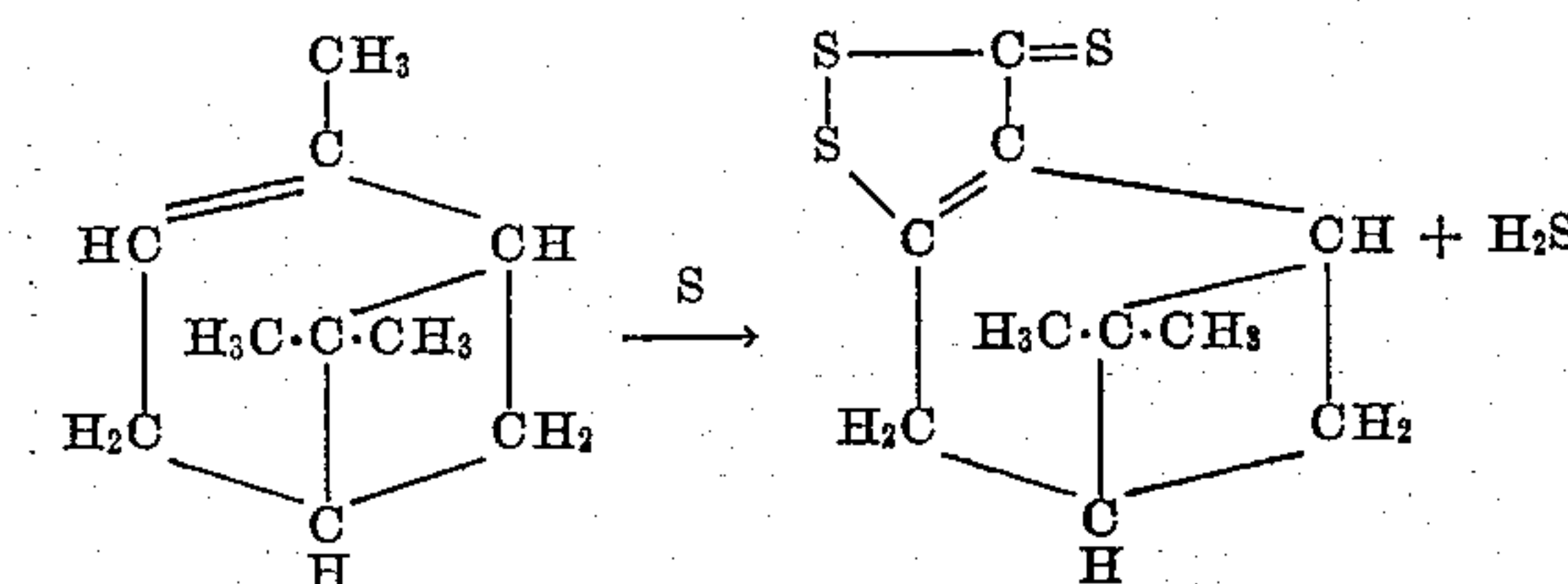
b. Isopropenylbenzene (alpha-methylstyrene) reacts with sulfur similarly to yield the isomeric 3-thiono-4-phenyl-1,2-dithiole.

c. 2,3-diphenyl-1-propene and 1,2-diphenyl-1-propene (alpha-methylstilbene) react with sulfur similarly to yield the same trithione, namely, 3-thiono-4,5-diphenyl-1,2-dithiole.

d. 1,3-diphenyl-1-propene, 1,1-diphenyl-2-propene and 1,1-diphenyl-1-propene do not react to form trithiones.

2. Unsaturated alicyclic hydrocarbons

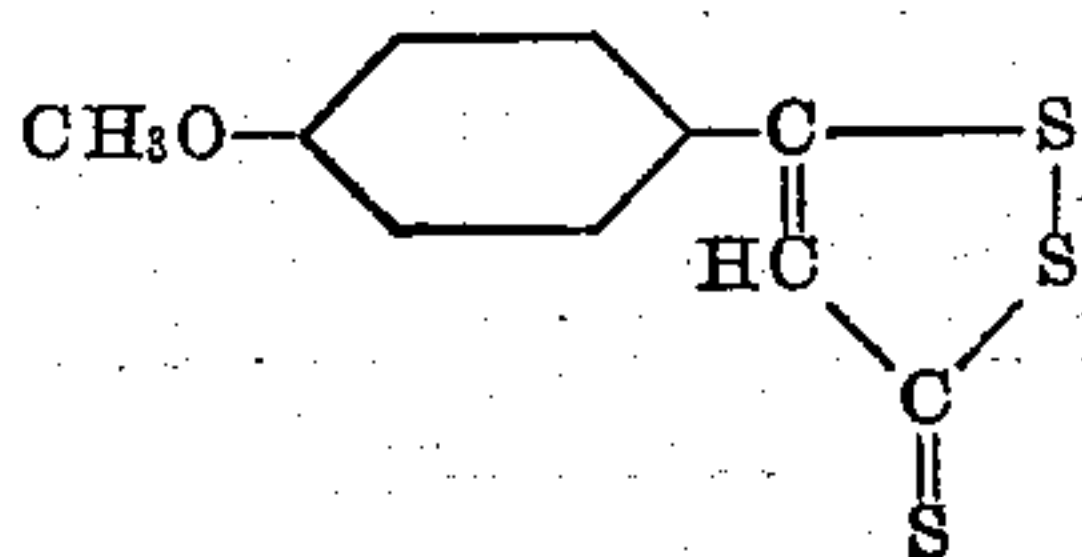
a. Pinene reacts readily with sulfur at about 200°–240° C. in accordance with the following equation



b. 2-para-methylcyclohexyl-1-propene reacts similarly with sulfur to yield the trithione, 3-thiono-4-p-methylcyclohexyl-1,2-dithiole.

3. Aryl-substituted alkenes containing polar groups on aryl radical

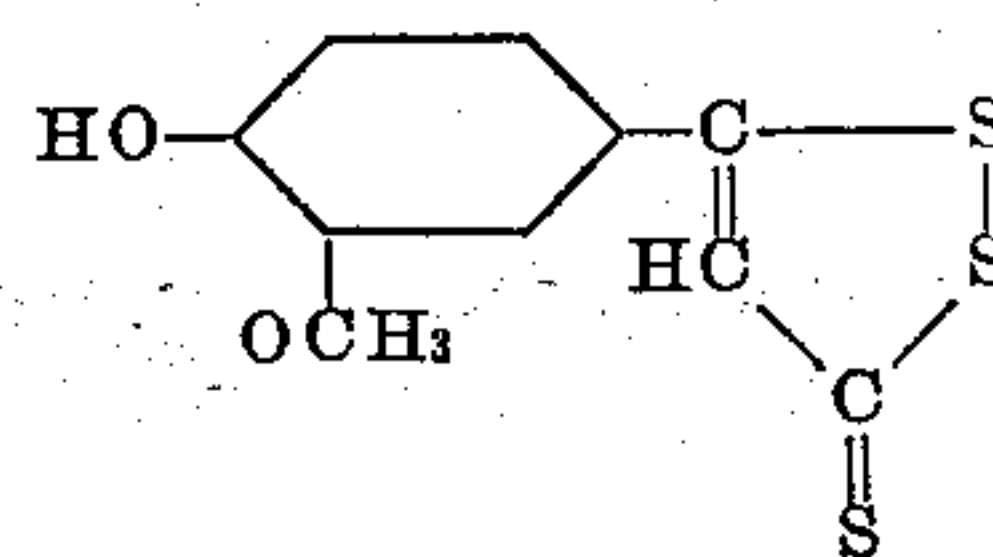
a. Both anethole (1-p-methoxyphenyl-propene) and its allyl isomer, estragole (3-p-methoxyphenyl-1-propene) react with sulfur at about 175°–250° F. (preferably about 210°–230° F.) to yield the same trithione, namely, 3-thiono-5-p-methoxyphenyl-1,2-dithiole:



b. Eugenol (3-(3-methoxy-4-hydroxyphenyl)-1-propene) and its propenyl isomer, isoeugenol (1-(3-methoxy-4-hydroxyphenyl)-1-propene) react with sulfur similarly to anethole, to yield the

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same trithione, namely 3-thiono-5-(3-methoxy-4-hydroxyphenyl)-1,2-dithiole:



It follows from the foregoing observations that trithione formation is effected from the reaction of unsaturated hydrocarbons with sulfur, under the indicated conditions, when and only when the unsaturated chain contains at least 3 carbon atoms, carbon atom 1 of which is primary (either initially or after allylic rearrangement), and carbon atom 3 of which is secondary (either initially or after allylic rearrangement), and that the chain contains at least four hydrogen atoms. The general formulae of such compounds capable of producing thiones are thus:



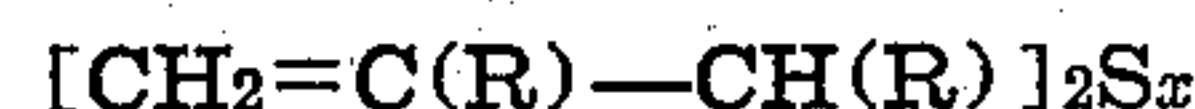
and



wherein the R's are radicals as defined in Formula I.

B. REACTION OF UNSATURATED MERCAPTANS AND POLYSULFIDES WITH SULFUR

The 2-mercapto or polysulfide of the substances corresponding to Formula II, namely, $\text{CH}_2=\text{C}(\text{R})-\text{CH}(\text{R})\text{SH}$, and



and the 1-mercapto or polysulfide of the substances of Formula III, namely



and $[\text{CH}(\text{R})=\text{C}(\text{R})-\text{CH}_2]_2\text{S}_x$, react with sulfur at about 175°–250° F. to yield corresponding trithiones, as is illustrated by the following:

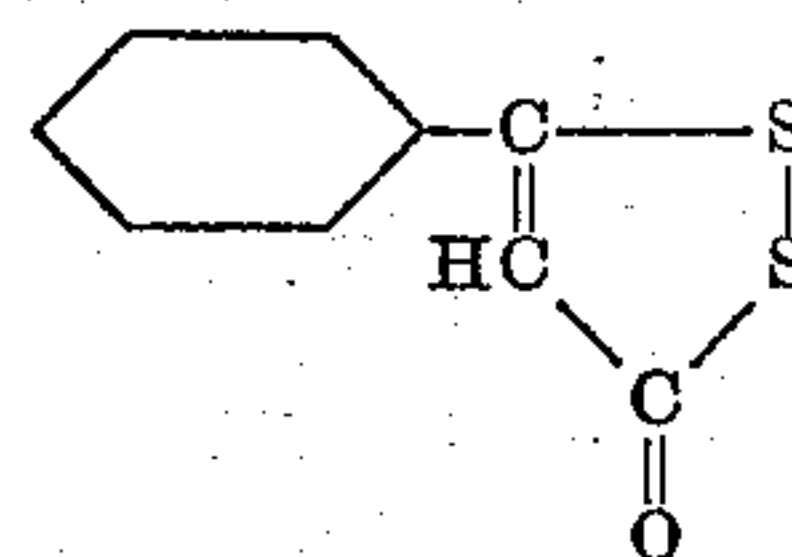
a. Cinnamyl mercaptan reacts with sulfur at 210–220° F. to yield the trithione, 3-thiono-5-phenyl-1,2-dithiole, identical with the trithione obtained by the reaction of allyl- or propenylbenzene with sulfur.

b. Similarly, cinnamyl disulfide reacts with sulfur to yield the same trithione.

c. Cinnamyl trisulfide, upon being rapidly heated to 220° C., yields the same trithione; a greater yield of the trithione is obtained when the cinnamyl trisulfide is heated with sulfur.

C. CHALCOGENONES FROM ALPHA, BETA-UNSATURATED CARBOXYLATES

a. Methyl cinnamate reacts with sulfur at about 250° C. to yield the chalcogenone, 3-oxo-5-phenyl-1,2-dithiole.



This chalcogenone is converted by reaction with phosphorus pentasulfide at elevated temperatures into the corresponding trithione.

b. Methyl cinnamate reacts at about 130° C. with a mixture of sulfur and phosphorus pentasulfide to yield the same trithione, namely, 3-thiono-5-phenyl-1,2-dithiole.

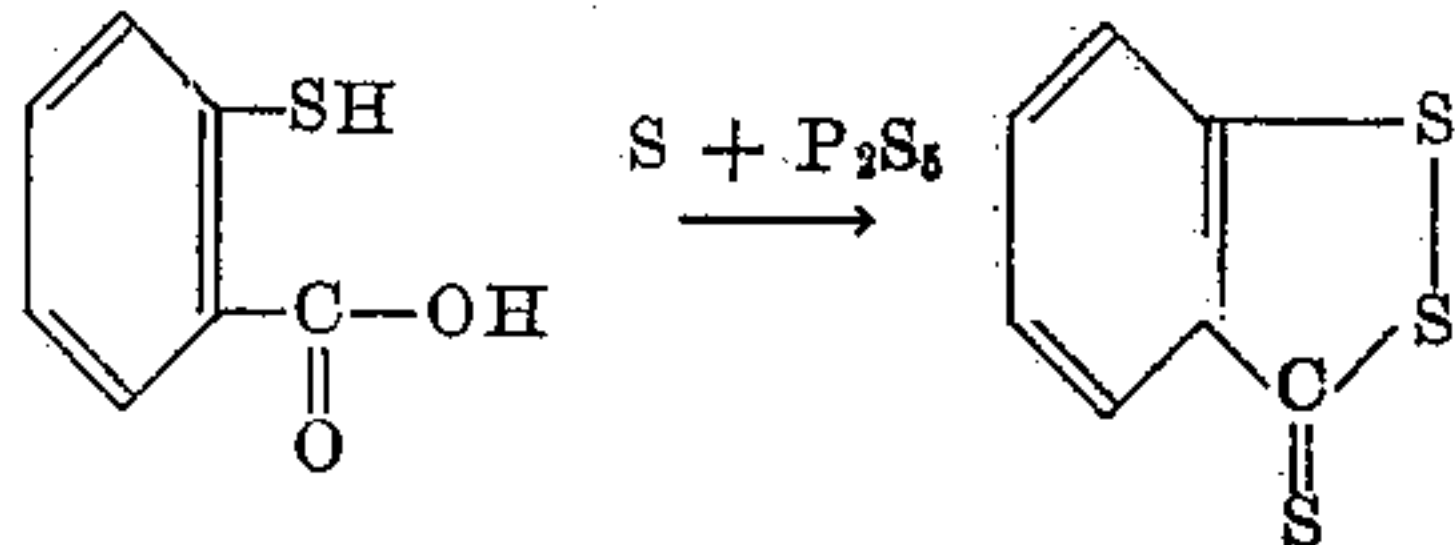
c. Ethyl p-methoxycinnamate reacts at 250°

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C. with sulfur to yield the chalcogenone, 3-oxo-5-p-methoxyphenyl-1,2-dithiole. This substance reacts with P_2S_5 at $130^\circ C.$ to yield the corresponding trithione, 3-thiono-5-p-methoxyphenyl-1,2-dithiole.

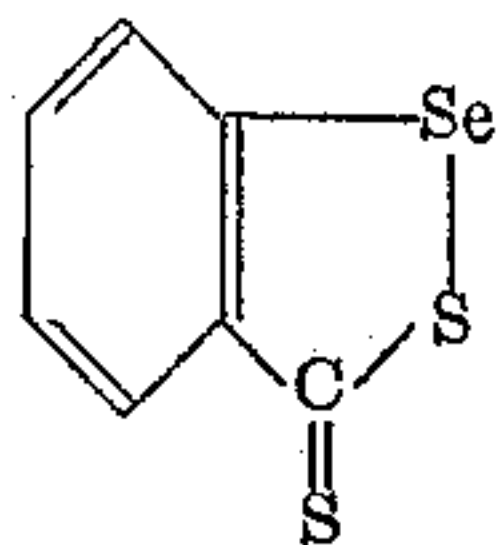
D. REACTION OF BETA-MERCAPTO-ALPHA, BETA-ETHYLENIC CARBOXYLATES AND POLYSULFIDES DERIVED THEREFROM.

a. Ortho-mercaptobenzoic acid reacts with free sulfur and phosphorus sulfides (P_2S_5) to yield the trithione, 2,3-dithiasulphindene (3-thiono-4,5-(alpha, delta-buta-1,3-dienylene)-1,2-dithiole):



b. The disulfide obtained by oxidation of o-mercaptobenzoic acid, namely, 2,2'-dithiobenzoic acid, $HOOC \cdot C_6H_4 \cdot S \cdot S \cdot C_6H_4 \cdot COOH$, reacts with phosphorus pentasulfide, with replacement of oxygen atoms of the $-COOH$ group by sulfur atoms and the formation of the same trithione as in D-a.

c. When the corresponding 2,2'-diselenobenzoic acid $HOOC \cdot C_6H_4 \cdot Se \cdot Se \cdot C_6H_4 \cdot COOH$, is reacted with phosphorus pentasulfide, the corresponding mixed chalcogenone is formed, namely, the substituted 3-thiono-1-seleno-2-thiole.



d. Similarly, 2,2'-diselenobenzoic acid, when reacted with phosphorus pentaselenide (P_2Se_5), yields the "triselenone," 3-selenono-4,5-(alpha, delta-buta-1,3-dienylene)-1,2-diselenole.

E. MISCELLANEOUS REACTIONS

1. Oxidation of "trithiones"

3 - thiono - 5 - p-methoxyphenyl- 1,2-dithiole (from anethole and sulfur) is oxidized with an oxidizing agent such as potassium permanganate to the corresponding 3-oxo-5-p-methoxyphenyl-1,2-dithiole.

As already indicated in D-b, the 3-oxo-1,2-dithioles are convertible by reaction with phosphorus sulfides and phosphorus selenides, for example P_2S_5 and P_2Se_5 , to the corresponding 3-thiono-1,2-dithioles and 3-selenono-1,2-dithioles, respectively.

2. Unsaturated ethers containing the required structures of Formulae II and III with sulfur or selenium

(1) Methallyl phenyl ether, when reacted with sulfur under the hereinbefore-indicated conditions, yields a trithione. Other methallyl ethers yield corresponding trithiones when reacted with sulfur.

(2) Propenyl and allyl ethers, such as the phenyl ethers, when reacted with sulfur under the trithione-forming conditions, yield corresponding trithiones, e. g., 3-thiono-5-phenoxy-1,2-dithiole.

3. Unsaturated ketones with sulfur

(1) Mesityl oxide, when reacted with sulfur under the trithione-forming conditions, yields

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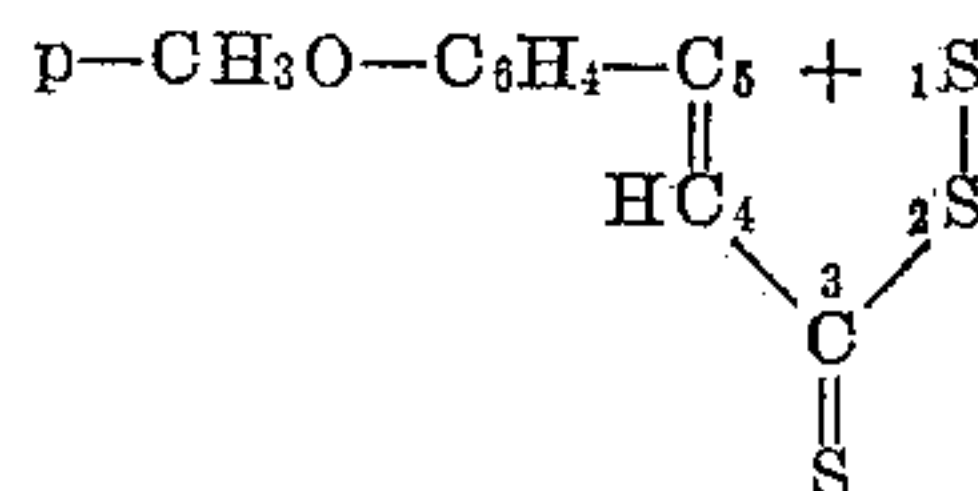
the trithione, 3-thiono-4-methyl-5-acetyl-1,2-dithiole.

(2) Dihydrocarvacrol, when reacted with sulfur, yields a trithione which is considered to be a 3 - thiono-4-(3-keto-4-methylcyclohexyl)-1,2-dithiole.

The reaction to form the "trithione" is generally carried out above $130^\circ C.$ and preferably in the range of from $180^\circ C.$ to $250^\circ C.$ and the ratio of the reactants is such that the chalcogenic compound is always present in an excess to the unsaturated starting material, and preferably is present in the ratio of from about 2:1 to 7:1, respectively, depending in part on the state of sulfuration of the organic compound to be converted to the "trithione."

To more clearly describe the trithiones of the present invention, the following examples of illustrative preparations are presented. It is to be understood, however, that various modifications can be resorted to without departing from the spirit of the invention.

Example I.—About 103.2 grams of anethole was reacted with about 89.9 grams of sulfur in an atmosphere of nitrogen and under agitation. The reaction mixture was heated to about $175^\circ C.$ with evolution of hydrogen sulfide and thereafter the temperature was increased to around $220^\circ C.$ and maintained at that temperature for about one hour. On cooling, a crystalline product was separated out and removed. To the cooled mixture, ether was added, resulting in separation of further crystalline product, the total product amount to about 80 g. The crystalline product was anethole-trithione(3-thiono-5(p-methoxy-phenyl)-1,2-dithiole) having the formula



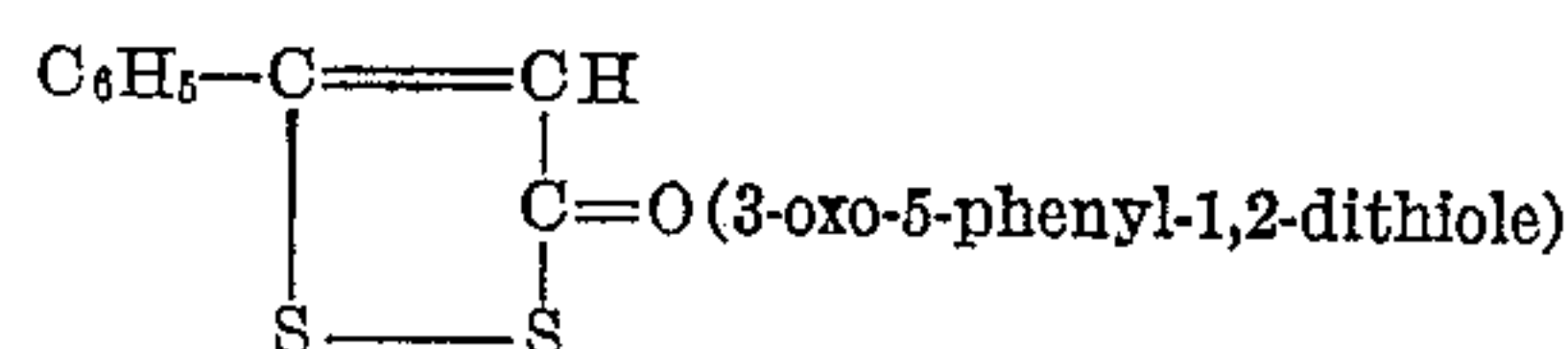
Anethole-trithione is oil-soluble and when added in minor amounts to a base lubricant it provides a lubricant possessing enhanced extreme pressure properties.

Example II.—(a) To 1 mol proportion of cinnamyl mercaptan was added about 4 gram atomic proportions of sulfur and the mixture was reacted for about 2 hours at a temperature of 210° – $220^\circ C.$ The resultant product was a crystalline material identified as 3-phenyl trithione (3-thiono-5-phenyl-1,2-dithiole).

(b) 3-phenyl trithione was also prepared by direct action of sulfur with dicinnamyl disulfide at a temperature of around about $220^\circ C.$ for over an hour.

(c) 3-phenyl trithione was also prepared by rapid heating of dicinnamyl trisulfide at a temperature of about $220^\circ C.$ The product is oil-soluble, stable and has good extreme pressure properties.

Example III.—One mol proportion of ethyl cinnamate was reacted with about 4 gram atomic proportions of sulfur at about $250^\circ C.$ to produce an oil-soluble product having good extreme pressure properties and having the general formula:



This product can be converted to phenyl trithione by reacting it with P_2S_5 at around $130^\circ C.$

for about one hour. Reaction with P_2Se_5 , instead of P_2S_5 , yields 3-selenono-5-phenyl-1,2-dithiole.

Example IV.—2,3-diphenyl-1-propene was reacted with sulfur under the conditions as described in Example I to form diphenyl trithione having good oil solubility and extreme pressure properties.

Example V.—Eugenol was reacted with sulfur under the conditions as described in Example I to form 3-thiono-5-(3-methoxy-4-hydroxyphenyl)-1,2-dithiole which product has good oil solubility, anti-wear and extreme pressure properties.

Example VI.—When eugenol is reacted with selenium substantially under the same procedure as described in Example I, 3-selenono-5-(3-methoxy-4-hydroxyphenyl)-1,2-diselenole is formed.

If instead of eugenol, isopropenylbenzene is reacted with selenium it forms 3-selenono-4-phenyl-1,2-diselenole. Both products are oil soluble and possess extreme pressure properties.

In general the "trichalcogenones" employed as extreme pressure additives in accordance with this invention are sufficiently soluble in mineral lubricating oils to present no blending problem. It is possible, however, to produce excellent extreme pressure lubricants by dispersing the additives in the lubricant in the form of a stable suspension and thus even those additives which are not readily soluble in the lubricating medium may be employed. Whether in the form of solutions or dispersions, suitable solubilizing agents may be added if necessary or desired.

For most purposes, the products need only be incorporated in amounts of less than 1 per cent by weight and preferably in amounts between 0.3 and 0.6 per cent by weight of the lubricating oil or grease to exert a marked improvement in the behaviour of the lubricant in service under extreme pressure conditions. Depending on the particular requirements of the lubricant, the additive may be used in quantities as small as 0.05 per cent or in larger amounts up to 5 per cent by weight of the lubricant.

Base oils to which compounds of this invention are added may be selected from a variety of natural oils such as paraffinic, naphthenic, and mixed base oils having a viscosity range, such as 90 SUS at 100° up to 250 SUS at 210° F. In addition, synthetic oils may be used such as polymerized olefins, alkylated aromatics; polymers and copolymers of alkylene glycols and alkylene oxides; organic esters of dibasic acid, e. g. 2-ethyl hexyl sebacate, dioctyl phthalate; other esters, e. g. ethyl, ricinoleate, butyl benzoate, trioctyl phosphate, polymeric tetrahydrofuran; polyalkyl silicone polymers, e. g. dimethyl silicone polymer, other silicone polymers; H_2S -adducts of unsaturated ethers and thioethers, e. g. H_2S adduct of dialkyl ether. Mixtures of natural and synthetic oils can be used. Under certain conditions of lubrication, minor amounts of a fixed oil such as castor oil, lard oil and the like may be admixed with a hydrocarbon oil and/or synthetic oil.

In addition, "trichalcogenones" of this invention can be added to improve grease compositions, such as Li, Na, Ca, Ba and Al soap greases of which such greases as Li stearate Li 12-hydroxy stearate, Na stearate greases are greatly improved by addition thereto of minute amount of a trithione, such as 3-thiono-5-p-methoxy-phenyl-1,2-dithiole. Instead of using soap as the gelling agent for making grease, any gelling agent

can be used such as inorganic silica or alumina gels, colloidal carbon, oleophilic clays, e. g. bentonite and the like. Mixtures of soap and other inorganic or organic gelling agents can be used in making grease.

To illustrate the pronounced improvement obtained in lubricating compositions by the addition thereto of trithiones, the following test is given:

Compositions of this invention were evaluated as extreme pressure agents by the use of the four-ball extreme pressure lubricating tester similar in principle to the Boerlage apparatus described in the magazine Engineering, volume 136, July 14, 1933. This apparatus comprises four steel balls arranged in pyramid formation. The top ball is rotated by spindles against the three bottom balls which are clamped in a stationary ball holder. The balls are immersed in the composition to be tested. Tests were run under conditions indicated in the table and compared with other outstanding extreme pressure agents.

FOUR-BALL E. P. LUBRICANT TESTER

[Fixed conditions: One minute tests at 1,500 R. P. M. steel on steel
Base oil: Refined mineral lubricating oil.]

Additive	Concentration of wt. AS	Welding Load, Kgs.
None	0.1	160
Sulfurized Sperm oil	0.1	200
3-thiono-5-p-methoxy phenyl-1,2-dithiole	0.1	250

The following mineral oil compositions containing 0.1-1% trichalcogenones when tested in the four-ball E. P. lubricant tester are found to be capable of withstanding loads as high or higher than the trichalcogenone (trithione) composition as noted in the above table. The test compounds indicated are: 3-oxo-5-phenyl-1,2-dithiole; 3-selenono-5-phenyl-1,2-dithiole; 3-thiono-5-phenyl-1,2-dithiole; 3-thiono-4-diphenyl-1,2-dithiole; 3-thiono-4-phenyl-1,2-dithiole; 3-thiono-5-(3-methoxy-4-hydroxy phenyl)-1,2-dithiole, 2,3-dithiasulphindene.

Compositions of this invention in addition to containing the trithiones as described may contain other additive agents such as pourpoint depressors, e. g. alkylated naphthalenes, thickeners, such as soaps and inorganic gels, oxidation inhibitors such as 2,4 dimethyl-6-tertiary butyl phenol and 2,6-ditertiary butyl-4-methyl phenol, sludge dispersers such as oil-soluble metal soaps and oil soluble metal phenates, anti-corrosion agents such as polycarboxylic acids obtained by condensing alkenes with maleic acid, viscosity index improvers such as polyisobutylenes and methyl methacrylate polymers, foam preventing agents such as polymeric organic silicones and metasilicates and anti-ring sticking agents such as basic metal soaps of alkylated salicylic acids. In particular the present trithiones are extremely useful in conjunction with other types of extreme pressure additives such as halogen and phosphorus-containing compounds. Thus there may be added to a blend of the present trithiones in lubricating oil such compounds as chlorinated paraffin wax, calcium dichlorostearate, dibutyl trichloromethane phosphonate, monoisopropyl trichloromethane phosphonate, monobutyl trichloromethane phosphonate-di(2-ethylhexyl)amine, tricresylphosphate, trichlorophenyl phosphate or 2,4-di(trichloromethyl)-6-nitro-1,3-benzodioxane. The presence of such halogen or phosphorus containing extreme pres-

sure additives exhibits a beneficial effect in that the extreme pressure activity of the blend is greater than with either additive alone.

We claim as our invention:

1. An oleaginous lubricating composition comprising a major amount of a lubricating oil base having incorporated therein a minor amount, sufficient to provide the composition with extreme pressure properties, of an organic trichalcogenone, selected from the class consisting of 3-chalcogenono-4-aryl-1,2 dichalcogenole, 3-chalcogenono-5-aryl-1,2 dichalcogenole, 3-chalcogenono-4,5 diaryl-1,2 dichalcogenole, 3-chalcogenono-4 alkoxyaryl-1,2 dichalcogenole, and 3-chalcogenono-5 alkoxyaryl-1,2 dichalcogenole, wherein each of the two ring chalcogen atoms has an atomic number of at least 16 and wherein each aryl substituent is a mono-nuclear aryl substituent, the chalcogen atoms being selected from the group consisting of sulfur and selenium atoms.

2. A lubricating composition comprising a major amount of a lubricating oil base having incorporated therein a minor amount, sufficient to impart extreme pressure properties to said base of an aromatic substituted trichalcogenone heteropenta-atomic ring compound containing three carbon and two chalcogen atoms of atomic number of at least 16 in the ring and one ketonic chalcogen atom attached to a ring carbon atom adjacent to one of the chalcogen atoms, the aromatic substituents of said material being mono-nuclear substituents, the chalcogen atoms being selected from the group consisting of sulfur and selenium atoms.

3. A lubricating composition comprising a major amount of a mineral lubricating oil base having incorporated therein a minor amount, suffi-

cient to impart extreme pressure properties to said base of an aromatic substituted trichalcogenic heteropenta-atomic ring compound containing three carbon and two chalcogen atoms in the ring and one ketonic chalcogen atom directly attached to a ring carbon atom adjacent to one of the ring chalcogen atoms, any aromatic substituents on said compound being mono-nuclear aromatic substituents, the chalcogen atoms being selected from the group consisting of sulfur and selenium atoms.

4. A lubricating composition comprising a major amount of a mineral lubricating oil containing a minor amount sufficient to impart extreme pressure thereto of 3-thiono-5-p-methoxyphenyl-1,2-dithiole.

5. A lubricating composition comprising a major amount of a mineral lubricating oil containing a minor amount sufficient to impart extreme pressure of 3-thiono-5-phenyl-1,2-dithiole.

6. A lubricating composition comprising a major amount of a mineral lubricating oil containing a minor amount sufficient to impart extreme pressure of 3-thiono-4,5-diphenyl-1,2-dithiole.

7. A lubricating composition comprising a major amount of a mineral lubricating oil containing a minor amount sufficient to impart extreme pressure of 3-thiono-5-(3-methoxy-4-hydroxyphenyl)-1,2-dithiole.

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VERNON WARNER DAVID.

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