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METHOD FOR PHOSPHATE COATING FERROUS METAL SURFACES AND FINISHING TREATMENT THEREOF

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ABSTRACT OF THE DISCLOSURE

A process for treating a phosphate coated ferrous metal surface which comprises rinsing the phosphate coating with a dilute aqueous solution of a primary phosphate selected from primary phosphate of ammonia, amines and mixtures thereof. The preferred phosphates are ammonium dihydrogen phosphate and triethanolamine dihydrogenphosphate, which phosphates are desirably present in the aqueous solution in an amount from about 0.1 to about 10 grams per liter.

This invention relates to an improved method for treating metal surfaces and more particularly it relates to an improved rinse solution for application to metal surfaces which have been treated to provide a protective and/or paint-base coating.

It is well known in the art to treat metal surfaces with a phosphate-containing solution, such as a zinc phosphate or iron phosphate solution, to form a phosphate coating on the metal surface, which coating acts as a corrosion preventive or paint-base coating. Typically, after phosphating, the coated surface is rinsed in hot or cold water and, thereafter, given a final rinse in dilute phosphoric acid and/or chromic acid. Although rinses of this type have been found to be effective in giving a corrosion resistant and/or paint-base coating, their use has not been without some undesirable effects. For example, with chromate rinses, i.e., rinses of chromic acid or of various salts thereof the rinsed surface may be discolored or stained and this may be objectionable in some cases, particularly where the rinsed surface is left unpainted or where a transparent or light colored protective coating is applied. Although this problem is not encountered in the use of phosphoric acid rinses, it has been found that their use may result in undue corrosion of equipment, particularly heating coils and portions of the circulating system in the treating vessels or tanks used. Notwithstanding these difficulties, however, rinses of this type are widely used since failure to use such rinses has often resulted in an appreciable decrease in the corrosion resistance of the coated metal surfaces. Accordingly, it is desirable to provide a rinse treatment for phosphate coated surfaces which provides the corrosion resistance of the presently used phosphoric acid and/or chromic acid rinses, but which is not subject to the disadvantages which may be encountered in using these rinse materials.

It is, therefore, an object of the present invention to provide an improved method for treating ferrous metal surfaces to provide a protective and/or paint-base coating on the metal surface.

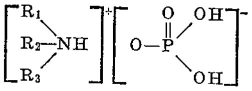
A further object of the present invention is to provide an improved rinse treatment for phosphate coated ferrous metal surfaces, which rinse treatment is not subject to the disadvantages which have heretofore been encountered when using chromic acid and/or phosphoric acid rinses.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Pursuant to the above objects, the present invention includes a process for treating a phosphate coated metal surface which comprises rinsing the phosphate coated surface with a dilute aqueous solution containing at least one water dispersible primary phosphate selected from the group consisting of primary phosphates of ammonia, primary phosphates of amines and mixtures thereof. The thus-treated surfaces have been found to be very effective in resisting stain or discoloration, particularly when the primary phosphate rinse solution is used after an unaccelerated phosphate coating solution, and are further found to improve the corrosion resistance of the phosphate coating.

More specifically, in the practice of the method of the present invention, a metal surface, having thereon a phosphate coating, is contacted with a dilute aqueous solution of a water dispersible primary or dihydrogen phosphate of ammonia and/or an amine and this solution is maintained in contact with the phosphated surface for a period of time sufficient to effect the desired rinsing of the phosphate surface. Various means for effecting contact between the rinse solution and the phosphate surface may be utilized, as for example immersion, spraying, flowing, flooding and the like. In general, satisfactory results have been obtained by spraying the rinse solution on the phosphate surface and this contacting technique is preferred. Contact times which are suitable to effect the desired rinsing of the phosphate surface may be from several seconds, e.g., 10, up to 1 to 2 minutes, with contact times within the range of about 30 seconds to 60 seconds being typical. It is to be appreciated, however, that contact times in excess of two minutes, e.g., 5 minutes or more, may be used without deleterious results.

The rinse solutions used in the present method are dilute aqueous solutions of a primary phosphate of ammonia and/or an amine. The primary phosphates used in formulating these rinse solutions may be characterized generally by the following structural formula:



wherein R_1, R_2 and R_3 are each selected from the group consisting of hydrogen, alkyl groups containing from about 1 to 8 carbon atoms, alkanol groups containing from about 1 to 8 carbon atoms and phenyl groups. These compounds may be classified generally as ammonium, mono-, di-, and trialkyl, alkanol and aryl dihydrogen or primary phosphates. Exemplary of specific compounds falling within this group which may be used in formulating the rinse solutions of the present invention are ammonium dihydrogen phosphate, methylamine dihydrogen phosphate, diethylamine dihydrogen phosphate, tributylamine dihydrogen phosphate, octylamine dihydrogen phosphate, dipropanol amine dihydrogen phosphate, triethanolamine dihydrogen phosphate, diheptanolamine dihydrogen phosphate, phenylamine dihydrogen phosphate, pentanolamine dihydrogen phosphate, trihexylamine dihydrogen phosphate, trimethanolamine dihydrogen phosphate, diphenylamine dihydrogen phosphate, as well as other similar mono- di-, and tri-, alkyl, alkanol and phenyl amine derivatives of the above.

As has been noted hereinabove these compounds are water dispersible and contain from about 1 to 8 carbon atoms in each alkyl or alkanol group. Additionally, it is to be appreciated that mixtures of two or more of the primary or dihydrogen phosphate salts may also be used. Of the above, the preferred phosphates are ammonium dihydrogen phosphate and triethanolamine dihydrogen phosphate, as well as mixtures of ammonium dihydrogen phosphate with triethanolamine dihydrogen phosphate.

The rinse solutions of the present invention are formulated as dilute aqueous solutions of the primary phosphate, typical examples of which have been set forth hereinabove. Desirably, these dilute solutions will contain the primary phosphate in an amount within the range of about 0.1 to 10 grams per liter, with amounts within the range of about 0.1 to 5 grams per liter being preferred. It is to be appreciated, however, that in some instances both greater and lesser concentrations may also be useful, e.g. 0.01 to 40 grams per liter. In general, concentrations of about 1 gram per liter have been found to be very suitable. Desirably, these dilute aqueous solutions are used at a temperature above about 15 degrees centigrade and are preferably used at temperatures within the range of about 60 to 75 degrees centigrade.

It is to be appreciated that the present invention includes not only the treatment of a phosphate coated metal surface with the aqueous rinse solutions which have heretofore been described but, additionally, includes the overall process wherein a metal surface is treated with a phosphate containing coating solution to form a phosphate coating on the surface and the thus-phosphate coated surface is thereafter rinsed with the aqueous primary phosphate rinse solutions. Accordingly, in the practice of this overall process, a metal surface and preferably a ferrous metal surface, is contacted with a phosphate containing coating solution so as to form a phosphate coating on the metal surface. The phosphate coating solutions which may be used are conventional and well known in the art and include acidic ferrous phosphate coating solutions, acidic zinc phosphate coating solutions, and alkali metal phosphate coating solutions, as well as other similar phosphate coating solutions which will produce either a zinc or iron phosphate coating on the ferrous metal surface treated. Desirably, prior to the application of the phosphate coating, the ferrous metal surfaces are first subjected to standard cleaning operations, utilizing alkaline cleaning solutions, and/or acidic pickling solutions, where these are necessary to effect derusting of the surface. Generally, as is common in the art, each of these cleaning operations will be followed by a water or neutralizing rinse to remove the residue of the various alkaline and acidic cleaning solutions from the metal surface and prevent contamination of the next processing solution. Once the desired zinc or iron phosphate coating has been formed on the metal surface, the phosphate coating is desirably rinsed with water and is, thereafter, rinsed with the aqueous dihydrogen phosphate rinsing solutions as have been described hereinabove. Ferrous metal surfaces which have been treated in accordance with the above procedure have been found to exhibit good corrosion resistance and, further, have been found to be substantially free of stains or discoloration. This freedom from staining or discoloration has been found to be particularly evidenced where the phosphate coating solution used is unaccelerated, i.e., does not contain the commonly used accelerating or oxidizing agents such as nitrate, nitrite, chlorate, bromate, and the like. Although staining problems are often less severe when using accelerated phosphate coated solutions, it has also been found that the use of the subject dihydrogen phosphate rinse solutions is effective in preventing what staining or discoloration does occur with the accelerated phosphate coating solutions.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are given in degrees centigrade and parts are by weight.

EXAMPLE 1

Articles having painted, rusted, steel surfaces were cleaned in hot alkali, rinsed in hot and then cold water, derusted in an acid pickling solution, rinsed in water and then neutralized and then water rinsed again. The cleaned steel surfaces were then immersed for 30 minutes in a conventional ferrous iron dihydrogen phosphate coating solution, which solution was at a temperature of about 98 to 100 degrees centigrade. The phosphate coated surfaces were then rinsed in water to remove any remaining acidic phosphatizing solution. A portion of the resulting phosphate coated steel pieces was then sprayed for about 45 seconds with an aqueous solution containing 2 grams per liter of ammonium dihydrogen phosphate, which solution was at a temperature of about 65 degrees centigrade. A second portion of the phosphate coated steel surfaces was similarly rinsed with a hot aqueous solution containing 1 gram per liter of ammonium dihydrogen phosphate. Thereafter, both portions of the rinsed steel workpieces were dried in an oven and were compared to similar phosphate coated steel workpieces which had been given no dihydrogen phosphate rinse, but had been dried in the oven immediately following the water rinse. It was found that the workpieces which had been given only the water rinse before drying were badly stained while those pieces which had been rinsed in the ammonium dihydrogen phosphate solution were found to be substantially free of stain.

By way of comparison, similar phosphate coated steel pieces were rinsed in a conventional chromic acid solution containing 0.25 gram per liter of CrO_3, chromic-phosphoric acid solutions containing 0.25 gram per liter of a 50—50 mixture of chromic and phosphoric acid and aqueous phosphoric acid solutions containing 2 grams per liter of H_3PO_4. After drying, those pieces which had been rinsed with the chromic or chromic-phosphoric acid mixtures were found to be badly stained. Although the pieces rinsed with the phosphoric acid showed little evidence of staining, the steam coils and other pipe work used in conjunction with the phosphoric acid rinse solution were found to be badly corroded. Attempts to eliminate this corrosion by including conventional pickling inhibitors in the rinse solution were not successful. It was further noted that such corrosion was not encountered in the equipment used with the ammonium dihydrogen phosphate rinses. Additionally, the corrosion resistance of the ammonium dihydrogen phosphate rinsed surfaces was found to be comparable to that of the chromic acid and phosphoric acid rinsed surfaces.

EXAMPLE 2

Slightly rusted, oiled steel was cleaned in a phosphoric acid-solvent cleaning solution, rinsed in cold water and then given a phosphate coating by immersion in a conventional zinc dihydrogen phosphate coating solution. The phosphate coated surface was rinsed in cold water and then given a final rinse by spraying for about 60 seconds with an aqueous solution containing 0.25 gram per liter of ammonium dihydrogen phosphate, which solution was at a temperature of about 70 degrees centigrade. The thus-rinsed steel was then dried in an oven. After drying, the steel surfaces were found to be completely free of staining or other discoloration while steel which had been similarly treated but with a hot water rinse substituted for the ammonium dihydrogen phosphate rinse was found to be badly stained, particularly on the horizontal surfaces and in the area of seams or welds.

EXAMPLE 3

The procedure of Example 2 was repeated with the exception that the dihydrogen phosphate rinse used contained 0.25 gram per liter of triethanolamine dihydrogen phosphate instead of the ammonium dihydrogen phosphate. After drying, the treated steel surfaces showed no evidence of staining or discoloration.

EXAMPLE 4

The procedure of Example 1 was repeated with the exception that the dihydrogen phosphate rinse solution used contained 1 gram per liter of ammonium dihydrogen phosphate and 1 gram per liter of triethanolamine dihydrogen phosphate. Comparable results were obtained.

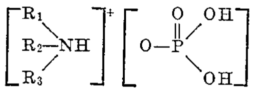
The procedure of the preceding examples is repeated using as the rinse solution aqueous solutions of phenylamine dihydrogen phosphate, dimethylamine dihydrogen phosphate, octanolamine dihydrogen phosphate, tripentanolamine dihydrogen phosphate, dibutylamine dihydrogen phosphate, and the like to obtain similar results.

What is claimed is:

1. A method for treating a ferrous metal surface having thereon a phosphate coating produced by coating said ferrous metal surface with a phosphate coating composition selected from the group consisting of acidic ferrous phosphate coating solutions, acidic zinc phosphate coating solutions and alkali metal phosphate coating solutions, which comprises contacting said surface with a dilute aqueous solution consisting essentially of from about 0.1 to about 10 grams per liter of at least one primary phosphate selected from the group consisting of primary phosphate of ammonia, primary phosphates of amines, each carbon chain of which contains from about 1 to 8 carbon atoms, and maintaining the phosphate coated surface in contact with the said aqueous solution for a period of time sufficient to effect rinsing of the phosphate coated surface.

2. A coated ferrous metal surface produced in accordance with the method of claim **1.**

3. The method as claimed in claim **1** wherein the primary phosphate in the dilute aqueous rinse solution has the formula



$$\left[\begin{array}{l} R_1 \\ R_2{-}NH \\ R_3 \end{array}\right]^+ \left[O{-}\overset{\overset{O}{\|}}{P}(OH)_2\right]$$

wherein R_1, R_2 and R_3 are each selected from the group consisting of hydrogen, alkyl groups having from 1 to 8 carbon atoms, alkanol groups having from one to eight carbon atoms, and phenyl groups.

4. The method as claimed in claim **3** wherein the primary phosphate is ammonium dihydrogen phosphate.

5. A coated ferrous metal surface produced in accordance with the method of claim **4.**

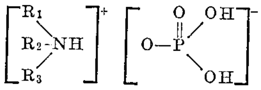
6. The method as claimed in claim **3** wherein the primary phosphate is triethanolamine dihydrogen phosphate.

7. A coated ferrous metal surface produced in accordance with the method of claim **6.**

8. A method for treating a ferrous metal surface to provide a protective coating thereon which comprises contacting said ferrous metal surface with a phosphate solution selected from the group consisting of acidic ferrous phosphate, acidic zinc phosphate and alkali metal phosphate coating solutions so as to form a protective phosphate coating on the surface and thereafter rinsing the thus-formed phosphate coating with a dilute aqueous solution consisting essentially of from about 0.1 to about 10 grams per liter of at least one primary phosphate selected from the group consisting of primary phosphates of ammonia and primary phosphates of amines, each carbon chain of which contains from about 1 to 8 carbon atoms.

9. A coated ferrous metal surface produced in accordance with the method of claim **8.**

10. The method as claimed in claim **8** wherein the primary phosphate in the rinse solution has the formula:



$$\left[\begin{array}{l} R_1 \\ R_2{-}NH \\ R_3 \end{array}\right]^+ \left[O{-}\overset{\overset{O}{\|}}{P}(OH)_2\right]^-$$

wherein R_1, R_2, and R_3, are each selected from the group consisting of hydrogen, alkyl groups containing 1 to 8 carbon atoms, alkanol groups containing from 1 to 8 carbon atoms and phenyl groups.

11. The method as claimed in claim **10** wherein the primary phosphate is ammonium dihydrogen phosphate.

12. A coated ferrous metal surface produced in accordance with the method of claim **11.**

13. The method as claimed in claim **10** wherein the primary phosphate is triethanolamine dihydrogen phosphate.

14. A coated ferrous metal surface produced in accordance with the method of claim **13.**

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