Patented Oct. 24, 1950

2,527,296

UNITED STATES PATENT OFFICE

2,527,296

RUST-PREVENTIVE COMPOSITIONS

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No Drawing. Application April 21, 1948, Serial No. 22,503

14 Claims. (Cl. 106—14)

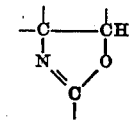
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The present application is a continuation-in-part of my co-pending application, Serial No. 607,677, filed July 28, 1945, now U. S. Patent No. 2,442,581, issued June 1, 1948, entitled "Rust-Preventive Compositions."

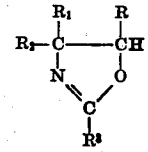
In the aforesaid co-pending application, compositions are disclosed that are adapted for use in the prevention of rusting of metals, particularly ferrous metals, upon exposure to humid atmospheres and other atmospheres conducive to rusting of metals. Briefly, the compositions disclosed in the aforesaid co-pending application comprise a suitable liquid vehicle in major proportion having dissolved therein a minor, but rust-inhibiting amount, of a salt formed by an acid ester of a phosphorus acid with an oxazoline compound. The present invention relates to compositions similar thereto but which, in addition, essentially contain a suitable metal sulfonate, the presence of such a sulfonate in combination with the aforesaid oxazoline salt having been found to provide a degree of rust-inhibiting characteristics many more times effective than would normally be expected from a summation of the individual effectiveness of the oxazoline salt or the metal sulfonate.

Broadly speaking, the compositions of this invention comprise a major proportion of a suitable liquid vehicle having dissolved therein a minor amount, sufficient to substantially inhibit rusting, of a rust-inhibiting agent comprising a metal sulfonate and a salt formed by an acid ester of a phosphorus acid with an oxazoline compound. In general, vehicles suitable for practicing the invention comprise organic liquids that are solvents for the metal sulfonates and the oxazoline salts embodied herein, and, additionally, are not per se effective to substantially induce corrosion of metal surfaces when applied thereto. In preferred embodiment, the vehicles employed are relatively non-drying organic liquids that have the aforesaid solvent characteristics and are substantially inert with respect to enhancing the rusting of metals upon exposure to atmospheres conductive thereto. In a still more preferred embodiment, liquid hydrocarbons are employed as vehicles for the rust-inhibiting agents of this invention. Illustrative thereof are mineral oils, fractions thereof, naphtha, aromatic solvents such as, V. M. and P. naphtha, benzol, and the like.

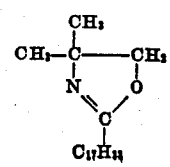
With reference to the salts embodied herein as a component of the rust-inhibiting agent, such salts may be prepared by subjecting to addition reaction conditions a blend comprising an oxazoline compound and an acid ester of a phosphorus acid. With respect to the oxazoline compounds suitable for preparing such salts, particularly effective types are the compounds known to the art as 2-oxazolines which contain the following radical:



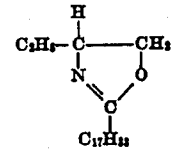
It is preferred to employ such oxazoline compounds in which one or more of the ring carbon atoms carries a long chain alkyl group, i. e., a long chain saturated or unsaturated hydrocarbon radical. More preferably, such oxazoline compounds are employed in which at least one of the ring carbon atoms carries an aliphatic group containing from about 4 to about 30 carbon atoms, as for example, such as may be obtained as the hydrocarbon residue from an acid of the fatty acid series. Although the invention contemplates use of such oxazoline compounds in which a long chain alkyl group is carried by any of the ring carbon atoms, in a still more preferred embodiment, oxazoline compounds are employed that carry a long chain alkyl group on the carbon atom between the nitrogen atom and the oxygen atom in the oxazoline ring. More specific illustrations of such compounds may be represented by the following structural formula:



wherein R, R_1, and R_2 may be hydrogen or alkyl and R^3 is alkyl and, more desirably, R^3 is of such chain length as may be obtained as the alkyl residue from a higher fatty acid as for example, lauric acid, oleic acid, stearic acid, and the like. Examples thereof are the oxazoline compounds produced by reacting oleic acid with 2-amino-2-methyl-1-propanol and having the following formula:



and the reaction product of oleic acid and 2-amino-1-butanol or 2-nitro-1-butanol having the following formula:



Other oxazolines which may be suitable and methods for their preparation are known, as for example, as displosed in U. S. Patents Nos. 2,372,409 and 2,372,410.

The acid esters suitable for reaction with the oxazolines to prepare the addition compounds employed as a component of the novel compositions may broadly be defined as partially esterified inorganic acids of phosphorus. In preferred embodiment, the esters are acid esters of phosphoric acid that contain, as the residue of an esterifying alcohol, a hydrocarbon group containing a relatively large number of carbon atoms, as for example, from about 4 to about 30 carbon atoms, and, more specifically that contain an aliphatic group containing about 8 to about 22 carbon atoms. Illustrative of esters falling within the more preferred embodiment are the mono- and di-esters of orthophosphoric acid that contain at least one hydrocarbon group having about 4 to about 22 carbon atoms. More specific illustrations thereof are the monoesters of orthophosphoric acid, such as monooctyl acid phosphate, monolauryl acid phosphate, monooctadecyl acid phosphate, and the like, and di esters, such as dioctyl acid phosphate, di-2-ethyl hexyl acid phosphate, dilauryl acid phosphate, dioctadecyl acid phosphate, and mixtures of such acid mono- and di-alkyl esters. Still further illustrations of suitable esters include acid esters of phosphoric acid that contain an aryl and/or an alkyl-substituted aryl radical, as for example, as may be illustrated by esters such as the mono- and dicardanyl acid esters of phosphoric acid.

As aforesaid, the rust-inhibiting agent embodied herein comprises a suitable metal sulfonate in combination with an oxazoline salt as aforedescribed. Such metal sulfonates desirably consist of alkali or alkaline earth sulfonates, such for example, as those derived from petroleum mahogany acids. One particularly effective compound of the latter type is sodium sulfonate, a composition of which is known in the art as "Petronate," containing about 60 to 65% of sodium sulfonate dissolved in a mineral oil.

In practicing this invention, various methods may be employed for preparing the novel rust-inhibiting compositions. One method is to prepare the oxazoline salt of an acid ester of a phosphorus acid, and incorporate the salt and the metal sulfonate into the solvent vehicle. Another method is to separately add the acid ester and the oxazoline compound to the oil whereupon these two substances react in the oil at room temperature to form, in solution, the addition product thereof. When the salt is thus formed, the metal sulfonate is added to the oil. When the latter method is employed for preparation of the rust-inhibiting compositions, it is preferred that the salt be formed in the vehicle prior to addition of the sulfonate in order to avoid the tendency of the acid ester to react with the sulfonate which would result in removal of acid ester from the reaction mixture, thus preventing the

desired combination of the acid ester with the oxazoline compound.

As aforesaid, the active rust-inhibiting materials generally comprise a minor proportion by weight of the compositions of this invention and, for most usages, the total concentration of the oxazoline salt and the sulfonate need not exceed about 10% by weight of the composition. Although amounts exceeding 10%, as for example, up to about 20%, of the rust-inhibiting ingredients may be employed, in most instances, such large amounts are unnecessary as smaller proportions are highly effective. Thus, in practicing the invention, the oxazoline salt may be employed in amounts ranging from about 0.1% to 10% and the metal sulfonate in amounts ranging from 0.5 to 15% based on the weight of the composition. However, for most purposes and in preferred embodiment, the oxazoline compound is employed in amounts ranging from about 0.25% to 3% and the metal sulfonate in amounts ranging from about 1% to 8%.

The oxazoline compounds, when used individually, have relatively little, if any, effectiveness in the inhibition of rusting of steel surfaces. Similarly, acid esters of phosphoric acid, if taken alone, are only moderately, if at all, effective in this respect. However, the oxazoline salts of such acid esters exhibit a degree of rust-inhibiting characteristics considerably in excess of the summation of the individual effectiveness, if any, of the individual components of the oxazoline salt. Moreover, and as is known to those skilled in the art, metal sulfonates such as the sodium salts of mahogany acids exhibit a certain degree of rust-inhibiting characteristics when applied to metals. However, as is evidenced by the data set forth hereinafter, use of a metal sulfonate in combination with an oxazoline salt, as aforedescribed, provides a degree of rust-inhibiting characteristics that is many more times effective than would be expected from a summation of the individual effectiveness of the oxazoline salt or the metal sulfonate when either of these materials is used individually in a concentration equivalent to use of a combination of the oxazoline salt with the metal sulfonate. The use of the metal sulfonate in combination with the oxazoline salt not only permits use of considerably less amounts of the oxazoline salt to obtain a high degree of rust inhibition, but use of such a combination results in considerable economies as the metal sulfonates are relatively inexpensive as compared to the oxazoline salts. A further, and important feature lies in the fact that these compositions form stable solutions. Obtainment of solution stability, as well as rust-inhibiting effectiveness, in compositions containing complex additives, constitutes a major problem in the art. The present discovery of components having compatible solubility characteristics, while at the same time exhibiting highly effective rust-inhibiting characteristics and other desired properties, is a major advance in the art.

Although the exact reasons underlying the highly effective rust-inhibiting characteristics obtained by practicing this invention are not fully known, it is believed that such results are apparently caused by co-action or interdependence between the additive components. The additive materials are highly polar in character which may account at least in part for the powerful rust-preventive properties. Presumably, this polar structure is also responsible for an additional desired characteristic possessed by these composi-

tions which is their strong wetting action upon and excellent adherence to metal surfaces to which they are applied. Modern usage of rust-preventive compositions for the purpose herein disclosed requires that they cling tenaciously to metal surfaces in a substantially unbroken film under quite adverse conditions, as for example, under high temperatures and humidities for extended periods of time, and in some cases, when exposed to more corrosive atmospheres such as salt spray or mist. The compositions of this invention not only adhere tenaciously to metal surfaces but provide protection thereof under a wide variety of adverse conditions as is apparent from the tests disclosed hereinbelow. An additional desired characteristic of the compositions disclosed herein is that they are not readily removable by water from metal surfaces to which the compositions have been applied.

In order to further describe the invention, the following example sets forth an illustrative embodiment of the highly effective rust-preventive characteristics provided by use of compositions such as embodied herein. In the example, the rust-preventive characteristics of the compositions described were determined by subjecting the compositions to the severe rust-inducing conditions of the humidity corrosion test described in "Army-Navy Aeronautical Specification Compound: Corrosion-Preventive; Air Craft Engine" AN–VV–C–576*b*. In accordance with the test, two freshly sand-blasted steel panels are coated on all surfaces with the test oil, drained for at least four hours in an atmosphere of 50 to 55% relative humidity at 25° C., and then subjected to a circulating atmosphere of 95 to 100% relative humidity at a temperature of 120° F. for 150 hours in a special humidity cabinet. At the end of the test period, the panels are removed from the humidity cabinet, cleaned with naphtha, and examined. The presence of any corrosion on the panels except within ⅛'' from any edge, evidences failure of the test composition.

Example I

A composition was prepared by dissolving in a mineral oil of SAE 40 grade 3% by weight of sodium sulfonate and 1% by weight of the addition salt formed by lauryl acid phosphates with an alkyl-substituted oxazoline prepared by reaction of oleic acid with 2-amino-2-methyl-1-propanol. Thus, the active rust-inhibiting agent was present in a total amount of 4% based on the weight of the oil. When subjected to the aforesaid humidity test, the metal panels were protected against rusting for more than 450 hours.

For purposes of comparison, and in order to illustrate the unexpected high degree of rust-inhibiting characteristics provided by use of the combination additive as compared to individual use of the components of such an additive, a composition was prepared by dissolving 4% by weight of sodium sulfonates in the SAE 40 oil, and another composition was prepared by dissolving 4% by weight of the aforesaid oxazoline-acid ester salt in the same grade oil. When subjected to the aforesaid humidity test, the protection provided by the composition containing only the sulfonate was about 65 hours, and, by the composition containing only the oxazoline salt, about 150–200 hours.

In order to further describe the invention, and to illustrate the excellent rust-inhibiting characteristics provided by practicing this invention under rust-inducing conditions differing from the conditions of the aforesaid humidity test, several compositions, as described in the following examples, were prepared and subjected to test in accordance with the test described in "USA 2–122 Oil, Lubricating, Preservative, Medium." Briefly, the test comprises immersing freshly sand-blasted steel panels in the oil under test at room temperature for one minute, draining the panels at 130° F. for 16 hours, and placing the panels in a special humidity cabinet maintained at 95–100% relative humidity at 100° F. The test composition is considered as passing the test if, at the end of 300 hours, corrosion has not occurred within ⅛'' from any edge of the panels.

Example II

A composition was prepared by blending a mineral oil of SAE 60 grade with 0.5% by weight of lauryl acid phosphates and 0.4% of an oxazoline compound formed by reaction of oleic acid with 2-amino-2-methyl-1-propanol, and stirring the blend until a homogeneous solution was obtained. Thereupon, 2.5% of "Petronate" (60–65% sodium sulfonate) was dissolved in the solution, thus providing a total additive concentration of about 2.4%. This composition, upon being subjected to the aforesaid humidity test (USA 2–122) protected the metal panels against rusting for at least 300 hours.

Example III

To a petroleum lubricating oil consisting of a blend of 50% solvent refined, acid treated, wax free neutral oil of 60 SUS at 100° F. derived from coastal crude and 50% non-viscous mid-continent solvent treated neutral of 85 SUS at 100° F., there were added 0.75% of dilauryl acid phosphate and 0.6% of the oleic acid 2-amino-2-methyl-1-propanol reaction product as aforedescribed. When the solution had become homogeneous, 8% of "Petronate" was added to and dissolved in the oil composition. When tested under the condition of the aforesaid humidity test at 100° F., this composition passed the requirements thereof, and also satisfactorily passed the salt water test set forth in the aforesaid USA specification 2—122 and the salt spray test set forth in Specification O. S. 1362. Briefly, the salt water test comprises totally immersing two sand-blasted steel panels in the test oil, draining the panels for 16 hours, and then totally immersing the panels for 20 hours in synthetic sea water. The test panels, after being removed from the sea water and dipped in acetone, must show no corrosion, except within ⅛ inch from any edge, if the test oil is to be considered as having passed the test. The salt spray test comprises dipping three test panels of freshly sand-blasted steel in the test oil, draining the same overnight at room temperature, then exposing the panels at room temperature to a fine mist of 4% aqueous sodium chloride solution for 24 hours. Any corrosion on the panel surfaces, except within ⅛ inch from any edge, indicates failure of the test oil to protect against rusting under the test conditions.

Example IV

In a manner similar to that set forth in Example III, compositions were prepared by dissolving in an SAE 30 grade oil, a total of 2.4% by weight of a combination additive comprising sodium sulfonate, the aforesaid reaction product of oleic acid with 2-amino-2-methyl-1-propanol, and lauryl acid phosphates in proportions as set forth in the following tabulation. When sub-

jected to the conditions of the aforedescribed humidity test, the compositions containing the combination additive protected the metal panels against rusting for at least 360 hours, as is set forth in the tabulation. Such a high degree of rust-preventive characteristics is completely unexpected from a summation of the individual effectiveness of the components of the combination additive as compositions based on the same oil containing only sodium sulfonate in 2.4% concentration or only the aforesaid phosphate and oxazoline compound in a total concentration of 2.4% in the same proportion as in the examples in the tabulation, failed in 216 hours or less when subjected to the humidity test.

Test Compositions by Weight				Total Additive Concentration	Humidity Test (Life in hours)
SAE 30 Grade Oil	Sodium Sulfonate	Acid Ester	Oxazoline Compound		
97.6	1.80	0.31	0.29	2.4	360
97.6	1.80	0.34	0.26	2.4	360

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will readily recognize that variations and modifications can be made. Such modifications and variations are to be considered to be within the purview of the specification and scope of the appended claims.

I claim:

1. A rust-preventive composition comprising a liquid hydrocarbon having dissolved therein (*a*) about 0.1 to about 10% by weight of said composition of a rust-inhibiting salt formed by an acid ester of phosphoric acid containing a hydrocarbon group of about 4 to 30 carbon atoms with an oxazoline compound containing an aliphatic group of about 4 to 30 carbon atoms and (*b*) an oil-soluble rust-inhibiting metal sulfonate from the group consisting of alkali and alkaline earth metal sulfonates in an amount of about 0.5 to 15% based on the weight of said composition sufficient to impart to said composition rust-preventive characteristics in excess of the sum of the individual effectiveness of the salt and sulfonate.

2. A composition, as defined in claim 1, wherein the liquid hydrocarbon is a mineral oil.

3. A composition, as defined in claim 1, wherein the salt is present in an amount of about 0.25 to about 3% and the sulfonate in an amount of about 1 to about 8%.

4. A composition, as defined in claim 1, wherein the acid phosphate is an alkyl acid phosphate.

5. A composition, as defined in claim 1, wherein the acid phosphate is lauryl acid phosphate.

6. A composition, as defined in claim 1, wherein the oxazoline compound is a 2-oxazoline in which a ring carbon atom is directly attached to the hydrocarbon residue of a fatty acid of about 4 to 30 carbon atoms.

7. A composition, as defined in claim 6, wherein the hydrocarbon residue directly attached to a ring carbon atom in the oxazoline is the hydrocarbon residue of oleic acid.

8. A composition, as defined in claim 1, wherein the metal sulfonate is derived from a petroleum mahogany acid.

9. A composition, as defined in claim 1, wherein the metal sulfonate is a sodium salt of petroleum mahogany acids.

10. A rust-preventive composition comprising a mineral oil having dissolved therein (*a*) about 0.1 to about 10% by weight of said composition of a rust-inhibiting salt formed by an acid ester of phosphoric acid containing a hydrocarbon group of about 4 to 30 carbon atoms with an oxazoline compound containing an aliphatic group of about 4 to 30 carbon atoms and (*b*) an oil-soluble rust-inhibiting alkali metal salt of a petroleum mahogany acid in an amount of about 0.5 to 15% based on the weight of said composition sufficient to impart to said composition rust-preventive characteristics in excess of the sum of the individual effectiveness of the salt and sulfonate.

11. A rust-preventive composition comprising a mineral oil having dissolved therein, by weight of said composition, about 3% of a sodium salt of petroleum mahogany acids and about 1% of a salt formed by lauryl acid phosphate with a 2-oxazoline containing the hydrocarbon residue of oleic acid.

12. A composition comprising a mineral oil having dissolved therein, by weight of said composition, about 1.5% of a sodium salt of petroleum mahogany acids and about 0.9% of a salt formed by lauryl acid phosphate with a 2-oxazoline containing the hydrocarbon residue of oleic acid.

13. A composition comprising a mineral oil having dissolved therein, by weight of said composition, about 5% of a sodium salt of petroleum mahogany acids and about 1.3% of a salt formed by lauryl acid phosphate with a 2-oxazoline containing the hydrocarbon residue of oleic acid.

14. A composition comprising a mineral oil having dissolved therein, by weight of said composition, about 1.8% of a sodium salt of petroleum mahogany acids and about 0.6% of a salt formed by lauryl acid phosphate with a 2-oxazoline containing the hydrocarbon residue of oleic acid.

JOHN W. BISHOP.

REFERENCES CITED

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

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Number	Name	Date
2,182,992	Lebo	Dec. 12, 1939
2,383,033	Adams et al.	Aug. 21, 1945
2,442,581	Bishop	June 1, 1948