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LUBRICANTS

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The present invention relates to compositions possessing corrosion and/or rust preventive properties. More particularly, the invention relates to oleaginous compositions which possess corrosion and/or rust inhibiting properties, particularly when such compositions are used in systems employing water or steam or which may become contaminated with water or steam.

In various equipment in which water or steam is used or which may become contaminated with water or steam during service or storage, rusting and/or corrosion 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 surfaces of such systems is a serious problem and therefore the 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 corrosion and/or rusting. Metallic products, prior to storage, are coated with an anti-rust material to prevent corrosion and/or rusting while in storage. Similarly, fabricated metallic articles and finished or semi-finished metallic stocks destined for shipment by rail or by water or to be stored, are protected against attack by moisture by coating such materials with anti-rust or slushing compounds.

It is an object of the present invention to provide an improved composition which will effectively inhibit or prevent the corrosion and/or rusting of metallic surfaces.

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

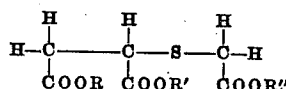
A further object of the invention is to provide a slushing composition which will effectively inhibit or prevent the rusting and/or corrosion of metal surfaces.

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 equipment in which water or steam may be present.

We have discovered that the foregoing objects can be attained by incorporating in organic compositions, particularly one containing a major proportion of an oleaginous material, such as a

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natural or synthetic hydrocarbon oil, a mineral oil, a vegetable, marine or animal oil, synthetic ester-type oils, or combinations thereof, a small amount, for example, from about 0.001% to about 2%, and preferably from about 0.002% to about 0.1% by weight, of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical, and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical. At least one of the alkyl radicals should contain at least 10 carbon atoms, and preferably from about 10 to about 16 carbon atoms.

Specific examples of compounds illustrative of compounds coming within the above general formula are the following:

- 1-decylcarboxy-3,4-dicarboxy-2-thiabutane
- 1-dodecylcarboxy-3,4-dicarboxy-2-thiabutane
- 1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane
- 1-cetylcarboxy-3,4-dicarboxy-2-thiabutane
- 1-octadecylcarboxy-3,4-dicarboxy-2-thiabutane
- 1,3-di-tetradecylcarboxy-4-carboxy-2-thiabutane
- 1,4-di-dodecylcarboxy-3-carboxy-2-thiabutane
- 1-decylcarboxy - 3 - tetradecylcarboxy - 4-carboxy-2-thiabutane
- 1-tetradecylcarboxy - 3 - butylcarboxy-4-carboxy-2-thiabutane
- 4-dodecylcarboxy-1,3-dicarboxy-2-thiabutane
- 4-tetradecylcarboxy-1,3-dicarboxy-2-thiabutane
- 3-cetylcarboxy-1,4-dicarboxy-2-thiabutane
- 3,4-di-dodecylcarboxy-1-carboxy-2-thiabutane

It is not intended to imply that all esters of the herein-described type serve with identical efficiency as anti-rust or anti-corrosion agents. While they are all effective they will exhibit some variation depending upon the nature and severity of the service to which they are subject, the nature of the metal to be protected, the relative solubility of the ester in the media which may be used for application of the ester to the metal surface and the relative stability of the ester at the service temperature.

Members of the herein-described class of compounds can be readily prepared by neutralizing maleic acid with an alkali metal hydroxide, such as sodium hydroxide, and adding to the neutralized product an alcoholic solution of a thioglycolate ester. The mixture is stirred at room

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temperature until titration with iodine indicates that the addition is substantially complete. The product is then acidified, preferably with an aqueous solution of hydrochloric acid, the acidified product extracted with a hydrocarbon solvent, such as ether or other low-boiling solvent, and the extract recovered by evaporation of the solvent. The preparation of 1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane, is given to illustrate the specific example of the method of preparation. Twenty-five hundredths moles of maleic acid is neutralized with a 15% sodium hydroxide solution and an alcoholic solution of tetradecyl thiolglycolate (0.25 mole) added to the neutralized acid. The mixture is stirred at room temperature until titration of a small sample of the reaction product with iodine indicates that the addition is substantially completed; this usually requires five to six hours. The mixture is then acidified with hydrochloric acid, extracted with ether, and the extract recovered by evaporation of the ether.

Although the esters of 1,3,4-tricarboxy-2-thiabutane of the type described herein can be suitably employed in organic compositions, particularly oleaginous compositions in general, to inhibit or prevent rusting and/or corrosion, for

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hibits rusting of the type above described. The rust-inhibiting characteristic of turbine oils containing these additives is demonstrated by the following test: Three hundred milliliters of the oil to be tested are placed in a 400 ml. lipless glass beaker and heated to about 140° F. in an oil bath and the oil stirred with a stirrer maintained at about 750 R. P. M. When the temperature of the oil sample reaches about 140° F., a cleaned test strip of cold rolled steel is suspended in the oil and stirring continued for 30 minutes to insure complete wetting of the steel specimen. Thirty milliliters of distilled water are then carefully added by pouring it down the side of the beaker, and stirring continued for forty-eight 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 A. S. T. M. Manual—1942, page 274, and identified as A. S. T. M.:D665-42T.

Samples of a turbine oil base, namely a hydrocarbon oil having a Saybolt Universal viscosity at 100° F. of about 150 seconds containing small amounts of various esters of 1,3,4-tricarboxy-2-thiabutanes were subjected to the above test and the following results obtained:

TABLE I

A. S. T. M. rust test

Ester	Additive Concentration (wt. per cent)					
	.002	.003	.005	.01	.02	.03
1-dodecylcarboxy-3,4-dicarboxy-2-thiabutane: Distilled Water.	Moderate.	None.....	None.	None.		None.
1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane: Distilled Water.		Moderate.	Slight.	None.	Slight.	Do.
Synthetic Sea Water.						Do.

the purpose of exemplifying the present invention the same will be described as applied to steam turbine lubricants for which highly refined hydrocarbon oils having Saybolt Universal viscosities at 100° F. of from about 125 seconds to about 250 seconds are employed.

With the advent of drastic refining treatments to produce more highly refined turbine oils having improved sludging resistant and emulsification properties, the desirable components of oils responsible for the wetting and therefore rust-inhibiting qualities of the oil were removed by these refining methods and the stable oils produced became inferior with respect to rust-inhibiting qualities. In steam turbines, rusting is usually encountered in the upper portions of oil reservoirs, and other parts of the system, caused by droplets of water coming in contact with the steel surfaces and displacing the oil with which the surface was covered. An oil will provide adequate protection against this rusting only if it wets the steel surfaces preferentially as compared with water. In the presence of oils which provide no protection coating, the steel surfaces are attacked by water with the formation of ferric oxide and black magnetic oxide. As the rusting progresses these oxides scale off and may be carried in suspension in the oil, often scoring bearings, plugging oil lines and often causing faulty operation or sticking of delicate governor parts. The need for non-rusting turbine oils is therefore great.

In accordance with the present invention the addition of small amounts of the herein-described thiabutanes to turbine oils effectively in-

In addition to the A. S. T. M. rust test the inhibited oils were subjected to the so-called Shell tenacity test. This test is carried out as follows:

At the end of the A. S. T. M. D-665-42T test, described above, the steel test specimen are removed from the oil, the oil is replaced with distilled water and the same test specimen then suspended in the beaker. Stirring is then continued at about 140° F. and the test specimen examined periodically for rusting.

The following samples were subjected to the above test and the results obtained tabulated in Table II:

Sample 1.—Control (mineral turbine oil base stock of about 150 S. S. U. at 100° F.).

Sample 2.—Control+0.02% 1-dodecylcarboxy-3,4-dicarboxy-2-thiabutane.

Sample 3.—Control+0.03% 1-dodecylcarboxy-3,4-dicarboxy-2-thiabutane.

Sample 4.—Control+0.02% 1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane.

Sample 5.—Control+0.03% 1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane.

TABLE II

Oil Sample	24 Hours	48 Hours
1.	Severe	None. Do. Do.
2.	Very Slight.....	
3.	None.....	
4.	do.....	
5.	do.....	

While the herein-described esters are especially well adapted for use in turbine oil compositions,

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they can be used in small proportions, namely up to about 2% or more, if required, as anti-rust or anti-corrosion agents for metals, in a wide variety of media, illustrated by 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, fuel oils;

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;

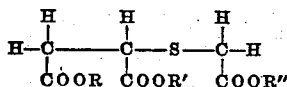
Protective coatings, slushing oils and greases in which part or all of the hydrocarbon oil may be replaced by metal soaps and/or waxes such as the ester-type waxes, mineral waxes such as petrolatum and paraffin waxes, pitches, tars, asphalt rosin.

The compositions, such as for example, the hydrocarbon oil compositions, in which the ester is used, can in addition contain V. I. improvers, viscosity-increasing agents, bloom producing agents, extreme pressure agents, antioxidants, dyes, and antiknock agents, as the case may be provided only that these additional agents do not enter into appreciable chemical reaction with the ester or precipitate it from the oils to which it has been added.

Thus, in turbine oils, we can in addition to an ester, 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-naphthylamine, di-alpha-naphthylamine, and the like. The antioxidant may suitably be used in a proportion in the range of about 0.001% to about 0.5% (by weight) based on the oil.

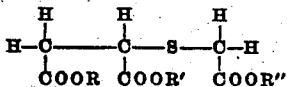
We claim:

1. An oleaginous material containing from about 0.001% to about 2% of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical having at least 10 carbon atoms.

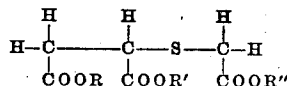
2. An oil containing from about 0.001% to about 2% of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical having at least 10 carbon atoms.

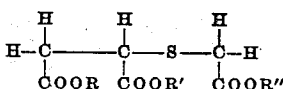
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3. A normally non-gaseous petroleum oil fraction containing from about 0.001% to about 2% of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical having at least 10 carbon atoms.

4. A hydrocarbon oil containing from about 0.001% to about 2% of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical having at least 10 carbon atoms.

5. A hydrocarbon oil containing from about 0.001% to about 2% of a dodecyl ester of a 1,3,4-tricarboxy-2-thiabutane.

6. A hydrocarbon oil containing from about 0.001% to about 2% of 1-dodecylcarboxy-3,4-dicarboxy-2-thiabutane.

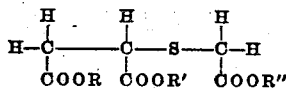
7. A hydrocarbon oil containing from about 0.001% to about 2% of a tetradecylester of 1,3,4-tricarboxy-2-thiabutane.

8. A hydrocarbon oil containing from about 0.001% to about 2% of 1-tetradecylcarboxy-3,4-dicarboxy-2-thiabutane.

9. A hydrocarbon oil containing from about 0.001% to about 2% of a cetyl ester of 1,3,4-tricarboxy-2-thiabutane.

10. A hydrocarbon oil containing from about 0.001% to about 2% of 1-cetylcarboxy-3,4-dicarboxy-2-thiabutane.

11. A composition consisting essentially of a hydrocarbon oil and from about 0.001% to about 2% of a 1,3,4-tricarboxy-2-thiabutane having the general formula



in which the substituents R, R' and R'' are selected from the group consisting of hydrogen and an alkyl radical and in which at least one of the R's is hydrogen and at least one of the R's is an alkyl radical having from 10 to 16 carbon atoms.

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