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[54] **METAL TREATING PROCESS**
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ABSTRACT: A process for phosphating iron and steel by treating it with a peroxide accelerated zinc phosphate solution. The phosphating solution used contains zinc, P_2O_5 , H_2O_2 , B_2O_3 and NO_3 . The desired amounts and ratios of these components are maintained in the solution by the controlled addition of zinc, P_2O_5 , NO_3 (as HNO_3) and sodium perborate.

METAL TREATING PROCESS

This invention relates to an improved process for phosphating metals and more particularly it relates to a process for the phosphating of ferrous metal surfaces which utilizes solutions based upon zinc phosphate and accelerated with peroxide.

In processes for phosphating ferrous metal surfaces, it has long been the practice to use phosphating solutions which are accelerated with one or more oxidizing agents, so that the phosphate coatings may be obtained, either by immersion or spraying, in shorter periods of time. The most frequently used oxidation accelerators have been nitrates, nitrites and chlorates, although it has also been proposed to use peroxide accelerators, particularly hydrogen peroxide, or mixtures of these with nitrates. Although those processes utilizing the nitrate and similar accelerators have long enjoyed considerable commercial success, for the most part, this has not been true of those processes which have utilized peroxide oxidizing agent accelerators.

In general, it has been found that the peroxide accelerated phosphating solutions are subject to the formation of excessive amounts of sludge during operation. This sludge not only has a detrimental affect upon the coating which is produced, but also results in an unacceptably high consumption rate of the phosphating chemicals in the treating bath. Additionally, in many instances continuous neutralization of the bath is necessary in order to maintain the phosphating solution at a pH which is above the equilibrium pH value. Although this super saturation of the solution, insofar as the zinc phosphate is concerned, may be maintained, it will, however, also result in an increase in the sludge formation in the bath. Thus, over long operating periods, with these peroxide accelerated baths, it has been almost impossible to obtain a uniform, hard, sludge-free coating.

It is, therefore, an object of the present invention to provide an improved process for phosphating metal surfaces which utilizes a zinc phosphate containing solution which is accelerated with peroxide.

A further object of the present invention is to provide an improved phosphating process, accelerated with peroxide, which is not subject to the disadvantages which have been encountered in the prior art processes of this type.

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 phosphating metal surfaces which comprises treating the metal surface with an aqueous phosphating solution containing 1 to 6 grams per liter zinc, 2 to 15 grams per liter P_2O_5 , 0.01 to 0.2 grams per liter peroxide, calculated as H_2O_2 , at least 1 gram per liter B_2O_3 and X anions, wherein X represents anions, other than phosphate, of an acid, which is at least as acidic as the first stage of phosphoric acid and where the X anions are present in an amount sufficient to provide a weight ratio of free P_2O_5 to total P_2O_5 of from about 0.08 to 0.20. The treatment of the metal surfaces with this phosphating solution, to obtain the desired zinc phosphate coating, is carried out at a temperature within the range of about 40° to 70° C.

More specifically, in the practice of the method of the present invention, a ferrous metal surface to be phosphated is contacted with an aqueous solution which contains 1 to 6 grams per liter zinc, 2 to 15 grams per liter P_2O_5 , 0.01 to 0.2 grams per liter peroxide, calculated as H_2O_2 , at least 1 gram per liter and preferably 1 to 10 grams per liter B_2O_3 and the X anions, in the amount sufficient to provide a weight ratio of free P_2O_5 to total P_2O_5 of from about 0.08 to 0.20 and preferably from about 0.12 to 0.16. Additionally, it is desirable that the above indicated amounts of the bath components be maintained during the treatment of the ferrous surfaces with this solution by adding zinc, P_2O_5 , X and sodium perborate in a weight ratio of Zn: P_2O_5 : sodium perborate (calculated as $NaBO_2 \cdot H_2O \cdot 3H_2O$) of 0.40-0.60:1:0.4-2.5 and by the addition of X, as HX, in the amount such that the weight ratio

of free P_2O_5 to total P_2O_5 in the total replenishing materials, exclusive of the sodium perborate, will be 0.35 to 0.65.

It is to be appreciated that in referring to the X anions, i.e., anions other than phosphate, of an acid which is at least as acidic as the first stage of phosphoric acid, nitrate, sulfate, and chloride, are exemplary of the anions which may be used. Of these, the preferred anions are the nitrate, which, in replenishing the treating solution, are added as nitric acid. Where X anions, other than nitrate are used, they will be added in amounts which are the chemical equivalent to the nitrate anions.

It is to be further appreciated, that in referring to the free P_2O_5 and total P_2O_5 content of the solution, the free P_2O_5 content may be determined by titrating a sample of the solution with 0.1 normal sodium hydroxide solution to the dimethyl-yellow end point. In this titration, it is found that 1 milliliter of the 0.1 normal sodium hydroxide solution corresponds to approximately 7.1 milligrams of free P_2O_5 . Additionally, the total P_2O_5 content of the bath may be determined using any of the known precipitation techniques or it may be determined from the amount of the 0.1 normal sodium hydroxide solution needed to titrate the sample from the dimethyl-yellow end point to the phenolphthaleine end point. In carrying out this titration, it is generally desirable to add concentrated potassium oxalate solution to the sample to avoid any undesirable precipitation during the titration. In this latter titration, it is found that 1 milliliter of the 0.1 normal sodium hydroxide solution corresponds to approximately 7.1 milligrams of total P_2O_5 .

In preparing the treating solutions of the present invention, as well as the replenishing solutions used during operation, appropriate aqueous concentrates containing the zinc, P_2O_5 , and the X anions in the desired proportions are used. Additionally, in making up the treating solutions, the peroxide may be added to the bath in any convenient form, as for example, as hydrogen peroxide, sodium perborate, sodium perphosphate, or the like. In replenishing the operating baths, however, the peroxide addition should be in the form of the sodium perborate ($NaBO_2 \cdot H_2O \cdot 3H_2O$), or in the form of a chemically equivalent mixture made up of alkali metal borates and H_2O_2 . In this manner, it has been found that the replenishment with the sodium perborate will maintain both the peroxide and the B_2O_3 content of the solution within the desired ranges. In making up the initial treating bath, however, in order to obtain initially the desired B_2O_3 concentration, the addition of other boric acid containing compounds, such as boric acid, or sodium borate, may also be desirable.

In addition to the above components, the phosphating baths of the invention may also contain other accelerating cations as are known in the art, such as, nickel, copper, cobalt, and the like. Film forming cations, other than zinc, may also be included in the phosphating baths. Exemplary of such materials are alkaline earth metals, various organic acids, such as the oxycarbonic acids, as well as acidic phosphoric acids esters of polyvalent alcohols and condensed phosphates, all of which affect the structure of the phosphate coating formed, as are well known to those in the art. Additionally, although the present solutions are particularly adapted to the treatment of ferrous metal surfaces, by the addition of activators such as simple and/or complex fluorides, nonferrous metals, such as aluminum or zinc, may also be treated. If desired, the present phosphating baths may also contain one or more suitable wetting agents.

In treating the metal surfaces in accordance with the method of the present invention, the phosphating solutions are brought into contact with the surface to be treated in any convenient manner, such as by immersion, spraying, roll coating, or the like. As has been previously indicated, during the contacting operations, the solutions are at a temperature within the range of about 40° to 70° C. Of these various contacting techniques, application by spraying is generally preferred and it has been found that at preferred solutions temperatures of from about 50° to 70° C., spraying times of from about 30

seconds to about 4 minutes are typical to effect the formation of the desired phosphate coating layers.

The phosphate coatings produced by the method of the present invention are fine grained, hard and particularly resistant to abrasion. Coating weights with the range of about 1 to 3 grams per square meter are typical of those produced by this process. Additionally, the coatings produced are found to provide a particularly suitable base for a subsequently applied electrophoretic paint or lacquer coating. In such instances, very good corrosion resistance and good paint or lacquer adhesion are found on the electrophoretically coated parts. Additionally, the coating produced by the present invention are also very well suited as a base for conventional paints, as well as a base for rubber and plastic coatings and may also be utilized to promote cold forming.

The coatings produced by the method of the present invention are found to be particularly advantageous in those cases where high corrosion resistance of the subsequently applied paint or similar coating is required, as for example on automobile bodies, refrigerators and the like. The method of the present invention is found to be further advantageous in that, unlike the conventional processes using nitrate-nitrite accelerators, toxic nitrous gases are not evolved during the operation of the process of the present invention. Not only are these nitrous gases an industrial health hazard to those working in the vicinity of the operating process but, additionally, treated parts which come into contact with such gases, particularly during stoppages or shutdowns of the phosphating process, exhibit a substantial decrease in their corrosion resistant properties. With the method of the present invention, these disadvantages are overcome.

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, parts and percents are by weight and temperatures are in degrees centigrade.

EXAMPLE 1

Steel automobile bodies were sprayed for 4 minutes at 60° C. with an aqueous alkaline cleaning solution containing 3 grams per liter borax, 0.2 grams per liter titanium ortho phosphate, 0.5 grams per liter disodium phosphate and 0.3 grams per liter of a nonionic wetting agent. After rinsing by spraying with cold water, the automobile bodies were phosphatized for 3.5 minutes at 50° C. by spraying with a solution having the following concentration:

25.5 grams per liter of a concentrate containing 12.5 percent by weight zinc, 27.2 percent by weight P_2O_5 , 10.5 percent by weight NO_3 and the balance water; 0.18 grams per liter $NaBO_2 \cdot H_2O \cdot 2.3H_2O$; and 5.6 grams per liter $Na_2B_4O_7 \cdot 10H_2O$. This solution had the following composition:

Zinc	3.2 grams per liter
P_2O_5	7.0 grams per liter
Peroxide (Calculated as H_2O_2)	0.04 grams per liter
B_2O_3	2.1 grams per liter
NO_3	2.7 grams per liter
Sodium	0.68 grams per liter
Free P_2O_5	100 grams per liter
Total P_2O_5	7.0 grams per liter
Acid ratio	0.14

After phosphating, the automobile bodies were rinsed first with cold then with warm water, containing 0.05 percent CrO_3 and were then subsequently, sprayed with deionized water and dried. Upon examination, the surfaces of the bodies were found to be covered with a densely packed, fine-crystalline strongly adherent layer having a coating weight of about 1.8 grams per square meter. This phosphate layer was found to be particularly abrasion resistant and the thus treated automobile bodies were electrophoretically painted without difficulty.

In order to maintain the efficiency of the phosphating bath during the above operation, the bath was replenished with a

concentrate containing 12.5 percent by weight zinc, 27.2 percent by weight P_2O_5 , 10.5 percent by weight NO_3 , and the balance water. The weight ratio of free P_2O_5 to total P_2O_5 in this replenishing concentrate was 0.47. Additionally the H_2O_2 content of the bath was maintained at a constant level by replenishing with $NaBO_2 \cdot H_2O \cdot 3H_2O$ in a weight ratio of zinc: P_2O_5 : $NaBO_2 \cdot H_2O \cdot 3H_2O$ which was equivalent to 0.46:1:1.1. It was found that even after a throughout of more than 100 square meters of steel surface per liter of the phosphating bath, uniformly satisfactory sludge free coatings were obtained.

EXAMPLE 2

Small steel parts including automobile hub caps, mud guards, and similar automobile components were cleaned in a continuous spraying arrangement with a cleaning composition having the composition as set forth in Example 1, for 2 minutes at 60° C. The parts were then rinsed in cold water and then phosphated by spraying at 62° C. for 2 minutes with a solution having the following composition:

22 grams per liter of a concentrate containing 12.4 percent by weight zinc, 27.1 percent by weight P_2O_5 , 12.9 percent by weight NO_3 and the balance water; 0.225 grams per liter $NaBO_2 \cdot H_2O \cdot 2.3H_2O$; and 6.2 grams per liter $Na_2B_4O_7 \cdot 10H_2O$. This solution contained 2.73 grams per liter zinc, 6.00 grams per liter P_2O_5 , 0.05 grams per liter peroxide (calculated as H_2O_2), 2.3 grams per liter B_2O_3 , 0.78 grams per liter sodium, 2.83 grams per liter NO_3 . The pointage, i.e., the milliliters of a 0.1 normal sodium hydroxide solution necessary to titrate a 10 milliliter sample of the bath to the phenolphthalein end point, was 13, while the free P_2O_5 was 0.9 grams per liter, the total P_2O_5 was 6.0 grams per liter and the acid ratio was 0.15.

After phosphating, these parts were rinsed in the manner described in Example 1 and while they were still wet were electrophoretically painted and the thus applied paint was cured. The painted parts were then subjected to the salt spray test based on the ASTM test B117-64. After 168 hours, rust penetrations of less than 1 milliliter were found on these parts. By way of comparison, another series of parts was phosphated using a conventional nitrate-nitrite accelerated zinc phosphatizing bath. These parts were processed in the same manner as the previous parts and subjected to the same test conditions. In the latter series of parts it was found that after 160 hours of testing, rust penetration of from 3 to 4 milliliters resulted.

During the operation of the above-phosphating baths, the bath was continuously replenished by means of a metering pump using a concentrate having the following composition:

Zinc	12.4 percent by weight
P_2O_5	27.1 percent by weight
NO_3	12.9 percent by weight
Balance	water

Additionally, a constant level of the H_2O_2 was maintained in the bath by replenishing with solid sodium perborate so that the weight ratio in the replenishment material between the concentrate and the sodium perborate is 4:1. In the replenishing materials the weight ratio of zinc: P_2O_5 : $NaBO_2 \cdot H_2O \cdot 3H_2O$ is 0.46:1:0.92 and the weight ratio of free P_2O_5 to the total P_2O_5 in the total replenishing material without the sodium perborate is 0.55. During the operation of the phosphating process, it was found that the consumption of the phosphate concentrate was about 18.0 grams per square meter of surface treated while the consumption of the sodium perborate was 4.5 grams per square meter of surface treated. The phosphate coating weights obtained during this operation of the process were within the range of about 1.4 to 1.6 grams per square meter.

While there have been described various specific embodiments of the present invention, the specific compositions and processes set forth herein are not to be taken as a limitation of the present invention but only as being exemplary of the invention and the manner in which it may be practiced.

What is claimed is:

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1. A method for the phosphate coating of metal surfaces which comprises treating the metal surface with an aqueous solution which contains from about 1 to 6 grams per liter zinc, 2 to 15 grams per liter P_2O_5 , 0.01 to 0.2 grams per liter peroxide, calculated as H_2O_2 , at least 1.0 grams per liter B_2O_3 and X anions in an amount to maintain the weight ratio of free P_2O_5 to total P_2O_5 in the solution within the range of about 0.08 to 0.20, wherein X denoted anions, other than phosphate, of an acid which is at least as acidic as the first stage of phosphoric acid, maintaining the solution at a temperature within the range of about 40° to 70° C. during the time of treatment and forming a zinc phosphate coating on the metal surfaces thus treated.

2. The method as claimed in claim 1 wherein the components of the treating solution are maintained in the desired range by replenishing the solution by the addition of zinc, P_2O_5 , X and sodium perborate, in a weight ratio of zinc: P_2O_5 :

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sodium perborate, calculated as $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, of 0.4–0.6:1:0.4–2.5 and by the addition of X anions as HX in an amount such that the weight ratio of free P_2O_5 to total P_2O_5 in the total replenishing materials, exclusive of the sodium perborate, is within the range of about 0.35 to 0.65.

3. The method as claimed in claim 2 wherein the amount of B_2O_3 in the treating solution is within the range of about 1 to 10 grams per liter.

4. The method as claimed in claim 3 wherein the weight ratio of free P_2O_5 to total P_2O_5 in the treating solution is within the range of about 0.12 to 0.16.

5. The method as claimed in claim 4 wherein the X anions are NO_3 .

6. The method as claimed in claim 5 wherein the metal surfaces treated are ferrous metal surfaces.

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