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COMPOSITION FOR AND METHOD OF COATING FERROUS METALS

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This invention relates to the treatment of metal surfaces, and particularly to the formation of protective phosphate coatings on the surfaces of iron and zinc and alloys thereof.

Phosphate coatings, to provide dependable paint-bonding and corrosion-resistant qualities, must be able to withstand intermittent or continuous assaults of moisture over long periods, and particularly they must be able to resist the attack of salt water, the most severely corrosive condition normally encountered. The coatings must be free from even the smallest defects that might provide foci for the initiation of corrosion, and they must especially be of a nature which inhibits the spread of corrosion from accidentally acquired scratches, etc., where the bare metal has been exposed.

In the art of phosphating metal surfaces, there has recently been an increasing interest in the use of phosphating compositions which contain alkali metal or ammonium dihydrogen phosphate as the basic phosphating ingredient, hereinafter referred to as "alkali metal phosphate" compositions, since these materials appear to be particularly suitable in the preparation of surfaces for the reception of paint, lacquer and other siccative coatings.

In the application of solutions of this type to metal surfaces, however, several operating details of the phosphating art assume great importance in a field where speed, convenience and economy are not only desirable but essential, and in one or more of these details the alkali metal phosphate solutions presently used generally fall short. Thus, a phosphating bath which during operation forms large amounts of "sludge" (insoluble reaction products and other insoluble material) requires frequent shut-down to remove the accumulated solids, cutting the overall speed of assembly-line processes. Moreover, in certain installations it is often preferred when possible to apply phosphate coatings by immersing the metal in a phosphating bath rather than by spraying the solution on the metal. However, the alkali metal baths are generally not suited to this type of application, and require the installation of expensive and sometimes inconvenient spray equipment before satisfactory coatings are obtained. A further operating detail is the shipping and storing of the phosphating material, which is usually supplied in concentrated form. It is preferred that the concentrate be a solid, for ease and economy of transport and storage, yet generally the alkali metal phosphate concentrates can only be supplied as concentrated, and often corrosive liquids, which increase shipping costs, require special containers and produce awkward storage problems.

The principal object of the present invention is to provide an alkali metal phosphate composition which not only produces a good base for the retention of siccative coatings but which is also highly resistant to the corrosive action of humidity and immersion in water.

Another object is to provide an alkali metal phosphate bath which operates with formation of only minimal

amounts of sludge. A further object is to provide an alkali metal phosphate solution which can be applied to the metal surface by the immersion technique as well as by spray application. A still further object is to provide a concentrated form of the phosphating composition which is solid and can be easily packaged and inexpensively transported.

All of these and other objects have been accomplished by the discovery that the use of a phosphating composition containing an alkali metal or ammonium dihydrogen phosphate together with a substantial amount of a pyrophosphate and a small amount of a soluble compound of arsenic or chromium, results in phosphate coatings on the metal surfaces which not only provide an excellent base for the retention of paint, lacquer, enamel or other siccative coating but which also are appreciably more resistant to the corrosive action of humidity and immersion in water.

The high degree of corrosion-resistance gained through the practice of this invention is well illustrated by the fact that steel coated in accordance therewith has demonstrated no spread of corrosion from scratches after exposure to a 20% salt spray at 95° F. for over ten days, the unscratched portions being entirely unaffected by the salt spray.

The phosphating solution of the present invention is aqueous in character and has three essential active ingredients as hereinabove indicated, these ingredients being (1) a dihydrogen phosphate which is selected from the group consisting of sodium, potassium and ammonium dihydrogen phosphate; (2) a pyrophosphate selected from the group consisting of sodium acid pyrophosphate and potassium acid pyrophosphate; and (3) a compound of arsenic or chromium which may be any soluble compound of tri- or penta-valent arsenic or trivalent chromium, such as Na_2HAsO_4, Na_2HAsO_3, $AsCl_5$, $Cr_2(SO_4)_3$, $CrCl_3$, etc. For certain purposes it may be desired to add other ingredients as hereinafter more particularly described. The particular components and the conditions for the successful practice of this invention will now be discussed in detail.

THE DIHYDROGEN PHOSPHATE

At least one such compound as aforesaid is considered as an essential component of the phosphating solution. The preferred compound is sodium dihydrogen phosphate because it is inexpensive and can be supplied conveniently as a stable powdered or granular material. However, the other named dihydrogen phosphates can be substituted for the sodium compound wholly or in part as may on occasion seem expedient.

The concentration of the dihydrogen phosphate in the phosphating solution is preferably calculated as chemical equivalents of sodium dihydrogen phosphate (NaH_2PO_4). On this basis, the concentration (expressed as NaH_2PO_4) should be from a minimum of about 5 grams to a maximum of about 24 grams per liter of solution, the preferred concentration being about 13 to 15 grams per liter.

THE PYROPHOSPHATE

Either sodium or potassium acid pyrophosphate or a mixture of the same should be present in the solution. It is again preferable that the concentration be calculated on the basis of the sodium compound ($Na_2H_2P_2O_7$). The concentration range contemplated for use (on this basis) is from about 1 to about 20 grams per liter of solution, the preferred concentration being about 9 to 10 grams per liter.

The precise function of the pyrophosphate in the solution is not accurately known, although its omission causes the procurement of coatings of generally unacceptable quality. It is known that the pyrophosphate hydrolyzes

to some extent under operating conditions to produce dihydrogen phosphate according to the equation

$$M_2H_2P_2O_7+H_2O\rightarrow 2MH_2PO_4$$

This hydrolysis is relatively slow, however, and unchanged pyrophosphate is normally present in the solution.

ACIDITY

The hydrogen ion concentration of the solution, conveniently expressed as pH, is controlled by the relative amounts of the ortho and the pyrophosphate present, the total effect being substantially that of a buffered solution. The normal operating pH should be within the range of about 4.1 to 6.5, it being understood that the pH of a freshly made solution will be in the lower part of this range, and will normally tend to increase during operation to a pH of about 5 to 5.5. The preferred operating range for pH is about 4.8 to 5.2.

In addition to the pH, the solution should be controlled with respect to total acidity, as determined by standard titration procedures, wherein a 10 ml. sample of the solution is titrated with 0.1 normal sodium hydroxide to a phenolphthalein end point. The total acidity is then represented by the number of milliliters of base used, this number usually being referred to as "points." The total acidity of the operating solution should be within the range of about 5 to 27 points, and preferably in the range of 17 to 22 points. The determination of total acidity is a convenient measure for the degree of depletion of the solution (during use), and the need for replenishment can be judged accordingly. Moreover, the pH can if necessary be adjusted to a particular range by addition of small amounts of an acid such as phosphoric acid or a base such as caustic soda. This is sometimes a convenient method of maintaining the pH within the preferred range when replenishment is still not needed.

ARSENIC OR CHROMIUM ADDITIVES

At least one compound of the group aforementioned is essential for attainment of the highly corrosion-resistant coatings in accordance with this invention. The concentration of arsenic or chromium compound in the phosphating solution is preferably calculated as the chemical equivalent of arsenic ion (As^{+5}). On this basis, the concentration should be from a minimum effective amount of about 0.02 gram to a maximum practical amount of about 0.2 gram per liter, the preferred concentration being 0.046 to 0.053 gram per liter (expressed as As^{+5}).

OTHER ADDITIVES

While the phosphating solution described will give desirable results in forming coatings on articles of iron, steel and zinc, it is usually preferably to include with the essential ingredients a compound of copper, for its accelerating effect and/or a nitrate which appears to further improve the corrosion resistance. The copper compound may, for example, be copper sulfate, cupric nitrate, cupric chloride, etc. It may be present in the bath in an amount of 0.002 to 0.013 gram copper ion per liter, the concentration being preferably about 0.0036 to 0.006 gram per liter.

The nitrate, which may for example be sodium, ammonium or potassium nitrate may be present in the bath in relatively large amounts, on the order of 1.5 to 7.3 grams nitrate ion per liter, an amount in the range of 4.4 to 5.1 grams per liter being preferred.

Other additives such as nitrites, sulfites or bromates may also be included in the bath if desired.

In practicing the present invention the metal stock to be coated, if not already substantially grease- and soil-free, should be cleaned by any standard, convenient method. After cleaning and, if necessary, rinsing, the metal is subjected to the phosphating solution, which may be applied by spray or as an immersion bath. The solution, which may be maintained at any temperature up to boiling, works best at temperatures between about 120° and 180° F. An application time of about 30 to 120 seconds is quite adequate to produce excellent coatings if the solution is sprayed.

Surprisingly, the solutions of this invention give remarkably good coatings when applied by the immersion technique, this being a distinct advantage over the previously known alkali metal phosphate baths, which have generally been considered only suitable in spray application. No obvious explanation for this unexpected advantage is apparent. The immersion time should be about one to five minutes to obtain a good coating.

AFTER-RINSE

A further process step which, while not absolutely critical, is in many cases preferred, is treatment of the coated article in a rinse solution which contains chromium. Rinses of this type are well known in the art, and their effectiveness in "sealing" the phosphate coating to insure its impermeability has led to their almost universal use in commercial phosphating processes. While adequate coatings are obtainable by the present process without using the rinse, it is generally desirable that such a rinse be used, in order to obtain highest quality coatings. A typical chromium-containing rinse may be a solution containing 0.1 to 2.0 grams CrO_3 and 0.03 to 0.20 gram H_3PO_4 per liter of rinse.

THE CONCENTRATE

It is well known in the phosphating field that from the economic standpoint it is desirable to provide a concentrated form of the phosphating compositions, for greater ease in storing and shipping. Often such a concentrate must take the form of a concentrated aqueous solution, since in these cases one or more of the ingredients is not conveniently available in solid form. In the present instance, while the phosphating composition herein disclosed may, if desired, be handled as a concentrated solution it is possible and generally preferable to supply all the ingredients as solids, so that the concentrate is a powdered, crystalline or granular mixture, which is chemically stable and non-caking on long storage.

In the solid concentrate the amounts of the different components correspond to the amounts present in the operating bath, and may be summarized as follows:

Component	Limits	Preferred Range
	Parts	*Parts*
Dihydrogen phosphate (calculated as NaH_2PO_4)	16–80	43–46
Pyrophosphate (calculated as $Na_2H_2P_2O_7$)	3–70	31–33
Arsenic or chromium compound (calculated as As^{+5})	0.06–0.6	0.17–0.22
Copper compound (optional) (calculated as Cu)	0.006–0.04	0.012–0.02
Nitrate (optional) (calculated as NO_3)	5.2–22	15–17

The operating bath can be prepared from the concentrate by simply dissolving the concentrate in water, the amount of concentrate being about 1 to 8 ounces per gallon and preferably about 3 to 5 ounces per gallon. A further advantage is that when the operating bath has become depleted through use, which is ascertainable as hereinabove mentioned by standard titration for total acidity, it may readily be replenished by addition of more of the concentrate, and this may be done at intervals or more or less continuously as desired. Replenishment in this manner is possible because apparently the components of the composition are depleted at about the same rate, without any awkward disproportionation that would entail laborious adjustments.

Following are several examples illustrating typical phosphating solutions made in accordance with the present invention.

Example I

	Grams
Monosodium phosphate (NaH_2PO_4)	13.5
Sodium acid pyrophosphate ($Na_2H_2P_2O_7$)	9.8
Sodium arsenate ($Na_2HAsO_4 \cdot 3H_2O$)	0.24

Water to make 1.0 liter.

Example II

Monosodium phosphate	14.0
Sodium acid pyrophosphate	9.8
$Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 2H_2O$	1.0

Water to make 1.0 liter.

Example III

Monopotassium phosphate (KH_2PO_4)	15.3
Sodium acid pyrophosphate	9.8
Sodium arsenate	0.24

Water to make 1.0 liter.

Example IV

Monosodium phosphate	13.5
Potassium acid pyrophosphate ($K_2H_2P_2O_7$)	11.2
Sodium arsenate	0.24

Water to make 1.0 liter.

Example V

Monosodium phosphate	6.0
Sodium acid pyrophosphate	7.0
Sodium arsenate	0.24

Water to make 1.0 liter.

Example VI

Monosodium phosphate	20
Sodium acid pyrophosphate	20
Sodium arsenate	1.4

Water to make 1.0 liter.

Example VII

Monosodium phosphate	20
Sodium acid pyrophosphate	10
Sodium orthoarsenite (Na_2HAsO_3)	0.15

Water to make 1.0 liter.

Example VIII

Monosodium phosphate	13.5
Sodium acid pyrophosphate	10.0
Sodium arsenate	0.25
Sodium nitrate ($NaNO_3$)	7.0

Water to make 1.0 liter.

Example IX

Monosodium phosphate	13.5
Sodium acid pyrophosphate	9.8
Sodium nitrate	6.6
Copper sulfate ($CuSO_4$)	0.012
Sodium arsenate	0.24

Water to make 1.0 liter.

Example X

Monosodium phosphate	13.5
Sodium acid pyrophosphate	9.8
Copper sulfate	0.012
Sodium arsenate	0.24

Water to make 1.0 liter.

Example XI

The dry concentrate form of the solution given in Example IX is made up as follows:

	Wt. percent
NaH_2PO_4 (powder)	44.9
$Na_2H_2P_2O_7$ (powder)	32.26
$NaNO_3$ (crystals)	22.0
$CuSO_4$ (powder)	0.04
$Na_2HAsO_4 \cdot 3H_2O$ (powder)	0.8
	100.00

The dry ingredients are thoroughly blended. This formulation is stable and will not decompose or cake up even after extended storage.

Example XII

The data given in Table I below was obtained in the following manner: Test panels cut from auto body stock steel (SAE 1010) were first cleaned in an alkaline cleaner, rinsed free of alkali and then sprayed with phosphating solutions according to the scheme:

	Panels
#1 solution of Example I	6
#2 solution of Example VIII	6
#3 solution of Example X	6
#4 solution of Example IX	6
#5 solution similar to Example I except that the pyrophosphate and arsenate is omitted	6
#6 solution similar to Example X except that the pyrophosphate is omitted	6

The spray treatment was for 1 minute and the solution temperature was 150° F. in each case. The panels were then water-rinsed, further rinsed in a solution containing 1 gram CrO_3 and 0.03 gram H_3PO_4 per liter and then dried. The coating weight was measured at this point. Each panel was then given 2 coats of a commercial refrigerator enamel. Two panels from each set were then subjected to (1) standard ASTM salt spray test (B–117–54T); (2) humidity test at 100% humidity and 110° F. for 1000 hours; and (3) water immersion test in distilled recirculated water at 115–120° F. for 500 hours.

TABLE I

Panel Series	Average Coating Weight (mg./sq. ft.)	Ratings		
		Salt Spray	Humidity	Water Immersion
1	44	E, G	E, E	E, E
2	37	E, E	E, E	E, E
3	50	E, E	E, G	E, G
4	47	E, E	E, E	E, G
5	19	P, P	G, G	F, F
6	33	F, VP	E, F	P, VP

(E=excellent, G=good, F=fair, P=poor, VP=very poor.)

The operation of phosphate coating baths is often troubled by the formation of copious precipitates, known in the trade as "sludge," which are composed principally of certain insoluble products of the reaction that takes place at the metal surface. The formulations of this invention have the advantage that remarkably little sludge is formed. This allows for prolonged continuous operation without need for shut-down, an important consideration for assembly-line practice.

Having described our invention, we claim:

1. A phosphating composition for forming phosphate coatings on iron, zinc and their alloys consisting essentially of a dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, an acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate and a small amount relative to the proportions of said first two ingredients of a soluble compound of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, the amount of said last mentioned ingredient being effective to improve the corrosion resistance of the phosphate coatings produced by said composition.

2. The composition of claim 1 wherein said metal ion is pentavalent arsenic.

3. A phosphating solution for forming phosphate coatings on iron, zinc and their alloys consisting essentially of a dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate

in amounts of 5 to 24 grams per liter, an acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate in amounts of 1 to 20 grams per liter, both based on chemical equivalents of the respective sodium compounds and a soluble compound of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium in amounts of 0.02 to 0.2 gram per liter based on chemical equivalents of arsenic ion.

4. A composition for preparing phosphating solutions consisting essentially of 16 to 80 parts dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, 3 to 70 parts acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate, parts being by weight based on chemical equivalents of the respective sodium compounds, 5.2 to 22 parts nitrate ion, 0.006 to 0.04 part copper ion and 0.06 to 0.6 part by weight of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, based on chemical equivalents of arsenic ion.

5. The composition of claim 4 wherein said dihydrogen phosphate is sodium dihydrogen phosphate, said acid pyrophosphate is sodium acid pyrophosphate and said nitrate ion is in the form of sodium nitrate.

6. The method of forming phosphate coatings on iron, zinc and their alloys comprising treating the surface of the metal with a solution consisting essentially of 5 to 24 grams per liter of dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, 1 to 20 grams per liter acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate, both based on chemical equivalents of the respective sodium compounds, and 0.02 to 0.2 gram per liter of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, said solution being at a temperature of 120 to 180° F.

7. The method of preparing surfaces of iron, zinc and their alloys for the reception of a siccative coating thereon comprising treating said surface at a temperature of 120 to 180° F. with an aqueous solution consisting essentially of 5 to 24 grams per liter of dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, 1 to 20 grams per liter acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate, both based on chemical equivalents of the respective sodium compounds, and 0.02 to 0.2 gram per liter of a metal iron of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, rinsing said treated surface with water and then further treating said surface with a solution containing 0.1 to 20 grams CrO_3 and 0.03 to 0.20 gram H_3PO_4 per liter.

8. A composition for preparing phosphating solutions consisting essentially of 16 to 80 parts dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, 3 to 70 parts acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate, parts being by weight based on chemical equivalents of the respective sodium compounds, and 0.06 to 0.6 part by weight of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, based on chemical equivalents of arsenic ion.

9. A phosphating solution for forming phosphate coatings on iron, zinc and their alloys prepared by dissolving in water from 1 to 8 ounces per gallon of a composition consisting essentially of 16 to 80 parts dihydrogen phosphate of the group consisting of sodium, potassium and ammonium dihydrogen phosphate, 3 to 70 parts acid pyrophosphate of the group consisting of sodium and potassium acid pyrophosphate, parts being by weight based on chemical equivalents of the respective sodium compounds, and 0.06 to 0.6 part by weight of a metal ion of the group consisting of pentavalent arsenic, trivalent arsenic and trivalent chromium, based on chemical equivalents of arsenic ion.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,954,309 September 27, 1960

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 4, for "iron" read -- ion --.

Signed and sealed this 11th day of April 1961.

(SEAL)
Attest:
ERNEST W. SWIDER
Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents