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PHOSPHATING SOLUTIONS FOR USE ON FERROUS METAL AND ZINC SURFACES

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ABSTRACT OF THE DISCLOSURE

Aqueous phosphating solutions containing phosphate ion, zinc ion, nickel, cobalt or copper ion, magnesium ion, nitrite ion and one or both of fluoride and chloride ions are useful for producing microcrystalline phosphate coatings on both ferrous metal and zinc (e.g., galvanized) surfaces, especially when their use is preceded by a titanium phosphate treatment. The resulting coatings improve adhesion of siccative organic coatings to the metal.

This invention relates to the treatment of metal surfaces, and more particularly to phosphating solutions used for such treatment. Still more particularly, it relates to an aqueous solution, suitable for producing a microcrystalline coating on both zinc and ferrous metal surfaces, containing as essential coating producing ingredients the following ions in the indicated concentrations:

(A) Phosphate—3–20 grams per liter
(B) Zinc—0.5–3.0 grams per liter
(C) Nickel, cobalt or copper—0.05–3.0, 0.003–0.7 or 0.003–0.04 grams per liter, respectively
(D) Magnesium—1–8 grams per liter
(E) Nitrite—0.01–0.25 gram per liter
(F) Fluoride and/or chloride—0.1–3.0 and 2–30 grams per liter, respectively.

Many varieties of solutions are known for the production of conversion-type phosphate coatings on metal surfaces. The simplest are the so-called "iron phosphate" solutions which in their simplest form contain only phosphate ion and accelerating or depolarizing ingredients such as nitrate, nitrite, chlorate, hydrogen peroxide and the like. They derive their name from the fact that iron from the metal surface being treated dissolves in the bath as it is used. More recently, solutions additionally containing zinc, manganese or lead have been developed. When these solutions are used, the metal contained therein is incorporated in the coating. Many other solutions are known which contain, in addition to the ions mentioned above, others which accelerate the solution's action or modify the coating, e.g., sodium, cadmium, copper, antimony, nickel, cobalt, cerium, ammonium, chloride, bromide, fluoride, sulfate, borate, perborate, chlorite and perchlorate. The coatings produced by these solutions serve as paint bases and corrosion-inhibiting substrates. Some of them, notably lead phosphate coatings, provide additional advantages such as weldability and improvement of drawing properties.

Phosphate coatings are advantageously formed on both ferrous metal (e.g., cold-rolled steel) and zinc (e.g., galvanized steel) surfaces. In general, however, the solutions used for steel treatment are of quite different composition than those used on zinc. For example, nitrate is frequently used as a depolarizer in solutions for use on ferrous metal but is generally unnecessary and may even be detrimental on zinc. On the other hand, nickel ions are useful in a solution for treating zinc or galvanized metal but accomplish little or nothing with ferrous metals. Therefore, it is common practice to employ entirely different solutions depending on the nature of the metal being treated.

In the manufacture of metal appliances and the like, parts are frequently phosphated at the end of the assembly line prior to painting and assembly. The fact that ferrous metals and zinc must be phosphated with different solutions requires the existence of at least two phosphating lines, or else requires considerable "down time" when switching from one type of metal to another. It would be much more convenient to use a single solution in a single phosphating bath regardless of the type of metal being run through, without the necessity for changing the solution, adding or removing ingredients or shutting down the line to switch from one solution to another.

A principal object of the present invention, therefore, is to provide new phosphating solutions of improved versatility.

A further object is to provide a phosphating solution which can be used on both steel and zinc surfaces without the necessity for changing, modifying or recharging the solution with a change in the metal being treated.

Still another object is to provide a phosphating solution which deposits a microcrystalline phosphate coating of improved crystal structure which adheres tightly to the metal surface being treated, serves as an excellent paint base and protects the surface from corrosion.

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

As indicated above, the phosphating solutions of this invention have six essential ingredients of which the first is, of course, the phosphate ion (Component A). This may be provided by phosphoric acid, which is usually the most convenient source. The commercially available 85% phosphoric acid is usually employed, although condensed acids such as pyrophosphoric, polyphosphoric and the like are also suitable as are salts such as ammonium dihydrogen phosphate, sodium dihydrogen phosphate, potassium dihydrogen phosphate and the like. The phosphate ion concentration is about 3–20 grams per liter and is usually about 3–15 grams per liter, at least in fresh solutions.

Zinc ion (Component B) may be provided by zinc oxide or by other water-soluble salts such as zinc nitrate, zinc fluosilicate and the like. The zinc ion concentration is about 0.5–3.0 grams per liter.

Nickel, cobalt and copper are considered equivalents as component C from the standpoint of function in the compositions of this invention. They vary, however, in the amounts used. Thus, the amount of nickel should be about 0.05–3.0 grams per liter and preferably about 0.1–3.0 grams per liter. Cobalt is used in smaller amounts (about 0.003–0.7 gram per liter) and copper in still smaller amounts (about 0.003–0.04 gram per liter). These metal ions may be furnished by any of the ordinarily used soluble salts thereof, typically the nitrate. Of the three metals, nickel is preferred.

The presence of magnesium (component D) is essential to the compositions of this invention, and may be furnished by magnesium oxide, magnesium nitrate, magnesium chloride or the like. The magnesium concentration is 1–8 grams per liter, preferably about 2.5–6.0 grams per liter.

The accelerator used in the solutions of this invention is the nitrite ion (component E) which may be present in very small amounts, generally about 0.01–0.25 gram per liter. It is most conveniently provided as sodium nitrite, but other soluble nitrites such as magnesium, potassium or the like may be used.

Component F, the final essential ingredient, is one or both of fluoride and chloride ions. The amount of fluoride should be about 0.1–3.0 grams per liter and preferably about 0.1–1.0 gram per liter. The required amount of chloride ion is 2–30 grams per liter, preferably about 7–15 grams per liter. It may occasionally be convenient to use both ions, in which case the concentration of each may be in the indicated ranges and usually on the low side thereof. Typical sources of fluoride and chloride ions are the sodium, potassium, magnesium or ammonium salts thereof, or other equivalent salts. Fluoride ion may also be provided in the form of a complex fluoride such as fluosilicate or fluoborate.

The compositions of this invention may also contain other ions which, while not essential to their function, come into the solution because of their presence in salts which it is convenient to use to provide the essential ions. Thus, it is frequently convenient to use nitrates of zinc, nickel and the like and therefore nitrate ion may be present in concentrations up to about 40 grams per liter. Nitrate serves, or course, as an accelerator or depolarizer similar to nitrite, but its presence is not necessary since the nitrite ion provides all the depolarizing effect required.

The phosphating solution is generally adjusted, before use, to a total acidity of about 5–30 points and a very low free acidity; usually about 0.1–5.0 points. The term "points" represents the number of milliliters of 0.1 N sodium hydroxide solution required to neutralize a 10 ml. sample of the phosphating solution. The indicator used to determine total acid is phenolphthalein; for free acid, it is modified methyl orange.

The phosphating solution may be prepared in the form of one or more concentrates, or as a dilute solution ready for use. When provided as a concentrate, nitrite ion must be excluded and added to the prepared solution just before use, since the highly acidic concentrate would convert nitrite to unstable nitrous acid.

Often, the coating action of the phosphating solutions of this invention can be improved by the addition of surface-active agents. These agents also serve as dispersants in the phosphating solution and help to maintain the ingredients in solution. Examples of suitable surface-active agents are the ethylene oxide condensates, particularly those containing about 3–25 polyoxyethylene groups, of which typical examples are polyoxyethylene derivatives of oleic acid and of alkyl phenols. Also useful are sodium alkyl sulfates and sulfonated hydrocarbons such as alkylnaphthalenesulfonic acid.

The following examples illustrate methods for the preparation of the phosphating solutions of this invention.

EXAMPLE 1

A concentrate is prepared from 45.9 parts of 85% phosphoric acid, 8.2 parts of 67% nitric acid, 1.2 parts of magnesium oxide, 8.7 parts of zinc oxide, 6.0 parts of nickel nitrate hexahydrate, 1.9 parts of zinc fluosilicate hexahydrate, and 28.1 parts of water. This solution is diluted with water to a concentration of 1.33%. To this solution is added a mixture of 29.7 parts of 67% nitric acid, 7.3 parts of magnesium oxide, 20.0 parts of sodium nitrite and 43.0 parts of water, in an amount sufficient to increase the magnesium ion concentration to 3.0 grams per liter.

EXAMPLE 2

A concentrate is prepared containing 35.4 parts of 75% phosphoric acid, 8.3 parts of 67% nitroic acid, 14.0 parts of zinc oxide, 8.4 parts of nickel nitrate hexahydrate, 6.9 parts of zinc fluosilicate hexahydrate, and 33.5 parts of water. A second solution is prepared containing 11.0 parts of magnesium oxide, 44.8 parts of 67% nitric acid, and 44.2 parts of water. These solutions are combined and diluted to give a working solution with a phosphate ion concentration of 4.56 grams per liter and a magnesium ion concentration of 3.32 grams per liter. Aqueous sodium nitrite solution (28%) is added in an amount sufficient to provide 0.06 gram per liter of nitrite ion.

EXAMPLE 3

The phosphoric acid-containing concentrate of Example 2 is combined with a solution containing 12.5% magnesium oxide, 63.0% of 20% muriatic acid and 24.5% water, and with the solution of sodium nitrite, in amounts suitable to provide 5.7 grams per liter of phosphate ion, 3.0 grams per liter of magnesium ion and 0.1 gram per liter of nitrite ion.

EXAMPLE 4

A solution is prepared containing 6.2 parts of 85% phosphoric acid, 8.3 parts of 67% nitric acid, 14.0 parts of zinc oxide, 3.5 parts of nickel nitrate hexahydrate, and 14.0 parts of water. A second solution is prepared containing 1015 parts of 67% nitric acid, 250 parts of magnesium oxide and 1000 parts of water. These solutions, and a 28% aqueous solution of sodium nitrite, are combined in proportions sufficient to provide 11.4 grams per liter of phosphate, 3.49 grams per liter of magnesium and 0.1 gram per liter of nitrite. Hydrofluoric acid is added in an amount sufficient to provide 0.3 gram per liter of fluoride ion.

EXAMPLE 5

A solution containing phosphoric acid, zinc oxide and nickel nitrate is prepared and combined with the magnesium- and nitric acid-containing solution of Example 4, the sodium nitrite solution of Examples 2–4 and hydrofluoric acid in amounts sufficient to provide 9.88 grams per liter of phosphate ion, 3.74 grams per liter of magnesium ion, 0.1 gram per liter of nitrite ion and 0.04 gram per liter of fluoride ion.

EXAMPLE 6

The procedure of Example 5 is repeated except that the magnesium- and nitric acid-containing solution is replaced by a magnesium chloride solution. The amounts used are sufficient to provide 9.5 grams per liter of phosphate ion, 4.1 grams per liter of magnesium ion, 0.1 gram per liter of nitrite ion and 10.8 grams per liter of chloride ion.

EXAMPLE 7

The procedure of Example 6 is repeated, except that hydrofluoric acid is added and the quantities of the various solutions are sufficient to provide 7.6 grams per liter of phosphate ion, 3.4 grams per liter of magnesium ion, 0.1 gram per liter of nitrite ion, 0.52 gram per liter of fluoride ion and 9.3 grams per liter of chloride ion.

In Table I are given the concentrations of the various ions in the solutions of Examples 1–7, together with some additional solutions according to this invention and four control solutions (Examples 10–13) not of this invention which are included for the sake of comparison in performance tests as described hereinafter. All concentrations are in grams per liter except for total acid and free acid, which are given in points as defined hereinabove.

TABLE I

Example	1	2	3	4	5	6	7	8	9	10	11	12	13
Phosphate	5.15	4.56	5.7	11.4	9.88	9.5	7.6	14.3	10.2	7.98	7.22	9.5	8.75
Nitrate	14.0	23	2.5	18.25	18.25				8.1	20.25	17.0	19.5	17.3
Nitrite	0.1	0.06	0.1	0.1	0.1	0.1	0.1	0.2	0.15	0.1	0.1	0.1	0.1
Fluoride	0.09	0.31	0.35	0.3	0.4		0.52						(*)
Chloride			9			10.8	9.3	21.5	15.2				
Zinc	0.98	1.56	2.1	2.76	1.80	1.02	1.02	2.5	0.82	1.74	1.62	1.32	1.32
Magnesium	3.0	3.32	3.0	3.49	3.74	4.1	3.4	1.3	6.7				
Nickel	0.16	0.50	0.50	0.43	0.27	0.28	0.24			0.45	0.42	0.28	0.31
Cobalt								0.21					
Copper									0.02				
Calcium										5.67	4.96	5.60	5.05
Total acid	17	12.4	14.5	25.5	21.6	17.7	15.5			18.8	16.5	20.8	19.7
Free acid		1.0	1.0	3.6	<2	0.4	0.7			1.3	1.4	1.7	1.9

* Hydrofluoric acid added to provide 0.3 gram per liter of fluoride, all of which precipitated as calcium fluoride.

In the accepted practice of phosphating metal articles, the metal surface is usually cleaned by physical and/or chemical means to remove any grease, dirt and oxides. It is strongly preferred, according to the present invention, that the chemical cleaning step include a titanium phosphate pretreatment of the type disclosed in U.S. Pat. 2,322,349; such a pretreatment promotes formation of a microcrystalline coating as described hereinafter.

The cleaned article is then rinsed with water and treated with the phosphating solution. The phosphating treatment may be by any of the commonly used techniques such as spraying, brushing, dipping, roller-coating and flow-coating. The temperature of the phosphating solution may vary from about room temperature to about 240° F.; the solutions of the present invention are conveniently used at about 150–180° F. and preferably about 160–165° F. The phosphating operation is carried out until a phosphate coating of the desired weight is obtained; this weight may be as little as 25 mg. per square foot of surface area but is preferably about 50–1000 and generally not more than about 300 mg. per square foot. Under most conditions, a coating within this weight range can be obtained when the duration of phosphate treating is between about 5 seconds and 10 minutes.

Upon completion of the phosphating operation, the metal article is generally rinsed with water and/or a hot, dilute aqueous solution of chromic acid. The chromic acid rinse appears to "seal" the phosphate coating and improve its utility as a base for the application of a paint or other siccative organic coating. A dilute aqueous solution of a metal chromate or dichromate, a chromic acid-phosphoric acid mixture, or a mixture of chromic acid with a metal dichromate may be used in place of the aqueous chromic acid. Also useful, especially on galvanized surfaces, are solutions containing partially reduced chromic acid such as those described in U.S. Pats. 3,282,744 and 3,404,045.

The effectiveness of the compositions of this invention for forming phosphate coatings on both ferrous metals and zinc surfaces is believed to result in part from the crystalline structure of the coating formed. Most of the previously known phosphating solutions form coatings with either an apatite or scholzite crystal structure. The apatite structure is represented by $(M^1)_{10}(OH)_2(PO_4)_6$, and scholzite by $(M_1)_2(M^2)(PO_4)_2 \cdot 2H_2O$. The identity of M^1 and M^2 in these formulas will depend on the metal ions present in the coating bath. Thus, a phosphate bath containing zinc ions will produce an apatite-like coating wherein M^1 is zinc. A phosphate solution containing zinc and calcium ions, such as that disclosed and claimed in U.S. Pat. 3,090,709, produces a coating of the scholzite type in which M^1 is zinc and M^2 is calcium. It will be noted that the scholzite crystal is a dihydrate; the water of crystallization is stable to temperatures in excess of those normally used in the drying process subsequent to phosphating, and so there is no change in crystal structure upon drying.

It has been found that the compositions of this invention produce a phosphate coating which, prior to drying, has predominantly a modified hopeite structure. Hopeite has the formula $Zn_3(PO_4)_2 \cdot 4H_2O$. When an ordinary hopeite crystalline coating is deposited on a metal surface and dried, it loses water of hydration at low temperatures and becomes loose and nonadherent. The compositions of this invention, however, produce hopeite crystals with partial substitution (generally up to about 20%) of magnesium for zinc. The presence of magnesium causes a change in the kinetics of drying so that the crystals lose only half their water of hydration, whereupon they are converted to thin needles which aggregate into thin bundles of parallel needles with strong epitaxial bonds to the metal surface. The dehydrated crystals are very small, generally microcrystalline.

The effectiveness of the compositions of this invention for forming phosphate coatings on metal is demonstrated by the Salt Fog Corrosion Test (ASTM B117) and the Detergent Test. In these tests, cold-rolled steel and galvanized steel test panels are cleaned at 160–165° F. with a cleaner of the following constitution:

	Percent
Sodium tripolyphosphate	27.3
Tetrasodium pyrophosphate	9.3
Sodium carbonate	2.2
Colloidal titanium orthophosphate	5.0
Anhydrous sodium metasilicate	51.2
Non-ionic polyoxyethylene emulsifiers	5.0

They are then rinsed with water, sprayed with the phosphating solution at 160–165° F., rinsed again with water, post-rinsed at 100° F. with a dilute aqueous chromic acid solution partially reduced with methanol, and finally rinsed with de-ionized water. The panels are then dried and painted with a white alkyd-melamine baking enamel.

In the Salt Fog Corrosion Test, the paint film on each panel is ruptured down to the bare metal by scoring a six-inch line on the surface of the panel. The score panel is placed in a cabinet containing a 5% aqueous sodium chloride solution at 95° F. Air is bubbled through the solution to produce a corrosive salt atmosphere which acts on the surface of the test panels, suspended above the level of the salt solution. The panels remain in this atmosphere for 120 hours after which they are removed, washed with water and dried with a cloth. A pressure-sensitive tape is then applied to each panel and removed suddenly. This procedure is repeated until no more paint can be removed in this manner. The loss of adhesion caused by corrosion from the scribed line is measured in thirty-seconds of an inch.

In the Detergent Test, the painted panels are immersed in a 1% synthetic detergent solution at 160° F. for the desired period, and are then removed and rated for blister size and frequency of blistering according to ASTM procedure B714. The blister size is reported as a number from 0 to 10, 0 representing large blisters and 10 representing no blistering. The frequency of blistering is designated as dense, medium dense, medium or few.

The results of the Salt Fog Corrosion and Detergent Tests, for the compositions of this invention (Examples 2–7) as compared with prior-art compositions not of this invention (Examples 10–13), are given in Table II.

TABLE II

Example	Metal	Coating weight, mg./sq. ft.	Salt fog corrosion test creep, 1/32 in.[1]	Detergent test	
				Time, hrs.	Rating
2	Steel	230	1.5	144	10.
	Galvanized	271	0.5	144	10.
3	Steel	193	0	144	10.
	Galvanized	190	0.5	144	10.
4	Steel	142	1.0	96	9 med.
	Galvanized	172	1.0	96	9 med.
5	Steel	122	0	96	9 med.
	Galvanized	165	1.0	96	10.
6	Steel	268	1.0	96	10.
	Galvanized	351	0	96	10.
7	Steel	138	1.5	96	9 dense.
	Galvanized	206	0	96	10.
10	Steel	123	0	96	9 med. dense.
	Galvanized	37	8.0	96	5 med. dense.
11	Steel	104	0	96	9 med. dense.
	Galvanized	28	7.0	96	7 med. dense.
12	Steel	178	0.5	96	9 med. dense.
	Galvanized	9	(2)	96	9 med. dense.
13	Steel	138	0.5	96	9 med. dense.
	Galvanized	15	(2)	96	6 med. dense.

[1] Average of 3 readings.

[2] Complete loss of adhesion.

The results in Table II show the superiority of the compositions of this invention for forming phosphate coatings on both steel and galvanized surfaces, as compared with known calcium-modified zinc phosphate solutions.

What is claimed is:

1. An aqueous solution, suitable for producing a microcrystalline coating on both zinc and ferrous metal surfaces, containing as essential coating-producing ingredients the following ions in the indicated concentrations:

(A) Phosphate—3–20 grams per liter
(B) Zinc—0.5–3.0 grams per liter
(C) Nickel, cobalt or copper—0.05–3.0, 0.003–0.7 or 0.003–0.04 grams per liter, respectively
(D) Magnesium—1–8 grams per liter
(E) Nitrite—0.01–0.25 gram per liter
(F) Fluoride and/or chloride—0.1–3.0 and 2–30 grams per liter, respectively.

2. A solution according to claim **1** wherein component C is nickel ion.

3. A solution according to claim **2** wherein the concentrations are approximately as follows:

(A) Phosphate—3–15 grams per liter
(B) Zinc—0.5–3.0 grams per liter
(C) Nickel—0.1–3.0 grams per liter
(D) Magnesium—2.5–6.0 grams per liter
(E) Nitrite—0.01–0.25 gram per liter
(F) Fluoride and/or chloride—0.1–1.0 and 7–15 grams per liter, respectively.

4. A solution according to claim **3** which additionally contains nitrate ion in an amount up to about 40 grams per liter.

5. A solution according to claim **4** wherein component F is fluoride ion.

6. A solution according to claim **5** wherein the fluoride ion is provided by a complex fluoride.

7. A solution according to claim **3** wherein component F is at least partially chloride ion.

8. A method of producing a microcrystalline phosphate coating on a ferrous meal or zinc surface which comprises contacting said surface with a solution according to claim **1.**

9. A method of producing a microcrystalline phosphate coating on a ferrous metal or zinc surface which comprises contacting said surface with a solution according to claim **3.**

10. A method according to claim **9** wherein the metal surface is previously treated with a cleaning solution containing colloidal titanium phosphate.

11. A method according to claim **10** wherein component F is fluoride and the solution additionally contains nitrate ion in an amount up to about 40 grams per liter.

12. A method according to claim **10** wherein component F is at least partially chloride ion.

13. A ferrous metal or galvanized article which contains on its surface a microcrystalline phosphate coating prepared by the method of claim **9.**

14. A metal article according to claim **13** which has been further provided with a siccative organic coating.

15. A ferrous metal or galvanized article which contains on its surface a microcrystalline phosphate coating prepared by the method of claim **10.**

16. A metal article according to claim **15** which has been further provided with a siccative organic coating.

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RALPH S. KENDALL, Primary Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,597,283 Dated August 3, 1971

Inventor(s) Charles T. Snee

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

Column 4, line 8, "nitroic" should read --nitric --; line 50, "0.04" should read --0.4--.

Column 5, line 60 "M_1" should read --M^1--.

Column 8, line 16, "meal" should read --metal--.

Signed and sealed this 28th day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents