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METHOD FOR PHOSPHATING FERROUS METALS

Wesley B. Upham, Hollywood, Fla., assignor to The Lubrizol Corporation, Wickliffe, Ohio, a corporation of Ohio

No Drawing. Continuation of application Ser. No. 619,962, Mar. 2, 1967, which is a continuation-in-part of application Ser. No. 494,889, Oct. 11, 1965. This application May 1, 1968, Ser. No. 725,957

Int. Cl. C23f 7/08

U.S. Cl. 148—6.15 3 Claims

ABSTRACT OF THE DISCLOSURE

Phosphating solutions containing zinc ions, ferrous ions and a saturated aliphatic hydroxy-substituted carboxylic acid such as tartaric or citric acid are especially useful in spray-phosphating operations for suppression of "blush rust."

This application is a continuation of copending application Ser. No. 619,962, filed Mar. 2, 1967, which in turn is a continuation-in-part of application Ser. No. 494,889, filed Oct. 11, 1965, now abandoned. The latter is a continuation of application Ser. No. 179,196, filed Mar. 12, 1962, now abandoned, which is itself a continuation-in-part of application Ser. No. 113,092, filed May 29, 1961, now U.S. Patent 3,116,178.

This invention relates to metal treatment, and more particularly to a new and improved method for forming zinc phosphate coatings on ferrous surfaces which comprises the steps of immersing the surface in a solution consisting essentially of 0.1%–2% zinc, 0.25%–4% PO_4, 0.02%–1% iron, and from about 0.002% to about 2% of at least one saturated, aliphatic polycarboxylic acid having 2–6 carbon atoms, the carbon atom adjacent to at least one carboxy group therein being substituted with a hydroxy radical, and maintaining said surface in said solution until a corrosion resistant coating is formed on said surface.

It is known in the metal finishing art to provide metal surfaces, especially ferrous surfaces, 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 as an excellent base for the later application of organic coatings such as paint, lacquer, varnish, primers, synthetic resins, enamel, and the like.

Such inorganic phosphate coating are generally formed on a metal surface by means of aqueous solutions which contain the phosphate ion and, optionally, certain auxiliary ions including metallic ions such as sodium, zinc, cadmium, iron, copper, lead, nickel, cobalt, and antimony ions, and non-metallic ions such as ammonium, chloride, bromide, nitrate, and chlorate ions. These auxiliary ions modify the character of the phosphate coating and adapt it for a wide variety of applications.

The preparation and use of aqueous phosphating solutions is well-known in the metal finishing art as shown by U.S. Patents 1,206,075, 1,247,668, 1,305,331, 1,485,025, 1,610,362, 1,980,518, 2,001,754, and 2,859,145.

Aqueous phosphating solutions are generally prepared by dissolving in water minor amounts of phosphoric acid and, optionally, a metal salt such as nitrate, phosphate, nitrite, sulfate, chloride, or bromide of sodium, zinc, cadmium, iron, nickel, copper, lead, or antimony. Ordinarily an oxidizing agent such as sodium chlorate, potassium perborate, sodium nitrate, ammonium nitrate, sodium chlorite, potassium perchlorate, or hydroxen peroxide is 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-slugging agents, coloring agents, and metal cleaning agents may also be incorporated in the phosphating solution. One common type of commercial phosphating bath which contains zinc ion, phosphate ion, and a depolarizer is made by dissolving small amounts of zinc dihydrogen phosphate, sodium nitrate, and phosphoric acid in water.

In order to provide the commercially satisfactory coating weights and coating speeds, an aqueous phosphating solution should generally have a total acidity within the range from about 5 to about 100 points, preferably from about 5 to about 50 points. It is possible, however, by certain special techniques to employ phosphating solutions having a total acidity substantially higher than 100 points, e.g., 125, 200, 250, or 300 points or more. The term "points total acidity" as employed in the phosphating art represents the number of milliliters of 0.1 normal sodium hydroxide solution required to neutralize a 10 milliliter sample of a phosphating solution in the presence of phenolphthalein as an indicator.

A particularly desirable and effective class of aqueous phosphating solutions or baths is set forth in copending application Ser. No. 373,449, filed *Aug.* 10, 1953, now U.S. Patent 3,090,709. It is intended that the disclosure of the said application be considered as forming a part of the present specification. The phosphating solutions described therein have a total acidity within the range from about 5 to about 100 points and contain as essential ingredients zinc ion, phosphate ion, nitrate ion, and an ion selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, cadmium, and barium ions. Such phosphating solutions provide a dense, adherent, micro-crystalline or amorphous phosphate coating which shows substantially no visible crystal structure at a magnification of 100 diameters and which is preferred for the purposes of the present invention.

One problem common to the known phosphating solutions and techniques is their tendency to form a thin film or iron oxide or "blush rust" on a ferrous metal surface. The blush rust phenomenon is particularly prevalent in spray-phosphating operations where the ferrous article is surrounded by a hot, humid atmosphere containing oxygen, water vapor, and fine droplets of the phosphating solution. Under these conditions, two competing reactions occur, viz, an oxidation of the ferrous surface by the water vapor-oxygen mixture and the desired reaction of the phosphating solution with the ferrous surface. The former reaction is believed to be responsible for the formation of blush rust.

Attempts have been made to suppress the formation of blush rust by the addition of passivating agents such as metallic nitrites and metallic dichromates to the phosphating solution. Although these efforts have been more or less successful in reducing the incidence of blush rust, they have introduced certain new problems, principally a greater rate of sludge formation in the phosphating bath in the case of nitrites, and a reduction in coating weights and coating speeds in the case of dichromates. Under certain operating conditions, metal dichromates passivate the ferrous surface to such an extent that it will no longer receive a phosphate coating.

It is therefore an object of the present invention to provide improved aqueous phosphating solutions.

A further object is to provide phosphating solutions which reduce the incidence of blush rust.

Another object is to provide a convenient and economical process for phosphating ferrous metal surfaces which reduces the formation of blush rust without adversely affecting the sludging or coating characteristics of the phosphating solution.

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

As previously indicated, the method of this invention involves the treatment of a ferrous metal surface with a phosphating solution containing zinc, phosphate, iron and a hydroxy-substituted polycarboxylic acid. The solution preferably also contains nitrate ion (about 0.25%–8.0%) and about 0.1%–4.0% of lithium, beryllium, magnesium, calicum, strontium, cadmium or barium ion. Best results from the standpoint of economy, excellent of the phosphate coating, and suppression of blush rust are obtained with a solution having a total acidity of about 5–50 points and containing as essential ingredients about 0.1%–0.6% of zinc ion; about 0.3%–1.5% of phosphate ion; about 0.1%–1.0% of ferrous ion; about 0.5%–6.0% of nitrate ion; about 0.1%–1.5% of calcium ion; and about 0.005%–1.0% of tartaric acid.

The organic acid used to suppress blush rust according to the method of this invention may be supplied conveniently as free acid or in the form of a salt thereof. Thus, for example, an addition to the phosphating solution of the free acid, its ammonium salt, or its light or heavy metal salt, such as a sodium, potassium, lithium, calcium, strontium, barium, copper, lead, or nickel salt, serves the purposes of the present invention. This is not to say that the acids and salts are of equal effectiveness. It has been found, for example, that certain salts are effective at lower concentrations than are the parent acids. It is also desirable in certain instances to use mixtures of different acids, different salts, or different acids and salts.

Examples of hydroxy-substituted polycarboxylic acids which are useful per se or in the form of salts for the purposes of this invention include malonic acid, malic acid, citramalic acid, tartronic acid, methyltartronic acid, tartaric acid, citric acid, dihydroxymaleic acid, 1,2-dihydroxyglutaric acid, 1,3-dihydroxyglutaric acid, mucic acid, malomalic acid, itamalic acid, and the like. Substituents such as chloro, bromo, fluoro, ester, ether, sulfide, nitroso, nitro, etc., may also be present in the acid.

Because of their commercial availability, stability in storage, and low cost, the alkali metal salts and especially the sodium and/or potassium salts are preferred as sources of the hydroxy-substituted polycarboxylic acid. A preference is expressed for sodium potassium tartrate (Rochelle salt) because of its effectiveness at very low concentrations.

The hydroxyaliphatic carboxylic acid compound (i.e., the acid or salt) is generally employed in an amount sufficient to impart at least about 0.002% by weight and preferably about 0.005%–2.0% of the acid to the phosphating solution. Amounts below about 0.002% appear to have little effect in reducing blush rust and amounts much over 2.0%, although effective, contribute little added protection and are uneconomical. From the standpoint of both economy and effectiveness, about 0.005%–1.0% is the particularly preferred range.

The presence of ferrous ion in the phosphating solution is also essential to the method of this invention. The ferrous ion may be provided by adding a ferrous salt to the solution, but it is preferably introduced by "breaking in" a solution containing the other ingredients by processing ferrous objects therein. After such processing, the solution inherently contains ferrous ion in the required percentage range.

The following table shows the compositions (excluding ferrous ion) of a number of phosphating solutions suitable for use in the method of this invention. All figures except "Points Total Acid" are percentages by weight.

Ingredient	Phosphating solution					
	A	B	C	D	E	F
PO_4	0.53	0.30	0.30	0.30	1.29	0.54
Zn	0.15	0.12	0.12	0.12	0.52	0.17
Ca	0.36	0.22	0.22	0.22	0.27	0.12
NO_3	1.3	0.82	0.82	0.82	1.41	0.71
Tartaric acid	0.0385	0.0039	0.035	0.030		
Citric acid					0.10	
Malic acid						0.25
Points total acid	12	8	8	8	30	12

The phosphating solutions in the table are prepared as follows:

Solution A.—100 ml. of water, 7.4 g. of 75% H_3PO_4, 2.7 g. of 42° Baumé HNO_3, 1.9 g. of ZnO, and 2.2 g. of 50% aqueous NaOH are thoroughly mixed and then diluted with water to make one liter of solution. 20 g. of $Ca(NO_3)_2 \cdot 3H_2O$ and 0.5 g. of Rochelle salt are then dissolved in this solution.

Solution B.—100 ml. of water, 4.2 g. of 75% H_3PO_4, 2.2 g. of 42° Baumé HNO_3, 1.5 g. of ZnO, and 1.8 g. of 50% aqueous NaOH are thoroughly mixed and then diluted with water to make one liter of solution. 12 g. of $Ca(NO_3)_2 \cdot 3H_2O$ and 0.05 g. of Rochelle salt are then dissolved in this solution.

Solution C.—This solution is prepared in the same manner set forth for Solution B, except that 0.35 g. of tartaric acid is used in lieu of the Rochelle salt.

Solution D.—This solution is prepared in the same manner set forth for Solution B, exept that 0.35 g. of sodium acid tartrate is used in lieu of the Rochelle salt.

Solution E.—14.2 g. of $Zn(NO_3)_2 \cdot 6H_2O$, 7.8 g. of 75% H_3PO_4, 4.2 g. of $ZnCl_2$, 8.7 g. of $NH_4H_2PO_4$, 14.3 g. of $Ca(NO_3)_2 \cdot 3H_2O$, and 1.0 g. of citric acid are dissolved in sufficient water to make one liter of solution.

Solution F.—4.98 g. of $Zn(NO_3)_2$, 6.88 g. of NaH_2PO_4, 6.32 g. of $Ca(NO_3)_2 \cdot 3H_2O$, and 2.5 g. of malic acid are dissolved in sufficient water to make one liter of solution.

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, or flow-coating may be employed, and that the temperature of the aqueous phosphating solution may vary within wide limits, e.g., from room temperature to about 212° F. In general, best results are obtained when the aqueous phosphating solution is used at a temperature within the range from about 150° F. to about 210° F. If desired, however, the aqueous phosphating bath may be used at higher temperatures, e.g., 225° F., 250° F., or even 300° F., by employing superatmospheric pressures.

In the ordinary practice of phosphating a metal surface, such surface is first cleaned by physical and/or chemical means to remove any grease, dirt, or oxides and then it is phosphated in the manner described above.

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 within the range from about 100 to about 1000 milligrams per square foot of surface area. The time required to form the phosphate coating will vary according to the temperature, the type of 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 the weight preferred for the purpose of the present invention will be within the range of from about one-quarter minute to about 15 to 20 minutes.

Upon completion of the phosphating operation, the phosphated article is rinsed, optionally, with water and/or a hot dilute aqueous solution of chromic acid containing

from about 0.01 to about 0.2 percent of CrO_3. The chromic acid rinse appears to "seal" the phosphate coating and improve its utility as a base for the application of paint, lacquer, varnish, and the like. In lieu of the dilute aqueous chromic acid, dilute aqueous solutions of metal chromates, metal dichromates, chromic acid-phosphoric acid mixtures, and chromic acid-metal dichromate mixtures may be used.

The method of this invetnion is illustrated by the following examples.

Example 1

Solution A and three similar solutions, one devoid of Rochelle salt (sodium potassium tartrate tetrahydrate) and the other two containing, respectively, twice and four times as much Rochelle salt as Solution A, were prepared and "broken in" by treating steel panels therewith until the ferrous ion concentration was about 0.036%.

Each of three 4-inch x 4-inch panels of cold-rolled 20-gauge SAE 1020 steel was placed in contact with a steel cone of fixed size and shape and then bent 180° along a 4-inch dimension. The bent panels were cleaned by immersion for 2 minutes at 190°–200° F. in an aqueous cleanser consisting of water plus 40 g./liter of a commercial, alkali-base cleanser. Thereafter, the three panels were immersed, respectively, in the three above-described phosphating solutions for 30 seconds at 175° F., suspended in the vapor above the phosphating solution for 2 minutes, rinsed with a dilute aqueous solution of chromic acid (0.5 g./liter of CrO_3), and rinsed with acetone to dry.

The panels were inspected and given a "blush rust rating" on a scale of 0 to 100, 0 representing a blush rust-free panel and 100 representing a panel completely covered with blush rust. The results were as follows.

Percent tartaric acid in the phosphating solution	Blush rust rating
None (control)	100
0.0385 (Solution A)	10
0.077	10
0.153	10

Example 2

Solution B and two similar solutions, one devoid of Rochelle salt and the other containing five times as much Rochelle salt as Solution B, were prepared and "broken in" as in Example 1.

Nine clean, solvent-degreased, 4-inch x 8-inch panels of 24-gauge cold-rolled steel were bent along their 4-inch dimension in the manner described in Example 1. Three sets of three panels each were phosphated, respectively, in a continuous spray-line apparatus according to the three schedules given below:

(a) Aqueous alkaline cleanser spray (1.5 oz./gal. of a commercial alkali-base cleanser) for 40 seconds at 175–180° F. Water spray for 3 minutes at 110° F. Solution B spray for 1.75 minutes at 160°–165° F. Water spray for 40 seconds at 120° F. Aqueous chromic acid spray (⅛ g. CrO_3/liter) for 40 seconds at 90° F.

(b) Like schedule (a), but using in lieu of Solution B a similar solution devoid of Rochelle salt.

(c) Like schedule (a), but using in lieu of Solution B a similar solution containing five times as much Rochelle salt.

After all three sets of panels had been phosphated, they were examined to determine the percent reduction in blush rust due to the presence of the tartaric acid anion. The results were as follows.

Percent tartaric acid anion (from Rochelle salt) in the phosphating solution	Percent reduction in blush rust (average of three panels)
None	Control
0.0039 (Solution B)	50
0.0195	75

Example 3

Solution C and two similar solutions, one devoid of tartaric acid and the other containing about twice as much tartaric acid as Solution C, were prepared.

In a manner like that described in Example 2, three sets of three bent steel panels each were spray-phosphated, respectively, with the above-noted phosphating solutions. An examination of the panels yielded the following data.

Percent tartaric acid anion (from tartaric acid) in the phosphating solution	Percent reduction in blush rust (average of three panels)
None	Control
0.035	25
0.075	50

Example 4

Solution D and two similar solutions, one devoid of sodium acid tartrate and the other containing twice as much sodium acid tartrate as Solution D, were prepared.

In a manner like that described in Example 2, three sets of three bent steel panels each were spray-phosphated. respectively, with the above-noted phosphating solutions. An inspection of the panels yielded the following data.

Percent tartaric acid anion (from sodium acid tartrate) in the phosphating solution	Percent reduction in blush rust (average of three panels)
None	Control
0.030 (Solution D)	50
0.060	50

What is claimed is:

1. A method for forming zinc phosphate coatings on ferrous surfaces which comprises the steps of immersing the surface in an aqueous solution comprising 0.1%–2% zinc, 0.25%–4% PO_4, 0.02%–1% iron, and from about 0.002% to about 2% of at least one saturated, aliphatic polycarboxylic acid having 2–6 carbon atoms, the carbon adjacent to at least one carboxy group therein being substituted with a hydroxyl radical, and maintaining said surface in said solution until a corrosion resistant coating is formed on said surface.

2. A method for forming zinc phosphate coatings on ferrous surfaces which comprises the steps of immersing the surface in an aqueous solution comprising 0.1%–2% zinc, 0.25%–4% PO_4, 0.02%–1% iron, and from about 0.002% to about 2% of at least one saturated, aliphatic polycarboxylic acid selected from the group consisting of citric acid, tartaric acid, malonic acid and malic acid, and maintaining said surface in sad solution until a corroson resistant coating is formed on said surface.

3. A method in accordance with claim 2 wherein said acid is citric acid.

References Cited

UNITED STATES PATENTS

3,116,178	12/1963	Upham.
3,268,367	8/1966	Nelson.
3,307,979	3/1967	Upham.

RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

148—6.16

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,458,364 Dated July 29, 1969

Inventor(s) Wesley B. Upham

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

Column 1, line 25, "abandoned" should read --U.S. Patent 3,307,979--.

Signed and sealed this 25th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents