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COMPOSITION AND METHOD FOR COATING METALLIC SURFACES

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The present invention relates to improved solutions for, and to an improved method of, coating the surfaces of zinc-coated steel and iron to provide thereon an adherent, corrosion-resistant coating suitable as a base for protective finishing materials such as paint, lacquer, varnish, enamel, etc. More specifically, the invention relates to improved phosphate coating solutions and to an improved method of coating the surfaces of zinc-coated iron and steel made by certain continuous commercial hot-dipping processes to provide smoother, more satisfactory coatings and to a method which is more satisfactory under the operating conditions prevailing in such processes.

The formation of phosphate coatings on iron and zinc is well known, for example, U. S. Patent No. 1,221,046 discloses the coating of zinc and its alloys by treatment with a solution of phosphoric acid containing a nitrate accelerator. The latter patent and U. S. Patent No. 2,121,574 allege that more uniform phosphate coatings are obtained when nickel or cobalt ions are added to the phosphoric acid solution. U. S. Patents 1,869,121 and 1,888,189 disclose that copper ion in certain concentrations is beneficial in speeding up the action of a phosphate solution on a zinc surface. The surfaces of certain zinc alloys containing aluminum, which are coated only with great difficulty in nickel-accelerated phosphate solutions, are said in U. S. Patent No. 2,591,479 to be easily coated when fluoborate ion is added to a phosphate solution in combination with nickel ions. While these and other known solutions deposit satisfactory coatings on most zinc and zinc alloy surfaces, it was found that in certain high speed, hot-dip zinc coating processes the known phosphate coating solutions produced coatings that were covered with multitudinous small raised areas of intense coating action. The latter phenomenon, known as "seediness," was not observed in the coating of electrogalvanized zinc surfaces or in other types of zinc coated ferrous surfaces, rather it was observed only with certain types of high-speed, continuous hot-dipped zinc surfaces such as those known commercially as "Zincgrip" or "Ti-Co," said to be obtained by the continuous hot-dip zinc coating process disclosed in U. S. Patent 2,197,622. The spots or raised pin-point areas of apparent intense coating action, when covered with paint or other protective finish, showed up as rough spots resembling a paint coating applied over a layer of sand or grit. The appearance of the finished product was highly unsatisfactory from a commercial point of view. Since this particular type of zinc-coated material is beginning to come into more common use for the production of articles to be painted or finished, the necessity for a satisfactory phosphate coating process and solution is acute.

In accordance with the present invention, however, it has been discovered that phosphate coating solutions containing nickel ion and a small proportion of soluble silicon preferably as the silicofluoride ion, are capable of producing heavy, uniform, adherent phosphate coatings substantially free of "seediness" on the above-mentioned types of continuous, hot-dipped zinc coated iron and steel.

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As a result smooth, attractive paint coatings which are tightly adherent and corrosion resistant can be applied to these particular types of zinc coated metal. Moreover, the coating solutions and process of this invention remove an important obstacle in an important industrial process. The present invention also provides stable, concentrated "make-up" and "replenisher" solutions of great utility in commercial coating processes.

The phosphate solutions of this invention comprise phosphate (PO_4) ion, an ion such as zinc and manganese in sufficient proportion to produce a dihydrogen phosphate with the (PO_4) ion, a small proportion of nickel ion, a small proportion of soluble silicon preferably introduced as a silicon-containing ion such as the silicofluoride (SiF_6) ion, and an oxidant such as nitrite or nitrate ions. In addition, the solution may contain a small proportion of coopper as an additional accelerator, if desired. As used in this specification and in the appended claims, the term "continuous hot-dipped, zinc-coated ferrous surface" is intended to include any iron, steel or other ferrous surface which has been provided with a zinc coating by the continuous method of U. S. Patent 2,197,622 or other hot-dipping methods which produce zinc coatings which aquire a "seedy" phosphate coating in known phosphate coating solutions.

The process of U. S. Patent No. 2,197,622 for applying a zinc coating on ferrous surface comprises the steps of oxidizing the ferrous surface to form a thin oxide film thereon having a color ranging from light yellow to purple and ranging as far as gray, then reducing the oxide film to a film of the pure metal and while the reduced film remains protected in a non-oxidizing atmosphere the surface, in a flux-free condition, is immersed in a molten zinc bath containing a minor quantity of aluminum to thereby form a zinc coating when the surface is withdrawn from the bath and allowed to cool.

The phosphate coating solutions which are improved by the addition of the combinations of nickel and silicon-containing ions contain as the essential coating-producing ingredients about 0.5 to 2.5% (w./vol.) PO_4 ion, at least sufficient zinc or manganese to form dihydrogen phosphate with the phosphate ion, and a suitable amount of an oxidizing ion such as the nitrate or nitrite ion or a mixture of nitrate and nitrite ions. The quantity of nitrate ion which is desirable is about 0.2 to about 1% with major benefits being obtained at about 0.3 to 0.5% NO_3. Where nitrite is used, substantially smaller quantities are required to produce acceleration and about 0.0002 to 0.008% NO_2 may be utilized.

Over the entire ranges of concentrations given above for the principal ingredients, soluble silicon is noticeably effective in reducing the number of seeds or raised spots. However, if the proportions of zinc and/or manganese and oxidant are too high, seed-free coatings cannot always be obtained. It is preferred, therefore, to utilize a bath containing less than about 0.4 to 0.5% zinc or manganese, less than about 0.5% nitrate ion, or less than about 0.005% nitrite ion. It is also preferable to utilize baths of this type which have a total acidity of less than 40 points (see Example 1 for method of determining total acidity) and a ratio of PO_4 ion to zinc or manganese ion of not more than 5:1.

The maximum benefit from the use of nickel ion and copper ion if utilized, lies in a critically small range, between about 0.01 and 0.4% for nickel and between about 0.0003 and 0.005% for copper. Since the higher concentrations of these ions, especially of copper, seem to favor increased seediness, it is preferred to utilize more moderate amounts of these substances, for example, less than 0.3% nickel and as little copper as is consonant with satisfactory coating rates, proportions of 0.0003 to 0.001% usually being most satisfactory. Due to the fact that both nickel and copper in the bath are depleted (as well as the coating producing constituents) as work is processed, it is desirable to maintain their effective working levels by replenishment. This is most conveniently accomplished by addition of a concentrated replenisher solution to be described below.

The nickel and copper ions can be provided by adding a salt which is soluble in the solution, for example, a carbonate, nitrate, chloride or sulfate. Likewise, the soluble silicon is added to the solution in the form of an acid such as hydrofluosilicic acid or a stable soluble salt such as the silicofluoride salts of sodium, potassium and ammonium.

The concentration of soluble silicon required for smooth, hard, and spot-free or seed-free phosphate coatings is very small. When as little as 0.03% of silicon is added, as sodium silicofluoride, the tendency to form "seedy" coatings is greatly reduced. However, with proportions less than 0.03% silicon, the number of spots sometimes is reduced but their size is increased. When more than 0.03% is utilized both the number and size of the spots are significantly reduced. In general, the proportion of silicon required for seed-free or substantially seed-free coatings increases as the acivity of the solution is increased, that is, as the concentration of zinc or manganese, nickel, copper, oxidant and the total and free acid content of the solution increases. For most purposes, 0.03 to 0.1% will suffice, with consistent commercially-acceptable coatings usually being obtained in commercial treating baths with as little as 0.04%. Silicon may be present in concentrations up to saturation, or in concentrations as large as the bath will tolerate without precipitation troubles. When introduced as silicofluoride the proportion of fluoride ion may limit the amount to be tolerated. In some cases, however, a small proportion of excess hydrofluoric acid will prevent precipitation troubles in the bath. The stabilizing effect of hydrofluoric acid is made use of in the formation of concentrated, stable make-up and replenisher solutions which can be stored and shipped without precipitation and which are simply diluted to make a new bath, or used as is for addition to an operating bath, as required. These concentrated solutions, of course, have utility for coating other types of zinc-coated ferrous surfaces.

The solutions of this invention containing the combination of nickel, copper and silicon in the ranges of concentration given above form hard, adherent, uniform and "seed"-free coatings on the particular types of hot-dipped, zinc-coated ferrous surfaces described above. The coatings produced have excellent resistance to corrosion and have excellent adherence properties for paints, lacquers, enamels, varnishes, and other protective coatings. The solutions of this invention can be utilized as an adjunct to the above-mentioned high speed "hot dip" zinc coating processes wherein sheet iron or steel in continuous strips are fed at high speeds successively through rolling mills, zinc coating stages and finally through the phosphate coating process. The solutions can be applied by immersion, spraying or any other suitable method. Bath temperatures required will usually vary between 130 and 180° F., with 130 to 160° F. being preferred.

Example 1

A separate make-up and a separate replenisher solution were built up containing the following materials:

	Make-Up, lbs.	Replenisher, lbs.
Zinc oxide (ZnO)	250.0	585
Nickel carbonate	375.0	175
Nitric acid (42° Bé.)	260.0	460
Phosphoric acid (75%)	1,120.0	2,140
Hydrofluosilicic acid (31.2%)	600.0	384
Hydrofluoric acid (60%)	38.0	18
Water to a total of	4,900.00	5,850.00

The above solutions were diluted with water in a ratio of 50 lbs./100 gallons to form solutions having the analysis:

Total Acidity	26.1	32.8
Free Acidity	2.8	6.1
Percent Silicon	0.04	0.03
Specific Gravity ° Bé.	35.5	44.3

The total acidity given above is the ml. of N/10 NaOH (points) determined by titrating a 10 ml. sample with N/10 sodium hydroxide to a phenolphthalein end-point whereas the free acidity is the ml. of N/10 sodium hydroxide (points) required to neutralize a 10 ml. sample to a bromophenol blue end point. The diluted, 35.5° Bé. make-up solution was placed in a tank and heated to about 130 to 180° F. A plurality of hot-dipped steel panels of brands known as "Zincgrip" or "Ti-Co," said to be made by the process of U. S. Patent 2,197,622, were immersed in the solution for about three minutes to "age" the solution (about 100 sq. ft. for every 4 liters of solution). The aging panels received especially adherent, hard and dense coatings which were completely smooth and uniform. Panels treated in a similar bath not containing the hydrofluosilicic acid were covered with white spots or seedy areas wherein the coating was built up above the surrounding surface. The original make-up bath was utilized for an extended period under commercial operating conditions during which time the original concentration was maintained by periodic additions of the undiluted replenisher solution. The processing sequence for this continuous operation was:

(1) Alkaline cleaner-spray or rinse at about 160° F.
(2) A second alkaline cleaner at about 150–160° F. (optional).
(3) Hot water rinse at 158° F.
(4) Phosphate treatment for about one minute at about 151° F.
(5) Water rinse at about 88° F.
(6) Chromic acid rinse at about 137° F.
(7) Air dry.

The panels continued to receive satisfactory phosphate coatings substantially free, and sometimes completely free, of seediness over a period of months of continued usage of the same bath. When these coated panels were painted with the usual primer and finish coats the finished stock showed excellent adherence of the paint, good corrosion resistance and an appearance entirely acceptable for commercial usage. When, however, similar hot-dipped zinc coated steel panels were coated in a bath similar to that of this example, except for the substitution of approximately equivalent amounts of hydrofluoric acid or hydrofluoboric acid, the phosphate coatings were objectionably "seedy." It is clear, therefore, that it was the soluble silicon and not the fluoride content that eliminated the seediness.

The "make-up" and "replenisher" solutions described in Example 1, above, are formulated so as to contain a balanced proportion of the ingredients and as high a total solids content as will not precipitate or crystallize out at 0° F. A dilution ratio of at least 1:1 is considered necessary for economy in shipping. Dilution ratios of at least 5, 10 or 15:1 or more are preferred. In the case of the "make-up," the concentrations of the ingredients are a simple multiple of the concentration of a working bath. In the "replenisher," however, the various ingredients are present in the ratio in which they are used up or removed from an operating bath. For example, the free acidity of the replenisher is higher than that of the make-up in order to maintain the free acidity of the operating bath. The phosphoric acid and zinc oxide, which are the principal coating-producing agents, are present in a higher proportion in the replenisher than in the make-up for the same reason. When these ingredients are combined in such high concentrations there is a tendency to form a precipitate, even at room temperature. This tendency is effectively overcome by the addition of sufficient excess hydrofluoric acid. For this purpose, only about 0.1 to 0.3% or more is required. When stabilized with hydrofluoric acid these solutions can be stored or shipped without special precaution and can be diluted with water to form excellent operating solutions. The replenisher, however, is preferably added to the operating bath "as is."

Example 2

A nickel activated bath having the following composition was employed to treat hot-dipped steel sheet:

	Grams/liter
Phosphoric acid, H_3PO_4 (75%)	13.7
Nitric acid, HNO_3 (32° Bé.)	3.6
Zinc oxide, ZnO	3.1
Nickel carbonate, $NiCO_3$	4.6
Boric acid, H_3BO_3	1.8
Hydrofluoric acid, HF (60%)	3.6

The above solution was heated to 130 to 180° F. in a suitable container. Hot dipped steel sheet prepared by the process described hereinabove, treated for one minute in this bath acquired adherent, hard and dense coatings averaging between about 250 and 350 mg./sq. ft. The coatings, however, were excessively "seedy" and after painting did not have a good appearance. Sodium silicofluoride in the amount of 3.5 lbs. per 100 gallons was then added and another series of panels were processed as before. The coatings produced were more uniform and so free of the objectionable seediness that painted panels prepared therefrom were of much better appearance. Paint adhesion and corrosion resistance were as good, if not better, than those coated in the bath without sodium silicofluoride.

What is claimed is:

1. An aqueous solution for coating a continuous hot-dipped, zinc-coated ferrous surface comprising as the essential coating-producing ingredients about 0.5% to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, at least one oxidizing ion from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2 to 1% nitrate ion and 0.0002% to 0.008% nitrite ion, and a silicon-containing ion in a proportion sufficient to produce at least 0.03% soluble silicon.

2. An aqueous solution for coating a continuous hot-dipped, zinc-coated ferrous surface consisting essentially of about 0.5% to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, at least one oxidizing ion selected from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2% to 1% nitrate ion and 0.0002% to 0.008% nitrite ion, and silicofluoride ion in a proportion sufficient to produce at least 0.03% soluble silicon.

3. An aqueous solution for coating a continuous hot-dipped, zinc-coated steel surface consisting essentially of 0.5% to 2.5% phosphate ion, zinc ion in a proportion from that sufficient to form dihydrogen phosphate with said phosphate ion, to not more than 0.5%, a ratio of phosphate ion to zinc ion of not more than 5:1, 0.01 to 0.4% nickel ion, 0.2% to 0.5% nitrate ion, and silicofluoride ion sufficient to produce at least 0.03% soluble silicon.

4. The method of providing seed-free phosphate coatings on continuous hot-dipped, zinc-coated ferrous surfaces comprising contacting the said surfaces with an aqueous solution comprising as the essential coating-producing ingredients about 0.5 to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, at least one oxidizing ion from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2 to 1% nitrate ion and 0.0002 to 0.008% nitrite ion, and a silicon-containing ion in a proportion sufficient to produce at least 0.03% soluble silicon.

5. The method of providing seed-free phosphate coatings on continuous hot-dipped, zinc-coated steel surfaces comprising contacting the said surfaces with an aqueous solution consisting essentially of 0.5 to 2.5% phosphate ion, zinc ion in a proportion selected from the range from that at least sufficient to form dihydrogen phosphate with said phosphate ion to not more than 0.5%, a ratio of phosphate ion to zinc ion of not more than 5:1, 0.01 to 0.4% nickel ion, 0.2 to 0.5% nitrate ion, and silicofluoride ion sufficient to produce at least 0.03% soluble silicon.

6. The method of providing seed-free phosphate coatings on continuous hot-dipped, zinc-coated steel surfaces comprising contacting the said surface with an aqueous solution containing as the essential coating-producing ingredients about 0.5% to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, at least one oxidizing ion selected from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2% to 1% nitrate ion and 0.0002% to 0.008% nitrite ion, and silicofluoride ion in a proportion sufficient to produce at least 0.03% soluble silicon.

7. An aqueous solution for coating hot-dipped, zinc-coated ferrous surfaces containing as the essential coating-producing ingredients about 0.5% to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, 0.0003 to 0.005% copper ion, at least one oxidizing ion selected from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2% to 1% nitrate ion and 0.0002% to 0.008% nitrite ion, and silicofluoride ion in a proportion sufficient to produce at least 0.03% soluble silicon.

8. The method of providing seed-free phosphate coatings on continuous hot-dipped, zinc-coated steel surfaces comprising contacting the said surface with an aqueous solution containing as the essential coating-producing ingredients about 0.5% to 2.5% phosphate ion, a metal ion of the group consisting of the zinc ion and the manganese ion in a proportion at least sufficient to form dihydrogen phosphate with said phosphate ion, 0.01 to 0.4% nickel ion, 0.0003 to 0.005% copper ion, at least one oxidizing ion selected from the group consisting of the nitrate ion and the nitrite ion in a concentration of about 0.2% to 1% nitrate ion and 0.0002% to 0.008% nitrite ion, and silicofluoride ion in a proportion sufficient to produce at least 0.03% soluble silicon.

References Cited in the file of this patent

UNITED STATES PATENTS

2,121,574	Romig	June 21, 1938
2,312,855	Thompson	Mar. 2, 1943
2,591,479	Ward	Apr. 1, 1952

FOREIGN PATENTS

606,109	Germany	Nov. 24, 1934
655,079	Great Britain	July 11, 1951