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CORROSION INHIBITING COMPOSITIONS

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1

This invention relates to corrosion inhibiting compositions for protecting metal surfaces, particularly those of ferrous and related metal or alloy products, from the corrosive action of air or oxygen in the presence of moisture or other aqueous liquids. More particularly, the present invention relates to corrosion inhibiting oil compositions adapted for use in systems which employ water or steam or which may become contaminated with water, steam or other aqueous liquids which normally cause corrosion and/or rusting of metal surfaces.

In various machines and industrial equipment in which water or steam or other aqueous liquids are used or which may become contaminated with such aqueous media, rusting or corrosion of the metal parts, particularly ferrous metal parts, is encountered, causing material damage to such equipment. For example, in internal combustion engines water due to condensation accumulates in the crankcase and frequently causes rusting and/or corrosion of the ferrous metal parts of such engines. In the operation of steam turbines rusting or corrosion of the ferrous metal parts of such systems is also a serious problem, and the prevention or inhibition of such rusting or corrosion is highly important. Corrosion due to the presence of aqueous medium is also a serious problem in the operation of textile machinery, in shock absorbers, in hydraulic lifts and the like. Although equipment of the foregoing type usually employs an oil of some sort, the oil film which may form on the ferrous metal surfaces does not provide adequate protection against rusting and/or corrosion by aqueous liquids, due to the partial displacement of this oil film from the metal surfaces by steam, water or other corrosive aqueous media.

It is an object of the present invention to provide an oil composition which will effectively inhibit or prevent the rusting or corrosion of metal parts of equipment which come in contact with water, steam or other corrosive aqueous liquids.

It is another object of the present invention to provide an oil composition which will inhibit corrosion of metal surfaces wherever the metal comes in contact with fluids causing or tending to cause corrosion of the metal surfaces.

Still another object of the invention is to provide an oil composition which will afford adequate protection against corrosion and/or rusting to metal surfaces exposed to the effects of moisture and oxygen jointly and normally tending to corrode and/or rust.

2

Another object of the invention is to provide an oil composition which will inhibit corrosion to ferrous metal surfaces by humid atmospheres.

Another object of the invention is to provide a method by which normally corrosive liquid mixtures having a corrosive constituent and a non-corrosive constituent may be treated to render the mixture as a whole non-corrosive.

A further object of the invention is to provide a method of preventing rusting and/or corrosion to metal parts of equipment in which water or steam is used or which may become contaminated with water, steam or other corrosive aqueous media.

Still another object of the invention is to provide a steam turbine lubricant which effectively inhibits or prevents the corrosion and/or rusting of metal surfaces of such steam turbine systems which come in contact with water or steam.

Other objects and advantages of the invention will become apparent from the following description thereof.

I have discovered that the foregoing objects can be attained by adding to an oil, preferably a mineral oil having a viscosity within the range suitable for steam turbine lubrication, small amounts; namely, from about 0.005% to about 0.1% of an alkylammonium naphthenate and preferably the primary and secondary alkylamine soaps of naphthenic acids in which each alkyl radical contains not more than about 16 carbon atoms and preferably from about 4 carbon atoms to about 12 carbon atoms. Illustrative specific examples of the alkylammonium naphthenates which can be employed in accordance with the present invention are the following:

Amylammonium naphthenate
Diamylammonium naphthenate
Dihexylammonium naphthenate
Octylammonium naphthenate
Dodecylammonium naphthenate
Didodecylammonium naphthenate
Decylammonium naphthenate

Although the alkylammonium naphthenates of the foregoing type all have to a definite degree corrosion and/or rust-inhibiting properties, all of them are not necessarily equivalent in their effectiveness. They may exhibit some variation depending on the nature and severity of the service in which they are employed, the nature of the metal to be protected, etc.

Alkylammonium naphthenates of the type above described can be readily prepared by warming and stirring a mixture of naphthenic acid with an equivalent amount of the desired amine

until the mixture becomes homogeneous. The alkylammonium naphthenate may, if desired, be formed in situ in the oil by the simple procedure of adding the desired alkyl amine, for example amylamine, and the naphthenic acid to the oil or other oleaginous material.

Naphthenic acids are complex mixtures of carboxylic acids which occur naturally in various crude petroleum oils, usually in proportions below 1 per cent, and which may be extracted therefrom by the use of alkalies. Extensive research has demonstrated that petroleum naphthenic acids fall into at least three general categories: (1) aliphatic acids having the general formula $C_nH_{2n}O_2$ and predominating in compounds wherein n is 6 to 7, (2) acids having the general formula $C_nH_{2n-2}O_2$ and shown to be cyclopentane derivatives $C_5H_9(CH_2)_xCO_2H$, where x generally varies from 1 to about 4 and wherein the cyclopentane ring may also contain one or more alkyl groups, (3) acids having the general formula $C_nH_{2n-4}O_2$, known to contain a bicyclic cycloaliphatic nucleus and containing about 12 to about 25 carbon atoms. The above classification presents a somewhat over-simplified picture. Some evidence has been adduced of the existence of even more complex acids in petroleum naphthenic acids, including tri- and tetra-cyclic cycloaliphatic-substituted aliphatic carboxylic acids. There is evidence that the molecular weights in the above classes overlap; thus, although the simple aliphatic acids predominate in C_6 or C_7 , small proportions of higher molecular weight fatty acids also occur and overlap into the molecular weights and boiling ranges of compounds falling into categories (2) and (3) above. Naphthenic acids obtained from different crudes and from various fractions of the same crude oil generally differ from each other somewhat in composition and character. For the purposes of the present invention the naphthenic acids obtained from petroleum or other sources can be suitably employed.

Although the alkylammonium naphthenates of the class described, when used in small amounts in hydrocarbon oils, are effective corrosion and/or rust inhibitors, when employed in systems which contain moisture or water or which may become contaminated by moisture or water, a preferred application of these alkylammonium naphthenates as corrosion and/or rust inhibitors is in the viscous, highly refined hydrocarbon oils, such as steam turbine oils which generally have Saybolt viscosities at 100° F. of from about 125 seconds to about 2000 seconds and higher. The drastic refining treatments required to produce more highly refined turbine oils having improved sludge resistance and emulsification properties removes the desirable components of oils responsible for the rust inhibiting qualities of the oil. The oils thus produced are inferior with respect to rust inhibiting qualities to moderately refined oils, which give fairly good protection against rusting. The steam turbine rusting is usually encountered in the upper portion of the oil reservoirs and other parts of the system, being caused by droplets of water coming in contact with the steel surfaces which have been covered by the oil and displacing a part or a portion of the oil. It is thought that most anti-rust additives suitable for use in turbine oil protect ferrous parts by plating out thereon and forming a thin film impervious to water. In the presence of oils which provide inadequate protection, the ferrous surfaces are attacked by the water with 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 causing faulty operation or sticking of the delicate governor parts. The need for non-rusting turbine oils is therefore great.

The anti-rust activity of turbine oils containing the salt of an aliphatic amine and an organic acid is demonstrated by the following test: 300 cubic centimeters of the oil to be tested are placed in a 400 cc. glass beaker and heated to about 163° F. in an oil bath and the oil agitated with a stirrer maintained at about 750 R. P. M. When the temperature of the oil sample reaches about 163° 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 cubic centimeters of distilled water are then carefully added by pouring it down the side of the beaker; stirring is continued for 48 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. This test is a modification of the American Society for Testing Materials Proposed tentative method of test for rust-preventing characteristics of steam-turbine oil in the presence of water, D665-42T. The method of carrying out this test is fully described in National Petroleum News, section 2, volume 34, number 30, July 29, 1942, page R-216.

The effectiveness of the salts of aliphatic amines and organic acids as corrosion inhibitors, as determined by the foregoing test, is demonstrated by the following results:

Sample No.	Composition	Extent of Rusting	Rating
1	Control	Severe	5
2	Control+0.05% Amylammonium naphthenate. ¹	None	1
3	Control+0.03% Amylammonium naphthenate. ¹	Very, very slight	1-2
4	Control+0.05% n-Butylammonium naphthenate.	Very slight	2-3
5	Control+0.05% Dibutylammonium naphthenate. ²	None	1
6	Control+0.03% Dibutylammonium naphthenate. ²	Very, very slight	1-2

¹ Prepared from naphthenic acid and the mixed mono-amylamines commercially available.

² Prepared from naphthenic acid and the mixed diamylamines commercially available.

In systems in which oil comes in contact with water, it is essential that any emulsification which may occur be of a quick breaking type. It is therefore important that any additive which may be used in such oils be of a type which will not cause stable emulsions to be formed. One of the advantages of employing the alkylammonium naphthenates for the herein described purpose is that they have substantially no tendency to cause stable emulsification. One of the standard methods of determining the emulsification tendency of oils under service conditions is the so-called Herschel Demulsification test, described in the Bureau of Standards Technological Paper No. 86 (1917). A petroleum oil used as a control, when subjected to the Herschel Demulsification test, gave a Herschel Demulsification number at 130° F. of 1620. The same oil containing 0.2% of alkylammonium naphthenate gave substantially the same result; namely, a Herschel Demulsification number at 130° F. of 1500, thus demonstrating the non-emulsifying properties of such soaps.

To inhibit the oxidative deterioration of the

oils susceptible to such deterioration small amounts of known antioxidants can be added to the oils in combination with the alkylammonium naphthenates. Antioxidants such as the polyhydric phenols and their alkyl derivatives, for example, catechol, tertiary-butylcatechol and octylcatechol, can be used. Other effective antioxidants are cresol, pyrogallol, hydroquinol, and other hydroxy condensed ring compounds and their alkyl derivatives, such as beta-naphthol, octyl beta-naphthol, amyl beta-naphthol, lauryl beta-naphthol, alpha-naphthol, cetyl alpha-naphthol, amyl alpha-naphthol and other alkyl derivatives of beta- and alpha-naphthols. Other antioxidants such as phenyl alpha-naphthylamine, diphenylamine, butyl para-aminophenol, etc., can be used. The amount of antioxidant employed will depend upon the effectiveness of the particular material used, but in general will range in quantity from about 0.001% to about 0.25%. Thus, I have found that a suitable turbine oil having a Saybolt Universal viscosity at 100° F. of from about 150 seconds to about 330 seconds exhibiting non-rusting properties and resistant to oxidative deterioration is one containing from about .005% to about .1% alkylammonium naphthenate and from about 0.02% to about 0.2% of N-phenyl-alpha-naphthylamine.

A turbine oil composition which gave extremely satisfactory results is one comprising a highly refined mineral oil having a Saybolt Universal viscosity at 100° F. of about 160 seconds, 0.1% phenyl-alpha-naphthylamine and 0.05% amylammonium naphthenate. This turbine oil when subjected to the Proposed method of test for oxidation characteristics of steam-turbine oils, directions for which have been published on pp. 17-20 of A. S. T. M. Standards on Petroleum Products Committee D-2, 1943, has lasted over 3300 hours. This stability is striking when compared with the life of a commercial turbine oil of about 800 to 900 hours. This turbine oil containing the phenyl-alpha-naphthylamine and the amylammonium naphthenate permitted only very slight rusting of the iron in the oil layer even after 3300 hours under the very drastic conditions of the A. S. T. M. turbine oil oxidation test, which is carried out at 203° F. in the presence of 20% water and copper and under conditions in which oil is saturated with oxygen and continuously agitated.

In addition to the alkylammonium naphthenates, the non-corrosive composition may, if desired, contain other adjuncts such as fatty acids, for example stearic acid, extreme pressure lubricants, sludge inhibitors, V. I. improvers, etc.

The alkylammonium naphthenates can also be used as corrosion and/or rust inhibitors in vegetable, animal, and marine oils, or in blends of such oils with hydrocarbon oils.

While I have illustrated the present invention by various specific examples thereof, it is not intended to limit the scope thereby except in so far as the same is defined by the following claims.

I claim:

1. A turbine oil consisting essentially of a highly refined hydrocarbon oil, from about 0.005% to about 0.1% of an alkyl amine soap of naphthenic acid, selected from the group consisting of primary alkyl amine soaps of naphthenic acids, and secondary alkyl soaps of naphthenic acids, in which each alkyl radical contains from about 4

carbon atoms to about 16 carbon atoms, and from about 0.001% to about 0.25% of an anti-oxidant selected from the group consisting of phenyl-alpha-naphthylamine, diphenylamine, and butyl para-amino-phenol.

2. A turbine oil consisting essentially of a highly refined hydrocarbon oil, from about 0.005% to about 0.1% of a primary alkyl amine soap of naphthenic acid in which the alkyl radical contains from about 4 carbon atoms to about 16 carbon atoms and from about 0.001% to about 0.25% of phenylalpha-naphthylamine.

3. A turbine oil as described in claim 2 in which the primary alkyl amine soap of naphthenic acid is mono-amylammonium naphthenate.

4. A turbine oil consisting essentially of a highly refined hydrocarbon oil, from about 0.005% to about 0.1% of a secondary alkyl amine soap of naphthenic acid in which each alkyl radical contains from about 4 carbon atoms to about 16 carbon atoms and from about 0.001% to about 0.25% of phenylalpha-naphthylamine.

5. A turbine oil as described in claim 4 in which the secondary alkyl amine soap of naphthenic acid is di-amylammonium naphthenate.

6. A turbine oil as described in claim 4 in which the secondary alkyl amine soap of naphthenic acid is di-dodecylammonium naphthenate.

7. A turbine oil consisting essentially of a highly refined hydrocarbon oil and from about 0.005% to about 0.1% of an alkyl amine soap of naphthenic acid selected from the group consisting of primary alkyl amine soaps of naphthenic acids and secondary alkyl amine soaps of naphthenic acids in which the alkyl radical contains from about 4 to about 16 carbon atoms.

8. A turbine oil consisting essentially of a highly refined hydrocarbon oil and from about 0.005% to about 0.1% of a primary alkyl amine soap of naphthenic acid in which the alkyl radical contains from about 4 to about 16 carbon atoms.

9. A turbine oil as described in claim 8 in which the primary alkyl amine soap of naphthenic acid is monoamylammonium naphthenate.

10. A turbine oil consisting essentially of a highly refined hydrocarbon oil and from about 0.005% to about 0.1% of a secondary alkyl amine soap of naphthenic acid in which each alkyl radical contains from about 4 to about 16 carbon atoms.

11. A turbine oil as described in claim 10 in which the secondary alkyl amine soap of naphthenic acid is di-amylammonium naphthenate.

12. A turbine oil as described in claim 10 in which the secondary alkyl amine soap of naphthenic acid is di-dodecylammonium naphthenate.

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