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CORROSION INHIBITORS AND COMPOSITIONS CONTAINING THE SAME

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This invention is directed to condensation products of alpha-halogenated aliphatic mono-carboxylic acids and 2,5-dimercapto-1,3,4-thiadiazole as new compositions of matter, and to compositions containing the same, which compositions possess corrosion and/or rust inhibiting properties.

In various equipment in which water and/or steam is used, or which may become contaminated with water or steam during service or storage, corrosion and/or rusting of the metal parts, particularly the ferrous metal parts, is encountered causing material damage to such equipment. For example, in the operation of steam turbines, rusting or corrosion of the metal parts of such systems is a serious problem, and hence, prevention or inhibition of such corrosion or rusting is highly important. Similar problems exist in the lubrication of certain types of marine engines.

The present invention is also applicable to anti-rust or slushing compositions for the protection of metals against atmospheric corrosion and/or rusting. Such anti-rust or slushing compositions are applied to metallic articles to be stored or for shipment to prevent rusting and/or corrosion thereof. Similarly, fabricated metallic articles and finished or semi-finished metal stocks destined for shipment by rail or by water are protected against attack by moisture by coating such materials with anti-rust or slushing compositions.

Accordingly, it is an object of the present invention to provide a composition which will effectively inhibit or prevent the rusting and/or corrosion of metallic surfaces.

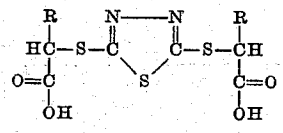
Another object of the invention is to provide a composition which will effectively inhibit or prevent the rusting and/or corrosion of metallic surfaces which come in contact with water and/or steam.

A further object of the invention is to provide a turbine oil which will effectively inhibit the rusting and corrosion of the metal surfaces of the system which come in contact with water or steam. Still another object of the invention is to provide a lubricant composition which will effectively inhibit or prevent the corrosion and/or rusting of metal surfaces of equipment employing such lubricant, particularly in equipment in which steam or water may be present.

Still another object of the invention is to provide a slushing composition which will prevent or inhibit the rusting and/or corrosion of metal surfaces.

The new compositions of matter of the present invention are the condensation products of an alpha halogenated aliphatic mono-carboxylic acid having at least 10 carbon atoms, and preferably from about 12 to about

25 carbon atoms, with 2,5-dimercapto-1,3,4-thiadiazole, which condensation product has the general formula



in which R is an alkyl radical of at least about 10 carbon atoms and preferably from about 12 to about 25 carbon atoms. Such compounds can be named as 1,3,4-thiadiazole-2,5-bis-(thia-alpha-aliphatic acids) or 1,3,4-thiadiazole-2,5-bis-(alpha-mercapto-aliphatic acids).

These condensation products can be readily prepared by refluxing for a period of 3 to 4 hours a mixture of one mole of an alkali metal salt of 2,5-dimercapto-1,3,4-thiadiazole and two moles of an alkali metal salt of the alpha-halogenated-aliphatic mono-carboxylic acid, decomposing the resultant salt of the condensation product with an excess of a mineral acid, for example, HCl, and extracting the free acid with a suitable organic solvent such as hexane, naphtha, and washing the hexane solution free of the mineral acid with water or a dilute aqueous alcohol solution. The organic solvent solution is then dried and the organic acid recovered by removal of the organic solvent by suitable means such as by evaporation under a vacuum.

Examples of alpha halogenated aliphatic fatty acids which can be used in the preparation of the above described condensation product are alpha-brom-lauric acid, alpha-chlor-lauric acid, alpha-chlor-myristic acid, alpha-brom-stearic acid, alpha-chlor-stearic acid, alpha-brom-arachidic acid, alpha-chlor-behenic acid, alpha-brom-behenic acid, alpha-brom-cerotic acid, alpha-chlor-mellissic acid, etc.

The preparation of the herein described condensation product is illustrated by the following examples.

Example I

Fifteen grams (0.1 mole) of 2,5-dimercapto-1,3,4-thiadiazole in 100 cc. ethanol was treated with 12.8 grams (0.2 mole) of KOH (87.9%) dissolved in 90 cc. ethanol. To the cooled suspension-solution were added 72.7 grams (0.2 mole) of alpha-brom-stearic acid and 11.2 grams KOH dissolved in 110 cc. ethanol with an additional 90 cc. ehtanol. The mixture was stirred and warmed on a steam bath and refluxed for 4 hours. The mixture was then diluted with about an equal volume of water and treated with an excess of concentrated HCl. The product acid, set free as an oil, was extracted with hexane and the hexane extract washed once with water and then with 20% ehtanol. The hexane solution was then dried over sodium sulfate, filtered and freed of hexane by evaporation. Recrystallization from a benzene-hexane solution yielded a light buff colored solid having a melting point of 81° C.

	N	S	Neutral Equivalent
Theory for $C_{38}H_{76}O_4S_2N_2$	3.92	13.44	357
Found	3.86	13.22	353

Example II

Forty-five grams (0.3 mole) of 2,5-dimercapto-1,3,4-thiadiazole in 300 cc. ethanol were treated with 33.6 grams (0.6 mole) of KOH in 150 cc. ethanol. To the cooled mixture were added 155.4 grams (0.6 mole) of alpha-brom-lauric acid and 33.6 grams KOH in 200 cc. ethanol and the mixture refluxed on a steam bath for 3 hours. The mixture was then acidified with 65 cc. concentrated HCl and the acid separated from the salt by filtration. The filtrate was evaporated under vacuum, and taken up in 250 cc. hexane, dried over Drierite, filtered and the hexane evaporated off. The recovered waxy solid was purified by crystallization from heptane. A solid having a melting point of 86–87° C., and the following analysis was obtained:

	N	S	Neutral Equivalent
Calculated for $C_{26}H_{46}N_2S_3O_4$	5.13	17.64	273
Found	4.93	17.2	264

The herein described condensation products find particular utility in oleaginous compositions to impart corrosion and/or rust inhibiting properties thereto. Although the condensation product described herein can be suitably employed in oleaginous compositions in general, particularly to inhibit or prevent rusting and/or corrosion, for the purpose of exemplifying the present invention the same will be described as applied to steam turbine lubricants for which highly refined oils having Saybolt Universal viscosities at 100° F. of from about 100 seconds to about 250 seconds are usually employed.

With the advent of drastic refining treatments to produce more highly refined turbine oils having improved non-sludging and emulsification properties, certain components of such oils, responsible for the wetting and therefore rust inhibiting properties of the oil are, however, removed. As a result, such oxidation-stable oils, produced by the drastic refining treatments, are inferior with respect to rust inhibiting qualities. Rusting in steam turbine systems is usually encountered in the upper portions of the oil reservoirs and other parts of the systems by virtue of droplets of water coming in contact with the metallic surfaces and displacing any oil which may be present thereon. Oil will provide adequate protection against such rusting only if it wets the metal surfaces preferentially as compared with water. As the rusting in steam turbine systems progresses the iron oxides formed may scale off and be carried in suspension in the oil; often scoring bearings, plugging oil lines and frequently causing faulty operation of delicate governor parts. The need for non-rusting turbine oils is therefore great.

In accordance with one embodiment of the present invention the addition of small amounts of a condensation product of the type herein described to turbine oils effectively inhibits rusting of the type above described. The rust inhibiting characteristic of turbine oils containing such additives is demonstrated by the following test:

Three hundred cubic centimeters of the oil to be tested are placed in a 400 cc. lipless glass beaker and heated to 140° F. in an oil bath and the oil stirred with a stirrer maintained at about 1000 R. P. M. When the temperature of the oil sample reaches 140° F. a cleaned strip of cold rolled steel is suspended in the oil and the stirring continued for 30 minutes to insure complete wetting of the steel specimen. Thirty cubic centimeters of distilled water are then carefully added by pouring it down the side of the beaker, and stirring continued for 24 hours. At the end of this period the specimen is removed from the beaker, washed with naphtha and visually inspected for the presence of rust. The method of carrying out this test is fully described in the A. S. T. M. Manual of 1953, page 292, and identified as A. S. T. M. Method D665–53T.

Samples of a turbine oil base, namely a highly refined hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of about 150 seconds, and samples of this oil containing small amounts of the condensation products of Examples I and II were subjected to the above test with the following results.

Additive	Weight percent	Degree of Rusting
None (control)		Severe rust.
Product of Example I	0.1	No rust.
Do	0.05	Do.
Do	0.03	Slight rust.
Do	0.01	No rust.
Product of Example II	0.1	Do.
Do	0.03	Do.
Do	0.01	Do.
Do	0.001	Do.

While the herein described condensation products are especially well adapted for use in turbine oil compositions they can be used in small proportions, namely from about 0.001% to about 1% in a wide variety of oleaginous bases such as by way of illustration, hydrocarbon oils, i. e. petroleum oils and synthetic hydrocarbon oils, aliphatic dicarboxylic acid esters, silicone polymers, 1,2 polyoxypropylene aliphatic ethers such as described in U. S. 2,488,644, esters of dihydroxy thioethers such as described in U. S. 2,451,895, and other oleaginous compounds. Illustrative of the media in which these additives can be employed are the following:

Motor fuels; for example, automobile or aviation gasolines, tractor fuels, diesel engine fuels, alcohol-containing motor fuels;

Lighting and heating fuels; kerosene stove oils, stove and lighting naphthas, furnace oils, fuels;

Solvent naphthas, cleaner naphthas, such as Stoddard solvent, V. M. and P. naphthas, hydroformed naphthas;

Lubricating and dielectric oils; motor oils, diesel oils, aviation engine oils, marine engine lubricants, gear oils, oil field machinery lubricants, ice-machine oils, steam cylinder lubricants, transmission oils, soluble oils, textile oils, cutting oils, turbine oils, insulating oils;

Lubricating greases; stable gel-like or solid dispersions of metal soaps in hydrocarbon oils;

Protective coatings; slushing oils and greases in which part or all of the hydrocarbon oil may be replaced by metal soaps, pitches, tars, asphalt, rosin, paraffin wax, etc.

The herein described compositions can in addition contain V. I. improvers, viscosity-increasing agents, bloom producing agents, extreme pressure agents, anti-oxidants, dyes, and anti-knock agents, as well as other rust or corrosion inhibiting agents such as, oil-soluble alkali metal sulfonates, for example sodium mahogany soap, etc., provided only that these additional agents do not enter into appreciable chemical reaction with the described condensation products or precipitate them from the oils to which they have been added.

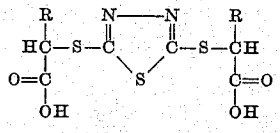
Thus, in turbine oils, we can in addition to the described condensation products, add an antioxidant such as the polyhydric phenols and their alkyl derivatives, for example, catechol, tertiary butyl catechol, octyl catechol, etc. Other effective antioxidants include beta-naphthol, amyl beta-naphthol, octyl beta-naphthol, lauryl beta-naphthol, alpha-naphthol, amyl alpha-naphthol, N-phenyl alpha-naphthyl-amine, di-alpha-naphthyl-amine and the like. The antioxidant may suitably be used in a proportion in the range of about 0.001% to about 0.25% (by weight) based on the oil.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

While the present invention has been described by reference to specific embodiments thereof, these are given by way of illustration only and the invention is not to be limited thereto, but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. As a new compound a 1,3,4-thiadiazole-2,5-bis-(thia-alpha-aliphatic acid) having the general formula

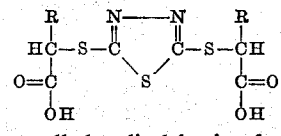


in which R is an alkyl radical of from about 10 to about 25 carbon atoms.

2. The compound, 1,3,4-thiadiazole-2,5-bis-(thia-alpha-lauric acid).

3. The compound 1,3,4-thiadiazole-2,5-bis-(thia-alpha-stearic acid).

4. A lubricant composition comprising a major proportion of a hydrocarbon oil and from about 0.001% to about 1% of a compound having the general formula



in which R is an alkyl radical having from about 10 to about 25 carbon atoms.

5. A lubricant composition comprising a major proportion of a hydrocarbon oil and from about 0.001% to about 1% 1,3,4 - thiadiazole - 2,5 - bis-(thia-alpha-stearic acid).

6. A lubricant composition comprising a major proportion of a hydrocarbon oirl and from about 0.001% to about 1% 1,3,4-thiadiazole-2,5-bis-(thia-alpha-lauric acid).

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