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TREATMENT OF METAL SURFACES

Erminio de Pretto, Milan, Italy, assignor to Società Generale per la Fosfatazione S. p. A., Milan, Italy

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The present invention relates to new and useful compositions in the treatment of metals such as iron and iron alloys, zinc and cadmium, particularly by coating the metals with a phosphate layer, and to a process of treating the metals.

The present invention is a continuation-in-part of my copending application Serial No. 223,166 filed April 26, 1951, now abandoned for "Process for the Preparation of Nitrophosphate Salts or Multi-Acid and Multimetallic Salts for the Nitrophosphatization of Iron, Its Derivatives and Alloys as Also of Cadmium and Zinc."

The formation of phosphate coatings on iron, zinc and cadmium substances by the use of free phosphoric acid and acidic phosphate compounds has been well known. An oxidizing agent is also employed in conjunction with the phosphoric acid and acid phosplate compounds for the formation of the phosphate coating. The most suitable oxidizing agent was found to be nitric acid plus nitrate salts. However, compositions containing phosphoric acid, nitric acid, phosphates and nitrates, although the same are effective in the treatment of the metal have been found to be disadvantageous in that the solutions have to be prepared fresh.

The use of nitrates in combination with phosphates for the formation of phosphate layers on metals shall herein be referred to as "nitrophosphating" and the solutions used for this purpose shall be referred to as "nitrophosphating solutions." Nitrophosphating has become well regarded and is used to a much greater extent at the present time than is simple phosphating because of the much greater speed of production of phosphate layers obtained by this method. For example, whereas simple phosphating requires a treatment time of from 60–90 minutes, the time required by the use of a nitrophosphating solution is reduced to from ½–4 minutes.

However, the lack of chemical stability of nitrophosphating solutions hitherto known has been a great disadvantage. The lack of stability is primarily due to a loss in total acidity which is apparently caused by a displacement of the nitric acid and is more pronounced, the greater the concentration of nitric acid. Due to the instability of the previously known solutions, it was impossible to obtain consistent efficiency and after standing a few days it required a great deal more of the solution to achieve the same effectiveness as with fresh solutions.

Many attempts have been made to overcome this difficulty. It was first attempted to overcome this difficulty by the addition of alkaline nitrates to the solution. However, this was unsuccessful. It was then attempted to overcome the difficulty by the addition of many different substances to the solutions, including glycerin, lanolin, ethylene oxide derivatives, and thiourea, all of which have proved to be unsuccessful for one reason or another.

It is therefore an object of the present invention to provide for the formation of nitrophosphating solutions containing free phosphoric acid, free nitric acid and phosphates and nitrates, which solutions are stable over long periods of time.

It is an additional object of the present invention to provide stable nitrophosphating solutions which retain maximum efficiency without substantial loss of acidity over long periods of time.

It is a further object of the present invention to provide a process of producing stable nitrophosphating solutions.

It is another object of the present invention to provide a process for the coating of metals with a phosphate layer.

With the above objects in view, the present invention mainly comprises an aqueous solution of at least one metallic phosphate, at least one metallic nitrate, phosphoric acid and nitric acid and at least one phosphoprotein. It has been found that the phosphoproteins which are the albumins derived from milk, eggs and plants in low concentration in the nitrophosphate solution give the desired stability to the solution so that the same has substantially constant activity over prolonged periods of time. The amount of the phosphoprotein is preferably less than the amount of the nitric acid and the phosphoric acid.

The present invention which comprises the utilization of milk, egg and plant albumins in combination with solutions for the production of phosphate layers on metals and particularly ferrous metals is mainly applicable to multi-acid and multi-metallic solutions which are used for the production of phosphate layers and which, as explained above are herein designated as nitrophosphating solutions. These solutions are designated as multi-acid because they contain more than one acid, namely both phosphoric acid and nitric acid. Preferably the solutions are also multi-metallic in that the phosphates and nitrates in the solution are of more than one metal, such as zinc, manganese, copper, nickel, etc.

The nitrophosphating solutions with the phosphoprotein added thereto are preferably prepared as liquid salt concentrates which are diluted before use with water so that the liquid salt concentrate is between 1–20% by weight of the final diluted solution. The liquid salt concentrate contains the phosphoprotein in an amount less than the amount of either the free nitric or the free phophoric acid and preferably between 0.3–2.5% by weight. Although greater amounts of phosphoprotein may be utilized, it has been found that as little as 0.3% by weight of the phosphoprotein will have a sufficient stability action and therefore greater amounts than 2.5% by weight are unnecessary. The preferred amount of phosphoprotein is between 0.5–1.0% by weight of the concentrate.

The amount of phosphate in the liquid salt concentrate, including both the metallic phosphates and the free phosphoric acid, may vary between 40–75% by weight of the concentrate. The amount of nitrate in the liquid salt concentrate, including both the metallic nitrates and the free nitric acid, may vary between 20–50% by weight of the concentrate. The amount of water in the liquid salt concentrate may vary between 3–18% by weight of the concentrate. As stated above, the amount of phosphoprotein, namely egg albumin, milk albumin and/or plant albumin, which exerts the stabilizing action on the nitrophosphating solution may vary between 0.3–2.5% by weight of the liquid salt concentrate. The proportion of metallic phosphate to free phosphoric acid and of metallic nitrate to free nitric acid may vary within extremely wide limits without in any way departing from the present invention. It is only essential that the solution contain nitric acid partially combined with a metal and partially in the form of free nitric acid and that it contain phosphoric acid partially combined with a metal and partially in the form of free phosphoric acid. The only limiting feature in this respect is that preferably the amount of total acidity of the solution is between 3–7

times the amount of the free acidity of the solution. It is also preferred that the nitrophosphating solutions contain nitric acid in an amount of from 3/10 to equal the amount of phosphoric acid. Solutions containing this high concentration of nitric acid were particularly difficult to stabilize, but the addition of the phosphoprotein to such solution according to the present invention, particularly in the amounts indicated, effects a complete stabilization of the solution.

Although the scope of the present invention is not meant to be limited by any theory as to how the stabilizing action of the phosphoprotein operates, it is believed that the same is partly due to a buffering effect. Nevertheless, it is mainly of interest to note, that the phosphoprotein according to the present invention maintains a constant and unvaried ratio between the undissociated and dissociated nitric acid.

The phosphoproteins, namely the milk, egg and plant albumins are well known and may be utilized according to the present invention no matter what process is utilized for the production of the phosphoprotein. The following, however, illustrates a process of obtaining the phosphoprotein milk albumin or lactalbumin from milk.

The milk is skimmed and centrifuged. The milk residue thus obtained is treated with sulfuric acid in an amount of 430–440 g. sulfuric acid per each 1000 liters of milk, thus forming a precipitate labile calcium phosphoprotein. Instead of sulfuric acid it is possible to utilize hydrochloric acid, however in the ratio of 665–670 g. hydrochloric acid per each 1000 liters of milk.

The obtained precipitate is washed with water, dried in hot air at a temperature greater than 47° C., and then pressed and ground to powder form. The resulting product is a white amorphous powder which is tasteless and has a density of about 1.25–1.26, is insoluble in water, alcohol and ether; soluble in alkaline solutions, partly soluble in concentrated acid solutions and completely soluble in dilute acid solutions. Therefore, upon dilution of the liquid salt concentrate containing the phosphoprotein, as above described, and heating at the hydrolysis temperature, i. e. 50–90° C. it is easily possible to completely dissolve the phosphoprotein contained in the concentrate.

Egg albumin and plant albumin may be prepared by substantially the same method as above described for the preparation of milk albumin; and the egg albumin and plant albumin are even more soluble in dilute acid solutions than is the milk albumin. Although egg, plant and milk albumin are all suitable according to the present invention for the stabilization of nitrophosphating solutions, the best results have been obtained with milk albumin. Although no exact chemical formula can be given for the milk albumin, it is known to consist of the following:

	Percent by weight
Animal fats	0.5–1
Protein substances (i. e. labile calcium phosphoprotein)	80–82
Moisture	10–12
Ash	5–7

The present invention mainly comprises the addition to a concentrated nitrophosphating solution which is diluted before use with water in an amount such that the concentrate is between 1–20% by weight of the final diluted solution, of a phosphoprotein, namely milk, egg and plant albumin in an amount of 0.3–2.5% by weight of the concentrate. The proportions of metallic phosphates, phosphoric acid, metallic nitrates and nitric acid may be varied within very wide limits in the solutions so long as the proportions are suitable to give the desired nitrophosphating properties. The present invention is concerned mainly with the addition of the phosphoprotein to the solution rather than with the specific proportions of other components of the solutions.

Nevertheless, the following examples are given to illustrate preferred liquid salt concentrates according to the present invention, the scope of said invention not however being limited to the specific examples given.

EXAMPLE I

A liquid salt concentrate is prepared containing the following components:

	Percent by weight
$Zn(H_2PO_4)_2 \cdot 2H_2O + H_3PO_4$	70
$Zn(NO_3)_2 + HNO_3$	24
Milk albumin	0.5
Water	5.5

The ratio of total acidity to free acidity of the above is 3:1. The weight of the free nitric acid is about 34% of the weight of the free phosphoric acid.

EXAMPLE II

A liquid salt concentrate is prepared containing the following components in the proportions indicated:

	Percent by weight
$Zn(H_2PO_4)_2 \cdot 2H_2O + Mn(H_2PO_4)_2 \cdot 2H_2O + H_3PO_4$	70
$Zn(NO_3)_2 + Mn(NO_3)_2 + HNO_3$	23
Egg albumin	1
Water	6

The ratio of total acidity to free acidity of the above is 7:1 and the weight of the free nitric acid is about 33% of the free phosphoric acid.

EXAMPLE III

A concentrate for nitrophosphating solutions is prepared containing the following components in the proportions indicated:

	Percent by weight
$ZnH_3(PO_4)_2 + Mn(PO_4)_2$	68
$Zn(NO_3)_2 + Mn(PO_3)_2 + Ni(NO_3)_2 + Cu(NO_3)_2 + HNO_3$	27
Plant protein (from soya beans)	0.3
Water	4.7

The ratio of total acidity to free acidity of the above is 4:1 and the weight of free nitric acid is about 40% of the weight of free phosphoric acid.

EXAMPLE IV

A concentrate for nitrophosphating solutions is prepared containing the following components in the proportions indicated:

	Percent by weight
$ZnH_3(PO_4)_2 + Mn(PO_4)_2$	44
$Zn(NO_3)_2 + Mn(PO_3)_2 + Ni(NO_3)_2 + Cu(NO_3)_2 + HNO_3$	44
Milk albumin	2.5
Water	9.5

The ratio of total acidity to free acidity of the above is 5.5:1 and the weight of the free nitric acid is about equal to the weight of the free phosphoric acid.

The following is illustrative of the preferred process of preparing a liquid salt concentrate according to the present invention:

Into an acid resistant vessel is placed concentrated nitric acid and concentrated phosphoric acid in a predetermined ratio as in any of the above examples, for example in a ratio of 70 parts phosphoric acid to 24 parts nitric acid as in Example I, and the acids are heated to a temperature of 70–80° C.; and a predetermined quantity of the phosphoprotein, such as milk, egg or plant albumin is added, i. e. 0.5 part by weight of the final concentrate as in Example I. Then the particular metals such as zinc, manganese, nickel or the like are added in a quantity such that the ratio of total acidity to free acidity of the final concentrate is between 3–7. In Example I the ratio of total acidity to free acidity is adjusted to 3:1.

The liquid salt concentrates of the present invention generally have a density which varies between 1.45–1.6 and have in suspension a reddish substance of colloidal consistency. The particles forming the suspension are the albumin. Upon dilution, these particles are dissolved and the clear solutions formed. The product is sold commercially in the form of the liquid salt concentrate which is diluted by the user in an amount such that the final solution contains the liquid salt concentrate in an amount of 1–20% by weight.

The liquid salt concentrate is preferably diluted in the proportion of 7–15% concentrate to 93–85% water. The solutions are used for the treatment of metals in an amount of about 1000 cc. per each square meter of surface to be nitrophosphated, requiring about eight hours of working time. It is not sufficient industrially if the solution remains in good condition for 1–2 days, but it is indispensable that the solution remain effective for the production of phosphate layers on the metal in accordance with a standard for 30 or more consecutive or alternate work days. This was impossible prior to the present invention. However, according to the present invention the solutions remain effective over extended periods of time and even for 1000 days or more.

There are various methods of measuring the efficiency of nitrophosphating solutions which allow for the determination of the efficiency of the stabilizing action of the phosphoprotein added to the nitrophosphating solutions according to the present invention. One method of measurement is based upon the measurement of the total acidity of the solution when fresh and after a certain time period. According to this method the total acidity of the diluted solution is determined by a standard acidimetric measurement in accordance with which the solution is titrated with 0.1 N NaOH using phenolphthalein as an indicator. For example, 10 cc. of the diluted solution are taken and 3 drops of phenolphthalien are added thereto. 0.1 N NaOH is then added until the color change of the phenolphthalien indicator. The number of cc. of NaOH required corresponds to the number of cc. of total acidity of the solution and is expressed as points of acidity. So, for example solution I diluted in a ratio of 7% concentrate to 93% water will have 45–46 points of total acidity and the same solution diluted in a ratio of 15% concentrate to 85% water will have a total acidity of 92–94 points.

The following tests illustrate the stabilizing action of the phosphoproteins according to the present invention.

Test A

A concentrate is prepared according to any one of Examples I, II, III or IV without the addition of the phosphoprotein thereto. The concentrate is diluted with water to form a 10% solution. The total acidity immediately after preparation is taken as 100%. After 48 hours it is found that the total acidity of the solution is between 92–95% of the original total acidity. After 10 days, heating the solution at 80° C. for 8 hours a day (a total of 80 hours of heating) the remaining total acidity is found to be 75–78% of the initial. The loss in total acidity is apparently due to the elimination of nitric acid.

Test B

A concentrate is prepared as in Test A with the addition of a phosphoprotein such as milk, egg or plant albumin in an amount of 0.5% by weight of the concentrate. The concentrate is diluted with water to form a 10% solution. The total acidity immediately after preparation is the same as in Test A and is taken as 100%. After 48 hours the solution is found to have no loss of total acidity, the total acidity still being at 100%. After 10 days, heating the solution at 80° C. for 8 hours a day (a total of 80 hours heating) the remaining total acidity is found to be between 95–97% of the initial total acidity.

Here too, the loss of total acidity is due to the elimination of nitric acid. However, as may be seen, the phosphoprotein achieves a profound stabilization of the solution.

Another method of determining the efficiency of the nitrophosphating solution is based upon the number of square meters of metal that is coated by a specified quantity of the solution.

In order for the phosphate layer on the surface of the metal resulting from treatments with the nitrophosphating solution to be satisfactory, it must meet certain requisites, as for example:

1. The thickness of the layer must be between 3–10 microns, the thinner the better;

2. The resistance to corrosion must be at least 80% of the resistance achieved by the same layer produced by a freshly prepared solution, namely on the first day of preparation.

3. The amount of iron must not be above a certain limit, and for example it should not exceed 1–2.5 g. per 1000 cc. of solution.

The more closely the solutions correspond to requisites 1, 2 and 3 mentioned above, the better the quality of the phosphate layer produced. It is an accepted principle in this field that a freshly prepared nitrophosphate solution has the property of generating nitrophosphate layers of optimum quality but that the quality becomes progressively worse as the solution becomes older and is 75–80% of the initial efficiency after a few days and is only 20–25% of the initial efficiency after 1000 days. The progressive lessening of efficiency becomes more pronounced after the second day of use of the solution and is probably due to a series of secondary chemical reactions to which the solution is subjected, for example the following:

a. Variation of the oxidimetric state which generally is constantly reduced as time passes. This is generally referred to as the RedOx potential;

b. Variation of the initial pH curve, the initial pH which may for example be between 2.1–3 depending upon the salt used and upon the relationship between the quantity of acid and the quantity of metals. The value fluctuates as the solution is used due to changes in the pH and the relationship between the nitric acid and the phosphoric acid as well as between free acidity and total acidity and the increase of iron content in the solution.

The addition of a phosphoprotein to the solution according to the present invention stabilizes both *a* and *b* above so that the solution retains its effectiveness for 1000 days or more and even after 1000 days the solution still maintains 80–85% of its initial effectiveness.

An additional means of determining the efficiency of the nitrophosphating solution which clearly establishes the stabilizing effect of the addition of the phosphoprotein to the solution is as follows:

Test C

A salt concentrate is prepared according to any one of Examples I, II, III and IV without any addition of phosphoprotein. The concentrate is diluted with water in an amount such that the concentrate is 10% of the final solution. The solution is therefore the same as in Test A above. This solution is used for the nitrophosphating of one square meter of metallic surface per each 1000 cc. of solution for 8 hours a day during 10 days and with daily replenishment of the consumed salt to the initial value. After the 10 days, the following checking determinations are made:

(1) The consumption of salt expressed as g./sq. m. is determined and for this solution is given an arbitrary value of 100.

(2) The protective value of the nitrophosphating layer obtained by this solution is determined from the 5th day on and for this solution is given the arbitrary value of 100.

Test D

A salt concentrate is prepared as in Test C however with the addition of 1% of milk albumin. The concentrate is diluted in water in an amount such that the concentrate is 10% of the final solution. This solution is therefore the same as in Test C above except for the phosphoprotein content. This solution is used for the nitrophosphating of 1 square meter of a metallic surface for each 1000 cc. of solution for 8 hours a day during 10 days and with daily replenishment of the consumed salt to the initial value. The following checking determinations are made and compared to the values obtained utilizing the solutions of Test C:

(1) The consumption of salt expressed as g./sq. m. is determined and compared with that of Test C above. Compared to the arbitrary value of Test C the amount of salt is 60. It is therefore aparent that by the addition of the phosphoprotein, the same amount of metal may be treated utilizing only slightly more than one half the amount required without the phosphoprotein.

(2) The protective value of the layer obtained by this solution is determined from the 5th day on and compared to that obtained in Test C. The value is found to be 250 as compared to the arbitrary value of 100 from Test C. It may therefore be seen that the protective layer obtained by the addition of phosphoprotein to the solution is about 2½ times that obtained without the phosphoprotein.

While the invention has been illustrated and described as embodied in treatment of metals, it is not intended to be limited to the details shown, since various modifications and structural changes may be made without departing in any way from the spirit of the present invention.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein, said phosphoprotein being present in an amount less than the amount of said free acids and at least in an amount of 0.3% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

2. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein, said phosphoprotein being present in an amount between 0.3–2.5% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

3. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of 3–18% water by weight, at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein, said phosphoprotein being present in an amount between 0.3–2.5% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

4. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of 3–18% water by weight, at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein, said phosphoprotein being present in an amount between 0.5–1.0% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

5. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein selected from the group consisting of milk, egg and plant albumins, said phosphoprotein being present in an amount less than the amount of said free acids and at least in an amount of 0.3% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

6. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein selected from the group consisting of milk, egg and plant albumins, said phosphoprotein being present in an amount between 0.3–2.5% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

7. A liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, said liquid salt composition essentially consisting of 3–18% water by weight, at least one metallic phosphate, at least one metallic nitrate, free phosphoric acid, free nitric acid and at least one phosphoprotein selected from the group consisting of milk, egg and plant albumins, said phosphoprotein being present in an amount between 0.3–2.5% by weight of said liquid salt composition, the total acidity of said liquid salt composition being between 3–7 times the free acidity thereof.

8. A process of producing a liquid salt composition adapted to be diluted with water in an amount such that said composition is between 1–20% by weight of the diluted solution which is adapted to be used for the treatment of metallic surfaces, comprising the steps of mixing concentrated nitric acid with concentrated phosphoric acid in an amount such that said nitric acid is between 3/10 to equal the amount of said phosphoric acid; adding a powdered phosphoprotein to the thus formed mixture in a predetermined quantity adjusted to be between 0.3–2.5% by weight of the final composition; and dissolving in said mixture having said phosphoprotein added thereto at least one metal selected from the group consisting of zinc, manganese, nickel and copper in an amount such that the total acidity of the resulting mixture is between 3–7 times the free acidity thereof.

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