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PHOSPHATE COATING PROCESS

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This invention relates to an improved method for forming phosphate coatings on metallic surfaces. More particularly, this invention relates to an improved method which concurrently partially replenishes the operating solution and maintains it in optimum coating condition on a continuous basis.

In the operation of phosphate coating processes of the type in which the metalic ion of the phosphate coating is derived from the coating bath, it is well understood that continuous operation of such a solution requires replenishment of the metallic ion which forms the coating as well as the other ingredients of the bath, including accelerating agent, and the acid providing constituent. Replenishing material, to date, has generally comprised concentrated admixtures of the coating solution ingredients with the proportions thereof adjusted to maintain the constituents in the coating solution as closely to their initial concentration as is possible. It will be apparent that such periodic addition causes a change in the concentration of the materials in the coating bath by the quantities of such materials which were contained in the replenishing material, and that the bath will necessarily continuously vary in the concentration of the coating forming components from a low concentration just prior to the addition of the replenishing material to a high concentration just after the addition of the replenishing material to the solution. No satisfactory system has been devised for a continuous addition of the replenishing material to the solution, inasmuch as variations in load of work being processed through the solution and other conditions vary the rate at which the coating chemicals are removed from the coating solution and therefore periodic replenishment responsive to prior chemical analysis has been generally employed. In the most important commercial phosphate solutions, namely zinc dihydrogen phosphate and manganese dihydrogen phosphate solutions, the replenishing material ordinarily includes zinc, phosphoric acid and accelerating agent, which may be nitrate, nitrite, chlorate, sulphite or the like. It is conventional to introduce the accelerating agent in the form of an alkali-metal salt, since these materials are commercially available and are inexpensive. The alkali-metal ion continuously introduced into the operating coating solution in the replenishing material creates operational problems in the solution. The alkali-metal ion for example in zinc phosphate solutions is known to cause subsequently applied paint to have the tendency to blister. Additionally sodium ions tie up phosphate ions in the coating solution and make such phosphate ions unavailable for forming phosphate coating on the surface. Such sodium phosphate presents the additional problem that it renders the ordinary analytical determination of the phosphate content of the coating solution, since the phosphate which is present as sodium phosphate is not available for coating formation. Thus, upon continued operation the determination of total phosphate in the solution becomes more and more inaccurate as a method of maintaining the solution in efficient coating forming condition, and it is necessary to add sufficient phosphate ions to continuously increase the total PO_4 content of the solution as the sodium ion concentration increases. It is also well understood that when operating coating phosphate solutions to form coatings on ferrous surfaces that a portion of the iron from the surface being coated becomes dissolved in the coating solution and its concentration tends to increase as the solution is continuously used. As the iron content of the bath, present as the ferrous ion, increases, the solution forms sludge and the disadvantages of the presence of sludge are fully appreciated. Moreover, in the operation of zinc or manganese phosphate coating solutions it is known that the zinc or manganese content of the coating is higher than the zinc or manganese content of any bath soluble form of zinc or manganese phosphate which can be used as the replenishing material. Thus, it is necessary to add zinc to the replenishing material in excess to that which can be added as zinc phosphate. This is nomally accomplished by introducing the oxidizing agent in the form of a zinc salt, such as zinc nitrate or zinc chloride, etc. While a portion of the oxidizing agent is consumed in the process of forming the coating, introduction of the accelerating agent in the form of the zinc salt provides an excess of the oxidizing agent or other anion over a continuous period of operation and the concentration of the oxidizing agent or other anion has a tendency to constantly rise. The effect of additional quantities of oxidizing agent or other anion in the bath is well known and it is therefore necessary to modify the other operating conditions to accommodate the increasing quantity of the oxidizing agent or other anion. It is well understood that the above operational disadvantages which flow from the periodic addition of a concentrated replenishing material should be eliminated and a method for continuously replenishing the coating metal ions without concurrently introducing undesirable cations and anions has long been sought by this art.

It is the primary object of this invention to provide an improved process which enables the replenishment of the coating metal ion and concurrently maintains the operating coating solution in optimum condition to efficiently form phosphate coatings on metallic surfaces.

Another important object of this invention is to provide a process for forming phosphate coatings on metallic surfaces which improves the efficiency of conversion of the coating chemicals in the solution to coating on the metallic surface, and thus reduces the overall chemical cost of forming any given quantity of coating.

Another object of this invention is to provide an improved phosphate coating process which is maintained in optimum coating forming condition with greater ease, and which renders the conventionally employed analytical determination of the total phosphate content of the solution a reliable indicator of the coating forming ability of the solution.

Another important object of this invention is to provide an improved phosphate coating process which enables substantially sludge-free operation of the phosphate coating solutions of the coating phosphate type, particularly zinc and manganese acidic phosphate coating solutions.

In accordance with this invention, it has been found that the above and related objects are realized by a process which, generally stated, comprises the steps of forming an ion-exchange resin containing the coating metal ion of the phosphate coating solution with which the bed is to be employed, and during operation of the phosphate coating solution passing a portion of the coating solution through the coating metal ion-containing bed to simultaneously introduce the coating metal ion to the solution and remove therefrom other cations which are present in the coating solution. The quantity of the coating solution which is passed through the coating metal ion-containing resin bed is continually adjusted in response to periodic analyses which are made on the operating coating solution, so as to maintain the coating metallic ion, the acidic constituents and the accelerator in substantially the initial concentrations which were present in the bath as formulated. By this method un-

desirable cations such as the alkali-metal ions, sodium, potassium, etc., and ferrous-iron are continuously removed from the solution and replaced by the coating metal ion zinc or manganese. The zinc or manganese ion is thus maintained in optimum concentration in the operating coating solution and gradual build up of the concentration of accelerating agent or inert anions is avoided.

The initial step of preparing a suitable ion-exchange resin bed for use in this process is accomplished by passing an aqueous zinc salt solution through an ion-exchange resin in hydrogen form for a sufficient time to substantially saturate or load the resin particles with the coating metal ion. For this purpose, any of the aqueous soluble salts of zinc or manganese may be employed, such as the sulphate, chloride, nitrate or the fluoborate salt. It is preferred, however, to employ the same salt solution which corresponds with the acid to be used in regenerating the resin, and since sulphuric acid is highly effective in regenerating highly acidic cation-exchange resins the use of zinc-sulphate or manganese-sulphate as the exchange resin saturants is preferred. The concentration of the coating metal salt saturating solution is not critical, but the use of a relatively concentrated solution is preferred in the interest of reducing the time required to convert the ion-exchange resin to a substantially loaded condition. It is satisfactory to employ a relatively dilute metal ion salt saturating solution, but it is preferred to use a solution containing at lease about 5%–10%, by weight, of the saturant salt. Good results have been obtained by using a 5%–10% zinc-sulphate aqueous solution. When using a more dilute solution it will be apparent that the ion-exchange resin can be converted into a substantially loaded or saturated condition by merely continuing to pass the saturant solution through the bed until it is in a saturated condition. With the ion-exchange resin in the metal ion coating loaded form it is necessary only to connect the resin bed with appropriate piping connections to the operating solution tanks to enable the passage of the selected quantity of operating solution through that bed during the operation of the coating solution. The coating solution is then formulated and as work is processed therethrough, a portion of the coating solution is continuously fed through the ion-exchange resin bed. Alternatively, the coating solution may be fed through the ion-exchange resin bed on a periodic basis, or if desired, the entire coating solution may be processed through the resin bed on a batch basis. A batch operation is less desirable than a continuous cycling of a portion of the operating solution through the ion-exchange resin bed, because it causes a relatively large change in the concentration of the coating chemicals in the solution, whereas a continuous partial circulation of the coating solution continuously maintains the solution substantially in its original form. By periodically analyzing the operating coating solution for its total acid content, a determination effected by titrating a 10 ml. sample of the coating solution against 0.1 N sodium hydroxide solution to a phenolphthalein end point, a reliable indication of the decrease in concentration of the PO_4 and other necessary ions in the solution is obtained and they can be satisfactorily replaced by periodic addition of a replenishing material in substantially conventional form. It will be understood that the addition of accelerating agent as an alkali metal salt or adjustment of the acidity of the solution with sodium hydroxide for example, is no longer detrimental to the coating efficiency of the solution since the continuous cycling of a portion of the operating solution through the ion-exchange resin bed removes the undesirable cations, sodium or the like. Such analyses indicates the concentration of the undesirable cations in the solution and constitutes a gauge by which the quantity of operating solution to be circulated through the ion-exchange resin bed can be adjusted to continuously maintain the concentration of such ions at a level below that which represents a problem to the formation of a corrosion resistant, high quality paint base coating.

It will be appreciated that the process of this invention is versatile and well adapted to accommodate widely varying quantities of work being processed through a given coating solution, changes in the type of contact between the solution and the work, the operating temperature or the like since the periodic analyses provide an accurate representation of the coating forming ability of the solution and by a simple modification in the quantity of the coating solution fed to the ion-exchange resin bed the changed condition is promptly accommodated.

As the ion-exchange resin bed is continuously used, the undesirable cations replace the zinc cation of the resin and the resin becomes less efficient in purifying and replenishing the operating solution. When the ion-exchange resin reaches a relatively low level of efficiency, the resin is easily regenerated to operating condition by treatment with sulphuric acid. When the ion-exchange resin contains a mixture of alkali metal ions and zinc ions the regeneration of the resin with sulphuric acid releases a mixture of sodium sulphate and zinc sulphate and this solution is normally discarded. Where the ion-exchange resin is operating in conjunction with a process in which it removes ferrous ions and thus in its spent condition contains ferrous ions and zinc ions, a regeneration with sulphuric acid releases an admixture of zinc sulphate and ferrous sulphate. From such a solution the zinc sulphate can be salvaged by the addition of zinc oxide and aerating this solution, for example, by bubbling air therethrough, to convert the ferrous sulphate into ferric hydroxide which is removed from the solution by filtration thus leaving zinc sulphate. Such zinc sulphate solution is then reusable to prepare the ion-exchange resin, in hydrogen form, to a form in which it is saturated or loaded with zinc ions. A similar procedure is effective when the ion-exchange resin contains a mixture of ferrous ions and manganese ions, by replacing the zinc oxide with manganese oxide and employing otherwise identical steps.

The below given examples are intended to illustrate the process of this invention in greater detail, but it is to be understood that the specific solutions used, the concentration of ingredients and the conditions employed are intended to be illustrative only, and not to represent the definitive limits of this invention which are set forth hereinabove and in the appended claims.

Example I

An aqueous acidic zinc phosphate coating solution was prepared and upon analysis found to contain 0.65% zinc, 1.34% PO_4, 0.5% NO_3, and to have pH of 2.5, and a total acid of 30.5 points. The total acid points are the number of ml. of 0.1 N NaOH required to titrate a 10 ml. sample of the solution to a phenol phthalein end-point.

An ion-exchange resin bed was prepared by passing a 10% zinc sulphate aqueous solution through a hydrogen form strongly acidic cation resin bed until the resin bed was substantially loaded with zinc ions, as determined by analyzing the zinc content of the solution entering the resin bed and leaving the same. The resin employed was Dowex 50–X8 resin which is a styrene-divinylbenzene resin which has been sulfonated with sulfuric acid, contains about 8% divinylbenzene and has a particle size in the range of about 20 to about 50 mesh.

The resin bed contained 3 lbs. of the zinc-form resin for each gallon of processed solution and was provided with suitable connections and a positive pressure pump to enable the regulated flow of a portion of the operating solution through the resin bed and return to the operating coating solution. Cold rolled steel in substantially flat panel form was processed through the above-described coating solution and coated with an av-

erage coating weight of approximately 2400 mg./sq. ft. by contacting the same for 20 mins. at approximately 200° F.

A portion of the bath having the above-stated composition was placed in a second coating tank and similar panels processed therethrough for comparative purposes. After processing 10 sq. ft. of panel surface through the bath without processing any portion of the coating solution through an ion-exchange resin bath, an analysis of the coating solution showed that the solution contained 0.46% ferrous iron, 0.16% zinc, 1.34% PO_4, 0.52% NO_3, and had a total acid of 29.4 and pH of 2.5. In comparison, by operating the coating solution provided with the ion-exchange resin processing facility and continuously passing a portion of the solution through the ion exchange column cold rolled steel was processed therethrough to form a coating averaging 2400 mg./sq. ft. in coating weight, until 100 sq. ft. had been processed through the bath and an analysis of the bath showed the composition to be the following: 0.45% ferrous iron, 0.18% zinc, 1.19% PO_4, 0.74% NO_3, and the solution to have a pH of 2.5 and a total acid of 30.5. The operating solution was substantially sludge-free and regeneration of the ion-exchange resin shows the resin to have accepted 52 grams of ferrous iron.

The coating solution having no ion-exchange resin bed connected thereto was continued to be used until 300 sq. ft. of cold rolled steel had been processed therethrough and an analysis of the bath at this point showed the following: 0.56% ferrous iron, 0.06% zinc, 1.33% PO_4, 0.50% NO_3 and to have a pH of 2.5 and a total acid of 30.0. The operating solution connected to the ion-exchange resin bed was operated until 300 sq. ft. of cold rolled steel had been processed therethrough and an analysis at this point showed the bath to contain the following: 0.38% ferrous iron, 0.13% zinc, 1.18% PO_4, 0.7% NO_3 and to have a pH of 2.5 and a total acid of 30.5.

Continued operation of the two solutions, with periodic replenishment as indicated by total acid determinations, was continued until thousands of sq. ft. of work had been processed through each bath. A total of the coating chemicals employed in the comparable baths showed that the solution having the ion-exchange column connected thereto operated substantially sludge-free during the continuous processing and employed 16 lbs. of coating chemicals per 1000 sq. ft. of surface coated, whereas the solution having no ion-exchange column connected thereto employed 20 lbs. of coating chemicals per 1000 sq. ft. of work processed therethrough.

Another zinc phosphate coating solution was formulated to produce relatively lightweight zinc phosphate coatings, suitable for use as a paint base and an analysis of the solution showed it to contain: 0.60% zinc, 1.02% PO_4, 1.30% NO_3, and to have a pH of 2.35, a total acid of 21, and a free acid of 4. The free acid was determined by titrating a 10 ml. sample of the coating solution against 0.1 N sodium hydroxide solution to a brom cresol-green end-point, the number given being the number of ml. of NaOH required to reach the end-point. Portions of this solution were positioned in the two coating tanks described above in Example I and operated at 180° F., so that the metal being processed therethrough was in contact with the solution for 5 mins. The average coating weight produced on the panels under these conditions was 450 mg./sq. ft. Processing cold rolled steel through the solutions showed the solution operated without the benefit of the ion-exchange column to have the following analysis after 30 sq. ft. of cold rolled steel had been processed therethrough: 0.35% ferrous iron, 0.25% zinc, 1.12% PO_4, 1.40% NO_3, and to have a pH of 2.4, a total acid of 20.4 and a free acid of 3.5. The coating solution having an ion-exchange column, of the same type described above in Example I connected thereto, after 98 sq. ft. of cold rolled steel had been processed therethrough had an analysis as follows: 0.11% ferrous iron, 0.15% zinc, 1.08% PO_4, 1.42% NO_3, a pH of 2.5, a total acid of 19.5 and a free acid of 3.5. Comparative operation of these two solutions showed that the solution operating without the ion-exchange column required 7½ lbs. of coating chemicals per 1000 sq. ft. of steel processed therethrough, and only 5 lbs. of coating chemicals per 1000 sq. ft. of steel processed therethrough was required in the operation of the coating solution having the ion-exchange column attached thereto.

Other solutions which have been satisfactorily operated with an ion-exchange column attached thereto in substantially similar arrangement to that described in Example I are set forth in the examples which follows:

Example II

A manganese phosphate solution as follows: 0.50% manganese, 1.3% PO_4, 0.5% NO_3, a pH of 2.55 and a total acid of 31.

Example III

A spray paint base solution as follows: 0.24% zinc, 0.28% NO_3, 0.54% PO_4, 0.001% NO_2 and a total acid of 9.8. This solution was sprayed on the work at 95° F.–110° F.

Example IV

A zinc phosphate solution for paint base coating formation by spray operation at 160° F., had the following analysis: 0.24% zinc, 0.35% ClO_3, 1.02% PO_4, and a total acid of 15.4.

What is claimed is:

1. A method for operating a phosphate coating bath of the type which forms on a metal surface a coating containing a metal ion derived from the coating solution which comprises the steps of forming an aqueous acidic phosphate solution containing a coating metal phosphate ion, treating an acidic ion exchange resin with an aqueous saturant solution containing the said coating metal ion until the said resin is substantially saturated with said metal ion, and passing at least a part of said coating solution through said resin bed to thereby remove from said coating solution cations other than said coating metal ion and to add to said solution said coating metal ion.

2. A process in accordance with claim 1 wherein ion exchange resin saturant solution is an aqueous zinc sulfate solution.

3. A method for continuously operating an aqueous acidic phosphate coating bath of the type which forms on a metal surface a coating containing a metal ion derived from the coating solution which comprises the steps of saturating an acidic ion resin with an ion selected from the group consisting of zinc and manganese ions, passing an aqueous acidic phosphate coating solution containing an ion selected from the group consisting of zinc and manganese and at least one additional ion selected from the group consisting of the alkali metal ions, ferrous and ferric ions, aluminum and the alkaline earth metal ions through said resin bed and controlling the quantity of said coating solution passed through said resin bed so as to remove substantially all of said other ions therefrom and replace the same with one of said ions selected from the group consisting of zinc and manganese.

4. A process in accordance with claim 3 wherein said coating solution is periodically passed through said resin bed and returned to the coating solution container.

5. A method for continuously operating an aqueous acidic phosphate solution of the type which forms on a metal surface a coating containing a metal ion derived from the coating solution which comprises the steps of forming an aqueous acidic coating solution containing PO_4, an accelerating agent and a metal ion selected from the group consisting of zinc and manganese, establish-

ing an acidic ion exchange bed and saturating the same with a metal ion selected from the group consisting of zinc and manganese, during processing of metallic parts through said coating solution to form a coating thereon continuously cycling a portion of said coating solution through said resin bed and regulating the quantity of said solution cycled through said bed so as to remove from said solution cations other than zinc and manganese ions and replace the same with the ion in said resin bed.

6. A method in accordance with claim 5 wherein said metal ion is zinc.

7. A process in accordance with claim 5 wherein said coating solution is periodically analyzed and the quantity of said solution fed through said resin bed is regulated so as to maintain said coating solution substantially free from ions other than said coating metal ion and periodically replenishing said coating solution responsive to said analyses so as to maintain the said PO_4, an accelerating agent and coating metal ion in substantially their initial concentrations.

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