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3,592,701

PROCESS FOR PHOSPHATING GALVANIZED METAL ARTICLES

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No Drawing. Continuation-in-part of abandoned application Ser. No. 323,134, Nov. 12, 1963. This application Nov. 30, 1967, Ser. No. 686,851

Int. Cl. C23f 7/12

U.S. Cl. 148—6.15 9 Claims

ABSTRACT OF THE DISCLOSURE

Phosphating solutions with a total acidity of about 5–850 points and consisting essentially of water, calcium ion (preferably about 0.01–8.0%), phosphate ion (preferably about 0.25–20.0%), and nickel ion (preferably about 0.005–2%) are useful for treating galvanized metal articles. These solutions may also contain about 0.01–26% of nitrate ion, about 0.001–0.1% of nitrite ion and about 0.1–1.0% of ammonium ion. They are applied by contacting the metal surface with the solution at a temperature of at least about 100° F.

This application is a continuation-in-part of copending application Ser. No. 323,134, filed Nov. 12, 1963, now abandoned.

This invention relates to improved metal treatment solutions, and more particularly to an aqueous phosphating solution adapted for phosphating galvanized metal articles, the active ingredients of said solution consisting essentially of phosphate ion, calcium ion and nickel ion.

It is well known in the metal finishing art that metal surfaces may be provided with an inorganic phosphate coating by contacting them with an aqueous phosphating solution. The phosphate coating protects the metal surface to a limited extent against corrosion and serves primarily as an excellent base for the later application of siccative organic coating compositions such as paint, lacquer, varnish, primers, synthetic resins, enamel and the like.

Such inorganic phosphate coatings are generally formed on a metal surface by means of aqueous solutions which contain the phosphate ion and, optionally, certain auxiliary ions such as sodium, manganese, zinc, cadmium, copper, antimony, ammonium, chloride, bromide, nitrate, sulfate and borate. These auxiliary ions modify the character of the phosphate coating and adapt it for a wide variety of applications. An oxidizing agent such as sodium chlorate, potassium perborate, sodium nitrate, sodium nitrite, ammonium nitrate, sodium chlorite, potassium perchlorate or hydrogen peroxide may be included in the phosphating solution to depolarize the metal surface being treated and thereby increase the rate at which the phosphate coating is formed on the metal surface. Other auxiliary agents such as anti-sludging agents, coloring agents and metal cleaning agents may also be incorporated in the phosphating solution. One common type of commercial phosphating solution which contains zinc ion, phosphate ion and a depolarizing agent is made by dissolving small amounts of zinc dihydrogen phosphate, sodium nitrate and phosphoric acid in water.

Such phosphating solutions have been useful in providing an adherent, integral phosphate coating on metal articles, particularly ferrous metal articles, thereby improving the adhesion thereto of a film of a subsequently applied siccative organic coating composition. However, they have not significantly improved the adhesion of a film of a siccative organic coating composition to a galvanized ferrous metal article. Thus, it is common knowlege in the metal finishing industry that paints, enamels, etc., adhere very poorly to zinc surfaces and that known aqueous

phosphating solutions which are adapted for the phosphating of ferrous surfaces do little to improve adhesion of paint to zinc surfaces. Although certain chemical treatments and physical surface treatments have been suggested as means for improving the adhesion of siccative organic coating compositions to zinc surfaces, they have not been fully satisfactory for the purpose and, consequently, have not achieved wide commercial acceptance.

A principal object of this invention, therefore, is to provide improved aqueous phosphating solutions.

Another object is to provide improved aqueous phosphating solutions which are adapted for phosphating zinc articles and metal articles containing zinc surfaces.

Another object is to provide a method for forming an adherent phosphate coating on zinc surfaces.

Still another object is to provide a method for improving the adhesion of siccative organic coating compositions to metal articles having zinc surfaces.

Other objects will in part be obvious and will in part appear hereinafter.

As indicated above, the essential ingredients of the aqueous phosphating solutions of this invention are phosphate, calcium and nickel ions. Optional ingredients, discussed more fully hereinafter, include the nitrate, nitrite, chloride and ammonium ions. Generally, the solutions have a total acidity of about 5–850 points (that is, about 5–850 ml. of 0.1 N sodium hydroxide solutions will neutralize 10 ml. of the phosphating solution, phenolphthalein being used as an indicator) and the active ingredients therein consist essentially of about 0.01–8.0% (by weight) calcium ion, about 0.25–20.0% phosphate ion, and about 0.005–2.0% nickel ion. The approximate compositions of preferred and particularly desirable solutions are given in Table I.

TABLE I

	Preferred concentration	Desirable concentration
PO_4^{-3}, percent	0.25–7.0	0.3–7.0
Ca^{+2}, percent	0.01–2.0	0.01–1.5
Ni^{+2}, percent	0.005–0.5	0.015–0.4
Points total acid	5–100	5–50

The importance of the acidity range is in the effect of acidity on coating weights and coating speeds. While the indicated ranges are usually most satisfactory, it is possible to employ aqueous phosphating solutions having a total acidity substantially higher than 100 points, e.g., 125, 200, 250 or 300 points or more. The use of these solutions sometimes permits the formation of a satisfactory phosphate coating on zinc surfaces in as short a time as one second. The commercial applications of such a rapid phosphating process are manifold. For example, it is well adapted for the continuous phosphating of cold-rolled strip galvanized at speeds consonant with those employed in modern, high production rolling mills. These phosphating solutions are also useful for coating zinc surfaces which have been treated to inhibit the formation of "white rust."

The phosphating solutions of this invention can be prepared by dissolving phosphoric acid and calcium and nickel salts in water in amounts sufficient to provide the desired weight percentages of the necessary ions. Any soluble calcium and nickel salts may be used; the presence of other ions in the solution (whether from salts, acids or bases) appears to have little or no detrimental effect. It is generally convenient to use calcium and nickel nitrates, and the nitrate ion in the solution may then function as an oxidizing agent to depolarize the metal surface and increase coating speed. The same or a similar effect is provided by nitrite ion. Ammonium and chloride ions may also improve the properties of the solutions Table II

gives the preferred and especially desirable approximate concentrations of these ions, when present.

TABLE II

	Percent	
	Preferred concentration	Desirable concentration
NO_3^-	0.01–26.0	0.01–4.0
NO_2^-	0.001–0.1	0.001–0.02
Cl^-	0.01–3.5	0.1–1.5
NH_4^+	0.01–2.0	0.1–1.0

Other ions such as sodium, potassium, bromide, sulfate, chlorate, perchlorate and perborate may also improve the properties of the phosphating solutions of this invention by increasing rust inhibiting capability, reducing sludging and the like.

The presence of calcium ion in the aqueous phosphating solutions of this invention is essential to the corrosion resisting and paint adhering properties of the coatings deposited on zinc surfaces. The nickel ion acts to improve the uniformity and appearance of the coating.

Specific examples of phosphating solution of the present invention are shown in Table III. Except for the "points total acid," the values given in the table indicate the percentages by weight of the various ions in the phosphating solution.

TABLE III

	Phosphating solutions							
Ion	A	B	C	D	E	F	G	H
Ca^{+2}	0.166	0.076	0.069	0.138	0.298	0.447	0.120	0.926
PO_4^{-3}	0.995	0.900	0.570	1.40	2.76	4.14	0.777	8.80
Ni^{+2}	0.010	0.404	0.0291	0.058	0.165	0.248	0.048	0.323
NO_3^-	0.344	-----	0.062	0.124	0.68	1.03	0.398	-----
NO_2^-	0.0133	0.0167	-----	-----	-----	-----	-----	-----
Cl^-	-----	0.489	-----	-----	-----	-----	-----	2.03
NH_4^+	-----	-----	-----	-----	-----	-----	0.156	-----
Points total acid	-----	10	12	25	60	91	24.5	-----

The preparation of the phosphating solutions set forth in Table III is effected in the following manner.

SOLUTION A

To 250 milliliters of water are added 2.3 grams of lime (72% calcium oxide), 13.7 grams of 75% commercial phosphoric acid, 4.5 grams of 42° Baumé nitric acid and 2.4 grams of nickel nitrate hexahydrate. Sufficient water is then added to yield 1 liter of solution, in which 0.2 gram of sodum nitrate is dissolved.

SOLUTION B

To 24.6 grams of water are added 1.4 grams of lime (72% calcium oxide) and 11.7 grams of 75% commercial phosphoric acid. The solution is then diluted by dissolving 4 parts (by volume) in 100 parts of water. To 1 liter of the diluted solution there is added 0.25 gram of sodium nitrite and 8.9 grams of nickel chloride.

SOLUTION C

To 87.3 grams of water are added 11.7 grams of lime (72% calcium oxide), 68.4 grams of 75% commercial phosphoric acid and 12.6 grams of nickel nitrate hexahydrate. This concentrate, having a specific gravity of 1.3, is diluted by dissolving 2 parts (by volume) in 100 parts of water.

SOLUTION D

The concentrate of solution C is diluted by dissolving 4.1 parts (by volume) in 100 parts of water.

SOLUTION E

To 943 grams of water are added 38 grams of 75% commercial phosphoric acid, 5.0 grams of 42° Baumé nitric acid, 5.8 grams of lime (72% calcium oxide) and 8.2 grams of nickel nitrate hexahydrate.

SOLUTION F

This solution is prepared by dissolving 57 grams of 75% commercial phosphoric acid, 7.5 grams of 42° Baumé nitric acid, 8.7 grams of lime (72% calcium oxide) and 12.3 grams of nickel nitrate hexahydrate in 914.5 grams of water.

SOLUTION G

This solution is prepared by dissolving 2.3 grams of lime (72% calcium oxide), 10.7 grams of 75% commercial phosphoric acid, 2.4 grams of nickel nitrate hexahydrate, 4.5 grams of 42° Baumé nitric acid, and 10 grams of ammonium dihydrogen phosphate in 970 grams of water.

SOLUTION H

To 830 grams of water there are added 121 grams of 75% commercial phosphoric acid, 23.4 grams of calcium chloride and 7.1 grams of nickel chloride.

The particular feature of the combination of ions which characterizes the phosphating solutions of this invention is that such solutions may be utilized to deposit uniform coatings on galvanized metal articles. Solutions which have been suggested previously as means for depositing phosphate coatings on galvanized ferrous metal articles deposit non-uniform crystalline coatings. However, the micro-crystalline coatings deposited by the phosphating solutions of this invention are smooth, uniform, and tightly bound to the metal article. As a result, the metal articles thus coated may be flexed and shaped without flaking of the coating. The smooth, uniform coating also provides protection against corrosion and is an excellent base for siccative organic coating compositions. Thus, the corrosion resisting and paint adherent properties of the coatings deposited by phosphating solutions of this invention on galvanized ferrous metal articles are superior to those deposited by the previously used aqueous phosphating solutions.

In view of the extensive commercial development of the phosphating art and the many journal publications and patents describing the application of phosphating solutions, it is believed unnecessary to lengthen this specification unduly by a detailed recitation of the many ways in which the phosphating step may be accomplished. Suffice it to say that any of the commonly used phosphating techniques such as spraying, brushing, dipping, roller-coating and flow-coating may be employed. The temperature of the aqueous phosphating solution may vary within wide limits, e.g., from about room temperature to about 240° F. In general, the best results are obtained when the aqueous phosphating solution is used at a temperature of at least about 100° F., generally about 120–200° F. If desired, however, the aqueous phosphating solution may be used at higher temperatures, e.g., 225° F., 250° F., or even 300° F., by employing super-atmospheric pressures.

In the accepted practice of phosphating metal articles, a surface is usually cleaned by physical and/or chemical means to remove any grease, dirt, or oxides. The cleaned article is then ordinarily rinsed with water before being subjected to the phosphating treatment. The phosphating operation is usually carried out until the weight of the phosphate coating formed on the metallic surface is at least about 25 milligrams per square foot of surface area and is preferably about 50–1000 milligrams per square foot. The time required to form the phosphate coating will vary according to the temperature, the concentration of the phosphating solution employed, the particular technique of applying the phosphating solution, and the coating weight desired. In most instances, however, the time required to produce a phosphate coating of a weight suitable for the purposes of this invention will be from about 5 seconds to about 10 or 15 minutes.

When phosphating metal surfaces with high total acid solution, the immersion technique is preferred. The manner can be a simple dipping technique or a continuously

moving kind of immersion exemplified by the immersion of moving zinc coated stock in the phosphating solution by means of submerged rollers or other devices which serve the same purpose. Similarly, plates of heavy gauge galvanized steel may be conveyed continuously through the phosphating solution. The temperature of the phosphating solution should preferably be about 150°–240° F. for rapid phosphating action, and the total immersion time is about 1–20 seconds. A more complete discussion of the utility of high total acid aqueous phosphating solutions is set forth in U.S. Pat. 3,144,360. It is intended that the disclosure of said patent be considered as forming a part of the present specification.

Upon completion of the phosphating operation, the phosphated metal article is generally rinsed with water and/or a hot dilute aqueous solution of chromic acid containing about 0.01–0.2% CrO_3. The chromic acid rinse appears to "seal" the phosphate coating and improve its utility as a base for the application of the siccative organic coating. Dilute aqueous solutions of metal chromates, metal dichromates, chromic acid-phosphoric acid mixtures, and chromic acid-metal dichromate mixtures may also be used in place of the dilute aqueous chromic acid.

After a galvanized metal article has been phosphated in accordance with the present invention, it is often desirable to apply a decorative and protective top-coat of a siccative organic coating composition such as paint, lacquer, varnish, synthetic resins, enamel, and the like. Examples of synthetic resins which may be used are the acrylic, alkyd, epoxy, and polyvinyl alcohol resins. The application of the organic coating composition can be effected by any of the ordinary techniques such as brushing, spraying, dipping, roller-coating, flow-coating, etc. The top-coated phosphated article is dried in the manner best suited for the particular siccative organic coating composition employed such as air-drying at ambient temperature, drying in a current of hot air, baking in an oven, or baking under a battery of infra-red lamps. In most instances, the thickness of the dried film of the siccative organic coating composition will be about 0.1–10 mils, most often about 0.3–5 mils.

A number of tests may be used to determine the efficacy of the aqueous phosphating solutions of this invention in improving the adhesion of films of siccative organic coating compositions to galvanized ferrous metal articles. The results of such tests indicate clearly the criticality of the nickel and calcium ions with respect to such adhesion.

EXAMPLE 1

Hot-dip galvanized 20-gauge SAE 1020 cold-rolled steel panels (4" x 8") are cleaned, phosphated with different phosphating solutions, and rinsed according to the schedule set forth in Table IV. All operations are conducted on a continuous conveyor-line apparatus.

TABLE IV.—SCHEDULE OF METAL FINISHING OPERATIONS

Operation No.	Description
1	Spray the panel for 30 seconds at 160°–170° F. with an aqueous alkaline cleaner compounded from 1 oz. of a commercial alkali-base cleaning composition and 1 gal. of water.
2	Spray rinse the panel for 15 seconds at 75°–85° F. with water.
3	Spray-phosphate the panel for 30 seconds at 140° F. with the selected aqueous phosphating solution.
4	Spray rinse the panel for 15 seconds at 75°–85° F. with water.
5	Spray rinse the panel for 15 seconds at 75°–85° F. with dilute aqueous zinc dichromate (1 gram CrO_3/liter).

Two galvanized steel panels are chosen at random from each phosphating operation, spray-coated with a commercial white alkyd bake-enamel and baked in an oven for 20 minutes at 320° F. The dried coating thickness is approximately 1 mil. The painted panels are line-scribed with a sharp instrument down to the bare metal and subjected to the salt spray test described in ASTM Procedure B 117–62. In this test, metal panels are exposed for a pre-determined time to the corrosive atmosphere of a mist or fog of 5% aqueous sodium chloride solution at 95° F. Corrosion generally starts at the scribed portion of the panel and then "creeps" under the paint causing it to blister and flake from the metal panel. The loss of paint is reported as the average loss from each side of the scribe in thirty-seconds of an inch.

After 120 hours exposure in the salt spray test, the panels which have been phosphated by the solutions of this invention (solutions A, C, and D) show paint losses from 0 to 1.5 thirty-seconds of an inch. On the other hand, the panels phosphated with similar solutions but containing no nickel ions, show paint losses of about 0–4 thirty-seconds of an inch. Panels treated with solutions similar to D but without calcium ions, also show greater paint loss than panels treated with solutions of the present invention. The results of the salt spray corrosion test as shown in Table V indicate that the aqueous phosphating solutions of this invinetion substantially improve the rust preventive properties of the panel coatings as demonstrated by the improved resistance to undercutting by corrosion from the scribe line.

Table V.—Salt spray test

Phosphating solution employed in Operation 3:	Paint loss in thirty-seconds of an inch
A	0.0.
	0.0.
C [1]	0.0 with medium blisters to 1.0.
	0.0 with medium blisters to 1.5.
D [2]	1.0 with couple of blisters to 2.0.
	0.0 with medium dense blisters to 1.5.
D	1.5.
	1.5.

[1] Operation 3 of metal finishing operation carried out at 110° F.

[2] Operation 3 of metal finishing operation carried out at 125° F.

EXAMPLE 2

One of the hot-dip galvanized cold-rolled steel panels selected at random from each of the phosphating operations of Example 1 is electrostatically spray-painted with a commercial, white alkyd enamel, and baked in an oven for 20 minutes at 320° F. The film of baked enamel measures about 1 mil.

The top-coated panel is then subjected to a water immersion test. In this test, the panels are completely immersed for 16 hours in a distilled water bath maintained at 160° F. Upon removal from the bath, each panel is inspected for blistering and rated on a scale of O (for very large) to 10 (for none at all). The concentration of blisters is also noted and this is indicated by a rating of "dense," "medium dense," "medium," or "light."

The results obtained in this test are set forth in Table VI. It will be noted that the phosphating solutions of this invention act as effective primers for siccative organic coatings.

Table VI.—Water Immersion Test

Phosphating solution employed in Operation 3:	Blister Rating
A	9 light.
C [1]	9 light.
D [2]	9 light.
D	8 medium.

[1, 2] As defined in Table V.

EXAMPLE 3

Top-coated panels are prepared in the manner set forth in Example 2 and subjected to the water immersion test described in that example. Thirty minutes after removal from the bath, each panel is "cross-hatched" with

a pointed steel instrument by making 11 parallel, 1-inch-long scribes 3/32-inch apart and a similar number of intersecting scribes at right angles thereto. Adhesive cellophane tape is then applied to the scribed area and removed suddenly. The pressure-sensitive adhesive tape application is repeated until no more paint can be removed in this manner. The cross-hatch section is then rated as to percent of enamel retained.

The results observed in this test are shown in Table VII. Again, the phosphating solutions of this invention were more effective than known phosphating solutions in promoting the adhesion of an enamel to a galvanized surface.

Table VII.—Cross-Hatch Adhesion Test

Phosphating solution employed in Operation 3:	Percent enamel retained
C[1]	90
D[2]	90
D	90
Solution like D but devoid of nickle ion	60

[1, 2] As defined in Table V.

EXAMPLE 4

The metal finishing operations outlined in Table IV are repeated on galvanized 20 gauge SAE 1020 cold-rolled steel panels except that the time for each operation is 33 seconds.

A commercial, white, thermoplastic, solution vinyl paint is applied to two of the galvanized panels from each phosphating operation in the following manner. A generous portion of the paint is placed on the panel, and the panel is coated by moving a ¼-inch wire-wound drawdown rod over the panel surface. The panels are then baked for 75 seconds at 450° F. The film of baked enamel measures about 1 mil. These panels are then subjected to the Olsen Cup Test which measures the adhesion of a coating composition to a galvanized metal surface under severe deformation conditions. This test consists of a device in which the coated test panel is securely clamped and then deformed. Access is provided to the panel through a 1-inch diameter circular opening. Through this opening, a ⅞-inch diameter rounded cylindrical piston is forced into the panel until the resulting dimple ruptures. The panel is removed and pressure-sensitive tape is applied to the convex surface of the dimple. After removal of the tape, the convex surface of the dimple is rated on a scale of 0 to 100, 100 indicating perfect adhesion and 0 indicating a complete loss of the coating composition (i.e., no adhesion). The results obtained in this test are shown in Table VIII.

Table VIII.—Olsen Cup Test

Phosphating solution employed in operation 3:	Adhesion rating
C[1]	90, 90
D[2]	90, 90
D	90, 90
Solution like D but devoid of calcium ion	50, 40
Solution like D but devoid of nickel ion	60, 40

[1, 2] As defined in Table III.

What is claimed is:

1. A method for forming an adherent phosphate coating on an article having zinc surfaces which comprises contacting said article, at a temperature of at least about

100° F., with an aqueous phosphating solution having a total acidity of about 5–850 points, the active ingredients of said solution consisting essentially of about 0.01–8.0% (by weight) calcium ion, about 0.25–20.0% phosphate ion and about 0.005–2.0% nickel ion.

2. A method for forming an adherent phosphate coating on an article having zinc surfaces which comprises contacting said article, at a temperature of about 100–240° F., with an aqueous phosphating solution having a total acidity of about 5–100 points, the active ingredients of said solution consisting essentially of about 0.01–2.0% (by weight) calcium ion, about 0.25–7.0% phosphate ion, about 0.005–1.0% nickel ion, and about 0.01–26.0% nitrate ion.

3. A method according to claim 2 wherein the phosphating solution has a total acidity of about 5–50 points and the active ingredients thereof consist essentially of about 0.01–1.5% calcium ion, about 0.3–7.0% phosphate ion, about 0.015–0.4% nickel ion, and about 0.01–4.0% nitrate ion.

4. A method according to claim 3 wherein the phosphating solution additionally contains about 0.001–0.1% nitrite ion.

5. A method according to claim 3 wherein the phosphating solution additionally contains about 0.001–0.2% nitrite ion and about 0.1–2.0% ammonium ion.

6. A method for improving the adhesion of a siccative organic coating composition to a galvanized metal article which comprises contacting said article at a temperature of at least about 100° F., prior to the application of said organic coating composition, with an aqueous phosphating solution having a total acidity of about 5–850 points, the active ingredients of said solution consisting essentially of about 0.01–8.0% (by weight) calcium ion, about 0.25–20.0% phosphate ion and about 0.005–2.0% nickel ion.

7. A method for improving the adhesion of a siccative organic coating composition to a galvanized metal article comprises contacting said article at a temperature of about 100–240° F., prior to the application of said organic coating composition, with an aqueous phosphating solution having a total acidity of about 5–50 points, the active ingredients of said solution consisting essentially of about 0.01–1.5 calcium ion, about 0.3–7.0% phosphate ion, about 0.015–0.4% nickel ion, and about 0.01–4.0% nitrate ion.

8. A method according to claim 7 wherein the phosphating solution additionally contains about 0.001–0.1% nitrite ion.

9. A method according to claim 7 wherein the phosphating solution additionally contains about 0.001–0.02% nitrite ion and about 0.1–2.0% ammonium ion.

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RALPH S. KENDALL, Primary Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,592,701 Dated July 13, 1971

Inventor(s) Howard G. Pekar

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 25, "0.2%" should read --0.02%--;
line 43, "1.5" should read --1.5%--.

Signed and sealed this 28th day of December 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

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