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ELECTROPHORETIC DEPOSITION ON ZINC ENRICHED METAL SURFACE

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5 Claims

ABSTRACT OF THE DISCLOSURE

A process for treating metal surfaces wherein a zinc enriched zinc phosphate coating is formed on the metal and, thereafter, the thus-coated surface is electrophoretically painted. The zinc enriched phosphate coating may be formed by plating zinc from a conventional zinc plating bath onto a zinc phosphate coating or by electrolyzing a zinc phosphate bath with the metal as cathode, to simultaneously deposit zinc and zinc phosphate.

This application is a continuation-in-part of our copending application Ser. No. 479,313, filed Aug. 12, 1965.

This invention relates to an improved method for coating metal surfaces and more particularly relates to an improved process for providing an electrophoretically applied paint coating on a ferrous metal surface.

With the recent development of water-soluble resin base paints, a great deal of work has been done on the application of such paint by electrophoresis. The electrophoretic application of paint involves the phenomena of electroosmosis and electrolysis, as well as electrophoresis. In this method, an electric current is passed through the paint while the article to be painted is made an electrode, usually the anode, in the paint. Normally, only one coat of paint may be applied by this method and heretofore, the technique has been used mainly to apply primer coats of paint. Such single-coat paint films, applied electrophoretically, have often failed to provide adequate corrosion resistance on ferrous metal surfaces, i.e., surfaces which are predominantly of iron.

It is known, of course, that zinc phosphate coatings have excellent corrosion resistance and these coatings have long been used as a base for paint on ferrous surfaces. These conventional zinc phosphate coatings have an appreciable electrical resistance, however, which in many instances, may limit the thickness of the paint film which may be deposited thereon by electrophoretic application techniques. Moreover, it has been found that a paint applied electrophoretically on a crystalline phosphate coating, as normally results from the application of a conventional zinc phosphate coating, often has an appreciable loss in gloss. Accordingly, up to the present time, conventional zinc phosphate coatings have generally not been satisfactory as a base for electrophoretically applied paint.

It is, therefore, an object of the present invention to provide an improved method of producing an electrophoretically applied paint coating on a ferrous metal surface.

A further object of the present invention is to provide an improved method for electrophoretically painting ferrous metal surfaces to obtain a protective paint film hav-

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ing a high gloss and which provides improved corrosion resistance.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a process for treating a ferrous metal surface which comprises forming on the ferrous metal surface a zinc phosphate coating containing metallic zinc and, thereafter, electrophoretically depositing a paint film on the zinc phosphate coated surface. It has been found that by first coating the ferrous metal surface with a zinc phosphate coating containing metallic zinc, the resulting coating has sufficient conductivity that, subsequently electrophoretic application of a paint film of the desired thickness may be easily accomplished. Moreover, the gloss of the thus-produced paint film is found to be maintained or even enhanced and improved corrosion resistance is imparted to the ferrous metal surface.

More specifically, in the practice of the present invention, the zinc phosphate coating containing metallic zinc may be formed on the ferrous metal surface to be treated in any convenient manner. For example, the ferrous metal surface may first be contacted with a conventional zinc phosphate coating solution so that a zinc phosphate coating is formed on the surface in the conventional manner. Thereafter, zinc may be deposited into the pores of the phosphate coating by electrodeposition from a conventional zinc plating bath. Alternatively, the surface to be coated may be contacted with a conventional zinc phosphate coating bath while passing an electric current through the bath, with the work to be coated as the cathode. In this manner, zinc is simultaneously deposited with the phosphate coating on the metal surface, thus forming the zinc phosphate coating containing metallic zinc. It is to be appreciated that other methods of forming a zinc enriched or zinc-containing zinc phosphate coating may also be used, as will be apparent to those in the art.

Various methods may be used for contacting the ferrous metal surface with the zinc phosphate coating solution, in order to form the desired zinc phosphate coating on the metal surface. Exemplary of such coating techniques are spraying, immersion, flooding, and the like. Although immersion techniques are generally preferred when the zinc enriched phosphate coating is produced by the simultaneous deposition of zinc in the pores of the phosphate coating, by passing a direct electric current through the coating solution with the work piece as a cathode, other coating techniques such as spraying and flooding may also be used.

Following the application of the zinc-enriched zinc phosphate coating on the metal surface, the surface is painted by the electrophoretic application of a suitable paint. This electrophoretic application of the paint may be carried out in various ways, as are known to those in the art. Typically, the coating solutions utilized are dilute aqueous solutions, having a solids content within the range of about 3 to 15 percent solids. The metal to be coated is preferably the anode and the voltages used are typically in the range of about 50 to 1,000 volts (direct current). Typical current densities used and coating times required are, respectively, from about 0.1 to 7 amperes per square foot and from about 10 seconds to about two minutes. Normally, the paint solution is at substantially room temperature, i.e., about 20 degrees centigrade, although

higher temperatures, such as those of 30 to 40 degrees centigrade or even higher, may be used if desired. The paint applied using these techniques are water-thinned resin paints which are, typically, aqueous solutions based on synthetic resins such as alkyd resins, acrylic polymers, melamine resins, epoxy ester resins, and the like. These aqueous resin solutions generally have a pH of about 9 and the solvent used is either water or an aqueous alcoholic mixture.

Various zinc phosphate solutions which are useful for forming protective coatings on ferrous surfaces, as are known in the art, may be used in the present process. Typically, these solutions are aqueous acidic solutions containing zinc ions and phosphate ions and may be formulated from zinc phosphate, zinc oxide, phosphoric acid, or other suitable sources of zinc ions and phosphate ions. Additionally, these solutions may also contain an accelerator or oxidizing agent, such as nitrate ions, nitrite ions, chlorate ions, peroxide ions, and the like, as are well known in the art. Additionally, other modifying ions may also be present in the solutions, such as ferrous ions, nickel ions, copper ions, alkaline earth metal ions, such as calcium ions, and the like.

In many instances, it has been found that wider variations in the bath operating conditions may be tolerated when using zinc phosphate coating solutions containing a chlorate accelerator. Accordingly, zinc phosphate solutions of this type are preferred and primary reference hereafter will be made to such solutions.

Exemplary of zinc phosphate solutions which may be used are those described in U.S. Patents 2,835,617, 3,090,709, 3,161,549, 2,813,812, 2,734,204, 3,015,594, 2,540,314, 2,514,149, 2,591,479, and 2,487,137. Although the specific concentration of the phosphate coating solutions used will depend on the type of coatings desired and the specific operating conditions utilized, in general it has been found to be desirable that the solutions used contain from about 0.5 to 3 percent by weight of phosphate (PO_4) and have a free phosphoric acid content within the range of about 0.3 to about 0.8 percent. Additionally, the accelerators and modifying ions are typically present in amounts within the range of about 0.0001 to about 5 percent by weight of the solution, depending upon the particular ions added and the nature of the coating which is desired.

The zinc phosphate coating solution may be applied in the conventional manner, solution temperatures from about room temperature up to the boiling point of the solution, i.e., about 20 degrees centigrade to 100 degrees centigrade, being suitable. Similarly, the contact times between the coating solution and the surface to be treated will be those which are normally used in applying zinc phosphate coatings and will vary according to the nature of the coating desired and the solution operating conditions. Typical contact times are from several seconds, e.g., 5 seconds, up to about 5 minutes or more, depending upon whether spraying or immersion application techniques of the phosphate coating are used.

Where the zinc enriched zinc phosphate coating is formed simultaneously with the deposition of the zinc phosphate coating by electrolyzing the zinc phosphate solution with the metal surface to be treated as the cathode, it has been found to be desirable if the solution temperatures are not in excess of about 85 degrees centigrade and preferably are within the range of about 20 to 70 degrees centigrade. Additionally, it has been found to be desirable that the current densities utilized in this simultaneous deposition of zinc and zinc phosphate are not substantially in excess of about 30 amperes per square foot, with current densities within the range of about one to about 15 amperes per square foot being preferred.

Where the zinc enriched zinc phosphate coating is formed by the electrodeposition of zinc onto the zinc phosphate coating formed on the metal surface, any of the conventional zinc plating baths may be used. As are

known in the art, these plating baths contain various soluble zinc salts, such as the sulfates, chlorides, cyanides, oxides, and the like. Additionally, as is known in the art, these plating baths may also contain other adjuvants for improving or enhancing the quality of the metallic zinc plate which is produced. These adjuvants include various other salts such as the alkali metal chlorides, ammonium chlorides, aluminum sulfates, alkali metal cyanides, the alkali metal hydroxides, acids, such as sulfuric acid, boric acid, acetic acid, including the alkali metal salts thereof, as well as various organic additives such as dextrin, and the like, as are known to those in the art. Exemplary of the various conventional zinc plating baths which may be used are those disclosed in U.S. Patent 3,133,005 and in the "Chemical Engineers Handbook," second edition, pages 2771 and 2773. The deposition of the zinc from the baths is effected by making the zinc phosphate coated surface the cathode in the bath and then passing a direct current through the bath to electroplate zinc onto the zinc phosphate surface. Typically, the current densities are within the range of about 5 to 100 amperes per square foot, while bath temperatures within the range of about 20 to 70 degrees centigrade may be used.

Thus, in forming the zinc-enriched zinc phosphate coating on the ferrous metal surfaces to be treated, the ferrous surface may first have formed thereon a zinc phosphate coating, using a conventional zinc phosphate coating solution in a conventional manner, and thereafter, the zinc phosphate coated surface is electroplated with zinc from a conventional zinc plating bath. Alternatively, the deposition of the zinc may be carried out simultaneously with the formation of the zinc phosphate coating, by making the ferrous metal surface to be treated the cathode in a conventional zinc phosphating bath and passing a direct current through the bath to effect the simultaneous deposition of the zinc and zinc phosphate. While other methods for forming a zinc-enriched zinc phosphate coating on the ferrous metal surface may also be used, it is to be appreciated that in each instance, the deposition of metallic zinc on the zinc phosphate coating will be carried out at least to the extent that the metallic zinc is deposited in the pores of the zinc phosphate coating.

Following the application of the zinc-enriched zinc phosphate coating to the ferrous metal surface, the thus-coated surface is then painted electrophoretically, in accordance with the procedure than has been set forth hereinabove. It is found that this method is superior to conventional zinc plating on the metal surface followed by painting of the zinc plated surface in that the cleaning of the ferrous metal surface is simpler than the cleaning required for conventional zinc plating, simple vapor degreasing normally being sufficient in the method of the present invention. Additionally, less metallic zinc is required on the surface to achieve the same degree of corrosion resistance than in the conventional zinc plating processes. Moreover, it is found that the adhesion of the electrophoretically applied paint to the zinc-enriched phosphate coating is improved over that obtained on conventional zinc plate.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are given in degrees centigrade and parts and percents are by weight. It is to be appreciated, however, that these examples are merely exemplary of the process of the present invention and are not to be taken as a limitation thereof.

Example 1

A conventional zinc phosphate processing solution was prepared containing about 0.24 percent zinc, and 1.02 percent PO_4 , and 0.35 percent chloride. The solution had a total acid pointage of about 20 and a free acid pointage of about 3.0. This aqueous treating solution was maintained at a temperature of about 60 degrees centigrade.

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Steel panels were vapor degreased and then immersed in the aqueous solution for two minutes. The panels were then removed from the solution, water rinsed, and made cathodes in a zinc-plating solution. This plating solution contained the following components in the amounts indicated:

Components:	Grams per liter
ZnSO ₄ ·7H ₂ O	250
NH ₄ Cl	16
Al ₂ (SO ₄) ₃	32
H ₃ BO ₃	20
Dextrin	13

Direct current was then passed through the plating solution at a current density of ten amperes per square foot until the pores in the phosphate coating were deposited with metallic zinc. Thereafter, a black, water-soluble, epoxy ester paint, containing 12 percent by weight solids, was electrophoretically applied to the coated panels, the paint application being carried out for two minutes at a voltage of 60 volts with the panels as the anode, the paint being at a temperature of about 20° centigrade. The painted panels were then heated for thirty minutes at about 150 degrees centigrade. The paint on the panels had a high gloss and a paint thickness, in $\frac{1}{1000}$ of an inch, of 1.05. Additionally, the surface roughness of the painted panels was within the range of 20 to 45 microinches.

Example 2

Using the zinc phosphate coating bath as in Example 1, vapor degreased steel panels were immersed in the bath, as in Example 1, but were simultaneously made cathodic while a direct current was passed through the bath at a current density of 2.5 amperes per square foot. The passage of current was continued until the pores of the zinc phosphate coating formed on the surface were deposited with metallic zinc. The thus-coated panels were then water rinsed, electrophoretically painted and heat cured, as in Example 1. The paint coating on the panels was found to have a moderately high gloss with a paint thickness, in $\frac{1}{1000}$ of an inch, of 0.75. Additionally, the surface roughness of the painted panels was within the range of 25 to 55 microinches.

By way of comparison, vapor degreased steel panels were given a phosphate coating, using the coating solution of Example 1, but without the subsequent plating of zinc from the zinc plating bath. These panels were water rinsed, dried, electrophoretically painted and heat cured as in Example 1. The paint film on these panels had a low gloss with a paint thickness, in $\frac{1}{1000}$ of an inch, of 0.65. Additionally, the surface roughness on the panels was within the range of 35 to 65 micro inches.

While there have been described various embodiments

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of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible and it is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A method for forming a protective coating on a ferrous metal surface which comprises forming on the metal surface a zinc phosphate coating containing metallic zinc, and thereafter, electrophoretically depositing a paint on the thus-coated surface.

2. The method as claimed in claim 1 wherein the ferrous metal surface to be treated is first contacted with an acidic zinc phosphate coating solution for a period sufficient to form a zinc phosphate coating on the surface and thereafter, metallic zinc is electrodeposited into the pores of the phosphate coating from a zinc plating bath.

3. The method as claimed in claim 1 wherein the ferrous metal surface to be treated is immersed in an acidic zinc phosphate coating solution and simultaneously made cathodic while a direct electric current is passed through the solution to deposit zinc simultaneously with the phosphate coating on the metal surface.

4. The method as claimed in claim 2 wherein the zinc plating bath comprises an aqueous solution of zinc sulfate.

5. The method as claimed in claim 4 wherein the electrophoretic deposition of the paint is carried out using voltages within the range of about 50 to 1,000 volts, current densities within the range of 0.1 to 7 amperes per square foot, for a period of time for about ten seconds to about two minutes.

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