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LUBRICATING OIL CONTAINING A MONOESTER OF A THIODIACETIC ACID

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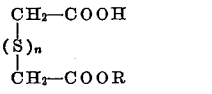
No Drawing. Application March 3, 1949, Serial No. 79,516

4 Claims. (Cl. 252—48.6)

1

This invention relates to lubricating oil compositions, and it is more particularly concerned with lubricating oils containing a multifunctional additive, namely, certain monoesters of thiodiacetic acids.

The monoesters of the thiodiacetic acids contemplated herein are compounds having the general formula,



wherein R is an aliphatic radical which has a normal chain length of at least about ten carbon atoms and n is a small whole number equal to at least one.

As is well known to those familiar with the art, rusting of ferrous metal surfaces is frequently encountered during the operation of steam turbines, particularly during the initial operation of new installations. Such rusting is most pronounced at points where the clearance between bearing surfaces is very small, such as in the governor mechanism. Manifestly, this constitutes a menace to the operational life of the turbine. When rusting is very severe, particles of rust may form on the main bearing surfaces, or be carried there by the circulating oil, and severely injure these bearings. This menace is usually caused by water entering the oil supply, as by condensation, and being entrained by the oil throughout the circulatory system, thereby coming into contact with ferrous metal surfaces.

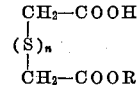
Very severe rusting conditions are encountered during the operation of marine turbines. This is due to the fact that the lubricating oil must circulate through the main drive gear system and the hydraulic system, as well as the turbine lubrication system. As a result, considerable quantities of sea water are entrained by the oil, rendering it more corrosive. Accordingly, it is desirable to obtain an additive which will prevent rusting under these severe conditions, as well as under the more mild conditions, i. e., where non-saline water is encountered.

In United States Letters Patent No. 2,371,207, there were disclosed as anti-rust agents dicarboxylic acids containing a thio or polythio linkage. These acids are generic to thiodiacetic acids. In order to be effective anti-rust agents in lubricating oil, however, it was specified that the acids must contain at least sixteen carbon atoms per molecule. The present invention is predicated on the discovery that monoesters of a dicarboxylic acid having a thio or polythio linkage and having appreciably less than sixteen carbon atoms per molecule are effective anti-rust agents. Monoesters of dicarboxylic acids have been proposed as anti-rust agents, as is well known. However, most monoesters have been ineffective when used in the presence of salt water.

2

It is well known that lubricating oils are susceptible to oxidation. Many substances have been proposed for use as additives to retard such oxidation, but, commonly, these substances are unifunctional and other substances must be added to the oil containing the anti-oxidant for the prevention of rust. Accordingly, it will be appreciated that an additive which will perform two or more functions, such as the prevention of rust and the prevention of oxidation, is particularly desirable and valuable. The monoesters which have been proposed heretofore do not possess such multifunctional properties. They are limited to anti-rust activity, and this is generally limited to non-saline water conditions.

In accordance with the present invention, it has now been found that certain monoesters perform several functions concurrently, namely, the prevention of rust and the prevention of oxidation. It has now been discovered that monoesters of thiodiacetic acids having the formula,

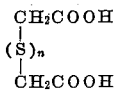


wherein R is an aliphatic radical which has a normal chain length of at least about ten carbon atoms, and n is an integer equal to at least one, when blended with a lubricating oil, concurrently impart the aforementioned desirable properties to the oil.

Accordingly, it is a broad object of the present invention to provide lubricants possessing a combination of desirable properties. Another object is to provide lubricating oil compositions which are resistant, concurrently, to rusting and to oxidation. A further object is to provide an additive which, when added to a lubricating oil, will impart both anti-rust and anti-oxidation properties thereto. A specific object is to provide a lubricating oil containing monoesters of thiodiacetic acid, in which the ester group has a normal chain length of at least about ten carbon atoms, which lubricating oil is resistant, concurrently, to both rusting and oxidation. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following detailed description.

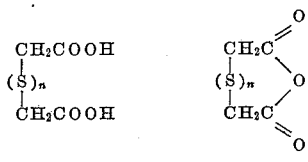
Broadly stated, the present invention provides

lubricating oils containing between about 0.01 per cent and about 10 per cent by weight of new monoesters of a thiodiacetic acid having the formula,



wherein R is an aliphatic radical which has a normal chain length of at least about ten carbon atoms; and n is an integer equal to at least one.

The thiodiacetic acids utilized herein, structurally speaking, consist of two molecules of acetic acid linked in the beta position by a thio group or a polythio group. As discussed in detail hereinafter, the monoesters of the present invention may be prepared from the thiodiacetic acid reactants or from the anhydrides thereof. Accordingly, the anhydrides of these acids may be used and are preferred. The thiodiacetic acid and anhydride reactants have the general formula, respectively:



wherein n is an integer equal to at least one. Within the broad concept of this invention, there may be any number of sulfur atoms in the thio linkage, however, about ten appears to be the upper limit of the preferred range of variation. Accordingly, n in the formulas, preferably, varies between one and about ten. Non-limiting examples of the thiodiacetic acid reactant are thiodiacetic acid; thiodiacetic acid anhydride; dithiodiacetic acid; dithiodiacetic acid anhydride; hexathiodacetic acid; and decathiodiacetic acid. These acids may be prepared in several ways well known in the art. For example, thiodiacetic acid is prepared by reacting chloroacetic acid with sodium sulfide. Its anhydride is prepared by the usual methods, such as by reaction with acid chlorides or by heating in vacuo.

The alcohol reactants utilizable for preparing the monoesters contemplated herein are the monohydric, aliphatic alcohols having at least about ten carbon atoms per molecule. They may be straight-chain or branched-chain, and saturated or unsaturated. As mentioned hereinbefore, however, the alcohol reactant must, upon esterification, produce a radical having a normal chain length of at least about ten carbon atoms. For example, an ester prepared using 3,9-diethyltridecanol-6, a monohydric alcohol having seventeen carbon atoms, was not effective for the purposes of the present invention. It will be noted that the longest normal chain in this alcohol contained only eight carbon atoms. Non-limiting examples of the alcohol reactant are decanol-1; undecanol-1; undecanol-2; undecene-1-ol-11; dodecancol-1; tridecanol-1; tetradecanol; hexadecanol-1; linoleyl alcohol; linolenyl alcohol; oleyl alcohol; octadecanol; phytol; erucyl alcohol; and myricyl alcohol.

The monoesters of the thiodiacetic acids contemplated herein may be prepared by any of the well known methods for preparing monoesters of dicarboxylic acids. For example, they may be prepared by reacting substantially equimolecular amounts of the alcohol reactant and the acid reactant with the removal of one mol of water

of esterification per mol of alcohol used. This process has the disadvantage that the monoester is contaminated with relatively large amounts of diester and unreacted acid reactant. From a practical point of view, however, these products contain sufficient monoester to be effective; and the diester and unreacted acid reactant present therein do not detract from the anti-rust and anti-oxidant activity of the monoester, although they contribute very little, if anything, towards the anti-rust and anti-oxidant action of the monoester. It is preferred, however, to prepare the monoester products by reacting substantially equimolar amounts of the alcohol reactant and of the acid anhydride reactant, because of the higher yield of monoester and the resulting relatively lesser contamination with diester. The particular reaction conditions for these esterification reactions are well known to those skilled in the art. Still another method of preparing monoesters of thiodiacetic acid involves the reaction of an ester of a haloacetic acid with thioglycolic acid, in the presence of a trialkylamine. This method is fully described in copending application, Serial No. 14,391, filed March 11, 1948, now United States Letters Patent No. 2,467,303. It must be strictly understood, however, that monoesters of thiodiacetic acids, as described herein, may be prepared by many other methods, and that all such monoesters are to be considered to be within the scope of the present invention, regardless of the method of preparing them.

Non-limiting examples of the monoesters contemplated herein are monodecyl thiodiacetate; monoundecyl hexathiodiacetate; monomyricyl thiodiacetate; mono-1-methyldecyl decathiodiacetate; monolinoleyl dithiodiacetate; monolinoleyl dithiodiacetate; monohexadecyl decathiodiacetate; monododecyl thiodiacetate; mono-1-methyldecyl dithiodiacetate; monooleyl thiodiacetate; monotridecyl decathiodiacetate; monoerucyl dithiodiacetate; monotetradecyl thiodiacetate; mono-1-methyldecyl hexathiodiacetate; monophytyl hexathiodiacetate; monododecyl dithiodiacetate; monooctadecyl thiodiacetate; mono-1-methyldecyl thiodiacetate; mono-10-undecenyl decathiodiacetate; monooctadecyl hexathiodiacetate; and monohexadecyl thiodiacetate.

In accordance with the present invention, the monoesters are added to a lubricating oil in concentrations ranging between about 0.01 per cent and about 10 per cent by weight. It is preferable, in most instances, to use a concentration varying between about 0.01 per cent and about 2 per cent. Concentrations of between about 0.05 per cent and about 2 per cent are used when operating in the presence of salt water; concentrations of between about 0.01 per cent and about 1 per cent are used when operating in the presence of non-saline water; and concentrations of between about 0.05 per cent and about 2 per cent are used when anti-oxidation activity is desired along with anti-rust protection.

The following specific examples are for the purpose of demonstrating the outstanding characteristics of the monoester additives of the present invention. It is to be strictly understood, however, that this invention is not to be limited to the specific monoesters or to the operations and manipulations set forth in the examples. A wide variety of other monoesters, as set forth hereinbefore, may be used in the lubricating oil compositions of the present invention, as those skilled in the art will readily understand.

EXAMPLE I

A mixture of dodecanol-1 and thiodiacetic acid anhydride, in a molar ratio of about 1:1.1, respectively, was heated at a temperature of 95–100° C. for about four hours. After cooling the reaction product, it was treated with sufficient water-immiscible solvent (e. g., about 400–500 parts of light petroleum ether or benzene) to dissolve it. The solution of ester product was then extracted with water until the aqueous extracts were substantially neutral to litmus paper, and then dried over a neutral inert drying agent, such as sodium or magnesium sulfate. After filtering the dried solution, the solvent was removed by vacuum distillation at a temperature of 95–100° C. under a pressure of 5–10 millimeters. The monododecyl thiodiacetate thus obtained contains a negliglible amount of didodecyl thiodiacetate, but its presence did not interfere with the anti-rust and anti-oxidation activities thereof. Pertinent test data for this monoester are set forth in Tables I and III.

EXAMPLES II THROUGH VIII

The monoctyl, monodecyl, monotetradecyl, monohexadecyl, monoheptadecyl, monooctadecyl, and monooleyl esters, respectively, of thiodiacetic acid were prepared in a manner similar to that set forth in Example 1. The monoheptadecyl ester used herein was prepared from an alcohol in which the longest normal chain contained eight carbon atoms, namely, 3,9-diethyltridecanol-6. Pertinent test data for these monoesters are set forth in Tables I and III.

EXAMPLES IX AND X

For purposes of comparison, didodecyl thiodiacetate and dihexadecyl thiodiacetate, respectively, were prepared by reacting the corresponding alcohol with thiodiacetic acid anhydride, in a molar ratio of about 2:1, respectively. The reaction was made at a temperature of about 80–100° C. for about six hours using a benzene reflux to remove the water of esterification. The reaction product was cooled and purified by extracting the acidic substances contained therein with a dilute aqueous solution of sodium hydroxide. The solvent was then removed from the raffinate by distillation under reduced pressure. The diester product thus obtained was substantially free of monester. Pertinent test data are set forth in Table I.

EXAMPLES XI THROUGH XIV

For further comparison purposes, the monooctyl, monodecyl, monododecyl and monooctadecyl esters, respectively, of thiodiacetic acid were prepared in the manner set forth in Example I. Pertinent test data are set forth in Tables II and III.

In order to demonstrate the outstanding character of the oil compositions contemplated herein, typical rust test data were obtained for oil blends containing the esters described in the examples. The oil used for test purposes was a blend of solvent-refined, Mid-Continent residual stock with a solvent-refined Mid-Continent Rodessa distillate stock. It had an A. P. I. gravity of 30.8, a flash point of 445° C., and a Saybolt Universal viscosity of 407.7 seconds at 100° F. This oil is suitable for use in steam turbines and the like, and the tests run on the oil blends simulate conditions which exist in turbine operations and analogous operations.

The test used to evaluate the esters was the ASTM Test D 665–44T. In this test, a cylindrical, polished steel specimen is suspended in 350 cubic centimeters of the oil under test, at a temperature of 140° F. After thirty minutes, 50 cubic centimeters of the oil are removed and 30 cubic centimeters of the distilled water (or 30 cubic centimeters of synthetic sea water) are added, and the mixture is stirred with an agitator revolving at 1000 R. P. M. throughout the test period. After 48 hours have elasped, the steel specimen is removed and examined for evidence of rusting. An oil passes the test when there is no trace of rust on that portion of the specimen which is immersed in the oil. The synthetic sea water used in this test contains 11.0 grams of magnesium chloride hexahydrate, 1.2 grams of calcium chloride, 4.0 grams of sodium sulfate, and 25.0 grams of sodium chloride per liter.

Test results on blends of representative monoesters of the present invention and of some of the corresponding diesters are set forth in Table I. Comparative test data for monesters of succinic acid are presented in Table II. It will be noted that succinic acid has a structure similar to that of thiodiacetic acid, with the exception of the thioether linkage.

TABLE I

Rust test data for lubricating oils containing esters of thiodiacetic acid

Example	Ester of Thiodiacetic Acid	N. N.[1]	Percent Conc.	Rust Test Results	
				Syn. Sea Water	Distilled Water
2	Monooctyl	117.6	0.10	Fail	Fail.
3	Monodecyl	143.1	0.10	Pass	
1	Monododecyl	125.4	0.10	do	
			0.05	Fail	Pass.
4	Monotetradecyl	141.5	0.10	Pass	
			0.05	Fail	Do.
5	Monohexadecyl	110.5	0.10	Pass	
			0.05	Fail	Do.
6	Monoheptadecyl	108.5	0.10	do	
			0.05		Do.
7	Monooleyl	105.1	0.10	Pass	
8	Monooctadecyl	111.7	0.10	do	
			0.05	do	Do.
			0.03	Fail	Do.
9	Didodecyl	7.05	0.10	do	
			2.00	do	
10	Dihexadecyl	1.73	0.10	do	

[1] Neutralization number=no. mg. KOH equivalent to 1 g. of substance.

TABLE II

Rust test data for lubricating oils containing esters of succinic acid

Example	Ester of Succinic Acid	N. N.[1]	Percent Conc.	Rust Test Results	
				Syn. Sea Water	Distilled Water
13	Monododecyl	161.7	0.15	Fail	Pass.
			0.10	do	
			0.05	do	
14	Monooctadecyl	144.0	0.15	do	Do.
			0.10	do	
			0.05	do	

[1] Neutralization number=no. mg. KOH equivalent to 1 g. of substance.

It will be apparent from the data set forth in Tables I and II that the monoesters of the present invention impart superior anti-rust properties to lubricating oils. It will be noted that the corresponding diesters exhibit no anti-rust properties in themselves. Likewise, although the monoesters of succinic acid impart anti-rust properties to the oils when tested in the presence of distilled water, they afford no protection against rusting in the presence of sea water.

The anti-oxidation activity of the monoesters of thiodiacetic acid was determined by means of the German tar test. The oil used was prepared by treating a Coastal distillate with 98 per cent sulfuric acid and oleum, followed by washing and percolation through clay. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Universal viscosity of 69 seconds at 100° F. This type of oil is susceptible to the formation of acidic bodies by oxidation. In the German tar test the oil blend under test is heated to about 120° C. and oxygen is bubbled therethrough for seventy hours. The amount of acidic bodies formed during this treatment is determined by titrating a sample of the oil with an alcoholic solution of potassium hydroxide. Results are expressed in terms of N. N. (neutralization number=number of milligrams of potassium-hydroxide required to neutralize one gram of oil). The test results are set forth in Table III. For comparison purposes, oil blends containing representative monoesters of succinic acid were tested in the same manner. The test results also appear in Table III.

TABLE III

Oxidation test data for oils containing monoesters of thiodiacetic acid and succinic acid

Example	Monoester	Percent Conc.	N. N.
2	Monooctyl thiodiacetate	1	0.65
3	Monodecyl thiodiacetate	1	0.70
1	Monododecyl thiodiacetate	Sat., <1	0.30
4	Monotetradecyl thiodiacetate	Sat., <1	0.83
5	Monohexadecyl thiodiacetate	Sat., <1	0.58
6	Monoheptadecyl thiodiacetate	1	0.32
8	Monooctadecyl thiodiacetate	Sat., <1	0.20
11	Monooctyl succinate	Sat., <1	6.3
12	Monodecyl succinate	1	18.1
	Blank, uninhibited oil		23.5

From the data in Table III, it will be apparent that the monoesters of thiodiacetic acid are superior to the corresponding monoesters of succinic acid, as oxidation inhibitors. In this connection, it must be noted that the monoesters themselves are acidic substances and that they, therefore, contribute to the titratable acidity. Viewed in this light, the excellent antioxidation activity of the monoesters of the present invention becomes manifest.

It will be apparent from the foregoing illustrative examples that lubricating oils containing the monoesters of the present invention possess good anti-rust and anti-oxidation properties. In addition to their function as additives, these monoesters are also useful as plasticizers and as intermediates for organic syntheses.

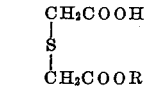
Mineral oil concentrates are also contemplated in this invention, such concentrates containing substantially larger amounts of the monoester than set forth hereinbefore. Thus, relatively large amounts, i. e., upwards of about ten per cent by weight and up to about 49 per cent, may be incorporated in an oil fraction. The oil concentrate thus obtained may thereafter be diluted with a suitable quantity of mineral oil prior to use, to produce a mineral oil composition containing the desired optimum concentration of the monoester.

It is to be understood that, in addition to the additive of the present invention, other oil addition agents may be incorporated in the oil composition, such as, for example, E. P. additives, pour point depressants, oiliness agents, etc.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope thereof, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

We claim:

1. A lubricating oil containing a small amount, sufficient to prevent rusting of ferrous metal surfaces, of a monoester of a thiodiacetic acid having the formula



wherein R is an aliphatic hydrocarbon radical which has a normal chain length of between about ten carbon atoms and about eighteen carbon atoms.

2. A lubricating oil containing a small amount

sufficient to prevent rusting of ferrous metal surfaces, of mono-n-ocetadecyl thiodiacetate.

3. A lubricating oil containing a small amount sufficient to prevent rusting of ferrous metal surfaces, of mono-n-hexadecyl thiodiacetate.

4. A lubricating oil containing a small amount sufficient to prevent rusting of ferrous metal surfaces, of mono-n-decyl thiodiacetate.

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EVERETT W. FULLER.

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