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INHIBITORS

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6 Claims. (Cl. 148—6.5)

This application is a continuation-in-part of my co-pending application Serial No. 242,419, now Patent No. 2,224,695, which is in turn a continuation-in-part of application Ser. No. 99,165, filed September 2, 1936.

The present invention relates to the art of treating metal and is particularly directed to an improved method of the treatment of metal surfaces to prevent corrosion and rust.

Many attempts are known in the prior art to provide rust and corrosion inhibitors for metals but these efforts heretofore have either proved unsatisfactory or too expensive in practice to warrant their wide commercial adoption.

The general objects of this invention are to provide a coating composition which is very simple in its use and application; one that is usable for metals directly without preliminary treatment or finishing operations; a compound which is inexpensive and generally reduces the cost of coating metal and a novel method to improve the art of inhibiting metals from corroding or oxidizing.

The specific object hereof is to provide a compound which will react with the metal to which it is applied to efficiently protect the surface of such metal and effectively prevent oxidation and corrosion.

In accordance with the present invention I have discovered that certain phosphorus-containing organic compounds in non-aqueous media are readily applicable to metal surfaces to inhibit corrosive action. For most purposes, I prefer to use derivatives of acids of phosphorus; and for certain purposes, the derivatives used are preferably of such nature that in contact with aqueous media they will yield a solution having a pH of below 7, my research and tests showing the most satisfactory results to be when the pH is between 4 and 6, in most cases.

The organic phosphorus compounds contemplated hereby are those which contain an oil-solubilizing organic radicle. Such oil solubilizing radicle may be any suitable aliphatic, cyclo-aliphatic or aromatic radicle, but will preferably contain a plurality of carbon atoms, advantageously four or more. A preferred type of oil-solubilizing radicle is that comprising those radicles which have the structure —O—R and more especially those which exist in the form of an ester.

In addition to the oil-solubilizing constituent, the compounds for use in this invention may advantageously contain a salt radicle. This salt radicle may be either organic or inorganic but for most purposes, I prefer inorganic salt radicles and

especially those consisting of metals. In general, the divalent metals will be found most desirable for my purpose and particularly those of group II of the periodic table of elements. The group of metals consisting of calcium, strontium, and barium are useful for my purpose in many cases; but for most purposes, I prefer an element of the group consisting of beryllium; magnesium; zinc; and cadmium.

Among the most effective inhibitors of my invention are those which contain at least one element of group VI (of the periodic table of elements) other than oxygen. This element may be either a member of the left-hand column of the elements in group VI, such as molybdenum or tungsten; or a member of the right-hand column, as for example, sulphur or selenium.¹ In general, I prefer those compounds which contain sulphur, as for example, the salt-esters of thio-acids of phosphorus.

In practicing my invention, I have found that many compounds of the acids of phosphorus are sufficiently active under favorable conditions to react chemically with metal surfaces to form adherent protective coatings.

A further advantage of the present discovery is the compatibility of certain derivatives of the acids of phosphorus in relatively pure state with oils and with vehicles used in coating materials, such as paints, varnishes, lacquers; and with other solvents partly or wholly immiscible with water. This is especially valuable in carrying out the invention as the corrosion inhibiting compound may be included in ornamental or preservative coating mixtures and applied to the surface to be treated without an extra operation. Still further, it has been found that the affinity of phosphorus compounds with paint, varnish, and lacquer coating materials generally improves the resulting coating and provides an effective bond or adherence thereof to the surface of the metal due to the reaction of such compounds with the metal.

In practice, a metal surface may be treated with a derivative of acids of phosphorus in an oil or other carrying vehicle to provide a thin coating on such surface. One very effective method comprises heating a coating liquid to a suitable temperature, immersing the article to be protected, and then cooling or drying in air the thin adherent coating upon the article which resulted

¹ Examples of compounds containing the former are the esters and salt-esters of phosphomolybdic acid and of phosphotungstic acid.

from the bath. The drying may be accelerated by placing the coated article in a suitable oven.

As examples of the new and preferred class of inhibitors and included within the scope of the present invention are the ester and ester-salt derivatives of the acids of phosphorus. Also included are certain of the organic derivatives of such acids, which derivatives may be of the aliphatic or aromatic type, and which derivatives will also have a pH of less than 7, preferably between 4 and 6. Specific examples of inhibitors contemplated by this invention are:

Tricresyl phosphate
Diphenyl phosphoric acid
Mono diphenyl phosphoric acid
Dilauryl phosphoric acid
Mono lauryl phosphoric acid
Mono-, di-, and tri-esters of:
 (Ortho) phosphoric acid
 Thio-phosphoric acid
 Phosphorous acid
 Thio-phosphorous acids
 Hypo-phosphorous acids
Mono-, di-, tri-, and tetra- esters of:
 Pyro-phosphoric acid
 Pyro-phosphorous acid
 Thio-pyro-phosphoric acids
 Thio-pyro-phosphorous acids
Mono-, and di- esters of: Hypo-phosphoric acid
Esters of:
 Meta-phosphoric acid
 Meta-phosphorous acid
 Thio-meta-phosphoric acids
 Thio-meta-phosphorous acids
Phenyl meta phosphate
Dichlor diphenyl phosphoric acid
Mono-tolyl phosphoric acid
Dinaphthyl phosphoric acid
Dichlor dinaphthyl phosphoric acid
Diethyl phosphoric acid
Dibutyl phosphoric acid
Tri-isobutyl phosphate
Diphenyl phosphorous acid
Diphenyl pyro-phosphoric acid
Sodium phenyl phosphoric acid
Lead phenyl phosphoric acid
Lead diphenyl phosphate
Lead dilauryl phosphate
Mono-ethyl phosphite
Di-ethyl phosphite
Mono-, di-, and tri-phenyl phosphites
Mono-, di-, and tri-aryl phosphites
Tri-ethyl phosphite
Tetra-ethyl ester of pyro-phosphoric acids
Ethyl meta phosphate
Mono-ethyl phosphoric acid
Mono- and di-thio-pyro-phosphoric acid derivatives
Mono- and di-thio-meta-phosphoric acid derivatives
Diphenyl thio-phosphoric acid
Diphenyl thio-phosphorous acid
Diphenyl thio-pyro-phosphoric acid
Phenyl meta-thio-phosphate
Ethyl thio-phosphite
Tri-ethyl thio-phosphite
Ethyl thio-meta-phosphate
Mono-ethyl thio-phosphate
Di-ethyl ester of tetrathio-phosphoric acid
and salts derived from any of the above-identified acid esters.

The inorganic-organic or thio inorganic-organic derivatives of the acids of phosphorus and of the acid salts thereof fall also within the general class of compounds and are useful to produce

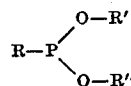
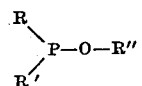
the present inhibitor. By way of example the following are cited:

Sodium phenyl phosphoric acid
Lead phenyl thio-phosphoric acid
5 Lead diphenyl phosphate
Lead dilauryl phosphate

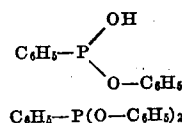
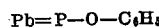
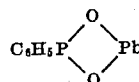
In the above described acids or salts, sulphur may be substituted for any or all of the oxygen atoms; organic or inorganic radicles for any or all hydrogen atoms; and metals for any or all hydrogen atoms to produce products which are useful for my purpose.

Other examples are found in certain metal and organic phosphides such as copper phosphide or 15 silver phosphide, tri-phenyl phosphide, phenyl-lead phosphides.

This invention also contemplates the use of derivatives of the acids of phosphorus in which an organic radicle is substituted for a hydroxyl 20 group of the original acid, that is, in which a carbon atom is directly attached to a phosphorus atom; for example:



in which R, R', R'' are hydrogen, or an organic radicle or a metal such as:



50 Still further compounds of the herein disclosed general class are the metallic or organic phosphomolybdates, phosphotungstates, ammonium phosphomolybdates and monoethyl phosphomolybdates.

55 Additional examples of these are as follows:
Derivatives of phosphomolybdic acid

Esters:

Monolauryl phosphomolybdate
Di-lauryl phosphomolybdate
Tri-lauryl phosphomolybdate
Tri-naphthenyl phosphomolybdate
Tri (poly-lauryl phenyl) phosphomolybdate

Ester-salts

65 The salts derived from the following esters by substituting magnesium, zinc and cadmium for the replaceable hydrogen;

Monolauryl phosphomolybdate
Di-lauryl phosphomolybdate
Dinaphthenyl phosphomolybdate
Di (poly-lauryl phenyl) phosphomolybdate
N-dilauryl-aniline dilauryl phosphomolybdate

Derivatives of phosphotungstic acid

Esters:

Monolauryl phosphomolybdate
 Di-lauryl phosphomolybdate
 Tri-lauryl phosphomolybdate
 Tri-naphthenyl phosphomolybdate
 Tri (poly-lauryl phenyl) phosphomolybdate

Ester-salts

The salts derived from the following esters by substituting magnesium, zinc and cadmium for the replaceable hydrogen:

Monolauryl phosphotungstate
 Di-lauryl phosphotungstate
 Dinaphthenyl phosphotungstate
 Di (poly-lauryl phenyl) phosphotungstate

N-dilauryl-aniline dilauryl phosphotungstate

With many of the foregoing acids of phosphorus it is to be noted that one or more of the hydrogen atoms may be replaced by organic or inorganic radicles and one or more of the hydrogen atoms may be replaced by a metal or metallic radicle, such as metallic oxide, and thus form a single compound useful for my purpose. Illustrative thereof are:

Cuprous monobutyl phosphite and cupric monophenyl trithiophosphite

Additional specific examples of compounds preferred for use as corrosion inhibitors in accordance with my invention are as follows:

Tri cresyl thiophosphates
 Tri (chlor-phenyl) thiophosphates
 Tri cyclohexyl thiophosphates
 Tri (methyl-cyclohexyl) thiophosphates
 Tri (amyl-cyclohexyl) thiophosphates
 Tri butyl thiophosphates
 Mono (poly-lauryl-phenyl) thiophosphoric acids
 Di (poly-lauryl-phenyl) thiophosphoric acids
 Mono naphthenyl thiophosphoric acids
 Di naphthenyl thiophosphoric acids
 Di (methyl-cyclohexyl) thiophosphoric acids
 Di (amyl-cyclohexyl) thiophosphoric acids
 Di phenyl thiophosphoric acids
 Di lauryl thiophosphoric acids

The magnesium, zinc and cadmium salts derived from the above examples of mono- and di-substituted thiophosphoric acids, e. g.:

Magnesium poly-lauryl-phenyl thiophosphates
 Zinc naphthenyl thiophosphates
 N-dilauryl-aniline dilauryl thiophosphates
 N-dicyclohexyl-aniline dicyclohexyl thiophosphates

In this specification it is to be understood that the term "radicle" is used to denote not only a group of atoms which can enter into a compound without undergoing decomposition, but a single radicle such as one containing one or more atoms of a single element in contrast with the "compound radicles."

The invention is capable of adaptation or practice in many varied forms and methods and the following are recited as illustrative embodiments of the same and not limitative of the scope thereof:

Example 1

The inhibiting compound consisting of the approximate mix of 5% diphenyl phosphoric acid

and 95% of a refined mineral oil (about 180 S. U. S. at 100° F.), which is heated to a temperature of about 180° C., has been found very satisfactory in treating steel sheets. The metals sheets or articles are dipped into the heated admixture where such compound attacks the surface of the metal to apply thereto a protective coating, and thereupon the metal article is removed from the bath and the surplus compound may be either wiped off or dried by air or heat to remove the oil vehicle. It will be understood that the diphenyl phosphoric acid has, during this process, attacked the surface of the metal and reacted chemically therewith to provide a homogeneous protective layer having pronounced corrosion-resisting properties.

As a result of the foregoing treatment of the metallic sheets it was found that the surface of such sheets had thereon an intimate strongly adherent coating which proved to be organic iron phosphate, the aforesaid diphenyl phosphoric acid having directly contacted the surface of the metallic sheets and having reacted therewith to produce upon the outer surfaces of such sheets this layer of organic iron phosphate.

It should be manifest that the very nature and formation of this protective coating is so intimately joined or alloyed to the surface of the metal as to be inseparable therefrom and hence, assured of its durability. The improved protective coating prevents the oxidation or corroding of the metal and is sufficiently ductile to permit certain working of such metal.

Example 2

An inhibiting compound is prepared by dissolving 0.25% tricresyl phosphate in a mineral lubricating oil (Penna. bright stock).

Example 3

An inhibiting compound is prepared by dissolving 0.25% of tri-isobutyl phosphate in bright stock.

A like admixture of diphenyl phosphoric acid, and oil, may be used to treat the surfaces of metallic articles in either heated or unheated condition. When the bath is unheated, the article dipped therein may require a slightly longer period of immersion and the method of drying may be slightly varied, such as by subjecting the coated article to heat to accelerate the chemical reaction of the compound with the metal itself. Many of the herein disclosed compounds are sufficiently acidic in nature to attack the metal without any heat or other accelerative aid.

The above examples are directed to the practice of the present invention in the mere surface treatment of metals to effectively prevent corroding or rusting thereof. Obviously, such metals may, thereafter, be used in any desired manner or may be ornamental or treated with other coating compositions, as for example, paints and lacquers.

The invention contemplates also the admixture of the above derivatives of the acids of phosphorous directly in certain paint, varnish, lacquer or enamel compositions, or other solvents partially or wholly immiscible with water. In employing the invention in such manner I have discovered that when a metallic surface is treated with a paint or the like, including one of the above derivatives of the acids of phosphorus, a very similar result is obtained to that described above in connection with Examples 1, 2 and 3. In other words, it is found that the said deriva-

tives of acids of phosphorus attack the metal surface being treated and produce the same reactionary effect regardless of the paint vehicle carrying such materials and thus provides an effective adherent organic protective coating on such metal.

As stated herein, the novel coating compound is preferably carried in non-aqueous media, such as petroleum oils and solvents, fatty oils, greases, waxes, or other organic solvents, or mixtures of the above such as are used as vehicles for paints, varnishes, lacquers, etc. Such compound will then react by itself or in contact with water or air with the surface of the metal to which the coating is applied, to produce thereon a protective coating. This coating consists of the reaction product of the metal and the acidic constituent of the compound. It has been found that certain of these compounds of phosphorus will attack the metal and produce a roughening of the metal and thereby greatly increase the adherent properties of such metal when an ornamental coating is applied thereto.

The invention also contemplates combining with the compound of phosphorus an organic derivative of an inorganic acid, e. g. sulphuric acid, silicic acid, nitric acid, or the like. These hydrolyzing agents are found to accelerate the attack on the metal surface and to greatly enhance the properties of such surface to hold coatings thereon.

Examples of the above mentioned organic derivatives of inorganic acids are:

Ethyl silicates
Phenyl sulphonic acid
Ethyl sulphuric acid
Lauryl sulphuric acid
Aniline sulphate

An example of the combination of one of the above with an acid compound of phosphorus is:

Sulphonated diphenyl phosphoric acid

It is very important to note that the processes involving the admixture of the novel inhibiting compound with another coating composition provides a more satisfactory bond or means of attachment of such other composition to metal surfaces. Obviously, if an ingredient of a coating composition does in itself react with and adhere to a metal surface, then such composition carrying this ingredient will become permanently adhered to the metal when applied.

As stated in the general outline of this invention, it is sometimes desirable that the derivatives of the acids of phosphorus to be used as the present novel inhibitor be of such nature that in contact with water they will yield a solution having a pH of below 7, preferably below 6 and above 4. Such materials are of sufficiently acidic nature as to react chemically with metal surfaces to form adherent protective coatings.

Because of the very nature of the acids of phosphorus and their derivatives it has been found that such agents as moisture, which ordinarily promotes corrosion, will, when attacking the metal surface treated by the present novel coating method, produce an accelerated reaction of such derivatives of phosphoric acids used in the coating with the metal to form a thin protective layer of organic metal phosphate, such as organic iron phosphate when used with steel or the like.

From the above description it has been shown that the compounds described, when incorporated in a coating composition, are all effective

and desirable corrosion and oxidation inhibitors.

The present invention is not limited to the specific examples given above, as they are to be construed as specific embodiments of the present invention and not limitations of the scope thereof. Likewise the quantities of materials employed and the procedure of preparation may be widely varied without departing from the scope of this invention, nor is it intended to limit the use of any member of the new class of inhibitors to any particular coating composition. The present invention is limited solely by the claims attached as a part of this specification.

The amount of the above-described derivatives of acids of phosphorus required for my purpose depends upon the nature of the compound, the kind of use, and the character of the vehicle. In the case of certain of the more active compounds, a very low percentage is sufficient, e. g. from 0.01 to 0.25%, and for most purposes, amounts up to about 5% are desirable. Usually only a minor amount need be used; but in the case of certain of the materials, for example, certain of the ester-salts (particularly those also useful as pigments or fillers) much higher proportions, up to 90% or more, may be found useful.

This application is a continuation-in-part of my co-pending application Serial No. 737,070, filed July 26, 1934, where I have disclosed that:

In order to protect bearings, gears, etc. from very severe overloads, it is sometimes advisable to use a halogen-containing compound which is so unstable as to be appreciably corrosive under normal conditions. Since chain compounds are generally more corrosive, i. e. more unstable than ring compounds, they are admirably suited for this purpose. In these circumstances the corrosive effect of such chain compounds and of halogenated organic ring compounds of the addition type for example, may be greatly inhibited by the addition of certain other oil-soluble compounds, such as (1) organic bases, aromatic and alkyl amines, triethanolamine, quinoline, etc., (2) organic phosphates, e. g., tri-butyl phosphate, tri-phenyl phosphate, tri-cresyl phosphate, etc. Also certain of the halogen and sulphur compounds referred to above have similar corrosion-inhibiting effects, notably, (1) the phosphates of chlorinated ring compounds, e. g. tri-chlorophenyl phosphate, (2) mercaptans and chlor-mercaptans.

It will be observed that in said application Serial No. 737,070, of which the present case is a continuation-in-part, I have given the following, viz.:

Organic phosphates

Tri-butyl phosphate
Tri-phenyl phosphate
Tri-cresyl phosphate

Phosphates of chlorinated ring compounds
Tri-chlorophenyl phosphate

as corrosion inhibitors and they are specific examples of organic compounds of phosphorus containing an oil solubilizing organic radicle.

In said application I have also disclosed for use in lubricants the following organic phosphorus compounds which are specific examples therein of the generic class of organic phosphorus compounds containing an oil solubilizing organic radicle to which the present application is particularly directed:

Tri-tertiary amyl phenyl phosphate
Triphenyl phosphite

Halogen derivatives of:

Tri-cresyl phosphate

Tri-phenyl phosphate

Tri-phenyl phosphite

Tri-tertiary amyl phenyl phosphate

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the composition and method herein disclosed, provided the ingredients or steps stated by any of the following claims or the equivalent of such stated ingredients or steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a compound containing phosphorus having an oil-solubilizing organic radicle with a separate organic derivative of a phosphorus-free inorganic acid, in an oil vehicle. 20

2. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a compound containing phosphorus having an oil-solubilizing organic radicle with a separate organic derivative of a phosphorus-free inorganic oxy acid, in an oil vehicle. 25

3. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a compound 30

containing phosphorus having an oil-solubilizing organic radicle with a separate organic derivative of an inorganic oxy acid of the class consisting of sulphuric acid, silicic acid, and nitric acid, in an oil vehicle. 5

4. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a compound containing phosphorus having an oil-solubilizing organic radicle with an oil-soluble compound of the class consisting of sulphonic acids and derivatives of sulphonic acids, in an oil vehicle. 10

5. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a salt-ester of an acid of phosphorus having an oil-solubilizing organic radicle with an oil-soluble compound of the class consisting of sulphonic acids and derivatives of sulphonic acids, in an oil vehicle. 15

6. A non-aqueous composition having the property of inhibiting corrosion of metal surfaces comprising the combination of a salt-ester of a sulphur containing acid of phosphorus having an oil-solubilizing organic radicle with an oil-soluble compound of the class consisting of sulphonic acids and derivatives of sulphonic acids, in an oil vehicle. 25

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