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LUBRICATING COMPOSITION

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9 Claims. (Cl. 252—48.2)

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This invention relates to the art of improving organic substances by incorporating therein a small amount of an added agent which stabilizes the organic substance against oxidation, or reduces corrosiveness of said substance to particular kinds of metallic surface, or acts to disperse sludge in said substance and prevent deposition of sludge on hot surfaces, or acts to prevent formation of sludge, or which functions to accomplish several of these objects.

More particularly, this invention relates to improving oils of lubricating viscosity, such as mineral oil, motor, gear and turbine lubricants, transformer oils, oil-soap greases, synthetic lubricating oil compositions, and the like, by adding thereto a small amount of an agent which stabilizes the oil against oxidation, or inhibits corrosion of cadmium-silver and lead-copper types of alloy bearings, or functions to prevent deposition of sludge and carbon on pistons and in piston ring slots of internal combustion engines, or functions to accomplish several of these results.

In the search for improved lubricating oils, several desiderata are present, varying in importance from one type of service to another. Enhanced film strength (i. e., the ability of a lubricant to maintain a film of lubricant between relatively moving surfaces at extremely high pressures), resistance to discoloration on exposure to the normal atmosphere, as in storage of a lubricant, resistance to oxidation on exposure to air or other oxidizing gases at high temperatures as in transformers and in the lubrication of cylinders of internal combustion engines and the working parts of steam and gas turbines, and resistance to fouling of cylinders of internal combustion engines, are among the desired properties of lubricants and other mineral oil compositions.

It is an object of the present invention to provide a new class of materials for addition to oxidizable organic substances to satisfy one or more of the desiderata mentioned above.

It is a further object of the invention to provide compositions of matter comprising in major part an oxidizable organic liquid and containing a small amount of added organic substance which as such greatly enhances resistance of the composition to oxidation.

It is a further object of the invention to provide lubricating oils and the like having high resistance to oxidation.

It is a further object of the invention to provide lubricating oils of enhanced resistance to oxidation and to formation and deposition of sludge, and of reduced tendency to corrode cadmium-silver, copper-lead and other similar bearing alloys.

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It is a particular object of the invention to provide lubricating oils which are of enhanced utility as lubricants at high temperatures and in the presence of oxidizing gases, by reason of enhanced resistance to oxidation and reduced tendency to form or to deposit sludge on hot metal surfaces.

It is a further particular object of the invention to provide improved lubricants for use in lubricating the pistons of internal combustion engines, especially of those engines, such as Diesel and aircraft engines, which operate under high compression and at high temperatures.

It is also an object of the present invention to provide a class of addition agents for lubricants which combine in marked degree a capacity to inhibit oxidation of the oil, corrosion of alloy bearing, and fouling of pistons of internal combustion engines.

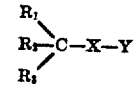
It is also an object of the present invention to provide new, oil-soluble improvement agents for oils of lubricating viscosity and a ready means of preparing the same.

It is also an object of the present invention to provide new combinations of lubricating oil improvement agents, by means of which still more marked improvements and a greater variety of improvements are obtained.

Still further objects will be apparent from the ensuing description and the appended claims.

We have discovered that a certain class of selenium compounds, embracing many compounds in themselves new, when present in small amount in a substantially non-reactive oxidizable organic substance, impart marked improvements to the organic substance.

These selenium compounds are the aliphatic selenomercaptans and salts of the same. Tellurium may be substituted for selenium, although the selenium compounds are preferred. These compounds may be represented by the formula:



wherein (reading from left to right), R_1, R_2 and R_3 are hydrogen or organic radicals (any two of which may be joined to form a single, bivalent

radical), C is an aliphatic carbon atom (i. e., a carbon atom other than a carbon atom forming part of a benzenoid ring), X is selenium or tellurium, and Y is hydrogen or a cationic salt-forming radical.

The simplest member of this class is methyl selenomercaptan, CH_3SeH. Although it is operative as an improvement agent when added in small amount to mineral lubricating oil and the like, it is volatile and not as well suited for use under conditions of high temperature as are higher molecular weight, less volatile compounds. Its salts, however, being less volatile, have a wider utility than the free selenomercaptan. Other similar low molecular weight selenomercaptans and telluromercaptans and their metal salts are likewise less desirable than the higher molecular weight (hence less volatile, less odorous and more oil-soluble) compounds. The preferred compounds of the invention are those containing 5 to 30 carbon atoms, most advantageously 10 to 30 carbon atoms in the molecule. As stated, the selenium compounds are preferred to the tellurium compounds.

Examples of selenium and tellurium compounds of the invention are n-butyl, n-amyl, 2-ethylhexyl, decyl, lauryl, cetyl, octadecyl, and "paraffin" selenomercaptans; 2-ethylhexyl, lauryl and octadecyl telluromercaptans; and the sodium, calcium, barium, and zinc salts of the foregoing selenomercaptans and telluromercaptans. Other radicals (e. g., other alkyl radicals such as ethyl, n- and isopropyl, isobutyl, isoamyl, hexyl, undecyl and tetradecyl, aralkyl radicals such as benzyl and cetylbenzyl and cycloaliphatic radicals such as cyclohexyl and methyl cyclohexyl), may be used in place of the above mentioned radicals, and the organic radical attached to selenium may contain an unsaturated group or may be substituted by a non-hydrocarbon substituent such as chlorine, hydroxyl, alkoxyl, amino, etc. Examples of other metals and non-metallic cationic salt-forming groups which may be used in place of the above-mentioned metals are potassium, lithium, the ammonium radical, strontium, aluminum, cadmium, cobalt, nickel, lead and thallium.

By "paraffin" as used herein to designate an organic radical is meant a radical derived from paraffin wax; e. g., paraffin selenomercaptan is a selenomercaptan (actually, a mixture of selenomercaptans), such as can be prepared by using chlorinated paraffin wax as the organic chloride, R·Cl, in equation (2) below.

By "aliphatic' as used herein without qualification to designate an organic radical atached to selenium or tellurium, is meant an organic radical whose attachment to selenium or tellurium is through an non-benzenoid carbon atom; e. g., octadecyl, benzyl and cyclohexyl selenomercaptans are all "aliphatic" selenomercaptans as "aliphatic" is herein defined.

The selenomercaptans can be prepared by the following series of reactions:

(1) $Na_2Se+Se \rightarrow Na_2Se_2$

(2) $Na_2Se_2+2R\cdot Cl \rightarrow R\cdot SeSe\cdot R+2NaCl$

(3) $R\cdot SeSe\cdot R+2H \rightarrow 2R\cdot SeH$

Sodium diselenide is prepared by reaction (1) and is reacted with an aliphatic chloride (RCl) in accordance with reaction (2) to yield an aliphatic diselenide (R·SeSeR). The aliphatic diselenide is reduced in accordance with reaction (3) to yield an aliphatic selenomercaptan.

In reactions (1), (2) and (3), potassium or other metal may be substituted for sodium, tellurium may be used instead of selenium and bromine or other replaceable element or radical may be substituted for chlorine. The group R is an aliphatic group. If a mixed diselenide is available, e. g., ethyl cetyl diselenide

$(C_2H_5\cdot SeSe\cdot C_{16}H_{33})$

it may be substituted for the symmetrical diselenide of reaction (3), yielding a mixture of selenomercaptans (e. g., ethyl and cetyl selenomercaptans).

The selenium and tellurium compounds of the invention may be used in amounts as low as 0.01% or less or as high as 5% or more, but preferably they are used in amounts of 0.1 to 2%, percentages being by weight based on finished composition. The amount will depend to some extent upon the nature of the oil being inhibited, the more difficultly-inhibited oils requiring the greater amounts; sufficient amounts are employed to reduce substantially the oxidative deterioration of the oil. Concentrates or stock solutions containing 5 to 50% or more of the selenium compound of the invention dispersed in an organic liquid (e. g., mineral lubricating oil) may be prepared for later blending with the substance to be stabilized to produce a finished product.

The selenomercaptans are incorporated in various oxidizable organic substances, particularly organic liquids, which substances are substantially unreactive with the added selenomercaptans so that the latter inhibiting agent is not dissipated by reaction with the substance to be inhibited but rather remains as selenomercaptan to inhibit oxidation. Thus, of the oxidizable hydrocarbon oils, those which are substantially completely free from olefins (which are said to react with selenomercaptans) are employed; thus, the substantially completely saturated hydrocarbon oils are preferably treated in accordance with the present invention, and unsaturated hydrocarbons, such as cracked gasoline, are excluded. Thus, the addition of selenomercaptans to lubricating oils causes no spontaneous reaction or color change; likewise the selenomercaptans remain unchanged in hydrocarbon solvents, such as petroleum ether, which is employed for extraction in the preparation of selenomercaptans. In other words, the selenomercaptans are employed in oxidizable organic substances which are stable to selenomercaptans, i. e., which are substantially free from groups normally reactive with selenomercaptans and telluromercaptans. Since the selenomercaptides do not react with unsaturated compounds as contrasted to selenomercaptans which apparently react with certain olefins such as in cracked gasoline, the selenomercaptides may also be used to inhibit oxidation of oxidizable unsaturated organic substances (analogous to the above-listed substances), such as cracked gasoline, etc., and unsaturated fats, fatty oils, and the like.

Illustrative of organic substances to which the selenium compounds of the invention may be added as stabilizers are petroleum products such as saturated gasoline, kerosene, lubricating oils and mineral oil-soap greases; saturated fats, fatty oils, rubber, aldehydes, ethers, terpenes, mercaptans, phenols and synthetic plastic or resinous materials such as urea-formaldehyde,

polyvinyl and phenol-formaldehyde resins. These and other organic materials undergo oxidation and deterioration (e. g., discoloration, sludge formation, thickening, etc.) under conditions ranging from mere exposure to air at normal atmospheric temperatures to intimate admixture with air or other oxidizing gases at temperatures of 300°–400° F. The inherent stability of the organic material toward oxidation will, of course, vary with the material. The selenium compounds of the invention will stabilize such materials under mild to extreme conditions of oxidation.

More particularly, the herein-described agents may be used advantageously in various types of oils, whether hydrocarbon or non-hydrocarbon, although their present field of chief utility is in viscous lubricating oils and greases made therefrom. The agents herein-described are particularly useful in motor oils for crankcase lubrication and the like such as in Diesel, aircraft, automotive and other engines operating at high temperatures, high pressures and high operating load conditions. These agents may also be employed in cutting oils, transmission oils, heat transfer fluids, hydraulic fluids, etc.

The additives of the present invention are particularly suitable for inhibiting the oxidative deterioration of polyether synthetic oils such as obtained from polymerization of lower molecular weight (e. g., C_2 to C_5) alkylene oxides, such as propylene and/or ethylene oxides and derivatives thereof to liquid products of lubricating oil viscosity. Likewise contemplated by the term "polyether synthetic oil" are the derivatives of such polymerization products, including the derivatives obtained by etherification and/or esterification of the hydroxy groups in the polymerization products. These polymers may also be described as liquid polyoxyalkylene compounds. The suitable polyether oils have average molecule weights ranging from about 500 to about 2500 or higher, and have viscosities ranging from about 40 S. S. U. to about 170 S. S. U. at 210° F. and somewhat greater or lesser. These oils may be used alone or in admixture with mineral lubricating oils or other suitable oils of lubricating viscosity.

The polyether synthetic oils may be obtained in various ways. Suitable oils may be obtained, for example, by the process described in U. S. Patent No. 1,976,678, whereby oxides of ethylene or propylene are polymerized at elevated temperatures in the presence of an alkaline catalyst and an inert organic diluent. Mixtures of certaintain polyoxyalkylene monohydroxy compounds resulting from the reaction under pressure of monohydroxy aliphatic alcohols with mixtures of oxides of ethylene and propylene are described in U. S. Patent 2,425,755. Certain dihydroxy polyoxyalkylene glycols or diols are described in U. S. Patent No. 2,425,845. In general, the polyether oils may be obtained by polymerization of lower molecular weight alkylene oxides or mixtures thereof under suitable reaction conditions, including the presence of a suitable catalyst, such as an alkali metal hydroxide or alcoholate and, preferably, in the presence of a reaction-initiating substance such as aliphatic, alicyclic and aromatic alcohols, including primary, secondary and tertiary alcohols, phenols, naphthols, heterocyclic alcohols, ether alcohols, polyhydric alcohols, water, etc.

A preferred class of polyether oils having substantial miscibility with mineral lubricating oil at low temperatures are derived from polymerization of 1,2-alkylene oxides having 4 to 8 carbon atoms, preferably in the presence of a hydroxyl-containing reaction-initiating compound, especially an aliphatic monohydroxy alcohol of relatively low molecular weight (i. e., 1 to 10 carbon atoms) which polyether oils are disclosed in copending application, Ser. No. 1,036, filed January 7, 1948, of George H. Denison, Jr., George J. Benoit, Jr., and Robert O. Bolt.

Another preferred class of polyether oils are the products of polymerization of an alcohol, preferably a monohydroxy alcohol, and a mixture of alkylene oxides containing propylene oxide and at least one oxide from the group of 1-butene oxide, 2-butene oxide and isobutene oxide, wherein the various oxides in the polymerizable mixture are not in excess of certain critical limits. Such polymerization products are disclosed in copending application of George J. Benoit, Jr., Serial No. 75,085, filed February 2, 1949.

The one or more hydroxyl groups in the above various polymers are often desirably etherified or esterified under suitable conditions. For example, an alcohol-initiated polymerization product of alkylene oxide, e. g., propylene oxide, contains free hydroxyl, which is suitably esterified with acetic acid or other low molecular weight fatty or other organic acid or anhydride thereof or the like.

While the polyether oils have superior characteristics such as high viscosity indices, certain of these oils have shortcomings (e. g., high affinity for water and low miscibility with mineral oil) which make them unsatisfactory as synthetic lubricants, and other particular polyether oils such as those of the above-mentioned copending applications overcome these and other disadvantages. The polyether oils are, however, generally unsatisfactory from the standpoint of resistance to oxidative deterioration. Not only do such oils readily oxidize or deteriorate under operating conditions in spark-ignition engines and the like, but such oxidative deterioration has been found to be difficult to inhibit. Further, some agents, which are apparently satisfactory in some tests to inhibit oxidation, promote disadvantageous side-reactions or otherwise deleteriously affect the desirable properties of a lubricant. For example, some agents are effective as oxidation inhibitors in polyether oils, but during use of the oils in engine operation the agents promote excessive gumming. Other compounds, e. g., sulfides, which are satisfactory oxidation inhibitors in mineral oils have substantially no inhibitory effect on the oxidation of polyether oils. In other ways, such as the initial rate of oxygen absorption, the polyether oils differ from mineral oils from the standpoint of oxidative deterioration.

The present aliphatic selenomercaptans and telluromercaptans and their salts have been found to bring about superior inhibition of oxidative deterioration of polyether oils without adversely affecting the other desirable properties of the polyether lubricants. As indicated hereinabove, either the selenomercaptans (and telluromercaptans) or their salts are employed with substantially olefin-free oils, but the selenomercaptides (and telluromercaptides) are preferably used with oils which tend to react with the free selenomercaptans (and telluromercaptans).

The following specific examples will serve further to illustrate the practice and advantages of the invention.

Example 1.—Preparation of high molecular weight selenomercaptans.—Methods described in the literature for preparing selenomercaptans are the reaction of sodium or magnesium hydroselenides with an alkyl halide or alkyl metal sulfate, and the reaction of aluminum selenide with alcohols at elevated temperatures. See, for example, J. Newton Friend's "Textbook of Inorganic Chemistry," vol. XI, part IV, page 1 (1937). These methods are disadvantageous because large amounts of dialkyl selenides and dialkyl diselenides are formed by side reactions. This necessitates the recovery of the selenomercaptan by distillation. When applied to the preparation of high molecular weight selenomercaptans, i. e., those containing about 10 carbon atoms or more, these methods of the prior art are especially disadvantageous because of the tendency of the high molecular weight selenomercaptans to decompose on distillation.

We have discovered a much superior method of preparing high molecular weight selenomercaptans which will now be described with reference to octadecyl selenomercaptan.

Dioctadecyl diselenide was prepared as follows: A mixture of 1 gram mole of sodium diselenide, 2 gram moles of octadecyl chloride and one liter of 95% ethyl alcohol were refluxed and stirred for nine hours. The reaction mixture was diluted with one liter of water and extracted with petroleum ether. The petroleum ether extract was dried over anhydrous sodium sulfate, filtered and concentrated on a steam bath. Two volumes of a 50% mixture of petroleum ether and acetone were added and the solution was cooled to promote crystallization of the dioctadecyl diselenide. A yield of 602 grams of dioctadecyl diselenide was obtained in the form of lemon yellow crystals melting at 52° C. to 55° C. *Analysis.*—Found: Per cent Se=22.3. Theoretical: Per cent Se=23.8.

A mixture of 30.4 grams of dioctadecyl diselenide and 34 mls. of 50% (by weight) sulfuric acid was heated to reflux temperature and 8.7 grams of zinc dust were added gradually with vigorous stirring. After addition of the zinc dust had been completed, 5 mls. of concentrated sulfuric acid were added and refluxing and stirring were continued until the zinc had completely reacted. On cooling the mixture to room temperature, octadecyl selenomercaptan separated as a white crystalline layer. This product was a white, waxy, crystalline solid melting at 36° to 40° C.

The octadecyl selenomercaptan so prepared can be reacted with alcoholic solutions of metal hydroxides or metal acetates to yield the desired metal selenomercaptide, or it can be dissolved in aqueous or aqueous-alcoholic sodium or potassium hydroxide and treated as described above.

Example 2.—Preparation of zinc octadecyl selenomercaptide.—The product of Example 1 (product of reducing 30.4 grams of dioctadecyl diselenide) was extracted with petroleum ether and the extract was washed with water, dried over sodium sulfate, filtered and mixed with 200 ml. of 95% ethyl alcohol. Petroleum ether was removed by distillation and 250 ml. of 95% ethyl alcohol were added to the residue. This mixture was heated to 150° F. and a solution of 18.3 grams of zinc acetate dissolved in 150 ml. of hot water was added slowly with stirring. A white precipitate formed, which was collected on a filter, washed with water, then with alcohol and then with petroleum ether and dried in vacuo over calcium chloride. A yield of 22 grams of zinc octadecyl selenomercaptide was obtained, being

65% of the crude dioctadecyl diselenide. This product was found to contain 20.7% Se (theoretical, 21.6%) and 8.91% Zn (theoretical, 8.95%). In subsequent preparations, the yield was raised to 84%. The product was a white solid soluble in chloroform and benzene, slightly soluble in alcohol.

Example 3.—Preparation of cadmium octadecyl selenomercaptide.—A solution of 70.4 grams of cadmium acetate dihydrate in 300 ml. of 50% ethyl alcohol was added slowly with stirring to a hot mixture of 160 grams of octadecyl selenomercaptan and 300 ml. of 100% ethyl alcohol. The precipitated cadmium octadecyl selenomercaptide was collected on a filter, washed with water, alcohol and acetone and dried in vacuo over calcium chloride. The product weighed 188 grams, representing a yield of 60% based on cadmium content. *Analysis.*—Found: Cd=8.7%, 8.8%; Se=16.6%, 16.8%. Theoretical: Cd=14.5%, Se=20.3%. After extraction with boiling petroleum ether, the product weighed 145 grams and assayed 11.5% Cd and 19.8% Se. The product was a white solid, soluble in chloroform and benzene and slightly soluble in alcohol. The product was about 80% pure.

Example 4.—Preparation of lead octadecyl selenomercaptide.—A hot solution of 91.2 grams of basic lead acetate ($Pb_2(OH)AC_3$) in 350 ml. of 50% ethyl alcohol containing 9 grams of glacial acetic acid was added slowly with stirring to a heated mixture of 200 grams of octadecyl selenomercaptan and 350 ml. of 100% ethyl alcohol. The precipitate was filtered off, washed with hot water, alcohol and petroleum ether. After drying in vacuo over calcium chloride the product weighed 205 grams, representing a yield of 78% based on lead content. *Analysis.*—Found: Pb=23.5%; Se=17.7%. Theoretical: Pb=23.8%; Se=18.1%. The product was a salmon colored solid, soluble in chloroform and benzene, and slightly soulble in alcohol.

Example 5.—Preparation of barium octadecyl selenomercaptide.—A slurry of 43 grams of barium oxide in 200 ml. of 95% ethyl alcohol and 5 ml. of water was added with stirring to a refluxing mixture of 180 grams of octadecyl selenomercaptan and 200 ml. of 95% ethyl alcohol. Refluxing was continued for twenty-five minutes and the reaction mixture was allowed to cool. The precipitate was collected on a filter, washed with alcohol and petroleum ether and dried in vacuo over calcium chloride. The product weighed 184 grams representing a yield of 77% based on barium content. *Analysis.*—Found: Ba=15.8%; Se=17.6%. Theoretical: Ba=17.1%; Se=19.7%. The product was slightly soluble in chloroform and benzene.

Example 6.—Preparation of nickel octadecyl selenomercaptide.—A hot solution of 69.2 grams of nickel bromide in 250 ml. of 50% ethyl alcohol was added with stirring to a heated mixture of 214 grams of octadecyl selenomercaptan and 350 ml. of 100% ethyl alcohol. Stirring was continued while a solution of 25.8 grams of sodium hydroxide in 150 ml. of hot water was added slowly. The precipitate was collected on a filter, washed with acetone and dried in vacuo over calcium chloride. The product weighed 242 grams. *Analysis.*—Found: Ni=6.8%; 6.8%; Se=16.1%, 16.2%. Theoretical: Ni=8.1%; Se=22.0%. Fractionation of the product showed it to be a mixture of nickel octadecyl selenomercaptide (38%), octadecyl selenomercaptan and dioctadecyl diselenide (37%) and inorganic nickel com-

pounds. The crude product was a granular, black solid, soluble in chloroform and benzene.

In each of the preparations described in Examples 1 to 6, above, the reaction mixture and product were blanketed by an atmosphere of nitrogen to prevent oxidation, until such time as the final product was prepared.

Example 7.—Oxidator tests.—Selenium compounds of the invention, also, for comparison, certain selenium compounds not of the invention, were dissolved in small amount in medicinal grade of white oil and submitted to an oxidation test in an apparatus of the type described by Dornte in "Industrial and Engineering Chemistry," vol. 28, page 26 (1936), oxygen being bubbled through the oil at atmospheric pressure. The temperature of the oil was 340° F. Results are given in Table I below, the "Induction period" being the time in hours required for 100 gms. of oil to absorb 1200 cc. of oxygen measured at S. T. P.

Table I

Additive	Se	Induction Period
	Per cent	*Hours*
Nil		0.05
0.08% Dioctadecyl diselenide	0.019	2.5
0.1% Dilauryl selenide	0.019	2.5
0.159% Dilauryl selenide	0.03	3.9
0.08% Octadecyl selenomercaptan	0.019	4.4
0.159% Zn octadecyl selenomercaptide	0.0344	4.8
0.149% Cd octadecyl selenomercaptide	0.03	2.1
0.166% Pb octadecyl selenomercaptide	0.03	0.8
0.153% Ba octadecyl selenomercaptide	0.03	3.9
0.138% Ni octadecyl selenomercaptide	0.03	3.6
0.086% Zn 2-ethyl hexyl selenomercaptide	0.051	1.8

It will be seen from the above table that all of the additives of the invention greatly improved the base oil. The free selenomercaptan was superior to dioctadecyl and dilauryl selenides. The metal selenomercaptides were not as effective oxidation inhibitors as the selenomercaptan, but several were as effective as dilauryl selenide and all of them greatly improved the base oil.

As oxidation inhibitors the free selenomercaptans are preferred to their salts, but their salts, especially the polyvalent metal salts, have in greater degree the property of functioning as "detergents" in motor lubricants; i. e., they promote cleanliness of pistons, piston rings and piston ring slots and retard piston ring sticking in internal combustion engines. This is shown in Example 8 in Tables II and III below.

Example 8.—Strip corrosion and engine tests.—Various oils, both uncompounded and compounded with small amounts of additives as indicated in Tables II and III below, were submitted to strip corrosion and engine tests as follows: In the corrosion tests, thin strips of copper-lead alloy of the type used in bearings of internal combustion engines are immersed in oil. The oil is maintained at 300° F. and air is blown through the oil during the test. Corrosion loss is noted after each test. Further details of this test appear in Farrington et al. U. S. Patent No. 2,349,817 at page 3, right-hand column, lines 17 to 37. The Lauson engine tests were carried out in the manner described in the same patent, page 3, left-hand column, lines 14 to 26, except that observations were made only at 30-hour intervals, crankcase (sump) temperature was 300° F., and the engine speeds were 1800 R. P. M. (Table II) and 1200 R. P. M. (Table III). The Wisconsin tests were carried out in a single cylinder air cooled Wisconsin engine, 2½ inch bore and 2¾ inch stroke, loaded by means of an electric induction motor. The engine was operated under extremely severe conditions, designed to develop fully the tendency of the crankcase lubricant to deteriorate with gum formation and piston ring sticking. Operation was at 1300 R. P. M.; upper cylinder temperature was maintained at 600° F.; crankcase oil temperature was maintained at 220° F. At periods of 30 hours the operations were interrupted and the condition of the piston and piston rings determined.

The results of these tests are set forth in Tables II and III below. In the tables, the concentration of each additive, if it is a salt, is given as millimols of metal per kilogram of oil; e. g., "14 mM/kg. Zn octadecyl selenomercaptide," which means 14 millimols of zinc, in the form of zinc selenomercaptide, per 1000 grams of oil. This particular salt was a relatively pure compound $(C_{18}H_{37}Se)_2Zn$, and has a molecular weight of 729. Therefore, 14 mM/kg. of this salt amounts to 1% by weight salt based on the oil. In most other cases the mM/kg. of metal can be similarly converted to per cent by weight of salt but in a few cases, e. g., calcium sulfonate, the molecular weight of the salt being unknown, it is impossible to convert mM/kg. of metal to per cent of salt.

Further with regard to Table II: The calcium sulfonate was a synthetic product made by chlorinating white oil, then condensing it with benzene, sulfonating the condensation product and converting the sulfonic acid to its calcium salt. The calcium phenate was prepared by condensing a butene polymer (average molecular weight about 194) with phenol and forming the calcium salt of the condensation product, as described in Examples 1 and 3 of Gardiner et al. U. S. Patent No. 2,228,661. The sulfurized calcium phenate was prepared by heating the same calcium phenate with sulfur, as described in Etzler et al. U. S. Patent No. 2,360,302. The zinc dicetylphenyl dithiophosphate was the product of reacting two moles of cetyl phenol, one mol of P_2S_5 and one mole of ZnO. The sulfurized diparaffin sulfide was the product of reacting chlorinated paraffin (22% chlorine) with sodium polysulfide to yield a product containing 14% sulfur and 3% chlorine and heating this sulfur- and chlorine-containing product with free sulfur in the proportions of 100 and 4.2, respectively, at 300° F. until all the sulfur dissolved. The said sulfur- and chlorine-containing product can be prepared in the manner described in Example 1 of Farrington et al. U. S. Patent No. 2,346,156. All the salts of Table II were normal salts. Base oil A was a solvent-refined SAE 30 paraffinic oil of California origin. Base oil B was a solvent-refined SAE 30 Mid-Continent oil. Oil C was a solvent-refined SAE 50 paraffinic oil of California origin.

In these tables, "PD No." designates piston discoloration number. By piston discoloration number is meant this: After 30 hours and again after 60 hours, the engine is dis-assembled and the piston is inspected. To a piston skirt which is completely black is assigned a PD No. of 800; to one which is completely clean is assigned a PD No. of zero; to those intermediate completely black and completely clean are assigned PD Nos. in proportion to the carbonaceous deposits. Actually, further refinements were employed in arriving at PD Nos. hereinbelow disclosed, but since the same method was used in every case it is unnecessary to describe these refinements.

Table II.—Strip corrosion and Lauson engine tests

Base Oil	Additives	Strip Corrosion—Wt. Loss, mgs.			Engine Tests—PD No.	
		24 hrs.	48 hrs.	72 hrs.	30 hrs.	60 hrs.
A	Nil	1.1	48.6	108.7	460	
A	14 mM/kg. Ca sulfonate	11.1	30.6	52.2	150	245
A	14 mM/kg. Zn octadecyl selenomercaptide	25.5	22.6	26.2	70	310
A	14 mM/kg. Cd octadecyl selenomercaptide	+3.3	+8.7	+6.6	130	165
A	14 mM/kg. Sulfurized Ca phenate				210	235
A	7 mM/kg. Zn octadecyl selenomercaptide+Sulfurized Ca phenate.	+5.1	+8.6	+11.3	110	215
A	7 mM/kg. Pb octadecyl selenomercaptide+Sulfurized Ca phenate.	+6.1	+4.5	+3.1	10	15
A	14 mM/kg. Ca phenate				225	330
A	7mM/kg. Zn octadecyl selenomercaptide+Ca phenate	8.8	19.7	32.0	20	25
A	7 mM/kg. Cd octadecyl selenomercaptide+Ca phenate	16.4	18.9	20.0	40	75
A	7 mM/kg. Ba octadecyl selenomercaptide+Ca phenate	91.0	92.9	98.5	80	85
A	7 mM/kg. Ca sulfonate+7 mM/kg. Zn octadecyl selenomercaptide.	+2.6	+6.3	+10.7	25	35

Table III.—Strip corrosion and engine tests

Base Oil	Additives	Strip Corrosion—Wt. Loss, mgs.			Engine Tests—PD No.		Type of Engine
		24 Hrs.	48 Hrs.	72 Hrs.	30 Hrs.	60 Hrs.	
B	Reference Compounding	1.1	1.4	2.9	80	200	Lauson.
B	4.5 mM/kg. sulfurized Ca phenate+4.5 mM/kg. Ca sulfonate+6 mM/kg. Zn octadecyl selenomercaptide.	+6.8	+8.1	+6.7	5	10	Do.
B	9 mM/kg. Ca phenate+6 mM/kg. Zn octadecyl selenomercaptide.				50	60	Do.
C	Nil	1.3	4.4	21.0	455		Wisconsin.
C	0.8% Octadecyl selenomercaptan+16 mM/kg. Ba m-cetoxy phenate.	1.3	7.0	16.6	75	105	Do.
C	16 mM/kg. Zn octadecyl selenomercaptide	0.1	+1.0	+12.6	215	320	Do.
C	8 mM/kg. Zn octadecyl selenomercaptide+8 mM/kg. Ba m-cetoxy phenate.	+9.5	+7.0	+6.0	140	145	Do.
C	8 mM/kg. Ca phenate+8 mM/kg. Zn octadecyl selenomercaptide.	8.1	26.9	41.4	115	145	Do.
C	14 mM/kg. Ca phenate+14 mM/kg. Zn octadecyl selenomercaptide.	17.8	18.1	31.4	105	135	Do.
C	24 mM/kg. Ca phenate+14 mM/kg. Zn octadecyl selenomercaptide.	5.8	4.2	7.2	130	155	Do.
C	7 mM/kg. Ba m-cetoxy phenate+7 mM/kg. Pb octadecyl selenomercaptide.	6.9	9.1	9.4	135	160	Do.

In Table IV below are given still further data, showing the performance of a low molecular weight selenomercaptide (zinc 2-ethyl hexyl selenomercaptide, made from 2-ethyl hexyl chloride) and of a high molecular weight selenomercaptide (zinc paraffin selenomercaptide, made from a chlorinated, low melting paraffin wax). Base oils A and C are the same as base oils A and C above.

Table IV

Base Oil		Strip Corrosion—Wt. Loss, mgs.			Engine Tests PD No.		Type of Engine
		24 Hrs.	48 Hrs.	72 Hrs.	30 Hrs.	60 Hrs.	
A	4.5 mM/kg. Ca sulfonate+4.5 mM/kg. sulfurized Ca phenate+6 mM/kg. Zn 2-ethyl hexyl selenomercaptide.	+11.5	+13.0	+12.5	0	0	Lauson.
C	20 mM/kg. Ca phenate+10 mM/kg. Zn 2-ethyl hexyl selenomercaptide.	7.8	3.6	2.3	160	225	Wisconsin.
C	8 mM/kg. Ca phenate+8 mM/kg. Zn paraffin selenomercaptide.	+9.4	+21.4	+21.4	40	80	Do.

The data in Tables II, III and IV illustrate, among other things, the following: Most of the selenium compounds of the invention functioned to inhibit corrosion of copper-lead bearings. All of them functioned to promote piston cleanliness, as shown by the PD numbers. Especially good results were obtained with combinations of addition agents, such as the phenate-selenomercaptide, sulfurized phenate-selenomercaptide and sulfonate-selenomercaptide combinations.

The "reference compounding" in base oil B was a multiple compounding which has passed exacting test requirements of Army Ordnance 2-104B Specification. The superiority of the compounding of the present invention is evident from Table III.

One or more selenium compounds of the invention may be used as the only added material present in an oxidizable organic substance or they may be used in conjunction with other additives. For example, the selenium compounds of the invention may be used advantageously in mineral lubricating oils in conjunction with metal salts of organic acids and/or metal salts of organo-substituted inorganic acids. These salts are used to improve various properties of lubricating oils, such as detergency, stability against oxidation, film strength, etc. Examples of such metal salts are calcium, barium, zinc and aluminum salts of cetylphenol; calcium, barium, zinc and aluminum salts of diamyl diphenol monosulfide; calcium, barium, zinc and aluminum salts of mono- and dicetyl esters of phosphoric acid; calcium, barium, zinc and aluminum salts of mono- and dicetylphenyl esters of dithio-

phosphoric acids; calcium, barium, zinc and aluminum salts of naphthenic acids; calcium, barium, zinc and aluminum salts of oil-soluble petroleum (mahogany) sulfonic acids; calcium, barium, zinc and aluminum salts of dibutyl dithiocarbamic acid; calcium, barium, zinc and aluminum salts of the reduced petroleum nitrogen base dithiocarbamates of Miller and Rutherford U. S. Patent No. 2,363,012. Other metals (e. g., sodium, lithium, magnesium and cobalt) and other acid radicals (e. g., aryl carboxylic acid, fatty acid, aliphatic polycarboxylic and thiophenol radicals) may be used instead of the aforementioned calcium, barium, zinc and aluminum metals and the aforementioned phenate, phenate sulfide, phosphate, thiophosphate, naphthenate, sulfonate and dithiocarbamate radicals, respectively. Thus, from 0.1 to 2% of selenium compound and from 0.1 to 2% of metal salt may be added to mineral lubricating oil, or greater amounts may be used to form a concentrate or stock solution.

The selenium and tellurium compounds of the present invention are also useful to improve the film strength of lubricants, as shown by the following data:

Table V

	Failure (Weeks Testing Machine, 600 R. P. M.) at—
	Pounds
Solvent refined SAE 30 oil	100
Solvent refined SAE 30 oil+0.51% octadecyl selenomercaptan	180
Solvent refined SAE 30 oil+0.56% Zn octadecyl selenomercaptide	340

In Table VI below are given the results of oxidator tests of various selenomercaptans and selenomercaptides in an alcohol-initiated propylene oxide polymer prepared as follows:

In a pressure vessel provided with means of agitation and heating, 0.75 part by weight of metallic sodium was added to 32.1 parts of 2-ethylhexanol, and the mixture stirred and heated to 200°–220° F. while sweeping out the hydrogen evolved with nitrogen. After hydrogen evolution ceased, the vessel and contents heated to 240° F. Propene oxide having a water content of less than 0.1% was then added until the pressure in the vessel was 40 p. s. i. (pounds per square inch). As the polymerization progressed, additional propene oxide was added to maintain the pressure at 40 p. s. i., while holding the temperature at 240° F., until 338 parts of propene oxide had been added. Thereafter the reaction mixture was stirred for an additional hour. After cooling, the product was neutralized with acetic acid and water-washed three times. The remaining water and light ends were removed from the oil phase by stripping at a pressure of about 25 mm. mercury with a pot temperature of about 300° F. The residue was then filtered, and on analysis gave the following results:

Viscosity at 100° F., 321 S. S. U. (Saybolt Universal seconds)
Viscosity at 210° F., 66.1 S. S. U.
Viscosity index, 144
Hydroxyl number, 50

The oxidation test was carried out in an apparatus of the type described by Dornte in "Industrial Engineering Chemistry," vol. 28, page 26 (1936), the sample being stirred while exposed to an atmosphere of oxygen. The "Induction period" is taken as time in hours at which 100 gram sample of oil begins to absorb oxygen rapidly.

Table VI

Additive	Se	Induction Period
	Per cent	
Nil		0.0
0.191% Octadecyl selenomercaptan	0.037	0.2
0.637% Octadecyl selenomercaptan	0.12	2.0
1.91% Octadecyl selenomercaptan	0.37	7.5
0.215% Zinc octadecyl selenomercaptide	0.037	0.1
0.720% Zinc octadecyl selenomercaptide	0.12	2.5
2.15% Zinc octadecyl selenomercaptide	2.37	6.5
1.76% Nickel octadecyl selenomercaptide	2.37	4.2
2.10% Barium octadecyl selenomercaptide	0.37	4.5
2.2% Thallium octadecyl selenomercaptide	0.37	3.5
2.55% Paraffin wax selenomercaptan	0.37	4.5
1.35% Zinc dodecyl selenomercaptide	0.37	2.0

It will be seen from the above table that all the additives when used in amounts greater than about 0.10% selenium content greatly improve the base oil.

This application is a continuation-in-part of our copending applications, Serial Nos. 59,027 and 59,028, filed November 8, 1948, which are in turn continuations in part of our now abandoned application, Serial No. 638,568, filed December 31, 1945.

We claim:

1. A lubricant comprising a major proportion of an oxidizable polyether oil of lubricating viscosity, which oil is substantially free from groups normally reactive with selenomercaptans and telluromercaptans, said oxidizable oil containing a small amount, sufficient to inhibit oxidation of said oil of a compound of the structure

R—X—Y

wherein X is selected from the group consisting of selenium and tellurium, R is an aliphatic group of 5 to 30 carbon atoms and Y is selected from the group consisting of hydrogen and the hydrogen equivalent of a cationic salt-forming group.

2. A lubricant comprising a major proportion of an oxidizable polyether oil of lubricating viscosity, said oil being a polymer of a lower molecular weight alkylene oxide, said oil being substantially free from groups normally reactive with selenomercaptans and telluromercaptans, said oxidizable oil containing a small amount, sufficient to inhibit oxidation of said oil of a compound of the structure

R—X—Y

wherein X is selected from the group consisting of selenium and tellurium, R is an aliphatic group of 5 to 30 carbon atoms and Y is selected from the group consisting of hydrogen and the hydrogen equivalent of a cationic salt-forming group.

3. A lubricant comprising a major proportion of an oxidizable polyether oil of lubricating viscosity, which is substantially free from groups, including unsaturated groups, normally reactive with aliphatic selenomercaptans, and a small amount sufficient to inhibit oxidation of said oil of an aliphatic selenomercaptan of 5 to 30 carbon atoms.

4. The lubricant composition of claim 3 wherein said polyether oil is an alcohol-initiated polymerization product of a lower molecular weight alkylene oxide.

5. The lubricant composition of claim 3 wherein the aliphatic selenomercaptan is present in a proportion of about 0.1 to about 5% by weight of the finished composition.

6. The composition of claim 1 wherein the compound having the structure

R—X—H

is present in the proportion of about 0.1 to 5% by weight of the finished composition.

7. The composition of claim 1 wherein in the compound of the structure

R—X—Y

Y is a metal, and said compound is present in the proportion of 0.1 to 5% by weight of the finished composition.

8. The composition of claim 1 wherein the added compound is zinc octadecyl selenomercaptide.

9. The composition of claim 3 in which the selenomercaptan is octadecyl selenomercaptan.

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