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PROTECTIVE COATINGS FOR NONFERROUS METALS

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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.

This application is a continuation-in-part of our copending patent application Serial No. 400,096, filed June 27, 1941. This continuation-in-part is primarily for the purpose of teaching the best methods of applying iron additions to phosphate solutions which have been found to be satisfactory.

The object of this invention is to provide upon zinc and other non-ferrous metal surfaces a dense, fine crystalline protective phosphate coating having good corrosion resistance.

Another object of this invention is to provide for applying to phosphate solutions for application to zinc and other non-ferrous metal surfaces to produce fine crystalline protective coatings thereon, iron in finely divided form to prolong the active life of the phosphate solution.

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 pres-

ent. 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 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 a high iron content during coating operation.

A convenient way of securing and maintaining the high concentration of ferrous iron is to suspend a mass of steel wool or iron filings within the solution in a porous receptacle such, for example, as a canvas bag. The iron content is maintained at a predetermined high concentration by reason of the extensive exposed surface of the steel wool or iron filings.

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, and this 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, it 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 which will go into solution will prolong the active life thereof. A further advantage to be obtained by making additions of iron which will go into 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.

By experience it has been found that good results may be obtained by applying to the phosphate solutions iron in a finely divided or powdered stage after the iron has been subjected to reduction in the presence of hydrogen. Reducing the iron in the presence of hydrogen has been found to render the iron extremely active so that it goes into solution quite rapidly and brings the iron content up to an optimum value. The hydrogen reduced iron may be distributed in the phosphate solution at predetermined intervals depending on the amount of use to which the solution has been applied. A small quantity of hydrogen reduced iron powder may be sprinkled in the solution at the beginning or end of every working day in case the solution is used extensively. The iron may be applied at more frequent or longer intervals as required. This form of iron is convenient in securing the benefits of this invention.

The following formula indicates a solution that has been employed with success in producing high grade coatings upon zinc metal surfaces:

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 metallic surface 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 economical, the solution prepared according to the formula produces desirable coatings superior to those of the prior art.

Zinc metal, galvanizant 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 solution is 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 coating bath has been operated for a prolonged period of time and the iron in solution has been greatly reduced so that signs of diminishing activity are evident, such as, for example, the time to produce a good coating of zinc becomes excessive, then the operator can easily replenish the bath solution by distributing a small amount of hydrogen reduced iron powder. Repeating the application of the hydrogen reduced iron powder from time to time will maintain the bath at a high degree of efficiency.

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 7½ 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, so 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.

While occasionally with prior art protective coating solutions there may be secured members that have coatings somewhat of the appearance of those produced by this process, a corrosion test in a steam chest reveals considerable difference in quality. The following is given as indicative. Samples of untreated zinc plate on a steel base were suspended in a steam chest containing steam at a temperature of 140° F. In less than twelve hours the entire surface was covered with a white zinc corrosion deposit. The same

type of zinc plated member was provided with a phosphate coating from a phosphate solution containing approximately 0.06% ferrous iron. On testing the coated metal in a steam chest at 140° F., white spots were apparent on the surface within twelve hours, although the corrosion had not spread over the entire surface in that time. When zinc-plated members treated with a hot phosphate solution saturated with ferrous iron corresponding to the above formula, were tested in a steam chest at 140° F. nearly fourteen days elapsed before any sample showed any sign of corrosion. A month in the steam chest was generally required to produce an extensive degree of corrosion. This last test indicates that the phosphate coating is sufficiently protective so that no other treatment would be required for many commercial applications.

In each of the above tests of the three different samples, the metal surface under test was without any organic finish. In a subsequent series of corrosion tests wherein lacquer coats were applied to the same three types of material in almost equivalent proportionality of corrosion resistance was obtained. Samples with the phosphate coating of this invention upon the zinc lasted twenty-eight times as long before showing corrosion as the zinc metal lacking this type of phosphate coating.

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 phenomena 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 the phosphate compositions 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 corrosion 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-75

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.

We claim as our invention:

1. The method of prolonging the active life of an aqueous solution comprising essentially an acid phosphate for producing a protective phosphate coating on zinc, cadmium and their alloys which comprises maintaining free ferrous metal in a form having an extensive surface in contact with the solution thereby maintaining from 0.10% and higher of dissolved iron in the solution while being applied to said metals.

2. The method of prolonging the active life of an aqueous solution comprising essentially an acid phosphate for producing a protective phosphate coating on zinc, cadmium and their alloys which comprises maintaining in the aqueous solution finely divided free iron which has been reduced in hydrogen thereby maintaining from 0.10% and higher of dissolved iron in the solution while being applied to said metals.

3. The method of maintaining the activity and prolonging the useful life of an aqueous acid phosphate coating solution suitable for producing protective coatings on surfaces of zinc, cadmium and their alloys which comprises suspending free ferrous metal in the solution while being applied to the surfaces in order to increase the amount of ferrous iron in solution above 0.10%, and heating the coating solution to a temperature of from 140° F. to 190° F.

4. In the process of providing a protective phosphate coating on the surfaces of zinc, cadmium and their alloys, the steps comprising applying to the surfaces an aqueous solution comprising as its essential ingredients a metal phosphate, free phosphoric acid and an oxidizing agent and free iron being present in the aqueous solution during application to the surfaces, the free iron being in a form having an extensive surface to provide for continuously maintaining a concentration of from 0.10% to saturation of dissolved iron thereby producing a hard and durable protective phosphate coating on the surfaces of the metals.

5. In the process of providing a protective phosphate coating on the surfaces of zinc, cadmium and their alloys, the steps comprising applying to the surfaces an aqueous solution comprising as its essential ingredients a metal phosphate, free phosphoric acid and an oxidizing agent and free iron reduced in hydrogen being present in the aqueous solution during application to the surfaces, the free iron being in a form having an extensive surface to provide for continuously maintaining a concentration of from 0.10% to saturation of dissolved iron thereby providing a hard and durable protective phosphate coating on the surfaces of the metals.

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