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## PROTECTIVE PHOSPHATE COATINGS FOR METAL SURFACES

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

The object of this invention is to provide for treating metal surfaces to expedite the process of forming corrosion-resistant phosphate coatings thereon.

Another object of this invention is to provide a composition capable of activating metal surfaces to improve the formation of corrosion-resistant phosphate coatings thereon.

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

The treatment of metallic surfaces with solutions or compositions which, under appropriate conditions, will deposit or form upon the metallic surface a protective phosphate coating is practiced extensively. Not only do these phosphate coatings protect the underlying metal from corrosion, but they constitute excellent surfaces for the successful application of organic finishes. The phosphate coatings occur as crystalline deposits to which organic finishes will bond and adhere more tenaciously than to the bare metal surface.

It is known in the prior art that metal surfaces, particularly surfaces of ferrous metal, may be provided with a protective phosphate coating by applying an aqueous solution containing phosphoric acid and metal phosphates. The time required to produce a satisfactory phosphate coating on the metal surface has usually been relatively lengthy but within recent years the time of treatment has been reduced to a fraction of an hour.

According to the present invention, the time necessary to produce a satisfactory phosphate coating on a metal surface by applying thereto a phosphate solution may be greatly reduced by pretreating the metal surfaces in order to activate the surface metal. It is my theory that under ordinary conditions the metal crystals exposed at the surface of a body of metal are characterized by different degrees of activity whereby some crystals are in a highly active state and will react speedily with a chemical applied thereto whereas other crystals on the same surface are in a relatively inactive state and react much more slowly or may not react at all with the given chemical applied thereto. The state of relative activity of a crystal probably determines the speed with which it will react with a phosphate solution to produce a phosphate coating. In the case of highly inactive or completely passive crystals, a protective phosphate coating may not even be produced after a prolonged contact with the phosphate solution. If the average crystal activity is low, poor coatings are obtained even after a long treatment. In most metals the surface crystals are not in a highly active state and would

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require long treatment with a phosphate solution to produce a coating. This theory of the nature of the reaction is explanatory and may not be necessarily controlling, and I do not wish to be bound thereby. However, experience indicates that some mechanism of the nature set forth herein is responsible for the unsatisfactory results previously met with in many instances in prior art practice.

The pre-treatment of this invention is believed to activate the metal at the surface of a body so that a large proportion or all of the exposed crystals are in a highly active state, whereby they react with a phosphate coating solution at a rapid rate. In some cases, metals that did not satisfactorily react with phosphate solutions to produce a protective phosphate coating will, when so pre-activated, acquire highly satisfactory coatings of phosphate. For instance, zinc metal ordinarily does not react with phosphate coating solutions to form satisfactory coatings. When subjected to the pre-treatment of this invention, zinc will react at a high rate with an applied phosphate solution to produce a fine crystalline coating having excellent protective properties.

The pre-treatment of the invention comprises the application to metal surfaces of an aqueous solution of ortho-disodium phosphate and zirconium dissolved in water. In some cases the addition of titanium to the solution produces unexpectedly improved results. In the absence of the zirconium or titanium, the disodium phosphate has negligible activating effect.

It has been found that ortho-disodium phosphate is the only material that may be combined with the zirconium, with or without titanium, to produce the desired activation of metal surfaces. Other phosphates have been tried and have been found substantially useless even when zirconium and titanium were present.

The zirconium is employed as a water soluble salt. The zirconium halides and zirconium sulphate are satisfactory for the purpose of the invention. Various other zirconium compounds may be employed. Since only a small amount of zirconium need be present in a large quantity of water in preparing the pretreating solution, the compound or zirconium selected need not be very soluble in water.

In some cases, a portion of the zirconium may be replaced by titanium with good results. Examples of titanium compounds suitable for this purpose are titanium tetrachloride, titanium trichloride, titanium hydroxide, titanium nitride and titanium potassium oxalate.

In producing the pretreating solution, the disodium phosphate and zirconium, with or without the titanium, are combined by dissolving to form an initial aqueous solution and slowly evaporating the solution to dryness. The zirconium and tita-

nium do not form an appreciably effective pretreating solution if simply added to the disodium phosphate without the step of evaporating to dryness.

The evaporated and dried disodium phosphate and zirconium composition so prepared may contain from about 0.005% up to 20% by weight of zirconium, the balance being disodium phosphate. It is used in a powdered form to facilitate dissolution in water. The dried composition may be stored indefinitely until desired for use. In preparing a pretreating solution, the dried composition is dissolved in water to produce an aqueous solution containing from about 0.1% to 2% of disodium phosphate and from about 0.001% to 0.1% of zirconium. If titanium is present, the total quantity of titanium and zirconium present may be from 0.001% to 0.1%. Zirconium and titanium may be present in larger amounts but no advantage is obtained due to the presence of such excess. A satisfactory commercial composition has been found to contain 1% disodium phosphate and 0.01% of zirconium or zirconium and titanium combined. In the aqueous solutions here described, the percentage of zirconium and titanium is that of the metal radical alone. A solution in the range of concentrations given will have a pH of from 8 to 8.5.

The pre-treatment solution prepared as indicated is particularly effective when applied to iron, steel and other ferrous metals. In my patent No. 2,310,239, issued February 9, 1943, a pre-treatment solution containing titanium was disclosed as particularly satisfactory in treating zinc. The present invention is based on a zirconium solution which exhibits desirable characteristics in treating zinc but its major advantages are revealed when applied to iron and steel surfaces. The zirconium present in the pretreating solution activates the ferrous metal to a much greater extent than titanium alone. However, when titanium is added to the zirconium, particularly to produce a solution having approximately 30% of titanium and 70% zirconium, exceptional results are obtained in treating ferrous metal.

Ferrous metal may be treated with the solution of disodium phosphate and zirconium either by spraying the solution on the metal surface or dipping the metal in the solution or in any other convenient manner. The time of treatment need be very brief. Usually, 10 to 15 seconds, is all that is required to satisfactorily activate the surface. In some cases, the activating solution may be applied for 45 seconds or even longer to the metal with some benefit.

The pretreated ferrous metal is treated with a conventional type of phosphate coating solution to cause the formation thereon of a protective phosphate coating. A typical coating producing solution for treating ferrous metal is the following:

|                           |             |       |
|---------------------------|-------------|-------|
| Manganese phosphate       | -----pounds | 1 3/4 |
| Phosphoric acid 83%       | -----do     | 5     |
| Sodium nitrate            | -----do     | 1/2   |
| Cupric nitrate            | -----ounce  | 1/4   |
| Water to make one gallon. |             |       |

The gallon of solution is further diluted with water to make a 3% solution thereof for use in applying to metal surfaces. Such a solution has a pH of from 8.0 to 9.0.

The main purpose of the sodium nitrate in the above formula is to provide an oxidizing agent to react with small amounts of nascent hydro-

gen 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 as well as a slower rate of reaction. 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, chlorates, and the like 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.

Numerous other solutions capable of producing phosphate coatings upon metal are known to the art and their reaction with activated metal surfaces is equally expedited to produce a protective coating.

When the preactivated metal is treated with the phosphate coating solution, a large quantity of gaseous bubbles appear when the solution is first applied. The bubbles consist mainly of hydrogen gas. With activated metal, the bubbling ceases after a fraction of a minute and it is believed that the coating reaction is substantially complete when this occurs. It may be desirable to prolong the application of the solution to the metal surface beyond the point at which the gaseous bubbles cease to be given off in order to assure the complete coating of the metal surface.

An examination under the microscope of the activated metal surface after the phosphate coating treatment shows that the surface is heavily and uniformly covered with small, fine crystals which are so closely disposed that they touch one another at many points. By comparison, the same ferrous metal, without having been given the preactivating treatment, after the phosphate coating composition has been applied under the microscope shows a much smaller total of relatively scattered crystals which are much larger and coarser. A great portion of the metal surface is without any crystals thereon. The corrosion-resistance afforded by this latter crystal coating is obviously much less than with the more complete crystal coatings formed on the pretreated metal surface.

The crystals are probably a ferro-ferric phosphate, though it is difficult to analyze the crystals with a sufficient accuracy to be certain of their exact chemical composition.

After an adequate crystalline phosphate coating has been produced upon the metal surface, the metal surface may be rinsed with clear water. For best results, the surfaces may be subjected to a sealing treatment by applying chromic acid solution thereto. An aqueous solution containing 7 1/2 ounces of chromic acid per 100 gallons of water is generally satisfactory for the purpose. A water rinse may not be necessary in this case since the chromic acid sealing treatment performs a rinsing function. The chromic acid solution need be applied to the metal surface for only a few seconds.

The metal, after rinsing or after the application of the chromic acid solution, may be dried by passing through a drying oven to prepare the

surface for subsequent operations such as the application of an organic finish. The drying operation may be dispensed with if the chromic acid sealing solution is heated to a temperature of about 190° or even higher, whereby sufficient heat is imparted to the metal so that the metal dries automatically in air upon removal from the solution.

The phosphate coating produced by the practice of this invention is extremely fine and velvety in appearance. A single coat of organic finish applied over the coating is sufficient to produce a smooth and highly protective finish thereon. Phosphate coatings produced without the preactivating treatment herein disclosed are of a much coarser structure and usually require two or more coats of organic finish to give a smooth surface and to furnish adequate corrosion protection.

While the zirconium preactivating treatment is particularly beneficial for treating iron, steel and other ferrous metal members, in the form of sheets, tubes, punchings, castings, forgings, and the like, it has advantages when applied to zinc, cadmium and other alloys and metals. For treating non-ferrous metals, the pretreating solution may be of the same composition as for treating iron and steel and the like, but the subsequently applied phosphate coating solution is usually modified to operate more satisfactorily with the metal being treated. These are well known in the art.

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 or taken in connection with the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. An aqueous solution for treating ferrous, zinc and cadmium metal surfaces to provide for improving the formation of protective coatings on the metal surface consisting of from 0.1% to 2% by weight of ortho-disodium phosphate and a total from 0.001% to 0.1% by weight of titanium and zirconium combined, the balance being water, the titanium and zirconium being present as water soluble compounds, the ortho-disodium phosphate, titanium compound and zirconium compound having been previously combined by dissolving them in water and evaporating to dryness.

2. A composition capable of activating metal surfaces when in aqueous solution consisting of from 0.005% to 20% by weight of zirconium and titanium, the zirconium and titanium being present as water soluble compounds, and the balance being ortho-disodium phosphate, the composition being the residue derived by dissolving in water the zirconium and titanium compounds and the ortho-disodium phosphate and evaporating the water solution to dryness.

3. A composition capable of activating ferrous surfaces when in aqueous solution consisting of from 0.005% to 20% by weight of zirconium and titanium, the zirconium and titanium being present as water soluble compounds, and the balance being ortho-disodium phosphate, the composition being the residue derived by dis-

solving in water the zirconium and titanium compounds and the ortho-disodium phosphate and evaporating the water solution to dryness, the ratio of weight of titanium to zirconium being about 3 to 7.

4. In the process of treating ferrous, zinc and cadmium metal surfaces, to provide corrosion resisting coatings thereon, the steps comprising, applying to the metal surface an aqueous solution consisting essentially of from 0.1% to 2% of ortho-disodium phosphate and from 0.001% to 0.1% of zirconium present as a water soluble compound, the ortho-disodium phosphate and the zirconium compound having been previously combined by dissolving them in water and evaporating to dryness, and the balance being water, to provide for activating the metal surface, and thereafter applying to the activated metal surface a solution comprising phosphoric acid, phosphates and an oxidizing agent to produce a phosphate coating thereon.

5. In the process of treating ferrous, zinc and cadmium metal surfaces, to provide corrosion resisting coatings thereon, the steps comprising, applying to the metal surface an aqueous solution consisting of from 0.1% to 2% by weight of ortho-disodium phosphate, and a total of from 0.001% to 0.1% of titanium and zirconium combined present as a water soluble compound, the ortho-disodium phosphate and the zirconium compound having been previously combined by dissolving them in water and evaporating to dryness, and the balance being water, to provide for activating the metal surface and thereafter applying to the activated metal surface a solution comprising phosphoric acid, phosphates and an oxidizing agent to produce a phosphate coating thereon.

6. In a solution for treating ferrous metal surfaces to provide for improving the formation of protective coatings on the metal surface comprising an aqueous solution consisting of from 0.1% to 2% by weight of ortho-disodium phosphate and a total of from 0.001% to 0.1% of titanium and zirconium each present as a water soluble compound, the ortho-disodium phosphate and the zirconium and titanium compounds having been previously combined by dissolving them in water and evaporating to dryness, the ratio of weight of titanium to the weight of the zirconium being about 3 to 7, and the balance being water.

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#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

| Number    | Name      | Date          |
|-----------|-----------|---------------|
| 1,254,263 | Oeschger  | Jan. 22, 1918 |
| 2,310,239 | Jernstedt | Feb. 9, 1943  |
| 2,312,855 | Thompson  | Mar. 2, 1943  |

#### OTHER REFERENCES

Gilman, "Inorganic Reactions" (1929), page 246.

Mellor, "Inorganic and Theoretical Chemistry," Vol. 7 (1927), pages 96, 97 and 163 to 165.