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HEAT RESISTANT PHOSPHATE COATINGS, METHODS AND ARTICLES PRODUCED THEREFROM

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This invention relates to methods of forming heat resistant phosphate coatings on metallic surfaces and to articles produced thereby.

Solutions of calcium phosphate or the like have been suggested for use in applying phosphate coatings, but heretofore they have been difficult to work with and for this reason have not been used extensively in actual practice or, at best, have been subordinated to other phosphates, such as those of the heavy metals, e.g., zinc or manganese phosphate. Coatings applied with the latter solutions decompose at temperatures of about 500° C.

It is an important object of the invention to provide thoroughly practical methods of forming heat resistant phosphate coatings on metallic surfaces, particularly ferrous metal and alloys thereof, from solutions of certain metal phosphates, which methods have widespread utility, being useful in protecting such surfaces from corrosion and from seizing during drawing operations and being pre-eminently satisfactory for isolation coatings on grain-oriented electrical steels.

Another object of the invention is to provide a non-hygroscopic product which can be put up in easily handled, marketable form from starting and replenishing the coating bath for the calcium phosphate solutions.

Still other important objects of the invention are the provision of articles of ferrous metals and alloys thereof having firmly adhered and uniformly distributed over the surfaces thereof phosphate coatings of unusual chemical and thermal stability; particularly the provision of grain-oriented electrical steels with chemically bonded isolation coatings which can withstand stress-relieving temperatures.

The above and other objects will become apparent during the course of the following description.

In accordance with the invention, solutions of certain metal monophosphates, particularly monocalcium and monobarium phosphate, having controlled concentrations are used in forming phosphate coatings of uniform quality on metallic surfaces, especially iron and steel including stainless steel. Unexpectedly it has been found that if such solutions are applied as a film and burned in, i.e., heated to elevated temperatures, especially fine crystalline and firmly bonded coatings are formed. The coatings formed according to the invention can withstand temperatures as high as 700–750° C. for relatively long periods without showing any marked change in their excellent properties. In nitrogen atmospheres, such as are used for stress-relieving, the coatings can be exposed to temperatures of 950° C. and even higher temperatures to 1200° C. and still exert their isolating effect upon the metal surface. Not only are the coatings formed by the methods of the invention heat resistant, but they exercise an extraordinary protection against corrosion as they are extremely dense. They are particularly useful during the annealing of iron and steel sheets in piles or wound strips as they prevent agglomeration or sticking, especially at elevated annealing temperatures when the danger of the sheets welding together is greatest. As far as can be determined the coatings consist principally of the corresponding water-free tertiary alkaline-earth phosphate,

e.g., water-free tertiary calcium phosphate, together with some phosphate of the metal treated, e.g., iron phosphate.

In the practice of the invention, the forming of such coatings is accomplished with phosphate solutions of calcium, barium, strontium, beryllium and aluminum and mixtures thereof; especially with monophosphate solutions of these metals. Monocalcium and monobarium phosphate solutions are preferred, both from the standpoint of economy and quality of coating obtained. The others, particularly monoaluminum phosphate solution are not as effective as the preferred solutions but can be satisfactorily employed as a replacement for the calcium or barium phosphate preferably and less desirably in lieu thereof. It has been found that the concentration of the dissolved phosphate of these metals in the solution must be at least 130 grams PO_4 per liter to produce layers having a thickness of about 10 microns and solutions having this lower limit of concentration are generally preferred. However, layers having a thickness of a few microns can effectively prevent sticking or agglomeration and solutions with as little as 80 grams PO_4 per liter of the phosphate of these metals produce such thinner layers. The lower limit of concentration of the phosphate of these metals is 70 grams PO_4 per liter and the upper limit is not more than 400 grams PO_4 per liter. Solutions that are at equilibrium with phosphoric acid at room temperatures or slightly above or below equilibrium with the dissolved phosphate are employed, and the total acidity of the solutions is thus indirectly given. The total acidity including phosphoric acid of each solution will be determined by that amount of free phosphoric acid, if necessary, which will just keep the phosphate in solution or that amount which will just avoid the formation of a precipitate. The equilibrium solubility of the phosphates increases upon the addition of phosphoric acid and whether free phosphoric acid is necessary will be determined by the particular phosphate employed and the concentration desired in the processing solution. The free phosphoric acid which corresponds to equilibrium, then, must be harmonized with the particular phosphate and concentration thereof which is used within the limits of the invention. As the concentration of phosphate of these metals approaches the upper limit, the bath tends to become too acid and the amount of phosphate in the coating of the metal being treated, e.g., iron phosphate, increases and the heat resistance of the coating suffers. For this reason, it is preferred that the concentration of the phosphate of these metals in the solution not exceed 340 grams PO_4 per liter. Toward the lower limit, i.e., 70 grams PO_4 per liter of the phosphate of these metals, the solutions have decreased wetting ability and form less uniform films so that the coverage of the burned-in coating is affected. It is highly desirable to work with solutions having a concentration of phosphate of these metals of at least 130 grams PO_4 per liter but nevertheless from the standpoint of economy a concentration of as low as 70 grams PO_4 per liter may be employed particularly if all that is needed is to prevent agglomeration during annealing. It has been found that if these coatings are to be used for protecting articles from seizing during drawing in conjunction with drawing lubricants, the phosphate of these metals in the solution should preferably be between 140 grams PO_4 per liter and 340 grams PO_4 per liter.

For regulating the thickness of the coating, various substances may be added to the solutions. If a very thin coating is desired, wetting agents may be used to decrease the thickness of the film to be burned in, and consequently the thickness of the resulting coating. For this purpose, wetting agents may be employed which are compatible with the particular phosphate solution. Non-ionic wetting agents are generally preferred. Good re-

sults were obtained with an oxyethylized aryl-alkyl alcohol with about 20 ethylene oxide groups sold under the trade name "EmulphorO." For the treatment of grain-oriented magnetic steels, e.g., grain-oriented transformer sheets, wetting agents are preferably not used as the material is extremely sensitive to the absorption of carbon. It is also possible to reduce the thickness of the layer or coating through lower concentrations of the dissolved phosphate but the uniformity of the coating suffers as mentioned and concentrations below the lower limit, viz., 70 grams PO_4 per liter, are avoided if possible.

On the other hand, if thicker coatings are desired, the concentration of the phosphate in the solution can be increased to produce thicker films and hence heavier coatings, but the increase in the thickness of the coating through this medium is possible only to a limited extent as indicated, that is, up to the preferred concentration of 340 grams PO_4 per liter, since otherwise too much of the phosphate of the metal treated will appear in the final burned-in coating. The thickness of the film to be burned in, and hence that of the final coating, can be controlled by the use of fillers. First the type of filler which becomes simply embedded in the coatings may be employed as for example, bentonite, mica, highly dispersed silica, alumina or magnesia. Also a type of insoluble filler may be employed which fuses with the base metal during the burning-in process, e.g., tertiary calcium phosphate. Through the formation of the phosphate layer and its bonding to the metal surface, these fillers are evenly applied and embedded in the coating and anchored with it. Thus they adhere firmly to the surface and form an even film which is considerably more firmly anchored than fillers which have been dusted or simply spread between layers or which have been applied by the flotation method. The fillers are preferably added to the solution in a fine dispersion. Soluble materials which form highly heat resistant oxides at the burning-in temperatures and which are compatible with the solutions of the invention may be added, e.g., certain soluble complex titanium or zirconium compounds may be added. Also, it is adavantageous to form the fillers "in situ" that is, forming the fillers during the burning-in process by the addition of soluble compounds which are deposited as insoluble and heat-resistant iron salts by reaction with the substrate being coated. These bed in the phosphate coating during the annealing process and make it possible to forego entirely or hold to small quantities the addition of inert fillers. Examples are boric acid or borates such as ammonium borate. Besides the borates polysilicates and polyphosphates may be employed, e.g., ammonium or alkali metal polysilicates and polyphosphates.

Other phosphates which decompose may be employed to advantage in the solution of the above-mentioned metal phosphates if the proportions of these other phosphates are maintained below 115 grams PO_4 per liter, as a maximum at any time and proportionately reduced as the concentration of the monocalcium or monobarium phosphate or the other alkaline-earth phosphates is decreased so that they always replace less than 50% of the phosphates of calcium, barium, or the other alkaline-earth phosphates including aluminum. For example, thermally decomposable phosphates, such as phosphates of ammonia or derivatives thereof such as urea; or phosphates such as aniline phosphates or organic esters of phosphates produce useful coatings when used with the said alkaline-earth phosphates in amounts not exceeding the above mentioned proportion. Such other phosphates provide additional sources of phosphoric acid during the burning-in treatment without raising the free acid content of the original solutions.

Such solutions as described above are applied to metal surfaces, e.g., iron and steel, including stainless steel, in conventional manner such as by dipping or by spraying. A significant feature of the methods of the present invention is the facility and quality of coatings on chrome-nickel steels which heretofore could not be covered uniformly with a phosphate layer using the customary phosphating methods. The metal surfaces with the film applied are subjected to elevated temperatures between 200° C. and 800° C. and preferably between 300° C. and 600° C. The burning-in temperature and time cannot be set forth exactly in advance since the speed of processing the material through the furnace, the thickness of the material to be treated and other factors which vary in the individual case are involved in the determination of the optimum temperature. Generally it has been found that with a sufficiently hot furnace and a baking temperature, e.g., 800° C. a finished coat can be obtained in a few seconds, while at 200° C. at least one or two minutes are required. Longer periods of time at the lower temperatures have been found to be not harmful. In the case of the treatment of grain-oriented electrical steels (e.g., Armco, a trademark), the methods of the invention are particularly advantageous since sheet metals or bands or grain-oriented steel have to be subjected to stress-relieving or annealing temperatures in order to relieve the stress of cold working and to attain maximum magnetic quantities. In such cases, it is possible to proceed with the burning-in of the film at the temperature required for stress relief which is of the order of 800° C. and under protective gas atmospheres of the order of 1000 to 1200° C. However, it is also advantageous in many cases first to burn in the film at a lower temperature and then proceed with the stress relief at the necessary higher temperature. The coatings formed according to the invention can stand the lower temperatures required for stress relieving without destruction. Where the stress-relieving is to impart grain-orientation and is carried out at temperatures above 850° C., however, destruction of or alteration of the type of coating occurs but surprisingly they still exert excellent isolating properties and prevent agglomeration of the piled sheets even at the higher temperatures. The coatings applied to grain-oriented electrical steels, such as cold rolled grain-oriented transformer sheet metal, function to isolate the individual layers during the processing through the annealing furnaces and prevent the individual layers from sticking to each other. The coatings also function subsequently as insulation coatings depending upon the stress-relieving temperatures for the grain-oriented steels as they have good electrical properties, i.e., they provide high inter-laminar resistivity and have minimum effects on the inter-lamination factor. The magnetic sheets or bands treated thereby are rust resistant and unaffected by oils so that they are suitable for use in air-cooled or oil-cooled transformers.

It is not necessary to start with pure compounds as technical monophosphates of the said alkaline-earth metals may be employed. In the case of calcium, superphosphate or double and triple superphosphate may be used as the starting materials. A feature of the invention is the provision of cheap starting materials for carrying out the methods of the invention in the case of calcium monophosphate, and the provision of a valuable starting and replenishing composition. Superphosphate is the decomposition product from tertiary calcium phosphate with sulphuric acid, and double and triple superphosphate are decomposition products from tertiary calcium phosphate and phosphoric acid. All of these products are standard by-products of the fertilizer industry. They contain all the impurities which were present in the raw phosphatic material. In providing starting materials for calcium phosphate solutions from these products, the superphosphate or the double or triple superphosphate are dissolved in water and the equilibrium solution appears by itself which contains in addition to the monophosphate of calcium, the amount of free phosphoric acid corresponding to equilibrium at room temperature. These solutions or brines contain sediments including tertiary

calcium phosphate which settle out and the brine is then separated from the residue. The brine can be used directly but preferably it is spray-dried by any of the well-known spray-drying processes. Through the manner and execution of the spray-drying process, pure monocalcium phosphate, soluble in water, is obtained out of the impure products. The monocalcium phosphate is obtained as a dry, powdered, nonhygroscopic product which holds the free phosphoric acid corresponding to equilibrium at room temperature through capillary action. As an example, 400 grams of commercial triple superphosphate were dissolved in one liter of water and allowed to settle. The resulting solution was separated from the insoluble impurities, including the tertiary calcium phosphate which developed through equilibrium. The equilibrium solution which was obtained after separation of the sediment had a concentration of monocalcium phosphate of 240 grams PO_4 per liter. The solution was spray-dried and a substantially pure monocalcium phosphate was obtained in which the free phosphoric acid corresponding to equilibrium was physically absorbed. Dry salts prepared as above are ready for shipping and a monocalcium phosphate solution, free of sediment, can be obtained therefrom in any desired concentration simply by dissolving the dry salt in water, and the resulting solutions are suitable for practicing the invention.

The following examples illustrate in detail the methods of the invention and the articles produced therefrom.

Example I

A solution was prepared which contained 151 grams PO_4 per liter of calcium monophosphate and 38 grams PO_4 per liter of urea phosphate. Samples of sheet metal of silicon steel having an analysis of approximately 3% silicon were dipped into the solution at room temperature. A film was produced on the surface of the samples of sheet metal and thereafter the surface having the film adhered thereto was subjected to temperatures of about 500° C. for from 30 seconds to 1 minute. A uniform, firmly fused, finely crystalline coating of from 4 to 6 microns was obtained.

Example II

Sheet metal samples which were treated as in Example I were tested in a 3% mist of salt spray and after 7 hours the phosphate layer was completely intact while sheet metals of the same quality but coated with a conventional zinc phosphate coating of 10 microns in thickness showed ample evidence of rusting. An uncoated sheet metal of the same material was almost completely rusted. Expressed in the notation system used by W. Machu in "Phosphatation, Scientific Basis and Techniques," 1952, page 291, Chemie Publishers, Weinheim (Bergstrasse), the corrosion test for the coatings materials are as follows:

For the burned-in layer	0
For the zinc phosphate layer	8
For the untreated metal	13

In this notation system, the state of corrosion is indicated by a number from 1 to 15, 1 to 5 meaning light beginnings of rust, 6 to 10 real beginnings of rust, and 11 to 15 actual and extensive rusting. After a treating time of one week, the burned-in layers obtained in Example I showed a notation of 2 with slight marginal corrosion, while the other samples had rusted completely.

Example III

A solution was prepared which contained 264 grams PO_4 per liter of calcium phosphate and 66 grams PO_4 per liter of urea phosphate, as well as 30 grams per liter of fine mica flour, The suspension at room temperature was applied to samples of sheet metal of the composition of Example I in the form of a thin film on the surface by spraying. The surface with the film applied was burned in for 60 seconds at 400° C. A phosphate layer of a thickness of about 8–10 microns was obtained.

Example IV

Samples of sheet metal, which were covered with a layer according to Example III were baked for 30 minutes at 700° C. without an ignition taking place. Only at 750° was there evidence of some slight decomposition through burning in. By way of comparison, an uncoated piece of sheet metal was given the same heating treatment. It began to turn blue at 350°, reddish at 500°, in less than two minutes.

Example V

Steel rods of 18/8 stainless steel were covered with a uniform thin phosphate layer, according to Example I. The rods had a diameter of 5.3 mm. and were in 6 drawings pulled to 2.1 mm. with a dry lubricant based on alkaline earth stearate. The cross-section was reduced 81.5%. The rods showed a shiny surface even after the sixth drawing.

For the purpose of comparison, uncoated rods of the same material were drawn with the same lubricant. After the second drawing deep grooves were seen to form, and no further drawings could take place.

Example VI

A cold rolled, grain-oriented 3% silicon magnetic steel band was put in a bath with a solution which contained 240 grams PO_4 per liter of monocalcium phosphate and 28 grams PO_4 per liter of free phosphoric acid and in which were suspended 30 grams per liter of mica. The band was removed from the solution with a liquid film firmly adhering thereto which remained uniformly distributed over the surface of the band even though the same was put up into the burning oven in a vertical position. It passed through the oven in from 30 to 60 seconds at 500° C. and a coating of a thickness of 8 microns consisting essentially of tertiary calcium phosphate was formed. The sheet metal band thus treated was used in assembling the core of a transformer and subjected to the necessary stress relieving temperatures after assembly without harm to the core or the electrical characteristics of the core.

Example VII

Steel strips were sprayed with the following solution:

81 grams PO_4 per liter of monocalcium phosphate
13.4 grams PO_4 per liter of equilibrium free phosphoric acid

The strips were then run through a pair of rollers to even the adhering film and processed through a furnace for 45 seconds at 550° C. The resulting burned-in phosphate coatings on the strips were of a few microns in thickness but nevertheless effective in protecting against agglomeration of the strips when annealed in stacked form.

In the manufacture of grain-oriented electrical steels, it has been customary to put some sheet metals after cold rolling and before applying the isolation coating through a stress relieving process at temperatures upwards of 800° C. in order to remove the stresses created in the cold working. With the methods of the present invention, such an intermediate step is avoided as it can be combined with the burning in of the coatings of the present invention. The magnetic band or sheet metal that has been cold rolled is processed in accordance with the invention and the film which is applied to the surface is burned in an oven heated to the temperature required for stress relieving. As is usual practice, the oven is kept under a protective gas atmosphere, e.g. nitrogen, so that higher temperatures can be used and in such cases the burned in coatings effectively isolate or prevent agglomeration of the bands or sheets at these higher temperatures.

Another feature of this invention is the discovery that after the stress-relieving or annealing treatment whether

the burned-in layers are formed on the metal surfaces simultaneously therewith or preliminary thereto and not withstanding that substantial decomposition or alteration in these layers occurs the thus annealed surfaces are particularly receptive to further burned-in layers without any preliminary cleaning. Thus the process described above not only prevents the agglomeration or sticking together of metal sheets in the annealing treatment but it prepares the metal surfaces in an especially beneficial way for subsequent reaction directly with phosphate coating solution, especially phosphate coating solutions that are burned-in on the metal surfaces. Subsequent burned-in layers are adherent and are anchored on the metal surfaces surprisingly without any preliminary treatment. In fact, it was completely unexpected to find that metal surfaces in the condition in which they are after the annealing treatment are more reactive to burned-in type phosphate coating solutions and receive more adherent burned-in layers than if they are subjected to an intermediary cleaning treatment. This discovery is of great commercial significance because such surfaces will no longer be subjected to annealing or stress-relieving temperatures and even though decomposition or alteration of the original burned-in layers has occurred, particularly if the higher temperatures and reducing atmospheres were employed to impart magnetic properties, such surfaces can be directly processed to provide subsequent burned-in layers for electrical insulating purposes. In the practice of this feature of the invention the same burn-in type phosphate coating solutions as above described and used to form the first burned-in layers are likewise employed for the application of the subsequent burned-in layers. The following example will explain this feature of the invention further.

Example VIII

For the manufacture of a grain-oriented transformer sheet, a rolled iron sheet containing silicon was covered with a film of a solution which contained 81 grams PO_4 per liter of calcium monophosphate in equilibrium with 13.4 grams PO_4 per liter of free phosphoric acid. The solution was evenly applied in a film which was burned in at 500–600° for 30 seconds. The rolled sheet was then annealed for several hours at 1100° C. in an atmosphere of pure hydrogen, as a result of which the desired grain orientation for the transformer sheet took place. The sheet was then slowly cooled in hydrogen, unrolled, stretched and without intermediary cleaning run through a solution containing:

114 grams PO_4 per liter of primary ammonium phosphate
124 grams PO_4 per liter of primary calcium phosphate
26.8 grams PO_4 per liter of free phosphoric acid
20 grams per liter of mica flour

An even film of this solution was formed on the surface. The sheet was then put through a burning-in zone, in which the solution film was burned-in on the metal surface at 600° C. for about 10 to 20 seconds. The result was a transformer sheet with an even electrical insulating coating which adhered well, was indissoluble, and protected at the same time against corrosion. The coating did not peel and resisted sufficiently the demands made on the sheet when used.

Sheets were also produced from the same solution of ammonium phosphate, calcium phosphate, phosphoric acid and mica flour and subjected to corrosive tests as well as electrical insulation tests. The results proved they would be entirely satisfactory for applications in which either or both conditions exist.

This application is a continuation-in-part of copending application of the same inventors, Serial No. 574,928 filed March 29, 1956, now abandoned.

What is claimed is:

1. A method of forming heat resistant coatings on a surface of ferrous metal and alloys thereof comprising contacting said surface with a solution containing as the essential coating producing ingredients between about 70 grams PO_4 per liter and 400 grams PO_4 per liter of calcium monophosphate, an amount of phosphoric acid sufficient to prevent the formation of a precipitate from the said monophosphate in said solution, and up to 50% based on said monophosphate of a thermally decomposable phosphate selected from the group consisting of ammonium phosphate, urea phosphate and aniline phosphate, said thermally decomposable phosphate being present in concentrations always less than 115 grams PO_4 per liter, and thereafter subjecting said surface to temperatures between about 300° C. to 1200° C. for a period of time sufficient to yield a firmly adherent phosphate coating on said surface.

2. A method of forming heat resistant coatings on a metallic surface which comprises the steps of (1) contacting said surface with an aqueous solution consisting essentially of at least about 70 grams PO_4/liter of a monophosphate of at least one metal selected from the group consisting of calcium, barium, strontium, beryllium and aluminum, (2) subjecting said surface to a temperature in the range of about 200° C. to about 1200° C. for a period of time sufficient to yield a firmly adherent burned-in phosphate coating on said surface, (3) cooling the said surface, (4) raising the temperature of the said surface sufficiently to effect annealing of the coated metal surface and cooling to thus effect said annealing, and thereafter repeating steps 1, 2 and 3 on said annealed surface.

3. A method of forming heat resistant coatings on a metal surface in accordance with claim 2 wherein said monophosphate is monocalcium phosphate.

4. A method of forming heat resistant coatings on a surface of a metal of the group of ferrous metals and alloys thereof comprising contacting said surface with an aqueous solution containing as the essential coating producing ingredients between about 70 grams PO_4 per liter and 400 grams PO_4 per liter of a monophosphate of at least one metal of the group consisting of calcium, barium, strontium, beryllium and aluminum, and an amount of phosphoric acid sufficient to prevent the formation of precipitates from the said monophosphate in said solution, up to 50% based on said monophosphate of a thermally decomposable phosphate selected from the group consisting of ammonium phosphate, urea phosphate and aniline phosphate, said thermally decomposable phosphate being present in a concentration less than 115 grams PO_4 per liter, and thereafter subjecting said surface to temperatures between about 200° C. and 1,200° C. for a period of time sufficient to yield a firmly adherent phosphate coating on said surface.

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