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RUST-INHIBITING LUBRICATING COMPOSITION

Herman D. Kluge, Wappingers Falls, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to a method of protecting metal surfaces against corrosion and rust formation in the presence of water and to an improved rust preventive composition.

It is recognized that the rusting of metal surfaces, and particularly the ferrous metals and alloys thereof, presents a serious problem in the maintenance and operation of industrial equipment and metal structures. This problem is most pronounced in the lubrication and preservation of machine and engine parts or other finished metal surfaces which are designed for operation under conditions of close space tolerances. It has recently been proposed to protect such metal surfaces from the formation of rust, e. g., ferric oxide, by applying to the metal surface a polar film of a dicarboxylic acid possessing one or more hydrocarbon ether radicals branching from the carbon chain linking the carboxylic group, in accordance with the disclosures of U. S. Patents Nos. 2,371,142 and 2,371,143, granted to Emmett R. Barnum and Ernest W. Zublin on March 13, 1945. Although many of the particular dicarboxylic acids proposed satisfactorily prevent the formation of rust or ferric oxide on metal surfaces subjected to the action of oxygen and water, they possess certain disadvantages which in most instances offset their rust inhibiting properties. It has been found that, as a general proposition, dicarboxylic acids substituted by ether-type radicals such as proposed by Barnum et al., while preventing formation of ferric oxide, enter into reaction with the iron of the metal surfaces and build up a solid, powdery deposit on the metal surfaces in lieu of ferric oxide rust. It is clearly evident that any appreciable build-up of the deposits resulting from this phenomenon will substantially offset any advantage gained from the rust-inhibiting characteristics of these acids.

It has now been discovered that a polar film of a dicarboxylic acid possessing at least 12 carbon atoms and containing at least one tertiary alkyl radical linked to the carbon chain between the carboxyl groups through an element such as oxygen, sulfur, selenium or tellurium, provides effective rust protection to the metal surfaces and particularly ferrous metals and prevents the formation of undesirable reaction product deposits. These acids find particular application in such compositions as flushing oils, steam turbine oils, greases, etc., where combined rust protection and lubrication of friction surfaces are required. However, they may also be incorporated in other oleaginous vehicles which serve as a medium for applying the inhibitor, e. g., spraying or brush application, to exposed metal surfaces such as steel structures and metal equipment for transit or storage.

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The acids of the invention may be further described as the dicarboxylic acids containing at least 12 carbon atoms and possessing the following descriptive formula:

$$\left[R{-}X{-}\right]_m C_n{-}Y_r \quad \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

wherein n and m are integers of at least one, X is an element of the class of oxygen, sulfur, selenium, or tellurium, R is tertiary alkyl radical, Y is either hydrogen or a hydrocarbon radical, and r is 0 or a whole number as required to satisfy the valence of 4 of each carbon atom of C_n. n is preferably greater than m and is usually within the range of 2 to 8, while m is usually within the range of 1 to 4. Thus, a tertiary alkyl "ether" radical (R—X—) is attached to at least one of the number of carbon atoms in the chain connecting the carboxyl groups. X is preferably a sulfur atom and when more than one tertiary alkyl "ether" radical is contained in the molecule, X may be the same or different elements of the class of O, S, Se or Te in the various "ether" radicals.

The majority of these aliphatic dicarboxylic acids exist in stereo-isomeric form and for purposes of the invention the cis form of the acid or the ones in which the carboxyl groups are in a plane symmetrical configuration are preferred. Furthermore, it is preferable that the acids contain a sufficient number of carbon atoms in the molecule to render them soluble or miscible in the oleaginous vehicle in which they are incorporated. The oleaginous vehicle referred to throughout the specification and claims is meant to include the hydrocarbon oils, fats, fatty oils, greases, lubricants, rust-proof bases, etc., which may be used as the medium of application of the rust inhibitor to the metal surfaces.

The amounts of acid which are incorporated in the oleaginous vehicle naturally depend upon the type of protection and the service to which they are applied. In general, it may be stated that amounts not materially greater than 3% by weight of the oleaginous vehicle as applied to the metal surfaces may be used with advantageous results. In lubricating compositions this amount may be substantially decreased and still provide adequate protection. Ranges of proportions between 0.01 and 1.0% by weight of the dicarboxylic acid in a lubricating oil may be used

where maximum rust prevention and minimum interference with the lubricating properties of the lubricant are required. It is to be expected that larger amounts of the dicarboxylic acid will be required in the preparation of the so-called rust-proof compounds where the sole function of the composition is to provide protection to exposed metallic surfaces and in the preparation of inhibitor concentrates which are used in compounding the rust preventive lubricating oils and rust-proof bases, etc.

The exceptional rust and reaction inhibiting properties of the dicarboxylic acids of the invention may be illustrated by the derivative results obtained in a modified ASTM rusting test using synthetic sea water. It is to be understood that the specific test results presented are merely illustrative of the advantages of the dicarboxylic acids of the invention and are not to be considered as limitations thereof. In this test a polished steel specimen is suspended in an agitated mixture of 300 ccs. of the oil to be tested and 30 ccs. of a synthetic sea water. The oil-sea water sample is maintained at 140° F. over an oil bath for 48 hours, after which time the steel specimen is removed, allowed to drain, and washed with precipitated naphtha and acetone, and the amount of rust observed. The synthetic sea water added to the test oil contains the following composition:

	Grams per liter
Magnesium chloride ($MgCl_2 \cdot 6H_2O$)	11.0
Anhydrous calcium chloride ($CaCl_2$)	1.2
Anhydrous sodium sulfate (Na_2SO_4)	4.0
Sodium chloride (NaCl)	25.0

In these particular tests a solvent-refined, acid-treated and filtered lubricating oil was used as the base oil in which was incorporated 0.03% by weight of the thiosuccinic acid derivatives. The results obtained are as follows:

Rusting test

Additive	Appearance of Steel Specimen
n-Dodecyl (lauryl) thiosuccinic acid.	No ferric oxide rust-heavy cream-colored powdery film.
Tertiary-dodecyl thiosuccinic acid.	No ferric oxide rust-slight trace of film.
Alkyl [1] thiosuccinic acid	Pin points of ferric oxide rust-heavy cream-colored powdery film.

[1] Average molecular weight of alkyl group = C^{12}.

The heavy powdery film obtained from the n-alkyl derivatives remained on the steel specimen even after removal of the test oil and washing with naphtha and acetone. In the majority of instances this film amounted to approximately 10 milligrams. To determine the composition of this powdery film twelve ASTM rusting tests, using distilled water, were run on an oil compounded with 0.03% n-octyl thiosuccinic acid.

137 milligrams of a cream-colored powdery film were obtained which analyzed as follows:

Found	Calculated	
	$Fe(Acid)_3$	$Fe_2(Acid)_3$
Fe=12.8	9.65	12.5
S=4.99–6.66	11.1	10.73

These results indicate that this heavy film is the result of the reaction of the iron and the normal alkyl thiosuccinic acid and is probably a mixture of the iron basic salt of the dicarboxylic acid. It may readily be seen that a build-up of insoluble reaction products such as obtained is particularly detrimental to the lubricating function of the oil on friction surfaces.

Obviously many modifications and variations of the invention, as hereinbefore 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 rust-inhibiting lubricating composition consisting essentially of an oleaginous liquid having lubricating properties as the predominant constituent, and 0.01–3.0% by weight on the basis of the oleaginous liquid of a tertiary dodecyl thiosuccinic acid sufficient to inhibit the formation on a steel specimen immersed in said composition in the presence of salt water of both ferric oxide rust, as well as a cream-colored powdery film which results from reaction of the iron with a n-dodecyl thiosuccinic acid, the said tertiary dodecyl thiosuccinic acid having the tertiary dodecyl radical linked through the sulfur atom to the carbon chain of the succinic acid between the carboxyl groups.

2. A rust-inhibiting lubricating composition according to claim 1, wherein the oleaginous liquid is a solvent-refined acid-treated mineral lubricating oil, and the tertiary dodecyl thiosuccinic acid is present in a proportion of 0.01–1.0% by weight based on the oil.

HERMAN D. KLUGE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,284,241	Werntz	May 26, 1942
2,293,580	Walker	Aug. 18, 1942
2,334,158	Fuchs et al.	Nov. 9, 1943
2,368,606	White	Jan. 30, 1945
2,369,641	Barnum	Feb. 20, 1945
2,371,142	Barnum et al.	Mar. 13, 1945
2,371,143	Barnum et al.	Mar. 13, 1945