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2,398,415

MINERAL OIL COMPOSITION AND THE LIKE

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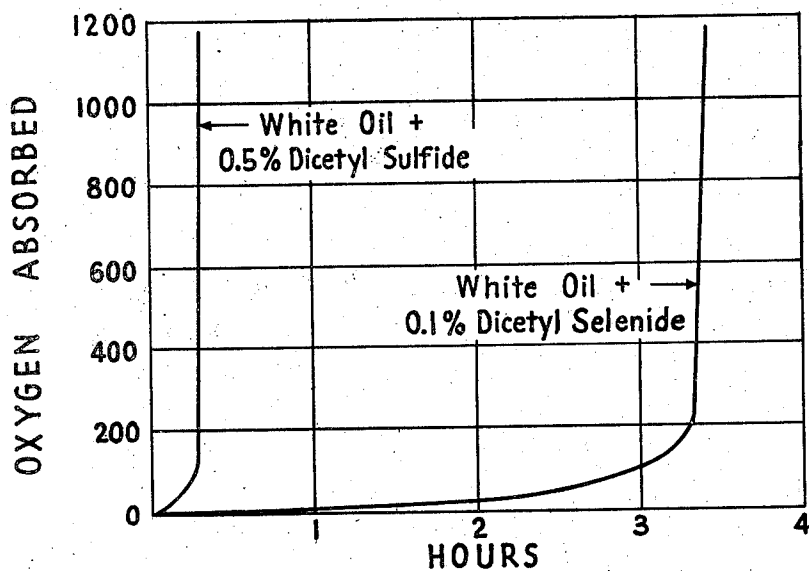


Fig. 1

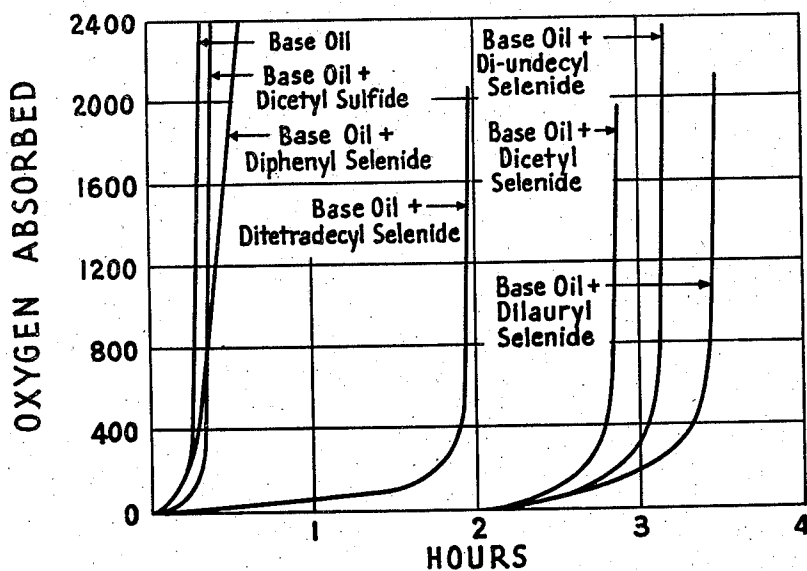


Fig. 2

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2,398,415

MINERAL OIL COMPOSITION AND THE LIKE

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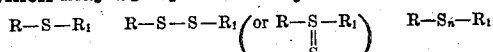
Application February 22, 1943, Serial No. 476,760

12 Claims. (Cl. 252-45)

This invention relates to the improvement of hydrocarbon oils by incorporating therein certain selenium or tellurium compounds.

This application is a continuation-in-part of our copending application Serial No. 432,040, filed February 23, 1942, now United States Patent No. 2,346,155, issued April 11, 1944.

In the art of compounding mineral oil lubricants such as crankcase oils, transmission oils, turbine oils, greases and the like, there has been accumulated a large body of knowledge concerning the benefits derived from incorporating in such oils small amounts of sulfur compounds. In particular, benefits have been shown to arise from adding small amounts of monosulfides (thioethers), and di- and higher polysulfides, which may be represented by the formulae



Monosulfides
(thioethers)

Disulfides

Higher
polysulfides

wherein R and R₁ represent like or unlike organic radicals selected from the group consisting of alkyl, aryl, alkaryl and aralkyl, and n represents an integer greater than two. Thus, Adams et al. U. S. Patent No. 2,110,281 proposes the use of di-alkyl monosulfides and di-alkyl disulfides in mineral oil, and other patents propose dibenzyl disulfide and a host of other organic monosulfide and polysulfide compounds.

It is now generally conceded that these simple sulfides (embracing by this term both mono- and polysulfides) are deficient as lubricant additives. This is not to say that they are ineffective; rather, the deficiency arises, in part at least, from the excessive demands put upon lubricants by current machine design and operation, and in part from the fact that such organic sulfides may perform well with one type of oil and poorly with another type of oil.

With regard to machine design and operation, many of the internal combustion engines of today operate at higher temperatures and higher compressions than heretofore with a resultant greater stress upon the lubricating oils and more rapid deterioration of these oils. Thus modern internal combustion engines, more especially those of the Diesel type, become fouled and develop piston ring sticking more quickly than the older engines when lubricated by the same oil. To complicate matters even further, certain of the bearings in the engines of today bear greater loads and are of the hard alloy type, such as cadmium-silver and copper-lead bearings. The higher loads on bearings demand better lubricant

performance, and the hard alloys mentioned supra, although preferable to the older babbitt bearings from the mechanical standpoint, are more readily corroded by certain mineral oils, by used oils in which acidic products of oxidation have accumulated, and by the action (believed to be an indirect, catalytic action rather than a direct corrosive action) of certain additives, such as calcium stearate and calcium naphthenate, which are sometimes added to oils to inhibit piston ring sticking and the like.

To meet the demand for better oils, the trend in that branch of the lubricant art which pertains to the use of organic sulfides has been to include with the organic sulfide an activating substance or functional grouping. Thus, as set forth in our copending application Serial No. 350,062, filed August 2, 1940, now United States Patent No. 2,346,153, issued April 11, 1944, by including in a mineral lubricating oil or the like along with a dialkyl thioether group, a partial ester of an acid of phosphorus or a salt of such partial ester, for example, calcium cetyl phosphate, a greatly improved performance results. Thus greatly reduced oxygen absorption and greatly reduced corrosion of copper-lead bearings are observed with oil containing cetyl ethyl thioether and calcium cetyl phosphate than with the same oil containing either of these additives alone. As set forth in our copending application Serial No. 350,063, filed August 2, 1940, now United States Patent No. 2,346,154, issued April 11, 1944, even greater improvement is obtained when a metal phenate such as calcium cetyl phenate is also included in the oil, along with the thioether and phosphorus compound. As set forth in Rosen United States Patents Nos. 2,085,045 and 2,216,752, better results are obtained with alkyl phenol sulfides and hydroxy substituted diaryl sulfides than with alkyl aryl sulfides and diaryl sulfides; that is, the functional group OH (also amino, etc.) enhances the potency of the sulfide group.

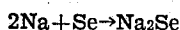
The general trend in the development of organic sulfide type inhibitors may, therefore, be summarized as an adding up or multiplication of functional groups, one being a sulfide type group and the other, which may be present in the same molecule as the sulfide group or in a different molecule, being another type of group or even a second sulfide group.

We have found, surprisingly, however, that when the higher dialkyl selenides or tellurides, those containing at least 8 carbon atoms in one alkyl group and preferably containing at least 8

carbon atoms in both alkyl groups, are added in small amount to hydrocarbon oils of lubricating viscosity, they exhibit, even alone (without the aid of activators or functional groups), effects which are observed with the corresponding di-alkyl sulfides, alkyl aryl sulfides and diaryl sulfides only in combination with activators or functional groups.

The following specific examples and the accompanying drawing will serve to illustrate the nature of the results that have been obtained in accordance with the present invention:

Example 1.—Dicetyl selenide was prepared stepwise as follows: In the first step, represented by the equation



sodium selenide was produced by reacting sodium and selenium in stoichiometric amounts in liquid ammonia and in the presence of an inert atmosphere (nitrogen). In the second step, represented by the equation



cetyl chloride was condensed with the sodium selenide in alcohol solution, also in an atmosphere of nitrogen. In both steps, after the reaction, solvent was removed by evaporation. The product of step 2 was washed free of NaCl with water, and the crude selenide so obtained was observed to stain copper metal black. This tendency can be destroyed and the selenide purified by heating the selenide with copper metal in an inert atmosphere and recrystallizing from petroleum ether. However, it has been found that the effect of the dialkyl selenides of the invention in blackening copper is of relatively minor significance in practice; hence, the crude product, washed free of NaCl, may be used.

The pure dicetyl selenide is a white, waxy odorless solid crystallizing in small lustrous plates and melting at 123–125° F. It is very soluble in most hydrocarbon solvents, for example petroleum ether, and it is practically insoluble in water and alcohol. These solubility properties are valuable from the standpoint of a lubricant additive since high solubility in hydrocarbon solvents and low solubility in water, together with the low volatility of the selenide, render it sufficiently soluble in mineral oils and insufficiently soluble in water to enable the refiner to provide an ade-

another portion of the same base oil there was dissolved 0.5% of dicetyl sulfide. These compounded oils were submitted to oxidation at 340° F. in an apparatus of the type described by Dornie in "Industrial and Engineering Chemistry," vol. 28, page 26 (1936), oxygen being absorbed by the oil under test at 340° F.

The results are tabulated below (Table I) and they are represented graphically in Figure 1 of the drawing, wherein abscissae represents time and ordinates represent volume of oxygen absorbed. Oxygen absorption in both Table I and Figure 1 is given in cubic centimeters of oxygen (S. T. P.) absorbed by 100 grams of oil in the stated time at 340° F. The vast improvement of dicetyl selenide over dicetyl sulfide, even though the latter was used in 5 times as great an amount, is evident.

Table I

Time, hours	Oxygen absorbed	
	White oil+0.5% dicetyl sulfide	White oil+0.1% dicetyl selenide
0.3.....	3,298	
0.5.....		13
1.0.....		13
1.5.....		19
2.1.....		29
2.9.....		76
3.3.....		180
3.40.....		559
3.42.....		987

Example II.—Dicetyl selenide, dicetyl sulfide and cetyl ethyl sulfide were blended with certain compounded oils known to be corrosive to copper-lead bearings. Corrosion tests on the various oils were made, with and without added sulfide or selenide. The corrosion tests were carried out as follows: Glass tubes 2 inches in diameter and 20 inches long were immersed in an oil bath, the temperature of which was automatically controlled to within $\pm 1^\circ$ of the 325° F. test temperature. Approximately 300 cc. of oil under test was placed in each tube and air was bubbled through it at the rate of 10 liters per hour. Strips of copper-lead bearing metal were placed in the oil. The weight loss of each strip was recorded. Before 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 results are given in Table II below:

Table II

Oil	Corrosion inhibitor	Wt. loss Cu-Pb strips in milligrams			Used oil inspection		
		24 hrs.	48 hrs.	72 hrs.	Viscosity increase	Neutralization No.	Naphtha insoluble
A.....	Nil.....	28.9	63.8	82.3	9.7	1.19	69
A.....	1.0% dicetyl sulfide.....	9.3	23.2	32.2	7.3	1.59	5
A.....	0.1% dicetyl selenide.....	11.2	22.7	30.0	7.5	2.18	51
A.....	0.25% dicetyl selenide.....	6.2	11.2	12.5	3.9	1.10	1
B.....	Nil.....	30.4	91.1	138.4	16.8	7.54	12
B.....	1.0% dicetyl sulfide.....	37.1	124.1	212.0	9.3	3.18	1
B.....	0.25% dicetyl selenide.....	13.7	35.2	48.3	5.5	0.72	1
C.....	Nil.....	34.1	88.6	106.3	7.4	1.03	28
C.....	1.0% cetyl ethyl sulfide.....	7.9	18.6	21.8	9.8	1.58	14
C.....	0.1% dicetyl selenide.....	8.1	17.6	20.6	3.8	2.27	0
D.....	Nil.....	11.0	30.5	44.0	7.6	1.28	45
D.....	1.0% cetyl ethyl sulfide.....	4.7	6.4	8.2	9.2	1.52	58
D.....	0.1% dicetyl selenide.....	0.1	+2.5	1.5	2.1	0.41	0

quate reserve of selenide in an oil without danger of its being leached out by water or lost through vaporization at elevated temperatures.

The dicetyl selenide thus prepared was dissolved in white oil of medicinal quality in the amount of 0.1% by weight of the selenide. In

Oils A, B, C and D referred to in Table II were all compounded oils, the base oil being a refined S. A. E. 30 Western oil. In oil A the compounding agent was 0.5% calcium cetyl phenate; in oil B the compounding agent was 1.0% of the same phenate; in oil C the compounding agents were

0.5% calcium cetyl phenate and 0.25% calcium cetyl phosphate, and in oil D the compounding agents were 0.5% sulfurized calcium cetyl phenate and 0.25% calcium cetyl phosphate.

From an inspection of Table II, it is evident that dicetyl selenide is a vastly more effective corrosion inhibitor than dicetyl sulfide and cetyl ethyl sulfide, and on the whole it provides a much better used oil inspection than these sulfides.

Example III.—A Western S. A. E. 60 aviation oil, with and without compounding agents, was submitted to test in a Lauson gasoline engine. The test was carried out as follows: A single cylinder Lauson gasoline spark ignition engine, 2% inch bore and 2½ inch stroke, loaded with a three-phase induction generator, 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. The engine was operated

Example IV.—A highly refined S. A. E. 30 Western oil and the same oil compounded with various inhibitors (both of the invention and not of the invention) were submitted to the 340° F. oxidation test described in Example I. The results are set forth in Tables IV and V below. In these tables the time is given in hours for the absorption of the indicated number of cubic centimeters of oxygen (S. T. P.) by 100 grams of oil. Except where otherwise indicated, the additive was dissolved in the oil in the amount of 0.1% by weight. The dilauryl selenoxide, being substantially insoluble, was suspended in the oil.

In Figure 2 of the drawing are set forth in graphic form the results obtained with the base oil and with the base oil compounded with several of the additives shown in Tables IV and V. In Figure 2, abscissae represent the time in hours and ordinates represent cubic centimeters of oxygen (S. T. P.) absorbed per 100 grams of oil.

Table IV

Time, hrs.	Nil	Oxygen absorbed by base oil plus—					
		Dicetyl sulfide	Diphenyl selenide	Cetylphenyl selenide	Dibenzyl selenide	Dicetyl selenide	Dilauryl diselenide
0.05	83						
0.15		20	0				
0.20	96						
0.25	522						
0.30	1,746		458				
0.32				728			
0.35		506	1,048	1,456			
0.40		1,380		3,022			
0.45		2,436				0	
0.50			1,706			0	0
1.00					630		
1.40							0
1.50					4,012		
1.55							0
2.00							21
2.50						174	
2.60						1,450	
2.90							44
3.00							40
3.50							152
4.00							571
4.30							1,906
4.40							
4.50							117
4.90							207
5.10							850

Table V

Time, hrs.	Oxygen absorbed by base oil plus—				
	Dipara- fin selenide	Dicetyl telluride	Bis (β - chloroethyl) selenide (0.15%)	Bis (β - hydroxyethyl) selenide (0.135%)	Dilauryl selenox- ide
0.25		0			0
0.40					0
0.50				22	
0.70				40	28
1.00		0		86	
1.35		0		101	
1.40					56
1.50					
1.60				484	180
1.65		37		800	
1.75		274			
1.78					194
2.00	44				2,748
2.20					
3.30		87			
3.50	1,590				

at 1200 revolutions per minute, the engine jacket temperature was maintained at 460° F., the crankcase oil temperature was maintained at 220° F. and the engine was operated for 30 hours after which the piston condition and the neutralization number of the used oil was determined. Results are set forth in Table III below:

Table III

Additives	P. D. No. ¹	Percent ring slot carbon	Ring condi- tion	Neut. No. of used oil
(1) None	455	40	Stuck	1.30
(2) 1.5% dicetyl selenide	515	100	Free	0.24
(3) 0.375% sulfurized Ca cetyl phenate + 0.125% Ca cetyl phosphate	200	60	Stuck	1.52
(4) Same compounding as (3) + 0.5% dicetyl selenide	115	0	Free	0.23
(5) Same compounding as (3) + 1.0% dilauryl selenide	70	0	do	0.83

¹ P. D. No. (Piston Discoloration No.) as used in the table above involves a careful inspection of the piston skirt and an estimate of the percentage of the skirt covered with black, dark brown or light brown gum. On the scale chosen a completely black piston is assigned a P. D. No. of 800 and a piston completely free from discoloration is assigned a P. D. No. of 0. Black gum on the piston skirt is estimated as being four times as detrimental to engine performance as light brown gum and a heavy deposit of black gum was in many cases observed to be the forerunner of piston seizure.

The curves of Figure 2 reveal strikingly the unusual performance of the higher dialkyl selenides of the present invention.

Example V.—The oxidation inhibiting effect of minute amounts of a dialkyl selenide of the present invention is shown in Table VI below. This table sets forth the results of a test on a highly refined white oil of extremely small amounts of dicetyl selenide. The test was car-

ried out as follows: 25 cubic centimeters of oil were placed in a cylindrical glass cell $4\frac{1}{2}$ inch long by $1\frac{1}{4}$ inch diameter. This cell was connected with a manometer and was immersed in an oil bath maintained at 275° F. The cell was disposed so that its axis was at a slight angle with the horizontal, and it was connected with an agitator (a windshield wiper motor) in such a manner that operation of the motor caused the cell to rock in the bath. The cell and manometer connection were freed of air and filled with oxygen prior to immersion in the oil bath. The instant of immersion was taken as zero time and agitation was commenced at this time. Manometer readings were taken until a pressure drop, due to absorption of oxygen, of 10 centimeters of mercury was recorded. The square root of pressure drop was then plotted against time and the intercept of the resulting curve with the time axis was taken as the inhibition period.

Results are set forth in Table VI below:

Table VI

Per cent dicetyl selenide	None	0.000001	0.0001	0.001	0.01
Inhibition period (minutes)	41	36	59	120+	120+

Example VI.—Oils A, B and C, with and without various selenides and a telluride, were submitted to the "Aluminum dish test." This test, which is very severe from the standpoint of gum formation, was carried out as follows: A weighed sample of oil (about 5 drops) was placed in an aluminum dish 2 inches in diameter which is flat on its lower face and slightly concave on its upper face, the dish having been thoroughly cleaned and dried before putting in the oil. The dish was then placed on an electric hot plate, the surface temperature of which was adjusted to the desired value. The dish was left on the hot plate for 20 minutes and was then removed and cooled to room temperature. The dish and deposit were then washed free of oil with petroleum ether and the residual gum was determined. The gum is expressed as percentage by weight of the original oil. Oil A was a Western SAE 60 aviation oil. Oil B was the same oil containing 0.375% of sulfurized calcium cetyl phenate and 0.125% of calcium cetyl phosphate. Oil C was a Western SAE 30 oil containing 0.5% of sulfurized calcium cetyl phenate and 0.25% of calcium cetyl phosphate.

Table VII

Oil	Additive	Gum formed at 550° F.	Gum formed at 600° F.	Gum formed at 650° F.
A	Nil	3.8	16.7	19.8
A	0.25% dicetyl selenide	2.5	11.0	18.2
A	0.50% dicetyl selenide	1.2	8.7	17.3
A	1.0% dicetyl selenide	0	4.4	13.6
A	2.0% dicetyl selenide	0	0.52	10.5
B	Nil	6.72	13.5	19.8
B	2.0% diundecyl selenide	0.79	8.1	13.05
B	2.0% dilauryl selenide	0.85	6.7	12.8
B	2.0% ditetradecyl selenide	0.35	7.5	10.4
B	2.0% dicetyl selenide	0.01	0.37	8.8
B	2.0% diheptadecyl selenide	0	5.7	14.9
B	1.0% dicetyl diselenide	0	1.8	8.6
B	2.0% dicetyl telluride	0	0	2.1
C	Nil	6.2	9.3	8.2
C	1.0% diparaffin selenide	0	0.3	4.1
C	2.0% dilauryl diselenide	0	0.2	3.2

It is known that a thioether of the type represented by dicetyl sulfide is not a very potent oxidation inhibitor if it is the only inhibitor present in an oil, but if an "activator" such as cal-

cium cetyl phosphate be present, the combination forms a potent oxidation inhibitor. It has been found, surprisingly, that the dialkyl selenides of the present invention do not behave in the same manner; they are potent inhibitors when acting alone, but their behavior in the presence of calcium cetyl phosphate and the like is very different from the behavior of the dialkyl sulfides in the presence of calcium cetyl phosphate and the like. This is illustrated by the data in Tables VIII and IX below, taken from oxidator tests the same as described in Example I.

Table VIII (no iron present)

Time, hrs.	Nil	Additives		
		0.5% Ca cetyl phosphate	0.1% dicetyl selenide	0.25% Ca cetyl phosphate+0.1% dicetyl selenide
0.05	33			
0.20	96			
0.25	522			
0.30	1,746	408		
0.33		1,192		
0.35		2,350		
1.00				48
1.70				242
1.80				712
1.85				1,518
2.00			174	
2.90			1,450	

Table IX (iron present)

Time, hrs.	Nil	Additives		
		0.25% Ca cetyl phosphate	0.25% dilauryl selenide	0.25% Ca cetyl phosphate+0.25% dilauryl selenide
0.20	176			
0.25	760			
0.30	1,648	868		
0.33		2,397		
0.35	3,288			
2.00			78	
2.80			286	
3.00				130
3.15			674	
3.25			1,374	
3.35			2,786	
4.00				260
4.50				934
4.75				1,524
4.85				3,274

Table VIII refers to oxidation tests carried out in the absence of iron while Table IX refers to the same oxidation tests carried out in the presence of iron. It will be seen that in the absence of iron (Table VIII), dicetyl selenide was more effective in the absence of calcium cetyl phosphate than in its presence, whereas from Table IX (in the presence of iron) it will be seen that dilauryl selenide was more effective in the presence of calcium cetyl phosphate than in its absence. Since iron is always present under conditions of actual use, as in the crankcase and cylinders, effective cooperation between the selenides or tellurides of the present invention and "activators" such as calcium cetyl phosphate may be expected.

The dialkyl selenides of the present invention effectively cooperate with other types of compounding agents, such as the combination of metal phenates and metal salts of organo substituted acids of phosphorus, as shown by Table X below. The base oil used in the tests exemplified by Table X was a refined SAE 30 Western oil. The strip corrosion test indicated was the

same as that described in Example II. As shown by the data of the table, the dialkyl selenides cooperate with the indicated compounding agents very much better than do the dialkyl sulfides.

one. Where n is 2 or more, both straight chain and branched chain groups are comprehended by $(X)_n$. The groups R and R_1 may be not only straight and branched chain saturated alkyl groups C_nH_{2n+1} , but also straight and branched

Table X

Additives	Wt. loss Cu-Pb strips			Vis. Increase 210° F.	Neut. No.	Naphtha insolubles
	24 hrs.	48 hrs.	72 hrs.			
0.5% Ca cetyl phenate+0.25% Ca cetyl phosphate.....	34.1	88.8	106.3	7.4	1.03	28
0.5% Ca cetyl phenate+0.25% Ca cetyl phosphate+1% cetyl ethyl sulfide.....	7.9	18.6	21.8	9.8	1.58	14
0.5% Ca cetyl phenate+0.25% Ca cetyl phosphate+0.2% dicetyl selenide.....	4.2	9.2	10.6	2.0	0.96	0
0.5% sulfurized Ca cetyl phenate+0.25% Ca cetyl phosphate.....	11.0	30.5	44.0	7.6	1.28	45
0.5% sulfurized Ca cetyl phenate+0.25% Ca cetyl phosphate+1% cetyl ethyl sulfide.....	4.7	6.4	8.2	9.2	1.52	58
0.5% sulfurized Ca cetyl phenate+0.25% Ca cetyl phosphate+0.1% dicetyl selenide.....	0.1	+2.5	1.5	2.1	0.41	0

In the specific examples and in the tables above are mentioned various sulfides, selenides, a telluride and a selenoxide. These are listed below and are identified as to structure or manner of preparation.

Monosulfides (R_1-S-R_2)

Dicetyl sulfide, $n-C_{16}H_{33}-S-C_{16}H_{33}-n$

Cetyl ethyl sulfide, $n-C_{16}H_{33}-S-C_2H_5$

Monoselenides (R_1-Se-R_2)

Normal (straight chain) monoselenides

Didecyl selenide, $n-C_{10}H_{21}-Se-C_{10}H_{21}-n$

Dicetyl selenide, $n-C_{16}H_{33}-Se-C_{16}H_{33}-n$

Dilauryl selenide, $n-C_{12}H_{25}-Se-C_{12}H_{25}-n$

Iso (branched chain) monoselenides

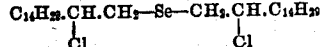
Diundecyl selenide, iso- $C_{11}H_{23}-Se-C_{11}H_{23}-iso$

Ditetradecyl selenide, iso- $C_{14}H_{29}-Se-C_{14}H_{29}-iso$

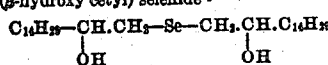
Diheptadecyl selenide, iso- $C_{17}H_{35}-Se-C_{17}H_{35}-iso$

Polar substituted monoselenides

Bis (β -chlorocetyl) selenide¹



Bis (β -hydroxy cetyl) selenide¹



Miscellaneous Monoselenides

Diphenyl selenide, $C_6H_5-Se-C_6H_5$

Cetyl phenyl selenide, $C_{16}H_{33}-Se-C_6H_5$

Dibenzyl selenide, $C_6H_5CH_2-Se-CH_2.C_6H_5$

Diselenides

Dilauryl diselenide, $n-C_{12}H_{25}-(Se)_2-C_{12}H_{25}-n$

Dicetyl diselenide, $n-C_{16}H_{33}-(Se)_2-C_{16}H_{33}-n$

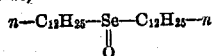
Monotellurides

Dicetyl telluride, $n-C_{16}H_{33}-Se-C_{16}H_{33}-n$

Miscellaneous selenides

Diparaffin selenide—prepared by condensing chlorinated paraffin wax with Na_2Se . Most probably a mixture of compounds corresponding to the formula $R-Se-R$, where R is a higher alkyl radical.

Dilauryl selenoxide,



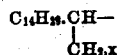
Wherever in the above examples and elsewhere herein a certain percentage of a component of an oil is given, percentage by weight based on the entire oil (oil + additives) is intended, unless otherwise specified.

As stated, dialkyl selenides and dialkyl tellurides containing at least 8 carbon atoms in an alkyl group, preferably containing at least 8 carbon atoms in each alkyl group, may be employed in accordance with the invention. These may be represented by the formula



wherein R and R_1 are like or unlike radicals of alkyl structure of which at least one contains not less than 8 carbon atoms, X is selenium or tellurium, and n is an integer at least equal to

¹ One or both of the polar substituted alkyl radicals may, however, have the structure



where $X=Cl$ or OH , and the "bis (β -chloro (or hydroxy) cetyl) selenide" may be a mixture of compounds.

chain unsaturated aliphatic groups C_nH_{2n-1} , C_nH_{2n-3} , etc., and also cycloalkyl or cycloaliphatic groups. That is, the groups attached to selenium and tellurium in the compounding agents of the present invention, may be saturated, unsaturated or cyclic aliphatic groups. Also, the groups R and R_1 may be substituted by aromatic groups, such as the phenyl, hydroxy phenyl and amino phenyl groups, provided such groups are spaced at least one carbon atom from the group $(X)_n$. Polar groups, such as chlorine, bromine, hydroxyl, ether, keto, amino, free carboxyl, metallo carboxyl, carboxy ester, mercapto, mercaptide, mono-, di and polysulfide, etc., may be substituted in the groups R and R_1 of the selenides and tellurides of the present invention. Two or more selenide or telluride groups $(X)_n$ may be present in the molecule.

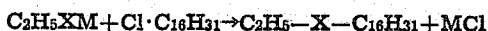
The following specific examples of selenides and tellurides, together with those specifically mentioned hereinabove, will illustrate the selenium and tellurium compounds of the present invention: decyl methyl monoselenide, cetyl ethyl monoselenide, octyl decyl monoselenide, di-eicosyl monoselenide; dioctyl diselenide, didecyl diselenide; diheptadecyl diselenide, dieicosyl diselenide; decyl methyl monotelluride, cetyl ethyl monotelluride, octyl decyl monotelluride, didecyl monotelluride, diundecyl monotelluride, dilauryl monotelluride, ditetradecyl monotelluride, dicetyl monotelluride, diheptadecyl monotelluride, dieicosyl monotelluride; dioctyl ditelluride, didecyl ditelluride, dilauryl ditelluride, dicetyl ditelluride; and the various mono- and polyselenides and mono- and polytellurides prepared by reacting sodium or other alkali metal mono- or polyselenides or mono- or polytellurides with halogenated, e. g., chlorinated, hydrocarbons, such as decyl chloride, dodecyl chloride, tetradecyl chloride, cetyl chloride, heptadecyl chloride, eicosyl chloride, chlorinated lubricating oil and chlorinated wax.

The selenides are preferred to the tellurides, because they are more stable and more easily prepared. However, the tellurides are highly effective as oil stabilizers and may be preferred in certain cases. Mixtures of selenides or tellurides are suitable, such as those prepared by condensing a metal selenide, polyselenide, telluride or polytelluride with a chlorinated or brominated mixture of hydrocarbons, for example, chlorinated or brominated lubricating oil or paraffin wax. It is not essential that all of the halogen be removed in the condensation reaction; thus a chlorine-containing dialkyl selenide or telluride or mixture of dialkyl selenides or tellurides may be used. Also, a mixture of selenides and tellurides may be used.

Suitable methods of preparing the dialkyl selenides and tellurides of the invention are as follows:

(1) From aliphatic halides and a metal selenide, telluride, polyselenide or polytelluride, by condensation in an inert solvent such as ethyl alcohol. This method is particularly suitable for the preparation of pure, simple selenides and tellurides such as dicetyl selenide and dicetyl telluride, and for the preparation of mixtures of selenides and/or tellurides, as from chlorinated wax.

(2) From the seleno and telluro analogues of the mercaptans; that is, from compounds of the type $RSeH$ and $RTeH$, where R is an aliphatic group. The compound $RSeH$ or $RTeH$, which may be termed a "seleno mercaptan" or a "telluro mercaptan," is converted to a metal "seleno mercaptide" or metal "telluro mercaptide," which is then condensed with a halogenated hydrocarbon, such as cetyl chloride, or a halogenated mixture of hydrocarbons, such as chlorinated wax, in the same manner as the halogenated hydrocarbons are condensed with metal selenides or tellurides. This method is especially suited to the preparation of mixed selenides or tellurides, such as cetyl ethyl selenide and cetyl ethyl telluride; for example, as follows:



wherein $X=Se$ or Te and M is a metal such as an alkali metal.

(3) Diselenides such as dilauryl diselenide can be readily and economically prepared by the following series of reactions:

- $MCN + Se \rightarrow MSeCN$
- $RX + MSeCN \rightarrow RSeCN + MX$
- $2RSeCN \rightarrow R-Se_2-R + (CN)_2$

In the above equation, M represents an alkali metal, preferably potassium; R represents an aliphatic group; and X represents a replaceable negative atom or radical, preferably chlorine. In carrying out this process, reaction (a) may be carried out in aqueous solution, reaction (b) may be carried out in ethyl alcohol, and reaction (c) is carried out by reacting the alkyl selenocyanate with caustic alkali in aqueous alcohol. This method does not yield as desirable a product, from the standpoint of lubricant additives, with chlorinated wax as it yields with some of the lower, purer alkyl chlorides, such as lauryl chloride and cetyl chloride.

(4) Selenium is dissolved in strong aqueous or alcoholic caustic soda or caustic potash solution to yield a mixture (in solution) of alkali metal selenides, polyselenides and selenites, possibly also other selenium compounds. It has been found that when this mixture is heated with a halogenated hydrocarbon or mixture of hydrocarbons, such as lauryl chloride or chlorinated wax, the product, comprising a complex mixture of selenides and probably including mono- and diselenides, perhaps also higher polyselenides, is an excellent lubricant additive.

As stated hereinabove, the selenides and tellurides of the present invention are not only compatible with but are also highly cooperative with other types of additives in hydrocarbon oils. Thus with metal salts of organo substituted phosphates in the presence of iron, the selenides and tellurides of the present invention yield a highly beneficial combination effect, and with metal salts of phenols, especially the polyvalent metal salts of the higher alkyl phenols, enhanced oil stabil-

ity results. Other types of additives with which the selenides and tellurides of the present invention may be used include the metal salts of organo substituted acids of boron, sulfur, and arsenic; the metal salts of carboxylic acids such as aryl carboxylic acids, fatty acids and polar substituted aliphatic mono- and polycarboxylic acids (calcium cetyl oxalate, calcium cetyl citrate, magnesium alpha hydroxy stearate, magnesium tartrate and the like). The additives of the present invention may be used in hydrocarbon oils in conjunction with sulfonates, such as the metal (calcium, magnesium, zinc, cadmium, aluminum, etc.) salts of aryl sulfonic acids of the "Nacconol" type (higher alkyl aryl sulfonic acids) or with petroleum sulfonates, such as calcium, magnesium, zinc, cadmium, or aluminum petroleum sulfonates.

The selenides and tellurides of the present invention are particularly useful in steam turbine lubricating oils in conjunction with rust inhibitors, especially the higher alkyl acid esters of polybasic aliphatic acids such as lauryl acid maleate, mono- or dicetyl citrate and the like.

The additives of the present invention, as seen from the above examples, in particular, Example V, are effective in amounts as low as 0.0001 per cent. Ordinarily concentrations of about 0.1 to 2 per cent will be used but larger and smaller amounts may be used. Amounts greatly in excess of 5% are ordinarily considered unnecessary except in forming a concentrate of the selenide or telluride with oil for later blending with more oil to produce a finished product. In such concentrates, the amount of selenide may be as high as 50% or higher.

The additives of the present invention may be used advantageously in oils generally, whether hydrocarbon or non-hydrocarbon, although their present field of chief utility is in viscous mineral oils and greases made therefrom. They may be used not only in lubricating oils for internal combustion engines, but also in transmission oils, turbine oils, cutting oils, spray oils and elsewhere. As for types of oil, the additives of the present invention may be used in paraffinic, mixed base and naphthenic petroleum lubricating oils; in oils of low or high viscosity; in oils resulting from olefin polymerization or the reduction or distillation of coal or coal products, oils from the hydrogenation of oxides of carbon, animal and vegetable oils, and synthetic lubricants such as amyl naphthalene. They may also be used to stabilize other organic products, such as fats, fatty oils, etc., against deterioration.

We claim:

1. A composition of matter, comprising an oil and a small amount, sufficient to stabilize the oil, of a compound of the type



where R and R_1 are like or unlike aliphatic radicals at least one of which contains not less than 8 carbon atoms, X is an element selected from the group consisting of selenium and tellurium and n has the value of 1 or 2.

2. The composition of claim 1, wherein X is selenium.

3. The composition of claim 1, wherein R and R_1 each contains at least 8 carbon atoms.

4. A composition of matter, comprising a hydrocarbon oil of lubricating viscosity and a small amount, sufficient to improve the oil, of a compound selected from the group consisting of dialkyl monoselenides and dialkyl diselenides

wherein at least one alkyl group contains not less than 8 carbon atoms.

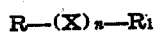
5. The composition of claim 4, wherein said compound is a monoselenide.

6. A compounded mineral lubricating oil comprising a small amount, sufficient to stabilize the oil, of a selenide of the type



where R and R₁ are like or unlike open chain aliphatic groups each of which contains not less than 8 carbon atoms and n has the value of 1 or 2.

7. A composition of matter, comprising an organic substance which tends to deteriorate in the presence of oxygen, and a stabilizing amount of a compound of the type



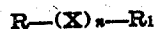
where R and R₁ are like or unlike aliphatic radicals at least one of which contains not less than 8 carbon atoms, n has a value of 1 or 2, and X is selected from the group consisting of selenium and tellurium.

8. A compounded lubricating oil, comprising a petroleum oil of lubricating viscosity and about 0.1 to 2% by weight based on finished oil of dicyl monoselenide.

9. A compounded lubricating oil, comprising a petroleum oil of lubricating viscosity and about 0.1 to 2% by weight based on finished oil of dilauryl monoselenide.

10. A compounded lubricating oil, comprising a petroleum oil of lubricating viscosity and about 0.1 to 2% by weight based on finished oil of diparaffin monoselenide.

11. A composition of matter useful for blending with hydrocarbon oils, comprising a concentrated dispersion in viscous hydrocarbon oil of a compound corresponding to the type



where R and R₁ are like or unlike aliphatic radicals at least one of which contains not less than 8 carbon atoms, n has a value of 1 or 2, and X is selected from the group consisting of selenium and tellurium.

12. A compounded lubricating oil, comprising a petroleum oil of lubricating viscosity and a small amount, sufficient to stabilize the oil, of a dialkyl monoselenide containing eight to twenty carbon atoms in each alkyl group.

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