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ART OF COATING ZINC

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This invention relates to the art of treating surfaces of zinc or its alloys in order to provide them with an adherent substantially insoluble coating of phosphates.

5 The principal objects of the invention are, first, to provide an article having a surface of zinc or its alloys with an improved phosphatic coating of greater uniformity in thickness and color and of greater suitability for the recep-
10 tion and retention of a final finish of paint, varnish, lacquer, japan or other similar organic protective material; second, to provide an improved method for the production of such articles, and, third, to provide improved materials for use in
15 producing such articles.

The invention also contemplates the production of a coating of the character described on articles of zinc or its alloys which will prevent certain deleterious effects which zinc normally
20 has upon organic protective materials applied thereto.

A further object of the invention is to produce a coating of more pleasing character and color.

25 Among the more detailed objects of the invention is the provision of a so-called "balanced" phosphatic treating solution which will coat zinc or its alloys much more uniformly than has heretofore been possible, and which will re-
30 sult in a coating better adapted to receive and hold a final finish of paint or the like.

Still another object is to produce coatings of the character described at a minimum expense and in a minimum of time.

35 The nature of the invention will be better understood and appreciated if attention is first directed to certain facts already familiar to those skilled in this art.

40 For example, it has long been known that a phosphatic coating can be produced on zinc by applying to it solutions comprising the ions of phosphoric and nitric acids. Such a process is described in United States Patent No. 1,221,046, and in carrying out the process therein disclosed
45 it is necessary to apply the solution to the zinc in a thin film and allow it to act for some time. The free acids attack the zinc, and, ultimately, there results a solution which is so reduced in acidity and reinforced with zinc ions that it becomes "balanced" with respect to the zinc, where-
50 upon the zinc then acquires a phosphatic coating.

55 The meaning of the term "balanced" as used in this art should be kept in mind and is explained as follows. If the solution is to produce

its coating in a reasonably short time, it should be no more acid than is necessary to prevent the precipitation of insoluble phosphates of the metals present until such time as it is allowed to act upon the attackable metal to be coated,
5 such as zinc. In other words, the solution should not contain an excess of hydrogen ion in order that it may act with reasonable rapidity.

But in the process of Patent No. 1,221,046 already referred to, great care must be exercised
10 in connection with the treatment of articles which are only thinly covered with zinc or its alloys, such, for example, as galvanized iron. If too much acid or acid of too great strength is applied to the surface of such an article, so
15 much zinc may be required to "balance" the solution that the entire zinc coating on the article may be removed before the phosphatic coating forms.

The art then discovered that by partial neu-
20 tralization of the free acids in the solution before applying it to the metal it was possible to avoid this difficulty. This was accomplished by the addition of metallic zinc, zinc oxide, zinc carbonate, etc., by means of which the solution
25 could be made initially nearly or entirely "in balance", so that it could begin to coat the zinc or its alloys as soon as it began to act upon them.

In addition to the foregoing, the art also dis-
30 covered that with such a "balanced" solution as described just above, an additional saving of time and materials could be effected if the solution were used dilute and hot, say somewhere in the neighborhood of from 120° F. to the boil-
35 ing point. However, the coatings produced in this way are very light in color, ranging from pure white to a light gray, and the coating action of the solution is extremely sensitive to
40 slight variations in the surface undergoing treatment. For instance, on an ordinary piece of zinc or a die-casting, some areas may be well coated and others may remain entirely bare, and on a piece of "spangled" galvanized iron this ir-
45 regularity of coating effect is especially noticeable and objectionable. In the latter case certain portions of every spangle escape coating at all, while other parts may be coated perfectly.

The present invention overcomes all of the difficulties in prior practice referred to above and,
50 briefly stated, it involves the discovery that far more satisfactory coatings of the character described can be produced by adding to the treating solution, in addition to the ingredients already discussed, certain compounds, soluble in the
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Formula No. 1

Zinc oxide	-----lbs.	1.530
Nickel carbonate	-----lbs.	0.248
Phosphoric acid, 75%	-----gallons	0.5000
Nitric acid, 38° Bé	-----do.	0.0487
Water, q. s. ad	-----do.	1.0000

solution, which will yield therein the cations of nickel and/or cobalt, the process of the invention consisting in subjecting the zinc surface to the action of a solution containing the negative ions of phosphoric acid as its major anion constituent, zinc ions as its major cation constituent, the cations of nickel and/or cobalt as a minor ionic constituent, and also the nitrate anion as a minor constituent.

Before proceeding to a detailed description of specific ways in which the invention can be realized, I should like to point out that very small quantities of the cations of nickel and/or cobalt markedly improve the evenness of the coating action without materially affecting the coating time; that larger concentrations produce darker coatings and slightly increase the time necessary to complete the coating; and that still higher concentrations cause a considerable increase in the coating time with the production of a thinner and generally less desirable coating of lighter color.

I am aware that metals less basic than iron have been added to phosphate coating solutions in order to accelerate the action and to color the resulting coating. For example, copper has been used as an accelerating agent in the production of phosphatic coatings on iron, but my experience has shown that the addition of copper to a "balanced" solution containing the ions of phosphoric acid, nitric acid and zinc, causes the deposited coating to be black and loosely adherent. Very small quantities of copper darken the coating somewhat and allow the production of adherent coatings, but such coatings have a greatly reduced corrosion resistance, and organic finishes applied thereto fail rapidly. The same observations apply for silver, mercury, antimony and other metals below hydrogen in the electromotive series.

Lead also has been proposed, but insofar as I am aware, this is the only metal which has been above hydrogen in the electromotive series. The metals below hydrogen are deposited at least partially in the metallic state and when present in the coating such metals, of which copper and silver are probably the most typical, all tend to produce smudgy and non-adherent coatings or else to impair corrosion resistance or paint life. Lead is a metal which is so slowly attackable by weak acids that it also is deposited largely in the metallic state when present in a phosphatic coating bath for zinc, and it is admitted by all those familiar with the art that lead cannot serve as a satisfactory coloring or accelerating agent.

In direct contrast to the foregoing, I have found that nickel and cobalt may be added to the treating solutions in considerable amounts without causing loosely adherent coatings and without impairing the corrosion resistance or paint preservative properties of the coating. In the practice of my invention I have been unable to find any nickel or cobalt in any coatings produced on the surface of zinc or its alloys by means of "balanced" solutions containing the ions of these metals, zinc, nitric acid and phosphoric acid, and it is to this fact that I ascribe the excellent corrosion resistance and paint preservative characteristics of my improved coatings.

As an illustration of the application of my process and solution in the production of excellent coatings on galvanized iron, for instance, the following example is given:

A concentrated stock solution is prepared in accordance with the following formula:

The zinc oxide and nickel carbonate are suspended in the water. The nitric acid and phosphoric acids are then gradually added with constant stirring. When all gassing has ceased, and the solution is clear, it is ready for use.

Approximately 8% by volume of this stock solution is now dissolved in water in a vat fitted with steam coils or other suitable heating means. The solution is preferably heated to approximately 160° F., and the galvanized iron sheets are immersed therein.

A rather violent evolution of hydrogen gas occurs on the surface of the sheet, which ceases almost entirely inside of about thirty seconds. The sheet is now removed, washed with clean water and dried in any convenient way, as by heating in a warm air oven.

The finished sheets will now be covered with an adherent, dark grey, smooth coating of excellent corrosion resisting and paint preservative properties. Certain types of zinc and zinc alloy surfaces are more easily coated by this solution than others. In the case of certain die-castings, for instance, the above solution may be applied at a somewhat higher temperature, not exceeding its boiling point. The solution may likewise be used at lower temperatures, if a longer time is available for coating.

The solution of Formula No. 1 gives a dark even coating of excellent smoothness. If a coating of lighter color is required less nickel may be used in the formula. It will be noted that in this formula one equivalent of nickel is present for each nine equivalents of zinc. Even at a nickel concentration of one equivalent of nickel to 100 equivalents of zinc the coating produced is much more uniform than when the nickel is absent.

As the proportion of nickel is increased the coating becomes darker in color until a ratio of approximately one equivalent of nickel to two equivalents of zinc is present. A greater proportion of nickel than this produces lighter colored and thinner coatings of less corrosion resistance and paint-preservative value.

Cobalt as a constituent of solutions of this kind acts very similarly to nickel. However, the darkening effect of cobalt is slightly less pronounced than that of the nickel. It may be substituted practically weight for weight for the nickel, as the two metals have nearly identical equivalent weights. The maximum darkening effect of the cobalt on the coating is reached at somewhat less than one equivalent of cobalt to one equivalent of zinc. However, no advantage seems to be obtained by using either nickel or cobalt in a proportion greater than one equivalent of nickel or cobalt to two equivalents of zinc.

It is to be noted that, other conditions remaining the same, the addition of either nickel or cobalt to the solutions in too great a quantity slows up the coating action somewhat. This retarding action is not appreciable up to a nickel or cobalt concentration of one equivalent to nine equivalents of zinc; at higher concentrations the retarding action is appreciable, and when one part of nickel or cobalt is present to two parts of zinc, retardation of coating is pronounced.

The nitrate ion may be varied in considerable degree without affecting the action of the solution materially. 0.12 equivalent of nitrate anion to one equivalent of combined metallic cations in the coating solution is found to be ample; but an amount of nitrate up to at least 0.40 equivalent to one equivalent of total metallic cations may be present without doing harm. As little as 0.05 equivalent of nitrate anion per equivalent of total metal cations is still enough to produce good results, but the coating of a very active zinc may reduce the nitrate in this case so that it may have to be replenished more rapidly than the other ingredients.

The presence of foreign cations and anions is not particularly harmful in my solutions, but no substance may be allowed to accumulate which disturbs seriously the ionic relationship of the solutions. For instance, moderate amounts of sodium, calcium, or other cations of highly basic metals may be present without harm: similarly moderate amounts of sulphate, borate, chloride, etc., are not particularly objectionable. Thus one may prepare a solution similar to Formula No. 1 except that cobalt takes the place of nickel, and that the nitrate and cobalt ions are added as sodium nitrate and cobalt sulphate respectively.

Such a solution is given below:

Formula No. 2

Zinc oxide	lbs.	1.500
Phosphoric acid, 75%	gallons	0.500
Sodium nitrate	lbs.	0.402
Cobalt sulphate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	lbs.	0.587
Water q. s. ad.	gallons	1.000

This solution can be prepared by suspending the zinc oxide in the water, stirring in the phosphoric acid until clear, and then dissolving therein the cobalt sulphate and sodium nitrate.

This solution may be diluted with water to a 5 to 10% strength, by volume and used hot, like the diluted Formula No. 1, to produce coatings on zinc base die castings, galvanized iron, etc. However, replenishment of the coating solution as it becomes depleted in strength may not be accomplished indefinitely with Formula No. 2. If this is attempted there will ultimately accumulate in the solution too great a quantity of sodium and sulphate ions.

It is obvious, therefore, that in order to avoid the necessity for more or less frequently discarding a solution which is continually used and replenished, one should supply the requisite ions as free as possible from foreign ions which may accumulate therein.

It has been discovered that the relative as well as the absolute rate of consumption of the constituents of my solutions in the coating operation varies somewhat with the composition and surface condition of the metal being coated. Thus the relative rates of depletion of zinc, nickel, and nitrate ions for example, may vary somewhat under various conditions. It may, therefore, be expedient in order to maintain a constant time and color of coating, to replenish the various ingredients in a continually reused solution, by means of separate additions of different materials, each bearing a preponderance of one or the other of the necessary ions. For instance, one may employ, as replenishing agents, as required, nickel nitrate, and zinc phosphate or concentrated solutions of these.

As stated above, solutions of the character described may be used to coat surfaces of zinc or

its alloys in the cold. This procedure becomes especially useful, for example in coating surfaces of galvanized iron forming portions of structures already erected, such as buildings, fences, etc.

In coating such structures one may use solutions such as the concentrate of Formula No. 1 diluted with water to, say, 20% strength, by volume. However, it may be found more convenient to use a solution especially prepared for the purpose.

A solution especially well adapted for use in coating such surfaces in the cold, especially when the solution is to be applied in a thin film as by brushing, spraying, flowing, etc., has the following composition:

Formula No. 3

Zinc oxide	lbs.	0.300
Phosphoric acid, 75%	gallons	0.140
Nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	lbs.	0.144
Isopropyl naphthalene sulfonic acid	do.	0.010
Methanol	gallons	0.100
Water, to make	do.	1.000

This material is best made by suspending the zinc oxide in the water, stirring in the phosphoric acid, and, when the solution is clear, dissolving the other ingredients therein.

The material is ready for use, and will be found to wet the metal surfaces very well and to coat them with reasonable rapidity.

The solution is simply applied to the surface to be coated and allowed to remain until visible action has ceased, which may take from five minutes to half an hour, depending on the prevailing temperature, nature of the metal, etc. The surface, after thorough rinsing with clean water, is allowed to dry, when it is ready for painting, etc.

It will be understood that the examples given are offered only by way of illustration, and are not to be taken as limiting the scope of the invention. One skilled in the art will readily appreciate that many variations are possible in the formulation of my solutions and in their mode of application, as well as in the products resulting from the application of the process and the solutions.

I claim:

1. A solution for coating zinc or its alloys comprising the anions of phosphoric and nitric acids and the cations of zinc and of a metal from the group consisting of nickel and cobalt.

2. A solution for coating zinc or its alloys comprising zinc ions as its major cation constituent, the negative ions of phosphoric acid as its major anion constituent, the cations of a metal of the group consisting of nickel and cobalt as a minor cation constituent, and nitrate anions as a minor anion constituent.

3. A balanced phosphatic solution for coating zinc or its alloys containing zinc cations and cations of a metal from the group consisting of nickel and cobalt, the ratio of zinc ions to the ions from said group being between approximately 100 and 2; and containing nitrate anions, the ratio of total cations to nitrate anions being between approximately 20 and 2.5.

4. The method of coating zinc or its alloys which consists in treating it with a solution containing the anions of phosphoric and nitric acids and the cations of zinc and of a metal from the group consisting of nickel and cobalt.

5. The method of coating zinc or its alloys which consists in treating it with a solution containing the negative ions of phosphoric acid as its major anion constituent, zinc as its major ca-

tion constituent, ions of a metal from the group which consists of nickel and cobalt as a minor cation constituent, and nitrate anions as a minor anion constituent.

5 6. The method of coating zinc or its alloys which consists in treating it with a balanced phosphatic solution containing zinc cations and cations of a metal from the group consisting of nickel and cobalt, the ratio of zinc ions to the
10 ions from said group being between approximately 100 and 2; said solution also containing nitrate anions, the ratio of total cations to nitrate anions being between approximately 20 and 2.5.

7. An article having a surface of zinc or zinc alloy and bearing thereon an adherent, insoluble phosphatic coating resulting from the treatment of claim 4.

8. An article having a surface of zinc or zinc alloy and bearing thereon an adherent, insoluble phosphatic coating resulting from the treatment of claim 5.

9. An article having a surface of zinc or zinc alloy and bearing thereon an adherent, insoluble phosphatic coating resulting from the treatment of claim 6.

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