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METHOD AND COMPOSITION FOR PRODUCING PHOSPHATE COATINGS ON METAL

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This invention relates to a method and composition for producing phosphate coatings on metal. More specifically, this invention concerns a method and material for producing on iron or steel a coating consisting predominately of iron phosphate.

For some years, the ferous metal coating art has distinguished sharply between the so-called coating phosphates and the so-called non-coating phosphates. The coating phosphates comprise those phosphates of metals such as zinc and manganese for example, which metals are incorporated into the coating as a result of the coating process. On the other hand, coating solutions of alkali metal dihydrogen phosphates are commonly referred to as the non-coating phosphates. They form fine grained, strongly adherent iron phosphate coatings on ferrous metal, and the alkali metal component of the phosphate coating chemicals does not enter into the coating formed on the surface of the metal. Examples of these non-coating phosphates are sodium, potassium, ammonium, etc.

As the phosphate coating art developed, many chemical accelerators were proposed and successfully used, both for the coating phosphates and for the non-coating phosphates. Such accelerators included nitrates and nitrites, as well as varieties of other substances, most of which acted as oxidizing agents and were gradually consumed in the process. The accelerators of the prior art have all had varying degrees of effectiveness in conjunction with the non-coating phosphates.

Various methods have been employed to prepare the surface of the metal prior to the deposition of the phosphate coating. Examples are solvent degreasing, alkali cleaning, emulsion cleaning, sand blasting, etc. Of the methods listed above for cleaning and preparing the surface of the metal, one very effective, economical and commercially used process is alkali cleaning, wherein the metal is subjected to the action of strong alkali solution containing alkali metal hydroxide, carbonate, phosphate, silicate, etc., or preferably mixtures thereof. Treating the metal in a strong alkali solution and subsequently rinsing in water before subjecting the ferrous metal to the phosphate coating bath affects the surface of the metal in such a manner that it is difficult to consistently produce a fine grained, uniform tenaciously adherent coating of iron phosphate on the metal when utilizing conventional non-coating phosphate baths. Also, the alkali carry-over from the rinse, into the phosphating solution, increases the pH of the bath which adversely affects the coating efficiency.

It is accordingly an object of this invention to overcome the difficulties just discussed. Another object is to provide a "non-coating" phosphate bath containing an accelerator which is very effective even when present in minute proportions. Still another object of this invention is to provide a method and solution for providing a fine, uniform, tenaciously adherent iron phosphate coating on a ferrous metal. Still another object is to provide a method of providing phosphate coatings on successive ferrous metal objects which carry small quantities of alkali on their surfaces, and of maintaining the phosphate coating bath at a proper pH notwithstanding such alkali carry-over.

Other objects and advantages of this invention will become apparent hereinafter.

In accordance with this invention ferrous metal objects to be coated are first subjected to an alkali cleaning operation, for example by treating the metal with a solution containing any proportions of the normal ingredients of an alkali cleaner such as caustic soda, soda ash, sodium phosphate, silicate, etc. Normally these solutions are hot when used. The cleaning step may be accomplished by immersion, spraying, or any other suitable procedure. The metal objects are then removed from the alkali cleaning solution and are rinsed in water.

It has been discovered that excellent, fine grained, uniform, tenaciously adherent iron phosphate coatings may be formed on the alkali treated metal surface after rinsing with water by treating the metal surface with a phosphate coating solution consisting essentially of alkali metal dihydrogen phosphate containing an accelerator which consists essentially of alkali metal nitrate combined with a small proportion of alkali metal molybdate. Preferably, the coating solution run-off is collected for re-use. It has further been discovered that, when the coating solution run-off is collected for re-use, it may be maintained at a substantially constant pH notwithstanding the build-up of alkali from the carry-over, by adding phosphoric acid to the solution.

In referring herein to "alkali metal" dihydrogen phosphates, "alkali metal" nitrate, and "alkali metal" molybdate, it is of course intended that the sodium, potassium and ammonium compounds of those radicals be included, together with lithium and the other well known alkali metals.

Alkali metal molybdates in accordance with this invention include the normal molybdates (MoO_4-2), the dimolybdates (Mo_2O_7-2), trimolybdates and other polymolybdates up to decamolybdates ($Mo_{10}O_{31}$-2) and above. For example, commercial ammonium molybdate is $(NH_4)_6Mo_7O_{24}.4H_2O$.

Although the relative proportions of the ingredients of the phosphate coating solution may vary within wide limits, such proportions in the concentrate are preferably as follows:

	Percent by weight
Phosphoric acid (75%)	1.00 to 6.0
Alkali metal dihydrogen phosphate	10.00 to 37.5
Alkali metal nitrate	2.00 to 13.5
Alkali metal molybdate	.04 to 1.2
Water to make 100.00.	

In the working solution, the preferred proportions are as follows:

	Percent by weight		
Phosphoric acid (75%)	0.124	to	.238
Alkali metal dihydrogen phosphate	0.922	to	1.050
Alkali metal nitrate	0.400	to	0.762
Alkali metal molybdate	0.0002	to	0.0005
Water	98.5538	to	97.9495
	100.0000		100.0000

An alkali such as sodium carbonate or sodium hydroxide and free phosphoric acid is incorporated into the coating solution, as required to maintain the preferred optimum pH range.

Example 1

In accordance with a preferred embodiment of this invention, a concentrated solution was prepared consisting of:

	Percent by weight
Phosphoric acid (75%)	4.00
Mono sodium dihydrogen phosphate	25.00
Sodium nitrate	10.00
Sodium molybdate (Na_2MoO_4)	0.05
Water	60.95
	100.00

The working solution was prepared by adding the above concentrate to water in the volume ratio of 3 parts concentrate to 97 parts water. The above solution will have a pH of between 2.9 and 3.3 depending upon the water used. The bath will deposit uniform fine grained, tenaciously adherent iron phosphate coating on ferrous metal. However, it is desirable to adjust the pH of the bath to about 4.2 by the addition of the proper amount of alkali such as soda ash or caustic soda and thereafter the continuous processing of ferrous metal through the bath will result in a gradual change in respect to pH, whereby the bath will operate between a pH of 4.2 and 5.8 and continue to produce uniform, fine grained, tenaciously adherent iron phosphate coatings. The desired pH range is 4.6 to 5.2, the recommended optimum pH being 4.8. A metal was prepared for the coating operation by alkali cleaning, followed by a water rinse. The working phosphate coating solution was then sprayed on the rinsed ferrous metal to produce an iron phosphate coating, after which the metal was rinsed with water, treated with chromic acid, and painted.

As small quantities of alkaline cleaner are carried from the alkali cleaning stage into the water rinse stage and from the rinse into the phosphate stage, the pH of the phosphate coating solution tends to rise above optimum. When this pH exceeds 5.2, sufficient phosphoric acid is added to the working solution to lower the pH to the optimum operating condition, preferably pH 4.5. One suitable material for adjusting this pH has the following composition:

	Percent
Phosphoric acid (75%)	83
Water	17

Successive metal objects coated in accordance with this example are quickly provided with fine grained uniform iron phosphate coatings of excellent adherence and bonding properties for the subsequent application of paint.

Other specific examples of working solutions in accordance with this invention are as follows:

Example 2

	Percent by weight		
Phosphoric acid (75%)	0.12	to	0.20
Mono sodium dihydrogen phosphate	0.90	to	1.00
Sodium nitrate	0.40	to	0.70
Water	98.57975	to	98.09955
Sodium molybdate	0.00025	to	0.00045
	100.00000		100.00000

Example 3

	Percent by weight		
Phosphoric acid (75%)	0.08	to	0.16
Mono sodium dihydrogen phosphate	0.45	to	0.90
Sodium nitrate	0.20	to	0.50
Water	99.2697	to	98.4392
Sodium molybdate	0.0003	to	0.0008
	100.0000		100.0000

Example 4

	Percent by weight		
Phosphoric acid (75%)	0.15	to	0.20
Mono sodium dihydrogen phosphate	0.90	to	1.05
Sodium nitrate	0.45	to	0.75
Water	98.4998	to	97.9996
Sodium molybdate	0.0002	to	0.0004
	100.0000		100.0000

Example 5

	Percent by weight		
Phosphoric acid (75%)	0.16	to	0.24
Mono sodium dihydrogen phosphate	0.75	to	1.10
Sodium nitrate	0.50	to	0.70
Water	98.5898	to	97.9597
Sodium molybdate	0.0002	to	0.0003
	100.0000		100.0000

Example 6

	Percent by weight		
Phosphoric acid (75%)	0.100	to	0.200
Mono potassium dihydrogen phosphate	0.750	to	0.900
Ammonium nitrate	0.300	to	0.750
Water	98.8498	to	98.1496
Potassium molybdate (expressed as $K_2Mo_{10}O_{31}$)	0.0002	to	0.0004
	100.0000		100.0000

Example 7

	Percent by weight		
Phosphoric acid (75%)	0.120	to	0.240
Ammonium dihydrogen phosphate	0.600	to	0.850
Potassium nitrate	0.250	to	0.500
Water	98.9289	to	98.4198
Ammonium molybdate (expressed as $(NH_4)_6Mo_7O_{24}$)	0.0001	to	0.0002
	100.0000		100.0000

Example 8

Product:	Percent
Monosodium dihydrogen phosphate	25
Sodium nitrate	10
75% phosphoric acid	4
Water	61
	100

The specific gravity of the above concentrate is 1.320 at 70° F.

To each 100 lbs. of the concentrate, 22.5 grams of technical sodium molybdate are added. This concentrate is added to the bath in the required volume to give the required total acid content. The bath is adjusted to the desired pH of 4.6 by the addition of Na_2CO_3 or NaOH, and metal articles are coated as heretofore described. The total acid is between 9 and 11 points. If the pH of the bath increases to 5.2–5.8, phosphoric acid is added to reduce the pH to 4.6.

Although specific forms of the invention have been described herein for the sake of clarity, it will be appreciated that equivalents may be substituted for the components and method steps specifically described, and that certain features of the invention may be used independently of other features, all within the spirit and scope of the invention as defined in the appended claims.

Having thus described my invention, I claim:

1. In a method of producing an adherent uniform phosphate coating on a ferrous metal, the steps which

comprise spraying said metal with an aqueous solution of alkali metal dihydrogen phosphate, and accelerating the coating action by incorporating into the solution an accelerator consisting of about 0.4 to 0.76% by weight nitrate and about .0002 to .0005% by weight molybdate ions.

2. An aqueous metal coating solution consisting essentially of about 0.922% to 1.05% by weight non-coating, alkali metal dihydrogen phosphate, about 0.40% to 0.76% by weight nitrate ions, and about 0.0002% to 0.0005% by weight molybdate ions.

3. A composition for coating ferrous metals consisting essentially of:

	Percent by weight
Phosphoric acid (75%)	1.00 to 6.0
Alkali metal dihydrogen phosphate	10.00 to 37.5
Alkali metal nitrate	2.00 to 13.5
Alkali metal molybdate	.04 to 1.2
Water to make 100.00.	

4. A composition for coating ferrous metals consisting essentially of:

	Percent by weight
Phosphoric acid (75%)	4.00
Sodium dihydrogen phosphate	25.00
Sodium nitrate	10.00
Sodium molybdate (Na_2MoO_4)	0.05
Water	60.95
	100.00

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