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PHOSPHATED METAL COATING

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This invention relates to improved phosphated metal coatings, and, while it includes such coatings on iron and steel, zinc, lead, copper and other metals, it will be described particularly in connection with coatings on iron and steel. While most important in connection with phosphate coatings, the invention is of great benefit in other types of coatings, particularly those comprising elements in the fifth group of the periodic system, such as, arsenates, vanadates and antimonates.

The invention consists essentially in treating metal carrying a coating of more or less insoluble phosphates, previously prepared in any way desired, with a solution of basic character, such solutions being more fully described below. The result is a coating showing a marked increase in the power to prevent rusting of the metal. As will be seen, a great latitude is possible in the choice of such basic solutions; nearly all of them are beneficial but some effect a much greater improvement than others in the rust inhibiting properties of the phosphate coat on the metal.

In various methods of providing ferrous metals with a thin protective layer of insoluble phosphates, the metal is treated with various solutions of acid phosphates of heavy metals. Acid phosphates of iron, manganese, zinc and copper have been used. The acid phosphate solution reacts on the metal with evolution of hydrogen and production of ferrous phosphate from the metal, the net result being the formation of a protective coating of insoluble phosphates. It has been found that these coatings retard development of rust but do not wholly prevent it, being more or less pervious and allowing moisture and air to gain access to the underlying metal. Alone, that is without oiling or varnishing, they do not give adequate protection to exposed metal. A phosphate coating is, however, an excellent substratum for paints and varnishes which do not bond well to smooth, clean, naked ferrous metal, this being particularly true of modern lacquers and enamels. Phosphating the metal is a useful preliminary step in varnishing and lacquering.

Zinc, lead, copper and other non-ferrous metals are treated in a similar manner to obtain protective phosphate coatings.

Solutions of acid phosphates of iron and other heavy metals suitable for treating ferrous and non-ferrous metals are made in various ways. A solution containing ferrous phosphate can be made by treating commercial phosphoric acid, in a somewhat diluted state, with iron filings or ferrous phosphate, zinc phosphate by treating the phosphoric acid with zinc filings, zinc oxid, zinc carbonate, or zinc phosphate, acid copper phosphate by dissolving various copper compounds in phosphoric acid, and manganese phosphate by saturating phosphoric acid with manganese acid phosphate, as well as in many other ways.

The protective phosphate coatings on ferrous metal are usually of complex nature, containing, in addition to iron phosphates formed from the metal, phosphates of other metals, complex coatings being more resistant. Manganese phosphate is considered a desirable component, and zinc phosphate also gives good coatings. A solution containing both may be conveniently made by attacking a mixture of zinc and manganese dioxid with phosphoric acid. In general acid phosphates of metals not above barium in the electromotive series may be used as coating agents, more particularly acid phosphates of barium, strontium, calcium, magnesium, aluminum, zinc, manganese, nickel, cadmium, lead, copper, arsenic, silver.

Phosphate coatings produced by any of the known methods consist of difficultly soluble metallic monohydrogen or secondary phosphates with, perhaps, in some cases a small proportion of the normal or tertiary phosphates. I have found that, by treating such phosphate coatings, regardless of how formed, with alkaline solutions of controlled alkalinity, a great improvement in resistance to the corrosive agencies causing rust is produced; there is an improvement in the rust inhibiting property of the coating. Depending on the nature of the coating, and also on the nature of the alkaline solution used, the improvement in rust inhibition ranges from 100 per cent to more than 2000 per cent as compared with the original coating.

It is well known that, in general, alkaline solutions are injurious to phosphate coatings and that even dilute caustic soda, say 2 to 5 per cent concentration, is capable of completely destroying such coatings. I have found, however, that, if the metalic surface carrying the phosphate coating be subjected to the action of an alkaline solution with limited alkalinity and for a brief period of time, a reaction takes place which makes the phosphate coating more basic than before and usually less soluble and that this increase in basicity of the coating results in a great increase in its resistance to corrosive influences. Secondary or mono-hydrogen phosphates are probably completely converted to normal or tertiary phosphates and, in addition, in most cases a certain proportion of the coating is actually converted into basic phosphates. It appears that the changed phosphates formed by the alkaline treatment of acid phosphate coatings provide much more perfect coverage and protection to the underlying metal than the mono-hydrogen phosphates or mixture of normal and mono-hydrogen phosphates which constitute the coating before the alkaline treatment. By way of illustration, several chemical equations are here given to show how the basicity of the coatings may be increased by various alkaline treatments. The coating

formed by the acid phosphate solution is basified in various ways.

(1) $3NaOH+3FeHPO_4\rightarrow Fe_3(PO_4)_2+Na_3PO_4+3H_2O$

(2) $2NaAlO_2+4ZnHPO_4\rightarrow 2NaOH+AlPO_4+2Zn_2(OH)PO_4+Na_3PO_4$

(3) $3Ba(OH)_2+4Cu_3(PO_4)_2\rightarrow 6Cu_2(OH)PO_4+Ba_3(PO_4)_2$

(4) $3Ba(AlO_2)_2+10Mn_3(PO_4)_2+12H_2O\rightarrow Ba_3(PO_4)_2+3Al_2(OH)_3PO_4+15Mn_2(OH)PO_4$

In Equation 1 involving a simple alkali as sodium hydroxide, there is actually some removal of P_2O_5 from the coating but the treatment increases the ratio of base to the P_2O_5 in the coating and betters the rust resistance of the coating. In Equations 2 and 3, the alkaline bath contains a metallic oxid which is capable of entering the coating, forming an insoluble phosphate. The weight of the coating is appreciably increased by the baryta or alumina taken up. In the 4th equation, a solution is utilized which contains positive and negative ions both comprising metals capable of entering the coating with formation of insoluble phosphates and this type of solution is decidedly superior to the other types of reagent. Both baryta and alumina are added to the coating. I have found a barium aluminate solution to be a highly advantageous reagent for improving the rust resisting power of phosphate coatings. In no case is the treating solution strongly alkaline.

Following is a discussion of a number of alkaline materials which have been found to be beneficial and concentrations are given in which benefits are known to be obtained. It is not intended to convey that concentrations below or above the concentrations given are necessarily injurious; in most cases beneficial effects are obtained with concentrations some distance outside the ranges given. Best results are obtained by the treatment in hot solutions, that is, at temperatures of 50–100° C., although cold solutions also give good results, and with a period of immersion ranging from one half minute to five minutes. It is difficult to get the full benefit of the treatment in less than thirty seconds and immersion for ten minutes or more does not seem to give results superior to those obtained with immersion periods of from two to five minutes.

The following alkaline or basic reagents in the concentrations noted are effective:

	Per cent
Potassium and sodium hydroxides	0.1 to 1
Potassium, sodium and ammonium normal carbonates	1 to 3
Trisodium phosphate and sodium borate	3
Ammonium hydroxid	1 to 10
Sodium and potassium cyanides	1
Sodium aluminate	½ to 1
Barium and strontium hydroxides (octahydrates)	1 to 5
Barium cyanid	2
Basic lead salts, such as, lead basic acetate	3
Ammoniacal solutions of metals below the alkaline earths, such as, zinc, nickel, cobalt and cupric hydroxid	1 to 3
Alkaline solutions containing metallic negative ions, such as sodium ferric tartrate	1
Strontium aluminate	1
Barium aluminate	1 to 5

Of the ammonium, sodium and potassium compounds mentioned, sodium or potassium aluminate appears to be decidedly superior to others in this group. Barium and strontium hydroxides are about equal to sodium aluminate in improving the quality of the coating, while barium aluminate, which has sufficient solubility for this treatment in hot water, effects great improvement in the coating.

In the treatment of an adherent coating consisting of phosphates of iron only, I have found an alkaline bath containing normal salts of alkaline reaction, or free hydroxides, or free hydroxides in the presence of a normal salt to give good results. Calcium hydroxide is not a good reagent for my purposes because it is too low in solubility. This is true also of magnesium and other simple hydroxides below strontium in the electromotive series. The soluble alkaline earth hydroxides, those of barium and strontium, give good results. A calcium salt, such as calcium nitrate, in the presence of ammonium hydroxide is beneficial although not nearly so much so as sodium aluminate and barium hydroxide.

With coatings consisting of mixed phosphates of metals, such as zinc and iron phosphates or manganese and iron phosphates or zinc, manganese and iron phosphates or iron and copper phosphates, all the reagents named in the table are effective in improving the coating. The treatment bath should not be too alkaline and should not contain ions which have an injurious or disintegrating effect on the coating. For example, the sulfid ion is injurious because it reacts with the metals of the phosphate coatings to form insoluble sulfids, such as ferrous sulfid. In the presence of air and moisture such sulfids will oxidize into soluble metal sulfates which are active in promoting the rusting of the coating. For some reason not entirely understood, silicates in the alkaline bath are somewhat injurious. Apparently the coating formed in this case is brittle and contains microscopic cracks.

It has been stated above that heretofore alkaline solutions have been found to be injurious to the coating. By way of example, it may be stated that hot 2 per cent sodium hydroxide solution disintegrates a coating containing phosphates of iron and manganese. When the alkaline bath contains barium, aluminum or other ions which are capable of becoming part of the coating as insoluble or basic phosphates, a somewhat higher degree of alkalinity may be resisted by the coating.

In coating the metal, the primary protective coating may be made with any of the stated acid phosphates depending on what kind of phosphate in the coating is deemed desirable. Acid phosphate of zinc, acid phosphate of manganese and acid phosphate of copper are all good coating agents. A solution containing acid phosphates of two or more metals may be used. In using acid phosphate of zinc, a strong solution made as described from commercial sirupy acid diluted with an equal volume of water and saturated with zinc may be employed as it is or it may be considerably diluted. A dilute solution containing as little as a fluid ounce of the strong solution per gallon of water is sometimes used. In using this diluted solution as a bath for metal coating, it may be replenished from time to time by adding a little more of the concentrated solution, using, say, a quarter of an ounce of the concentrated solution per gallon of the bath as and when required. The concentrated liquid may also contain acid phosphate of iron. A high ratio of zinc to phosphoric acid is desirable; it is de-

sirable to have as much zinc as is consistent with a clear solution.

The treatment of ferrous metal with metallic acid phosphate solutions results in an evolution of hydrogen and formation of ferrous phosphate. The gassing is inconvenient and a depolarizer is desirable unless the work is to be made an anode in an electrolytic circuit. With a depolarizer in solution and gassing restrained, coatings of better physical character are obtained; they are less pervious. The coating action is quicker. The presence of a small amount of ferric iron both in the coating and in the acid phosphate solution is advantageous. In the solution it exercises a depolarizing action, lessening the evolution of hydrogen. With depolarization and obviation of a "gas blanket" denser and less pervious coatings are made and operation is quicker. As ferric iron is reduced to ferrous in depolarization, propositions looking towards reoxidation are sometimes advanced. Air blowing has not been successful for various reasons and the addition of alkali chromates, permanganates, etc., loads the bath with salines. Potassium, ammonium and sodium nitrate are undesirable for the same reason. Manganese dioxid makes the bath muddy.

I have, however, found that by maintaining a small concentration of hydrogen peroxide in the coating bath, the advantages are secured without the disadvantages, the peroxide leaving no residue other than water. Hydrogen peroxide strips the coatings, if present in any large amount, say, 1 per cent or more. But I have found that in concentrations of the order of 0.05 to 0.1 per cent, its action is wholly beneficial. The coating action is accelerated. With any of the acid phosphate baths described or now in use, the presence of peroxide in this concentration results in the formation of denser, better protective coatings. Their cohesion to the underlying metal is better. These bettered coatings are, however, greatly improved by the alkaline after-treatments hereinbefore described.

It is found that the phosphate coating is of better physical and chemical character when it contains a plurality of bases, this being one of the reasons for preferring a coating bath of acid phosphate of zinc to one of acid phosphate of iron. A variety of other heavy metal oxids have been found useful in these coatings. Both manganese and copper in the form of soluble acid phosphates give good results and an admixture of these acid phosphates with zinc phosphate gives good results.

In making a solution of acid phosphate of manganese for treating iron, ordinary commercial liquid concentrated phosphoric acid (1:5) is diluted with water, manganese oxid or carbonate added and the mixture raised to the boiling point. Good proportions are from 200 to 300 gallons of water, one gallon of phosphoric acid and six pounds of manganese oxid. A solution of acid phosphate of copper can readily be made by dissolving copper oxid, hydroxide or carbonate in phosphoric acid.

In a practical embodiment of the present process of providing ferrous metal with a rustproof coating, useful either alone or as a substratum for lacquer, paint and varnish, or for an enameled finish, clean sheet metal is dipped into a hot bath of acid phosphates containing a concentration of phosphates equivalent to about 1 per cent of P_2O_5. Any of the described acid phosphate solutions may be employed. Good coatings are made with an acid phosphate solution containing both zinc dihydrogen phosphate and manganese dihydrogen phosphate in a molecular ratio of about 2:1. In such a bath, there is usually some iron dihydrogen phosphate present in amount equal to about 1 per cent of the total phosphates. If this amount be not present in the bath as originally made, the bath will pick it up from the ferrous metal surface being coated as the work progresses. Hydrogen peroxide added to the bath in a concentration less than 0.1 per cent has a depolarizing action and accelerates the formation of a coating. The bath just described will quickly form on ferrous surfaces an adherent coating of low solubility consisting mostly of the secondary or monohydrogen phosphates of zinc, mangenese and iron, most or all of the iron phosphate in the coating coming from action on the metallic surface.

Another method of producing phosphate coatings consists of subjecting the ferrous metal to the action of a bath containing manganese dihydrogen phosphate, manganese nitrate and a relatively small proportion of acid phosphates of iron. A trace of soluble copper in the coating bath is sometimes beneficial.

After a phosphate coating has been developed on the ferrous surfaces by any of the methods described, or usual in the art, the coated metal is washed and then dipped into one of the alkaline baths already described. I generally use a solution of barium aluminate chemically equivalent to three per cent of $Ba(OH)_2.8H_2O$. The ratio of aluminum to barium in these solutions is not of great importance; it may vary from that of the meta-aluminate to that of the tribarium ortho-aluminate. All give excellent results. However, the other alkaline solutions mentioned may also be employed.

In certain comparative tests to illustrate the principles involved in the present invention, clean sheet steel was used for comparison. This particular metal rusts badly with a single dipping in water and drying. In providing this steel with various phosphated coatings, including those described, the metal was generally improved in its resistance to rust. The various coatings, however, before the alkaline treatment, differed considerably among themselves, some showing no more resistance than the naked metal, while others withstood several wettings before a heavy development of rust appeared. On treatment of the coatings with weak alkaline solutions free of sulfid ion, the resistance was greatly increased.

To give some idea as to the improvement effected by the alkaline treatment of phosphated surfaces as described, some details are given of the rusting tests on various surfaces repeatedly wet with water and allowed to dry out between wettings. In this test, clean metal rusts badly with a single wetting and takes a rating of zero. The various phosphate coatings, which include all those above described, show ratings ranging from 8 to 15 on the basis of repeated wettings required to bring the sample down to a zero rating. The same coatings, when treated with one tenth per cent caustic soda, 3 per cent ammonia or 1 per cent sodium cyanide, show ratings of 42 to 75 or five times the rust resistance of the untreated coatings. When the alkaline treatment consisted of barium hydroxide or strontium hydroxide or sodium aluminate the ratings ranged from 70 to 120. This indicates an eight-fold increase in rust resistance. When the alkaline treatment

was with a barium aluminate solution, the ratings ranged from 175 to 225, which is about 20 times better than the rating of the untreated coatings. It is believed that the figures just given afford a good relative measure of the rust inhibiting properties of the surfaces under test. All other alkaline treatments herein mentioned and a few not mentioned were included in the test and all of them improved the ordinary phosphate coatings, although none of them showed as good results as the soluble alkaline earth aluminates.

It will be evident that various combinations of the alkaline materials referred to herein are possible and that, in general, excellent results are to be obtained from the treatment of phosphated metal coatings with the mixed reagents in solution.

What I claim is:—

1. The method of improving the corrosion resistance of an adherent protective and bonding coating consisting of at least one difficultly soluble phosphate on the surface of a metal selected from the group consisting of ferrous metals, zinc, lead and copper, said coating being produced by the reaction with said metal of a solution consisting principally of at least one dihydrogen phosphate of a metal not above barium in the electromotive series, which comprises treating the phosphate coating with a dilute aqueous solution having an alkalinity substantially greater than that of a saturated solution of potassium chromate but insufficient to injure the said coating, and which reacts with said phosphate coating and increases the basicity and corrosion resistance thereof.

2. The method of claim 1, wherein the said aqueous solution contains an active ingredient having at least one constituent which forms an insoluble phosphate and which enters into said coating by combining with the phosphate thereof.

3. The method of claim 1, wherein the said solution contains at least one active ingredient selected from the group consisting of normal salts having alkaline reaction, metallic hydroxides more soluble than calcium hydroxide, and normal salts plus a free base more soluble than calcium hydroxide.

4. The method of claim 1, wherein the said alkaline solution contains an active ingredient having at least one constituent selected from the group consisting of barium, strontium and aluminum.

5. The method of claim 1, wherein the said alkaline solution contains barium aluminate as an active ingredient.

6. The method of claim 1, wherein the difficultly soluble phosphate coating comprises a monohydrogen phosphate which reacts with an ingredient of said solution to form a phosphate at least as basic as tertiary phosphate.

7. The method of claim 1, wherein the said difficultly soluble phosphate coating comprises iron monohydrogen phosphate which reacts with an ingredient of said solution to form a phosphate at least as basic as tertiary iron phosphate.

8. As a new article of manufacture, a metal article having a surface of a metal selected from the group consisting of ferrous metals, zinc, lead and copper, said surface being provided with an adherent protective and bonding coating consisting principally of at least one difficultly soluble phosphate more basic than the monohydrogen phosphate of said surface metal and produced by basification of an adherent coating previously formed on said surface by the reaction therewith of a solution consisting principally of at least one dihydrogen phosphate of a metal not above barium in the electromotive series.

9. The article of claim 8, wherein the final difficultly soluble phosphate coating is at least as basic as tertiary phosphate.

10. As a new article of manufacture, an article having a ferrous metal surface provided with an adherent protective and bonding coating consisting principally of difficultly soluble phosphates at least as basic as tertiary iron phosphate and comprising at least one basic element selected from the group consisting of barium, strontium and aluminum, said element being combined with a previously formed adherent phosphate coating produced by the action on said ferrous metal surface of a solution consisting principally of at least one dihydrogen phosphate of a metal not above barium in the electromotive series.

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