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COMPOUNDED OIL

Bruce B. Farrington, Victor M. Kostainsek, and
George H. Denison, Jr., Berkeley, Calif., assign-
ors to Standard Oil Company of California,
San Francisco, Calif., a corporation of Dela-
ware

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This invention relates to a new and useful composition of matter. More particularly, the invention involves liquid lubricating compositions for use in internal combustion engines of modern design using hard metal bearings which are susceptible to corrosion by highly refined lubricants under severe operating conditions. The invention provides a novel corrosion inhibited oil having deleterious corrosive and other effects inhibited even under the higher bearing pressures, the higher rotating speeds, the higher engine temperatures and the like, caused by relatively recent changes in engine design. The prevention of undue corrosion by lubricants encountering these conditions is increasingly difficult for three principal reasons.

The first reason is that the newer bearing metals are, in general, more susceptible to the destructive agents of a corrosive nature even though these metals are harder and capable of carrying higher loads than were the conventional Babbitt bearings. Typical of these corrosion-susceptible newer bearings are those composed of cadmium-silver or copper-lead alloys supported upon a steel back. Others of these relatively new bearing metals are cadmium-nickel alloys and the so-called high lead bearings.

The second reason for increasing difficulty in preventing corrosion is that the changes in engine design have required concurrent marked advances in methods of refining lubricating oils to yield products having high viscosity index or other desired properties. This demand for oils having lesser change in viscosity with changes in temperature, i. e. higher viscosity index, has been met by refining lubricants by certain selective solvent refining or selective solvent extraction processes wherein the lower viscosity index hydrocarbons are selectively dissolved. The selective solvent refining processes are operated to concentrate in one fraction, usually the undissolved lubricant fraction, those compounds of a "paraffinic" nature which show a smaller change in viscosity upon change in temperature. Selective solvent extraction processes have been found in many cases to yield an oil which, although satisfactory from the standpoint of viscosity index, is over-refined as respects stability at higher temperatures. This is particularly true where the selective solvent refinement is carried to a point which yields high viscosity index products.

By "over-refined" oils it is intended to designate those oils from which naturally-occurring inhibitors normally present in the oil have been removed at least to an extent which materially

reduces the stability of the oil against deterioration at higher temperatures or which substantially increases corrosiveness of the oil on modern bearing metals. Over-refined oils are not necessarily high viscosity index oils since oils of intermediate viscosity index are sometimes produced from quite low viscosity index stocks by a severe refinement which causes a substantial reduction in the natural inhibitor content of the oil and thereby produces an oil having a correspondingly reduced stability. From the above it should be apparent that over-refined oils are not limited to those produced by solvent extraction. Other refining processes, e. g. sulfuric acid treatment to produce white oils, remove naturally-occurring inhibitors originally in the oil when the treatment is sufficiently severe and thereby produce over-refinement with the attendant difficulties herein discussed.

In general, over-refined oils may be characterized as having natural inhibitors removed to the point where the corrosiveness of the oil is greater than about 40 mgs. on a 1" x 2" coarse-grained copper-lead bearing in a 72-hour corrosion test (subsequently described in more detail) run under the following conditions:

Air rate----- 300° F.
Temperature----- 30 liters per hour
Catalyst----- 10 gms. of steel wool and a
6" x 1" copper strip

The foregoing 40 mgs. loss in the 72-hour corrosion test may be designated as a corrosion index of 40.

The solvent refined oils referred to above, and especially the over-refined oils, are not the only type of oils which become definitely corrosive to the newer bearing metals under normal but severe conditions of use in internal combustion engines. It has been found that a corresponding adverse reaction, namely, corrosion of alloy bearing metals such as cadmium-silver alloys, also occurs in paraffinic base oils which have not been solvent refined or over-refined. These corrosion difficulties sometimes cause bearing failure after only a few thousand miles of operation. The higher the viscosity index of the lubricating oil the more pronounced, in general, is the tendency to corrosion of the kind referred to above. Generally speaking, the problem is encountered in oils having viscosity indexes of 75 and higher, and becomes of major magnitude in oils having a viscosity index of 80 to 85 or higher.

Thirdly, the newer engines require that the crankcase lubricants operate under significantly

higher temperatures than heretofore required. It is found that lubricating oils, which are satisfactory and non-corrosive on newer alloy bearings at lower temperatures heretofore normally encountered, become unduly corrosive to these same bearings at the higher temperatures. These higher temperatures approach the borderline of stability of organic compounds and relatively small increases in temperature therefore magnify many-fold the difficulties of inhibiting corrosion and other deterioration, such as formation of "varnish," carbon, or sludge.

Problems in lubrication of internal combustion engines have been further multiplied by the necessity for addition of stabilizers capable of inhibiting the deterioration of the lubricating oil at elevated temperatures. As engine conditions became more severe, piston ring sticking, "varnish" formation on pistons and cylinder walls, and deposition of hard carbon on the piston wall above the top piston ring, have caused trouble in engine operation. These particular difficulties are met by incorporation of stabilizing agents such as aryl metal oxides (metal phenates), salts of aryl carboxylic acids, salts of polycarboxylic acids which preferably have been partially esterified, salts of alkyl carboxylic acids containing a polar group (e. g. mercapto, thio-keto, thioether, amino, cyano, phosphino, oxyketo, and hydroxy groups, and the like) near a carboxyl group of the acid, and metal alcoholates. These types of stabilizers are relatively non-corrosive and some have a corrosion inhibiting action under less severe lubricating conditions.

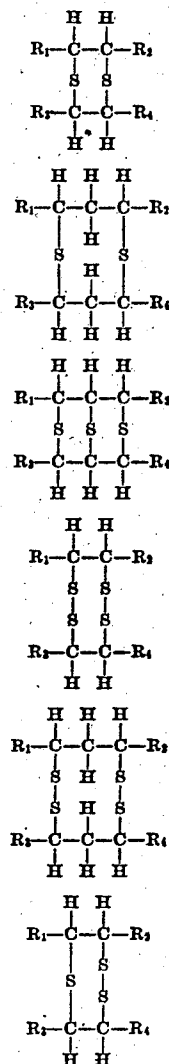
In naphthenic base lubricating oils, or even in oils of intermediate refinement and intermediate viscosity index (e. g., a viscosity index of less than 75) which are not over-refined, various corrosion inhibitors are highly effective under severe service. However, when an over-refined or high viscosity index oil (e. g. of 80 viscosity index or more) is used as a base stock and when the oil is to do service under extreme conditions on corrosion-sensitive alloy bearings, the difficulties presented have seemed almost insurmountable. Thus there was presented a combination of circumstances not previously encountered, namely: (a) the necessity for lubricating corrosion-sensitive hard alloy bearings, (b) the desirability of using a base oil stock inherently more corrosive to such bearings than lower viscosity index or less highly refined oils, and (c) more severe operating conditions, as respects temperature and speed, than the lubricating engineer had previously been requested to meet.

Under this new combination of circumstances it was found that the above-mentioned non-corrosive stabilizers against deterioration at elevated temperatures catalyzed corrosion by the oil although these compounds remained non-corrosive in themselves. Also, it was discovered that various corrosion inhibitors found to be effective to prevent corrosion even by the over-refined or higher viscosity index stocks in the absence of the stabilizers were not effective as anti-catalysts to destroy the catalytic corrosion of the stabilizers in such oils. In other words, the anti-catalytic action of an inhibitor in uncompound hydrocarbon oils formed no adequate basis for predicting that the same inhibitor would selectively "poison" the stabilizing agent of compounded oils and destroy the agent's catalysis of corrosion without also destroying its catalytic stabilizing action against deterioration at elevated temperatures.

A feature of this invention comprises the provision of a lubricating oil containing a new combination of additives. This new combination of additives is highly effective, both as respects stabilization against deposition of adhesive or resinous materials at elevated temperatures and prevention of corrosion of alloy bearings, when incorporated in over-refined lubricating oils and oils having a viscosity index higher than 75, e. g. a viscosity index of 80 to 85 or higher. Since the new combination of additives is effective even in hydrocarbon lubricating oils which are relatively non-responsive to corrosion inhibitors and stabilizers, the combinations disclosed in more detail hereinafter are exceedingly powerful additives for more responsive oils, such as naphthenic or mixed base lubricants containing naturally-occurring inhibitors in normal quantities or in oils having a viscosity index of less than 80.

The corrosion inhibitors of this invention comprise long carbon chain multi-bridged thioalkyl compounds, and the preferred type is termed herein "alkyl polythio-dimero."

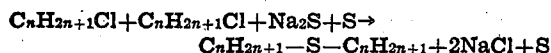
These inhibitors are exemplified by compounds of the following type formulae:



wherein at least R₁ or R₂ is a long carbon chain and preferably at least R₃ or R₄ is also a long carbon chain. All four of these radicals, R₁, R₂, R₃ and R₄, need not be long chains; for example, R₂

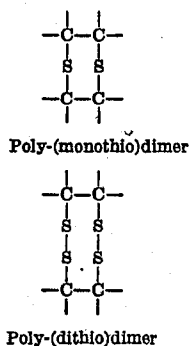
and R_4 may be short chains or even hydrogen when R_1 and R_3 are long chains. Compounds in which only one of the radicals, e. g. R_1 , is a long carbon chain are not precluded. Likewise, these radicals may contain cyclic substituents such as an aromatic or naphthenic substituent. However, such carbocyclic substituents, if present, should be positioned in a long chain on a carbon atom relatively distant from the bridged sulfur group or groups since it is desired that the sulfur groups possess substantially the properties of bridged thioalkyl substituents.

The term "dimer" as used herein designates a type of product such as produced by linking together two molecules of hydrocarbon structure by a condensation reaction. Such a reaction is illustrated by condensation of a chlorinated hydrocarbon with an inorganic sulfide whereby a chlorine atom from each of two molecules is displaced and a divalent sulfur atom takes up the free valence of each molecule to thereby connect the molecule together, thus:



The carbon chains so condensed need not be identical or of the same number of carbon atoms to fall within the meaning of the term "dimer" as used herein. Similarly, the term "trimer" is used to designate compounds in which three molecules are connected by such a condensation reaction.

The term "alkyl polythio-dimer" designates a condensation product of two molecules of hydrocarbon structure in which at least two sulfur atoms independently bridge and connect alkyl carbon chains. Such a dimer is produced by a condensation of two polyhalogenated alkyl molecules in which at least two halogen atoms are split out from each alkyl molecule and at least two sulfur atoms form connecting links between the free valences of the two molecules. A significant distinguishing characteristic of these compounds is that at least two carbon atoms of a chain separate the terminal valences of the bridging sulfur atoms, thus:



The term "multi-bridged" as applied to these compounds requires that there be more than one sulfur bridge between at least one pair of the condensing molecules. The term "thiomer" is used to cover generically such sulfur bridged polymers whether they be dimers or trimers. Thiomers of a liquid consistency, even though very viscous at ordinary atmospheric temperatures, are preferred and mixtures which are predominantly dimers or trimers yield the best results.

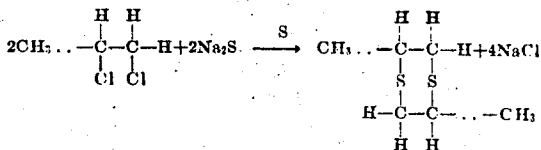
The foregoing type formulae exemplify the preferred type of compounds insofar as it is indi-

cated that the bridging sulfur atoms are on carbon atoms near each other in a long carbon chain. However, modifications at present less preferred but within the scope of the invention in its broader aspects include multi-bridged thio compounds in which the terminal valences of the sulfur bridges are separated by more than two intervening carbons of the chain. As previously indicated, at least one long carbon chain should be present in the compounds. By "long carbon chain" it is intended to designate a carbon chain having eight to ten or more carbon atoms, and preferably twenty or more carbon atoms. Relatively straight chains are preferred, although branching in the chain is not precluded; for example, butene and isobutene polymers yield long carbon chains having some branches but are suitable for the purposes of this invention. Paraffin wax is an illustration of a composition containing long carbon chains of outstanding value for synthesis of the corrosion inhibitors herein disclosed.

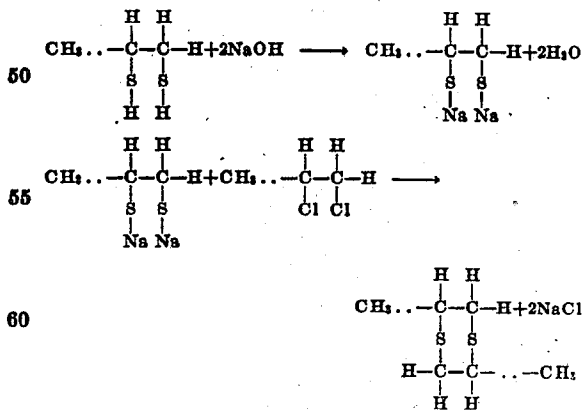
The corrosion inhibiting thiomers of this invention may contain organic or inorganic substituents in one or more of the carbon chains. Examples of such substituents are the halogens (chlorine, bromine and iodine), ester groups, hydroxyl groups, and metal carboxylate groups.

The corrosion inhibitors of this invention may be prepared by various methods. The following are equations for exemplary reactions:

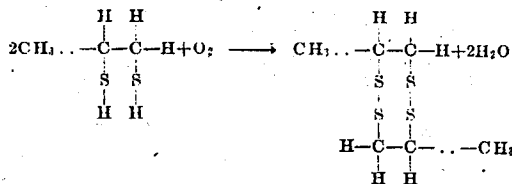
(1) Reaction of halogenated long chain hydrocarbons and an inorganic sulfide in the presence of added sulfur:

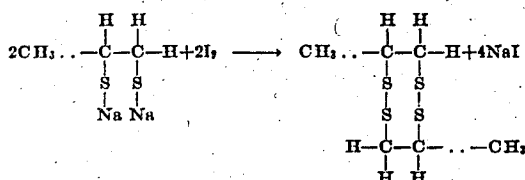
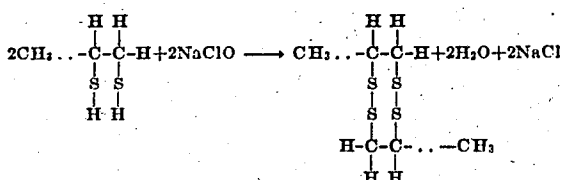


(2) Preparation of a mercaptide and reaction with a halogenated hydrocarbon, one or both being long chain compounds:



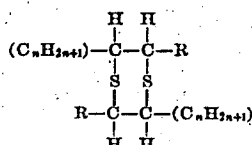
(3) Oxidation of polymercaptan or polymercaptide with various oxidizing agents:





The following specific type compounds illustrate corrosion inhibitors of this invention:

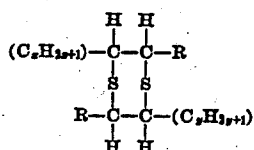
(a) Di-(monothio) dimers—



where R is hydrogen or $\text{C}_n\text{H}_{2n+1}$:

2,5-di-hexyl dithiane-1,4
2,5-di-octyl dithiane-1,4
2,5-di-decyl dithiane-1,4
2,5-di-dodecyl dithiane-1,4
2,5-di-tetradecyl dithiane-1,4
2,5-di-cetyl dithiane-1,4
2,5-di-octadecyl dithiane-1,4
2,5-di-eicosyl dithiane-1,4
2,5-di-docosyl dithiane-1,4
2,5-di-tetracosyl dithiane-1,4
2,5-di-hexacosyl dithiane-1,4
2,5-di-octacosyl dithiane-1,4
2,5-di-tricontyl dithiane-1,4
2,5-di-paraffin wax dithiane-1,4

(b) Mixed di-(monothio) dimers—



where R is hydrogen or $\text{C}_n\text{H}_{2n+1}$:

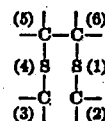
2-decyl 5-dodecyl dithiane-1,4
2-decyl 5-tetradecyl dithiane-1,4
2-decyl 5-cetyl dithiane-1,4
2-decyl 5-octadecyl dithiane-1,4
2-decyl 5-eicosyl dithiane-1,4
2-decyl 5-docosyl dithiane-1,4
2-decyl 5-tetracosyl dithiane-1,4
2-decyl 5-hexacosyl dithiane-1,4
2-decyl 5-octacosyl dithiane-1,4
2-decyl 5-tricontyl dithiane-1,4
2-decyl 5-paraffin wax dithiane-1,4
2-paraffin wax 5-amyl dithiane-1,4
2-paraffin wax 5-hexyl dithiane-1,4
2-paraffin wax 5-octyl dithiane-1,4
2-paraffin wax 5-decyl dithiane-1,4
2-paraffin wax 5-dodecyl dithiane-1,4
2-paraffin wax 5-tetradecyl dithiane-1,4
2-paraffin wax 5-cetyl dithiane-1,4
2-paraffin wax 5-octadecyl dithiane-1,4
2-paraffin wax 5-eicosyl dithiane-1,4

2-paraffin wax 5-docosyl dithiane-1,4
2-paraffin wax 5-tetracosyl dithiane-1,4
2-paraffin wax 5-hexacosyl dithiane-1,4
2-paraffin wax 5-octacosyl dithiane-1,4
2-paraffin wax 5-tricontyl dithiane-1,4

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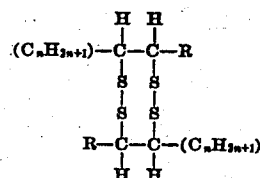
In the foregoing terminology, standard nomenclature was utilized and the members of the nucleus of the dimers are numbered as follows:

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(c) Di-(disulfide) dimers—



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where R is hydrogen or $\text{C}_n\text{H}_{2n+1}$:

3,7-di-hexyl tetrathiocane-1,2,5,6
3,7-di-octyl tetrathiocane-1,2,5,6
3,7-di-decyl tetrathiocane-1,2,5,6
3,7-di-dodecyl tetrathiocane-1,2,5,6
3,7-di-tetradecyl tetrathiocane-1,2,5,6
3,7-di-cetyl tetrathiocane-1,2,5,6
3,7-di-octadecyl tetrathiocane-1,2,5,6
3,7-di-eicosyl tetrathiocane-1,2,5,6
3,7-di-docosyl tetrathiocane-1,2,5,6
3,7-di-tetracosyl tetrathiocane-1,2,5,6
3,7-di-hexacosyl tetrathiocane-1,2,5,6
3,7-di-octacosyl tetrathiocane-1,2,5,6
3,7-di-tricontyl tetrathiocane-1,2,5,6
3,7-di-paraffin wax tetrathiocane-1,2,5,6

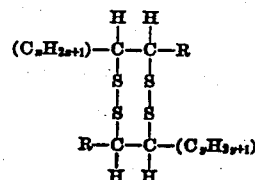
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(d) Mixed di-(bridged dithio) dimers—

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where R is hydrogen or $\text{C}_n\text{H}_{2n+1}$:

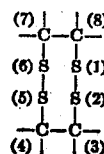
3-decyl 7-dodecyl tetrathiocane-1,2,5,6
3-decyl 7-tetradecyl tetrathiocane-1,2,5,6
3-decyl 7-cetyl tetrathiocane-1,2,5,6
3-decyl 7-octadecyl tetrathiocane-1,2,5,6
3-decyl 7-eicosyl tetrathiocane-1,2,5,6
3-decyl 7-docosyl tetrathiocane-1,2,5,6
3-decyl 7-tetracosyl tetrathiocane-1,2,5,6
3-decyl 7-hexacosyl tetrathiocane-1,2,5,6
3-decyl 7-octacosyl tetrathiocane-1,2,5,6
3-decyl 7-tricontyl tetrathiocane-1,2,5,6
3-decyl 7-paraffin wax tetrathiocane-1,2,5,6

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In the foregoing terminology, standard nomenclature was utilized and the members of the nucleus of the dimers are numbered as follows:

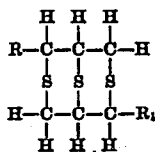
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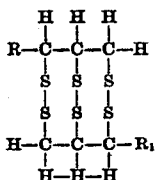
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Additional types of compounds illustrating the invention in its broader aspects are:

Tri-(bridged monothio)dimers—

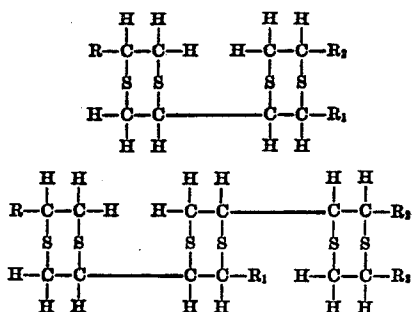


Tri-(bridged disulfide) dimers—



where R and R₁ are radicals of hydrocarbon structure.

The invention is not limited to dimers but, where the carbon chains are less than twenty carbon atoms long and yield oil-soluble products, higher polymers are useful. Thus the trimers and tetramers are contemplated—



where R, R₁, R₂ and R₃ are radicals of hydrocarbon structure.

However, it is preferred that the compound or mixture of compounds should be liquid at ordinary atmospheric temperature. For this reason, dimers, trimers or mixtures of dimers and trimers are at present utilized.

It has been discovered that a reaction product comprising an unknown mixture of thiomers is an outstanding corrosion inhibitor. This reaction product contains a mixture of different sulfides which cooperate in some unknown manner to produce a powerful corrosive inhibiting action effective at high temperatures and in high viscosity index oils. The reaction product is believed to be a mixture of multi-bridged thiomers, monothio ethers, dithio ethers and probably a small proportion of trithio ethers. This particular reaction product is one of applicants' preferred species. The reaction product is herein designated "paraffin wax thiomers" and comprises the product of the reaction of a halogenated paraffin wax (preferably containing from about 15 to about 25% chlorine) and an inorganic sulfide such as sodium sulfide or polysulfide.

In order to illustrate the invention and facilitate the practice thereof by those skilled in the

art, the following examples of methods of preparing wax thiomers are given:

PREPARATION OF CHLORINATED WAX

Crude white scale wax is melted and heated to about 150° to 200° F. and chlorine gas is passed through the melt. The temperature is preferably kept between these limits by adjusting the rates of heating and inflow of chlorine. The density of the mix increases rapidly as the chlorination proceeds and the gravity of the reaction product is thus a measure of the degree of chlorination. When the chlorine content of the wax has reached a desirable percentage the flow of chlorine gas is cut off and the mixture is blown with either nitrogen or air until substantially free of either chlorine gas or hydrogen chloride. The chlorinated wax is a straw-colored liquid which slowly darkens on standing. Exemplary inspections of such chlorinated waxes are as follows:

Batch	Per cent Cl	Gravity, °A. P. I.
1.....	27.5	9.0
2.....	28.1	8.9

PREPARATION OF WAX THIOMERS

Utilizing a chlorinated wax such as the above, the wax thiomers may be prepared as follows:

EXAMPLE 1

The proportions of the reactants are given in the table below:

Reactants	Grams	Gram moles
Chlorinated wax (27.5% chlorine).....	8,520	16
Sodium sulfide (60-62% Na ₂ S).....	3,760	29.5
Sulfur.....	693	21.7
Alcohol.....	19,000	414
Water.....	3,185	176

¹ 23,600 cc.

The sodium sulfide utilized was approximately a trihydrate and the amount of water added was just sufficient to produce Na₂S.9H₂O.

In preparing the wax thiomers the chlorinated wax and alcohol are first thoroughly mixed in a vessel equipped with a stirrer and a reflux condenser. The sodium sulfide is dissolved in the heated water. The sulfur is added and the mixture boiled and stirred until the sulfur dissolves in the aqueous solution. This aqueous solution is added to the alcoholic solution of the chlorinated wax and the whole is refluxed at 185° F. (atmospheric pressure) for twenty hours. The reaction product is then washed with water until free of alcohol and inorganic salts and then dried by air-blowing it at elevated temperature. After drying, the final product is filtered.

In a preferred embodiment of the invention the reaction is carried out under conditions such that substantially all the chlorine in the chlorinated wax is removed. In order to facilitate production of this type of product it is preferred that the chlorinated wax contain only about 16% chlorine.

The following table gives analytical results on the various batches of paraffin wax thiomers pre-

pared with some variations in the method of operation:

Method ¹	Vis. at 100°	Percent S	Molecular weight
1	1,825	12.0	724
2	3,313	13.6	660
1	1,740	11.1	500
2	1,685	12.0	827
1	1,711	11.8	650
1	1,680	11.4	753
1	1,867	11.5	703
1	1,922	11.6	746
1	1,677	11.2	750
3	1,998	10.4	697
2	2,003	11.6	

¹ Method 1—Both alcohol and water are used as in the description given above. Method 2—Only alcohol is used as a solvent, and the sodium sulfide and sulfur are added directly to the chlorinated wax in alcohol. Method 3—Half the quantity of alcohol and water are used.

EXAMPLE 2

To insure a wax thiomers substantially free of chlorine the following process was utilized:

Chlorinated wax in this example contained 16% chlorine and anhydrous sodium sulfide was used. No water was added and the alcohol was anhydrous. The proportions were as follows:

Reactants	Grams	Gram moles
Chlorinated wax (16% chlorine).....	800	1.9
Sodium metal.....	100	4.35
Alcohol (100%).....	1,600	35
Sulfur.....	69.4	2.16

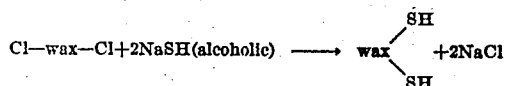
The sodium was dissolved in 800 grams of alcohol and half of the resulting sodium ethylate solution saturated with hydrogen sulfide to yield anhydrous sodium hydrosulfide. To this solution the other half of the sodium ethylate was added. The chlorinated wax was dissolved in 800 grams of alcohol and heated to 160° F. The alcoholic reaction product of sodium ethylate and sodium hydrogen sulfide (anhydrous sodium sulfide) was added and the sulfur stirred in. The whole mixture was refluxed for nineteen hours, washed, dissolved in ethyl ether and dried with anhydrous sodium sulfate. After filtering, the ether was evaporated off.

Yield grams..... 701
Viscosity at 100° F..... 1224
Per cent S..... 12.6
Per cent Cl..... 1.8

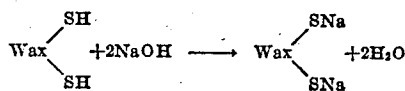
EXAMPLE 3

According to this method wax multi-bridged monothio dimers may be prepared as follows:

Chlorinated wax (15 to 25% chlorine) was reacted with an alcoholic solution of sodium hydrosulfide to yield wax mercaptan by the reaction—

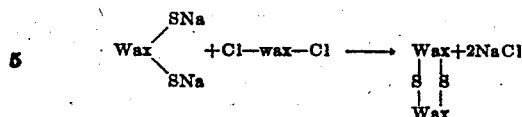


The wax mercaptan is then converted to alkaline metal mercaptides by reaction with caustic soda or sodium ethylate as follows:



The wax mercaptide is then reacted with additional chlorinated wax (15 to 25% chlorine) in

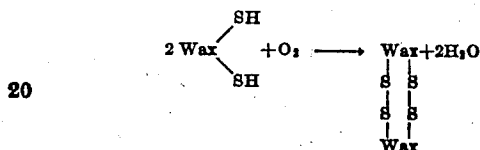
alcoholic solution to give a wax multi-bridged disulfide—



A typical product of this method had a molecular weight of 873, a sulfur content of 6.8%, and a chlorine content of 2.2%.

EXAMPLE 4

A wax multi-bridged disulfide may be prepared from the wax mercaptans of Example 3 by oxidation of the mercaptans as follows:



Oxidizing agents other than oxygen may be utilized; for example, iodine, alkali hypochlorites or hypochlorous acid.

EXAMPLE 5

Dissolve 100 grams of wax polymercaptan (16.4% S, 2.5% Cl, molecular weight 370, viscosity at 100° F.=210.1) in 400 cc. of petroleum ether. Slowly stir in 496 grams of a 5.25% by weight NaClO aqueous solution and thoroughly agitate for about one hour. Separate the aqueous layer, wash the petroleum ether solution with water, dry, filter and evaporate off the petroleum ether to leave a wax multi-bridged disulfide containing 16.4% sulfur.

EXAMPLE 6

A wax multi-bridged disulfide containing 12.9% sulfur and 1.8% chlorine was prepared by the method of Example 5 utilizing 100 grams of wax polymercaptan (12.3% sulfur, 1.9% chlorine, molecular weight 530, viscosity at 100° F.=153.5) and 410 grams of the sodium hypochloride solution.

The proportions of the corrosion inhibitors disclosed herein may vary from about 0.1% to about 2% by weight based on the oil. In the less corrosive and more stable oils 0.25% is sufficient, while in more corrosive and less stable oils 1% or more may be necessary. The lighter grades of lubricating oils require somewhat more compounding. In an oil such as a solvent refined S. A. E. 30 lubricant from Kettleman Fields, California crude, 0.25% of the corrosion inhibitor has been found sufficient even in the presence of other stabilizers such as metal phenates.

In general, it has been found that the corrosion inhibitors of this invention are outstanding and not the mere equivalent of the various other sulfides. For example, the same corrosion inhibiting action in over-refined or high viscosity index lubricating oils is not obtainable with ordinary thioethers or disulfides of the type formulae:



respectively. The multi-bridged sulfur structures give a corrosion inhibiting action, particularly in over-refined oils or oils having a viscosity index greater than 75, under conditions where various other thioethers and disulfides of the conventional structure are not fully satisfactory. For example, an S. A. E. 10 lubricating oil from a

certain Colombian crude is a particularly difficult oil to adequately stabilize against corrosion. In such an oil, a monothioether of the type—



is not equivalent to paraffin thiomers as shown by the following data:

Oil	Test 1, 325° F., strip corrosion test—mg. wt. loss, fine grained Cu-Pb, 72 hours	Test 2, 300° F., strip corrosion test—mg. wt. loss, coarse grained Cu-Pb, 72 hours	Test 3, bearing corr. test in high speed Diesel engine—mg. wt. loss per full connecting rod	
			66 hrs.	246 hrs.
Colombian S. A. E. 10+0.5% sulfurized metal phenate+0.25% metal organo-phosphate+1.0% cetyl ethyl sulfide	26.0	—	55	204
Colombian S. A. E. 10+0.5% sulfurized metal phenate+0.25% metal organo-phosphate+1.5% cetyl ethyl sulfide	12.2	88.2	40	150
Colombian S. A. E. 10+0.5% sulfurized metal phenate+0.25% metal organo-phosphate+1% paraffin wax thiomers	8.6	24.9	9.5	31

¹ By extrapolation.

Likewise, a disulfide of the type formula—



is not the equivalent of a paraffin wax thiomers having substantially the same sulfur content. This is illustrated by the following data:

Oil	Test 2, 300° F., strip corrosion test, mg. wt. loss, coarse grained Cu-Pb, 72 hours
Colombian S. A. E. 10+0.5% sulfurized metal phenate+0.25% metal organo-phosphate+1.0% paraffin wax thiomers (11.5% sulfur)	25
Colombian S. A. E. 10+0.5% sulfurized metal phenate+0.25% metal organo-phosphate+1.0% disulfide (R-S-S-R ₁) (12.3% sulfur)	85

From these data it is evident that the paraffin wax thiomers is from four to eight times as effective as cetyl ethyl sulfide, and over three times as effective as a conventional dialkyl disulfide structure with about the same sulfur content in the inhibiting agent. The limit established by the Caterpillar Tractor Company in the high speed Diesel engine corrosion test is 50 mg. in 246 hours for oils of "exceptional quality." The above data show that paraffin wax thiomers are capable of producing an oil meeting the test for exceptional quality, whereas the other sulfides, although highly effective as corrosion inhibiting agents, do not yield an oil of exceptional quality with Colombian base stocks. As stated above, it should be borne in mind that this Colombian base stock is very difficult to handle from the corrosion standpoint, and this particular type of oil was selected for the above tests in order to emphasize the exceptional properties of the corrosion inhibiting agents herein disclosed.

The strip corrosion data above given were obtained in corrosion tests carried out in the following manner: Glass tubes two inches in diameter and twenty inches long were immersed in an oil bath, the temperature of which was automatically controlled to within $\pm 1^\circ$ F. of the test temperature indicated. Approximately 300 cc. of oil under test was placed in each tube and air was bubbled through it. Strips of the different types of the bearing metals were placed in the oil. The weight loss of each strip was recorded. Be-

fore weighing, each strip was washed in petroleum ether and carefully wiped with a soft cotton cloth. The duration of the test was 72 hours. The loss in weight in milligrams in the foregoing corrosion test is termed the corrosion index of the oil.

In test 1 the temperature was 325° F. as indicated. Ten liters of air per hour were bubbled

through the test oil and a copper catalyst was utilized.

In test 2 the temperature was 300° F. as indicated. 30 liters of air per hour were bubbled through the test oil and both a copper strip and 10 grams of steel wool were placed in the oil as catalysts. The bearing metal subjected to corrosion in test 2 was a strip of coarse-grained copper-lead bearing. This second type test is the one designated previously for characterizing over-refined oils.

Test 3 is carried out in a high speed Diesel engine by operation under the following conditions:

R. P. M.	1400
40 Brake horsepower	32
Jacket temperature	°F. 200
Oil sump temperature	°F. 210
Air to radiator	°F. 125
45 Oil change	hours. 60

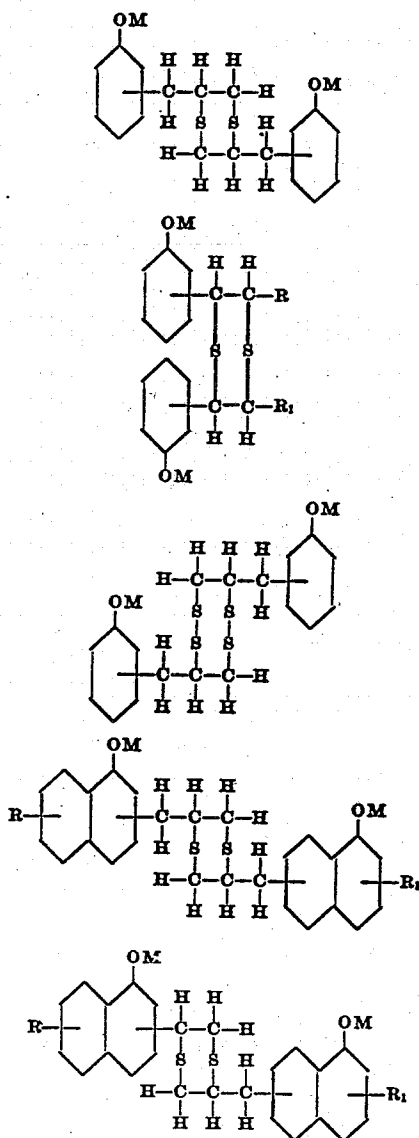
The corrosion inhibitors of this invention need not be single pure compounds. As a practical matter, the thiomers are usually mixtures of different compounds. When all of the carbon chains in the thiomers are long the mixtures contain dimers predominantly with smaller proportions of higher homologues such as trimers or even tetramers. As the number of long chain molecules in the thiomers is increased, viscosity also increases and oil solubility decreases until a point is reached where normally solid substantially oil-insoluble products are obtained. It is possible to obtain oil dispersions of the solid products but a liquid viscous readily oil-soluble thiomers is preferred, as previously noted.

The present invention also provides multi-functional additives for lubricants. Such multi-functional compounds are capable of simultaneously inhibiting piston ring sticking or varnish formation and reducing corrosion. Examples of such multi-functional additives are aryl metal oxides containing a multi-bridged thio grouping and metal carboxylates containing such a grouping. In general, the presence of multi-bridged sulfur grouping in metal salts of oil-soluble organic acids imparts multi-functional characteristics thereto.

Examples of aryl metal oxides containing multi-bridged sulfur are:

ARYL METAL OXIDES CONTAINING MULTI-BRIDGED THIOALKYL GROUPS

EXEMPLARY TYPE FORMULAE



where R and R₁ are radicals of hydrocarbon structure.

EXAMPLES

(1) Metal alkyl phenate di-(alkyl monothio)-dimers—

- Calcium salt of 2,5-di-(hydroxy phenyl) hexyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) octyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) decyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) dodecyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) cetyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) octadecyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy phenyl) eicosyl-1,4-dithiane

Calcium salt of 2,5-di-(hydroxy phenyl) paraffin wax-1,4-dithiane

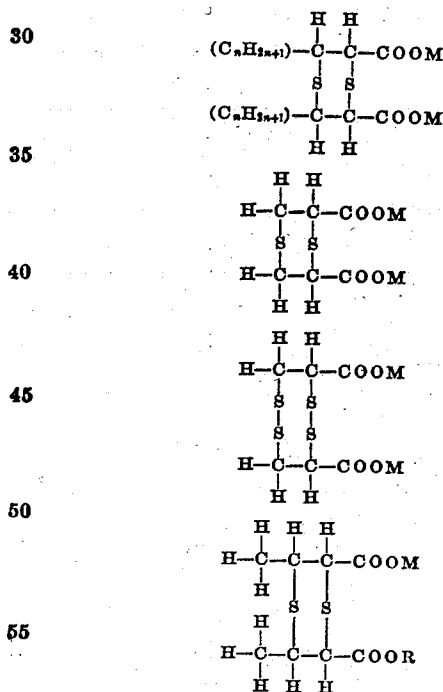
(2) Metal alkyl naphtholate di-(alkyl monothio) dimers—

- Calcium salt of 2,5-di-(hydroxy naphthyl) hexyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) octyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) decyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) dodecyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) cetyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) octadecyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) eicosyl-1,4-dithiane
- Calcium salt of 2,5-di-(hydroxy naphthyl) paraffin wax-1,4-dithiane

Other metals may be substituted for calcium, e. g. barium, strontium, magnesium, aluminum, zinc, tin and chromium.

25 ALKYL METAL CARBOXYLATES CONTAINING MULTI-BRIDGED THIO GROUPS

EXEMPLARY TYPE FORMULAE



where R is a radical of hydrocarbon structure.

EXAMPLES

- Aluminum salt of 2,6-di-octyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-decyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-dodecyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-cetyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-octadecyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-eicosyl-1,4-dithiane-3,5-dicarboxylic acid
- Aluminum salt of 2,6-di-paraffin wax-1,4-dithiane-3,5-dicarboxylic acid

Aluminum salt of 2,6-di-hexadecenyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-octyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-decyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-dodecyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-cetyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-octadecyl-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-eicosyl-1,4-dithiane-3,5-dicarboxylic acid

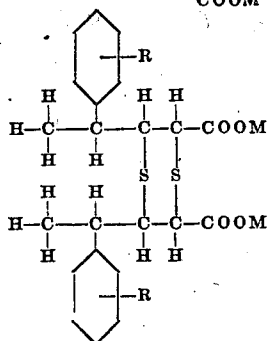
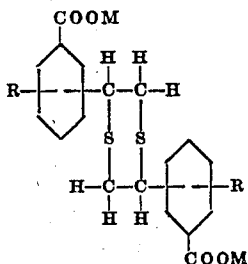
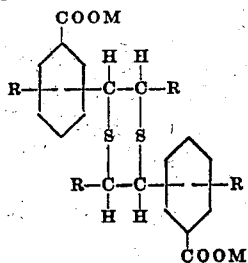
Zinc salt of 2,6-di-paraffin wax-1,4-dithiane-3,5-dicarboxylic acid

Zinc salt of 2,6-di-hexadecenyl-1,4-dithiane-3,5-dicarboxylic acid

Other metals may be substituted for aluminum or zinc, e. g. calcium, barium, strontium, magnesium, tin and chromium.

METAL SALTS OF ARYL CARBOXYLIC ACIDS CONTAINING MULTI-BRIDGED THIOALKYL GROUPS

EXEMPLARY TYPE FORMULAE



where R is a radical of hydrocarbon structure.

EXAMPLES

Calcium salt of 1,4-dithiane-2,5-di-(hexyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(octyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(decyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(dodecyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(cetyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(octadecyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(eicosyl phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(paraffin wax phenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(hexyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(octyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(decyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(dodecyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(cetyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(octadecyl hydroxyphenyl carboxylic) acid

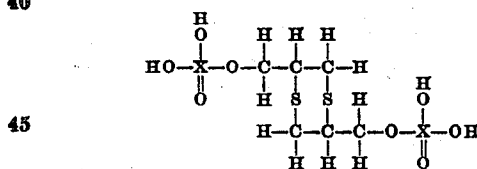
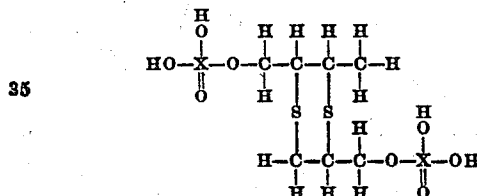
Calcium salt of 1,4-dithiane-2,5-di-(eicosyl hydroxyphenyl carboxylic) acid

Calcium salt of 1,4-dithiane-2,5-di-(paraffin wax hydroxyphenyl carboxylic) acid

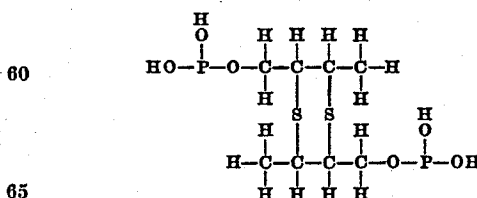
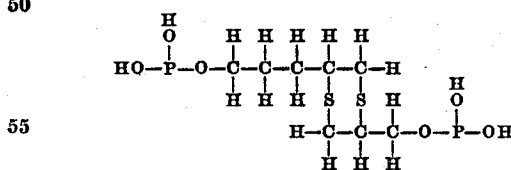
Other metals may be substituted for calcium, e. g. barium, strontium, magnesium, aluminum, zinc, tin and chromium.

METAL SALTS OF ORGANO-INORGANIC ACIDS CONTAINING MULTI-BRIDGED THIO GROUPS

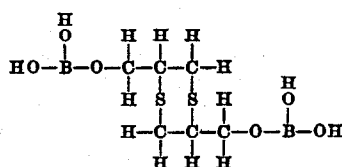
Exemplary are metal salts of acids of the following type formulae:

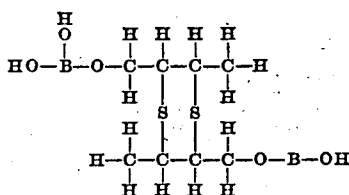


where X is preferably phosphorus, but may be arsenic or antimony.



where P is phosphorus.





where B is boron.

EXAMPLES

- Calcium salt of 1,4-dithiane-2,5-di-(octyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(decyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(dodecyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(tetradecyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(cetyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(octadecyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(eicosyl phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(paraffin wax phosphoric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(octyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(decyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(dodecyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(tetradecyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(cetyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(octadecyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(eicosyl phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(paraffin wax phosphorous) acid
- Calcium salt of 1,4-dithiane-2,5-di-(octyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(decyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(dodecyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(tetradecyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(cetyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(octadecyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(eicosyl boric) acid
- Calcium salt of 1,4-dithiane-2,5-di-(paraffin wax boric) acid

Other metals may be substituted for calcium, e. g. barium, strontium, magnesium, aluminum, zinc, tin and chromium.

The foregoing multi-functional addition agents may be prepared by various methods. For example, the same type of reactions disclosed at page 3 of this specification may be applied to these compounds by chlorinating the alkyl portion of the molecule and reacting the chlorinated product with an alkali metal sulfide containing added sulfur to obtain the multi-bridged monothio compounds. When a multi-bridged disul-

fide group is desired, then a mercapto group may be introduced into the alkyl portion of the molecule of these compounds and the resulting poly-mercaptans oxidized to yield multi-bridged disulfides.

Reference has been made in the foregoing specification to the effectiveness of the inhibitors of this invention for selectively "poisoning" certain stabilizers to minimize the catalytic action thereof on corrosion without destroying the desired catalytic action of such additives in stabilizing the lubricating oil against deterioration at elevated temperatures. Types of stabilizing agents previously mentioned are aryl metal oxides (metal phenates), salts of aryl carboxylic acids, salts of polycarboxylic acids which preferably have been partially esterified, salts of alkyl carboxylic acids containing a polar group near a carboxyl group of the acid, and metal alcoholates. Incorporation of the multi-bridged thioalkyl compounds heretofore disclosed in hydrocarbon oils having a viscosity index greater than 75 or over-refined oils enhances the responsiveness of these oils to the immediately foregoing types of stabilizers. Thus the multi-bridged thioalkyl compounds act as sensitizers in high viscosity index or over-refined hydrocarbon oils for stabilizing agents of the anti-piston ring sticking type. The corrosion inhibitors herein disclosed are accordingly multi-functional and are therefore both a sensitizer and an inhibitor of corrosion.

The corrosion inhibitors hereinbefore disclosed cooperate with aryl metal oxides to give a superior oil. Examples of aryl metal oxides are polyvalent metal salts of phenols of the type formula—



in which *u*, *v*, *w*, *x* and *y* are selected from the group consisting of hydrogen or radicals of hydrocarbon structure. The phenol preferably contains at least one alkyl group having more than four carbon atoms. The term "radicals of hydrocarbon structure" is intended to include alkyl, aryl, aralkyl, alkaryl or cyclic nonbenzenoid groups which may or may not contain inorganic substituents. Likewise, this term includes radicals which contain hydroxyl groups, ether, thioether, keto, thioketo or carboxyl groups.

The aryl metal oxides also may be metal salts of polynuclear phenols, e. g. salts of polyaryl naphtholates.

Examples of specific aryl metal oxides are alkaline earth metal salts of phenols containing a decyl, dodecyl, tetradecyl, cetyl, octadecyl, eicosyl or wax substituent; aluminum salts of phenols containing a decyl, dodecyl, tetradecyl, cetyl, octadecyl, eicosyl or wax substituent; magnesium salts of phenols containing a decyl, dodecyl, tetradecyl, cetyl, octadecyl, eicosyl or wax substituent; and similar salts of alkyl substituted polyhydroxy phenols. Other metals, e. g. tin, zinc, cadmium, chromium, iron, cobalt and nickel, may be substituted for the foregoing metals.

These compounds may be prepared by methods disclosed in the art. The following data exemplify the effectiveness of the corrosion inhibitors

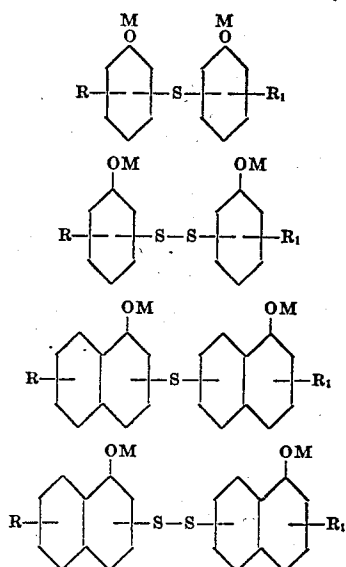
herein disclosed in reducing the corrosivity of lubricants containing aryl metal oxides:

Oil	300° F. corr. test—mg. wt. loss, coarse grained copper-lead		
	24 hrs.	48 hrs.	72 hrs.
Colombian S. A. E. 10 (VI=77).....	24.7	55.8	105.8
Colombian S. A. E. 10 (VI=77)+0.5% calcium cetyl phenate.....	129.1	160.2	191.4
Colombian S. A. E. 10 (VI=77)+0.5% calcium cetyl phenate+1% paraffin wax thiomers.....	8.0	25.4	33.5

Sulfurized metal phenates are particularly useful in combination with the multi-bridged sulfur corrosion inhibitors herein disclosed. The sulfurized metal phenates may be formed by reaction of the foregoing aryl metal oxides, particularly polyvalent metal salts of mononuclear phenols, with a small amount of sulfur. About $\frac{1}{10}$ to $1\frac{1}{2}$ gram atoms of sulfur per mol of metal phenate may be utilized in carrying out the sulfurization reaction. Preferably, the weight of sulfur is equivalent to about $\frac{1}{2}$ to 1 gram atom per mol of the phenate. The reaction of the sulfur and metal phenate is desirably carried out in an organic solution. For example, the metal phenate may be dissolved in a small amount of a hydrocarbon oil to form a concentrated solution of 50% by weight or more of the phenate in the oil. The preferred proportion of sulfur is then added to this solution, the reacting ingredients stirred and heated at 300° to 320° F. for about one hour, or until substantially complete reaction is obtained as indicated by the fact that a copper strip will show only a reddish-purple coloring after five minutes' submersion in the reaction mixture at 300° F.

Examples of aryl metal oxides which may be sulfurized are calcium, barium, strontium, magnesium, zinc, cadmium, aluminum, tin, chromium, iron, cobalt and nickel aryl metal oxides.

The corrosion inhibitors of this invention also cooperate with aryl metal oxides containing aryl sulfide substituents to yield a superior oil. Examples of such aryl metal oxides are illustrated by the following type formulae:



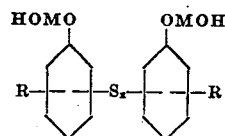
where R and R₁ are radicals of hydrocarbon structure and M is a metal, preferably a poly-

valent metal such as calcium, barium, strontium, magnesium, aluminum, zinc, tin and chromium.

The effectiveness of the corrosion inhibitors of this invention in combination with the above type sulfide substituted aryl metal oxides is shown by the following data:

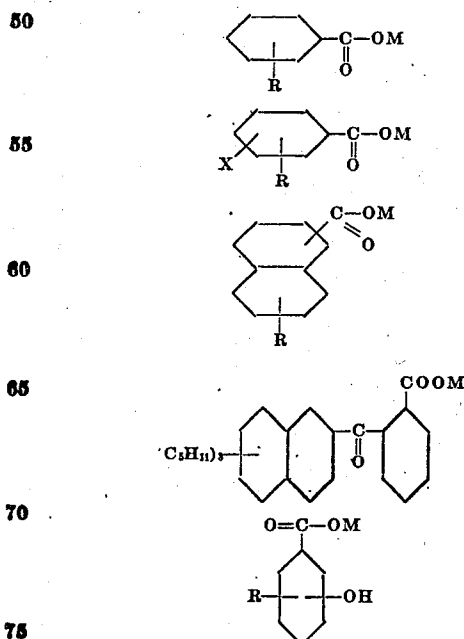
Oil	325° F., strip corr. test—mg. wt. loss		
	24 hrs.	48 hrs.	72 hrs.
Solvent refined oil base S. A. E. 30 (VI=86)+0.75% metal phenate disulfide.....	17.2	27.3	32.1
Solvent refined oil base S. A. E. 30 (VI=86)+0.75% metal phenate disulfide+1% paraffin wax thiomers.....	1.5	3.7	6.4
Standard Diol HD (VI=37).....	29.3	89.4	112.2
Standard Diol HD (VI=37)+1% paraffin wax thiomers.....	12.3	15.1	16.1

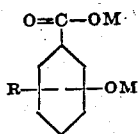
An oil solution of a metal phenate containing an aryl sulfide group and of the type listed in the foregoing table may be obtained under the trade-name "Paranox 56," a product of Standard Oil Company of New Jersey. $2\frac{1}{2}\%$ of the Paranox 56 may be added to the oil to obtain 0.75% by weight based on the oil of the metal phenate containing an aryl sulfide substituent. The Standard Diol HD referred to in the above table is an oil sold under that brand name by Standard Oil Company of New Jersey and is believed to contain a small amount of a compound of the type formula:



where R is an alkyl radical, M is an alkaline earth metal, and x is 1 or 2. In any event the paraffin wax dimer is operative both with the type of compounds mentioned and with the oils having the brand names indicated.

Salts of aryl carboxylic acids and the corrosion inhibitors disclosed herein may be utilized in combination to give a superior lubricant. Salts of this type are exemplified by the following type formulae:



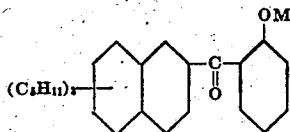


where R is a radical of hydrocarbon structure; M is a metal, e. g. calcium, barium, strontium, magnesium, cadmium, zinc, aluminum, tin, chromium, iron, cobalt or nickel; and X is a substituent such as $-\text{NH}_2$, $-\text{NR}_2$, $-\text{OH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{NO}_2$, $-\text{OM}$, $-\text{SH}$, $-\text{CN}$, $-\text{OCN}$, $-\text{SCN}$, and the like.

The effectiveness of this combination is illustrated by the following data:

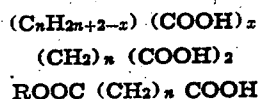
Oil	325° F., strip corr. test— mg. wt. loss		
	24 hrs.	48 hrs.	72 hrs.
Kettelman (Calif.) S. A. E. 30 (VI=86) + 0.5% calcium polyamyl naphthoyl benzoate	50.7	154.9	179.5
Kettelman (Calif.) S. A. E. 30 (VI=86) + 0.5% calcium polyamyl naphthoyl benzoate + 1% paraffin wax thiomers	11.9	12.3	12.3
Socony-Vacuum RD8-203 (VI=64)	28.7	75.7	107.1
Socony-Vacuum RD8-203 (VI=64) + 1% paraffin wax thiomers	24.5	48.7	52.3

The calcium polyamyl naphthoyl benzoate referred to in the above table is a compound of the type formula—



The Socony-Vacuum RD8-203 is an oil believed to contain a small amount of a tin salt of a paraffin wax substituted salicylic acid. In any event, the paraffin wax thiomers is operative with such salts and in the compounded oil of this name.

Salts of polycarboxylic acids in combination with the corrosion inhibitors disclosed herein may be utilized to yield superior lubricants. Exemplary type formulae of polycarboxylic acids from which these salts may be formed are as follows:



in which n may be zero or a whole number generally from 1 to 8 inclusive, x is a whole number from 1 to n , and in which there may or may not be alkyl, aryl, aralkyl or carbocyclic substitution to increase oil solubility. Improved salts of this type are obtained when n is greater than 1 and the acid contains a polar group substitution in a position alpha, beta, gamma, delta or epsilon to the carbon atom of the salt-forming carboxylic acid group. The term "polar group" as used herein includes the following:

Metallo-carboxyl, $-\text{COOM}$
 Hydroxyl, $-\text{OH}$
 Amino, $-\text{NH}_2$
 Oxy, $-\text{OR}$
 Metallo-oxy, $-\text{OM}$
 Keto, $=\text{O}$
 Thio keto, $=\text{S}$
 Mercapto, $-\text{SH}$
 Cyano, $-\text{CN}$

Cyanate, $-\text{OCN}$
 Thiocyanate, $-\text{SCN}$

and the like.

The effectiveness of this combination is illustrated by the following data:

Oil	325° F., strip corr. test— mg. wt. loss		
	24 hrs.	48 hrs.	72 hrs.
Kettelman (Calif.) S. A. E. 30 (VI=86) + 0.5% calcium cetyl citrate	2.5	3.5	4.3
Kettelman (Calif.) S. A. E. (VI=86) + 0.5% calcium cetyl citrate + 1% paraffin wax thiomers	0.8	2.6	3.8

Calcium, barium, strontium, magnesium, zinc, cadmium, aluminum, tin, chromium, iron, cobalt and nickel salts of the polycarboxylic acids, preferably partially esterified, may be utilized. Examples of acids from which such salts may be prepared by known methods are: oxalic acid, malonic acid, isosuccinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid, fumaric acid, maleic acid, malic acid, tartronic acid, tartaric acid, citric acid, aminosuccinic acid and the like. It is preferred that each of the above acids be partially esterified and that the metal salts be a salt of a partially esterified acid.

Examples of salts of alkyl carboxylic acids containing a polar group near a carboxyl group of the acid are: the calcium, barium, strontium, magnesium, zinc, tin, aluminum, chromium, iron, cobalt and nickel salts of alpha, beta or gamma hydroxy lauric, myristic, palmitic, stearic and arachidic acids; the calcium, barium, strontium, magnesium, zinc, tin, aluminum, chromium, iron, cobalt and nickel salts of alpha, beta or gamma thio, mercapto, mercaptide or thiono substituted lauric, myristic, palmitic, stearic and arachidic acids; and the calcium, barium, strontium, magnesium, zinc, tin, aluminum, chromium, iron, cobalt and nickel salts of alpha, beta or gamma amino substituted lauric, myristic, palmitic, stearic and arachidic acids. The effectiveness of these salts in lubricating oils may be enhanced by use in combination with the multi-bridged thioalkyl compounds herein disclosed.

Examples of metal alcoholates which may be added to hydrocarbon oils together with the multi-bridged thioalkyl inhibitors comprise the alkali, alkaline earth, aluminum and heavy metal alcoholates, e. g. sodium, potassium, calcium, barium, strontium, magnesium, zinc, cadmium, tin, aluminum, chromium, iron, cobalt and nickel alcoholates. Examples of alcohols utilized to form the metal alcoholates are the higher alcohols, such as amyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, ceryl, myricyl and unsaturated alcohols, such as are derived from lanolin.

For purposes of clarity and emphasis it is again pointed out that each of the multi-bridged thioalkyl compounds, and particularly the paraffin wax thiomers hereinbefore disclosed, may be utilized either as a corrosion inhibitor or as a sensitizer for hydrocarbon oils to be stabilized with any of the aryl metal oxides, salts of aryl carboxylic acids, salts of polycarboxylic acids, salts of alkyl carboxylic acids containing a polar group, and the metal alcoholates above disclosed. In some instances, as for example in over-refined or high viscosity index oils having a viscosity index greater than 75, the principal function of the

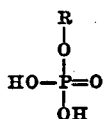
thiomers may be that of a sensitizer rather than a corrosion inhibitor. In other instances, as when the hydrocarbon oil being stabilized is only moderately refined or has a viscosity index less than 75 and the service to be encountered by the compounded oil is severe or with corrosion-sensitive bearings, the principal function of the thiomers may be that of a corrosion inhibitor. In still other situations the thiomers may serve as multi-functional agents to both inhibit corrosion and sensitize the base oil to stabilization with the salt-type inhibitor.

The proportion of the salt-like inhibitors, that is, of the aryl metal oxides, salts of aryl carboxylic acids, salts of polycarboxylic acids, salts of alkyl carboxylic acids containing a polar group, and the metal alcoholates above disclosed, may vary from about 0.1% to 2% by weight in the finished oil. From approximately .5% to 1.5% is usually preferred.

Another aspect of this invention comprises the provision of an activator for the multi-bridged thioalkyl compounds disclosed herein. These activators enhance the effectiveness of the thiomers herein disclosed in a manner which has not been explained and is not understood. The activators preferably comprise either an acid ester, that is, a partially esterified acid of a strong acid-forming element such as phosphorus, or of a weak acid-forming element such as arsenic, antimony, or boron, or a salt of acids of these strong or weak acid elements containing an organic substituent. Acid esters or salts of partial esters of acids of silicon and of metacarbonic or orthocarbonic acids are also contemplated within the broader aspects of the invention. Either the acid ester alone, or the salt alone, or mixtures of salts and acid esters of any of the foregoing may be used as an activator. These types of activators, when utilized in combination with the foregoing multi-bridged thioalkyl compounds, enhance the corrosion inhibiting or sensitizing action thereof. This is true even though the activator may not, when added alone, be a sensitizing agent for the oil being stabilized.

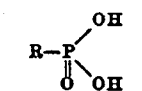
Illustrative activators which may be added to hydrocarbon oils, such as mineral lubricating oil, according to this invention comprise metal salts in which the metals are selected from groups II, III, IV and VI of Mendelyev's Table of the Elements. Specific examples of such metals are: calcium, barium, strontium, magnesium, zinc, tin, cadmium, aluminum, chromium, iron, cobalt and nickel. Likewise, the alkali metal and ammonium salts are not precluded.

The salts of substituted acids of phosphorous utilized as activators and illustrating the derivatives of strong acid-forming elements are preferably formed from substituted oxyacids of pentavalent phosphorous of the following type formula:

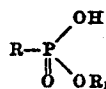


where R may be alkyl, aryl, alkaryl, aralkyl or cyclic nonbenzenoid radicals. Substituted phosphoric acids containing at least twelve carbon atoms are preferred, but where the salts are sufficiently soluble in oil, acids containing fewer carbon atoms may be utilized. Examples of preferred type acids are alkyl or alkaryl substituted phosphoric acids having at least twelve carbon atoms in the molecule. It is to be understood that the

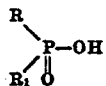
broader aspects of the invention include salts of other types of acids of phosphorus containing more than twelve carbon atoms. Additional examples of such substituted oxyacids of phosphorous are as follows:



Phosphonic acid



Monoester of phosphonic acid



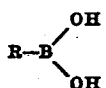
Phosphinic acid

where R and R₁ may be alkyl, aryl, alkaryl, aralkyl or cyclic nonbenzenoid groups which, in turn, may be pure hydrocarbon constituents or oxygenated hydrocarbons such as alcohols, ketones, esters and ethers, or hydrocarbons containing substituents such as halogens (chlorine, bromine, iodine), amino, or nitro groups. Likewise R and R₁ may be an oil-soluble heterocyclic constituent, for example, a radical containing a nitrogen ring.

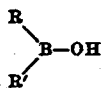
In general, salts of substituted derivatives of acids of phosphorus, such as phosphorous acid, H₃PO₃; hypophosphoric acid, H₂P₂O₆; orthophosphoric acid, H₃PO₄; pyrophosphoric acid, H₄P₂O₇, and the sulfur analogues of these acids fall within the broadest aspects of the invention. By "acids of phosphorus containing an organic substituent" or by "substituted acids of phosphorus" wherever used herein it is intended to designate acids of phosphorus containing an organic group of the types previously listed. The organic groups may be either directly attached to the phosphorus atom of the compound or attached thereto through an intervening atom, such as oxygen or sulfur. The term "oxyacids of phosphorus" is used to designate throughout the specification and claims acids of phosphorus in which only an oxygen atom may intervene between the hydrogen and phosphorus atoms of the parent acid.

Additional examples of activators comprising derivatives of weak acid-forming elements are metal salts or acid esters derived from acids selected from the following groups:

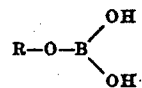
TYPE 1.—ACIDS OF BORON CONTAINING AN ORGANIC SUBSTITUENT



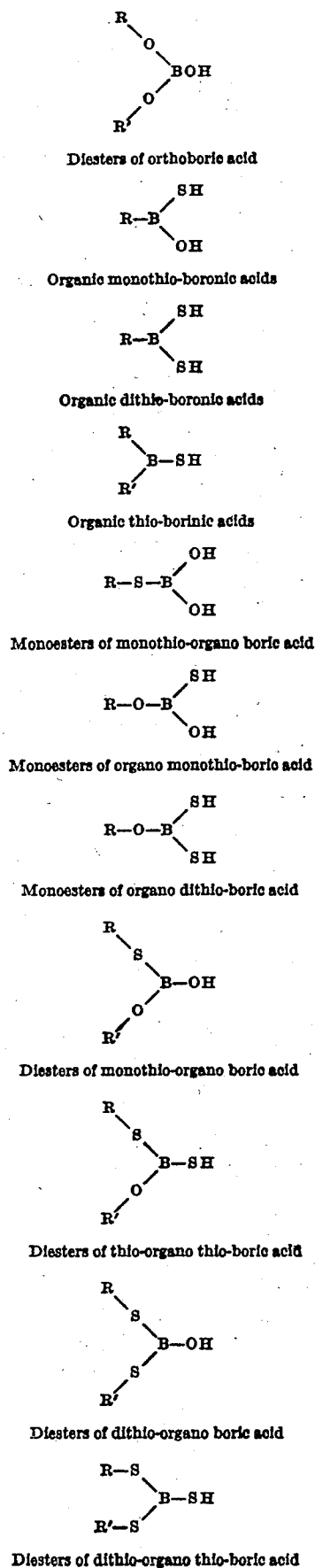
Organic boronic acids



Organic borinic acids

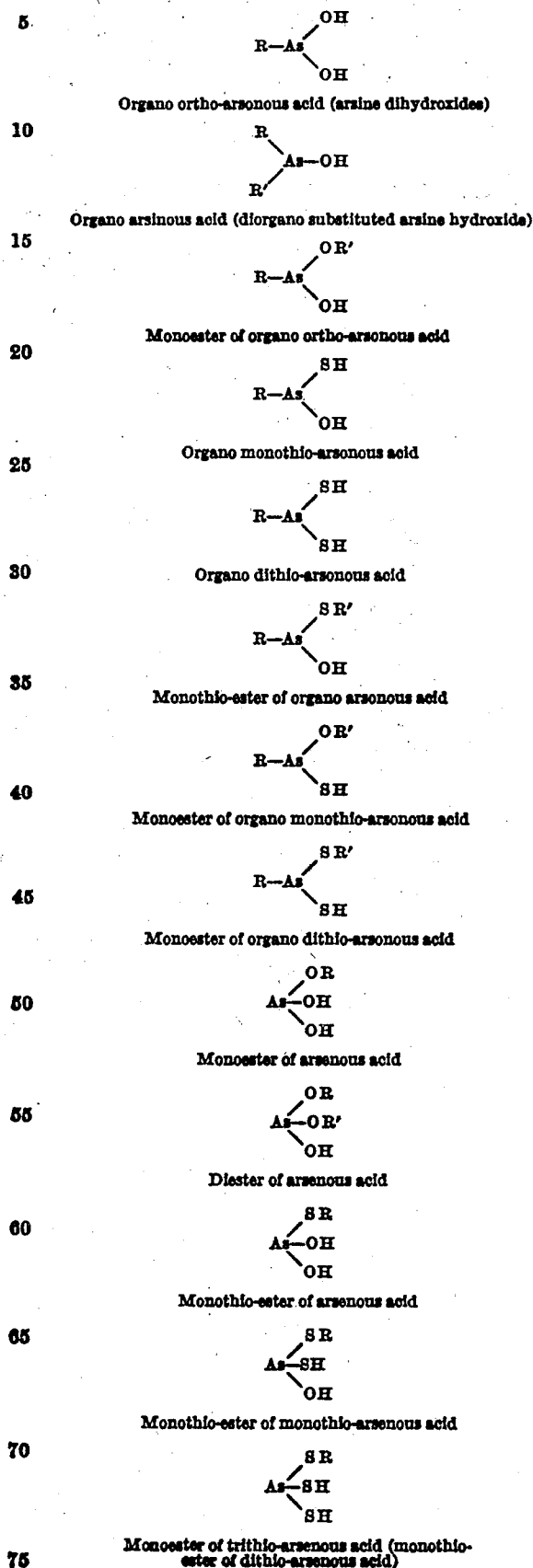


Monoesters of orthoboric acid

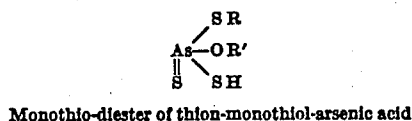
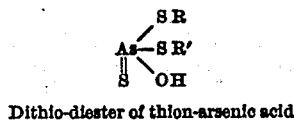
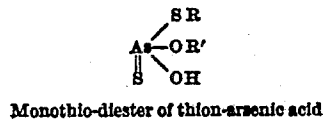
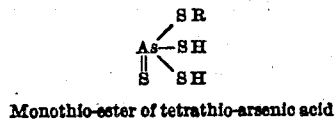
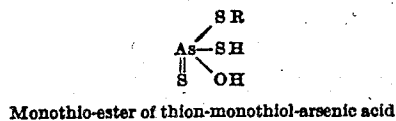
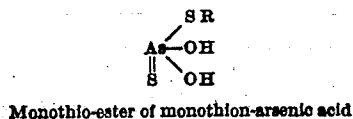
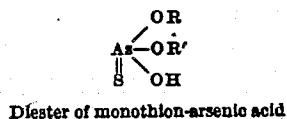
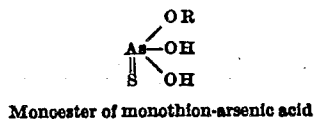
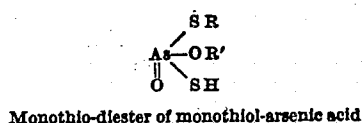


TYPE 2.—ACIDS OF ARSENIC CONTAINING AN ORGANIC SUBSTITUENT

A.—Trivalent arsenic

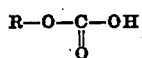


$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{OR}' \\ \diagdown \\ \text{OH} \end{array}$		$\begin{array}{c} \text{SH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{SH} \end{array}$	
Monothio-diester of arsenous acid	5	Organo dithiol-arsenic acid	
$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{SR}' \\ \diagdown \\ \text{OH} \end{array}$		$\begin{array}{c} \text{SR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
Dithio-diester of arsenous acid	10	Monothio-ester of organo arsonic acid	
$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{OR}' \\ \diagdown \\ \text{SH} \end{array}$		$\begin{array}{c} \text{SR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{SH} \end{array}$	
Monothio-diester of monothio-arsenous acid	15	Monothio-ester of organo thiol-arsenic acid	
B.—Pentavalent arsenic		$\begin{array}{c} \text{OR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{SH} \end{array}$	
$\begin{array}{c} \text{OH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	20	Monoester of organo thiol-arsenic acid	
Organo arsonic acid		$\begin{array}{c} \text{R} \\ \diagup \\ \text{As}-\text{OH} \\ \diagdown \\ \text{R}_1 \quad \text{S} \end{array}$	
$\begin{array}{c} \text{R} \\ \diagup \\ \text{As}-\text{OH} \\ \diagdown \\ \text{R}' \quad \text{O} \end{array}$	25	Diorgano substituted thion-arsinic acid	
Disubstituted organo arsinic acid		$\begin{array}{c} \text{R} \\ \diagup \\ \text{As}-\text{SH} \\ \diagdown \\ \text{R}' \quad \text{S} \end{array}$	
$\begin{array}{c} \text{OR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	30	Diorgano substituted dithio-arsinic acid	
Monoester of organo arsonic acid		$\begin{array}{c} \text{R} \\ \diagup \\ \text{As}-\text{SH} \\ \diagdown \\ \text{R}' \quad \text{O} \end{array}$	
$\begin{array}{c} \text{OH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{OH} \end{array}$	35	Diorgano substituted thiol-arsinic acid	
Organo thion-arsenic acid		$\begin{array}{c} \text{OR} \\ \diagup \\ \text{As}-\text{OH} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{SH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{OH} \end{array}$	40	Monoester of arsenic acid	
Organo thion-monothiol-arsenic acid		$\begin{array}{c} \text{OR} \\ \diagup \\ \text{As}-\text{OR}' \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{SH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{SH} \end{array}$	45	Diester of arsenic acid	
Organo trithio-arsenic acid		$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{OH} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{OR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{OH} \end{array}$	50	Monothio-ester of arsenic acid	
Monoester of organo thion-arsenic acid		$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{SH} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{SR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{OH} \end{array}$	55	Monothio-ester of monothiol-arsenic acid	
Monothio-ester of organo thion-arsenic acid		$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{SH} \\ \diagdown \\ \text{O} \quad \text{SH} \end{array}$	
$\begin{array}{c} \text{SR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{SH} \end{array}$	60	Monothio-ester of dithiol-arsenic acid	
Monoester of organo trithio-arsenic acid		$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{OR}' \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{OR}' \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{S} \quad \text{SH} \end{array}$	65	Monothio-diester of arsenic acid	
Monoester of thion-monothiol-arsenic acid		$\begin{array}{c} \text{SR} \\ \diagup \\ \text{As}-\text{SR}' \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	
$\begin{array}{c} \text{SH} \\ \diagup \\ \text{R}-\text{As} \\ \diagdown \\ \text{O} \quad \text{OH} \end{array}$	70	Dithio-diester of arsenic acid	
Organo monothiol-arsenic acid	75		

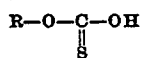


TYPE 3.—CARBONIC ACIDS CONTAINING AN ORGANIC SUBSTITUENT

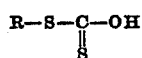
A.—Metacarbonic acid



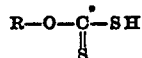
Partial ester of carbonic acid



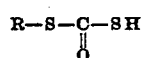
Partial ester of thion-carbonic acid



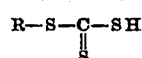
Monothio-ester of thion-carbonic acid



Monoeester of thiol-thion carbonic acid

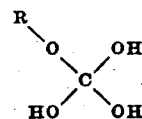


Monothio-ester thiol of thiocarbonic acid

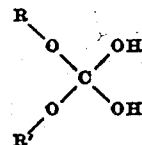


Partial ester of trithio-carbonic acid

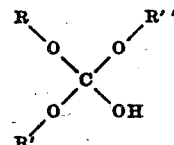
B.—Orthocarbonic acid



Monoeester of orthocarbonic acid

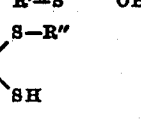
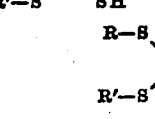
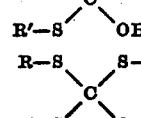
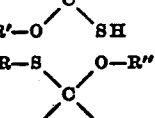
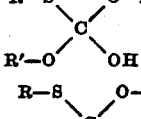
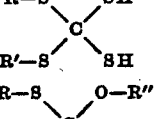
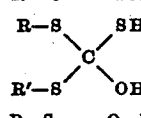
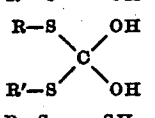
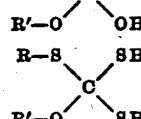
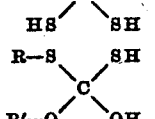
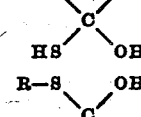
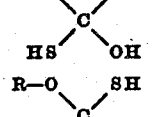
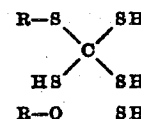
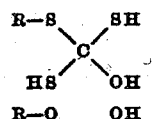
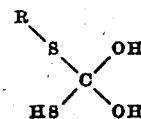
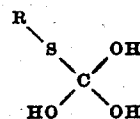


Diester of orthocarbonic acid



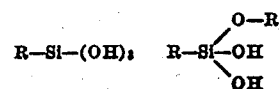
Triester of orthocarbonic acid

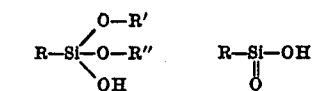
and corresponding sulfur derivatives such as—



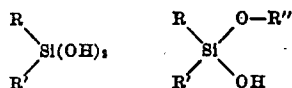
TYPE 4.—ACIDS OF SILICON CONTAINING AN ORGANIC SUBSTITUENT

A.—Mono-organo acids of silicon





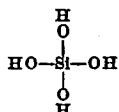
B.—Diorgano acids of silicon



C.—Triorgano acids of silicon



D.—Partial esters of mono-orthosilicic acid



In all of the foregoing type formulae R, R' and R'' are radicals of hydrocarbon structure. It is understood that by the term "hydrocarbon structure" it is intended to include hydrocarbon groups containing polar radicals such as OH, SH, Cl, NH₂ and COOH. Likewise, this term includes radicals containing ether, sulfide and ester groups.

It should be borne in mind that in the foregoing type formulae all of the acids listed may not exist as such and that it is the esters or salt-like derivatives thereof with which the present invention is concerned. Accordingly, existence of the free acid in a stable form is not a prerequisite to the preparation of the derivatives thereof contemplated herein. It should also be observed that various of the salt-like derivatives are relatively insoluble in organic solvents such as hydrocarbon oils. However, oil-solubility is not an absolute prerequisite for utility of the present invention in its broadest aspects, as will be explained in more detail hereinafter; nevertheless, oil-soluble compounds are preferred. Some of the salt-like compounds and esters are unstable at high temperatures. When the compounded oil is to encounter high temperature conditions during use compounds known or found to be more stable at elevated temperatures should be selected.

Activating agents contemplated within the broader aspects of the invention are in general salts, and preferably polyvalent metal salts, of the following acid reacting compounds: organic substituted derivatives of acids of boron, such as orthoboric, H₃BO₃; mesoboric, H₄B₂O₅; metaboric, H₂B₂O₄; dihydrotetraboric, H₄B₂O₇; hexahydrotetraboric, H₆B₄O₉ (once called pyroboric acid); dihydrotetraboric, H₂B₄O₇; hexahydrohexaboric, H₆B₆O₁₂; dihydrohexaboric, H₂B₆O₁₀; hexahydro-octaboric, H₆B₈O₁₅; dihydro-octaboric, H₂B₈O₁₃; dihydrodecaboric, H₂B₁₀O₁₆; dihydrododecaboric, H₂B₁₂O₁₉; organic substituted derivatives of acids of arsenic, such as alkyl arsine hydroxides or oxides, alkyl arsine sulfides, dialkyl arsine hydroxides or oxides, dialkyl arsine sulfides, aryl arsine hydroxides or oxides, alkaryl arsine hydroxides or oxides, aryl or alkarylarsine sulfides and sesquisulfides, diaryl arsine hydroxides or oxides, dialkaryl arsine hydroxides or oxides, diaryl or dialkaryl arsine sulfides, alkyl arsonic acids, alkyl arsine disulfides, alkyl arsinic acids, aryl arsonic acids, aryl di-arsonic acids, halogenated aryl arsonic acids, nitroaryl arsonic acids, 75

amino aryl arsonic acids, hydroxy aryl arsonic acids, carboxy aryl arsonic acids, alkaryl arsonic acids, alkaryl diarsonic acids, halogenated alkaryl arsonic acids, aryl arsinic acids, alkaryl arsinic acids, aryl trithio-arsonic acids, alkaryl trithio-arsonic acids, aryl arsine disulfides, and alkaryl arsine disulfides; organic substituted carbonic acids, such as monoesters of metacarbonic acids, mono-, di- and tri-esters of orthocarbonic acids, including the thio derivatives of both the meta and ortho acids; organic substituted acids of silicon, such as mono-, di- and tri-organo acids of silicon, and partial esters of mono-orthosilicic acid; organic substituted acids of germanium, such as trisubstituted germanols, germanonic acids, and germanic acid anhydrides; organic substituted acids of tin, such as organo stannonic acids and organo thio-stannic acids; organic substituted acids of antimony, such as organo stibinous acids, organo stibonic acids and organo stibinic acids; and analogous weak acids of bismuth, chromium, molybdenum, and manganese in those instances where organo salt-forming acids are obtainable.

The proportion of activating agents herein disclosed which may be added according to the principles of the present invention may vary depending upon the uses involved and the properties desired. As little as 0.05% by weight of various of the compounds gives measurable improvements. From approximately 0.1% to 2% of the compounds may be added to liquid lubricants. In general, from approximately 0.25% to 0.75% has been found preferable, particularly when used in conjunction with from approximately 0.25% to 1% of an aryl metal oxide and 0.5% to 1.5% of the paraffin wax thiomers.

A preferred embodiment of this invention provides a mineral oil composition containing three types of components, namely:

- (1) A metal salt of an organic acid in an amount sufficient to inhibit deterioration of the oil. This type of stabilizing agent has been previously disclosed herein in detail and examples given of aryl metal oxides, salts of aryl carboxylic acids, salts of polycarboxylic acids which preferably have been partially esterified, salts of alkyl carboxylic acids containing a polar group near a carboxyl group of the acid, and metal alcoholates. These salts, as hereinbefore disclosed, may be used in this preferred embodiment;
- (2) A corrosion inhibitor and/or a sensitizer in an amount sufficient substantially to reduce corrosion and/or enhance the responsiveness of the hydrocarbon oil to the stabilizing action of the metal salt stabilizer. When the base oil being stabilized is of high viscosity index or over-refined, this second ingredient usually functions primarily as a sensitizer. When the base oil is of low viscosity index or low refinement, the ingredient may serve primarily as a corrosion inhibitor. In moderately refined or moderate viscosity index base oils, this type of ingredient serves both as a sensitizer and a corrosion inhibitor. The corrosion inhibitor and/or sensitizer is a long carbon chain multi-bridged thioalkyl compound of the type previously disclosed herein. The many examples given in this specification may be utilized in the present preferred embodiment of the invention but, as previously indicated, the paraffin wax thiomers are outstanding.

(3) An activator for the sensitizer and/or corrosion inhibitor for increasing the effectiveness thereof. The activators comprise either an acid ester, that is, a partially esterified acid of phosphorus, arsenic, antimony or boron, or a salt of acids of these elements containing an organic substituent, as disclosed hereinbefore. The salts of other analogous organo-inorganic acids disclosed herein are not precluded as activators and fall within the broader scope of the invention.

The following data on oils compounded with the above three types of ingredients are illustrative:

TABLE I

325° F. strip corrosion test on S. A. E. 30 oil from Kettleman crude (California) +0.5% sulfurized calcium cetyl phenate+0.25% calcium cetyl phosphate+0.25% thiomers

Multi-bridged thiomers compounding agency							Cu-Pb wt. loss mmg.			Viscosity increase at 210° F.	Neut. No.	Naphtha insoluble
Vis. at 100° F.	Mol. wt.	Percent S	Percent Cl	Percent Cl in orig. wax	Percent by wt. in oil	Preparation by—	24 hrs.	48 hrs.	72 hrs.			
1753	680	12.2	11.5	26	0.25	Reaction of chlorinated paraffin wax with sodium sulfide.	11.0 0.7	30.5 1.7	44.0 4.4	7.6 4.4	1.28 0.83	45 1
3031 1012	936 504	13.3 7.5	10.3 3.7	26 15.4	0.25 0.25	Reaction of chlorinated lubricating oil with sodium sulfide.	+0.3 3.6	0.0 11.0	1.4 14.2	7.6 7.8	0.46 1.94	2 16
913	850	10.9	.7	16	0.25	Oxidation paraffin wax polymercaptan to disulfide.	0.6	2.2	2.6	3.2	1.61	-----
590	873	6.8	2.2	16	0.25	Reaction wax polymercaptide with chlorinated wax.	6.3	16.7	19.1	7.1	1.15	10

TABLE II

300° F. strip corrosion test (coarse grained bearings) on S. A. E. 10 oil from Colombian crude +0.5% sulfurized calcium cetyl phenate+0.25% calcium cetyl phosphate+1% thiomers

Multi-bridged thiomers compounding agency							Cu-Pb wt. loss mmg.			Viscosity increase at 210° F.	Neut. No.	Naphtha insoluble
Vis. at 100° F.	Mol. wt.	Percent S	Percent Cl	Percent Cl in orig. wax	Percent by wt. in oil	Preparation by—	24 hrs.	48 hrs.	72 hrs.			
1753	680	12.2	11.5	26	0.1	Reaction of chlorinated paraffin wax with sodium sulfide.	0.4 0.4	112.4 9.8	259.4 29.6	3.4 2.5	4.18 1.57	71 27
1561	550	11.1	12.6	26	1	Reaction of chlorinated paraffin wax with sodium sulfide (iron present).	3.7	17.8	34.4	2.0	1.32	27
1224	1525	12.6	1.7	16	1	Reaction of chlorinated paraffin wax with sodium sulfide.	0.2	6.7	12.6	1.9	1.30	18
2886	1500	18.0	1.0	16	1	Reaction of chlorinated paraffin wax with sodium sulfide (+ extra sulfur).	+3.1	+3.2	+3.7	1.5	0.84	17
1012	504	7.5	3.7	15.4	1	Reaction of chlorinated lubricating oil with sodium sulfide.	3.7	22.1	65.9	2.1	2.19	25
590	873	6.8	2.2	16	2	Reaction wax polymercaptide with chlorinated wax.	2.0	15.6	20.6	2.6	1.43	24
14330	1364	14.9	3.0	-----	1	Oxidation paraffin wax polymercaptan to disulfide.	12.0	25.6	48.2	-----	-----	9

The strip corrosion tests in Tables I and II were carried out in the same manner as described previously for 325° F. and 300° F. corrosion tests, respectively.

In the compounded oils containing the combination of three additives as above described, the proportions may be as previously indicated, namely, from about 0.1% to 2% by weight, and preferably from approximately 0.5% to 1.5% by weight based on the oil, of the salts of organic acids; from about 0.1% to about 2% by weight based on the oil of a corrosion inhibitor and/or sensitizer, and preferably from about 0.25% to 1.5% thereof; and from as little as 0.05% to 2% by weight based on the oil of the activator, from approximately 0.25% to 0.75% being preferable.

may nevertheless be highly useful and extremely advantageous in conjunction with the operation of internal combustion engines having corrosive-resistant bearing metals. Likewise, combinations of compounding agents which are not sufficiently powerful to stabilize a particular oil stock under the most extreme conditions may, nonetheless, be highly advantageous in such oils where the environment to be encountered is not so severe. The present invention in its broader aspects is therefore not limited to the particular compounding agent or combination of ingredients giving the greatest stability or passing all of the very severe tests which have been devised. The invention embraces various of the less advantageous additives or combinations thereof which may find utility in particular applications where all pos-

sible improvements in properties of the oil may not be required or where the standard of performance may not be so high.

The compounding agents and combinations of this invention appear at present to find their greatest utility in over-refined or highly paraffinic mineral lubricating oil stocks, which stocks have heretofore been the most difficult to stabilize. However, it is to be understood that the invention is not limited to such base stocks since advantages herein disclosed may be obtained with moderately refined or less paraffinic lubricating oils or even low viscosity index lubricants.

The compounded hydrocarbon oils of this invention may be utilized as turbine oils, cable oils, electric switch oils, transformer oils and the like, as well as in crankcase lubricants for internal combustion engines and especially Diesel engines. The compounding agents of this invention may also be added to hydrocarbon oils containing additional ingredients, such as pour point depressants, oiliness agents, extreme pressure addition agents, blooming agents, compounds for enhancing the viscosity index of the hydrocarbon oil, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease, as in the case of mineral castor machine oils or other compounded liquid lubricants.

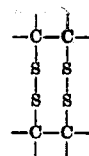
In the foregoing disclosure an upper limit of approximately 2% by weight based on the oil of each of the compounding agents has been indicated as sufficient for a finished oil. The present invention also embraces solutions containing more than 2% of the novel combination of compounding agents. Concentrates containing high percentages of the additives of this invention comprise a convenient method of handling the compounding agents, and the concentrated solutions may be sold and used as addition agents for lubricants in general. Thus mineral oil solutions containing as much as 50% or more by weight of the compounding agents may be prepared. Such concentrated solutions are adapted for dilution with hydrocarbon lubricating oil to yield a finished product containing, for example, from approximately 0.5% to 1.5% by weight of a metal phenate; from approximately 0.25% to 1.5% by weight of a paraffin wax thiomers; and from approximately 0.25% to 0.75% by weight based on the oil of a metal salt of an acid of phosphorus containing an organic substituent. Concentrated solutions of the additives in organic solvents capable of dilution with mineral lubricating oil to form a homogeneous mixture containing the above proportions of compounding agents comprise a part of this invention.

While the character of the invention has been described in detail and numerous examples of the compounds given, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

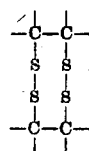
1. A viscous hydrocarbon oil containing from approximately 0.1% to 2% by weight based on the oil of a polyvalent metal salt of an organic acid, from approximately 0.1% to 2% by weight

based on the oil of a multi-bridged thioalkyl compound containing the chemical group—



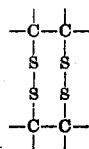
10 said compound having at least one long carbon chain, and from approximately 0.05% to 2% by weight based on the oil of a metal salt of an inorganic acid containing an organic substituent.

15 2. A viscous hydrocarbon oil containing a corrosion inhibitor comprising a multi-bridged thioalkyl compound containing the chemical group—



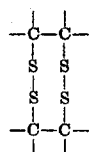
20 said compound having at least one long carbon chain and being present in the oil in amount sufficient to inhibit corrosiveness of the oil.

25 3. A lubricating oil having a corrosion index greater than about 40 containing a corrosion inhibitor comprising a multi-bridged thioalkyl compound containing the chemical group—



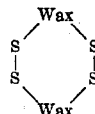
30 said compound having at least one long carbon chain and being present in the oil in amount sufficient to inhibit corrosiveness of the oil.

35 4. A viscous hydrocarbon oil having a viscosity index greater than approximately 75 and a corrosion inhibitor comprising a multi-bridged thioalkyl compound containing the chemical group—



40 said compound having at least one long carbon chain and being present in the oil in amount sufficient to inhibit corrosiveness of the oil.

45 5. A viscous hydrocarbon oil containing a corrosion inhibitor comprising a petroleum wax thiomers containing the chemical group—



50 said petroleum wax thiomers being present in the oil in amount sufficient to inhibit corrosiveness of the oil.

55 6. A hydrocarbon oil containing an aryl metal oxide containing a multi-bridged thioalkyl substituent characterized by more than one sulfur bridge between alkyl carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms, there being a sufficient amount of said multi-bridged thioalkyl substituent in the oil to inhibit corrosiveness of the oil.

60 7. A hydrocarbon oil containing a metal salt

of an aryl, carboxylic acid containing a multi-bridged thioalkyl substituent characterized by more than one sulfur bridge between alkyl carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms, there being a sufficient amount of said multi-bridged thioalkyl substituent in the oil to inhibit corrosiveness of the oil.

8. A hydrocarbon oil containing a metal salt of an organo-inorganic acid containing a multi-bridged thioalkyl substituent characterized by more than one sulfur bridge between alkyl carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms, there being a sufficient amount of said multi-bridged thioalkyl substituent in the oil to inhibit corrosiveness of the oil.

9. A composition comprising a hydrocarbon lubricating oil subject to deterioration and to formation of adhesive deposits at elevated temperature, an aryl metal oxide in an amount sufficient substantially to inhibit said deterioration, and an inhibitor capable of reducing the catalysis of corrosion by said aryl metal oxide without destroying the stabilizing action thereof, said inhibitor comprising a multi-bridged thioalkyl compound containing at least one long carbon chain.

10. A composition comprising a hydrocarbon lubricating oil subject to deterioration and to formation of adhesive deposits at elevated temperature, a salt of an aryl carboxylic acid in an amount sufficient substantially to inhibit said deterioration, and an inhibitor capable of reducing the catalysis of corrosion by said salt of an aryl carboxylic acid without destroying the stabilizing action thereof, said inhibitor comprising a multi-bridged thioalkyl compound containing at least one long carbon chain.

11. A composition comprising a hydrocarbon lubricating oil subject to deterioration and to formation of adhesive deposits at elevated temperature, a metal alcoholate in an amount sufficient substantially to inhibit said deterioration, and an inhibitor capable of reducing the catalysis of corrosion by said metal alcoholate without destroying the stabilizing action thereof, said inhibitor comprising a multi-bridged thioalkyl compound containing at least one long carbon chain.

12. A composition comprising a hydrocarbon lubricating oil, a corrosion inhibitor comprising a multi-bridged thioalkyl compound containing at least one long carbon chain, and an activator for enhancing the effectiveness of said corrosion inhibitor comprising a salt of an organo substituted acid of an element selected from the group consisting of phosphorus, arsenic, antimony and boron.

13. A composition comprising a hydrocarbon lubricating oil subject to deterioration and to formation of adhesive deposits at elevated temperature, a metal salt of an organic acid in an amount sufficient substantially to inhibit formation of said adhesive deposits, a multi-bridged thioalkyl sensitizer for the hydrocarbon oil capable of enhancing its responsiveness to the stabilizing action of said metal salt, and an activator capable of enhancing the effectiveness of said thioalkyl sensitizer.

14. A composition comprising a hydrocarbon lubricating oil subject to deterioration and to

formation of adhesive deposits at elevated temperature, a metal salt of an organic acid in an amount sufficient substantially to inhibit formation of said adhesive deposits, a multi-bridged thioalkyl sensitizer for the hydrocarbon oil capable of enhancing its responsiveness to the stabilizing action of said metal salt, and an activator comprising a salt of an acid of phosphorus containing an organic substituent, said phosphorus acid salt being capable of enhancing the effectiveness of said thioalkyl sensitizer.

15. An addition agent for lubricating oils which comprises a concentrated solution in an organic solvent of a polyvalent metal salt of an organic acid, a multi-bridged thioalkyl compound, and a polyvalent metal salt of a substituted acid of phosphorus containing an organic substituent, said concentrated solution containing more than 2% by weight based on the oil of each of said three ingredients, said solution being capable of dilution with mineral lubricating oil to form a homogeneous mixture containing from approximately 0.1% to 2% by weight based on the oil of the polyvalent metal salt of an organic acid, from approximately 0.1% to approximately 2% by weight based on the oil of the multi-bridged thioalkyl compound, and from approximately 0.05% to 2% by weight based on the oil of the polyvalent metal salt of a substituted acid of phosphorus containing an organic substituent.

16. A composition comprising a compounded hydrocarbon oil subject to deterioration and to formation of adhesive deposits at elevated temperature, said compounded oil containing a metal salt of an organic acid in an amount sufficient substantially to inhibit said formation of adhesive deposits, and a corrosion inhibitor capable of reducing corrosivity of said compounded oil without destroying the inhibiting action of said metal salt, said corrosion inhibitor being a multi-bridged thioalkyl compound characterized by more than one sulfur bridge between carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms.

17. A composition comprising a compounded hydrocarbon oil subject to deterioration and to formation of adhesive deposits at elevated temperature, said compounded oil containing an aryl metal oxide in an amount sufficient substantially to inhibit said formation of adhesive deposits, and a corrosion inhibitor capable of reducing corrosivity of said compounded oil without destroying the inhibiting action of said aryl metal oxide, said corrosion inhibitor being a multi-bridged thioalkyl compound characterized by more than one sulfur bridge between carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms.

18. A composition comprising a hydrocarbon oil, a corrosion inhibitor capable of reducing the corrosivity of said oil, said inhibitor being a multi-bridged thioalkyl compound characterized by more than one sulfur bridge between carbon chains, at least one of said chains containing at least about 8 alkyl carbon atoms, and an activator for enhancing the effectiveness of said corrosion inhibitor, said activator being a salt of an organo-inorganic acid.

BRUCE B. FARRINGTON.
VICTOR M. KOSTAINSEK.
GEORGE H. DENISON, JR.