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MINERAL OIL COMPOSITIONS AND THE LIKE

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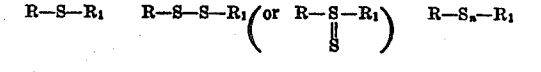
4 Claims. (Cl. 252—45)

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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 (which issued April 11, 1944, as U. S. Patent No. 2,346,155) and of our copending application Serial No. 476,760, filed February 22, 1943 (which issued April 16, 1946, as U. S. Patent No. 2,398,415).

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 R_1 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

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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 issued as U. S. Patent No. 2,346,153), 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 issued as U. S. Patent No. 2,346,154), 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 U. S. 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 dialkyl sulfides, alkyl aryl sulfides and diaryl sulfides only in combination with activators or functional groups.

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

Example I.—A highly refined SAE 30 Western oil and the same oil compounded with various inhibitors (both of the invention and not of the invention) were submitted to an oxidation test in apparatus of the type described by Dornte in "Industrial and Engineering Chemistry," vol. 28, page 26 (1936). In this test, oxygen at atmospheric pressure was bubbled through the oil, which was maintained at 340° F. The results are set forth in Tables I and II 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 amount of 0.1% by weight. The dilauryl selenoxide, being substantially insoluble, was suspended in the oil.

Table I

Time, Hrs.	Nil	Oxygen Absorbed By Base Oil Plus						
		Dicetyl Sulfide	Diphenyl Selenide	Cetylphenyl Selenide	Dibenzyl Selenide	Dicetyl Selenide	Dilauryl Diselenide	Didecyl Selenide
0.05	33							
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						
0.50			1,706			0		
1.00						0		0
1.40					630			
1.50							0	
1.55					4,012			
2.00								0
2.50							21	
2.60						174		
2.90						1,450		
3.00								44
3.50							40	
4.00								152
4.30								571
4.40								1,906
4.50							117	
4.90							207	
5.10							850	

Table II

Time, Hrs.	Oxygen Absorbed By Base Oil Plus				
	Diparaffin Selenide	Dicetyl Telluride	Bis (β-chlorocetyl) Selenide (0.15%)	Bis (β-hydroxycetyl) Selenide (0.135%)	Dilauryl Selenoxide
0.25		0			
0.40				0	
0.50					0
0.70			22		
1.00		0		40	28
1.35		0		86	
1.40			101		
1.50					56
1.60				180	
1.65			484		
1.75		37		800	
1.78		272			
2.00	44				194
2.20					2,748
3.30	67				
3.50	1,590				

Example II.—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 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 III

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	1.0% Diparaffin sulfoselenide	0	0.5	3.1
C	2.0% Dilauryl diselenide	-------	0.2	3.2

In the specific examples and in the tables above are mentioned various sulfides, selenides, a telluride, a sulfoselenide 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
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:
[1] Bis (β-chlorocetyl) selenide,

$$C_{14}H_{29}\cdot CH(Cl)\cdot CH_2—Se—CH_2\cdot CH(Cl)\cdot C_{14}H_{29}$$

[1] Bis (β-hydroxy cetyl) selenide,

$$C_{14}H_{29}\cdot CH(OH)\cdot CH_2—Se—CH_2\cdot CH(OH)\cdot C_{14}H_{29}$$

Miscellaneous monoselenides:
Diphenyl selenide, C_6H_5—Se—C_6H_5
Cetyl phenyl selenide, $C_{16}H_{33}$—Se—C_6H_5
Dibenzyl selenide, $C_6H_5\cdot CH_2$—Se—$CH_2\cdot C_6H_5$
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—$C_{16}H_{33}$—Te—$C_{16}H_{33}$—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.
Diparaffin sulfoselenide—Prepared by condensing chlorinated paraffin wax with the product of dissolving selenium in aqueous or alcoholic solution of sodium sulfide or polysulfide.
Dilauryl selenoxide, n—$C_{12}H_{25}$—Se(=O)—$C_{12}H_{25}$—n

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

$$C_{14}H_{29}\cdot CH(CH_2\cdot x)—$$

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

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

$$R—(X)_n—R_1$$

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 one. Where n is 2 or more, the group X_n may be homoatomic (only selenium atoms or only tellurium atoms) or heteroatomic (at least one element of the group selenium and tellurium plus at least one other element of the group oxygen, sulfur, selenium and tellurium), and both straight chain and branched chain groups are comprehended by $(X)_n$. The groups R and R_1 (the "alkyl" groups) comprehend not only straight and branched chain saturated groups C_nH_{2n+1}, but also straight and branched chain unsaturated aliphatic groups C_nH_{2n-1}, C_nH_{2n-3}, etc., and also cycloalkyl or cycloaliphatic groups. That is, by "alkyl" as used to identify the groups attached to selenium and tellurium in the compounding agents of the present invention, it is meant to include saturated, unsaturated and 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 alkyl group as herein defined. 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:

$$C_2H_5XM + Cl \cdot C_{16}H_{31} \rightarrow C_2H_5—X—C_{16}H_{31} + MCl$$

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

The following specific examples will illustrate the preparation and properties of the selenium and tellurium compounds of the invention.

Example III.—Dicetyl selenide

$$(C_{16}H_{33}—Se—C_{16}H_{33})$$

was prepared stepwise as follows: In the first step, represented by the equation

$$2Na + Se \rightarrow Na_2Se$$

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

$$2C_{16}H_{33}Cl + Na_2Se \rightarrow C_{16}H_{33}—Se—C_{16}H_{33} + 2NaCl$$

normal 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 in the presence of decolorizing charcoal. However, it has been found that the effect of the dialkyl selenides of the invention in blackening copper is of relatively little 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 adequate reserve of selenide in an oil without danger of its being leached out by water or lost through vaporization at elevated temperatures.

Example IV.—Dicetyl telluride

$$(C_{16}H_{33}—Te—C_{16}H_{33})$$

was prepared in the same manner as dicetyl selenide in Example I, except that tellurium was substituted for selenium in chemically equivalent amount. It was also found advantageous to isolate the telluride after the second step (condensation of cetyl chloride with sodium telluride) by chilling the alcoholic solution and filtering and then extracting the residue with petroleum ether and evaporating the petroleum ether. Purification by copper treatment was also employed for final purification.

The telluride so prepared consisted of white odorless crystals, melting point 43° to 44.5° C.

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 stability 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. These metal salts of organic acids and of organo-substituted inorganic acids will ordinarily be used in amounts of about 0.5 to 2% by weight based on finished oil.

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 selenium and tellurium additives of the present invention 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, rubber, mineral oil-soap greases, aldehydes, ethers, terpenes, mercaptans and phenols, against deterioration.

We claim:

1. A compounded lubricating oil, comprising a petroleum oil of lubricating viscosity and about 0.1 to 2% by weight based on finished oil of dicetyl monotelluride.

2. 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 monotelluride.

3. 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 monotelluride.

4. A compounded lubricating oil, comprising an oil of lubricating viscosity and about 0.1 to 2% by weight based on finished oil of a dialkyl monotelluride selected from the group consisting of dicetyl monotelluride, dilauryl monotelluride and diparaffin monotelluride.

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