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CORROSION INHIBITION

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This invention relates to corrosion inhibitors for metals and particularly to corrosion inhibitors which inhibit rust formation in ferrous metals occurring as the result of exposure to the effect of moisture and oxygen.

It is well known that the surfaces of metals, particularly the surfaces of ferrous metals, normally tend to corrode with the formation of rust when subjected to the effect of moisture and oxygen. Many methods have been proposed for preventing or inhibiting such corrosion and rust formation. One of the commonest methods proposed has comprised coating the metallic surfaces with a thin film of an oily material such as lanolin, vaseline, and similar materials. While such oily materials are to some extent effective, they have not proved to be entirely satisfactory in practice.

It is frequently desirable to apply to metal surfaces and particularly to ferrous metal surfaces lithographic inks, paints, lacquers, and the like. When the metal surfaces are preserved with oily materials, it is generally necessary to remove such oily materials from the metallic surfaces prior to application of lithographic inks, paints, lacquers and the like as such oily materials greatly decrease the receptivity of the metal surface for inks, paints, lacquers and the like.

It is an object of this invention to provide a new and improved method for the protection of metal surfaces from corrosion. Another object is to provide a new and improved method for the treatment of metallic surfaces so as to effect the inhibiting of corrosion on the surface, and at the same time not decrease the receptivity of the surface for lithographic inks, paints, and the like. Another object is to provide a new and improved process for the treatment of ferrous metal surfaces so as to prevent the rusting of same. Another object is to provide new articles of commerce. A still further object is to develop corrosion inhibitors for ferrous metals which can be applied from simple aqueous systems. Another object is the treatment of ferrous metal surfaces to prevent their corrosion and further to prepare same for subsequent painting. Another object is to provide an improved process for painting. A further object is to provide metals and particularly ferrous metals, the surfaces of which will have a lesser tendency to be corroded and rusted, and which at the same time will have a high receptivity for lithographic inks, paints, lacquers and the like. Another object is to provide certain new and useful compositions of matter and new articles of manufacture. Other objects will be apparent from the following description of the invention.

These objects are accomplished by coating the surfaces of metals and particularly the surfaces of ferrous metals with a thin film of a composi-

tion containing a phosphoric acid salt of a long chain aliphatic amine having at least one long chain aliphatic group of at least 8 carbon atoms attached directly to the amino nitrogen. These long chain aliphatic amine phosphates may be otherwise designated as those derived from a hydrogen orthophosphate, for example orthophosphoric acid or a mono or dihydrogen phosphate, and a primary, secondary or tertiary amine having at least one long chain group of at least 8 carbon atoms attached directly to the aminonitrogen. The amine phosphates may also be obtained by reacting in the presence of water the salt of an aliphatic amine having at least one long chain group attached directly to the amino nitrogen with a water soluble metallic salt of orthophosphoric acid. The phosphates formed may be either acid or neutral salts.

These phosphates when separated have been found to be exceptionally useful compounds. When applied to metal surfaces and particularly ferrous metal surfaces they have been found to have a marked rust-proofing effect. Furthermore, the surface becomes more receptive to paint films and paint films applied directly thereon adhere very well to the metal. The phosphates form colloidal solutions in water at elevated temperatures and may be used in this form for treating the metal surfaces.

The following examples set forth certain well defined instances of the application of this invention. They are not, however, to be considered as limitations thereof since many modifications may be made without departing from the spirit and scope of this invention. Examples I and II illustrate the method of preparing the compounds used in this invention. In these examples the parts given are parts by weight. The remaining examples illustrate the treatment of metallic surfaces so as to provide the improvements obtained by the use of this invention.

Example I

Two hundred parts of the mixture of alkyl amines obtainable by catalytically hydrogenating the nitriles derived from coconut oil fatty acids are added with stirring over a period of 15 to 20 minutes to 375 parts of 28.4% aqueous solution of H_3PO_4 . The temperature is maintained at between 25° and 30° C. during the addition of the amine to the phosphoric acid solution. The reaction goes to completion in a short time, after which the mixture is chilled and filtered with pressure. The acid salt obtained in this way is washed with cold water and dried in an oven at 120° C. A product of satisfactory purity for many purposes may be obtained by drying the original reaction product without washing.

The product is an amber-colored, hard, waxy solid. It has no definite melting point but is

quite soft (grease-like) at 100° C. It is substantially insoluble in cold water but at 100° C. water dissolves three-tenths its weight of the product readily. The product is insoluble, hot or cold, in carbon tetrachloride, ethyl acetate, toluene or dioxan, but is soluble, hot or cold, in methanol.

Example II

Two hundred parts of n-dodecylamine are added with stirring to 312 parts of a 17% aqueous solution of H₃PO₄. The reaction goes to completion in a short time after which the phosphate is separated by filtration and is then dried.

Example III

Twenty-gauge steel sheet, free from rust and grease, was dipped in a hot 1:1 ethyl alcohol-water solution containing 4% hexadecylammonium dihydrogen phosphate and then allowed to dry in the open air. Steel panels so treated were exposed outdoors along with similar steel panels similarly treated with other commonly used protective materials. The results of this exposure are collected in the following table:

Treatment of panel	Corrosion rating *	
	1 week	3 weeks
No treatment.....	0	0
Mineral oil (4%) in toluene.....	1	0
Petrolatum (4%) in toluene.....	0	0
Castor oil (4%) in acetone.....	9.5	1
Hexadecylammonium dihydrogen phosphate (4%) in 1:1 ethyl alcohol-water solution.....	10	8

*Rating 10=no visible rust; 0=surface covered completely with rust.

Example IV

Steel sheet which was first phosphatized by the usual process known as "Bonderiting," whereby a definite layer of iron phosphate is produced on the surface, and then sprayed with 4% octadecylamine in toluene solution was exposed out-of-doors for three months. At the end of this period this treated steel was entirely rust-free, while steel sheet which had been similarly phosphatized but treated with light mineral oil was rusted heavily. Sheet which received no treatment subsequent to phosphatizing was covered with rust over its entire surface.

Example V

A brass sheet which had been freed of dirt and grease was treated by dipping the sheet in a 4% aqueous solution of dodecyl ammonium dihydrogen phosphate maintained at 90° C. The sheet after treatment had a pleasing satin finish. The treated sheet and similar untreated sheets were exposed to an industrial atmosphere indoors for a month. At the end of this period, the untreated sheets were badly tarnished while the treated sheets possessed their original pleasing appearance.

The amines which are useful in making the products of this invention may be classed as the long-chain aliphatic amines having said aliphatic group attached directly to the amino nitrogen atom, particularly those amines having at least 8 carbon atoms per amino nitrogen. This includes the secondary and tertiary as well as the primary mono, di, and polyamines. Octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl amines and hexadecamethylene diamine and octadecamethylene diamine are examples of amines that can be used, and amines containing an unsaturated chain such as octenyl, decenyl, do-

decenyl, hexadecenyl and octadecenylamine are also suitable. Technical mixtures are sometimes used, as for example amines which correspond respectively to the alkyl alcohols obtained by the catalytic hydrogenation of coconut oil acids and sperm oil. Monoamines having at least one long chain of less than twenty-five carbon atoms attached directly to the amino nitrogen atom are preferred because of availability and cost considerations, and monoamines containing at least one chain of from eight to eighteen carbon atoms attached directly to the amino nitrogen atom are particularly well suited to most of the applications where these products find use.

Phosphoric acid salts of alkylamines having a hydrocarbon chain of from 8 to 18 carbon atoms attached directly to the amino nitrogen have been found to be particularly useful in the following instances: (1) The treatment of steel subjected to high humidity and the corrosive action of perspiration, for example, during the handling of steel during fabrication, inspection, and packing; (2) the treatment of steel requiring temporary protection during exposure to weathering; (3) the treatment of plated iron or steel articles which may be subject to corrosion due to plating defects.

The following types of long-chain aliphatic ammonium phosphates having said aliphatic group attached directly to the amino nitrogen come within the scope of this invention:

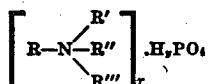
Monoalkylammonium dihydrogen phosphates
 Monoalkylammonium monohydrogen phosphates
 Neutral monoalkylammonium phosphates
 Dialkylammonium dihydrogen phosphates
 Dialkylammonium monohydrogen phosphates
 Neutral dialkylammonium phosphates
 Trialkylammonium dihydrogen phosphates
 Trialkylammonium monohydrogen phosphates
 Neutral trialkylammonium phosphates

While it is preferred to employ the long chain amine phosphates in which the long chain group is an alkyl group of at least 8 carbon atoms this long chain group may be substituted with such substituents as halogen, hydroxy, nitro, alkoxy, carboxyl or ester groups. However, from the standpoint of cost and availability the compounds where the long chain aliphatic group is hydrocarbon are preferred.

Compounds of these types are illustrated by the following:

Trihexylammonium dihydrogen phosphate
 Di(trihexylammonium) monohydrogen phosphate
 Tri(trihexylammonium) phosphate
 Dioctylammonium dihydrogen phosphate
 Di(dioctylammonium) monohydrogen phosphate
 Tri(dioctylammonium) phosphate
 Octadecylammonium dihydrogen phosphate
 Di-octadecylammonium monohydrogen phosphate
 Tri-octadecylammonium phosphate
 12-chloro-octadecylammonium dihydrogen phosphate
 12-hydroxy octadecylammonium dihydrogen phosphate
 12-methoxyoctadecylammonium dihydrogen phosphate
 9,10-octadecenylammonium dihydrogen phosphate
 Ethyldecylammonium dihydrogen phosphate
 Di(dimethyldodecylammonium) monohydrogen phosphate
 Tri(ethylmethyloctylammonium) phosphate

The majority of the specific compounds enumerated above all fall under the general formula:



where—

x may be 1, 2 or 3

$x+y=3$

R —an aliphatic radical having 8 to 24 carbon atoms and connected directly to the amino nitrogen through single bonded carbon, and preferably is hydrocarbon

R' , R'' , and R''' , are hydrogen or aliphatic radicals of 8 to 24 carbon atoms connected directly to the amino nitrogen through single bonded carbon and preferably are hydrocarbon.

The first two examples cited above describe the preparation of these substituted ammonium acid phosphates from phosphoric acid and free amine, but the phosphoric acid may be replaced by inorganic acid phosphates such as the mono or disodium compounds, the corresponding potassium or ammonium salts and even compounds of those heavy metals which form soluble salts with phosphoric acid and the halogen or other mineral acids. Inorganic acid phosphates do not react directly with the free amines to give the desired compounds, but must be used with salts of the amines, and the metal salts formed in this double decomposition should be soluble to facilitate separation from the precipitated phosphate. When prepared in this way the substituted ammonium phosphate is usually washed free of inorganic salts before drying, although this is not always essential.

Example IV illustrates the formation of the substituted ammonium phosphate on the surface metal by first forming a surface layer of metal phosphate and then applying the amine. Acidic gases of the atmosphere may take part in this reaction.

It has been indicated that fairly concentrated solutions and low temperatures are preferred to increase the yield of material obtained. In many cases, however, it is not necessary to isolate the product at all since it can be used in the original reaction medium, and under these circumstances temperature control offers no advantages.

The long-chain alkylammonium dihydrogen phosphates are particularly useful as anticorrosion agents for ferrous metal surfaces. They are useful in protecting such surfaces as steel sheet, wire, tubing, and various manufactured articles. The monohydrogen phosphates can likewise be used for these purposes, and as acid-accepting constituents of coating composition films. When the long-chain alkylammonium phosphates are applied in solution, the preferred concentration lies between 2 and 10%, respectively; however, solutions containing as low as 1% or up to 20% of these compounds may sometimes be used. The lower alcohols such as ethanol and methanol may be used as solvents, but water heated to 60° C. or more is equally suitable in most cases. The choice of solvent must be made, however, with regard to physical properties of the particular alkylammonium phosphate which is to be used, since in general these compounds become more soluble in organic solvents and less soluble in water as the hydrocarbon content of the molecule increases.

Although these compounds will usually be applied to metal surfaces by means of a solution using such well known processes as dipping, spraying, wiping, and brushing, it will be de-

sirable at times to use other methods of application. A material which melts at reasonably low temperatures and which undergoes no decomposition in the region of its melting point may be applied in the liquid form without a diluent of any kind, provided that the application of the material is so regulated that the final protective film conforms to the desired thickness limits. These compounds may also be applied to the metal surface as a finely divided solid and the protective layer be formed by fusing the solid particles to a continuous coating at a suitable temperature. The protective agent may also be emulsified or dispersed in a liquid which is not a true solvent and applied to metal surfaces in this form, with the evaporation of the carrier occurring subsequently. In some instances it has been found that oils of various types may serve as carriers for the protective agent, and in such cases it is not intended that the carrier be removed by evaporation as is the practice when solvents or dispersions are used.

Long-chain aliphatic amines are effective anticorrosion agents in themselves, as has been disclosed in the copending application of Clifford K. Sloan, filed May 13, 1939, Serial No. 273,578, and it is well known from the prior art that phosphoric acid is a rust-proofing agent. However, the products disclosed in this invention do more than merely combine the properties of these two compounds for these products contain certain new and valuable properties which are not found in either the long-chain amines or in phosphoric acid. For example, the amines alone have an adverse effect on adhesion of subsequently applied paint films, and phosphoric acid also tends to weaken the bond between paint and metal. Paints adhere very well to metal coated with the acid salts of this invention, however, and such metal is not only protected effectively against corrosion during long periods of storage but can be painted over directly without any preliminary cleaning treatment. This property of the acid salts distinguishes them from ordinary protective films of oil and grease which must be removed completely before paint can be applied.

When a paint film is subsequently to be applied to the metal surface, it is preferred that the film or layer of anti-corrosive deposited on the metal surface be of such thickness that one pound will coat approximately 20,000 square feet of metal. A film of about this thickness may readily be obtained by dipping the metal into a 4% solution of the protective agent. Films of a thickness such that one pound will coat approximately 10,000 square feet or of a thickness such that one pound will coat approximately 80,000 square feet may also, but less preferably, be used. These thicknesses may be obtained by dipping a sheet of steel into 8% and 1% solutions of the agents, respectively.

Another advantage of the compounds described herein is the absence of excessive reactivity. Phosphoric acid alone is too reactive to be used in the protection of zinc and cadmium plated metals, and it will also attack copper plate and produce objectionable discoloration. A long-chain alkyl-ammonium acid phosphate, on the other hand, provides excellent protection for such products without affecting the appearance or luster of the metal.

Still another advantage resides in the solubility characteristics of these compounds, which permits them to be applied as anticorrosion agents from aqueous solutions although the thin, ori-

ented surface films deposited in this way are quite insoluble and even strongly water repellent. Other anti-corrodents can be put into solution only in organic solvents, which represents an added expense and in many cases requires special precautions because of the fire hazard.

These compounds are particularly well adapted to the protection of ferrous metal articles, such as bolts, nuts, nails, wire, sheets, tools, fine machinery parts, bearings, cutlery, gears, fire arms, metallic cases, etc., and to the treatment of ferrous metal articles which have been provided with a surface coating of some other metal or alloy, such as chromium, copper, nickel, cadmium, zinc, brass, aluminum, tin, lead, etc. In addition to such uses, these compounds may be applied to the surfaces of other metals and alloys, particularly those used for structural shapes and articles of commerce such as rods, tubes and sheets. Among such metals are zinc, brass, bronze, aluminum, tin, copper, pewter, lead, magnesium, cadmium, "duralumin", nickel, etc.

This application is a continuation-in-part of our copending application Serial No. 273,580, filed May 13, 1939.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. The process for the prevention of atmospheric corrosion of metal surfaces capable of corrosion, which comprises treating the said surfaces with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain.

2. A process for the prevention of iron oxidation which comprises treating the area susceptible oxidation with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain.

3. A process for the prevention of iron oxidation which comprises treating the area susceptible to oxidation with a long chain alkylammonium dihydrogen phosphate.

4. In a process of painting metal surfaces comprising the steps of treating said metal surfaces to clean and prepare same for the reception of the paint film, the improvement which comprises coating said metal surface with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain.

5. In a process of painting metal surfaces comprising the steps of treating said metal surfaces to clean and prepare same for the reception of the paint film, the improvement which comprises

coating said metal surface with a long chain alkylammonium dihydrogen phosphate.

6. As an article of manufacture a body having a metal surface susceptible to atmospheric corrosion, at least a part of which surface is coated with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain.

7. As an article of manufacture a body having a surface susceptible to iron oxidation, at least a part of which surface is coated with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain.

8. As an article of manufacture a body having a surface susceptible to iron oxidation, at least a part of which surface is coated with a long chain alkylammonium dihydrogen phosphate.

9. As an article of manufacture a body having a surface susceptible to iron oxidation, at least a part of which surface is coated with a long chain amine salt of ortho-phosphoric acid, said long chain being a hydrocarbon chain and having superimposed on at least a part of said coated surface a paint film.

10. As an article of manufacture a body having a surface susceptible to iron oxidation, at least a part of which surface is coated with a long chain alkylammonium dihydrogen phosphate and having superimposed on at least a part of said coated surface a paint film.

11. As an article of manufacture, a body having a metal surface susceptible to atmospheric corrosion and containing copper, at least a part of which surface is coated with a dodecylamine salt of ortho-phosphoric acid.

12. The article of claim 11 characterized in that the said surface is coated with the salts derived from orthophosphoric acid and the technical mixture of amines corresponding respectively to the alkyl alcohols obtained by the catalytic hydrogenation of coconut oil acids.

13. The article of claim 8 characterized in that the long chain alkyl ammonium dihydrogen phosphate is hexadecyl ammonium dihydrogen phosphate.

14. As an article of manufacture, a body having a surface susceptible to iron oxidation, at least a part of which surface is coated with a dodecylamine salt of orthophosphoric acid.

15. The article in accordance with claim 14 characterized in that the surface is coated with the mixture of alkyl amine salts obtained from ortho-phosphoric acid and the alkyl amines obtained by the catalytic hydrogenation of the nitriles derived from coconut oil fatty acids.

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