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PROCESS FOR THE APPLICATION OF THIN, CONTINUOUS PHOSPHATE LAYERS ON METAL SURFACES

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5 Claims

ABSTRACT OF THE DISCLOSURE

A process for the application of continuous phosphate coatings on iron, steel and zinc surfaces. The layers are of a thickness of one micron or less and are of particular hardness. These coatings are produced by spraying on the metal surfaces an aqueous solution containing, aside from zinc-, phosphate- and nitrate ions, NO_2^- ions, water-soluble glycerophosphate and nonionic detergents, all in predetermined amounts in very narrow limits. For the coating of zinc surfaces, an addition of a fluoro-complex is opportune. The ratio of total acid to free acid is to be held at 8 to 12. In the process according to the invention, a pretreatment, e.g., degreasing, not only is not required but actually may be deleterious. Phosphate layers of 0.5 micron readily can be attained.

This application is a streamlined continuation of our copending United States patent application Ser. No. 710,760, filed Mar. 6, 1968, and now abandoned.

The invention relates to a process for the application of hard, dense and continuous zinc phosphate layers on iron, steel, zinc and their alloys by means of nitrate-containing zinc phosphate solutions, whereby these layers have a thickness of less than 1 micron and preferably less than 0.8 micron.

The application of phosphate coatings on iron, steel and zinc from nitrate- and zinc phosphate-containing solutions for the improvement of corrosion resistance, adhesion of organic coatings and facilitating of cold shaping or deformation is known. The phosphate layers usually are of 3 to 15 micron thickness, and thicknesses of less than 3 microns, down to approximately 1.5 microns, are attained only under special conditions, e.g., by the addition of polymeric phosphates. The phosphate coatings thus produced provide good protection against corrosion, but the adhesion of organic coatings subsequently applied is not as good as with thinner iron phosphate layers, particularly upon ensuing deformation. Iron phosphate coatings are applied by means of solutions which form discontinuous coatings on the metal surfaces, thus do not meet all practical requirements. These coatings have thicknesses of 0.1 to 1 micron but are deficient in the prevention of corrosion.

Phosphatization solutions have been disclosed for rust protection treatments which contain glycerophosphoric acid. The latter is said to shorten the treatment times and to lower the sludge formation in the bath.

It also has been practiced for a considerable time to add detergents to zinc phosphatizing solutions in order to cleanse the surfaces simultaneously with the phosphatization.

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The processes named above all provide phosphate coatings of conventional thickness.

It is the object of the invention to provide iron, steel and zinc surfaces with hard, dense and continuous layers of zinc phosphate having a thickness of less than 1 micron. This is accomplished by spraying these surfaces for 0.5 to 10 minutes at temperatures ranging from 35 to 90° C. with aqueous solutions which contain, beside zinc-, phosphate- and nitrate ions, as effective amounts, 0.005 to 0.05 weight percent of NO_2^- , 0.01 to 0.2 weight percent of a water-soluble organic phosphorus compound selected from the group of glycerolmonophosphoric acid and its water-soluble salts, and 0.002 to 0.075 weight percent of a nonionic detergent, whereby these solutions have a proportion of total acid to free acid of 8 to 12. The surfaces thus treated may be post-passivated with chromic acid and/or phosphoric acid or with water-soluble acid chromates and/or phosphates. Post-passivation is an optional step.

The solutions employed in carrying out the invention contain zinc-, phosphate- and nitrate ions in the conventionally used proportions and concentrations. These concentrations and proportions are balanced so that the solutions have an acid ratio of total acid (in points): free acid (in points) of 8 to 12. Points of total acid are designated as milliliters of N/10 NaOH required for the titration of 10 ml. of bath solution, using phenolphthalein as indicator; and points of free acid are designated as milliliters of N/10 NaOH required for the titration of 10 ml. of bath solution using methylorange as indicator. At an acid ratio of less than 8, a continuous coating does not form on the metal surfaces, and if the proportion exceeds 12, the layers are of conventional thickness and soft. The concentration of the treating solution generally is selected so that the point value of the total acid is between 5 and 30 points.

It is necessary that the nitrite, glycerophosphate and nonionic detergents additives are within the narrow limits named above. "Glycerophosphates" are to be understood to denote glycerolmonophosphoric acid and its water-soluble salts, primarily its alkali- and ammonium salts. The preferred nitrite addition lies between 0.01 and 0.03 weight percent. When these limits are exceeded in either direction, faultless layer formation is not obtainable or the layers become thick, soft and less dense. The specific thickness of the coating layers according to the invention is above 2 and preferably at approximately 3, the specific thickness being expressed as layer weight-layer volume.

Any nonionic detergent may be used in the process according to the invention. Preferred are the customary ethylene oxide adducts of fatty alcohols, alkylphenols, polyglycerols (OH-value 900-1200) and polypropylene glycols, or ethylene oxide-propylene oxide adducts of fatty alcohols, alkylphenols and polyglycerols (OH-value 900-1200).

The amount of ethylene oxide and/or propylene oxide per OH-group of the above mentioned compounds is preferably about 5-40 mols, and the molecular weight of the ethylene oxide adducts of polypropylene glycols is preferably about 950-3000. Such products are usually known under the trademark "Pluronic." Anionic detergents are not suited for the process.

When zinc or its alloys are to be treated with the solutions according to the invention, and addition of 0.01 to 0.25 weight percent of complex fluorides has been found particularly advantageous and is a special embodiment of the invention. Suitable complexes are fluoroboric acid or fluorosilicic acid. The employment of simple fluorides or hydrogen fluoride is inopportune.

The process according to the invention is carried out by spraying. Effective pressures are 1.5 to 3 atmospheres. Effective spray temperatures range from 35 to 90° C.,

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and the effective treatment times from 0.5 to 10 minutes. Particularly suitable treatment times are 1 to 5 minutes, longer times yielding harder coatings. While an extension to 10 minutes is not harmful, no special advantages are gained beyond 5 minutes.

It is a particular feature of the invention that the customary degreasing of the surfaces to be treated not only is not required but in general even has a deleterious effect on the coating layer formation. Only when excessive grease contamination is present on the surfaces, a pretreatment is indicated, and this pretreatment is carried out with the solutions according to the invention in like concentration as used for the phosphatization itself or in slightly lower concentration. The main reason for this pretreatment is the prevention of the contamination of the treatment solution, which otherwise can be re-used, not the effect on the metal surfaces. If such a pretreatment is carried out, the time for phosphatization can accordingly be shortened.

The layers produced may be post-passivated in the customary manner using dilute aqueous chromic and/or phosphoric acid solutions or their water-soluble acid salts.

The process according to the invention yields zinc phosphate layers on the metal surfaces which have a thickness of less than 1 micron and principally of less than 0.8 micron. Thicknesses as low as 0.5 micron can readily be attained. The continuous layers impart to the surfaces good corrosion resistance and excellent adhesion to organic coatings, i.e., coatings of paints, lacquers and synthetic resin compounds. These adhere well even upon ensuing deformation. The phosphate layers also are unaffected by bending and cold deformation of the metals and are suited for electrical insulation.

The process greatly simplifies the phosphatization procedure because cleansing, degreasing and rinsing steps are omitted as unnecessary.

The coating layers produced have been found particularly useful as preparatory steps for electrophoretic coating.

The invention now will be more fully explained by the following examples. However, it should be understood that these are given merely by way of illustration, and not of limitation, and that it is intended to cover all modifications and variations which do not constitute departures from the spirit and the scope of the invention as herein-after claimed.

The solutions named in the examples are aqueous, and any remainders in percentages of given compositions are to be considered water. Percentages are by weight, and temperatures in degrees centigrade. The tests in the tables performed according to "DIN" standards are those set by a German official standardizing society and denote "Deutsche Industrienormen" (German Industrial Standards), comparable to those set by the ASTM.

EXAMPLE 1

Greased, cold rolled steel sheets were treated in a spraying booth with a 3 percent solution of the concentrate named below at 65-75° for approximately 3 minutes at a spray pressure of 1.8 atmospheres.

The solution contained:

	Percent
ZnO	10
H ₃ PO ₄ (75%)	32
HNO ₃ (62%)	10
Na ₂ -glycerophosphate · 5.5 H ₂ O (50%)	1.5
Alkylphenol-ethylene oxide-propylene oxide adduct	0.17

The treating solution had 13.9 points total acid, and the acid ratio of total to free acid was adjusted to 10. Sodium nitrite was added continuously, balanced to the

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throughput, so that the NO₂⁻ concentration in the solution was kept constant at 0.015%.

The phosphate coating layer thus produced had a thickness of 0.5 micron and a coating weight of 1.5 g./m.². It was hard, continuous and uniform. The phosphatization solution was replenished with the concentrate named above.

After phosphatization, the metal surfaces were rinsed with water, post-passivated with very dilute chromic acid-phosphoric acid solution, rinsed with fully deionized water, and subjected to electrophoretic coating.

The adhesion of the organic coating thus applied and the corrosion resistance of the metal surfaces were excellent, as established by a comparison with the following phosphatizing solutions A to D.

Using these solutions A to D, steel sheets from the same batch as used above were first degreased and then treated in the same manner as above, up to and including electrophoretic coating.

Solution A:	Percent
ZnO	10
H ₃ PO ₄ (75%)	32
HNO ₃ (62%)	10

The concentration was 3 percent. The acid ratio was adjusted to 10. Sodium nitrite continuously was added, balanced to the throughput, maintaining an NO₂⁻ concentration of 0.015% in the solution. This corresponds to the conditions named above.

Solution B:	Percent
ZnO	10
H ₃ PO ₄ (75%)	32
HNO ₃ (62%)	10
Na ₂ -glycerophosphate · 5.5 H ₂ O (50%)	1.5

The same concentrations, acid ratio and sodium nitrite addition were maintained as for solution A.

Solution C:	Percent
ZnO	10
H ₃ PO ₄ (75%)	32
HNO ₃ (62%)	10

The concentration was 3 percent, the acid ratio 10. Sodium nitrite and water-soluble polymeric phosphate as thin-layer component were continuously added.

Solution D:	Percent
ZnO	10
H ₃ PO ₄ (75%)	32
HNO ₃ (62%)	10
HBF ₄	2

The concentration was 3%, the acid ratio adjusted to 10. Sodium nitrite was added continuously to maintain the NO₂⁻ concentration in the solution constant at 0.015%.

After phosphatization, the sheets treated with solutions A to D were treated the same as the sheets coated according to the invention and subjected to electrophoretic coating with the same organic coating compound. The results of coating tests are listed in Tables 1 and 2.

TABLE 1

Product	Depth, mm.	Percent chipped grid boxes
According to invention.	10	No chipping or peeling to rupture of metal
A.	10	30% (appr.) of coating chipped off.
B.	10	10% (appr.) of coating chipped off.
C.	10	Do.
D.	10	Do.

NOTE.—(1) Ruled grid test according to DIN 53 151: None of the sheets exhibited release of the organic coating from the substrate, regardless of which solution had been used, i.e., no peeling or chipping occurred. (2) Eriksen cupping test according to DIN 50 101, combined with the above ruled grid test.

TABLE 2

Corrosion Test in Kesternich-Device according to DIN 50 018

Product	Exposure (hours)					
	15	23	25	30	39	42
According to invention.....	Slight rust in cross cut.	Same as 15 plus slight rust at edges.	Same as 23.....	Same as 23.....	Light rust over entire surface, coating adheres, no blisters.	Coating attacked, slight blistering, 20% rust.
A.....	Slight rust in cross cut and on edges.	Heavy rust in cross cut and on edges, entire coating surface rough.	Heavy rust extending from cross cut over entire surface, blisters on entire surface on face.	Same as 25.....	Coating rough all over; 40% rust on entire surface.	Coating destroyed, rust 100%.
B.....	Slight rust in cross cut.	Strong rust in cross cut and on edges.	Increased rust in cross cut; coating adheres.	do.....	Coating smooth, 20% rust over entire surface.	Coating very rough, 50% rust.
C.....	do.....	Heavy rust in cross cut and on edges.	Same as 23.....	Increased rust in cross cut; coating adheres.	do.....	Do.
D.....	Heavy rust in cross cut; light rust on edges.	Same as 15.....	do.....	Same as 25.....	Slight rust over entire surface, coating slightly rough.	30% rust, coating rough over entire surface.

EXAMPLE 2

Heavily greased iron sheets were pretreated with a 5% solution of a concentrate, the proportions of which are given below, at 60° for 1 minute at a spray pressure of 2.2 atmospheres and immediately thereafter phosphatized with the same solution, without an intermediate rinse. The acid ratio of the solution was 11, and the NO₂ concentration kept constant at 0.023% by continuous addition of sodium nitrite. After phosphatization, the sheets were rinsed with water and dried with hot air. The phosphate layer formed was very hard, had a thickness of approximately 0.7 micron and a weight of 1.8 g./m.².

The solution used contained:

	Percent
ZnO	6
H ₃ PO ₄ (75%)	23
HNO ₃ (62%)	5
Na ₂ -glycerophosphate·5.5 H ₂ O (50%)	1
Fatty alcohol ethylene oxide adduct	0.32

For purposes of comparison, preliminary degreasing was carried out with a solution (E) of one-half the concentration of the spraying solution and with (F), a customary weakly alkaline metal cleanser. Otherwise, the sheets which were from the same batch as used above, were treated in exactly the same manner. The phosphate coatings on the sheets degreased with (E) had a thickness of 1 micron and a coating weight of 1.8 g./m.²; those degreased with (F) had a thickness of 1.2 microns and a weight of 2.1 g./m.². These latter coatings (F) were perceptively softer than those obtained in the other two processes.

EXAMPLE 3

Hot-galvanized iron sheets were sprayed with a 5% solution of the following contents:

	Percent
ZnO	10
H ₃ PO ₄ (75%)	35
HNO ₃ (62%)	8
Na ₂ -glycerophosphate·5.5 H ₂ O (50%)	1.5
HBF ₄	2
Ethylene oxide-propyleneglycol adduct	0.5

The acid ratio was adjusted to 9, and sodium nitrite continuously added to the solution to maintain the NO₂-concentration constant at 0.01%. The treating temperature was 65°, and the spray pressure 2 atmospheres.

The phosphate layer thus obtained had a thickness of 0.5 micron and a coating weight of 1.4 g./m.².

After the phosphatization, the sheets were rinsed with tap water and, for purposes of ensuing treatment, e.g., application of a coating, with deionized water.

When under like conditions, iron sheets were used in lieu of galvanized sheets, the phosphate coating had a thickness of 0.7 micron and a weight of 1.8 g./m.².

The coatings were very hard, continuous and uniform, regardless of whether they were formed on iron or galvanized plate. They imparted good corrosion resistance and excellent adhesion to organic coatings.

Like results were obtained on zinc and galvanized surfaces when, in lieu of fluoroboric acid, an equivalent amount of fluorosilicic acid was used, whereby these amounts may range from 0.01 to 0.25 weight percent of the total solution.

Likewise the same results were obtained, if other water-soluble glycerophosphates, such as mono-sodium salt of glycerol-monophosphoric acid, mono- and dipotassium or mono- and diammonium salt of glycerolmonophosphoric acid are used instead of disodium glycerophosphate.

The detergents used in Examples 1, 2 and 3 were respectively an adduct of dodecylphenol with 9 mol ethylene oxide and 8 mol propylene oxide, an adduct of oleyl-alcohol with 12 mol ethylene oxide, and Pluronic L 62 of Wyandotte Chemicals Corporation.

However, instead of these compounds any customarily nonionic detergent as named in the specification, may be used.

We claim:

1. A process for depositing continuous, dense and hard phosphate layers of from 0.5 to 1 micron thickness on iron and steel surfaces which consists essentially of spraying said surfaces at temperatures ranging substantially from 35° C. to 90° C. for a sufficient time with a phosphatizing aqueous solution of zinc, phosphate and nitrate ions having a ratio of total acid to free acid, in points, of 8 to 12, and a total acid concentration, in points, of between 5 and 30; said aqueous solution further containing 0.005 to 0.05 weight percent of NO₂ ions; 0.01 to 0.2 weight percent of a water-soluble organic phosphorus compound selected from the group consisting of glycerol-monophosphoric acid and its water-soluble salts; and 0.002 to 0.075 weight percent of a nonionic detergent.

2. The process as defined in claim 1, wherein said time is substantially 0.5 to 10 minutes.

3. The process as defined in claim 1, wherein said solution is sprayed onto said surfaces without prior treatment.

4. The process as defined in claim 1, wherein the spray pressure is substantially 1.5 to 3 atmospheres.

5. A process for depositing continuous, dense and hard phosphate layers of from 0.5 to 1 micron thickness on undegreased iron and steel surfaces which consists essentially of spraying said surfaces, in the absence of any prior treatment, with an aqueous solution for approximately 0.5 to 10 minutes at a temperature of substantially 35° C. to 90° C., and at a spray pressure of substantially 1.5 to 3 atmospheres; and rinsing said surfaces with water; said solution consisting essentially of a phos-

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phatizing solution of zinc, phosphate and nitrate ions having a point ratio of total to free acid of 8 to 12, and a total acid concentration, in points, of between 5 and 30; and further containing 0.01 to 0.03 weight percent of NO_2 ions, 0.01 to 0.2 weight percent of a water-soluble organic phosphorous compound selected from the group consisting of glycerolmonophosphoric acid and its water-soluble salts and 0.002 to 0.075 weight percent of a nonionic detergent.

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