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EXTREME PRESSURE LUBRICANT COMPOSITIONS

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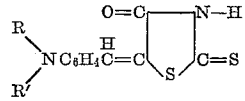
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5 Claims. (Cl. 252—47.5)

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.

In a commonly-owned copending application, Serial No. 392,502, filed November 16, 1953, in the names of Herman D. Kluge and Thomas C. Roddy, Jr., it is disclosed that rhodanine and its 5-hydrocarbon-substituted compounds impart excellent extreme pressure properties and protection against silver corrosion to lubricating compositions. The subject invention involves the discovery that 5-alkylaminobenzylidenerhodanines, also identified as 5-alkylaminobenzylidene-2-thiono-4-keto-thiazolidines, impart extreme pressure properties and protection against silver corrosion 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 and anticorrosive properties thereto of a 5-alkylaminobenzylidenerhodanine compound of the general formula



wherein R is either hydrogen or an aliphatic radical and R′ is an aliphatic radical; aliphatic radical includes both alkyl and alkenyl groups. The 5-alkylaminobenzylidenerhodanine usually constitutes 0.01 to 2.0 percent of the total lubricating composition.

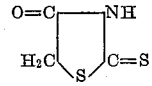
The increasing speeds and torques available in modern automotive equipment have caused increased bearing pressures and rigorous service conditions on the gear teeth of hypoid gears and on other instances of metal-on-metal contact. As a consequence, the extreme pressure requirements of lubricants have 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 sulfurhalogen 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 5-alkylaminobenzylidenerhodanines is that they impart anticorrosive properties to the resulting lubricant composition. These 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 5-alkylaminobenzylidenerhodanines 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 and anticorrosive properties of lubricants when present in concentrations as low as 0.1 to 1.0 weight percent.

Rhodanine is the common chemical name of 2-thiono-4-ketothiazolidine, which has the following structural formula:



Rhodanine compounds containing an alkylaminobenzylidene radical on the 5 position and used in the lubricant compositions of this invention are exemplified by the following: 5-p-dimethylaminobenzylidenerhodanine, 5 - p - methylaminobenzylidenerhodanine, 5 - m - dipropylaminobenzylidenerhodanine, 5-o-ethylaminobenzylidenerhodanine, 5-o-methylbutylaminobenzylidenerhodanine, 5-p-di-isobutylaminobenzylidenerhodanine, 5-m-hexylaminobenzylidenerhodanine and 5-p-di-1-butenylbenzylidenerhodanine.

It will be noted that the amino group contains at least one alkyl substituent. The aliphatic substituents on the amino group may contain 1 to 15 or more carbon atoms, but normally contain 1 to 6 carbon atoms. As is evident from the foregoing list of compounds, alkylamino group can be meta, ortho or para to the methylene group attached to the 5 position on the rhodanine nucleus.

The incorporation of 5-alkylaminobenzylidenerhodanine 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 rhodanine compounds 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 5-alkylaminobenzylidenerhodanines 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 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, alkenyl succinic, 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 molar 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 5-alkylaminobenzylidenerhodanines have a wide variety of applications. Since these compounds impart anti-wear, exceptional extreme pressure, antioxidant and anticorrosive properties to lubricant compositions even when present in very small concentrations, the lubricating compositions of this invention are designed for a wide variety of uses. A partial list of their uses 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. Greases containing 5-alkylaminobenzylidenerhodanines find application as chassis greases, ball and roller bearing grease, rail and flange lubricants, all types of gear lubricants, traction motor lubricants and all types of bearing lubricants.

5 - alkylaminobenzylidenerhodanine compounds 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 lube oil compositions, 5-alkylaminobenzylidenerhodanine compounds are used in conjunction with one or more of the following type 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 alkenyl succinic 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 additives with which 5-alkylaminobenzylidenerhodanine compounds are associated 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 5-alkylaminobenzylidenerhodanine compounds 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. ±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 1" x .25" 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 strip is 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 Hours	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, the test is repeated and the oil is rated 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 5-alkylaminobenzylidenerhodanine compounds on the silver corrosion properties of the above base oil is shown in Table I.

TABLE I

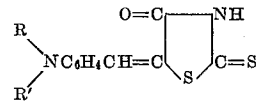
EMD corrosion test (24 hr.)

	Silver Wt. Change, mg.	Silver Appearance	Rating
Base oil	−14	Black flaky deposit.	5
Base oil +0.25% 5-(p-dimethylaminobenzylidene) rhodanine (filtered).	0	Black powdery deposit.	2

Obviously, many modifications and variations of the invention as above 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.

I claim:

1. A lubricating composition comprising a mineral lubricating oil having lubricating properties as the major component and a minor amount sufficient to impart extreme pressure and anticorrosive properties thereto of a 5-alkylaminobenzylidenerhodanine compound having the general formula



wherein R is selected from the group consisting of hydrogen and an aliphatic radical and R′ is an aliphatic radical.

2. A lubricating composition as described in claim 1 in which said 5-alkylaminobenzylidenerhodanine comprises 0.01 to 2.0 percent of the total composition.

3. A lubricating composition as described in claim 1 in which said rhodanine compound is 5-p-dialkylaminobenzylidenerhodanine.

4. A lubricating composition according to claim 1 in which the aliphatic radicals desginated by R and R′ contain 1 to 6 carbon atoms.

5. A lubricant composition according to claim 1 in which said rhodanine compound is 5-(p-dimethylaminobenzylidene) rhodanine.

References Cited in the file of this patent

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2,213,804 Lincoln et al. ---------- Sept. 3, 1940