

## UNITED STATES PATENT OFFICE

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## APPLICATION OF PHOSPHATE PROTECTIVE COATINGS TO NONFERROUS METALS

John C. Lum, Union, N. J., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

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1 Claim. (Cl. 204—56)

1

This invention relates to the art of producing corrosion resistant coatings on the surface of zinc and similar metals. The invention is particularly useful in the production of protective phosphate coatings in a rapid and economical manner. Such coatings are valuable in the preparation of zinc metal surfaces for the reception of an organic surface finish.

The object of this invention is to provide for increasing the iron in solution in an aqueous bath for applying protective phosphate coatings on non-ferrous metals.

A further object of the invention is to provide means for continuously replenishing the iron in solution in an aqueous bath for applying protective phosphate coatings on non-ferrous metals.

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

At the present time it is a fairly extensive practice to treat metallic surfaces with composition which will, under appropriate conditions, deposit upon the metallic surface a protective phosphate coating. By applying a solution containing metallic phosphates and free phosphoric acid, the metal will acquire a surface coating of the phosphate deposited as a fine crystalline layer having predetermined protective characteristics. Heretofore, the drawbacks to the phosphate treatment resided in that the time of treatment of the metal surface usually was somewhat prolonged and in some instances certain metals acquired the phosphate coating only with great difficulty. In some cases, particularly with zinc metal and zinc alloys, phosphate coatings have not been extensively applied as a commercial practice, since unsatisfactory coatings of phosphates were deposited upon the metal.

It has been discovered that the application of satisfactory coatings upon zinc base metals may be secured by the application of a particular composition, herein disclosed. Furthermore, the protective phosphate coating upon zinc base metals is produced in a short period of time by applying the composition at a predetermined temperature.

In the prior art, the commercial practice has been to prepare a solution containing iron, generally as ferrous phosphate, in a concentration of from 0.03% to 0.06%. Included in the solution is a certain quantity of zinc phosphate and an oxidizing agent. Free phosphoric acid is also present. The prior art solutions were applied at room temperature. The phosphate coating that was formed after a prolonged immersion, which was necessary under the conditions, is of a coarse

2

crystalline nature, the crystals being visible to the naked eye. Furthermore, the crystals were deposited as a non-uniform layer with unequal corrosion protection upon the surfaces of the zinc member.

It has been discovered that uniformly distributed, fine-grained phosphate coatings having crystals that are substantially invisible to the naked eye may be produced upon zinc metal surfaces by employing a phosphate coating solution having a higher ferrous iron content than heretofore present. It is desirable to employ a solution containing more than 0.10% of ferrous iron and preferably the iron content should run near the saturation point which is approximately 0.30% iron. Therefore, phosphate coating solutions for zinc and other non-ferrous metals should be initially prepared with a high iron content.

When phosphate solutions are employed to treat zinc and other non-ferrous metals in producing a protective phosphate coating, the ingredients of the phosphate solution are consumed in proportion to the amount of surface treated. However, some of the ingredients of the phosphate solution are consumed at a different rate than other ingredients. In particular, when zinc, zinc alloys and other non-ferrous metals are being treated, iron dissolved in the solution is more rapidly depleted than any other ingredient. When the iron has been practically all consumed, the ability of the solution to produce protective coatings is greatly diminished or entirely exhausted, even though the solution otherwise contains sufficient amounts of other phosphate coating forming ingredients therein. An important feature of the invention is the maintenance of high iron content during coating operation.

Continually or regularly replenishing the dissolved iron is both economical and highly beneficial to the process of producing phosphate coatings on zinc and the like. It has been found that the dissolved iron should be present in quantities of from 0.10% to saturation for good results. If iron is added in one way or another to a solution which has been depleted of dissolved iron by extensive use, the solution will be in a condition for use in treating more zinc metal and the like with as good results, or in some cases better results, than achieved with a fresh solution. Instead of wasting the phosphate solution because of unsatisfactory results due to a low iron content the simple addition of a small amount of iron to the solution will prolong the active life thereof. A further advantage to be

obtained by making additions of iron to the phosphate solution is that the activity is maintained at a predetermined high level as compared to conventional solutions and processes which continually deteriorate in efficiency as the iron in solution is depleted without being replenished.

It has been found that phosphate solutions may be replenished to maintain iron therein in quantities of from 0.10% to 0.30% by applying there-to one or more ferrous plates to the solution. When at least one of the ferrous plates, for example a steel plate, is made anodic in contact with the solution, iron is rapidly dissolved and builds up the iron content of the solution to the saturation point.

Where the coating baths are employed continuously, a small electrical current may be passed continuously through the plates. In other cases, the plates may be inactive for a portion of the time and a heavy enough electrical current passed through them for a predetermined period of time to put sufficient iron into solution. The electrolysis of the ferrous plates is necessary only when the iron content of the solution is approaching a low value.

It is preferable to insert two steel plates fairly close together, making one the anode and the other the cathode, and suitably connecting them to a source of direct current. A direct-current generator, an alternating-current rectifier or even batteries may be employed as the source of direct current for this purpose. In such a combination, the anodic ferrous plate will dissolve rapidly in the solution while the ferrous plate that is energized as the cathode will have deposited thereon the non-ferrous metal that progressively accumulates by being dissolved from the objects under treatment. For example, where zinc plates are being processed to produce a phosphate coating thereon, zinc is dissolved and builds up in the bath. The direct-current treatment of the solution deposits zinc from the solution on the cathode plate, thereby removing excess zinc from solution.

As an example of the practice of the invention, zinc members were treated in a phosphate solution. The following formula indicates a composition that has been employed with success in producing high grade protective phosphate coatings upon the zinc metal surfaces:

|                                                                                                                      | Per cent     |
|----------------------------------------------------------------------------------------------------------------------|--------------|
| Iron .....                                                                                                           | 0.10 to 0.30 |
| Zinc phosphate .....                                                                                                 | 0.04         |
| Sodium nitrate .....                                                                                                 | 0.2 to 2     |
| Phosphoric acid sufficient to give a solution having one part of free phosphoric acid to 6 parts of total phosphate. |              |

The sodium nitrate in the above formula constitutes an oxidizing agent which it is believed reacts with nascent hydrogen resulting from the reaction of the zinc and the solution. Nitrites and other oxidizing agents may be used to accomplish the same function. The oxidizing agent removes the nascent hydrogen from the metallic surface which would otherwise prevent satisfactory deposition of protective phosphate at that point.

In treating surfaces of zinc metal with the solution represented by the formula, it has been discovered that the reaction is greatly expedited by heating the solution above room temperature. A temperature of from 140° F. to 190° F. will give a much more rapid reaction than would be obtained by employing the solution at a room temperature of from 70° F. to 80° F. It will be

appreciated, however, that even at room temperature though the reaction is rather slow and not as economical, the solution prepared according to the formula produces desirable coatings superior to those of the prior art.

Zinc metal, galvanized members, or zinc plated articles may be subjected to the action of the solution in order to produce protective coatings upon the metal. In some cases zinc alloys containing a preponderant proportion of zinc and metals chemically related to metallic zinc such, for example, as cadmium, may also be treated with the solution for this protective coating.

The zinc base metallic surfaces to be treated are rendered free of surface grease, dirt and other impurities which would tend to inhibit the production of a satisfactory coating by subjecting the surfaces to a cleansing operation. Trichlorethylene vapor degreasing processes have been satisfactory for this purpose. Alkaline cleaning solutions are also productive of a good surface for subsequent coating. Other methods of cleaning surfaces precedent to treating with phosphate solutions are known to the art and need not be detailed herein.

When the metal is subjected to the solution, a great quantity of gaseous bubbles are emitted. These bubbles are produced for a period of time of approximately forty seconds at the termination of which time a velvety appearing, fine crystalline coating has been produced upon the entire surface. It is believed that the coating process is substantially complete upon the cessation of the bubbling, but five or ten seconds, or even longer immersion after termination of bubbling may be beneficial. The solution may be applied by spraying or the surface may be immersed in a tank of the solution.

After the bath has been operated for a prolonged period of time, the iron in solution will be greatly reduced so that signs of diminishing coating activity are evident, such for example as a less satisfactory or less complete protective coating on the zinc being produced or else the time to produce a good coating on the zinc becomes excessive. The operator then can immerse in the solution two iron plates connected in circuit with a source of direct current. Passing electrical current between the plates and through the solution causes iron to dissolve from the anode plate and zinc to deposit on the cathode plate.

It is not necessary to wait until the iron content is low before adopting these measures, but as mentioned above, the iron or steel plates may be set in permanently in the solution and current passed continuously so as to maintain a predetermined high iron concentration. A rheostat or other control means may be placed in the electrical circuit to provide for securing an adequate control of the amount of iron being dissolved to compensate for the iron removed from solution.

As an example of the effectiveness of such a process, the following is cited. A bath for applying a phosphate coating on zinc was analyzed and found to contain 0.138% of iron. A pair of plates of approximately one square foot surface area were immersed in the bath and 50 amperes of electrical current passed through them. After ten minutes operation, the bath when analyzed contains 0.186% iron.

It will be appreciated that the steel or iron that is used for the plates is preferably a relatively pure iron free from deleterious impurities.

which may adversely affect the phosphate coating bath. Plates of Armco iron, which is a relatively pure grade of iron available to the trade, are entirely satisfactory for the practice of the invention.

The coated metal surface may be rinsed after removal from the phosphate solution in clear rinse water. For the best coating results, the phosphate coated zinc metal surfaces have applied thereto a sealing treatment consisting of a chromic acid solution. Chromic acid solutions containing a concentration of  $7\frac{1}{2}$  to 12 ounces of chromic acid per 100 gallons may be applied to the phosphate coated zinc surface for a few seconds to produce the desired sealing. The chromic acid solution may be dried by passing the zinc metal members through a drying oven. Alternatively, it has been found that by heating the chromic acid solution to a temperature of 190° F., or even higher, sufficient heat is imparted to the member, that after removing the metallic member from the chromic acid solution, drying occurs spontaneously due to the stored heat. The phosphate coated zinc base metal may be put into service at once or it may be further processed with organic finishes.

An inspection of the treated heat surface shows a uniform, blue-gray, fine crystalline phosphate coating distributed over the entire surface. All irregularities and recesses of the zinc surface are covered with the phosphate coating. The treated metal has acquired a highly protective coating which is also suitable for successful paint and lacquer application.

One of the major benefits of the high iron content phosphate coating solution is the improvement in the hardness of the phosphate coating on plated zinc. It is a known phenomenon that electroplated zinc coatings are usually relatively soft. If such soft zinc plate is treated with a phosphate solution containing 0.06% iron for instance, a soft, easily removable phosphate coating is generally produced. When the iron content of the phosphate solution is above 0.10%—particularly over 0.15% iron—the phosphate coating on the soft zinc electroplate will be considerably harder. It will resist scratching and abrasion from handling quite satisfactorily.

It has been particularly desirable to provide an intermediate phosphate coating between zinc metal and organic finishes due to the nature of the reaction between the finish and metallic zinc. It is a well-known phenomenon that paint or other organic material applied to zinc surfaces may be readily removed from a simple scraping operation. There is no bonding of the organic finish to the zinc metal surface, in fact, it appears as if there is a definite separation between the zinc metal and any coating of organic material. The fine crystalline phosphate coatings upon zinc base metals as produced by treating with the phosphate solutions herein disclosed are highly satisfactory bases for the subsequent application of an organic finish. The organic finish keys into the crystalline coating and a bond between the organic finish and the phosphate coating is produced which retains the organic finish satisfactorily. Whenever the organic finish is inadvertently scraped or scratched, the underlying phosphate coating limits the spread of cor-

rosion products underneath the organic film to prevent lifting and separation of the finish away from the zinc metal. The combination of the fine crystalline protective coating and an organic finish subsequently applied produces articles of commerce having great resistance to deterioration, particularly in humid atmospheres. The life of apparatus produced in this manner is greatly extended over that heretofore available.

It is particularly desirable to employ the composition disclosed in this invention for producing phosphate coatings in combination with an activating pre-treatment disclosed in Patent No. 2,310,239, issued February 9, 1943, to George Jernstedt, and assigned to the same assignee as this application.

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 limiting sense.

I claim as my invention:

The process of treating members of non-ferrous metal selected from the group of metals consisting of zinc, cadmium and alloys in which zinc and cadmium predominate, in an aqueous acidic phosphate solution containing from 0.10% to 0.30% of dissolved iron to provide for applying protective phosphate coatings containing iron on the members, the steps comprising immersing the non-ferrous metal members in the solution to react therewith to produce thereon a protective iron-containing phosphate coating, the iron content of the solution being decreased thereby and some of the non-ferrous metal being dissolved in the solution, introducing into the solution ferrous members, connecting a source of direct current to the ferrous members to render one ferrous member cathodic and the other anodic, the anodic ferrous member being dissolved in the solution whereby to replenish the ferrous metal content of the solution to a value of from 0.10% to 0.30%, and zinc or cadmium being deposited out of solution on the cathodic member.

JOHN C. LUM.

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