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METHOD OF EXPEDITING CHEMICAL
COATINGS ON METALRobert R. Tanner, Birmingham, Mich., assignor
to Parker Rust Proof Company, Detroit, Mich.No Drawing. Application October 13, 1944,
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8 Claims. (Cl. 148—6)

This invention relates to a method whereby corrosion-resistant and paint-bonding chemically formed coatings are produced in an extremely short interval, especially upon sheets or other elongated metal stock of substantially uniform cross section. One form of apparatus adapted to carry out the method claimed herein is disclosed and claimed in my co-pending application, for "Apparatus for rustproofing metal" filed August 21, 1941, Serial No. 407,775.

Many methods of rendering metal resistant to corrosion are known and have been used. Various methods of application of the coating solutions have been employed in the art. Immersion, spraying and flowing are those most widely used.

In the rust-proofing art, making use for the most part of phosphate coating solutions, processing times have been speeded up until in most plants where large amounts of production are processed the time has been cut to approximately one minute. Such reduction in time has been obtained for the most part by the use in the processing solution of oxidizing agents of a suitable kind, such as nitrates. Up to the present-time, it had been thought that the processing time had been cut as much as commercially practicable.

In order to obtain the best results from a corrosion-resistant and paint-bonding coating, it is necessary that the coating be substantially uniform and adherent over the entire surface treated. If this is not the case, then the paint adhesion and general quality of the completed article will be inferior.

It is more or less characteristic of rust-proofing solutions to start their reaction with a metal surface unevenly and, in the first few seconds of treatment, what coating is formed tends to be non-adherent. Continued processing, however, results in an increase in adhesion and the uneven appearance of the coating disappears. In the past, various attempts to reduce the processing time materially below one minute by the methods described have been discouraged by the difficulties just enumerated, among other factors.

However, I have found that it is possible to cut the required processing time of a rust-proofing solution down to as low as two seconds and still obtain a continuous, adherent, and uniform coating. Such speeds have been attained on flat

stock, for which this method is particularly adapted, although it might be employed with other elongated stock of substantially uniform cross section, particularly where a thin, dense coating is desired which will still remain useful after the stock is bent or otherwise worked. The method consists in contacting the flat stock with a series of resilient members or with members surfaced with resilient material, which members are wet with the coating solution and which exert some pressing action on the surface of the metal. Thin, uniform deposits may be obtained by passing the flat stock, while being coated, between the members so that a repeated forceful contact is made with the surface of the sheet while the coating action is taking place.

It is not entirely understood how the action of the resilient surfaced members accelerates the coating action but, nevertheless, it is a fact that a satisfactory coating is obtained in much shorter time than where the same solution is simply sprayed or flowed on the work or the work is immersed in the solution.

One function of the resilient surfaces which contact the sheet appears to be that of aiding in cleaning the metal surfaces. Stock which is to be processed is sometimes oiled and in other instances is furnished in a "dry" condition, that is unoiled. In the former case, a cleaning procedure takes place before attempting to coat the sheet. Where a dry sheet is available, the cleaning step usually is not considered necessary.

In either case, the surface of the metal is such that the coating solution does not attack it with complete uniformity. Therefore, the coating action is retarded, at least in spots, until such time as the chemical action of the solution starts over the entire surface.

It may be that the resilient members, in forcibly contacting the surface to be coated, dislodge the thin layer of impurities so that the coating can start forming immediately, thus making possible the employment of exceptionally short processing periods. Whatever the reason, the described treatment brings the solution into chemically reactive contact with the surface of the metal, so that an exceptionally fine grained, uniform and adherent coating results in a minimum of time.

This reduction in the processing time has made

it possible to install the process in steel mills where thin gauge steel is processed at a speed of about one hundred and fifty feet a minute or faster, and where longer processes hitherto employed elsewhere either could not be employed or at the best would greatly retard the output of production.

In a specific embodiment of the invention, flat thin gauge steel stock is started through a series of rubber rolls, the rolls being wet with a phosphate solution of the following approximate composition:

Free acidity	3.0
Total acidity	20.0
ClO ₃	per cent 1.0
Zn	do 0.5
NO ₃	do 0.7
PO ₄	do 1.0
Cu	do 0.005
pH	2.2

The values for free and total acidity refer to the number of cc. of N/10 sodium hydroxide required to titrate a 10 cc. sample of the solution when methyl orange and phenolphthalein are used, respectively, as indicators.

The rolls exert some pressure on the metal surface and are spaced so that the work is repeatedly subjected to the squeezing action of the rolls while wet with the phosphate coating solution, so that a uniform, corrosion-resistant, paint-bonding, phosphate coating is obtained by reaction with the metal surface. This may be obtained in about ten seconds, although in some cases it may be desirable to process for thirty seconds. Best results seem to be obtained where the rolls are spaced apart so that in between rolls the flat stock may be wet with the coating solution. The interval between rolls may be about one second.

In the above example, the rolls were driven in such a manner that each one had a peripheral speed substantially equal to that of the linear speed of the metal being treated. Where an appreciable differential exists between the metal and the rolls, the coating produced for some reason is streaked and varies in density and weight from place to place. In many instances, the initial coating is so loosely adherent that rubbing contact removes the coating from most of the surface as fast as formed, and prevents the speedy formation of a satisfactory coating, while a rolling contact expedites formation of the coating over all portions of the surface, and leaves the coating in place to become quickly more adherent as the coating proceeds.

Attention should be paid not only to the speed at which the rolls are driven but also to their effective diameter. A difference in this dimension either in the original rolls or brought about by unequal application of pressure may cause sufficient differential in speed to result in the formation of a non-uniform coating.

The invention is equally applicable to the treatment of flat zinc-coated stock, and acceleration accompanied by the formation of an adherent, uniform coating is also obtained in this instance. However, the problems encountered in coating zinc are somewhat different from those usually involved in coating iron. Zinc surfaces are usually more reactive with phosphate and similar coating solutions than iron surfaces, but are even more subject to spotted or irregular reactions for obscure or unknown reasons. Therefore, in coating zinc, the production of a

continuous coating, while the coating is still thin at all points, is more important than increasing the total amount of coating produced in a given time. For this purpose, a rubbing as well as pressing contact has been found desirable.

The following specific example illustrates the advantages of the invention as applied to the production of phosphate coatings:

A stock solution prepared by dissolving

	Pounds
42° Bé. nitric acid	145
75% phosphoric acid	1470
Zinc oxide	360
Nickel carbonate	58

and adding water to 31.6° Bé. at 80° F., was diluted with water in proportion of water—100 gallons, stock solution—3.5 gallons. The solution was heated to between 160° and 175° F. and was pumped through a series of spray nozzles located in such a manner so as to direct the solution against the surfaces of 4 sets of 4" diameter rubber rolls equally spaced so that the distance from the entrance to the exit rolls was 19 inches. The rolls were arranged parallel and in line so that a sheet of metal could be passed between successive pairs while in contact with the coating solution. The rolls were driven at successively increasing rates, the relative speeds being in the ratio of 1:1.4:1.7:2.0, that is, the final set was driven at twice the speed of those at the entrance and the intermediate sets at intermediate speeds. The speed of the machine as a whole was such that the time required for a given point on a sheet of metal to pass through the entire series of rolls was four seconds.

Steel sheets having an electroplate of zinc .00002" in thickness were directed through the machine. In every case they received a hard, uniform, extremely fine grained and tightly adherent phosphate coating.

A determination showed that the coating weight amounted to 68 mg. per sq. ft. of surface treated.

It has not been found possible by flowing, spraying or immersing in such solutions, without the slipping contact to produce on zinc surfaces reliably and consistently a uniform adherent phosphate coating weighing as little as 100 mg. per sq. ft. Even with ordinary rubber rolls having a peripheral speed substantially the same as the speed of the zinc surface in contact therewith, a much heavier coating results. Where the rolls are of considerable diameter, or soft, or both, so that there is considerable flattening of the roll in contact with the zinc surface, there is sufficient squeezing or slipping action between the rubber and zinc to reduce the coating thickness as much as is necessary, in some instances, such slipping action taking place both at the entrance and exit sides of the bite of the rollers.

Advantages similar to those described in connection with the examples have also been obtained where manganese acid phosphate instead of zinc phosphate is employed in the solution in combination with an accelerator for the coating action.

Although special emphasis has been given to the use of the invention in connection with the formation of phosphate coatings, it is also useful in improving coatings formed by other acid solutions which react with zinc surfaces to produce insoluble compounds of zinc and of the acid present. For example, a solution containing 50 grams

ferric oxalate and 10 grams oxalic acid per 8 liters of water heated to 140° F. and applied for 10 seconds to a zinc plated surface during the application of slipping rubber rolls, provided a coating decidedly superior in adhesion to the coating produced where no rolls were employed. At the same time a very uniform coating was obtained having a weight approximately 40% of that produced in the same length of time without the rolls.

It will be seen from the foregoing that a method has been devised whereby a uniform, smooth and tightly adherent salt coating may be formed on zinc, while it is still less than 100 mg. per sq. ft. in weight, by means of an accelerated acidulous coating solution.

While the immediately foregoing description has dealt with coating zinc, somewhat similar results may be obtained in coating aluminum where an exceptionally thin and still uniform coating is desired. For example, an acid phosphate solution containing approximately

	Per cent
Zinc	.5
Ferrous iron	.2
Nitrate	1.0
Ammonium acid fluoride	.4

was heated to 170° F. and simply flowed over an aluminum sheet for a period of thirty seconds. A coarsely crystalline coating was produced between the crystals of which large areas of uncoated metal appeared when viewed with a microscope. In spite of the discontinuous condition the large size of the individual crystals produced a coating weight of 145 mg. per sq. ft. of surface.

When the same solution was applied to similar metal sheets in like manner but with the sheets subjected to the effect of slipping rubber rolls, the coating obtained was perfectly continuous over the entire sheet, was composed of extremely fine crystals and had a weight of but 40 milligrams per sq. ft. of surface.

In addition to the acceleration obtained by my invention, another highly advantageous result lies in the ability to produce exceptionally thin coating. The rolls are apparently effective in causing the formation of unusually small crystals in the coating so that the surface of the metal is quickly protected from further action. Also, as indicated above, instead of the relatively non-adherent and uneven coating often produced by previous methods in the first few seconds of coating action, a continuous, adherent and relatively uniform coating is produced in these few seconds. Thin coatings of this type are valuable where the stock is to undergo various forming and drawing operations and it is necessary that the coating be substantially all retained for its protective and paint-bonding properties. They are especially valuable where the coated metal is also to be painted before forming. In this case, any loss of coating adhesion would also result in a loss of the paint, since the paint is bonded to the coating. A further advantage in forming the thin coating resides in the saving of chemicals required to produce it over those consumed in the formation of heavier types. Ordinary phosphate coatings such as customarily applied to fabricated parts weigh from about 250 to 2000 mg. per square foot of surface, whereas by following the present invention, coatings weighing as little as 50 mg. per square foot of surface have been produced and have proven entirely satisfactory for paint-bonding purposes.

As will be seen from the specific examples given for coating iron with rolls having the same peripheral speed as the speed of surface being coated and for coating zinc and aluminum with a rubbing as well as pressing action, the inclusion of the rubbing feature depends upon the action desired. It may be added that the effect of the rubbing depends upon the pressure exerted and the relative speed of the surfaces, or in other words, upon the amount of friction. This may be adjusted in accordance with the effect desired.

The yielding contact disclosed has two major effects. It facilitates the coating action on portions where the action is slow to start and, especially where there is considerable friction, it keeps the coating from building up too rapidly in the portions where it starts first in proportion to its building up on other places. The degree of rubbing action should be adjusted to the degree of adhesion of the coating to the metal and to the final thickness of coating desired. The less the adhesion, the less is the friction which should be applied, while more friction is useful if a thinner coating is to be produced. By increasing the rubbing action, a coating of almost any desired thickness may be produced.

My invention, although its use has been described chiefly in connection with the application of phosphate coating solutions to iron, zinc and aluminum, may also be employed and similar advantages obtained in connection with phosphate coatings on other metals such as copper and brass, and with other types of solutions which produce corrosion-resistant and paint-bonding coatings by reaction with the metal surface. That is, when these other solutions produce objectionably uneven and/or non-adherent coatings in the time suitable for commercial purposes, the invention facilitates the production of a relatively uniform, adherent coating in the time permitted. These other coating solutions include oxalic and similar organic acids, and solutions of inorganic acids and oxidizing agents which produce coatings on metals, the coatings in this instance being predominantly oxides of the metal treated, sometimes including oxides of other metal in solution.

In fact, apparently any coating produced upon a metal surface by reaction therewith of a chemical solution appears to be improved by the repeated forcible pressure of the solution onto the surface, usually with a properly adjusted degree of rubbing action.

In a process where the entire coating is formed in a few seconds, it will be readily apparent that even momentary delay in the starting of the action of the solution has a material effect on the coating produced, while any irregularity in the time of attack by the chemical solution is reflected by an irregularity in the final coating. Also, any initial lack of adherence of the coating is detrimental. In relatively long coating operations, a few seconds difference in the time of attack is obviously less important in the final result, and the continued action may remedy initial lack of adherence.

The number of rolls to be employed will vary with the varying effect of applying the varying solutions and metal surfaces, as well as with the varying effect of one pair of rolls. The effect of one pair of rolls varies with their resiliency, the degree of pressure, their diameter and the speed of operation. Apparently greater speeds are permissible with increased size of rolls. The pressure should not be so excessive as to completely

dry the surface, and the film of solution should be pressed onto the surface for a period sufficient to allow some reaction. Therefore, the optimum speed and pressure varies with the nature of the solution employed and the kind and condition of the metal surface, and with the temperature, as well as with variation of the mechanical conditions. Therefore, no specification of speed or pressure is feasible for optimum results under all conditions, but illustrative examples may be given.

When coating iron with an accelerated phosphate solution such as described above, it was found that a pair of 2 inch, relatively hard, rubber rolls with steel cores gave better results when run at a speed of 20 feet a minute than where run at 40 feet a minute, while softer 8 inch rolls gave as good results when speeded up to 90 feet a minute.

Although rubber surfaced rolls have been mentioned in connection with specific examples of the invention, cloth surfaces or other yielding materials compatible with the coating solution might be used, resilient blades may take the place of rolls, or other means may be used where convenient. The metal sheets of commerce do not present perfectly even flat surfaces, and are unevenly contacted when run between even very carefully trued and polished steel rolls. Steel cores coated with rubber or wound with cloth make apparently even contact. The degree of yielding necessary in order to get this uniform contact is obviously dependent upon the amount of irregularity of the surface to be coated. That is, the yielding must be sufficient to enable the pressing surface to conform to the configuration of the metal surface being coated.

In coating wire, it might be drawn through rolls, but the entire surface of the wire might be evenly contacted more readily by members surrounding the wire and resiliently pressing against all sides thereof, and the members might be either movable or stationary in accordance with the result desired, and similar arrangements may be applied wherever desired to obtain the repeated contacts in the most convenient manner.

In addition to producing the desired type of coating in a short time, the rolls also serve, where individual sheets are processed, to convey the sheets by virtue of their motion and frictional contact. The rolls are equally effective, however, whether single sheets are processed or where a continuous sheet or strip is conveyed through them by an exterior mechanism.

While an action of the rollers has been described as a cleaning action, it should be understood that it is not like, and does not take the place of, the ordinary cleaning operations customary in preparing metal surfaces for rust-proofing.

My process starts with metal surfaces as clean as have been hitherto submitted to the phosphate coating operation, and then, by repeatedly pressing the solution against the surface, the solution is promptly brought into chemically reactive contact with the entire surface.

This application is a continuation-in-part of my prior applications Serial No. 406,484, filed August 12, 1941; Serial No. 482,193, filed Apr. 7, 1943; and Serial No. 482,194, filed April 7, 1943.

Although it is readily understood from the description of the invention that it is capable of considerable variation in its use, and that different kinds of solutions may be employed and various metals may be treated, the preferred form of

my invention involves its use for the treatment of steel or zinc plated steel with phosphate coating solutions whose action is accelerated so the coating is produced in a period not exceeding thirty seconds, and where slippage between the contacting surfaces is directly proportional to the initial adhesion of the coating to the metal and inversely proportional to the thickness of the desired coating.

What I claim is:

1. The method of producing a visible paint-bonding coating upon a metal surface which comprises subjecting the surface to a solution of coating chemicals adapted to react with said surface and produce a visible paint-bonding coating thereon in less than one minute and subjecting each portion of the surface, while that portion is being coated, to pressures by the surface of a solid which yields to conform to the configuration of the metal surface, and repeating the pressures enough times and with enough force to improve the quality of the coating produced in less than a minute.

2. A method in accordance with claim 1 and wherein the coated surface is of ferrous metal and the solution is a phosphate coating solution, and comprising the application of the repeated pressures by non-slipping, rolling contact.

3. A method in accordance with claim 1 and wherein the coated surface is of zinc metal and the solution is a phosphate coating solution, and comprising the combination of rubbing with the application of the repeated pressures.

4. A method in accordance with claim 1 and comprising the combination of rubbing with the application of the repeated pressures and the use of a degree of rubbing directly proportioned to the adhesion of the coating to the metal surface.

5. A method in accordance with claim 1 and comprising the combination of rubbing with the application of repeated pressures and the use of a degree of rubbing inversely proportioned to the thickness of coating desired.

6. The method of producing a visible paint-bonding coating upon an elongated article having a longitudinal metal surface accessible to a roller, which comprises passing said surface, wet with a solution containing coating chemicals adapted to react with the surface and produce thereon a visible coating in less than one minute, against a succession of rolls with yielding surfaces, and employing sufficient pressure to improve the coating action of the chemicals.

7. The method of producing a visible paint-bonding coating upon a sheet having a metal surface which comprises passing said surface, wet with a solution containing coating chemicals, against a succession of rolls with yielding surfaces, said chemicals being adapted to produce a visible coating on said surface in less than one minute and the rolls being applied with sufficient force and frequency to improve the adherence of the coating produced.

8. The method of producing a visible paint-bonding coating upon a sheet having a surface of metal of the group consisting of iron, zinc and their alloys, which comprises forming on said surface a phosphate coating in less than 30 seconds by the action of a phosphate solution containing an oxidizing agent, and during said action passing the sheet between successive rollers, and applying the rollers with sufficient force and frequency to accelerate the formation of a continuous adherent coating.

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