

1

2,713,558

LUBRICATING COMPOSITIONS

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This invention relates to lubricants, and more particularly to mineral lubricating oil compositions which are suitable for lubrication under extreme operating conditions such as under extreme pressure and wear conditions.

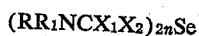
It is well known that the high pressure occurring in certain types of gears and bearings may cause a film of lubricant to rupture with consequent damage to the machinery. It has been shown that base lubricants, such as mineral oil and/or synthetic oil, can be improved, with regard to their protective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

It is known that certain elements or compounds of elements of the type of chlorine and phosphorus are capable of imparting extreme pressure properties to lubricants, which may be lubricating oils and greases, when blended therewith. Among the compounds heretofore used are phosphoric acid esters, free or loosely bound sulfur, and certain chlorinated organic compounds.

It has now been discovered that improved extreme pressure lubricants are obtained by incorporating into a base lubricant a minor amount of an oil-soluble selenium N-organo-substituted thiocarbamate, which may be either the divalent or tetravalent selenium thiocarbamate (including both mono- and di-thiocarbamates). The N-organo substituent(s) is an oleophilic organic radical and usually is a hydrocarbon radical, generally attached to the N-atom by an acyclic or alicyclic C-atom (or two such C-atoms in the case of heterocyclic N-containing structures and thiocarbamates from secondary amines). The divalent selenium thiocarbamates are preferred for the purpose of the invention. Still further, it has been found that mixtures of the selenium salts and a thiuram polysulfide are particularly effective in providing extreme pressure properties in lubricating oil compositions thereof. As a still further aspect of the invention, it has been found that the selenium carbamates are particularly effective in providing lubricating oils with outstanding extreme pressure properties when used together with metal salts, such as lead naphthenate, either with or without the thiuram polysulfide.

Thus, whereas, in a comparative evaluation in a standardized test, lead naphthenate, known to be an extreme pressure agent, reached a scar diameter of 2 mm. at only 200 kilograms load and welded at 300 kg., divalent selenium dibutylthiocarbamate gave a scar of about 2 mm. only after a load of 400 kg. was applied and welding did not occur until a load of 600 kg. was applied.

The selenium thiocarbamates are represented by the general formula:

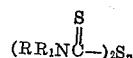


wherein n is a whole number from 1 to 2, R is a hydro-

2

carbon radical, such as alkyl, aralkyl, cycloalkyl or heterocyclic radicals, and R_1 is hydrogen or the same as R , X_1 and X_2 are selected independently from oxygen and sulfur, at least one of them being sulfur. The preferred class of compounds of the foregoing are the divalent selenium salts of hydrocarbyldithiocarbamic acids, represented by the formula $(R_2R_3NCSS)_2Se$, wherein R_2 and R_3 are the same or different acyclic and/or alicyclic hydrocarbon radicals, the total number of carbon atoms of R_2 and R_3 per molecule being from about 8 to about 20.

The thiuram polysulfides which are useful in combination with the selenium salts of this invention can be represented by the general formula:



wherein R and R_1 have the same designations as specified in connection with the selenium thiocarbamates and preferably correspond to the R 's of the thiocarbamate and n is at least 2, usually from 2 to 4.

Thiuram sulfides can be prepared by any suitable means, such as described in U. S. Patents 2,251,686, 2,286,690, 2,423,310, 2,464,799, and 2,647,145.

The selenium thiocarbamates are preparable by known methods. Thus, an aqueous solution of an alkali metal (sodium) selenite can be reacted with an aqueous solution of an alkali metal (sodium) thiocarbamate, such as sodium dibutylthiocarbamate, and the mixture acidified, with the precipitation of divalent selenium dibutylthiocarbamate. Alternatively, an alcoholic (methanolic) solution (dispersion) of selenium dioxide can be reacted with a suitable amine, such as dicyclohexylamine, and carbon disulfide. The amine and carbon disulfide react to give a corresponding dicyclohexyldithiocarbamate, which reacts further with the selenium dioxide to give the tetravalent selenium dicyclohexyldithiocarbamate; this latter on heating is converted to the divalent selenium dicyclohexyldithiocarbamate and dicyclohexylthiuram disulfide. Carbon oxysulfide (carbonyl sulfide) can be used in the place of the carbon disulfide to prepare the mono-thiocarbamates, the product usually being a mixture of the thiolcarbamate and the thionocarbamate. The amine is either a primary or a secondary amine, the thiocarbamates from the secondary amines being preferred. As already stated, the N-atom should be attached directly to an acyclic or alicyclic C-atom of the substituent radical. This C-atom may be either primary, secondary or tertiary and it may have hydrocarbon radicals attached thereto which are acyclic, alicyclic or aromatic, to yield radicals such as n -butyl, secondary butyl, tertiary butyl, the amyls, cyclohexyl, cyclohexylmethyl, benzyl, and the like. Also, two C-atoms attached directly to the N-atom, as in a secondary amine, may form a heterocyclic structure with the N-atom, the R and R_1 substituents in such a case forming a single hydrocarbylene (e. g., tetramethylene, pentamethylene) radical, as in pyrrolidine and piperidine. Suitable amines of this type are heterocyclic petroleum nitrogen bases. The preferred amines include the alkyl, alkaryl, aryl, cyclic and heterocyclic amines such as monoamyl, butyl, octyl, cyclohexyl, phenyl, morpholine amines; and dimethyl, diethyl, diisopropyl, dibutyl, diamyl, dioctyl, dicyclohexyl, dibenzyl, diphenyl ethyl, dipyrindyl, dimorpholine amines.

The following examples illustrate methods of preparing the divalent selenium carbamate compounds for use in compositions of this invention.

A molar portion of selenium dioxide dissolved in isopropanol was reacted in a glass vessel with a molar portion of carbon disulfide and dibutylamine for a period of about one hour. The reaction is exothermic and therefore the amine should be added at a rate to avoid sub-

stantial rise in temperature. The resulting product, after removal of the alcohol by vaporization, is an equimolar mixture of divalent selenium dibutyldithiocarbamate and tetrabutyl thiuram disulfide. If desired, the tetrabutyl thiuram disulfide can be separated from the mixture and the selenium salt used as the oil additive in compositions of this invention. However, it is preferred to use the mixture as the oil additive without recourse to separation.

Other specific divalent selenium salts together with their corresponding thiuram disulfides which can be used in compositions of this invention include divalent and tetravalent (divalent preferred) selenium dimethyl mono- and dithiocarbamates; diethyl mono- and dithiocarbamates, diamyl mono- and dithiocarbamates; dihexyl mono- and dithiocarbamates; dioctyl mono- and dithiocarbamates; N-ethyl-N-phenyl mono- and dithiocarbamates; dicyclohexyl mono- and dithiocarbamates; monocetyl mono- and dithiocarbamates; di(cetylphenyl) mono- and dithiocarbamates; dibenzyl mono- and dithiocarbamates; diamyl-piperidyl mono- and dithiocarbamates; dibutyl carbamate; dihexyl carbamate; dicyclohexylcarbamate; and monocetylcarbamate.

The oil-soluble selenium salts with or without the corresponding thiuram polysulfides can each be used in amounts ranging from 0.01% to 10% and preferably from 0.1% to about 5% by weight in various types of lubricating oils such as natural and synthetic hydrocarbon oils, synthetic polar containing lubricants such as esters of polycarboxylic acids, polyalkylene oxide polymers, silicon polymers and mixtures thereof, said oils ranging in viscosity from 50 SUS at 100° F. to above 200 SUS at 210° F.

A particularly preferred embodiment of this invention is provided by combining the above type of additives with an oil-soluble metal salt of a cyclic carboxylic acid such as the polyvalent metal salts of naphthenic acid, abietic acid, rosin acid of which preferred are the lead, tin, aluminum and zinc salts of naphthenic and abietic acids.

The naphthenic acids and their refined product can be prepared by the processes described in U. S. Patents 2,200,711, 2,214,438, 2,296,039, and 2,537,576. The molecular weight of the naphthenic acid can vary from 200 to above 1000 and preferably from 350 to 600.

The salts as described above such as lead naphthenate and the others can be used in amounts ranging from 0.01% to 10% and preferably from 0.1% to about 5% by weight.

The general formulation of compositions of this invention can be represented by:

	Amount, percent wt.	
	Broad Range	Preferred Range
<i>Primary additives</i>		
Se salts of thiocarbamic acids.....	0.01-10	0.1-5
<i>Secondary additives</i>		
Thiuram sulfide.....	0.01-10	0.1-5
<i>Optional additives</i>		
Salts of carboxylic acids and/or organic compounds containing inorganic acid radicals, e. g. lead naphthenates, sulfonates, etc.....	0-10	0.1-5
<i>Base</i>		
Natural oil, e. g., mineral oil, fuel oil, synthetic oil, fixed oils and mixtures thereof.....	Balance	Balance

The following examples are suitable compositions for the practice of this invention in which the selenium is divalent unless otherwise indicated.

Example 1: Percent by Wt.
Se dibutyldithiocarbamate 6.6

Example 1—Continued
Pb petroleum naphthenate (MW 450)..... 6.7
Mineral lubricating oil (SAE 30)..... Balance

Example 2:
Se dibutyldithiocarbamate 5
Pb petroleum naphthenate 5
Di(2-ethylhexyl)sebacate Balance

Example 3:
Se dibutyldithiocarbamate 1.5
Tetrabutylthiuram disulfide 1.5
Pb petroleum naphthenate 3
Mineral lubricating oil (SAE 30)..... Balance

Example 4:
Se dibutylmonothiocarbamate 3.5
Pb petroleum naphthenate 5
Phenyl- α -naphthylamine 0.1
Mineral lubricating oil..... Balance

Example 5:
Se dihexyldithiocarbamate 1
Pb petroleum naphthenate 2
Mineral lubricating oil Balance

Example 6:
Se dibenzylthiocarbamate 1.2
Pb petroleum sulfonate 2.5
2,6-ditert-butyl-4-methylphenol 0.1
Mineral lubricating oil Balance

Example 7:
Se dicyclohexyldithiocarbamate 1.8
Al petroleum naphthenate 1
Mineral lubricating oil Balance

Example 8:
Se monobutyldithiocarbamate 1
Zn petroleum naphthenate 1.5
Mineral lubricating oil Balance

Example 9:
Se dibutylmonothiocarbamate 0.25
Pb abietate 1
Tetrabutylthiuram disulfide 0.25
Mineral lubricating oil Balance

Example 10:
Tetravalent Se dibenzylthiocarbamate 0.5
Pb petroleum sulfonate 1.5
Mineral lubricating oil Balance

Example 11:
Se dibenzylmonothiocarbamate 2.5
Pb abietate 1.8
Mineral lubricating oil Balance

Example 12:
Se diethylmonothiocarbamate 0.75
Tetraethylthiuram disulfide 0.75
Pb petroleum naphthenate 3
Mineral lubricating oil (SAE 30)..... Balance

Example 13:
Se dibutyldithiocarbamate 0.5
Pb petroleum naphthenate 0.5
Fuel oil Balance

Example 14:
Se diethylmonothiocarbamate 0.75
Tetraethylthiuram disulfide 0.75
Al petroleum naphthenate 3
Mineral lubricating oil (SAE 30) Balance

Example 15:
Tetravalent Se dicyclohexyldithiocarbamate .. 0.5
Pb petroleum sulfonate 1.5
Di(2-ethylhexyl)sebacate Balance

Example 16:
Se dihexyldithiocarbamate 0.5
Pb petroleum naphthenate 0.25
Pb petroleum sulfonate 0.25
Mineral lubricating oil Balance

Example 17:
Se dibutyldithiocarbamate 0.5
Tricresylphosphate 0.25
Pb petroleum naphthenate 0.25
Mineral lubricating oil Balance

Example 18:

	Percent by weight
Se dibutyldithiocarbamate	6.6
Mineral lubricating oil	Balance

Example 19:

Se dibutyldithiocarbamate	3.3
Tetrabutylthiuram disulfide	3.3
Mineral lubricating oil	Balance

The synergistic effects produced by the additive blend of this invention are clearly shown by the following additional data, also obtained on the four-ball EP tester. The flash temperature parameter is the maximum value reached by the ratio $P/d^{1.4}$, where P is the applied load in kilograms and d is the scar diameter in millimeters at the end of 10 second running.

Base Oil	Percent w. Selenium Dibutyl Dithio-Carbamate	Percent w. Tetrabutyl Thiuram Disulfide	Percent w. Lead Naphthenate	Flash Temp. Parameter	Mean Hertz Load, kg
Mineral Oil	0	0	0	160	15
Do.	3	0	0	220	68
Do.	5	0	0	195	69
Do.	0	0	1	155	18
Do.	0	0	3	150	
Do.	3	0	5	145	
Do.	3	0	1 (Ex. 21)	295	
Do.	3	0	2 (Ex. 22)	340	92
Do.	3.3	0	6.7 (Ex. 23)	350	94
Do.	5	3.3	5 (Ex. 24)	360	93
For Comparison: Mineral Oil	3% Zinc Dibutyl Dithio-carbamate.	0	3	205	40
Do.	3% P_2S_5 -terpene Reaction Product.	0	3	210	

Example 20:

Se dibutyldithiocarbamate	1.5
Mineral lubricating oil	Balance

Example 21:

Se dibutyldithiocarbamate	3
Pb petroleum naphthenate	1
Mineral lubricating oil	Balance

Example 22:

Se dibutyldithiocarbamate	3
Pb petroleum naphthenate	2
Mineral lubricating oil	Balance

Example 23:

Se dibutyldithiocarbamate	3.3
Tetrabutylthiuram disulfide	3.3
Pb petroleum naphthenate	6.7
Mineral lubricating oil	Balance

Example 24:

Se dibutyldithiocarbamate	5
Pb petroleum naphthenate	5
Mineral lubricating oil	Balance

Compositions of this invention were evaluated for their extreme pressure properties by use of the four-ball extreme pressure lubricant tester as described in Engineering, vol. 136, July 13, 1953. This apparatus comprises four steel balls arranged in a pyramid formation. The top ball is held in a chuck and rotated against the three bottom balls which are clamped in a stationary ball holder. The balls were immersed in the composition to be tested. Tests were run under conditions indicated in the following table and compared with other outstanding extreme pressure compounds.

Four-ball evaluation of E. P. compositions

[Fixed conditions: One minute, 1500 R. P. M. at ambient temperature, steel on steel. Base lubricant: Refined mineral oil]

Additive	Amount (Percent) Wt.	Scar Diameter (mm.) at Various Loads (Kg.)												
		20	40	60	80	90	100	140	200	300	400	500	600	700
Selenium dibutyl-dithiocarbamate..... +	6.6	-----	-----	.53	-----	-----	-----	-----	.91	-----	1.05	-----	1.3	1.7
Lead naphthenate (Example 1).....	6.7	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Selenium dibutyl-dithiocarbamate.....	3.3	-----	-----	.53	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tetrabutylthiuram disulfide.....	3.3	-----	-----	-----	-----	-----	-----	-----	.91	-----	-----	-----	-----	-----
Lead naphthenate (Example 23).....	6.7	-----	-----	-----	-----	-----	-----	-----	-----	-----	1.05	-----	1.3	1.7
Selenium dibutyl dithiocarbamate..... Do	6.6	.32	-----	.54	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Tetrabutylthiuram disulfide (Example 19).....	3.3	.32	-----	.54	-----	-----	-----	-----	-----	-----	2.07	2.18	W*	-----
Dodecyl diselenide.....	3.3	-----	-----	-----	-----	-----	-----	-----	-----	-----	2.07	2.18	W*	-----
Tributyl selenonophosphate.....	4.4	-----	.40	.45	.58	.69	-----	1.60	-----	-----	-----	-----	-----	-----
Lead Naphthenate.....	1	-----	-----	-----	.66	-----	2.32	-----	3.12	2.20	W*	-----	-----	-----
P ₂ O ₅ treated castor oil.....	10	.26	-----	.38	-----	-----	1.21	-----	2.03	W*	-----	-----	-----	-----
None.....	.2P	.29	-----	.65	-----	-----	.85	W*	-----	-----	-----	-----	-----	-----
		.30	.38	1.80	W*	-----	-----	-----	-----	-----	-----	-----	-----	-----

W* means welding of the four balls has occurred.

W* means welding of the four balls has occurred.

7

amount of a mineral lubricating oil and from about 0.1% to about 5% each of an oil-soluble divalent selenium dialkyldithiocarbamate, a polyalkyl thiuram disulfide and up to 10% of an oil-soluble metal naphthenate.

6. A lubricating composition comprising a major amount of a mineral lubricating oil and from about 0.1% to about 5% each of an oil-soluble divalent selenium dibutyldithiocarbamate and tetrabutyl thiuram disulfide.

7. A lubricating composition comprising a major amount of a mineral lubricating oil and from about 0.1% to about 5% each of an oil-soluble divalent selenium divalent dibutyldithiocarbamate, tetrabutyl thiuram disulfide, and up to 10% of an oil-soluble lead naphthenate.

8. A lubricating composition comprising a major amount of mineral lubricating oil, from about 3% to about 6.6% of a divalent selenium dibutyl dithiocarbamate, up to about 3.3% of tetrabutyl thiuram disulfide and up to about 6.7% of lead naphthenate.

8

9. A lubricating composition comprising a major amount of mineral lubricating oil, from about 0.1% to about 6.6% of divalent selenium dibutyl dithiocarbamate from about 0.1% to about 3.3% of tetrabutyl thiuram disulfide and from about 0.1% to about 6.7% of lead naphthenate.

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