United States Patent Office 2,796,402 Patented June 18, 1957

2,796,402

EXTREME PRESSURE LUBRICANT COMPOSITIONS

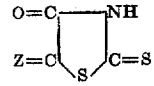
Herman D. Kluge, Wappingers Falls, N. Y., and Thomas C. Roddy, Jr., Port Arthur, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application November 16, 1953, Serial No. 392,502

14 Claims. (Cl. 252—47.5)

This invention relates to lubricating compositions characterized by antioxidant properties, freedom from corrosion and exceptional extreme pressure and anti-wear properties. More particularly, this invention discloses a novel lubricant additive which imparts a number of desirable properties to lubricating compositions.

The novel lubricating compositions of this invention comprise an oleaginous material having lubricating properties as the major component and a minor amount, sufficient to impart extreme pressure properties thereto, of a 2-thiono-4-ketothiazolidine compound of the general formula



wherein Z is selected from the group consisting of



and R''=

said R and R' being radicals selected from the group consisting of hydrogen and monovalent hydrocarbon residue and said R'' being a bivalent hydrocarbon residue having both valences on a single carbon atom. Monovalent hydrocarbon residue comprises aliphatic groups, aryl radicals, alkaryl radicals, aralkyl radicals, cycloaliphatic radicals and alkyl-substituted cycloaliphatic radicals. Bivalent hydrocarbon residue having both valences on the single carbon atom comprises alkylidene, cycloalkylidene and aryl alkylidene radicals. Advantageously, the hydrocarbon residue contains 1 to 20 carbon atoms.

The 2-thiono-4-ketothiazolidine component of the lubricating composition usually constitutes 0.01 to 2.0 percent of the entire lubricating composition. The incorporation of the 2-thiono-4-ketothiazolidine compound in lubricating compositions imparts exceptional extreme pressure and anti-wear properties in addition to improving the antioxidant and anticorrosive properties of the resulting lubricant composition.

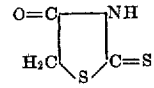
The increasing speeds and torques available in modern automotive equipment have caused increased bearing pressures and rigorous service conditions on the gear teeth of hypoid gears and on other instances of metal to metal contact. As a consequence, the extreme pressure requirements of lubricants have steadily risen and it has been necessary to incorporate extreme pressure agents in a great number of greases and lubricating oils. The most effective extreme pressure agents known prior to the instant invention were of the active sulfur, active halogen or combined active sulfur-halogen type. Active sulfur extreme pressure compounds are exemplified by sulfurized fatty acids and organic disulfides; an example of an active chlorine agent is chlorinated paraffin wax; combined active sulfur-chlorine agents are exemplified by sulfo-chlorinated sperm oil. These extreme pressure agents which require a concentration of about 3 to 15

percent of the total lubricant composition in order to be effective have the disadvantage that they tend to be corrosive and require the presence of oil-soluble corrosion inhibitors.

An outstanding advantage of 2-thiono-4-ketothiazolidine and its derivatives is that they impart anticorrosive properties to the resulting lubricant composition. The 2-thiono-4-ketothiazolidine compounds are particularly effective in combating corrosion of the silver bearings encountered in diesel engines and have displayed significant ability to combat the corrosive effects of active sulfur and active chlorine type compounds.

Another outstanding property of the 2-thiono-4-ketothiazolidine compounds of this invention is their effectiveness in very small concentrations. In contrast with the 3 to 15 weight percent concentration required for the display of extreme pressure properties by active sulfur and active chlorine compounds, the novel additives of this invention greatly enhance extreme pressure properties of lubricants when present in concentrations as low as 0.1 to 1.0 weight percent.

Rhodanine is the common chemical name of the 2-thiono-4-ketothiazolidine compound which is the initial member of the series of compounds which impart extreme pressure, anticorrosive and antioxidant properties to the lubricant compositions. The structural formula for rhodanine is



As far as can be ascertained, the groups which are essential to the functioning of rhodanine and its derivatives as extreme pressure, anticorrosive and antioxidant agents are the =C=S, =N—H and =C=O groups. The H atoms on the five position in the rhodanine ring structure can be substituted with a wide variety of hydrocarbon radicals and the resulting compound still retains its function as an extreme pressure agent possessing antioxidant and anticorrosive properties. Compounds in addition to rhodanine itself which are used in the lubricant compositions of this invention are exemplified by the following: 5-methyl-2-thiono-4-ketothiazolidine, 5,5-diethyl - 2 - thiono - 4 - ketothiazolidine, 5 - (2 - propenyl) - 2 - thiono - 4 - ketothiazolidine, 5 - (1 - butenyl)-2 - thiono - 4 - ketothiazolidine, 5 - benzal - 2 - thiono-4-ketothiazolidine, 5 - (1 - naphthyl) - 2 - thiono - 4 - ketothiazolidine, 5,5 - di(2 - ethylhexyl) - 2 - thiono - 4-ketothiazolidine, 5 - hexadecyl - 2 - thiono - 4 - ketothiazolidine, 5 - octylidene - 2 - thiono - 4 - ketothiazolidine, 5,5 - di(p - tolyl) - 2 - thiono - 4 - ketothiazolidine, 5(2-methylcyclohexyl) - 2 - thiono - 4 - ketothiazolidine, 5,5-di(2 - butyl) - 2 - thiono - 4 - ketothiazolidine, 5 - phenyl-2 - thiono - 4 - ketothiazolidine and 5 - cyclohexylidene-2-thiono-4-ketothiazolidine.

The incorporation of rhodanine and its 5-substituted compounds imparts exceptional extreme pressure properties as well as antioxidant and anticorrosive properties to both greases and lube oil compositions. The concentration of the additive in both greases and oils is usually within the 0.01 to 2.0 weight percent concentration range; in general, concentrations of additives in the upper portion of the cited range are used in grease compositions, whereas concentrations in the lower part of the prescribed limits are employed in lube oil compositions.

The oleaginous lubricating base can be a hydrocarbon mineral oil, a synthetic lubricating base or mixtures thereof. If a hydrocarbon mineral oil is the base, it is either a paraffin base or a naphthene base fraction which advantageously has undergone solvent refining to improve its lubricity and its viscosity-temperature relationships. For certain applications such as greases, straight

vacuum distillate lube fractions that have not undergone extensive solvent refining are employed as the lubricating base in which rhodanine and its derivatives are incorporated. In general, it can be stated that a wide variety of lube oil fractions are contemplated for use in the lubricating compositions of this invention; for example, paraffin base and naphthene base lube oil fractions having an SUS viscosity at 100° F. between 50 and 5,000 may be used as the base oil in the compositions of this invention.

The synthetic lubricating bases are usually of the ester or ether type. High molecular weight, high boiling liquid aliphatic dicarboxylic acid esters possess excellent viscosity-temperature relationships and lubricating properties and are finding ever increasing utilization in lube oils and greases adapted for high and low temperature lubrication; esters of this type are used in the formulation of jet engine oils and of greases designed for low temperature operation. Examples of this class of synthetic lubricating bases are the diesters of acids such as sebacic, adipic, azelaic, alkenylsuccinic, etc.; specific examples of these diesters are di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, di-2-ethylhexyl adipate, di-n-amyl sebacate, di-2-ethylhexyl-n-dodecyl succinate, di-2-ethoxyethyl sebacate, di-2'-methoxy-2-ethoxyethyl sebacate (the methyl Carbitol diester), di-2'-ethyl-2-n-butoxyethyl sebacate (the 2-ethylbutyl Cellosolve diester), di-2-n-butoxyethyl azelate (the n-butyl Cellosolve diester) and di-2'-n-butoxy-2-ethoxyethyl-n-octyl succinate (the n-butyl Carbitol diester).

Polyester lubricants formed by a reaction of an aliphatic dicarboxylic acid of the type previously described, a glycol and a monofunctional aliphatic monohydroxy alcohol or an aliphatic monocarboxylic acid in specified mol ratios are also employed as the synthetic lubricating base in the compositions of this invention; polyesters of this type are described in U. S. 2,628,974. Polyesters formed by reaction of a mixture containing specified amounts of dipropylene glycol, sebacic acid and 2-ethylhexanol and of a mixture containing adipic acid, diethylene glycol and 2-ethylhexanoic acid illustrate this class of synthetic polyester lubricating bases.

Polyalkylene ethers as illustrated by polyglycols are also used as the lubricating base in the compositions of this invention. Polyethylene glycol, polypropylene glycol, polybutylene glycols and mixed polyethylene-polypropylene glycols are examples of this class of synthetic lubricating bases.

The sulfur analogs of the above-described diesters, polyesters and polyalkylene ethers are also used in the formulation of the lubricating compositions of this invention. Dithioesters are exemplified by di-2-ethylhexyl thiosebacate and di-n-octyl thioadipate; polyethylene thioglycol is an example of the sulfur analogs of the polyalkylene glycols; sulfur analogs of polyesters are exemplified by the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

The lubricant compositions containing rhodanine or its 5-substituted derivatives have a wide variety of applications. Since rhodanine and its prescribed derivatives impart anti-wear, exceptional extreme pressure, antioxidant and anticorrosive properties to lubricant compositions even when present in very small concentrations, rhodanine-containing lubricants, either of hydrocarbon base or synthetic base type, are designed for a wide variety of uses. A partial lis' of the uses for rhodanine-containing lube oils is as follows: motor oils for lubrication of internal combustion auto engines, airplane oils, diesel oils, jet engine oils which are usually of the synthetic base variety, cutting oils, grinding oils, cylinder oils, hydraulic oils, automatic transmission fluids and valve oils. Rhodanine-containing greases find application as chassis greases, ball and roller bearing greases, rail and flange lubricants, all types of gear lubrication, traction motor lubricants and all types of bearing lubricants.

Rhodanine and its 5-substituted derivatives are compatible with a wide variety of additives employed in the formulation of lube oils and greases. In most applications of the lubricants of this invention other additives will be incorporated to help the lubricant meet the specifications prescribed for a specific utilization. Accordingly, in most applications in lube oil compositions rhodanine and its derivatives will be used in conjunction with one or more of the following types of additives: detergents, illustrated by salts of petroleum sulfonates and divalent alkaline earth metal salts of alkylphenols; antioxidants as illustrated by phenothiazine and polyalkyl-substituted phenols; corrosion inhibitors such as sulfurized terpenes; anti-rust agents as illustrated by alkenylsuccinic acids; extreme pressure agents as illustrated by aryl phosphates, sulfurized oils and fats, chlorinated hydrocarbons and sulfo-chlorinated hydrocarbons and organic acids. In greases, the most common additive with which rhodanine and its derivatives will be found are antioxidant and extreme pressure agents; antioxidants are exemplified by phenyl alpha-naphthylamine; extreme pressure agents are similar to those employed in lube oils.

The effectiveness of rhodanine and its derivatives in combating silver corrosion was demonstrated in the EMD corrosion test which is used to determine the corrosiveness of heavy duty lubricating oils toward silver metal. The test gives an indication whether the oil is suitable for use in EMD (Electromotive Division) diesel engines containing silver plated wrist pin bushings.

The EMD corrosion test is run by placing silver strips or silver-plated wrist pin bushings in the sample of oil under test which is maintained with stirring at 300 R. P. M. at a temperature of 300° F. + or −2° F. The appearance and weight changes of the strips or bushings are determined periodically with 24 and 72 hours being the most common test periods employed. If the silver-plated wrist pin bushing, which has an approximate size of 3" x ¼", is used, it is pretreated at a temperature of about 140° F. with acetic acid-hydrogen peroxide solution comprising 3 parts glacial acetic acid and 1 part 30 percent hydrogen peroxide solution to remove lead flashing from the surface. After complete removal of the lead as determined by visual observation, the bushing is immersed in distilled water, dried, polished with steel wool, cleaned with lintless paper and weighed. In the following tests, silver strips which have a surface area equivalent to that of exposed silver on the bushing, specifically 3.50" x 0.75" x 0.005", were employed. With the silver strips, the acetic acid-hydrogen peroxide treatment is eliminated and the strips are directly polished with steel wool, cleaned with lintless paper and weighed to the nearest mg.

In the test, all observations and weight changes are recorded; on the basis of the observation and weight changes, the oil is rated according to the following classifications:

Appearance and Wt. Change of Silver Specimen After 72 Hrs.	Classification
Appearance Unchanged:	
Max. 5 mg. wt. change	1
6–25 mg. wt. change	4
Over 25 mg. wt. change	5
Discoloration or non-scaly non-flaking deposit on strip:	
Max. 5 mg. wt. change	2
6–25 mg. wt. change	3
Over 25 mg. wt. change	5
Scaly or flaking deposit on strip	5

If strips from duplicate tests do not fall in the same classification, repeat test singly and rate the oil as 2 of the 3 strips indicate.

The base oil used in the EMD corrosion test was a heavy duty lube oil containing a high concentration of detergent and inhibitor; the reference oil was an SAE 40 grade mixture having a V. I. of 55 and comprising 47.2 percent solvent refined paraffin residuum, 41.0 percent acid refined naphthene distillate fraction and 11.8

percent solvent refined paraffin distillate, and containing 2.4 percent basic barium sulfonate, 0.75 percent zinc alkyl dithiophosphate, 0.37 percent barium alkyl dithiophosphate and 0.225 percent neutral terpene-P_2S_5 reaction product. The additives used in the above composition are well known lubricant additives, which are more particularly described as follows: Basic barium sulfonate designates products resulting from the reaction of petroleum sulfonic acids with barium hydroxide in such proportions that the resulting mixture contains one free hydroxyl group. Divalent metal alkyl dithiophosphates, specifically, zinc and barium alkyl dithiophosphates, are formed by neutralization of the reaction product of phosphorus pentasulfide and monohydroxy alcohols, particularly lauryl alcohol, cyclohexanol and capryl alcohol, with an excess of powdered metal or metal oxide. A neutral terpene-P_2S_5 product is obtained by oxidation of the reaction product of P_2S_5 with a terpene such as pinene, limonene, terpinene, dipentene and mixtures thereof.

The effect of rhodanine and its 5-substituted derivatives on the silver corrosion properties of the above base oil is shown in Table I.

TABLE I

EMD corrosion test (24 hr.)

	Silver Wt. Change, mg.	Silver Appearance	Rating
1. Base oil	−14	Black flaky deposit.	5
2. Base Oil + 0.25% Rhodanine (blend filtered).	+1	Gray powdery deposit.	2
3. Reblend of (2)	0	Very slight gray stain.	2
4. Base Oil + 0.25% 5-butylidene Rhodanine.	0	Slight gray powdery deposit and peacock stain.	2
5. Base Oil + 0.25% 5-octylidene Rhodanine.	0	Gray powdery deposit.	2

The extreme pressure properties of rhodanine and its derivatives in turbine oils was demonstrated by the Falex pop-up test, the Falex wear test and the mean Hertz load test.

The Falex pop-up test is run on a Falex machine, which is a standard tester; the testing procedure is as follows:

Duration	Until failure.
Test temperature	210° F.
Oil charge	55 cc.
Speed	290 R. P. M. or 19 ft. per min.

The steel pin, steel blocks and boat are cleaned with Stoddard Solvent and dried. The blocks are placed in the jaws at a V-block angle of 86 to 106°, and the pin fastened to the driving shaft. The test lubricant is poured in the boat and heated to test temperature. The test is started and run for 3 minutes at 300 lb. load; the test is then run for 1 minute at a load of 500 lbs.; the load is increased in 250 lb. increments every 1 minute until seizure occurs (sudden rise in torque—pop-up). The operator takes readings every minute and reports the time in minutes and seconds of seizure load, torque, condition of blocks and pin.

The Falex wear test is carried out on the same piece of equipment in the following manner:

Duration	2 or 3 hrs.
Test temperature	As specified, usually 250 or 300° F.
Oil charge	55 cc. per run.
Speed	290 R. P. M. or 19 ft. per min.

The specified blocks having a V-block angle of 86 to 106° and pin are cleaned with Stoddard Solvent and dried. The oil in the boat is brought to the specified test temperature. The load is applied by means of a hydraulic loading device. The test is started and run at half load for ten minutes. It is then run for 2 hours at full load. The load is checked at 15 minute intervals, the temperature and torque are recorded, the weight loss on test specimens at the end of test is measured and the loss is recorded.

The mean Hertz load test is described in U. S. 2,600,058.

The reference turbine oils used in the above tests were naphthene base oils which had been subjected to a refining treatment comprising acid treatment, neutralization, steaming and brightening by air blowing. Both base oils had an SSU viscosity at 100° F. of 485 to 515 and at 130° F. of 185 to 205, a °API gravity of 20.5 to 23.5 and a pour of −10° F. maximum. One of the oils, designated Base Oil "A," is uninhibited, whereas the other oil, designated Base Oil "B," is inhibited against rust and oxidation. The inhibited Oil "B" contains 0.3 weight percent 4-methyl-2,6-ditertiary-butylphenol which acts as an oxidation inhibitor, 0.033 weight percent of an anti-rust concentrate comprising approximately 45.5 weight percent C_{10} to C_{12} alkenyl succinic acid, 7.5 weight percent dilauryl acid orthophosphate, 47 percent lube oil and 0.001 weight percent kerosene concentrate containing about 12 weight percent dimethyl silicone.

The improvement wrought by the incorporation of rhodanine and 5-substituted rhodanines on the extreme pressure properties of turbine oils is shown in Table II.

TABLE II

Extreme pressure tests on turbine oils

	Falex Pop-up lb. (specimen face load)	Falex 2 Hr. Wear, 250°F, steel on steel, 200 lb. load; mg. wt. loss	Mean Hertz Load, kg.
Base Oil "A"	500, 700	scuffed	<14
Base Oil "A" + 0.25% 5-octylidene-rhodanine.	1,000, 750	8, 8	31
Base Oil "B"	500, 500	excessive	14
Base Oil "B" + 0.25% rhodanine.	1,250, 1,250	20, 25	25

The data in Table II clearly show that very small amounts of rhodanine and 5-octylidene rhodanine effect a substantial improvement in the extreme pressure properties of turbine oils. The substantial improvements in the Falex pop-up test, mean Hertz load test and the Falex two-hour wear test effected by 0.25 percent of rhodanine compound are particularly significant.

The effectiveness of rhodanine in improving the extreme pressure properties of synthetic hydraulic oils was demonstrated by the mean Hertz load test, the seizure-weld test and the one-hour wear test. The seizure-weld test is a measure of the extreme pressure properties of a lubricant, and is included in Government Specification MIL-L-7808; the test is run on the Shell four-ball machine.

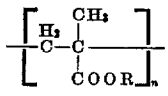
The one-hour wear test is also run on the Shell four-ball machine, and is effected under the following conditions:

Duration	1 hour at each load.
Test temperature	No heat control.
Oil charge	15 cc.
Speed	1,800 R. P. M.

The balls, first grade SKF steel, are cleaned with Stoddard Solvent and MEK, then dried; the lower balls are locked in position and a fresh 10 to 15 cc. charge of test oil is poured into the test cup. A one-hour run at 1,800 R. P. M., 140 ft. per min., is made at 1, 10 and 40 kg. loads. The scar diameters of the three lower balls are measured horizontally and vertically and the average of the six readings is taken. From this, the conversion of scar diameter in millimeters is obtained. The torque counter readings are taken at the end of 1, 10, 30 and 60 minutes.

The base hydraulic oil comprises 82.5 weight percent

di(2-ethylhexyl) azelate, 0.5 percent phenothiazine, 17 percent of a methacrylate ester polymer having the following general formula



wherein R is a butyl radical and *n* is an integer greater and 1, and 150 parts per million of dimethyl silicone. This mixture is characterized by high V. I. and good corrosion resistance. The effect of a small concentration of rhodanine on the extreme pressure properties of this synthetic base hydraulic oil is shown in Table III.

TABLE III

Extreme pressure tests on synthetic hydraulic oils

	Mean Hertz Load	Seizure-Weld	One Hour Wear		
			1 kg.	10 kg.	40 kg.
Base oil	20	Fail	0.406	0.615	0.851
Base oil+0.1% Rhodanine	39	Pass	0.165	0.396	0.470
Base oil+0.2% Rhodanine	54	Pass	0.178	0.257	0.389

The ability of rhodanine to improve the extreme pressure properties of grease mixtures was demonstrated in a mixed lithium-calcium base grease. The base grease comprised 20.7 percent of a fatty acid soap mixture comprising 60 weight percent lithium soap and 40 weight percent calcium soap formed by saponification of a fatty acid mixture containing 3 parts of hydrogenated castor oil and 1 part of triple pressed stearic acid, 77.1 percent of a base oil comprising 3 parts of di(2-ethylhexyl) sebacate and 1 part of a naphthene base oil having an SSU viscosity at 100° F. of 96 to 104, a gravity °API of 27 to 31 and a pour of 25 maximum, 1.5 percent glycerine, 0.2 percent excess lithium hydroxide and 0.5 percent of a stabilizer comprising 95 percent diphenylamine and 5 percent salicylal amino guanidine oleate. The mean Hertz load test was used to illustrate the effect of rhodanine on the extreme pressure properties of the grease. The effect of rhodanine on the extreme pressure properties of this base grease designated Li-Ca low temperature grease is shown in Table IV.

TABLE IV

Extreme pressure tests on grease

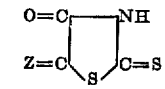
	Mean Hertz Load
Li-Ca Low Temp. Grease	20
Li-Ca Low Temp. Grease+1% Rhodanine	45

The 25-unit improvement in mean Hertz load effected by the incorporation of 1 percent rhodanine in the Li-Ca low temperature grease is particularly noteworthy. It has been necessary to use 5 to 10 percent of prior art extreme pressure agents in order to effect an improvement of this magnitude.

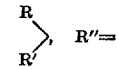
Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating composition comprising an oleaginous material selected from the group consisting of hydrocarbons, esters, polyethers, and mixtures thereof having lubricating properties as the major component and a minor amount sufficient to impart extreme pressure properties thereto of a 2-thiono-4-ketothiazolidine compound having the general formula



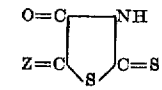
wherein Z is selected from the group consisting of



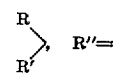
said R and R' being selected from the group consisting of hydrogen and a monovalent hydrocarbon radical and said R'' being a divalent hydrocarbon radical having both valences on a single carbon atom.

2. A lubricating composition as described in claim 1 in which said 2-thiono-4-ketothiazolidine compound comprises 0.01 to 2.0 percent of the total composition.

3. A lubricating composition comprising a hydrocarbon mineral oil having lubricating properties and a minor amount sufficient to impart extreme pressure properties thereto of a 2-thiono-4-ketothiazolidine compound having the general formula



wherein Z is selected from the group consisting of



said R and R'' being selected from the group consisting of hydrogen and a monovalent hydrocarbon radical and said R'' being a divalent hydrocarbon radical having both valences on a single carbon atom.

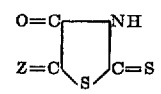
4. A lubricating composition as described in claim 3 in which the 2-thiono-4-ketothiazolidine compound is rhodanine.

5. A lubricating composition as described in claim 3 in which the 2-thiono-4-ketothiazolidine compound is 5-alkylidene rhodanine.

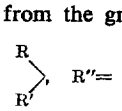
6. A lubricating composition as described in claim 3 in which the 2-thiono-4-ketothiazolidine compound is a 5-substituted rhodanine having at least one aliphatic hydrocarbon radical on the 5 position.

7. A lubricating composition as described in claim 3 in which the 2-thiono-4-ketothiazolidine compound is a 5-arylalkylidene rhodanine.

8. A lubricating composition comprising an oleaginous ester-type lubricating base as the major component and a minor amount sufficient to impart extreme pressure properties thereto of a 2-thiono-4-ketothiazolidine compound having the general formula



wherein Z is selected from the group consisting of



said R and R' being selected from the group consisting of hydrogen and a mono-valent hydrocarbon radical and said R'' being a divalent hydrocarbon radical having both valences on a single carbon atom.

9. A lubricating composition as described in claim 8 in which the 2-thiono-4-ketothiazolidine compound is rhodanine.

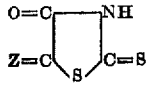
10. A lubricating composition as described in claim 8 in which the 2-thiono-4-ketothiazolidine compound is 5-alkylidene rhodanine.

11. A lubricating composition as described in claim 8 in which the 2-thiono-4-ketothiazolidine compound is a

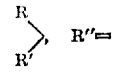
5-substituted rhodanine having at least one aliphatic hydrocarbon radical on the 5 position.

12. A lubricating composition as described in claim 8 in which the 2-thiono-4-ketothiazolidine compound is a 5-arylalkylidene rhodanine.

13. A lubricating grease composition comprising a mixed mineral oil-ester lubricating base, a fatty acid soap mixture in an amount sufficient to thicken said lubricating base, and a minor amount sufficient to impart extreme pressure properties thereto of a 2-thiono-4-ketothiazolidine compound having the general formula



wherein Z is selected from the group consisting of



said R and R′ being selected from the group consisting of hydrogen and a mono-valent hydrocarbon radical and said R″ being a divalent hydrocarbon radical having both valences on a single carbon atom.

14. A lubricating grease composition according to claim 13 in which said 2-thiono-4-ketothiazolidine compound is rhodanine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,154,096	Loane	Apr. 11, 1939
2,213,804	Lincoln et al.	Sept. 3, 1940