

# UNITED STATES PATENT OFFICE

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## METHOD OF COATING FERROUS METAL WITH A WATER INSOLUBLE METALLIC PHOSPHATE

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This invention relates to the art of applying phosphate coatings to the surface of iron or steel, and particularly to the art of producing these coatings on a succession of pieces by treating them with an aqueous acid phosphate solution such, for example, as zinc phosphate.

Among the objects of the invention the following are particularly noted:

1. The provision of a process for coating a series of pieces of ferrous metal with great rapidity and at a minimum of expense.

2. The provision of a method for producing coatings of extreme uniformity on a long succession of pieces, by means of a solution which is continually used for the purpose and always maintained in perfect operating condition. In connection with this object it is the aim of the invention to maintain the solution entirely uniform with respect to its coating characteristics, even though the solution may undergo a considerable change in its chemical composition.

3. The provision of a method by means of which it is possible to achieve a very rapid coating operation without resorting to the use in the coating solution of accelerating agents, such as metals less basic than iron and/or oxidizing agents such as nitrates, permanganates, etc., which, heretofore, have been commonly employed in phosphatic coating operations. My invention thereby makes possible ease of control and economy of operation, and avoids the presence of deleterious metals in the resultant coating.

4. The provision of a method which is especially suited to the production of very fine-grained, smooth phosphatic coatings on chemically cleaned iron or steel surfaces such as surfaces which have been cleaned in an alkaline cleaning solution, without necessitating drying, rubbing, wiping, or brushing prior to or during their treatment with the phosphatic solution.

The solution employed in the process of the present invention may comprise a phosphate of a metal such as zinc or manganese. For certain practical and commercial reasons I prefer to use zinc phosphate, because of its more ready availability and relatively lower cost. Therefore, in the following description, I will refer to zinc phosphate, although it is to be understood that the same principles may very well be applied to other metals of a similar nature.

Briefly stated, the process, in its preferred form, comprises subjecting a succession of iron or steel pieces serially to the action of an aqueous zinc phosphate solution, while substantially continuously adding to the solution, regulated quantities of the zinc phosphate solution and of a water solution of a salt of nitrous acid, which additions are made in an amount which is sufficient to maintain the metal content and the pH

of the solution substantially constant and also substantially free of dissolved iron.

The presence of small amounts of foreign anions in the solution is generally quite harmless, but large amounts of sulphates, chlorides, or ions of other strong acids must be avoided.

Foreign cations, especially of metals more basic than zinc, are almost entirely without influence on the process. For instance, large quantities of the ions of alkalis and ammonium do no harm.

A satisfactory continuous operation of the coating process on a succession of surfaces depends on maintaining the solution constantly in its optimum condition. However, certain factors, to be discussed below, which are directly helpful in accelerating and improving the coating action are antagonistic to the maintenance of the solution in the best possible working condition. Some compromises, therefore, have been found to be necessary in order to maintain uniformity of results in the continuous operation of my process, and my invention makes possible the adoption of these factors with their incidental advantages in spite of what otherwise would be their disadvantages.

Before proceeding with a more detailed description of my improved process, I wish to state that extensive experiments have shown that when a dilute solution of zinc phosphate, which is substantially saturated at room temperature, is heated for some time, it gradually precipitates a phosphate of zinc containing a higher ratio of zinc to phosphorus than the solution from which it precipitates. In other words, the hot solution is supersaturated with respect to the zinc phosphate which precipitates. As the precipitation proceeds, the solution rises in hydrogen ion concentration (falls in pH) due to the greater proportionate loss of zinc. This action continues until the solution has again reached equilibrium at the elevated temperature.

The rate at which such a hot zinc acid phosphate solution loses its supersaturation is accelerated by a number of factors such as the presence of crystalline precipitates of certain kinds, violent agitation, high temperature, and the presence of certain dissolved materials, notably dissolved iron.

I have discovered that rapid coating of iron or steel surfaces with solutions of this character proceeds best when the solution is supersaturated. I have likewise discovered that the utmost speed of coating action is obtained by rapidly renewing the film of solution actually in contact with the surface which is being coated. This can be accomplished by any means which causes a rapid relative motion of the solution and the surface, but I prefer, because of its simplicity and its effectiveness in producing this result, to impinge the solution onto the surface.

To this end I employ suitable spraying equipment and a pump for circulating the solution from a reservoir to the spraying nozzles, the solution which runs down from the work being caught in suitable troughs and subsequently returned to the reservoir for recirculation. Equipment of this kind is well known in the art and need not be specifically described or illustrated, especially since it can take any one of a number of forms, dependent upon the particular installation.

The highest coating speed is likewise favored by elevation of temperature, up to the boiling point, and for best results the temperature of the solution should be quite accurately controlled. However, as above indicated, elevated temperatures have a tendency to cause the solution to lose its supersaturation, for which reason I prefer a temperature somewhere between 160° F. and 190° F., because my experience has shown that a temperature within this range will yield coatings in a period which is sufficiently brief without causing the extremely rapid loss of supersaturation which occurs at higher temperatures.

Violent agitation of the solution tends to speed up somewhat the rate at which it loses its supersaturation and falls in pH. Nevertheless, rapid renewal of the film of solution actually in contact with the surface of the metal, and the more or less violent agitation which it necessitates, is still considered desirable, since the great increase in coating rate so obtainable is a sufficient advantage to more than compensate for the additional difficulty which it entails in the proper maintenance of the solution. Rapid circulation by means of a pump and the violent agitation incident thereto as well as to the impingement from spray nozzles such as suggested above, present this problem of loss of supersaturation, but even so I consider them to be desirable.

In addition, the elevation in temperature, as mentioned above, has a bearing upon the loss of supersaturation, but here again I prefer to use the temperatures indicated above in connection with my improved process.

In the continuous operation of my process another problem arises in that the solution, in acting upon the iron or steel surfaces of a succession of pieces, dissolves some of the iron, and I have discovered that this dissolved iron has such an accelerating effect upon the rate of loss of supersaturation as to make its removal essential.

The removal of the iron from the solution may be effected in a number of ways, such, for example, as by the addition to the solution of chemicals capable of precipitating the ferrous iron or of oxidizing the ferrous iron to ferric iron, the latter being practically insoluble in the solution. Furthermore, adequate aeration of the solution may also be employed in removing the iron. I prefer, however, to precipitate the iron by adding a suitable chemical, and the chemical I employ has an added function which will be described below. I wish it to be understood, however, that whatever aeration takes place in the carrying out of my process, especially where the solution is impinged upon the work, may have an important bearing upon the precipitation of insoluble ferric iron, and to the extent that aeration accomplishes this end, I am enabled to save expense by employing a minimum quantity of the preferred chemical to be described below.

As a result of the operation of the various factors described above, there exists, during the coating operation, a continuous tendency for the solution to become more acid, i. e., to fall in pH.

At the same time the solution tends to become depleted in zinc content, partly due to useful deposition of insoluble zinc phosphate on the metal to be coated, and partly to the continual precipitation of zinc phosphate from the solution in its attempt to relieve the supersaturation. For these reasons, it has been found necessary, in order to maintain the solution in perfect operating condition, to continually add to the solution a substance or substances capable of preventing this increase in hydrogen ion concentration (fall in pH) as well as a substance or substances capable of maintaining at a substantially constant value the zinc content of the solution.

While it is possible to add these substances intermittently, yet such addition may allow the composition of the solution at certain times to fall outside the optimum range. Moreover, owing to the effects of local concentration, etc., on adding comparatively large amounts of restoring chemicals at one time, the local balance of the solution is so disturbed that zinc is uselessly lost and chemicals uselessly consumed. A marked increase, both in the uniformity of the coatings obtained, as well as in economy of chemical consumption, is obtained by adding both types of chemicals substantially continuously. This is especially true of the chemical for maintaining the pH substantially constant.

It is likewise preferable to add the chemicals to the coating solution at a location where it is in a state of vigorous agitation.

The solution is capable of operating successfully at a given pH over a considerable range of zinc concentrations, but at a given zinc concentration the solution operates correctly only within a narrow pH band. Too high a pH, in general, causes useless precipitation of zinc phosphate, while too low a pH causes the process to become inoperative.

The precipitating agent which I prefer to employ is a salt of nitrous acid, because such material will function not only as a medium for converting ferrous iron into insoluble ferric iron, but also as an agent for maintaining the pH of the solution substantially constant. Sodium nitrite is particularly suitable for the purpose, and I prefer to introduce it as a freshly prepared water solution. Barium nitrite or calcium nitrite may also be employed, or some other water soluble salt of nitrous acid.

As above pointed out, effective aeration of the solution, such as occurs during an impinging method of applying the solution to the surface to be treated, will have a marked effect on the precipitation of ferric iron, and the extent to which this effect can be availed of, will, of course, make possible a corresponding reduction in the quantity of the nitrite solution which may be required.

It will be noted that the continuous addition of the precipitating chemical may give rise to the presence in the solution of quantities of certain materials (principally monosodium phosphate) which will steadily increase as the process continues, so that the chemical composition of the solution, which may start out, for example, merely as a solution of acid zinc phosphate, will alter markedly with time. However, in spite of this alteration, its coating effect will remain substantially constant as long as the pH and the zinc content are maintained substantially unaltered and the solution is kept substantially free of iron.

As a specific example I will now describe my improved process as it may be applied to the coating of a succession of steel stampings such as automobile fenders, hood covers, splash guards, gasoline tank covers, etc.

The stampings, as they come from the press, are generally contaminated with oil, grease, and/or drawing compound, and sometimes with rust. Unless the rusting is severe, the parts may be satisfactorily coated without removal of the rust. If severely rusted, the parts may be subjected to pickling or other de-rusting treatment before entering the cleaning and coating system to be described.

Grease, etc., should be removed from the articles to be coated by my process. This may be accomplished by any of the well-known conventional means such as wiping or washing with a solvent, vapor degreasing, or alkaline cleaning.

Although my improved process of producing a uniform coating on a long series of surfaces is not dependent for its success on a particular type of cleaning procedure, yet the production of extremely uniform coatings on surfaces originally contaminated non-uniformly with grease, dirt, etc., is facilitated by a cleaning procedure that leaves the surfaces uniform with respect to residual contamination. This can be accomplished by solvent cleaning methods, but the simplicity and economy of alkaline cleaning makes this method preferable.

After being properly cleaned and prepared for the coating operation, the stampings are subjected to a coating solution such, for example, as the following:

*Formula No. 1*

Zinc oxide	-----pounds	1. 667
Phosphoric acid, 75%	-----gallon	0. 500
Water	-----gallon	0. 500

The foregoing is a concentrated solution, and for use should be diluted with water until the concentration of the formula is about 2% by volume.

The diluted solution is placed in a suitable tank which is preferably equipped with means for controlling the temperature of the solution. As indicated above, the temperature may vary considerably, but I have found that a temperature in the neighborhood of 180° F. will produce excellent results.

Measured at room temperature, the above solution has an initial pH of about 2.5.

Inasmuch as I prefer to impinge the solution against the surface of the stampings, any suitable spraying equipment may be provided, the details of which are not illustrated, because they may take various forms, dependent upon individual requirements.

Circulation of the solution through the tanks to the spraying nozzles or jets is preferably provided for by means of a centrifugal pump, and the material which runs down from the work is collected in suitable troughs and returned to the tank or reservoir from which the solution is pumped.

The stampings to be coated are subjected to the impinging action of the jets of solution at a rate such as will provide for a treatment of from thirty seconds to one minute, although this period may vary considerably, depending upon conditions and the temperature of the solution.

While the stampings are being coated, the pumping system is kept in continuous operation in order to provide for continuous circulation of the

solution from the tank to the impinging nozzles or jets, and from the jets to the work, and then back again to the tank.

Equipment of the kind described is familiar to those skilled in this art, but I should like to point out that a substantially continuously operating conveyor system of any suitable sort is particularly well adapted for use with my improved process, the stampings being carried past the impinging nozzles at a steady and uniform rate, and the coating action taking place in a remarkably short period of time.

As soon as the coating operation is begun, I immediately add to the solution regulated quantities of the solution of Formula No. 1, and also of a water solution of a salt of nitrous acid, preferably sodium nitrite. These additions are made preferably at a point where the solution is in more or less violent agitation so as to insure thorough mixing with the body of the solution.

The rate at which these solutions are introduced is regulated so as to maintain the zinc content and the pH of the coating solution substantially constant and also substantially freed of dissolved iron. To this end suitable determinations of the zinc content and of the pH may be made in any desired manner known to this art.

For example, the zinc content of the solution may be determined electrolytically or chemically. A convenient method consists in titrating a small sample of the solution with standard potassium ferrocyanide in accordance with the directions given in standard chemical text books.

The pH may be determined colorimetrically or potentiometrically by any standard method. The potential of the glass electrode vs. a saturated calomel electrode furnishes a convenient measure of the pH of the solution.

The zinc content of the solution may be varied over a considerable range without appreciably affecting the operation of the process, but for each zinc concentration there exists an optimum pH from which only narrow departures are allowable. The minimum pH (maximum hydrogen ion concentration) which is allowable to secure good coatings in the time allowable, varies a little with the type of metal to be coated, and the method of cleaning employed. The correct pH likewise varies with the temperature at which the coating solution is maintained.

Exact values of the pH at which the solution should be operated for each zinc concentration and temperature are difficult to specify. Typical values are given for several temperatures in Table 1, below. These values are for normally reactive steel, thoroughly alkali cleaned. A little experimentation will enable the operator to find the correct values for his conditions, and, once found, these need only to be maintained to insure perfectly uniform coating throughout.

TABLE NO. 1

*Typical pH values for various zinc concentrations and temperatures*

Zinc concentration grams per liter	Temperature, °F.		
	170°	180°	190°
1	2.82	2.80	2.67
2	2.68	2.61	2.43
3	2.55	2.42	2.18
4	2.41	2.23	-----

The above values are average for successful operation on ordinary sheet steel, alkali cleaned.

Values more than 0.1 pH unit below these give definitely less satisfactory coatings; values more than 0.1 pH above this can only be maintained at the expense of excessive precipitation of zinc.

5 For solvent-cleaned steel values about 0.1 pH unit lower may be used to obtain excellent coatings. However, my experience has shown that a solution which operates perfectly with alkali-cleaned steel will likewise operate perfectly with  
10 solvent cleaned steel, if both are reasonably free of grease and uniformly cleaned.

After the stampings have been coated they may be washed and then dried, whereupon they are ready for the application of any desired finish, such as paint, varnish, lacquer, japan, or the like.

The zinc restoring solution may be the concentrated solution of Formula No. 1, and the sodium nitrite solution may contain about 60  
20 grams of sodium nitrite per liter of water.

The addition of the solutions as described, so as to maintain the zinc content and the pH of the treating solution at substantially constant values, will, at the same time, serve to keep the  
25 solution substantially free of dissolved iron, the concentration of which latter should be kept below approximately 5 grams per liter. The use of the sodium nitrite solution described serves at the same time to insure the complete precipita-  
30 tion of the soluble iron, which is changed from the ferrous state to the ferric state, in which latter state it precipitates and can be removed from the solution from time to time.

The sodium nitrite solution mentioned above is  
35 only typical, and I wish it to be understood that solutions of any convenient strength may be employed, so long as they are added in proper quantities to accomplish the purpose in view.

Similarly, the zinc-containing solution used for  
40 maintaining the zinc concentration of the coating solution may likewise be varied considerably in composition and in concentration. It is convenient, however, to use the same solution as was originally used for making up the original coating  
45 solution.

Solutions of the phosphates of other coating metals except, of course, ferrous phosphate may be substituted for the zinc solution given in Formula No. 1, and by way of illustration the follow-  
50 ing may be employed:

*Formula No. 2*

Manganous carbonate-----pounds--	2.35
Phosphoric acid, 75%-----gallon--	0.500
55 Water-----do-----	0.500

In using this solution in my improved process, the pH and the manganese content of the coating solution are maintained constant at appropriate values in a manner entirely analogous to the maintenance of the pH and the zinc content of the coating solution of the given example.

In any case, the content of coating metal in the working solution is determined by standard chemical methods forming no part of the present  
65 invention. Rapid methods of chemical analysis, such as titrations, are naturally to be preferred.

My improved process is capable of giving the finest-grained and smoothest coatings on surfaces which have been alkali-cleaned and rinsed, with-  
70 out drying, wiping, brushing or mechanical treatment either prior to or during the coating operation, which is a distinct and marked advantage over previous processes known to me, which, for the production of the smoothest coating, require  
75 that the work be solvent-cleaned and wiped or

brushed before coating, or, at least, if it be alkali-cleaned, that it be dried and solvent-wiped before being coated, or that it be mechanically rubbed during the coating operation. This advantage makes it possible to combine the apparatus stages,  
5 in which the pre-cleaning is performed, into one continuous unit with the coating stage, which, of course, effects a corresponding saving in floor space and a marked economy in construction and equipment costs.  
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What I claim is:

1. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which comprises spraying a succession of pieces  
15 with a zinc phosphate solution; collecting the run-off for re-use in the spraying operation; and substantially continuously adding to the solution regulated quantities of zinc phosphate and of a soluble salt of nitrous acid sufficient to maintain  
20 the sprayed solution substantially constant as to zinc content and pH and also substantially free of dissolved iron.

2. The method of claim 1 wherein the solution is maintained at a substantially constant tem-  
25 perature within the range of approximately 160° F. to 190° F.

3. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which  
30 comprises spraying a succession of pieces with a zinc phosphate solution; collecting the run-off for re-use in the spraying operation; and substantially continuously adding to the solution regulated quantities of zinc phosphate solu-  
35 tion and of an aqueous solution of sodium nitrite sufficient to maintain the sprayed solution substantially constant as to zinc content and pH and also substantially free of dissolved iron.

4. The method of claim 3 wherein the solu-  
40 tion is maintained at a substantially constant temperature within the range of approximately 160° F. to 190° F.

5. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the  
45 substantially continuously operable method which includes spraying a succession of pieces with an aqueous acid phosphate coating solution which is substantially free of dissolved iron, collecting the run-off for re-use in the spraying operation,  
50 and substantially continuously adding to the solution regulated quantities of the acid phosphate and of a soluble salt of nitrous acid sufficient to maintain the sprayed solution substan-  
55 tially constant as to its metal content and pH and also substantially free of dissolved iron.

6. The method of claim 5 wherein the solution is maintained at substantially constant tempera-  
60 ture within the range of approximately 160° F. to 190° F.

7. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which includes spraying a succession of pieces with  
65 an aqueous acid phosphate coating solution which is substantially free of dissolved iron, collecting the run-off for re-use in the spraying operation, and substantially continuously adding to the solution regulated quantities of aqueous acid phosphate coating solution and of a water solu-  
70 tion of a salt of nitrous acid sufficient to maintain the sprayed solution substantially constant as to its metal content and pH and also substantially free of dissolved iron.

8. The method of claim 7 wherein the solution  
75

is maintained at substantially constant temperature within the range of approximately 160° F. to 190° F.

5 9. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which comprises spraying a succession of pieces with a manganese phosphate solution; collecting the run-off for re-use in the spraying operation; 10 and substantially continuously adding to the solution regulated quantities of manganese phosphate and of a soluble salt of nitrous acid sufficient to maintain the sprayed solution substantially constant as to manganese content and pH 15 and also substantially free of dissolved iron.

10. The method of claim 9 wherein the solution is maintained at a substantially constant temperature within the range of approximately 160° F. to 190° F.

11. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which comprises spraying a succession of pieces with a manganese phosphate solution; collecting the run-off for re-use in the spraying operation, and substantially continuously adding to the solution regulated quantities of manganese phosphate solution and of an aqueous solution of sodium nitrite sufficient to maintain the sprayed solution substantially constant as to manganese content and pH and also substantially free of dissolved iron.

12. The method of claim 11 wherein the solution is maintained at a substantially constant temperature within the range of approximately 160° F. to 190° F. 15

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CERTIFICATE OF CORRECTION.

Patent No. 2,132,883.

October 11, 1938.

GERALD C. ROMIG.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 24, for "freed" read free; page 4, first column, line 27, for "5" read .5; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of December, A. D. 1938.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.

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12. The method of claim 11 wherein the solution is maintained at a substantially constant temperature within the range of approximately 160° F. to 190° F.

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