

UNITED STATES PATENT OFFICE

2,080,299

INHIBITING CORROSION OF METALS

Anthony F. Benning, Penns Grove, N. J., Lawrence G. Benton and Richard G. Clarkson, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application April 12, 1935,
Serial No. 16,106

10 Claims. (Cl. 91—68)

This invention relates to the protection of metals from corrosion, and more particularly to the protection of ferrous metals from the effects of moisture and oxygen jointly.

It is well known that metal surfaces, particularly ferrous metals, are subject to corrosion from the effects of moisture and of oxygen, and many methods of preventing or inhibiting such corrosion have previously been proposed. For example, it has long been known that an oil film will preserve the metal surface from atmospheric corrosion for considerable periods of time. Various compositions based upon this principle are disclosed in the patent and technical literature. This method of protection has the disadvantage that if an oil of low viscosity is used the oil tends to drain off and ultimately to rupture the film. Corrosion then proceeds at a rapid rate at the point of rupture. As an alternative, an oil of very high viscosity may be used, but in this case the oil is difficult to apply and difficult to remove.

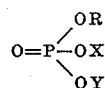
It is an object of the present invention to provide a new and improved method of treating metal surfaces materially exposed to the effects of moisture and oxygen jointly and normally tending to corrode, in order to inhibit such corrosion. A further object is to provide a new and improved method of treating ferrous metals to prevent corrosion by humid atmospheres. A still further object is to provide new and improved corrosion-inhibiting and rust-preventing compositions of matter which may be used in coating metal surfaces, particularly ferrous metal surfaces, for preservation from corrosion. Other objects will appear hereinafter.

These objects are accomplished by applying to the metal surfaces materially exposed to the effects of moisture and oxygen jointly, certain neutral and acidic organic esters of phosphorus acids. By the expression "organic esters" we mean to include esters of aromatic hydroxy compounds such as phenols, as well as those of aliphatic and cycloaliphatic alcohols, both saturated and unsaturated. This expression is intended to cover the free esters as well as ester salts. In general, these organic phosphorus esters may be described as compounds in which the hydroxyl group ($-\text{OH}$) of a phosphorus acid such as, for example, ortho-phosphoric acid, meta-phosphoric acid, pyrophosphoric acid, phosphorous acid, hypophosphorous acid, thiophosphoric acid and other phosphorus acids containing a hydroxyl group, is substituted or replaced by the radical $-\text{OR}$, where R represents a carbon radical. One

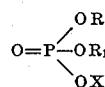
or all of the hydroxyl groups may be replaced by a carbon radical in this manner. The resultant compound may contain free hydroxyl groups attached to the phosphorus atom or atoms, or the hydroxyl groups may be neutralized with salt-forming groups such as alkali metals, ammonia or amines. It will be recognized that the molecule of the organic phosphorus ester may contain more than one phosphate, phosphite, or other phosphorus acid residue.

The various organic phosphorus esters may be described by chemical structure as mono-, di-, tri-esters, etc., according to the number of ester radicals per phosphorus atom. Taking phosphoric acid as typical, the mono-, di- and tri-esters may be given the following formulas:

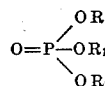
Mono-ester



Di-ester



Tri-ester



where R, R_1 and R_2 represent the same or different carbon radicals, and X and Y represent hydrogen or salt-forming radicals.

In practicing the invention we may employ any one of the following organic esters of phosphorus acids and mixtures thereof: cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters. We may also employ the less volatile lower aliphatic esters in mixtures with the other esters of the type described.

The organic esters of phosphorus acids may be applied in several ways. We may dip or rub the metal surface in a composition consisting of one or more of the aforesaid organic esters. An

alternative method which we prefer is to apply to the metal surface a composition comprising a large proportion of an oil admixed with a relatively small proportion of one or more of the organic esters of phosphorus acids. By the term "oil" we mean to include liquid mineral hydrocarbons as well as liquid glycerides or waxes of animal or vegetable origin.

It has also been found that metallic surfaces may be protected against corrosion due to aqueous solutions by the addition to the said solutions of one or more of the aforesaid organic esters of phosphorus or an admixture of such an ester with an oil. In this modification of the invention, it is advantageous to have present in the aqueous solution one or more of the common emulsifying agents such as soap, sulfonated animal, vegetable or mineral oils or synthetic products such as fatty alcohol sulfate esters.

Among the compounds which we have found to be especially suitable in inhibiting and preventing corrosion of metal surfaces are the di- and tri-aryl esters of phosphorus acids, the mono- and di-long chain aliphatic hydrocarbon esters of phosphorus acids, mixed organic di-esters of phosphorus acids containing a long chain aliphatic hydrocarbon group, and mixtures of any of these esters. Of the aliphatic esters, those containing a carbon chain of at least 8 carbon atoms have proven to be most effective and, of these, the mixed esters and mixtures of esters containing long chain aliphatic groups, for example, 10 to 18 carbon chain derivatives, are generally preferred.

In the addition of the free esters or salts thereof to oils and other media to produce corrosion-preventing compositions, the use of as small amount as 0.05% will have an appreciable effect. For practical purposes, however, it will generally be found desirable to use at least 0.2%. Generally speaking, moreover, the amount of organic phosphorus ester added to the oil or other media will be largely dependent upon the particular metal surface treated, the area of the metal surface, and the nature of the conditions to which it is exposed. In general, we preferably treat the metal surface with an oil-containing composition in which the proportion of organic ester of the phosphorus acid or salt thereof varies within the range of about 0.5% to about 10.0%. For most ordinary purposes, such as for protection of guns, tools and the like, compositions containing 1% to 2% organic phosphorus ester will be satisfactory.

It will be recognized that a variety of tests might be employed to establish the efficacy of our invention. In general, the methods of testing which we have devised were based upon the treatment of metal surfaces under moisture and oxygen conditions to which they would be exposed in actual practice. However, in order to increase the speed of the tests, various expedients were employed to increase the rate at which corrosion would take place.

In order to more clearly illustrate the invention and the benefits of the results obtained thereby, the following examples are given. The quantities are stated in parts by weight.

Example I

Gun barrels were dipped in oil and then suspended in a large, loosely covered container, the bottom of which was covered with water. A mixture was prepared of 1 part of dicresyl phosphate and 99 parts of light naphthenic oil (spindle oil), and this mixture used to coat the

surface of the gun barrel. A second, exactly similar gun barrel was coated with the untreated spindle oil, and both coated gun barrels suspended in the previously described container for two months. At the end of the test period, no rust was found on the gun barrel coated with treated oil, but the other gun barrel was badly rusted at several points.

Example II

Steel wood-working tools were oiled with a mixture of 2 parts of dilorol phosphate and 98 parts of a light lubricating oil. The tools remained untarnished after standing several months in a moist atmosphere. Similar tools oiled with the untreated oil tarnished in a few weeks. The dilorol phosphate above referred to was obtained by esterifying commercial lauryl alcohol which is a mixture consisting largely of dodecyl alcohol but also containing some decyl and tetradecyl alcohols, with phosphorus pentoxide. The esterification product contained both monoalkyl and dialkyl esters with the latter predominating.

Example III

A portion of an automobile fender was sandpapered so as to remove all enamel, under-coating, etc. One portion was coated with a medium viscosity lubricating oil; another portion coated with a solution of 2 parts dicetyl phosphate in 98 parts of the same oil; a third portion was coated with the dilorol phosphate composition described in Example II; and a fourth section was untreated. The automobile was then subjected to ordinary exposure conditions. After twenty-four hours, the untreated section was spotted with rust, and after one week it was deeply pitted. After two weeks the section coated with lubricating oil was rusted in several places. After one month's service, the portion coated with the oil solution of dicetyl phosphate was bright and clean. The portion treated with dilorol phosphate had a dull grayish cast but was not rusted.

Example IV

To illustrate that the compositions disclosed are also effective in decreasing the corrosion of steel and other metals by aqueous solutions as well as by moist air, the following experiment was carried out:

A 35% solution of glycerin in water was divided into three portions. To one portion, designated A, was added 0.5% of its weight of a mixture of 95 parts of a commercial self-emulsifying oil (composed of sulfonated petroleum and mineral oil) and 5 parts ortho-toluidine. To the second portion, designated B, was added 0.5% of its weight of a mixture of 94 parts of the same self-emulsifying oil, 5 parts ortho-toluidine and 1 part of tricresyl phosphate. To the third portion, designated C, was added 0.5% of its weight of a mixture of 94 parts of the same self-emulsifying oil, 5 parts of ortho-toluidine and 1 part dilauryl phosphate.

The three solutions were placed in three flasks, each fitted with a reflux condenser and a tube for admitting air below the surface of the liquid. Two small, polished, previously weighed strips of metal, one of brass and the other of steel, were placed in each flask. Air was blown through the inlet tube and the flasks were heated in a large oil bath to a temperature of 85° C. The test was continued at this temperature and with a constant treatment of air for 600 hours. At the end of this time, the metal strips were

removed from the flask, cleaned thoroughly, dried and weighed.

The steel strip from solution A was found to have lost 23.4 milligrams per square inch of surface, and the brass strip from the same solution 34.0 milligrams per square inch of surface. The loss of the steel strip and the brass strip of solution B was 0.0 milligram and 27.0 milligrams, respectively. In solution C, the steel strip lost 7.8 milligrams per square inch and the brass strip 20.4 milligrams per square inch.

The foregoing examples are merely illustrative of the results obtained with a few of the various organic esters of phosphorus acids. Other organic esters of phosphorus acids coming within the scope of our invention are the following: the mono- and di-oleyl phosphates and mixtures thereof; the mono- and di-stearyl phosphates and mixtures thereof; the mono- and di-octyl phosphates and mixtures thereof; the mono- and di-ocenoil phosphates and mixtures thereof; mixed lauryl octyl phosphate (di-ester); trimethyl ricinoleyl phosphate; mono- and di-cetyl phosphates and mixtures thereof; mono- and di-lorol phosphates; mono- and di-hydroxy stearic acid phosphates; lauroxy ethanol phosphate; ethyl-lauryl phosphate; ethyl-phenyl phosphate; butyl-cresyl phosphate; butyl lauryl phosphate; mixed phosphate esters of lorol and ocenoil; lauryl-cyclohexyl phosphates; dicyclohexyl phosphate; methyl-cyclohexyl phosphate; cyclohexyl phosphate; the mono-phosphate of the diglyceride obtained by the partial hydrolysis of linseed oil; cyclohexyl-cresyl phosphate; lauryl-monoglyceryl ether diphosphate; cetyl-monoglyceryl ether monophosphate; oleyl-monoglyceryl ether monophosphate; stearyl-monoglyceryl ether monophosphate; lauryl-phenyl phosphate; lauryl-cresyl phosphate; oleyl-cresyl phosphate; oleyl-phenyl phosphate; mixed diethyl phosphate and dilauryl phosphate; mixed triethyl phosphate and mono- and dilauryl phosphates; mixed mono- and di-butyl phosphates and dilauryl phosphates; phenyl-cresyl phosphate; diphenyl phosphate; phenyl-dicresyl phosphate; dicresyl phosphate; triphenyl phosphate; tri-nitrophenyl phosphate; mixed tertiary amyl phenyl phosphates; trinaphthyl phosphate; mixed dodecahydro-diphenylol propane phosphates; mixed mono- and di-decahydro-beta-naphthyl phosphates; mixed tetrahydro-beta-naphthyl phosphates; dibutyl amine salt of mixed phosphates of lorol; benzyl-amine salt of mixed phosphates of lorol; amyl-amine salt of mixed phosphates of lorol; alpha-naphthyl-amine salt of dilorol phosphate; cyclohexyl-amine salt of dilorol phosphate; lauryl-amine salt of dilorol phosphate; mixtures of mono- and di-lorol phosphites; triphenyl phosphite; dilorol-dithiophosphate; mono- and di-lauryl thiophosphates; di-phenyl-thiophosphate; dicetyl-thiophosphate, dicresyl-thiophosphate, tricresyl-thiophosphate; and corresponding compounds of other phosphorus acids.

In the foregoing examples, the term "ocenoil" is intended to include a mixture of primary aliphatic alcohols containing mostly oleyl alcohol but also containing other alcohols having 12 to 18 carbon atoms. A typical mixture of this type ordinarily has an iodine number of about 50. The term "lorol" is intended to include a mixture of primary aliphatic alcohols such as is ordinarily obtained by the carboxylic reduction of coconut and/or palm kernel oils. This mixture ordinarily contains mostly lauryl alcohol

together with some octyl, decyl and myristyl alcohols. A typical mixture of this type has a boiling range of 140° C. to 190° C. at about 50 mm.

The compounds employed in accordance with the invention are, in many instances, known in the art and the general methods for making them are also known and described in the literature. These methods generally comprise treatment of alcohols, unsaturated aliphatic compounds or phenols with phosphorus chlorides or with phosphorus oxychlorides or oxides such as phosphorus pentoxide. Other methods involve treatment of an oxidized mineral or natural oil with phosphorus oxyhalides and a catalyst such as aluminum chloride. Phosphate and phosphite esters can also be obtained by treatment of oils containing ethylene linkages or hydroxy groups with phosphorus halides, oxyhalides, oxides and sulfides.

Where the various organic esters of phosphorus acids are liquids, they may be employed alone for the purpose of preventing or inhibiting corrosion. Where they are solids, they may be used in a non-corrosive carrying medium, preferably a liquid carrying medium in which they are soluble. Readily dispersible carrying media may be employed, such as non-corrosive liquids or semi-liquids. Soft-film forming carriers are usually preferred. In general, it is preferable, even where the organic phosphorus ester is a liquid, to use it in conjunction with a readily dispersible carrying medium, preferably one in which it is soluble or miscible. Ordinarily, it has been found, as previously indicated, that a relatively large amount of a liquid carrier containing a relatively small amount of the organic phosphorus ester will give satisfactory results. For the purposes of this invention, it is preferable that the liquid carrier be one of relatively low volatility, as, for example, light oils of the spindle oil type and light lubricating oils, medium viscosity lubricating oils, (for instance, S. A. E. 30), glycerin-diphenyl and diphenyl-oxide, although the invention does not preclude the use of these compounds in benzene, solvent naphtha, gasoline and other liquids which are non-corrosive to metals and in which the compounds may be dissolved, dispersed or emulsified.

One method of preparing suitable compositions is to dissolve or disperse the organic phosphorus esters directly in a suitable oil, preferably a soft-film forming oil. Another method is to prepare them in the form of aqueous emulsions. Similarly, the composition may consist of the organic ester emulsified with oil and water. Any of the usual types of emulsions may be employed, such as those previously described.

The invention is very advantageous in protecting metal surfaces, particularly ferrous metal surfaces, from the corrosive effect of moisture and oxygen jointly. While its most desirable application thus far has been in the protection of metal surfaces from the action of moist air, it is also useful, as previously indicated, in protecting metals against the corrosive action of water.

The expression "long chain aliphatic" as employed in the specification and claims means an aliphatic radical containing eight or more carbon atoms. The term "carbon radical" is used to define a radical in which the bond joining the radical to the remainder of the molecule is from a carbon atom.

As many apparently widely different embodi-

ments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A method of inhibiting corrosion of a metal surface materially exposed to the effects of moisture and oxygen jointly and ordinarily tending to corrode which comprises treating said metal surface with a rust-proofing composition comprising a non-hardening oil and an organic ester of a phosphorus acid selected from the class of esters consisting of cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters, said long chain aliphatic radicals containing at least eight carbon atoms.

2. A method of inhibiting rust formation on a ferrous metal surface materially exposed to the effects of moisture and oxygen jointly and normally tending to rust which comprises treating said ferrous metal surface with a rust-proofing composition comprising a soft film-forming oil having dispersed therein an organic ester of a phosphoric acid selected from the class of esters consisting of cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters, said long chain aliphatic radicals containing at least eight carbon atoms.

3. A method of inhibiting corrosion of a metal surface materially exposed to the effects of moisture and oxygen jointly and ordinarily tending to corrode which comprises treating said metal surface with a rust-proofing composition comprising a soft film-forming oil having dispersed therein a di-ester of a phosphoric acid in which at least one esterifying radical is a long chain aliphatic hydrocarbon radical containing at least eight carbon atoms.

4. A method of inhibiting rust formation on ferrous metal surfaces materially exposed to the effects of moisture and oxygen jointly and normally tending to rust which comprises treating said metal surfaces with a rust-proofing composition comprising a soft film-forming oil having dispersed therein a di-ester of a phosphoric acid in which at least one esterifying radical is a long chain aliphatic hydrocarbon radical containing at least eight carbon atoms.

5. A method of inhibiting rust formation on ferrous metal surfaces materially exposed to the effects of moisture and oxygen jointly and normally tending to rust which comprises treating said metal surfaces with a rust-proofing composition comprising a soft film-forming oil and di-lorol phosphate.

6. A rust-proofing composition for metals comprising a soft-film forming oil containing an organic ester of a phosphorus acid selected from the class consisting of cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters, said long chain aliphatic radicals containing at least eight carbon atoms.

7. A rust-proofing composition for metals comprising a soft-film forming oil containing an organic ester of a phosphoric acid selected from the class consisting of cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters, said long chain aliphatic radicals containing at least eight carbon atoms.

8. A rust-proofing composition for metals comprising an emulsion containing a non-hardening oil and an organic ester of a phosphorus acid selected from the class consisting of cycloaliphatic and long chain aliphatic mono-esters; simple and mixed long chain aliphatic, cycloaliphatic and aromatic di-esters; mixed long chain aliphatic-aromatic di-esters; mixed cycloaliphatic-aromatic di-esters; simple and mixed aromatic tri-esters; mixed long chain aliphatic-lower aliphatic poly-esters containing not more than one long chain radical; mixed cycloaliphatic-lower aliphatic poly-esters containing not more than one cycloaliphatic radical; and mixed lower aliphatic-aromatic poly-esters, said long chain aliphatic radicals containing at least eight carbon atoms.

9. A rust-proofing composition for metals comprising essentially a soft-film forming oil and about 0.05% to about 10% di-lorol phosphate.

10. A rust-proofing composition for metals comprising essentially about 2 parts of di-lorol phosphate dissolved in about 98 parts of light lubricating oil.

ANTHONY F. BENNING.
LAWRENCE G. BENTON.
RICHARD G. CLARKSON.