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ART OF COATING METAL SURFACES WITH A WATER INSOLUBLE METALLIC PHOSPHATE

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

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This invention relates to the art of producing phosphate coatings on metal surfaces, and more specifically to the production of such coatings on ferrous metal surfaces, and the present application is a continuation in part of my earlier application Serial No. 228,401, filed September 3, 1938.

The objects and advantages of the invention will be more clearly understood and appreciated if the following facts are kept in mind. Because of certain contaminants generally found on the surfaces of metal articles which are to be phosphate coated it is practically the universal custom in this art to clean such surfaces before the coating process per se is applied, since it is almost impossible to produce coatings of uniformly constant and satisfactory character without first cleaning the metal to be coated. The most common contaminants which occur on practically all fabricated articles such as steel stampings, machined pieces, etc., are grease, oil and solid dirt of one kind or another. On iron or steel, rust and scale also are frequently encountered, and if present they are generally removed by acid treating operations known as "pickling". Furthermore, a pickling operation, if required, generally precedes whatever cleaning step may be necessary to remove such contaminants as grease and oil.

Probably the most convenient and economical method for removing grease, oil, solid dirt, etc., is the process loosely known in the art as "alkali cleaning". In this process, the surfaces to be cleaned are treated with solutions of alkaline chemicals such as caustic soda, soda ash, trisodium phosphate, borax, sodium silicate, etc. These solutions may also contain emulsifying agents such as soap, solvents such as kerosene, etc., and they may be used hot or cold and the work may be immersed in the solution or may be sprayed therewith. In its most usual form the alkaline cleaning process employs hot dilute solutions of a mixture of alkalies, with or without soap or other emulsifying agent.

Alternative methods for removing these contaminants make use of solvents such as hydrocarbons, chlorinated hydrocarbons, etc., and these may be included under the general term of "solvent cleaning". These methods may involve dipping the work to be cleaned into a solvent, wiping it with a rag soaked in a solvent, or exposing the cold work to the vapor of a solvent, this latter being known as "vapor degreasing". Combinations of these various solvent cleaning methods are also frequently employed.

I have discovered that the phosphate coating process per se is quite sensitive to the method of first cleaning the surfaces which are to be coated. For example, experience shows that alkali cleaned surfaces are slower to coat, that they acquire their coating less evenly, and are coated with a rougher and more crystalline coating than surfaces which have been solvent cleaned. Furthermore, surfaces which have been wiped or brushed before, during or after solvent cleaning, or during the coating operation have been found to acquire a still smoother coating, and with even greater ease.

I have further discovered that the rates at which chemicals must be added to maintain the coating solution in proper working condition are markedly affected in some unaccountable manner by the condition of the cleaned surface just prior to the coating operation. This is especially true of spray processes such for example as the process which is disclosed and claimed in my prior Patent 2,132,883, issued October 11, 1938, and which will be discussed more fully hereinafter.

The type of steel or iron being coated also has an influence on the finished coating as well as upon the rate at which the replenishing chemicals must be added to the coating solution.

In addition to the foregoing it is obvious that the carry-over of certain residues of the cleaning operation or solution on the surface to be coated into the coating solution proper will tend to upset the balance of the coating solution as well as to impair the quality of the resultant coating.

I have made attempts to obviate all of the foregoing difficulties by carefully and repeatedly rinsing the cleaned surfaces before the coating operation takes place, but with the greatest of care in this rinsing step and even with the employment of absolutely pure and neutral rinsing water unaccountable variations in results have still been encountered especially in rapid processes such as modern production methods demand.

By many very careful experiments I have established the fact that the variations in the quality of the finished coating as well as in the amounts of chemicals needed in replenishing the coating bath are in some way directly related to or associated with changes in the acidity or alkalinity of the rinse water just preceding the coating operation. Such changes may be due to any one of a number of causes which are difficult to eliminate in practice, such as a change in the shape and size of the surfaces to be coated, with a consequent change in the carry-over of cleaning

solution; change in the smoothness of the surfaces, which has a similar effect; change in the pressure of the water supply feeding the rinsing tanks; change in the composition of the cleaning solution, including accumulation of suspended dirt, etc.

In addition, I have also discovered that changes such as the foregoing present a problem which is more acute where alkali cleaning is employed than in processes where other types of cleaning have been followed, so that my invention is particularly applicable to methods which include alkali cleaning.

With all of the foregoing in mind, it can be said that the principal object of the present invention is to effect a marked saving in the consumption of chemical used in the coating process. Further objects are the production of coatings of greater uniformity on a long succession of surfaces, reduction in the amount of suspended solids in the coating solution (usually referred to as "sludge"), greater ease of rinsing of the coated surfaces, less frequent cleaning of heating coils, etc., in the coating solution reservoir, besides other objects which will appear to those skilled in this art, in connection with the following description of the invention.

Basically considered, my invention resides in the discovery that the foregoing difficulties may be largely overcome and the objects of the invention consistently obtained if the hydrogen ion concentration of the rinse water used to remove the residues of the cleaning operation just prior to the coating step is maintained between approximately pH 4.2 and pH 6. However, the optimum range within these limits may vary somewhat depending upon the type of steel being processed. I do not know with what property of the steel the optimum pH of the rinse water is to be correlated, but many experiments and observations have shown that it will vary slightly depending upon the type of steel being processed. For instance, I have found that with many of the steels most commonly encountered where phosphate coating is employed, best results may be obtained if the range is maintained between approximately pH 5 and pH 6, although with some steels an improvement in result is noted if a somewhat lower pH is employed, although in no instance have I found that a pH of less than approximately 4.2 is beneficial.

The means by which the pH of the rinse water prior to the coating operation is kept within this range may be any known to the chemist, but as a practical matter, where alkali cleaning is employed, I find it distinctly advantageous to counteract the tendency of the alkali carried over from the cleaning operation to raise the pH of the rinsing water prior to the coating step, by feeding back some or all of the final rinse water which is employed after the coating operation. This final rinse water obviously contains acid coating solution and by feeding back some or all of such rinse water to the rinsing step which follows the alkali cleaning operation it is generally possible to maintain the pH within the range specified without the addition of any other acid or acid salt. However, if some supplemental acid or acid salt is necessary, it may be added in the form of acetic acid, sodium hydrogen sulphate, hydrochloric acid, etc., although I prefer to add phosphoric acid or admixtures of phosphoric acid with one of its salts, because this is the acid employed in the coating solution.

As stated before, my invention is peculiarly adapted for use in connection with the so-called spray process of phosphatic coating, and furthermore, it is markedly advantageous in connection with a spray process which utilizes an aqueous acid phosphate coating solution other than ferrous phosphate, such, for example, as zinc phosphate or manganese phosphate. Beyond this it is unusually beneficial in processes of this kind, where the coating solution is maintained substantially free of dissolved iron by suitable additions of a salt of nitrous acid, such as sodium nitrite, in accordance with the disclosure contained in my prior Patent No. 2,132,883, issued October 11, 1938. Therefore, by way of specific example, I will describe my invention as it is applied in connection with a spray process of the character mentioned.

Specifically, the following description involves the coating of a succession of stamped and welded refrigerator cabinets and doors.

The pieces were ground smooth on the welded joints and were then hung on a monorail conveyor of a conventional four tank processing machine, the apparatus being arranged so that the pieces or stampings to be coated passed successively through the four compartments of the machine. In each of the four compartments the surface of the pieces was subjected to the action of jets of liquid, forced by a pump from a collecting tank beneath the stampings through appropriate pipes and spray nozzles, the excess liquid draining from the surfaces, returning to the tank from which it had been drawn.

The first tank of the washing machine contained a hot dilute solution comprising sodium metasilicate and caustic soda. The second tank contained hot rinse water and was provided with means for repeatedly and continuously changing the water as required. The third tank contained the coating solution, maintained at a temperature of 170° F. In this instance, the coating solution was zinc phosphate, which, during operation, was continuously replenished by adding thereto, through a flow meter, a solution of zinc phosphate. To this tank also was substantially continuously added, through a flow meter, a water solution of sodium nitrite sufficient to maintain the solution substantially free of dissolved iron. The fourth tank contained hot rinse water which could be continually changed by introducing a stream of fresh water.

The coating solution for tank No. 3 was formed by diluting to about fifty times its original volume a concentrated solution constituted as follows:

Formula No. 1

Zinc oxide	pounds	1.500
75% phosphoric acid	gallons	0.500
Water, to make	do	1.000

Replenishment of the coating solution during the coating operation was made by continuously adding, as needed, to the coating solution in tank No. 3 regulated quantities of the concentrated zinc phosphate solution of Formula No. 1. Hourly analyses were made to determine the rate of addition.

As soon as the stampings were started through the system, there was added to the solution in tank No. 3 substantially continuously, also through a flow meter, a solution of sodium nitrite containing 2 pounds of sodium nitrite to each gallon. The additions were made at that minimum rate which was necessary to maintain the sprayed solution substantially free of dis-

solved iron, so as to produce uniformly, perfectly coated stampings, any tendency toward imperfect work being corrected by regulating the flow of the nitrite solution. A little experience in the operation of such a process soon demonstrates to the operator how to regulate the flow of the nitrite solution so as to obtain such uniformly and perfectly coated stampings, but it might here be said that one factor in guiding the operator to the desired results is the maintenance of a substantially constant pH in the coating solution.

In order to prevent the rinse water in tank No. 2 from becoming alkaline, overflow from tank No. 4 from the final rinse water after the coating operation was conducted back to tank No. 2, to take the place of the addition of fresh water to such tank. Generally speaking, the pH of tank No. 2 can nearly always be maintained within the specified range, i. e., pH 4.2 to pH 6, by so feeding back from tank No. 4 to tank No. 2, the neutralizing and buffering action of the feed-back rinse water being sufficient for this purpose. However, if necessary, additional acid chemical may be supplied to tank No. 2 in order to maintain the desired pH therein. I have found, as stated above, that this can be done in various ways, although I prefer to use phosphoric acid or a small amount either of the solution of Formula No. 1 given above or of a little of the diluted coating solution used in tank No. 3.

It is to be noted that when experience has been gained in the operation of this process, actual determination of the pH of the rinse water following the alkali cleaning by electrometric or colorimetric means is not necessary. Observation of the coated work emerging from the coating system and of the necessary rates of chemical feed will serve as sharp indices of the condition of the water in the No. 2 rinse tank.

In order to demonstrate the economy of chemicals possible with my invention, the following contrast in operating conditions represents actual experience. Instead of following the procedure outlined, pure water only was fed into both rinsing tanks Nos. 2 and 4, and during this period approximately 3 to 4 gallons of the zinc phosphate solution of Formula No. 1 per hour were required by the coating solution of tank No. 3 under the conditions of operation then existing. Coincidentally, the necessary rate of feed of the sodium nitrite solution into this same tank varied irregularly from 4 to 7 gallons per hour or more while the number and area of the pieces being coated remained quite constant. When the overflow from the final rinse water was conducted to tank No. 2, to take the place of fresh water, an immediate improvement in economy and uniformity of chemical requirements became apparent. For example, the flow of sodium nitrite solution required was generally but 3 to 3½ gallons per hour and the same of zinc phosphate solution. But even with this arrangement, occasional unaccountable variations in the amounts of the reagents required by the coating tank were noted and careful observation showed that these variations were directly associated with fluctuations in the pH of the rinse water in tank No. 2.

For instance, many experiments have demonstrated that whenever the pH of the water in tank No. 2 was outside the range of pH 4.2 to pH 6 the chemical requirements increased sharply. For example, with some steels, when the water in this tank was deliberately held at pH 4, by suitable chemical additions, the consumption of sodium nitrite solution was 6 gallons per hour, and when the pH was held at 6.5 the consumption of nitrite solution was 4 gallons per hour. A corresponding increase in the consumption of zinc phosphate was also noted under these conditions. But when the pH was kept between 4.2 and 6 the consumption of nitrite solution was only 2 to 2.5 gallons per hour, and the consumption of the concentrated zinc phosphate solution of Formula No. 1 was only about 3 gallons per hour.

As stated, such control was many times possible simply by feeding back rinsings from rinsing tank No. 4 to rinsing tank No. 2, but when this procedure did not give the necessary control small quantities of phosphoric acid or other acids were added as required, or small amounts of the solution of Formula No. 1 or of the coating solution in tank No. 3. Regardless of the type of addition, the results were always the same, provided the pH of the rinsing tank No. 2 was maintained substantially constant between pH 4.2 and pH 6.

The above example is merely illustrative of the effect of the pH of the rinse water immediately preceding the coating step and, as stated above, while experience has shown that reasonable economy in chemical consumption may be maintained at any point within the range of pH 4.2 to pH 6, yet the optimum pH for any given instance may vary somewhat with the type of steel being processed. As already indicated, some steels have been found to coat most economically when the pH is maintained as low as 4.2, although with other steels improvement is noted when the pH is maintained between 5 and 6.

I claim:

1. In the art of coating a ferrous metal surface by treating it with an aqueous acid phosphate coating solution where the said surface is first cleaned with an alkaline cleaning solution, the method which includes the step of rinsing the surface after said cleaning operation with an aqueous solution having an acidity within the range pH 4.2 to pH 6 before treating it with the said coating solution.

2. The method of claim 1 wherein the coated surface is rinsed after treatment with the coating solution and wherein rinsings from the coated surface are employed in the maintenance of the specified pH of the rinsing solution used in the rinsing operation which follows the alkaline cleaning operation.

3. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the method which includes cleaning the surface with an alkaline cleaning solution, rinsing the surface after said cleaning operation with an aqueous solution having an acidity within the range pH 4.2 to pH 6, spraying a succession of pieces so cleaned and rinsed with an aqueous acid phosphate coating solution which is substantially free of dissolved iron, collecting the runoff for reuse in the spraying operation, 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 substantially constant as to its metal content and also substantially free of dissolved iron.

4. The method of claim 3 wherein the coated surface is rinsed after treatment with the coating solution and wherein rinsings from the coated surface are employed in the maintenance of the specified pH of the rinsing solution used in the

rinsing operation which follows the alkaline cleaning operation.

5. In the art of coating ferrous metal surfaces with a water insoluble metallic phosphate, the substantially continuously operable method which includes the following steps applied to a succession of pieces, i. e., cleaning the surfaces with an alkaline cleaning solution; rinsing the surfaces with an aqueous solution having an acidity within the range pH 4.2 to pH 6; spraying the surfaces with a zinc phosphate solution; collecting the run-off for reuse in the spraying operation; and substantially continuously adding to the solution regulated quantities of zinc phosphate solution 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.

6. The method of claim 5 wherein the coated surface is rinsed after treatment with the coating solution and wherein rinsings from the coated surface are employed in the maintenance of the specified pH of the rinsing solution used in the rinsing operation which follows the alkaline cleaning operation.

GERALD C. ROMIG.