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CORROSION RESISTANT COATING FOR METAL SURFACES

John C. Lum, Union, and George Jernstedt,
Bloomfield, N. J., assignors to Westinghouse
Electric & Manufacturing Company, East
Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to the art of producing corrosion resistant coatings upon the surfaces of iron, zinc, cadmium and other metals and alloys thereof.

This invention relates more particularly to the rapid and efficient production of phosphate coatings upon the surfaces of metals. Protective phosphate coatings of this type are of great economic importance in the preparation of metal surfaces for the reception of an organic finish.

The object of this invention is to provide for expediting and improving the application of protective phosphate coatings on metal surfaces by subjecting the metal to a preactivating treatment.

Another object of this invention is to provide a composition capable of activating metal surfaces to improve the process of forming corrosion resistant coatings.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It is an extensive practice to treat metallic surfaces with solutions or compositions which under appropriate conditions will deposit or form upon the metallic surface a protective phosphate coating. These phosphate coatings protect the underlying metal from corrosion, rusting and other deterioration. In addition, the phosphate coatings are of value, in that they constitute an excellent base for the application of organic finishes to the metal surfaces. Due to the crystalline nature of the phosphate coatings upon the metal, the organic finishes will bond and adhere more tenaciously thereto than to the bare metal surface. Peeling of the paint due to inadequate bonding is greatly diminished when protective phosphate coatings are employed. In addition, the separation of the organic finish from the metal surface due to corrosion of the surface metal beneath the organic finish is greatly reduced, since the protective phosphate coatings inhibit corrosion.

In the prior art, phosphate coatings have been produced upon metal surfaces by applying a solution containing phosphoric acid and phosphates. The time involved in treating the metal surface in order to secure adequate protective coatings usually has been lengthy and even within recent years has constituted a fraction of an hour. Upon some metals, for example, zinc, the treatment has been extremely lengthy and even so the protective phosphate coating has been relatively unsatisfactory.

According to this invention, it has been discovered that the time necessary for a complete and adequate reaction between the metal surface and a composition capable of developing a phosphate coating thereon may be greatly reduced by subjecting the metal surface to a preliminary activating treatment. When treated with an activating solution of the type described herein, bare metal surfaces have imparted thereto certain characteristics whereby they are activated so that the normal or modified phosphate coating compositions will form an exceedingly durable and complete phosphate film or coating thereon with great rapidity, for example, in a minute or less.

A further advantage obtained by the activation of metal surfaces is the formation of satisfactory phosphate coatings upon metals which heretofore did not lend themselves to the formation of good phosphate coatings. As an example, zinc, which ordinarily is not regarded as capable of being consistently satisfactoryily treated with phosphate coating compositions, is now readily and fully treatable in a minute or less when activated by the preliminary treatment herein disclosed.

Furthermore, it has been noticed that surfaces that have been activated by a preliminary treatment acquire a much better protective phosphate coating than the same phosphate coating solution would produce on unactivated surfaces. The activated surfaces acquire coatings which are characterized by a finely crystalline deposit whose individual grains cannot be distinguished with the naked eye. These fine crystalline layers are clearly superior in corrosion resistance and other properties to the same metal treated to produce phosphate coatings without an activating treatment.

It is well known to those skilled in the art that zinc, galvanized iron and electroplated zinc surfaces cannot be treated with uniformly satisfactory and consistent results with conventional phosphate solutions. Numerous attempts to modify the phosphate solutions in order to produce an adequate protective phosphate coating consistently on zinc surfaces have been generally unsuccessful from a commercial standpoint. This invention in contrast to the prior art difficulties with zinc, produces phosphate coatings on zinc that are almost velvety smooth and good inhibitors of the corrosion of the underlying zinc metal. Zinc so treated may be painted with a single coat of an organic finish which will adhere tenaciously for great periods of time under all types of humidity and other difficult test conditions.

In the practice of this invention, metal surfaces to be subsequently subjected to a treatment productive of a crystalline phosphate coating are activated by pretreating the metal with a solution composed of disodium phosphate containing small quantities of water soluble compounds of lead, tin and arsenic. In the absence of these water soluble compounds of lead, tin and arsenic, the disodium phosphate has negligible activating effect.

In the specification and claims, the term "metal" will be used with reference to arsenic, though strictly speaking this is not true of the element.

In preparing a satisfactory solution of disodium phosphate and one or more compounds from the group selected from tin, lead, or arsenic, the following process has been found to be most preferable. Orthodisodium phosphate is dissolved in water, preferably to form a nearly saturated solution. A small amount of one or more water soluble salts of the group consisting of tin, lead or arsenic is added to this solution in an amount ranging from ½ of 1% of the weight of the disodium phosphate up to 10% of the weight of disodium phosphate or even more. Arsenic oxides, lead acetates, tin chlorides and tin sulfates are examples of salts usable for the purpose. The solution so prepared is evaporated to dryness by slow heating. The residue may be broken up, preferably finely pulverized, in order to facilitate dissolving in water in subsequent operations.

It has been found that disodium orthophosphate is the most desirable material in producing the activating solution. Other dialkali potassium salts, for example, dipotassium phosphate, may be employed in the same manner.

The dried composition resulting from the evaporation described above is dissolved in water to prepare the activating solution. It has been found that the best results have been obtained when the solution contains from 0.1% to 2% of a dialkali phosphate, such as disodium phosphate, and the quantity of the soluble salt selected from the group described above ranges from 0.005% to 0.05%. However, the salt content may be varied from this preferred range with activation being obtained. The pH of the solution within the range set forth will vary from 8.0 to 8.5

The metal surface to be treated is initially thoroughly cleansed. One suitable treatment is cleaning in vapors of chlorinated solvents such as trichlorethylene and the like. Alternatively, the metal surface may be electrocleaned or subjected to alkaline detergents with thorough washing with clean water before applying the activating solution.

The thoroughly cleaned metal surface may be dipped into the disodium phosphate metallic salt activating solution or the solution may be sprayed over the metallic parts or applied in any desired manner. The surfaces need be subjected for about only 10 seconds to the activating solution in order to acquire a satisfactory degree of activation. However, applications of activating solution for 45 seconds or more are beneficial. It is believed that the metal surface does not acquire any protective coating during this stage of the process.

The member is removed from the activating solution and a conventional or a modified phosphate coating forming solution is applied. For use with zinc metals, a solution containing iron in an amount from 0.03% to 0.30%, zinc phosphate about 0.04% and phosphoric acid to produce a 20 point solution and comprising 1:8 of the total phosphate content, and the remainder water is one example of a solution suitable for use with zinc. In some cases an oxidizing agent, such as a nitrate in amount from 0.2% to 1% may be present in order to remove any nascent hydrogen bubbles which form on the metal surfaces.

Application of the phosphate coating composition causes a heavy discharge of gaseous bubbles from the metal surfaces. It is believed that the cessation of such bubbling, which occurs in about 30 seconds, is a sign that the phosphate coating reaction is substantially complete. It is generally desirable, however, to prolong the application of the solution to the metal surface for a brief period of time beyond this point in order to insure complete formation of the phosphate coating.

The metal may be removed from the phosphate coating composition and subjected to heat in order to dry the surface. In some cases, the metal coming from the phosphate coating bath may be treated with chromic acid as a sealing coating and thereafter dried. Again the metal may be subjected to a hot chromic acid solution at a temperature of around 190° F. and thus acquire sufficient heat so that the metal dries automatically in the air after removal from the solution.

The treated dry surface will reveal on examination an almost velvety appearing crystalline coating of remarkable uniformity. The naked eye is unable to distinguish separate crystals. Under the microscope, a high magnification is necessary in order to disclose the separate crystals. The microscope particularly reveals the exceptional improvement produced by applying the activating solution prior to the phosphate coating composition. Without the preliminary activating treatment, the coatings are composed of relatively coarse crystals and the coverage of the metal surface is noticeably irregular. Large uncoated spaces between the crystals are dispersed at very frequent intervals. When initially subjected to the activating treatment, the metal acquires a much finer crystalline coating which under the microscope reveals very few open spaces and the coverage is more effective than that on the unactivated metal.

Steel and iron surfaces may be subjected to the activating solution in the same manner as zinc. The activated ferrous metal surfaces will respond better to a treatment by a phosphate solution differing somewhat from the previous solution. A typical formula for ferrous metals is given herein:

Manganese phosphate	pounds	1¾
Phosphoric acid 83%	do	5
Sodium nitrate	do	½
Cupric nitrate	ounce	¼

Sufficient water to make one gallon of solution. The gallon of solution is diluted with water to make a 3% solution.

The main purpose of the sodium nitrate in the above formula is to provide an oxidizing agent to react with small amounts of nascent hydrogen which are produced when the solution reacts with the metal surface. Unless the hydrogen is oxidized or removed as large bubbles of hydrogen gas, the nascent hydrogen adheres to the metal surface and blankets the action of the solution. Therefore, a non-uniform coating may result. The oxidizing agent will immediately react with the bubbles of nascent hydrogen and remove them from the surface of the metal. Other oxidizing agents, such as sodium or potassium nitrite, are suitable for this purpose.

Zinc phosphate may be introduced to replace a part of the manganese phosphate in the solution for treating ferrous metals. Generally, the presence of one or more of the group consisting of zinc, copper and manganese greatly expedites the reaction of the ferrous metal with the phosphate solution.

Besides ferrous metals and zinc, other metals such as cadmium and alloys of these metals are similarly responsive to the activating treatment to acquire phosphate coatings of the finely crystalline nature herein disclosed.

Corrosion tests have revealed a decided improvement in the corrosion resistance of the phosphate coatings as secured to the practice of the invention in this case. In a steam chest at 140° F. ordinary zinc plating on a steel base will turn completely white after 12 hours. The same kind of zinc plated member given in a standard phosphate treatment without an activating treatment resists corrosion in the steam chest somewhat better. After 12 hours a few white spots will be apparent on the surface of such phosphate surface coated zinc. However, in zinc plated steel similar to members subjected to the above tests when given an activating pretreatment followed by a phosphate surface treatment as herein detailed, at least 14 days elapsed before any sample showed a sign of corrosion in a steam chest operating at 140° F. Generally, the members are capable of withstanding a month in the steam chest before any extensive degree of corrosion is evidenced in the metal given the activating pretreatment.

When the same three materials were additionally coated with an organic finish, an almost equivalent proportionality was obtained. Samples to which an activating treatment was applied to zinc prior to a phosphate treatment lasted over 25 times as long at 140° F. in a steam chest before failure of the organic finish was observed, as compared to the other types of material.

Not only is the corrosion resistance secured by the application of a preliminary treatment of the metal, but superior surface characteristics are obtained as compared to prior art phosphate coatings. A single coating of organic finish is frequently sufficient to give complete and uniform coverage of zinc surfaces produced by this invention. Zinc surfaces treated without activating had so rough a surface that two or more applications of organic finish have been necessary to secure a satisfactory surface finish. Therefore, the invention introduces a saving in the amount of organic finish necessary to finally complete the article.

Since certain changes may be made in the above invention and different embodiments of the invention may be made without departing from the scope thereof, it is intended that all matter contained in the above described disclosure shall be interpreted as illustrative and not in a limiitng sense.

We claim as our invention:

1. An activating solution for treating metal surfaces to improve the subsequent formation of protective phosphate coatings on the metal surfaces comprising, in combination, an aqueous solution containing as its essential components a dialkali metal phosphate and water soluble metal salts selected from the group of metals consisting of tin, lead and arsenic.

2. An activating solution for treating metal surfaces to improve the subsequent formation of protective phosphate coatings on the metal surfaces comprising, in combination, an aqueous solution containing as its essential components from 0.1% to 2% of disodium phosphate and from 0.005% to 0.05% of a water soluble metal salt selected from the group of metals consisting of tin, lead and arsenic.

3. An activating solution for treating metal surfaces to improve the subsequent formation of protective phosphate coatings on the metal surfaces comprising, in combination, an aqueous solution containing as its essential components from 0.1% to 2% of disodium phosphate and water soluble metal salts selected from the group of metals consisting of tin, lead and arsenic.

4. A composition capable of activating metal surfaces comprising essentially, in combination, a dialkali metal phosphate and a water soluble metal salt selected from the group of metals consisting of lead, tin and arsenic.

5. A composition capable of activating metal surfaces composed essentially of disodium phosphate and a water soluble metal salt selected from the group of metals consisting of lead, tin and arsenic.

6. A composition capable of activating metal surfaces composed essentially of disodium phosphate and a water soluble metal salt selected from the group of metals consisting of lead, tin and arsenic, the metal phosphate and the metal salt being derived from a water solution of both evaporated to dryness.

7. The method of applying protective phosphate coatings to metal surfaces which comprises, in combination, applying an aqueous solution of a dialkali metal phosphate and a water soluble salt of a metal selected from the group consisting of lead, tin and arsenic, the aqueous solution activating the metal surface, and thereafter subjecting the activated metal surface to a solution of phosphoric acid, phosphates and an oxidizing agent to produce an effective corrosion resistant phosphate coating thereon.

8. The method of applying protective phosphate coatings to metal surfaces which comprises, in combination, applying an aqueous solution of from 0.1% to 2% of disodium phosphate and from 0.005% to 0.05% of a water soluble salt of a metal selected from the group consisting of lead, tin and arsenic, the aqueous solution activating the metal surface, and thereafter subjecting the activated metal surface to a solution of phosphoric acid, phosphates and an oxidizing agent to produce an effective corrosion resistant phosphate coating thereon.

9. The method of applying protective phosphate coatings to metal surfaces which comprises, in combination, applying an aqueous solution of disodium phosphate and a water soluble salt of a metal selected from the group consisting of lead, tin and arsenic, the aqueous solution activating the metal surface, and thereafter subjecting the activated metal surface to a solution of phosphoric acid, phosphates and an oxidizing agent to produce an effective corrosion resistant phosphate coating thereon.

JOHN C. LUM.
GEORGE JERNSTEDT.