

## UNITED STATES PATENT OFFICE

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## CORROSION INHIBITORS

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This application is a continuation-in-part of my copending application, Serial No. 671,123, filed May 20, 1946, now abandoned, which in turn was a continuation-in-part of my then copending application, Serial No. 369,227, filed December 9, 1940, now Patent No. 2,400,573, dated May 21, 1946; which application was a continuation-in-part of my then copending application Serial No. 99,165, filed September 2, 1936, now abandoned.

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.

In general, objects of this invention are to provide a coating composition which is very stable 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.

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 compounds, generally known as the phosphide compounds, in non-aqueous media are readily applicable to metal surfaces to inhibit corrosion action. More particularly, this invention is concerned with organic phosphide types of compounds containing a metal group, and still more specifically the organo-metallic phosphides. For most purposes, it is preferred to employ an organo-metallic phosphide of such nature that in contact with an aqueous media they will yield a solution having a pH of below about 7, my research and tests showing the most satisfactory results to be when the pH is between about 4 and 6, in most cases. For reasons not too clearly understood the organo-metallic phosphides give particularly good results in inhibiting corrosion of such metals as for example ferrous types, bearing metals of copper-lead, cadmium-silver, or analogous types.

For the purposes of this specification and the appended claims, the term "organo metallic phosphide" is intended to include those compounds in which the metal substituent is solely attached to

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the phosphorus atom, and such compounds must contain at least one organic radical attached to the phosphorus atom.

Generally, the organo-metallic phosphides can be represented by the following structural formula:



where M is a mono-, di- or polyvalent metal, R is an organic radicle, hydrogen, or halogen, at least one of which is an organic radicle, and "a" and "b" can be either one or two, and "c" can be up to 4, depending on the valence of the metal. To illustrate this point, when M is a divalent metal, "a" is 1, "b" can be either 1 or 2, and "c" can be either 1 or 4, in accordance with the following subgeneric structural formulae:



In the case of a monovalent metal represented by M in the above structural Formula (a), the numerical values of "a" and "b" and "c" in said formula will vary in accordance with the following subgeneric structural formulae:



The organo-metallic phosphides can have present therein metals from groups I and II of the periodic system, namely the alkali or alkaline earth metals. Other polyvalent metals also can be suitably employed, however, it is preferable to use metals from groups I and II of the periodic system.

The halogen present in the phosphides of this invention generally can be of any halogen, but it is preferred to employ chlorine as the halogen contained in the organo-metallic phosphides.

The organic radicles as previously mentioned can be one or more "R's" in the generic structural Formula (a) given hereinabove. In a more particular identification of the types of organic radicles present in the organo metallic phosphides, the table below enumerates examples thereof in an order of convenience rather than preference. It is preferred to employ oil solu-



bilizing organic radicles, which contain a plurality of carbon atoms, advantageously about 4 or more.

TABLE I

*Organic radicles*

- I. Aliphatic
  - A. Hydrocarbon
    1. Acyclic
      - a. propyl
      - b. butyl
      - c. amyl
      - d. the radicles of other homologous compounds enumerated above.
    2. Cyclic
      - a. Cycloparaffins
        - (1) cyclopentyl
        - (2) cyclohexyl
  - II. Aromatic
    - A. Benzene series
      - (1) phenyl
      - (2) methyl phenyl
      - (3) radicles of other homologous compounds of benzene
    - B. Naphthalene series
      - (1) naphthyl
      - (2) methyl naphthyl
      - (3) other homologous radicles of naphthalene
  - III. Oxygen bearing radicles  
The OR group where R can be any of the aliphatic radicles enumerated under I and II
  - IV. Halogen bearing radicles  
The halogen, for example chlorine, can be present in any of the organic radicles listed under I, II, and III above.

Examples of organo-metallic phosphides found applicable for the purposes of this invention include:

Calcium amyl phosphide  
Barium octyl phosphide  
Zinc octyl phosphide  
Barium cresyl phosphide  
Barium benzyl phosphide  
Magnesium chlorophenyl phosphide  
Phenyl lead phosphide

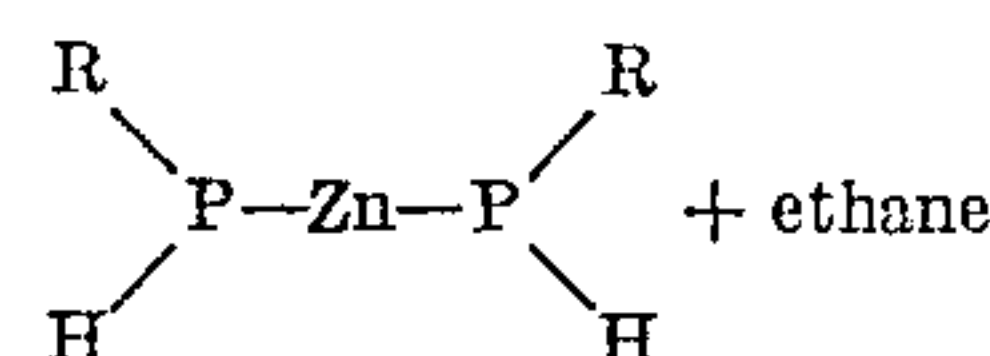
It is not to be inferred that all organo-metallic phosphides are equivalent in efficacy, but that under certain conditions some organo-metallic phosphides are more desirable than others.

In order that a better understanding can be obtained of my invention, two illustrative examples of methods of preparation will be given. It should be understood that the examples are given by way of illustration and not by way of limitation.

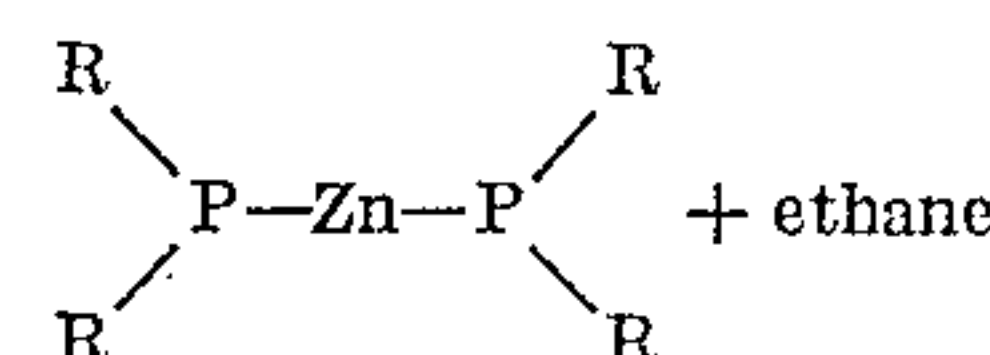
An organic phosphine which may be either  $RPH_2$  or  $R_2PH$  is reacted with an alkali metal such as sodium or potassium to produce a phosphide. The alkali metal is dissolved in liquid ammonia. The alkali dissolves in liquid ammonia without reaction. The organic phosphine is then introduced slowly into the solution. When using an organic phosphine of the formula  $RPH_2$  and when using equal molecular portions of the organic phosphine and metal there will be produced a compound having the formula  $RPHM$ . However, when 1 mol of the organic phosphine  $RPH_2$  is combined with 2 mols of the metal, a phosphide having the formula  $RPM_2$  is produced. When utilizing an organic phosphine of the formula  $R_2PH$ , 1 mol thereof will be used for a mol of metal and the phosphide produced will have the formula  $R_2PM$ .

A second method for the preparation of the phosphides is by means of the reaction of an organic phosphine with zinc diethyl. Accordingly, to this method an organic phosphine of the formula  $RPH_2$  is introduced to the liquid zinc diethyl and at room temperature or only

slightly above room temperature the reaction will proceed to the production of



When using an organic phosphine of the formula  $R_2PH$  the reaction thereof with zinc diethyl will result in the following:



A further advantage of the present discovery in the compatibility of certain organo-metallic phosphides 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 organo-metallic phosphide 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 an organo-metallic phosphide 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 from the bath. The drying may be accelerated by placing the coated article in a suitable oven.

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 with the surface of the metal to which the coating is applied, to produce thereon a protective coating. It has been found that certain of these organo-metallic phosphides 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 physically combining with the organo-metallic phosphide 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 the silicates, nitrates, sulphates, and the sulphonates and ester and salts of the sulphonates. The sulphonates and ester and salts thereof are the preferred derivatives of inorganic acid which may be used in combination with the organo-metallic phosphides.

In the following table are listed specific examples of types of sulphonic acids, esters and



salts which are useful in accordance with the principles of this invention.

TABLE II

## Sulphonic acids, e. g.:

Benzene sulphonic acid  
Naphthalene sulphonic acid  
Amyl naphthalene sulphonic acid  
Capryl benzene sulphonic acid  
Lauryl benzene sulphonic acid  
Lauryl sulphonic acid  
Cetyl sulphonic acid  
Petroleum mahogany sulphonic acids

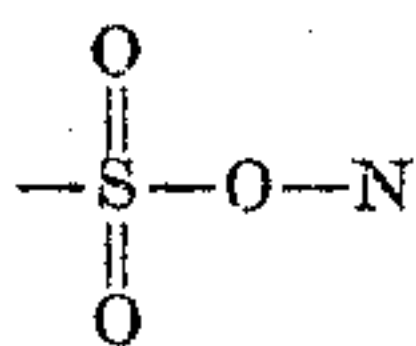
## Esters of sulphonic acids, e. g.:

Butyl ester of benzene sulphonic acid  
Benzyl ester of benzene sulphonic acid  
Chlor-benzyl ester of benzene sulphonic acid  
Phenyl ester of lauryl sulphonic acid  
Ethyl ester of cetyl sulphonic acid  
Phenyl ester of petroleum mahogany sulphonic acid

## Salts of sulphonic acids, e. g.:

Calcium salt of petroleum mahogany sulphonic acid  
Barium salt of petroleum mahogany sulphonic acid  
Magnesium salt of petroleum mahogany sulphonic acid  
Aniline salt of petroleum mahogany sulphonic acid  
Calcium salt of lauryl benzene sulphonic acid  
Zinc salt of capryl benzene sulphonic acid

From the foregoing it will be observed that the particular derivatives of sulphuric acid listed are characterized by the formula



Where M is hydrogen (acids), an organic radical (esters) or a metal (salts).

Other specific examples of the above mentioned organic derivatives of inorganic acids are:

Ethyl silicates  
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 an example of a composition which may be employed for the purposes of the present invention, calcium amyl phosphide may be employed in combination with the calcium salt of petroleum mahogany sulphonic acid in a non-aqueous oil vehicle.

As stated in the general outline of this invention, it is sometimes desirable that organo-metallic phosphides 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 organo-metallic phosphides 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 organo-metallic phosphides used in the coating with the metal to form a thin protective layer.

While I have presented theories to explain the action of organo-metallic phosphides as corrosion inhibitors, it should be understood that I do not intend to be bound thereby. The theories have been solely presented with the view of aiding the advancement of the arts as much as possible.

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 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 organo-metallic phosphides 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, particularly those useful as pigments or fillers much higher proportions, up to 90% or more, may be found useful.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

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

1. A corrosion inhibitor for metal surfaces comprising the combination of an oil-soluble organo-metallic phosphide, which compound has a metal substituent solely attached to phosphorus and contains at least one organic radical selected from the class consisting of hydrocarbon and halogen-containing hydrocarbon radicals, and a non-aqueous oil vehicle.

2. The corrosion inhibitor of claim 1 is further characterized by yielding a pH value below 7 when in contact with an aqueous media.

3. A corrosion inhibitor for metal surfaces comprising the combination of an oil-soluble organo-metallic phosphide compound having the general formula  $M_aPbR_c$  wherein M is a metal solely attached to P and R is selected from the group consisting of hydrogen, halogen, hydrocarbon, and halogen-containing hydrocarbon radicals having a valence of one, which compound contains at least one organic radical; a and b can be either one or two, and c is not less than one or more than four, such compound when in contact with an aqueous media yields a solu-



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tion having a pH of below 7; and a non-aqueous oil vehicle.

4. A corrosion inhibitor in accordance with claim 3 in which M is a bi-valent metal.

5. A corrosion inhibitor in accordance with claim 3 in which M is a metal of group 2 of the periodic table.

6. A corrosion inhibitor for metal surfaces comprising in combination, an oil-soluble organo-metallic phosphide having the following general formula:



wherein M is a bivalent metal and R is a hydrocarbon group having valence of one, which compound upon contact with an aqueous media yields a solution having a pH of below 7; and a non-aqueous oil vehicle.

7. A corrosion inhibitor for metal surfaces comprising in combination (a) an oil-soluble organo-metallic phosphide, which compound has a metal substituent solely attached to phosphorous and contains at least one organic radical selected from the class consisting of hydrocarbon and halogen-containing hydrocarbon radicals, and upon contact with an aqueous media yields a solution having a pH of below 7; (b) an organic compound selected from the group consisting of organic sulphonic acids, esters of organic sul-

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phonic acids, and salts of organic sulphonic acids; and (c) a non-aqueous oil vehicle.

8. A corrosion inhibitor for metal surfaces comprising in combination (a) calcium amyl phosphide, and (b) a non-aqueous oil vehicle.

9. A corrosion inhibitor for metal surfaces comprising in combination (a) calcium amyl phosphide, (b) calcium salt of petroleum mahogany sulphonic acid, and (c) a non-aqueous oil vehicle.

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