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METHOD OF COATING METALS WITH AMINE PHOSPHATE COATING AND COMPOSITION THEREFOR

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14 Claims. (Cl. 148—6.16)

This invention concerns the treatment of surfaces of mild steel, zinc, and aluminum for the purpose of producing thereon a protective coating without the necessity of pretreatment of the metal surface. The invention concerns particularly the coating of steel, zinc, and aluminum by the chemical action of a phosphate containing bath on the metal surface wherein the phosphate is an amine phosphate.

This application is a continuation-in-part of my prior copending application, Serial No. 209,323, filed February 3, 1951, for Amine Phosphate Coating Solutions, now abandoned.

It is common practice in the art of metal coating to treat metal surfaces with acidic solutions of phosphates where the phosphate may be phosphoric acid or a salt of phosphoric acid. It is also known that in particular instances an organic phosphate may be used in a non-aqueous solution and in other instances may be used to provide a source of phosphoric acid by the decomposition of the organic phosphate at an elevated temperature. In connection with organic phosphates, for example, Prutton in U. S. Patent No. 2,224,695 discloses that esters and ester salt derivatives of phosphoric acid may be used to form a coating of an organic iron phosphate on the surface of a metal where the ester is used in a non-aqueous media. Further, he discloses that the presence of moisture accelerates the reaction of such organic phosphates in the formation of an organic iron phosphate coating.

An essential feature of the present invention lies in the use of an aqueous medium and the formation of a metal phosphate coating rather than an organic metal phosphate coating.

Phosphates have been classified as "coating phosphates" or "non-coating phosphates" depending on whether the cation associated with the phosphate becomes an essential constituent of the coating or whether the phosphate formed is substantially that of the metal coated. The difference between these two coating mechanisms can become very important from an economic point of view when the cation associated with the phosphate is derived from a relatively expensive source. Again using the above-mentioned patent by way of example, the coating formed is an organic iron phosphate. Therefore, the phosphate was used as a coating phosphate and the concentration of organic material would be depleted constantly during use. It is a feature of the present invention that an organic phosphate is used as a non-coating phosphate.

An additional serious problem which is encountered in this art concerns the nature of the metal surface to be treated. The effectiveness of the best coating baths known is impaired considerably when the metal surfaces are dirty or contain finger marks, grease and other residues not normally soluble in the coating bath. This problem has been solved to some extent by pretreatment of the metal surfaces with grease solvents, and blasting, etc. In general, however, the effectiveness of coating baths has been linked closely with the effectiveness of metal pretreatment.

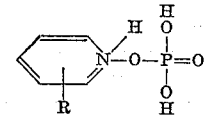
It is, therefore, an object of this invention to provide a composition for the forming of an adherent metal phosphate coating on the surface of mild steel, zinc, or aluminum without requiring the extensive pretreatment of the metal surface now found necessary.

It is a further object of this invention to provide a preliminary cleaning coating for mild steel, zinc, or aluminum which can be readily converted to the standard phosphate coatings of the art or can be given a standard chromic acid rinse to form in both cases excellent paint bases without the necessity of the extensive pretreatment now required for the formation of these later coatings.

It is also an object of this invention to provide for the formation of a metal phosphate coating in a one-step process; to provide for the formation of such a coating to be followed up by the use of a standard coating phosphate bath in a two-step process, or by a chromic rinse for a two-step process; or to provide for the formation of such a coating to be followed up by both the use of a standard coating phosphate bath and chromic rinse for a three-step process where the one-, two-, and three-step processes produce a superior result in both cleaning and coating the metal and providing excellent paint bases and drawing and wear-resistant surfaces.

It has now been found that the foregoing and related objects may be achieved with an aqueous coating bath which is maintained at a pH between 3 and 6 and which comprises as the principal coating-forming ingredient a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01 percent phosphoric acid in the coating bath. Improved quality coatings may be obtained by adding to such aqueous solutions, controlled proportions of certain oxidizing agents.

The preferred heterocyclic amine phosphates for the purposes of this invention are pyridine and substituted pyridine phosphates having the following structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, and wherein each of the foregoing hydrocarbon radicals may contain hydroxyl, bromo, chloro, sulfo and nitro substituent groups. It is to be understood that the lead line attaching R to the ring is illustrative only and is intended in its conventional sense to connect R to the ring; that is, R may be attached to any one of the 5 carbon atoms in the ring. The pyridine phosphates above shown may be used in quantities yielding at least about .01% of a phosphate ion up to quantities which saturate the solution. The preferred concentration is about .05% to .15% phosphate ion.

Particularly good results have been obtained with pyridine having no R group ring substituent.

In aqueous solution, it will be understood that the amine phosphates of the above given structure are in actuality in the form of ions of pyridine or substituted pyridine in equilibrium with phosphate ions such that the heterocyclic amine may occupy any one of the three displaceable hydrogen positions of the phosphoric acid radical. When one of the hydrogens of the phosphoric acid radical is substituted by one heterocyclic amine group, the resulting aqueous solution has a pH of approximately 4.2. When 2 of the displaceable hydrogens of the phosphoric acid radical are substituted by heterocyclic amines, the pH of the aqueous solution approaches 7. As indicated hereinabove, the operating range of pH of the solutions of this invention is restricted to between 3 and 6. It will

be understood, therefore, that in order to achieve a pH of 3 in an aqueous solution of heterocyclic amine phosphates having the above given structure, it is necessary that there be a slight excess of free phosphoric acid in the solution. Solutions having a pH of about 6 contain a mixture of monoamine phosphates and diamine phosphates or in other words, the solution contains a slight excess of amine over that required to replace 1 hydrogen ion, but less than is required to fully replace 2 hydrogen ions of each phosphoric acid radical.

An amine phosphate ionizes very rapidly in aqueous media to yield the equilibrium proportions of the amine phosphate, phosphoric acid and amine. Similarly, phosphoric acid reacts rapidly in aqueous media with the same amine to yield the same equilibrium proportions. Therefore, the phosphate may be added as a mixture of the equivalent proportions of phosphoric acid and heterocyclic amine of the above given structure. In most instances where the pH of a solution is to be corrected downwardly, it is desirable to add phosphoric acid to serve the dual purpose of increasing the acidity, and of increasing the concentration of phosphate ions. Similarly, and where the pH is to be corrected upwardly, an alkali metal phosphate, carbonate, oxide, hydroxide or the like is most suitable. From the foregoing, it will be apparent that the composition of the solutions and the relative proportions of heterocyclic amines and phosphates which are contained therein are specifically dependent upon the recited pH.

Coatings of exceptionally good quality may be obtained from the solutions of this invention when there is incorporated therein limited quantities of certain oxidizing agents. Although the presence of oxidizing agents is not necessary in order to achieve the objects of the invention, particularly adherent and paint receptive coatings result from the use of an oxidizing agent and this coating may be improved even further by the subsequent treatment of the coating with a chromic rinse. Preferred oxidizing agents and the operating ranges of concentrations in the solutions of this invention are as follows:

	Percent
Chlorate	.5–4
Bromate	.2–2
Nitrite	.005–.4
Sulfite	.05–.5

Other oxidizing agents which may be employed but which are somewhat inferior to the above preferred oxidizing agents for commercial reasons include sodium meta nitrobenzene sulfonate in concentrations of .1 to 4 percent and hydrogen peroxide in concentrations of .001 percent to .05 percent. Within the above given ranges, the specific percentage for each of the various oxidizing agents which is most suitable from the standpoint of quality as well as economy may vary considerably, but the optimum percentage is quite easily determined in each specific instance since the improved coatings resulting from the use of oxidizing agents are in each instance heavier coatings than are produced with the amine phosphate itself. This statement should not be interpreted as implying that there is any relationship between coating weight and quality of coating, for actually there is not. In this specific case, however, the improved quality coatings derived by the adding of an oxidizing agent are heavier coatings and, thus, the coating weight may be taken as a reference standard to determine the proper percentage of oxidizing agent to yield an improved quality coating.

The composition of the present invention may be painted or sprayed on the metal surface, or the metal may be immersed in a bath of the coating composition. The temperature of the solution and the time of contact between metal and solution is not critical. Temperatures of about 130°–170° F. are most suitable for coating metal in a relatively short time but temperatures down to room temperature can be used. Visible coatings are formed on both steel and zinc, but the coating on aluminum, although an excellent paint base, cannot be seen by visual inspection. The aluminum phosphate coating is probably transparent because of its extreme thinness.

As indicated previously, an advantage is gained from the use of the compositions of this invention in those cases in which it is desired to form on the surface one of the well-known phosphate coatings such as is produced with a zinc phosphate solution. When zinc phosphate coatings or other metallic phosphate coatings produced from coating-phosphate solutions are desired, the zinc phosphate solution may be applied directly to the metal which has been preliminarily coated in accordance with the method of the present invention. In many instances the preliminarily formed coating will dissolve in the coating-phosphate bath and be replaced by the phosphate coating from the second bath because the latter baths are normally run at quite high acidities. The improved coating which results from such a two-step method, appears to owe its quality to the nature of the surface which resulted from the preliminary treatment in accordance with the method of this invention. That is, the use of the composition of the present invention not only coats the metal but thoroughly cleans it and provides an excellent base for an additional or alternative coating.

The phosphate coatings produced by the method of this invention as well as phosphate coatings of the conventional zinc phosphate type resulting from the above described two-step method, may be further improved by treating the coatings with a hexavalent chromium rinse in accordance with conventional methods and with chromic acid concentrations which are standard practice in this art.

The following examples are given to more clearly illustrate the method and the solutions of this invention. In the below given examples the term "point solution" refers to the milliliters of one-tenth normal sodium hydroxide which is required to neutralize a 10 ml. sample of the solution to the phenolphthalein endpoint.

Example 1

A series of solutions was made up as follows:

a. 40 grams pyridine and 23.5 ml. 75% phosphoric acid were made up to 6 liters with water, giving a pH of 5.4;

b. Pyridine and phosphoric acid were combined with water to produce a 20 point solution having a pH of 3.0;

c. 47 grams methyl pyridine and 23.5 ml. 75% phosphoric acid were made up to 6 liters with water, giving a pH of 5.4;

d. 62 grams, 2 methyl, 5 ethyl pyridine and 23.5 ml. 75% phosphoric acid were made up to 6 liters with water giving a pH of 5.4;

e. 54 grams dimethyl pyridine and 23.5 ml. 75% phosphoric acid were made up to 6 liters with water giving a pH of 5.4;

f. 78.5 grams of phenyl pyridine and 23.5 ml. 75% phosphoric acid were made up to 6 liters with water, giving a pH of 5.4;

g. The pH of solution "*b*" was altered by the addition of varying proportions of pyridine to produce pH values between 3 and 6.

Each of the preceding solutions at a temperature of 160° F. was sprayed on the surface of a cold rolled mild steel panel for a period of one minute, the steel panels having received no preliminary treatment. The coatings produced were very adherent and varied in color from grayish white to dark gray with an outside thin, light tan, dusty film. The coating weight varied from approximately 15 to 100 mg. per square foot of surface area, and in each instance was essentially iron phosphate. The coatings were then rinsed with hexavalent chromium solutions in accordance with standard practice and the resulting coatings were found to be excellent paint bases.

Example 2

Each of the solutions described in Example 1 was modified by adding thereto varying proportions of chlorate, nitrite, bromate and sulfite oxidizing agents within the ranges of concentrations hereinabove indicated, and the processing carried out in the manner indicated under Example 1. Definite improvement was noted in each of the coatings, and the coating weights were in each case substantially greater than the corresponding examples without the oxidizing agent.

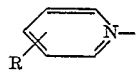
Example 3

Solutions having the compositions indicated under Example 1 were sprayed upon the surface of a cold rolled mild steel panel at a temperature of 160° F. for one minute. The treated panels were then subjected to spraying by a conventional zinc phosphate coating solution containing a nitrate accelerator at 160° F. for about one minute.

The zinc phosphate coatings produced were rinsed with a standard hexavalent chromium solution. The coatings produced were found to have excellent corrosion resistance, resistance to humidity and to be an especially satisfactory base for paint.

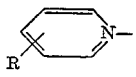
What is claimed is:

1. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous solution consisting essentially of phosphoric acid, water, and a substituted heterocyclic amine phosphate having the structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, the pH of the solution being between about 3 and 6, said solution containing at least .01% phosphate ion.

2. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous solution consisting essentially of phosphoric acid, water, a small amount of an oxidizing agent, and a substituted heterocylic amine phosphate having the structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, the pH of the solution being between about 3 and 6, said solution containing at least .01% phosphate ion.

3. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous acidic solution consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the said solution, the pH of the solution being between about 3 and 6.

4. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous acidic solution consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the said solution, and a small amount of an oxidizing agent, the pH of the solution being between about 3 and 6.

5. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous acidic solution having a pH between about 3 and 6 and consisting essentially of pyridine phosphate which yields at least about .01% of a phosphate ion in the said solution.

6. A method for cleaning and coating a metal of the class consisting of mild steel, zinc and aluminum which comprises the step of contacting the surface of the metal with an aqueous solution consisting essentially of a heterocyclic amine phosphate, wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the solution, the said solution having a pH of between about 3 and 6.

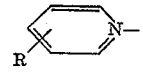
7. A method for cleaning and coating a metal of the class consisting of mild steel, zinc and aluminum which comprises the step of contacting the surface of the metal with an aqueous solution consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the solution, an oxidizing agent in an amount sufficient to result in an increase in coating weight, the said solution having a pH between about 3 and 6.

8. A method for cleaning and coating a metal of the class consisting of mild steel, zinc and aluminum which comprises the step of contacting the surface of the metal with an aqueous solution consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the solution, an oxidizing agent in an amount sufficient to result in an increase in coating weight, the said solution having a pH between about 3 and 6 and thereafter rinsing the coated surface with a hexavalent chromium solution.

9. A method for forming a phosphate coating on the surface of a metal of the class consisting of steel, zinc and aluminum which comprises the steps of contacting the surface of the metal with an aqueous acidic solution having a pH of about 3 to 6 and consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the solution whereby the said solution chemically reacts with the metal surface to form an inorganic phosphate coating thereon, thereafter contacting the coated surface with an aqueous acidic phosphate solution consisting essentially of a phosphate of the class of coating-phosphates to thereby form a second phosphate coating on the surface.

10. A method for forming a phosphate coating on the surface of a metal of the class consisting of steel, zinc and aluminum which comprises the steps of contacting the surface of the metal with an aqueous acidic solution having a pH of about 3 to 6 and consisting essentially of a heterocyclic amine phosphate wherein nitrogen is the sole hetero atom which yields at least about .01% of a phosphate ion in the solution whereby the said solution chemically reacts with the metal surface to form an inorganic phosphate coating thereon, thereafter contacting the coated surface with an aqueous acidic phosphate solution consisting essentially of a phosphate of the class of coating-phosphates to thereby form a second phosphate coating on the surface, and thereafter rinsing the coated surface with a hexavalent chromium solution.

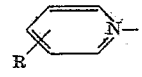
11. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous solution consisting essentially of phosphoric acid, water, and a substituted heterocyclic amine phosphate having the structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, and wherein each of the foregoing hydrocarbon radicals contain at least one substituent selected from the group consisting of hydroxyl, bromo, chloro, sulfo and nitro, the pH of the solution being be-

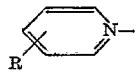
tween about 3 and 6, said solution containing at least .01% phosphate ion.

12. A composition for coating a metal of the class consisting of mild steel, zinc and aluminum comprising an aqueous solution consisting essentially of phosphoric acid, water, a small amount of an oxidizing agent, and a substituted heterocyclic amine phosphate having the structure:



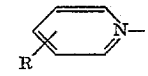
wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, and wherein each of the foregoing hydrocarbon radicals contain at least one substituent selected from the group consisting of hydroxyl, bromo, chloro, sulfo, and nitro, the pH of the solution being between about 3 and 6, said solution containing at least .01% phosphate ion.

13. A method for cleaning and coating a metal of the class consisting of mild steel, zinc and aluminum which comprises the step of contacting the surface of the metal with an aqueous solution consisting essentially of phosphoric acid, water, a small amount of an oxidizing agent, and a substituted heterocyclic amine phosphate having the structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, the pH of the solution being between about 3 and 6, said solution containing at least .01% phosphate ion.

14. A method for cleaning and coating a metal of the class consisting of mild steel, zinc and aluminum which comprises the step of contacting the surface of the metal with an aqueous solution consisting essentially of phosphoric acid, water, a small amount of an oxidizing agent, and a substituted heterocyclic amine phosphate having the structure:



wherein R is a ring substituent selected from the class consisting of hydrogen and hydrocarbon radicals having less than 7 carbon atoms and of the group consisting of alkyl, aryl and cycloalkyl, and wherein each of the foregoing hydrocarbon radicals contain at least one substituent selected from the group consisting of hydroxyl, bromo, sulfo, and nitro, the pH of the solution being between about 3 and 6, said solution containing at least .01% phosphate ion.

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