Patented Aug. 10, 1943 2,326,309

UNITED STATES PATENT OFFICE

2,326,309

METHOD OF PRODUCING PHOSPHATE COATINGS ON FERROUS METAL ARTICLES

Gerald C. Romig, Elkins Park, Pa., assignor to American Chemical Paint Company, Ambler, Pa., a corporation of Delaware

No Drawing. Application January 22, 1941, Serial No. 375,448

11 Claims. (Cl. 148—6.5)

The present application is in the nature of a continuation-in-part of my earlier copending application Serial No. 322,176, filed March 4, 1940.

This invention relates to the art of applying phosphate coatings to ferrous surfaces and especially to the production of coatings of this type which are to be used as a base for paint or the like. Typical instances are the coating and finishing of automobile bodies and fenders; refrigerator, radio and other cabinets; washing machine parts, etc.

As is well known, in industrial fields of the kind mentioned, modern mass production methods generally demand extreme rapidity of operation. Furthermore, the results must be uniform over a long succession of pieces and the process must be dependable so as to avoid all interruptions to production schedules. My invention, therefore, is particularly concerned with meeting these requirements.

Other objects of the invention are to provide a process of the character described which will produce a firmly adherent coating so that the subsequently applied final finish of paint or the like is securely anchored; to produce a coating which will increase the life of the final finish under all of the various corrosive influences which may be encountered in service; to produce a coating which is chemically inert toward the constituents of the usual final organic finish of paint, as well as chemically stable toward the corrosive agents normally met with; to produce a coating which is sufficiently smooth so as not to interfere with the smoothness and luster of the final finish, as well as one which requires the least possible number of finish coats; and to produce a phosphate coating which is relatively thin. This latter is particularly important because inorganic coatings of the character produced by this invention are generally rather hard and somewhat brittle in nature and if excessively thick they are liable to lessen the resistance of the final finish to impact, bending or other stresses. My invention, therefore, is adapted to provide a coating which completely covers the metal without, however, being so thick as to chip off readily and unduly injure the final finish in case the metal is subjected to distortion sufficient to crack the coating.

As stated above, the invention is intended to provide a process of the character described which will produce a coating with great rapidity. As a practical matter, this means that in order to meet the demands of modern mass production methods, the coating treatment should generally be completed within substantially one minute, and, in no case, should exceed approximately ten minutes and preferably should be not greater than five minutes. My invention makes this possible and at the same time provides a process which can be operated practically continuously on a twenty-four hour a day basis without interruptions due either to chemical or mechanical difficulties or limitations.

It is also an object of my invention to provide a phosphate coating process which is susceptible of very precise control by the use of simple means for accurate maintenance of operating conditions and with the use of equipment which can be readily incorporated into the modern production line, the equipment preferably being of such nature that the work may be passed through the process on standard conveying mechanisms.

Another object of my invention is to provide a phosphate coating process which, if desired, can be employed without the necessity of heating the coating solution so as to avoid the cost and other disadvantages incident to the employment of heating elements. In association with this object, it is an aim of the invention to provide a process in which the production of sludge in the coating solution during the course of its use is reduced to a minimum, as well as to modify the character of whatever sludge is produced so that shut-downs for the purpose of removing sludge either from the tanks used to hold the solution or from pipes, spray nozzles or pumps, etc., used in spraying it, are practically eliminated.

In connection with all of the foregoing, it is also an object of the invention to provide a method which is substantially "foolproof" and which is economical to operate not only from the servicing standpoint but also from the standpoint of chemical consumption.

In carrying out my improved process, I employ zinc phosphate as the coating metal phosphate. A concentrated solution may be prepared by dissolving zinc oxide in 75% phosphoric acid according to the following formula:

Formula No. 1

Zinc oxide	pounds	1.5
Phosphoric acid, 75%	gallon	0.5
Water	do	0.5

This concentrated solution may be diluted with water to the degree required or desired within the compass of the following instructions.

The solution when used must be substantially supersaturated with respect to zinc phosphate,

i. e., to that zinc phosphate which would be the solid phase in equilibrium with the solution at the temperature of use. If the diluted solution of Formula No. 1 is not sufficiently supersaturated, it may be brought to a condition of supersaturation by the addition of a chemical capable of raising the pH of the solution. Any chemical otherwise harmless to the solution and capable of neutralizing phosphoric acid in the bath may be used for this purpose. As illustrations of compounds which may be employed, sodium hydroxide, zinc carbonate and sodium carbonate have proven satisfactory as they are inexpensive, harmless to the solution, and readily available. The degree of supersaturation desirable will be further discussed below, but it will be pointed out here that the supersaturated solution of zinc phosphate referred to above spontaneously hydrolizes, and if nothing is done to restore the supersaturation hydrolization will continue until the solution reaches a state of equilibrium. The pH of a supersaturated solution is higher than that of the solution in equilibrium at the same temperature; that is, the spontaneous hydrolization of the solution is accompanied by a fall in pH. The difference between the pH of a supersaturated solution and that of the fully hydrolized solution is a convenient index of the degree of supersaturation. When a solution is spoken of herein as having a pH above equilibrium it will be understood that the solution in question, were it allowed to reach equilibrium at the same temperature, would hydrolize and would fall to a lower pH.

The solution must be applied to the surface of the work to be coated at a temperature substantially below the boiling point and preferably below 190° F. Indeed, it is desirable to employ the solution at temperatures even considerably below 190° F., especially where, among other things, reduction in sludge is an important consideration. However, the maintenance of a substantially constant working temperature has been found to give the most satisfactory results. Ordinary living or room temperatures will often produce the best results, provided certain factors are properly adjusted in accordance with the instructions to be given below. Incidentally I might say that I have found it to be practically impossible to maintain the necessary degree of supersaturation at temperatures higher than approximately 190° F.

The solution should also contain hydrogen peroxide in an amount and for the purpose to be discussed more fully below.

In carrying out the process of the present invention the composition of a coating solution which will produce the desired type of coating in a short period of time is greatly affected by a variety of factors no one of which can be materially altered without affecting others. However, after extensive experimentation and investigation, I have established certain general principles which will now be discussed.

The pH at which the solution will coat satisfactorily varies inversely with the temperature and the amount of zinc. But the pH of the solution at equilibrium varies in substantially the same way, decreasing with an increase in temperature or an increase in zinc phosphate in the bath and vice versa. Accordingly, while the actual pH necessary to produce satisfactory coating action will vary with the temperature, the zinc content and other ingredients of the zinc phosphate bath, the amount which the pH should be above equilibrium for the particular solution being used will always be substantially the same.

I have found that the coating effect of a zinc phosphate solution containing hydrogen peroxide is improved by any addition, however small, of a neutralizing agent for phosphoric acid. But an appreciable amount of neutralizing agent is necessary to produce within about one minute as good coatings as are usually demanded commercially. In the continuous use of a commercial solution, the zinc and phosphoric acid must be replenished. This replenishment is customarily accomplished by adding a relatively concentrated solution of zinc phosphate. In order to keep the zinc dissolved, the replenishing solution customarily contains enough phosphoric acid to combine with the zinc to form $Zn(H_2PO_4)_2$ and some excess over that amount. In commercial practice, I have found it desirable to add somewhat more neutralizing agent than that calculated to be necessary to neutralize said excess acid. The neutralizing agent is best added to the coating solution separately, since it would result in precipitating zinc if added directly to the concentrated zinc phosphate solution. In general, it has been found that the pH should be maintained more than .1 above the pH at equilibrium in order to continuously produce commercially satisfactory coatings under usual working conditions.

The amount of hydrogen peroxide may be varied greatly. Any detectable amount produces some improvement in the coating action, but under ordinary commercial conditions, as much as .004% is required to produce a satisfactory coating within the time allowed. Some added hydrogen peroxide continues to improve the results, but equal added increments have successively less effect until a point is soon reached where no further improvement is obtained by increasing the amount of hydrogen peroxide, although still greater amounts may be used without noticeable impairment of the results.

By continued increase of hydrogen peroxide, a point is reached where the phosphate coating produced is thin and hard and exhibits no white scratch when tested with the fingernail (a commonly employed method of testing phosphate coatings). Continued increase of hydrogen peroxide, after the thin, hard coating is produced, causes the phosphate coating to be underlain with a dark oxide layer and to be overlain with a loose, non-adherent powder; still more peroxide inhibits the formation of the desired phosphate coating, the surface being covered with a blue to reddish-blue oxide film.

The above described results of too much peroxide may assist in detecting the difficulty when too much peroxide has been added by accident; but ordinarily such conditions will not be even closely approached, since considerations of economy ordinarily will prevent increase of the peroxide above the point where such increase shows improved results, and the variation in peroxide above that point which results in no material change in the resulting coating is wide enough so that the operator can easily keep the solution within that range.

The amount of peroxide which can be tolerated without bad effects varies with the temperature at which the solution is used, the amount of zinc phosphate in the solution, and the amount the pH is raised above equilibrium. For example, when coating ferrous surfaces, with a solution containing .865% zinc and neutralized

to a pH of 2.9 at a temperature of 80° F., passable coatings may be produced with as much as .096% hydrogen peroxide in the solution, while if the pH is only 2.75 on the one hand or 3.05 on the other, the limit for hydrogen peroxide is about 0.75%, other conditions being the same. At the same temperature, a solution containing .289% zinc and neutralized to approximately the same extent above equilibrium, that is to a pH 3.13 to 3.43, will tolerate only about .045% hydrogen peroxide. A solution with the same amount of zinc and at a temperature of 175° F. and neutralized to a pH of from 2.32 to 2.62 tolerates only in the neighborhood of .03% hydrogen peroxide. At the same temperature, but with a zinc content of only .1445% and a pH of from 2.45 to 2.75, the upper limit for hydrogen peroxide is not much above .02%.

The process may be employed by immersing the work in the solution, but the preferred method is to spray the solution onto the work, allow it to run off, collect, recirculate and respray. While it may be operated in this way at a somewhat higher temperature, it is advisable for economic reasons to employ a temperature not over 130° F.

Too little zinc in the solution results in little coating action, so that for the commercially desirable coating action within one minute, at least .1% of zinc in the solution is desirable. While larger amounts of zinc increase the coating effect somewhat and allow larger amounts of hydrogen peroxide to be used without exceeding the beneficial amount, the greater zinc content results in greater deposit of sludge and is more wasteful of chemicals.

For producing satisfactory coatings economically by the spray method described, it is recommended to keep the zinc content between .1% and .5%. For these limits, it is recommended that the hydrogen peroxide be kept within from .004% to .024%. Too little hydrogen peroxide results in a loose, poorly adherent coating, and too much results in a thin, hard coating becoming overlain with loose powder and finally producing an oxide coating, so that one skilled in the art can readily discover and remedy a departure from the working limits under the particular conditions employed, but for regular operation the hydrogen peroxide may be very easily maintained well within these limits.

As has been noted, it is preferred to keep the solution at a pH at least .1 above equilibrium for the particular solution employed, and in connection with discussion of limits of tolerance of hydrogen peroxide, a range of about .3 in pH was mentioned. While the pH should be maintained somewhat above the lower limit for best results, and so as to avoid dropping below that limit due to unavoidable variations, any increase above the pH necessary to produce a good coating, within the time and under the conditions being employed, is wasteful, since it results in rapidly increasing deposition of sludge as the pH is increased, and also requires a rapidly increasing addition of neutralizing agent in order to maintain the pH. The difficulty in this respect rapidly increases as the temperature is raised, and is one reason for recommending not over 130° F. for economical employment of the spray method. The rapidity of hydrolization and consequent deposition of sludge and the necessity for adding neutralizing agent to maintain the pH are increased by the agitation of the solution incident to spraying.

The hydrogen peroxide in the solution may be added as such, or may be generated within or without the solution, by any means well known to the chemist. For instance, the hydrogen peroxide may be generated by adding to the solution sodium peroxide, barium peroxide, zinc peroxide, sodium perborate, sodium percarbonate, sodium perphosphate, sodium persulphate, etc.

If the addition of any of the above reagents causes an undesired disturbance in the pH of the solution, such disturbance may be avoided by adding along with the reagent or separately, phosphoric acid or other non-deleterious acid in quantity sufficient to overcome the disturbing effect of the reagent.

It will readily be understood that during the coating of a succession of surfaces, the solution will become depleted in zinc and in phosphate due to the deposit of these constituents on the surfaces being coated, as well as to a certain unavoidable loss of zinc phosphate which precipitates spontaneously from the supersaturated solutions used in my improved process. Hydrogen peroxide is also continuously consumed both by its action on the metal surfaces during the coating process and by its action on any ferrous phosphate which may enter the solution by the action of the solution on any iron or steel surfaces in process. Ferrous phosphate is thus converted into ferric phosphate which, being only very slightly soluble in the solution, precipitates therefrom as it is formed. Hydrogen peroxide likewise spontaneously decomposes in the solution into oxygen and water, although this process is rather slow at the pH's and temperatures prevailing in my solutions. The losses just referred to in zinc phosphate and hydrogen peroxide must be replaced continually if the bath is to be maintained at its original concentration with respect to these ingredients.

Although phosphoric acid is consumed by the action of the solution on the metal surfaces, there is a tendency for the solution to gain in free phosphoric acid due to the continuous hydrolysis of zinc phosphate, as well as to the liberation of free phosphoric acid which accompanies the oxidation of any ferrous phosphate and its subsequent precipitation as ferric phosphate. Free acid is also added when the solution is replenished in zinc and in phosphate by the addition of the solution of Formula No. 1 which contains free phosphoric acid.

In view of this, in order to maintain the pH of the solution within the proper limits, it has been found necessary, especially in commercial practice, to add from time to time or continually a substance capable of counteracting this tendency toward a fall in pH. Among such substances are common alkaline chemicals such as sodium hydroxide, sodium carbonate and other substances capable of neutralizing phosphoric acid.

As previously stated, the hydrogen peroxide may be added to the solution as such, or may be introduced in the form of any chemical, otherwise harmless to the solution, which is capable of liberating hydrogen peroxide when introduced into the solution. A number of examples of such chemicals have been given hereinbefore.

Such of these chemicals as, on decomposition by the solution, introduce into it no anions at

all or only anions of acids much weaker than phosphoric acid, have the property not only of liberating hydrogen peroxide when added to the solution, but also of neutralizing and thus preventing the accumulation of free phosphoric acid, i. e., a fall in pH. The examples given with the possible exception of sodium perphosphate and sodium persulphate are of this character. In the case of sodium percarbonate, carbon dioxide is also liberated which, being a gas, escapes from the solution. In the case of sodium perborate, boric acid is liberated, which, being an extremely weak acid, does no harm in the solution.

The results obtained in my process seem to be suitable for any type of ordinary iron or steel with the exception of special alloys which are very acid resistant, such as stainless steel. However, it may be remarked that the kind of physical treatment of steel, such as the degree of cold working, temperature of annealing, type of slushing oil used to protect the steel in transit, etc., has some effect on the ease with which the desired coating is obtained. Certain highly polished steels produced by a fairly heavy finishing pass between very highly polished rolls, for instance, are difficult to coat unless they are first slightly etched or unless the surface is slightly roughened as by sanding, etc. However, ordinary steels such as are used for the fabrication of sheet metal stampings are readily coated.

My improved process lends itself particularly well to operations in the cold and by this I intend to refer to solutions to which no supplemental heat is applied. However, the conditions of operation sometimes raise the temperature of the solution up to the neighborhood of 120° F. to 140° F. because the pieces to be treated are frequently warm at the time that they are contacted with the solution due to previous cleaning steps to which they may have been subjected. Heat introduced in this way is merely an incident to the functioning of a complete series of coating steps and does not involve the use of any supplemental heat. However, the maintenance of a substantially constant temperature has been found to be desirable and to this end appropriate means may be employed when desired.

In general the cooler the solution the less will be the formation of sludge. Furthermore, whatever sludge is formed is of a different character than that which is customarily encountered when operating at higher temperatures. With my solutions when used cold the sludge is deposited in a light crystalline form which does not adhere nor grow to a heavy coating upon any surfaces with which the solution may come into contact. Hot solutions have a tendency to deposit sludge which adheres rather firmly and grows to a substantial thickness upon such surfaces as the walls of the tanks and the orifices of the nozzles. This improvement in sludge quality greatly mitigates the troubles incident to the sludge, since the loose, non-adherent quality of the sludge produced when the solution is cold avoids plugging of the nozzles and piping and makes it possible easily to flush it out of tanks and pipe lines with a stream of water and eliminates the necessity for mechanical removal of sludge by hammering, chipping, etc. Furthermore, because of the very much lower rate at which zinc phosphate precipitates from supersaturated cold solutions, the absolute quantity of sludge formed is greatly reduced with the cold solutions of my invention.

The elimination of heating coils likewise eliminates another serious disadvantage which is otherwise present. Owing to the high temperature of the surface of the heating coils themselves, they rapidly become coated with an adherent, heat-insulating scale which so interferes with the passage of heat into the solution that they must be cleaned at comparatively frequent intervals if the proper temperature of the solution is to be maintained. Moreover, this local heating tends to cause the precipitation of zinc phosphate, with a consequent loss of zinc, and furthermore, a loss of supersaturation.

In carrying out the process of the present invention, it will be understood, of course, that the parts to be coated should preferably be cleaned before being subjected to the action of the solution. This may be accomplished by any of the well known conventional means, but the type of cleaning known as emulsion cleaning is preferred. Contrary to what might have been expected, alkali cleaning when compared to emulsion cleaning seems to increase the amount of neutralizing agent required and the amount the pH must be raised above equilibrium in order to produce a good coating.

From the above, it will be readily seen that the method is capable of variations as to the amounts of the various ingredients employed in the solution, and the process may be used by immersion or spraying and at any temperature below about 190° F. But it has been pointed out that the spray method is generally found most convenient; that emulsion cleaning is preferable; that practical consideration limits the concentration of zinc phosphate in the solution, the degree of neutralization and the amount of hydrogen peroxide content.

In commercial installations especially with emulsion cleaning or its equivalent, it has been found that commercial satisfaction is given by a process of spraying at a temperature below 130° F. and replenishing the solution so as to maintain the zinc content about .25% and not under .1% or over .5%, with a peroxide content in the solution of between .004% and .024%, and neutralized to an extent which will result from adding caustic soda in an amount preferably not varying more than 20% above or below 1.04 lbs. per gallon of the concentrated solution of zinc phosphate described above. In any case, when that concentrated solution is used, a neutralizing agent should be used in an amount exceeding to some extent that necessary to neutralize all phosphoric acid more than that required by calculation to form $Zn(H_2PO_4)_2$ in the materials added for replenishment.

To illustrate, if neutralization is achieved by caustic soda, the reaction may be calculated as follows:

$$H_3PO_4+NaOH \rightarrow NaH_2PO_4+H_2O$$

Considering the molecular weights, it will be seen that approximately .4 lb. caustic soda are required to neutralize 1 lb. of H_3PO_4. In $Zn(H_2PO_4)_2$ the weight of zinc is approximately one-third of the PO_4 calculated as H_3PO_4. Consequently, the amount of caustic soda necessary to neutralize the concentrated solution to the PO_4 to Zn ratio of $Zn(H_2PO_4)_2$ will be obtained, in pounds of caustic soda, by multiplying the pounds of H_3PO_4 in the solution added by .4, thus obtaining the amount of caustic that would be required if no zinc were added, and then subtracting from that amount 1.2 times

the pounds of zinc, to determine how much the amount of caustic necessary is reduced by the presence of the zinc. As will be seen, this calculation will hold good for any concentrated solution containing H_3PO_4 in excess of that required to form $Zn(H_2PO_4)_2$ with the zinc present, and some excess of H_3PO_4 is necessary to keep the zinc in solution in the concentrated solution. This calculation holds true regardless of the form of the replenishing materials in which the Zn and P_{O_4} are added.

While any amount of caustic in addition to that calculated by the above formula gives beneficial results, it has been noted that it has been preferred, under the commercial conditions so far encountered in the use of this process by spraying, to employ the caustic in an amount not varying more than 20% above or below 1.04 lbs. to the gallon of the concentrated solution given above in which there is 1.2 lbs. zinc and 5 lbs. phosphoric acid. The equivalent in neutralizing effect of 1.04 lbs. of caustic to one gallon of the concentrated solution described above may be given for any other replenishing materials by the formula—

X lbs. NaOH=(.4×lbs. H_3PO_4)
minus (.8×lbs. Zn)

I claim:

1. The method of coating a ferrous surface which consists in subjecting the surface to a solution of acid zinc phosphate containing hydrogen peroxide and maintaining the operating pH of the solution by substantially continuous addition of a neutralizing agent for phosphoric acid, the solution being applied at a temperature not above 190° F.

2. The method of coating a ferrous surface which consists in spraying on the surface a solution of acid zinc phosphate containing hydrogen peroxide and maintaining the pH of the solution above equilibrium to produce on said surface a paint bonding phosphate coating within one minute, the solution being applied at a temperature not above 190° F.

3. The method of coating a ferrous surface which consists in subjecting the surface to a solution of acid zinc phosphate containing from .004% to .024% hydrogen peroxide and having an operating pH at least .1 above equilibrium, the solution being applied at a temperature not above 190° F.

4. The method of coating a ferrous surface which consists in subjecting the surface to a solution of acid zinc phosphate containing hydrogen peroxide and having a pH above that of equilibrium, and replenishing the solution with materials including ingredients which will replenish the hydrogen peroxide and the acid zinc phosphate and including a neutralizing agent for phosphoric acid in the bath, the ingredients of the replenishing material being selected and proportioned so that the pH of the solution is maintained more above equilibrium than it would be maintained if replenished with pure zinc dihydrogen phosphate and maintaining the solution at a substantially constant temperature not above 190° F.

5. The method of coating a ferrous surface which consists in subjecting the surface to a solution of acid zinc phosphate containing hydrogen peroxide and having a pH above that of equilibrium, and replenishing the solution with materials that replenish the hydrogen peroxide in the solution, that include as their chief coating chemicals the ingredients of zinc phosphate, and that include neutralizing material for phosphoric acid in the bath in a quantity greater than the quantity having a neutralizing effect equivalent to the pounds of caustic soda given by the following expression: pounds NaOH equals (.4×lbs. H_3PO_4) minus (1.2×lbs. Zn) in which the "pounds H_3PO_4" equals the weight of the PO_4 compounds in the materials calculated as H_3PO_4, and "pounds Zn" equals the weight of the zinc in the added materials calculated as metallic zinc, and applying the solution at a temperature not exceeding 190° F.

6. The method of coating a ferrous surface which consists in subjecting the surface to a solution of acid zinc phosphate containing hydrogen peroxide and having a pH above that of equilibrium, and replenishing the solution with materials that replenish the hydrogen peroxide in the solution, that include as their chief coating chemicals the ingredients of zinc phosphate, and that include neutralizing material for phosphoric acid in the bath in a quantity within 20% plus or minus of the quantity having a neutralizing effect equivalent to the pounds of caustic soda given by the following expression: pounds NaOH equals (.4×lbs. H_3PO_4) minus (.8×lbs. Zn) in which the "pounds H_3PO_4" equals the weight of the PO_4 compounds in the materials calculated as H_3PO_4, and "pounds Zn" equals the weight of the zinc in the added materials calculated as metallic zinc, and applying the solution at a temperature not exceeding 190° F.

7. The method of coating an iron or steel surface which consists in spraying the surface with a solution of acid zinc phosphate containing hydrogen peroxide, and replenishing the solution with materials that replenish the hydrogen peroxide in the solution, that include as their chief coating chemicals the ingredients of zinc phosphate, and that include neutralizing material for phosphoric acid in the bath in a quantity within 20% plus or minus of the quantity having a neutralizing effect equivalent to the pounds of caustic soda given by the following expression: pounds NaOH equals (.4×lb. H_3PO_4) minus (.8×lb. Zn) in which the "pounds H_3PO_4" equals the weight of the PO_4 compounds in the materials calculated as H_3PO_4, and "pounds Zn" equals the weight of the zinc in the added materials calculated as metallic zinc, and applying the solution at a temperature not exceeding 130° F.

8. The method of coating an iron or steel surface which consists in spraying on the surface a solution of acid zinc phosphate containing from .1% to .5% of zinc and from .004% to .024% of hydrogen peroxide and replenishing the solution with materials that replenish the hydrogen peroxide in the solution, that include as their chief coating chemicals the ingredients of zinc phosphate, and that include neutralizing material for phosphoric acid in the bath in a quantity within 20% plus or minus of the quantity having a neutralizing effect equivalent to the pounds of caustic soda given by the following expression: pounds NaOH equals (.4×lbs. H_3PO_4) minus (.8×lbs. Zn) in which the "pounds H_3PO_4" equals the weight of the PO_4 compounds in the materials calculated as H_3PO_4, and "pounds Zn" equals the weight of the zinc in the added materials calculated as metallic zinc, and applying the solution at a temperature not exceeding 130° F.

9. The method of coating an iron or steel surface which consists in cleaning the surface with

emulsion cleaner, spraying on the surface a solution of acid zinc phosphate containing from .1% to .5% of zinc and from .004% to .024% of hydrogen peroxide and replenishing the solution with materials that replenish the hydrogen peroxide in the solution, that include as their chief coating chemicals the ingredients of zinc phosphate, and that include neutralizing material for phosphoric acid in the bath in a quantity within 20% plus or minus of the quantity having a neutralizing effect equivalent to the pounds of caustic soda given by the following expression: pounds NaOH equals (.4×lbs. H_3PO_4) minus (.8×lbs. Zn) in which the "pounds H_3PO_4" equals the weight of the PO_4 compounds in the materials calculated as H_3PO_4, and "pounds Zn" equals the weight of the zinc in the added materials calculated as metallic zinc, and maintaining the solution at a substantially constant temperature not over 130° F.

10. A supersaturated acid zinc phosphate solution for coating ferrous surfaces in less than ten minutes, said solution containing from .1% to .5% zinc and from .004% to .024% hydrogen peroxide.

11. An acid zinc phosphate solution for coating ferrous surfaces, said solution containing from .1% to .5% zinc and from .004% to .024% hydrogen peroxide and having a pH from .1 to .4 above equilibrium.

GERALD C. ROMIG.

CERTIFICATE OF CORRECTION.

Patent No. 2,326,309. August 10, 1943.

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, first column, line 6, for "0.75%" read --.075%--; page 5, second column, lines 47 and 48, for "lb." read --lbs.--; 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 5th day of October, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.