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MINERAL OIL COMPOSITION

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This invention relates to mineral oil compositions and more specifically relates to mineral oil compositions for ferrous metal surfaces in an environment where such surfaces are also subject to contact with water and in consequence are likely to rust.

As is well known to those familiar with the art, when iron is exposed to moisture, which generally contains some dissolved oxygen and carbon dioxide, a mixture—rust—predominantly comprised of iron oxides and carbonates forms on the surface of the iron. Naturally, this is to be avoided in the operation of most machinery wherein iron surfaces are in close engagement, inasmuch as rust formation seriously impairs the operating efficiency thereof. As an illustration, difficulties have been experienced during the operation of steam turbines, particularly during the operation of new steam turbines, in view of rust formation on ferrous metal parts. The combination of fresh (not previously used) oil, clean, new metal surfaces and moist conditions of operation, each of which characterizes the operation of new steam turbines, appears particularly conducive to rusting difficulties. Particles of rust formed on or carried to the bearing surfaces of small clearance, such as the governor, for example, tend to cause sticking, which renders them inoperative. In cases of severe rusting, bearings may be damaged.

This rusting phenomenon under conditions of the type outlined above is evidently the result of improper or inadequate "wetting" of the metal surfaces with oil, thus permitting a preferential contact of the surfaces with water which is present. As a result, considerable investigation has been carried on in an effort to develop oils which will preferentially "wet" the metal parts in the presence of water. One expedient developed and used in the past to prevent rusting under these conditions has been to mix with the new oil several per cent of an oil which has been previously used in turbine operation for a considerable period of time. The oxidation products in the used oil cause the oil to "wet" more adequately and better adhere to the metal surfaces. Such an expedient, however, not only introduces those oxidation products which inhibit rusting but introduces as well other oxidation products, which promote the formation of sludge and acidity and increase emulsifying tendencies, all of which are undesirable in turbine operation and the like.

Also developed as a result of such investigations are mineral oil compositions containing small amounts of materials such as acids, degreas (wool grease), glycerides and esters. Of the latter class

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of additives, esters, many are but slightly effective and some are even ineffective as rust inhibitors. Apparently, inaccurate and confusing terminology has been used heretofore in describing such esters as rust inhibitors for use in mineral oil; they are more accurately described as corrosion inhibitors. As is well known to those familiar with the art, rust formation and corrosion are two distinct phenomena. Rust formation is defined hereinabove and distinguishes from corrosion which is a process of gradual disintegration or decomposition of a metal surface and which may occur in the presence or absence of moisture. Many esters which have been described as rust inhibitors are, in fact, effective only against corrosion, being ineffective against rust formation. This relationship is illustrated hereinafter.

We have discovered that esters of oleyl alcohol and malic acid and particularly dioleyl malate, when admixed or dissolved in mineral oil in small amounts, are outstandingly effective in preventing rust formation on ferrous metal surfaces when in contact therewith in the presence of water.

We have also discovered a method of inhibiting the rusting of ferrous metal surfaces in an environment wherein water is present. The method contemplated herein involves contacting the ferrous metal surfaces with a mineral oil fraction normally incapable of preventing rusting of the said surfaces and maintaining in the oil fraction a small amount of an ester of oleyl alcohol and malic acid, and preferably dioleyl malate.

Esters of the type contemplated herein are well known in the art and it is believed that there is no need for a discussion herein of methods of preparation thereof. It is to be understood, however, that the neutral ester, dioleyl malate; the partial ester, monooleyl malate, and mixtures of the neutral and partial esters can be used for the purposes of this invention.

That dioleyl malate is outstanding as a rust inhibitor is shown below by results obtained with various esters in a typical rust test. In this test, the oil used was one obtained from a mixed Mid-Continent and Coastal distillate refined by treatment with 70 pounds of 98 per cent sulfuric acid per barrel, neutralized, washed and percolated through clay. The oil had a specific gravity of 0.879, a flash point of 385° F., and a Saybolt Universal viscosity of 152 seconds at 100° F. The oil is suitable for use in turbines and the test with the oil and oil blends thereof simulates the conditions which exist in turbine operation. The test involves placing a small disc of polished steel having a slightly cupped (concave) upper surface in

a sample of the oil, or oil blend thereof, at room temperature and then placing a drop of distilled water on the cupped surface of the disc. When the oil alone is used, the steel disc showed definite signs of rust within 15 minutes. The amount of ester used in each test is expressed in terms of per cent in the table. It will be noted that most of the tests were made on mixtures of the normal and partial esters. The percentage is given of the partial ester present in each case, and it is obvious that the percentage of the neutral ester can be ascertained by subtracting from 100 per cent the percentage of partial ester present. The condition of the steel disc used in each case and the period of time over which the condition was observed are indicated below in the table.

Table

Ester	Conc., Wt. per cent	Effect	Time, Hrs.
Dioleoyl malate containing 8% monooleoyl malate.	0.05	No Rust	18
Dioleoyl malate containing 26% monooleoyl malate.	0.05	do	18
Di-2-ethyl-hexyl malate.	0.2	Rust	1/4
Diamyl tartrate containing 4% monoamyl tartrate.	1.0	do	1/4
Dioctyl tartrate containing 7% monoctyl tartrate.	1.0	do	1/4
Dilauryl tartrate containing 5.3% monolauryl tartrate.	0.05	do	1/4
Dicetyl tartrate containing 5.5% monocetyl tartrate.	0.05	do	1
Dioctyl tartrate containing 4.3% monocetyl tartrate.	0.05	do	2
Dioleoyl succinate containing 8% monooleoyl succinate.	0.50	do	1
Diamyl maleate.	1.0	do	1/4
Dibutyl phthalate.	1.0	do	1/4
Dioleoyl phthalate containing 19% monooleoyl phthalate.	0.50	do	1/4
Distearyl phthalate containing 21% monoestearyl phthalate.	0.50	do	1
Oleoyl acetate.	0.50	do	1/4
Oleoyl levulinate.	0.50	do	1/4
Butyl ricinoleate.	0.5	do	1/4
Isoamyl stearate.	1.0	do	1/4
Methyl dichlor palmitate.	1.0	do	1/4
Benzyl p-hydroxy benzoate.	0.5	do	1/4
Methyl anthranilate.	0.3	do	1/4

It will be apparent from inspection of the results shown in the table that dioleoyl malate is greatly superior to related esters in inhibiting rust formation. Even closely-related esters, such as di-2-ethyl-hexyl malate, dilauryl tartrate, dicetyl tartrate, etc., are effective in preventing rust formation for only relatively short intervals or are totally ineffective. For example, when the same amounts of dioleoyl malate and dilauryl tartrate are used, no rust is formed in an 18 hour test period with dioleoyl malate, whereas rust is formed within 1/2 hour with dilauryl tartrate. Similarly, when 0.2 per cent (4 times the quantity used of dioleoyl malate) of di-2-ethyl-hexyl malate is used, rust is formed within 1/4 hour.

Heretofore, many of the esters shown in the table above, such as the succinates, phthalates, etc. have been described in the art as rust inhibitors. From the foregoing test results, it will be clear that they have been inaccurately described. Some do, however, possess the ability to inhibit corrosion of metal surfaces.

The esters contemplated herein may be used in amounts of from about 0.01 per cent to about 1.0 per cent depending upon the conditions to which the oils containing them are submitted. In general, however, satisfactory results will be obtained when amounts of the order of 0.05-0.10 per cent are used.

As contemplated herein, the esters of oleoyl alcohol and malic acid of this invention may be used alone in mineral oils and may also be used

in mineral oils containing one or more other addition agents. They may be used in conjunction with other mineral oil addition agents such as, for example, oxidation inhibitors, film strength improving agents, oiliness agents, etc. Typical of such additives are the well-known phenols, amines, sulfides, organic compounds of phosphorus, organic compounds of chlorine, etc.

It is to be understood that although we have illustrated the invention with certain preferred mineral oil blends, the invention is not restricted to the specific examples given but includes within its scope whatever changes fairly come within the spirit of the appended claims.

This application is a continuation-in-part of application Serial No. 457,082, filed September 2, 1942 (now abandoned).

We claim:

1. A mineral oil composition comprising a mineral oil fraction normally incapable of preventing rusting of ferrous metal surfaces in the presence of water, and in admixture therewith a minor proportion, from about 0.01 per cent to about 1.0 per cent, of a mixture of neutral and partial esters of malic acid and oleyl alcohol containing about 8 per cent to about 26 per cent of partial ester.

2. A mineral oil composition comprising a mineral oil fraction normally incapable of preventing rusting of ferrous metal surfaces in the presence of water, and in admixture therewith a minor proportion, sufficient to inhibit said rusting, of a mixture of neutral and partial esters of malic acid and oleyl alcohol containing at least about 8 per cent of partial ester.

3. A mineral oil composition consisting of a mineral oil fraction normally incapable of preventing rusting of ferrous metal surfaces in the presence of water, and a minor proportion, sufficient to inhibit said rusting, of a mixture of dioleoyl malate and monooleoyl malate, said mixture containing at least about 8 percent of monooleoyl malate.

4. The method of inhibiting the rusting of ferrous metal surfaces in an environment wherein the said surfaces are contacted with a mineral oil fraction normally incapable of preventing rusting thereof and wherein water is present, which comprises contacting said surfaces with said mineral oil fraction containing a minor proportion, sufficient to inhibit said rusting, of a mixture of neutral and partial esters of malic acid and oleyl alcohol said mixture containing at least about 8 per cent of partial ester.

5. The method of inhibiting the rusting of ferrous metal surfaces in an environment wherein the said surfaces are contacted with a mineral oil fraction normally incapable of preventing rusting thereof and wherein water is present, which comprises contacting said surfaces with said mineral oil fraction containing a minor proportion, from about 0.01 per cent to about 1.0 per cent, of a mixture of neutral and partial esters of malic acid and oleyl alcohol said mixture containing at least about 8 per cent of partial ester.

6. The method of inhibiting the rusting of ferrous metal surfaces in an environment wherein the said surfaces are contacted with a mineral oil fraction normally incapable of preventing rusting thereof and wherein water is present, which comprises contacting said surfaces with said mineral oil fraction containing a minor proportion, sufficient to inhibit said rusting, of a mixture of dioleoyl malate and monooleoyl malate said mixture

containing at least about 8 per cent of said mono-
oleyl malate.

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