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MINERAL OIL COMPOSITION

Everett W. Fuller, Woodbury, and Ralph V. White, Pitman, N. J., and Bertrand W. Story, Freehold, N. Y., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

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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 outline 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, degras (wool grease), glycerides and esters. Of the latter class 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.

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We have discovered that esters of a particular group of esters, 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. These esters are characterized by limited alcohol and acid groupings and are defined as those which are obtained from a long-chain aliphatic alcohol having at least eighteen carbon atoms and a hydroxy-substituted, aliphatic dicarboxylic acid.

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 one or more of the esters defined above.

Typical esters of the class contemplated herein are dioleyl malate, dioleyl tartrate, distearyl malate, distearyl tartrate, dioleyl tartronate, distearyl mesoxalate, etc. Stated in another manner, the alcohol groups of the said esters are represented by oleyl, stearyl, etc.; and the acid groups thereof are represented by malate, tartrate, tartronate, mesoxalate, etc. These esters 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 neutral esters in which the two carboxyl groups are completely esterified, and partial esters in which one of the two carboxyl groups is esterified, can be used for the purposes of this invention.

That the esters contemplated herein are outstanding as rust inhibitors 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

	Conc., Weight per cent	Effect	Time, Hours
A. *Ester of a long-chain alcohol, 18 or more carbon atoms, and a hydroxy-substituted aliphatic dicarboxylic acid*			
Dioleyl malate containing 8% monooleyl malate.	0.05	No rust	18
Dioleyl malate containing 26% monooleyl malate.	0.05	do	18
Dioleyl tartrate containing 20% monooleyl tartrate.	0.05	do	18
Dioleyl tartrate containing 97% monooleyl tartrate.	0.05	do	18
Dioleyl tartrate containing 10% monooleyl tartrate.	0.10	do	18
Dioleyl tartrate containing 5% monooleyl tartrate.	0.15	do	18
Dioleyl tartrate containing 2.7% monooleyl tartrate.	0.25	do	18
Distearyl tartrate containing 2% monostearyl tartrate.	0.30	do	18
B. *Esters of alcohols having less than 18 carbon antoms, and a hydroxy-substituted aliphatic dicarboxylic acid*			
Di-2-ethyl-hexyl malate	0.2	Rust	¼
Diamyl tartrate containing 4% monoamyl tartrate.	1.0	do	¼
Dioctyl tartrate containing 7% monooctyl tartrate	1.0	do	¼
Dilauryl tartrate containing 5.6% monolauryl tartrate	0.05	do	½
Dicetyl tartrate containing 5.5% monocetyl tartrate.	0.05	do	1
Dicetyl tartrate containing 4.3% monocetyl tartrate.	0.05	do	2
C. *Esters of a long-chain alcohol, 18 or more carbon atoms, and a polycarboxylic acid not substituted with a hydroxy group or groups*			
Dioleyl succinate containing 8% monooleyl succinate.	0.50	do	1
Dioleyl phthalate containing 19% monooleyl phthalate.	0.50	do	½
Distearyl phthalate containing 21% monostearyl phthalate.	0.50	do	1
D. *Miscellaneous esters*			
Oleyl acetate	0.50	do	¼
Oleyl levulinate	0.50	do	¼
Butyl ricinoleate	0.50	do	¼
Diamyl maleate	1.0	do	¼
Dibutyl phthalate	1.0	do	¼
Isoamyl stearate	1.0	do	¼
Methyl dichlor palmitate	1.0	do	¼
Methyl anthranilate	0.3	do	¼
Benzyl p-dyhroxy benzoate	0.5	do	¼

It will be apparent from inspection of the results shown in the table that the esters contemplated herein, those of group A, are greatly superior to related esters in inhibiting rust formation. Even closely-related esters, such as di-2-ethyl-hexyl malate, dilauryl tartrate, dicetyl tartrate, dioleyl succinate, etc. (groups B and C) are effective in preventing rust formation for only relatively short intervals or are totally ineffective. For example, when the same amounts of dioleyl tartrate, dilauryl tartrate and dicetyl tartrate are used, no rust is formed in an 18 hour test period with dioleyl tartrate, whereas rust is formed within ½ to 2 hour periods with dilauryl and dicetyl tartrates, respectively.

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

Pure or partial esters of long-chain alcohols having at least eighteen carbon atoms and of hydroxy-substituted aliphatic dicarboxylic acids, 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 with amounts of the order of 0.05–0.10 per cent.

As contemplated herein, the esters 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, sufficient to inhibit said rusting, of a mixture of neutral and partial esters of a hydroxy-substituted aliphatic dicarboxylic acid and a long-chain aliphatic alcohol having at least eighteen carbon atoms, said mixture containing at least 2 per cent of a 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 a hydroxy-substituted aliphatic dicarboxylic acid and a long-chain aliphatic alcohol having at least eighteen carbon atoms, said mixture containing about 2 per cent to about 97 per cent of a partial ester.

3. 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 a hydroxy-substituted aliphatic dicarboxylic acid and a long-chain aliphatic alcohol having at least eighteen carbon atoms, said mixture containing from about 2 per cent to about 97 per cent of a partial ester.

4. 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 a hydroxy-substituted aliphatic dicarboxylic acid and a long-chain, unsaturated aliphatic alcohol having at least eighteen carbon atoms.

5. 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 a hydroxy-substituted aliphatic dicarboxylic acid and oleyl alcohol.

6. 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 tartaric acid and a long-chain, unsaturated aliphatic alcohol having at least eighteen carbon atoms.

7. 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 dioleyl tartrate and monooleyl tartrate.

8. 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 and maintaining in said mineral oil fraction a minor proportion, sufficient

to inhibit said rusting, a mixture of neutral and partial esters of a long-chain, aliphatic alcohol having at least eighteen carbon atoms and of a hydroxy-substituted aliphatic dicarboxylic acid.

9. 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 and maintaining in said mineral oil fraction a minor proportion, from about 0.01 per cent to about 1.0 per cent, of a mixture of neutral and partial esters of a long-chain aliphatic alcohol having at least eighteen carbon atoms and of a hydroxy-substituted aliphatic dicarboxylic acid, said mixture containing about 2 per cent to about 97 per cent of a partial ester.

10. 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 and maintaining in said mineral oil fraction a minor proportion, sufficient to inhibit said rusting, of a mixture of dioleyl tartrate and monooleyl tartrate.

EVERETT W. FULLER.
RALPH V. WHITE.
BERTRAND W. STORY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,993,737	Graves	Mar. 12, 1935
2,134,736	Rueter	Nov. 1, 1938
2,158,096	Werntz	May 16, 1939
2,204,598	Humphreys	June 18, 1940
2,204,601	Kavanagh	June 18, 1940
2,370,299	Farrington	Feb. 27, 1945
2,370,300	Farrington	Feb. 27, 1945

Certificate of Correction

Patent No. 2,443,578. June 15, 1948.

EVERETT W. FULLER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 31, for the word "outline" read *outlined*; column 3, line 49, in the table for "antoms" read *atoms*; line 74, for "dyhroxy" read *hydroxy*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of December, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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