United States Patent Office 2,816,075 Patented Dec. 10, 1957

2,816,075

LUBRICATING OIL COMPOSITIONS

Ellis K. Fields, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

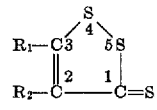
No Drawing. Application June 1, 1954, Serial No. 433,789

2 Claims. (Cl. 252—45)

This invention relates to lubricating oils of improved properties and particularly to lubricating oil compositions containing aryl substituted trithiones in amounts effective to improve the base oil with respect to bearing corrosion.

Although a wide variety of chemical additives have been proposed and used as bearing corrosion inhibitors in lubricating oil compositions, the requirements of an additive combining a high degree of effectiveness with satisfactory oil solubility and stability in use under a wide variety of conditions have not been satisfied. I have discovered that aryl substituted trithiones are effective inhibitors of bearing corrosion when incorporated in lubricating oil compositions. The resulting compositions are stable in use, and the inhibitors have the advantage that they may be reproduced readily to specification since they are simple chemical compounds rather than the complex reaction products of unknown chemical constitution of ordinary usage.

The trithiones have the following chemical formula:



where at least R_1 or R_2 is an aryl or substituted aryl group and the other may be hydrogen or an alkyl or substituted alkyl group. The trithiones may be readily prepared in quantity and in a commercially satisfactory manner by the process disclosed in my co-pending application SN 433,788 filed June 1, 1954. According to the process there disclosed, an alkyl substituted aromatic of cumene type structure is reacted with sulfur in the presence of a small amount of an aryl guanidine as a catalyst. The reaction is conducted at a temperature of about 140°–230° C. for a period of time sufficient to complete the reaction. The reaction mixture is cooled; the crystalline product is filtered free and may be washed with benzene or other light hydrocarbon solvent.

The new inhibitors are distinguished structurally by the presence of 2 sulfur atoms in the 5 membered heterocyclic ring and by the presence of an additional side chain sulfur attached as a free sulfide group to the unsubstituted carbon atoms of the ring. The structural configuration of sulfur in my inhibitors may be significant because I have found that they are surprisingly superior to the disulfide heterocyclic type inhibitor disclosed in Lincoln and Byrkit Patent 2,213,804 when evaluated for bearing corrosion inhibiting properties. The aryl substituent may be in the number 2 or number 3 ring position, numbering counter-clockwise from a ring sulfur atom to the adjacent ring carbon atom. The aryl substituent may be a simple phenyl group, a substituted phenyl group or a naphthalene group. The substitution of the aryl group may be utilized to modify favorably oil solubility and film forming properties of the additives but should not be inconsistent with use of the additive in lubricating compositions. For example, alkyl phenyl substituted trithiones such as 2-(p-t-butyl phenyl) trithione and alkoxy phenyl trithiones such as 3-(p-methoxy phenyl) trithione have particular effectiveness as bearing corrosion inhibitors for use in lubricating oil composition. The number 3 carbon atom of the ring also may be substituted as will be the case when the hydrocarbon employed in the preparation of the trithione is more than 3 carbon atoms in the chain, i. e., for side chain aromatics higher than cumene. Other substituents such as oxygen, nitrogen or halogen containing groups, for example, may be present in the inhibitor molecules provided such groups do not impair effectiveness or oil solubility and stability.

The trithione inhibitors are ordinarily added to the base oil in small amounts, say in the range of about 0.01 to 2 weight percent of the oil and usually in the range of about 0.1 to 1 weight percent. In practice, the lubricating oil compositions of my invention will ordinarily contain other compatible additives. Thus, the finished oil compositions may contain in varying amounts one or more additives such as an oil soluble detergent, an anti-oxidant, a viscosity index improver, a pour depressant and the like. In addition, where the solubility of the trithione inhibitor in oil is low as is the case with 2-phenyl-trithione, for example, it is advantageous to use an oil soluble detergent to solubilize it.

I shall illustrate the application of my invention in more specific form by describing the preparation of specific trithione inhibitors and by reference to corrosion test data on oil blends containing representative trithione inhibitors. I do not intend to limit the invention however to the specific materials and details expressly described.

In the example, illustrating the preparation of the trithiones, a copper strip corrosion (ICCS) test was employed as a measure of the degree of completion of the reaction. The copper strip corrosion was run by suspending a small strip of polished copper in a 1% solution of the product to be tested in an inert hydrocarbon such as high boiling ligroin or refined oil. The solution is heated for 1 hour at 212° F. Free sulfur will cause the strip to turn black. A determination of relative corrosivity is obtained by comparison with a scale of standard strips numbered from 0 to 12. A perfect strip is rated 0, and a corrosion number of 2 to 6 on the scale is an indication of complete reaction of the sulfur charged.

EXAMPLE I

A mixture of 400 grams of sulfur, 1100 grams of p-cymene and 5 grams di-orthotolylguanidine was refluxed at 180–185° C. for 11 hours. The copper strip corrosion (ICCS) on a sample at this time was 5. The mixture was cooled to 10° C., and the red crystals of 2-(p-methyl phenyl)-trithione formed were collected on a filter, washed with 100 cc. cold benzene and sucked dry. The yield was 355 grams, of product of melting point 119–120° C. A sample was recrystallized from benzene for analysis and had a melting point of 122–123° C. Analysis:

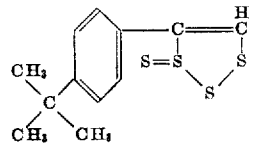
	C, percent	H, percent	S, percent	mol. wt.
Calculated for $C_{10}H_8S_3$	53.60	3.57	42.83	224
Found	54.00	3.80	42.60	229

Unreacted cymene, 575 grams, was recovered by distillation of the filtrate.

EXAMPLE II

p-t-Butyl cumene, B. P. 220–224° C. was prepared according to H. Barbier, Helvetica Chim. Acta 19, 1345

(1936). A mixture of 105.6 grams (0.6 mole) of p-t-butyl cumene, 28.8 grams of (0.9 mole) sulfur and 0.4 grams (0.3%) of di-o-tolylguanidine was stirred at 184° C. for 24 hours, cooled to 5° C. for 4 hours and filtered, giving 21 grams of red crystals. Seventy grams p-t-butyl cumene B. P. 77–82° C./4.2 were recovered from the filtrate. The crystals were recrystallized from 5W lubricating oil, giving brilliant golden leaflets, M. P. 145° C. which analyzed for 2-p-t-butyl phenyl trithione



Analysis.—Calculated for $C_{13}H_{14}S_3$: C, 58.61%, H, 5.27%; S, 36.09%; molecular weight, 266. Found: C, 59.25%; H, 5.20%; S, 35.70%; molecular weight, 262.

A number of representative trithiones including the products of Examples 1 and 2 were evaluated for effectiveness as bearing corrosion inhibitors by incorporation in a lubricating base oil and subjecting to a stirring sand corrosion test (SSCT). The base oil was an SAE–30 distillate from a mid-continent crude oil which had been propane-dewaxed and chlorex solvent extracted. The oil blends tested contained detergent type additive of the type comprising alkali metal and alkaline earth metal salts of phosphorous pentasulfide-butylene polymer reaction products in concentrations ineffective to influence corrosivity of the base oil under the conditions of the SSCT test.

The SSCT test is conducted as follows: A copper-lead test specimen is lightly abraded with steel wool, washed with naphtha, dried and weighed to the nearest milligram. The cleaned copper-lead test specimen is suspended in a steel beaker, cleaned with a hot tri-sodium phosphate solution, rinsed with water and acetone and dried. 250 grams of the oil to be tested, together with 0.625 grams lead oxide and 50 grams of a 30–35 mesh sand are charged to the beaker. The beaker is then placed in a bath or heating block and heated to a temperature of 300° F. (±2° F.) while the contents are stirred by means of a stirrer rotating at 750 r. p. m. The contents of the beaker are maintained at this temperature for twenty-four hours, after which the copper-lead test specimen is removed, rinsed with naphtha, dried and weighed. The test specimen is then replaced in the beaker and an additional 0.375 grams of lead oxide added to the test oil. At the end of an additional twenty-four hours of test operation the test specimen is again removed, rinsed and dried as before, and weighed. The test specimen is again placed in the beaker together with an additional 0.250 grams of lead oxide and the test continued for another twenty-four hours (seventy-two hours total). At the conclusion of this time, the test specimen is removed from the beaker, rinsed in naphtha, dried and weighed. The loss in weight of the test specimen is recorded after each weighing. A weight loss of 200 mg. or less in 48 hours and 500 mg. or less in 72 hours is allowable.

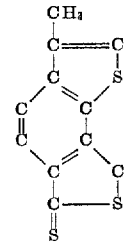
The test data are tabulated in Table I as follows:

Table I

Trithione	ICCS Number	Concentration in Base Oil, percent	SSCT, wt. loss, mgs.	
			48 hours	72 hours
2-phenyl-	3	[1] 0.75	28	233
2-(p-methyl phenyl)-	2–3	[1] 0.75	147	358
3-(p-methoxy phenyl)-	2–3	[2] 0.50	11	28
2,3-(methyl thiophenobenzo)-	1–2	[1] 0.75	42	158
2-p-t-butyl phenyl-		[3] 1.0	1	2
Blank [3]			669	

[1] Contains 3.3% of a neutral barium salt of a phosphorous pentasulfide-butylene polymer reaction product.
[2] Contains 1.65% of a potassium salt of a phosphorous pentasulfide-butylene polymer reaction product.
[3] Contains 5.98% of an alkaline barium salt of a phosphorous pentasulfide-butylene polymer reaction product.

From the data of the above table, the effectiveness of the trithiones as bearing corrosion inhibitors is apparent. Although the 2,3-(methyl-thiophenobenzo)-trithione of the table was prepared from *dl*-limonene the resulting product analyzed for a fused ring aryl substituted trithione of the following apparent structure:



and hence is within the intended scope of the invention.

To further test the effectiveness of the aryl substituted trithiones as bearing corrosion inhibitors, a blend of p-t-butyl phenyl trithione in the SAE–30 base oil at 1% concentration, containing 5.44% of an alkaline barium salt of a phosphorous pentasulfide-butylene polymer reaction product, was tested by the procedure of the L–4 engine test. (C. R. C. Designation L–4–545, C. R. C. Handbook, 1946 edition, Coordinating Lubricants Research Council, New York, N. Y.) The bearings were smooth with weight losses of 0.097, 0.034 and 0.113 grams respectively. The oil rated by varnish and sludge deposits passed the test satisfactorily. The detergent type additive employed is representative of the class disclosed in U. S. Patent No. 2,316,082 to Loane and Gaynor, and compatibility and advantageous cooperation between it and the new bearing corrosion inhibitor was apparent under engine test conditions.

I claim:

1. A lubricating oil composition which consists essentially of a lubricating oil normally corrosive to bearing surfaces and a small amount effective to inhibit bearing corrosion of 2-(p-t-butylphenyl)-trithione.

2. A lubricating oil composition which consists essentially of a detergent containing lubricating oil normally corrosive to bearing surfaces, and a small amount effective to inhibit bearing corrosion of 2-(p-t-butyl phenyl) trithione.

References Cited in the file of this patent

UNITED STATES PATENTS

2,653,910 Airs et al. ---------- Sept. 29, 1953