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## PHOSPHATE COATING SOLUTION AND METHOD OF COATING FERRIFEROUS METAL

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The present invention relates to the art of producing a phosphate conversion coating on a ferriferous metal surface and is particularly concerned with that type of conversion coating which is produced by treating the surface of the metal with alkali metal phosphate solutions.

In this disclosure the term "alkali metal phosphate" is to be understood as including both sodium and potassium phosphates as well as ammonium mono and ammonium dihydrogen phosphates.

In this art as heretofore practiced the alkali metal phosphate coating baths have been employed as aqueous solutions having pH values ranging from approximately 3.2 to 6.2 although, as a general rule, a somewhat narrower pH range has been employed, say from about 4.7 to 6.0. Furthermore, it has been customary practice to include one or more of the so-called accelerating agents such, for example, as chlorates, nitrates, nitrites and peroxygen compounds which, as is well known, operate to reduce the time required for coating formation.

In prior practice another factor has also been important and that is that the type of solutions just described have had to be heated to temperatures ranging from about 170° to 180° F. in order that they may produce the desired coatings within a reasonable period of time—say from 1 to 3 minutes.

Other problems have also arisen in connection with the practices of the prior art. For instance, while nitrite ion has been recognized as an accelerating agent in baths of the type described, its use, generally speaking, has been restricted to combinations with other well known accelerators. This restricted use of the nitrite ion is a reflection of certain inherent disadvantages associated with its behavior in coating solutions of this type. For example, where an insufficient amount of accelerator is employed, no apparent coating is produced on ferriferous surfaces. Conversely, if too great an amount is employed a phenomenon known in the art as "white spot" is produced on the metal being treated and, eventually, no coating of any appreciable value can be obtained.

With nitrite accelerated alkali metal phosphate coating solutions it has been observed also that the coatings produced are lighter in weight by as much as 20% to 25% as compared to coatings resulting from the use of chlorates or peroxygen compounds as accelerators, which lighter weight coatings are not as suitable for pre-paint use since their corrosion resistance is definitely inferior to that of heavier coatings.

More recently it has been found that the use of bromates as accelerating agents not only yields heavier coating weights than are obtained with nitrites but also permits the use of lower reaction temperatures on the order of 150° to 160° F., although some sacrifice in coating weight results from the use of such lower bath temperatures. However, bromate accelerated baths often produce coatings which are mottled or otherwise uneven in appearance, which uneven appearance frequently affects the appearance of the treated metal surface after it has been given a final siccative finish such as paint or the like.

With all of the foregoing limitations of the prior art in mind the principal object of the present invention may be said to reside in the provision of an improved nitrite accelerated alkali metal phosphate coating process by

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means of which it is possible to produce, on ferriferous metal surfaces, highly corrosion resistant and extremely effective paint-bonding coatings at lower temperatures than has been possible heretofore.

A concomitant object of this invention is the provision of a solution for and a method of applying phosphate conversion coatings to ferriferous metal surfaces of more uniform appearance and of greater weight than has ever been possible heretofore with any of the nitrite accelerated alkali metal phosphate coating baths familiar to the art.

How the foregoing objects and advantages as well as others which may appear hereinafter are attained will become apparent in connection with the following description.

The present invention is based upon the discovery that if at least 0.3 gram/liter of a saturated alkyl secondary amine of the formula:  $H-N-(C_nH_{2n}X)_2$  wherein X is selected from the group consisting of hydrogen and hydroxyl, and  $n$  is an integer of from 2 to 4 inclusive, is added to a nitrite accelerated alkali metal phosphate coating solution having a pH of from 4.0 to 5.8, such solution can be employed as a coating bath in the treatment of ferriferous metal surfaces to produce an extremely uniform highly corrosion resistant coating of substantially greater weight than heretofore possible in this art even when customary or normal treating cycles of 1 to 3 minutes are employed and, furthermore, that these improvements in result can be obtained at appreciably lower coating bath temperatures than have ever been practical heretofore.

As noted hereinabove, at least 0.3 gram/liter of the specified secondary amine must be incorporated into the coating solutions of this invention. Where less than this minimum amount is utilized no appreciable coating will result and the benefits of this invention will be completely lost.

Although use of as little secondary amine as 0.3 gram/liter yields the desired coatings at lower operating temperatures, it has been discovered that 0.5 gram/liter is a preferred minimum in order to insure, at all times throughout operation of the bath, that a sufficient amount of this additive is present.

So far as the upper limit of secondary amine is concerned it has been found that there is no apparent deleterious effect from the use of as much as 30 grams/liter of these compounds. Use of even higher amounts thereof are limited in some instances by solubility considerations, but where a particular secondary amine falling within the generic formula listed hereinabove is soluble in an infinite degree, such, for example, as diethylamine, no limitation on the amount used has been found. In the interests of economy, however, it is preferred not to exceed about 1 gram/liter of secondary amine in the coating solutions of this invention.

Typical secondary amines which fall within the generic formula listed above include the diethyl, dipropyl and dibutyl-amines as well as the diethanol, dipropanol and dibutanol amines.

With respect to the amount of nitrite ion (calculated as  $NO_2$ ) which should be utilized in association with the secondary amines above described, certain rather unexpected factors have been discovered which will now be described. Where the quantity of secondary amine employed in the solution ranges from 0.3 to approximately 1 gram/liter it is essential that the grams of nitrite ion per liter of coating solution should lie within the range determined by the following equations:

A. For the minimum amount of  $NO_2$ ,

$$\frac{0.3}{\text{Molecular weight of amine used}} \times 46$$

B. For the maximum amount of NO<sub>2</sub>,

$$\frac{1}{\text{Molecular weight of amine used}} \times 46$$

Where the quantity of secondary amine employed is greater than approximately 1 gram/liter it is necessary to employ not less than the minimum quantity of nitrite ion as calculated by Equation A, while at the same time the maximum quantity of NO<sub>2</sub> may go well beyond the amount which is determined by Equation B. Indeed, just as soon as more than approximately 1 gram/liter of secondary amine is employed there seems to be no need to limit the quantity of nitrite ion which can be utilized in the bath and as much as 10 grams/liter of NO<sub>2</sub> has been found to produce completely satisfactory results. The only limitation on the upper quantity would seem to be imposed by considerations of economy and unnecessary wastage of this salt. Furthermore, I have found that use of relatively large excesses of nitrite ion relative to the amount of secondary amine employed where the content of the latter is approximately 1 gram/liter or more has, somewhat surprisingly, made it possible to greatly increase coating weights without impairment of their quality. In short, with my process I find that coating weights can be substantially increased by increasing the quantity of nitrite employed although this advantage cannot be realized to its fullest extent except where the bath contains more than approximately 1 gram/liter of the secondary amine.

To refer again to Equations A and B, in situations where the quantity of amine lies between 0.3 and 1 gram/liter the following specific example is suggested. Where diethylamine is employed and is utilized in an amount of from 0.3 to 1 gram/liter, then the amount of nitrite ion which is required must lie between the limits determined by substituting the molecular weight of diethylamine (73.14) in the equations. This will give a range for the nitrite (NO<sub>2</sub>) of 0.18 to 0.63 gram/liter of coating solution. However, where the amount of amine employed is greater than 1 gram/liter it is only necessary to be sure that at least 0.18 gram of NO<sub>2</sub> per liter is employed, although many times more than the maximum of 0.63 gram/liter is entirely practical and, as stated above, as much as 10 grams/liter of NO<sub>2</sub> have been found to produce completely satisfactory results. This fact was completely unpredictable insofar as prior art experience with nitrite accelerated alkali metal phosphate coating solutions is concerned, and I have discovered that by increasing the nitrite content coating weights of more than twice that normally realized heretofore can be obtained with my invention.

The nitrite ion may be introduced into the alkali metal phosphate coating solution as a salt, such, for example, as an alkali or alkaline earth metal salt. Due to commercial availability the sodium salt is preferred. However, the only limitation on the salt used is that the cation portion thereof exhibit no deleterious effect upon the coating reaction.

So far as control over the nitrite content of the improved phosphate coating solutions of this invention is concerned, this is readily accomplished either by a permanganate titration in acidic medium or by an iodometric titration according to well established art practices.

With respect to control of the secondary amine content of my improved coating solutions, it has been found that a visual control is both adequate and reliable so long as the coating solution contains nitrite ion and is not deficient in alkali metal phosphate ion or pH. For example, where coating quality begins to deteriorate as evidenced by thinner coatings being produced on ferrous surfaces, a nitrite titration is immediately taken and, if such titration shows the presence of nitrite ion, it is only

necessary to add at least 0.3 gram/liter of secondary amine in order to restore the bath to its original and desired coating ability. Where the nitrite titration shows a deficiency of this accelerator, it is preferred practice to add nitrite without adding secondary amine, since results with this process show that the secondary amines are not consumed in the coating reaction, and that the only loss thereof is through entrainment or drag-out during coating operations.

As noted hereinabove, the alkali metal phosphate coating solutions of this invention must be maintained within a pH range of 4.0 to 5.8. Where pH values of less than 4.0 are employed the solution exhibits an undesirable etching action on the ferrous metal surfaces thereby impairing coating formation. Conversely, where the solution pH is permitted to rise above about 5.8, the coatings produced will be found to be thin and powdery, while still further pH increases will result in no coating being produced upon the metal surfaces. A preferred pH range for operating the process of this invention has been found to be from 4.5 to 5.7 since optimum coatings are produced within this narrower pH limitation.

Adjustment of the coating solution pH may be made, where needed, by the addition of small increments of either phosphoric acid or sodium hydroxide according to well established art practices.

One of the outstanding improvements derived from the process of this invention is the ability to obtain coatings on ferrous metal surfaces at temperatures of from 120 to 150° F. As noted hereinabove prior usage of alkali metal phosphate coating solutions necessitated the employment of coating temperatures of 170 to 180° F. in order to obtain satisfactory results. The reduced operating temperatures made possible by the improvements of this invention represent considerable economic advantages to the coating industry.

The 120 to 150° F. operating temperature range applies to dip, spray or roller coating applications and, while no harmful results are obtained by use of coating temperatures above 150° F., that is temperatures of 170 to 180° F., or even higher, excessive temperatures have been found to result in reduced coating weights, and such temperatures are completely unnecessary and represent an economic waste when utilizing the present process. Temperatures below the minimum of 120° F. should not be used since it has been found that the desired coating weights will not be obtained at such low temperatures within reasonable operating cycles.

So far as the length of time of treatment is concerned, it has been found that the coating cycle will provide the desired coatings when operated for as little time as 30 seconds to as much time as 5 minutes. However, the preferred operating cycle is from 1 to 3 minutes utilizing a temperature of from about 135 to 145° F. Use of lower treating temperatures will necessitate longer contact times, while, conversely, use of slightly higher treating temperatures will require shorter contact cycles.

In order to contrast the results obtainable with the process of the present invention with results obtained from a typical prior art nitrite accelerated alkali metal phosphate coating solution, the following tests were conducted:

A tap water solution was prepared containing, per liter, 10 grams of monosodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>). The pH of this solution was 5.2.

Portions of this alkali phosphate solution were then utilized for the treatment of clean, cold-rolled steel panels utilizing contact cycles of 2 minutes and coating temperatures of 140° F., except for Example #2 which utilized a temperature of 175° F. and Example #3 which utilized a temperature of 120° F., the Example #2 temperature being typical of that used in the prior art. Secondary amines and nitrite accelerator (as NaNO<sub>2</sub>) were

added to these solutions prior to coating utilization in accordance with the following table:

Table I

Example	Secondary Amine		NO <sub>2</sub> , Grams per liter	C.W. mg./Ft. <sup>2</sup>	Panel Appearance
	Type	Grams/liter			
1			0.62	36	Streaked, non-uniform red-gold coating, deep blue.
2			0.62	36	
3	diethylamine	1.0	0.62	49.6	Do.
4	diethanolamine	1.0	0.44	50.9	Do.
5	diisopropanolamine	1.0	0.34	46.0	Do.
6	dibutylamine	1.0	0.35	59.5	Do.
7	dibutylamine	0.5	0.18	51.3	Do.

Following coating each panel was subjected to an immediate water rinse after which a dilute chromic acid rinse was utilized in accordance with well established art practice. A baking enamel was then applied to these panels, and following a curing cycle they were subjected to standard salt spray tests (ASTM-B11757T), the results of which showed substantial improvement in corrosion resistance in favor of the secondary amine-nitrite produced coatings in comparison with coatings resulting from prior art practice.

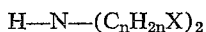
From the foregoing tests it is readily apparent that the use of nitrite accelerated alkali metal phosphate coating solutions, which solutions also contain an amount of secondary amine from the class described, produced coatings of higher weight and superior corrosion resistance at lower temperatures than could heretofore be obtained with nitrite accelerators.

It is within the purview of this invention to employ an amount of wetting agent in the improved alkali metal phosphate coating solutions of this invention, if desired, since, as is well known in the art, such wetting agents serve to improve the solution's ability to wet thoroughly the entire metal surfaces introduced therein.

I claim:

1. In the art of forming a phosphate conversion coating on a ferriferous metal surface wherein an aqueous alkali metal phosphate coating solution is applied to the surface to form the coating: the method which comprises including in the coating solution, as addition agents, the following ingredients:

(1) from 0.3 to 1 gram/liter of a saturated alkyl secondary amine of the formula:



wherein X is selected from the group consisting of hydrogen and hydroxyl, and n is an integer of from 2 to 4 inclusive and

(2) nitrite ion (calculated as NO<sub>2</sub>) within the range determined by the following equations:

(A) For the minimum amount of NO<sub>2</sub>,

$$\frac{0.3}{\text{Molecular weight of secondary amine used}} \times 46$$

(B) For the maximum amount of NO<sub>2</sub>,

$$\frac{1}{\text{Molecular weight of secondary amine used}} \times 46$$

maintaining the pH of said solution at from 4.0 to 5.8; and maintaining the temperature of the solution at not less than 120° F.

2. The method of claim 1 wherein the temperature of the solution is maintained at from 120° F. to 150° F.

3. The method of claim 1 wherein the temperature of the solution is maintained at from 135° F. to 145° F. and the treatment is continued for from 1 to 3 minutes.

4. The method of claim 1 wherein the pH is maintained at from 4.5 to 5.7.

5. In the art of forming a phosphate conversion coat-

ing on a ferriferous metal surface wherein an aqueous alkali metal phosphate coating solution is applied to the surface to form the coating: the method which comprises including in the coating solution, as addition agents, the following ingredients:

(1) upwards of 1 gram/liter of a saturated alkyl secondary amine of the formula: H—N—(C<sub>n</sub>H<sub>2n</sub>X)<sub>2</sub> wherein X is selected from the group consisting of hydrogen and hydroxyl, and n is an integer of from 2 to 4 inclusive and

(2) a quantity of nitrite ion (calculated as NO<sub>2</sub>) which is not less than

$$\frac{0.3}{\text{Molecular weight of secondary amine used}} \times 46$$

maintaining the pH of said solution at from 4.0 to 5.8; and maintaining the temperature of the solution at not less than 120° F.

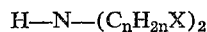
6. A bath for use in forming a phosphate conversion coating on a ferriferous surface, said bath consisting essentially of:

(1) an aqueous alkali solution of phosphates from the class which consists of sodium, potassium, and ammonium mono and dihydrogen phosphates in coating producing concentration and

(2) the following ingredients as addition agents:

(A) not less than 0.18 gram/liter of nitrite ion (calculated as NO<sub>2</sub>) and

(B) not less than approximately 1 gram/liter of saturated alkyl secondary amine of the formula:



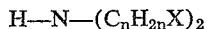
wherein X is selected from the group consisting of hydrogen and hydroxyl, and n is an integer of from 2 to 4 inclusive.

7. A bath for use in forming a phosphate conversion coating on a ferriferous surface, said bath consisting essentially of:

(1) an aqueous alkali solution of phosphates from the class which consists of sodium, potassium, and ammonium mono and dihydrogen phosphates in coating producing concentration and

(2) the following ingredients as addition agents:

(A) from 0.3 to 1 gram/liter of saturated alkyl secondary amine of the formula:



wherein X is selected from the group consisting of hydrogen and hydroxyl, and n is an integer of from 2 to 4 inclusive and

(B) nitrite ion (calculated as NO<sub>2</sub>) the quantity of ion being within the range determined by the following equations:

(1) For the minimum amount of NO<sub>2</sub>,

$$\frac{0.3}{\text{Molecular weight of amine used}} \times 46$$

(2) For the maximum amount of NO<sub>2</sub>,

$$\frac{1}{\text{Molecular weight of amine used}} \times 46$$

References Cited in the file of this patent

UNITED STATES PATENTS

2,298,280	Clifford et al. ....	Oct. 13, 1942
2,318,605	Goebel et al. ....	May 11, 1943
2,328,540	Hochwalt .....	Sept. 7, 1943
2,333,206	Sloan .....	Nov. 2, 1943
2,574,955	Bishop .....	Nov. 13, 1951
2,835,618	Keller et al. ....	May 20, 1958
2,840,498	Logue et al. ....	June 24, 1958