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CHROMATE-FREE BRIGHT DIP FOR ZINC AND CADMIUM SURFACES

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ABSTRACT OF THE DISCLOSURE

A dry pulverulent composition and an aqueous solution prepared therefrom are disclosed for use as a bright dip bath for zinc and/or cadmium surfaces to improve resistance of such surfaces to oxidation, staining and/or corrosion. The essential components of the composition and bath are a soluble nitrate salt, a water soluble fluoride salt, and if needed a salt of sulfuric acid and/or sulfamic acid to lower the pH of an aqueous solution prepared from the composition to not over 4.0. Citric acid is preferably also included as a chelator for iron and other divalent metals. Thus the essential composition is chromate-free in contrast to the prior art; however, the composition may contain a trivalent chromium component serving as a base to produce a conversion coating, which provides improved corrosion resistance without the pollution problems attendant upon the use of hexavalent chromium bright dips of the prior art. Maximum corrosion resistance requires the presence of hexavalent chromium in the composition, but there is still provided a unique advantage over the prior art since excellent salt spray corrosion resistance is obtained with only minute amounts of hexavalent ion. Acid soluble oxidation resistant dyes may also be incorporated to provide a blue conversion coating.

BACKGROUND OF THE INVENTION

This invention relates to compositions for and methods of brightening the surfaces of zinc and cadmium metals and their alloys, usually for the purpose of enhancing the activity of such surfaces for subsequent treatment; e.g., phosphating, chromating, plating, dyeing, painting or waxing. Increasing the resistance of the surfaces to corrosion is a complementary purpose of the foregoing, if not the sole controlling purpose of the treatment. The invention here is directed more particularly to the achievement of these results without employment of chromate compositions; this is, without need more especially for hexavalent chromium ions in the treatment compositions, since such hexavalent chromium introduces troublesome and expensive pollution problems in the disposal of spent treatment solutions.

The compositions and procedures used in the prior art for the brightening of zinc and cadmium surfaces are quite extensive, as articles having such surfaces are mass-produced in the automotive, appliance and hardware industries. Most prior bright dip baths employ nitric acid, but the problems of safely preparing and handling nitric acid containing baths are well known. Variations have therefore been introduced utilizing nitrate salts instead of the liquid acid. This has reduced one of the problems but another problem has remained since even the acid-salt modified bright dips have continued to require hexavalent chromates in their make up. These chromates have been utilized to meet functional specifications in the way of resistance to corrosion of the treated surfaces, usually measured by salt spray tests. Chromates, and particularly hexavalent chromium compounds, are a source of environmental pollution occasioned by the dumping of waste or spent bright dip baths. Trivalent

chromium can be controlled relatively easily. However, costly processing of the spent baths is involved in converting any hexavalent chrominum to a non-deleterious form and precipating it prior to disposal if pollution is to be avoided, and governmental regulations are making this more and more mandatory.

A major purpose of the present invention is the provision of pulverulent compositions for use in making up bright dips for zinc and cadmium surface articles, and aqueous baths made therefrom. A corollary purpose is to avoid the disadvantages and hazards of liquid nitric acid and chromates previously required, while providing compositions which are nevertheless effective to give excellent brightening capacity for the zinc and cadmium surfaces, and for imparting good corrosion resistance to them.

Summary of the Invention

It has been discovered that dry pulverulent compositions can be prepared which, when dissolved in the appropriate amount of water, give excellent bright dip baths. Zinc or cadmium surface articles momentarily dipped in such solutions, even under normal ambient temperature conditions, exhibit unusual brightness and luster of the surface. Such compositions, apart from being in dry, pulverulent form and thus more safely handled than liquids, have the further advantage of eliminating the necessity of chromium compounds entirely, or at least hexavalent chromium compounds, without sacrificing satisfactory corrosion resistance of the treated surface.

Briefly and in general, the novel compositions comprise a nitrate salt in predominant amount, more especially an inorganic nitrate such as sodium, potassium or ammonium, or alternatively urea nitrate. The nitrate serves as the primary polishing component in the composition. The composition also includes a soluble fluoride, more especially sodium, potassium or ammonium fluoride or bifluoride, which normally serves as a buffer but which may also be used to adjust the necessary bath acidity. Preferably such requirement is fulfilled by incorporation of an acid salt component, as for example, an acid salt of sulfuric or sulfamic acid, in amount sufficient to produce a solution pH not over 4.0 when the composition is dissolved in the appropriate amount of water to produce the bright dip bath. Such an acid salt is usually not required where urea nitrate is used, since hydrolysis of this makes the added acid salt unnecessary. Preferably the composition also contains a chelating agent such as citric acid, although this is not always essential. Where coloration of the finish is desired, as a white-bright finish for example, a chromium trioxide compound such as chrome alum or other form of trivalent chrome salt to form a thin gelatinous conversion coating can also be included. The coatings containing a trivalent chromium compound have more corrosion resistance than the compounds without this. Omega chrome cyanide (Mordant Blue No. 3) added to the bright dip bath containing trivalent chromium will produce a bluish coating by absorption of the dye into the conversion coating.

The proportioning of the foregoing materials will vary substantially in the compositions depending on the ultimate requirements of the treated surface. Thus the nitrate may represent as little as about 15% by weight of the total composition, and up to as much as 99.8% where urea nitrate is used, since this serves both as the nitrate ion source as well as providing the necessary bath acidity. Since the nitrate ion serves as the primary brightening agent, preferably it ranges from 15% to 85% where an inorganic nitrate is employed, or from 50% to 85% where urea nitrate is used. The acid salt may likewise vary in amount, ranging upwards to 80% by weight, providing always that the resultant bright dip bath prepared by dis-

solving the composition in water will have a maximum pH of not over 4.0. Preferably the pH will be under 3.0 and of the order of 1.0–2.5. In general, a level of 15% to 35% by weight of the acid salt is desired. The fluoride salt is usually present in minor amount which may be as low as about 0.2% but preferably is from 0.2% to 2% by weight to serve as a buffer. In those instances where it is also relied upon to supplement the acid salt component, it will be present in greater amount up to 15% (preferably 13%) by weight. Generally speaking, when a trivalent chromium component is included, this will vary to as much as 15% by weight of the total composition, with a preferred range of 0.5% to 10%. Where a citrate complexer is used, this also will range up to 15%, with a preferred range of 0.2 to 10%. Finally inclusion of up to 15% (preferably 0.5% to 10%) by weight of an organic dye such as omega chrome cyanide (Mordant Blue No. 3) or similar acid soluble organic dye resistant to oxidation, is contemplated.

To prepare a bright dip bath utilizing the foregoing compositions, they are dissolved in water. From as little as ⅓ ounce of the pulverulent composition per gallon of bath solution, up to about 6 ounces of composition per gallon of solution, is found to be effective. Obviously the effectiveness of the bath, in terms of its brightening and corrosion inhibiting effects, will depend in part at least upon the concentration. Although some effect will be noted at concentrations lower than ⅓ ounce per gallon, the effect is not considered significant or sufficient for general practical purposes, either because of excessive treatment time required or the use of elevated bath temperatures, both contributing to higher processing costs. This is apart of course from such other considerations as reduced brightness and corrosion inhibited surface characteristics. On the other hand, concentrations greater than about 6 ounces per gallon of solution do not appear to produce any significant improvement and are thus economically of lesser importance. A preferred operating range is from ½ to 4 ounces per gallon of solution.

Both zinc and cadmium metal surfaces, as well as predominantly zinc or cadmium based alloy surfaces, can be brightened in the bath compositions of the invention under normal ambient temperature conditions of the treatment solution, and up to temperatures approaching the boiling point of the solution. The bath compositions are also quite tolerant in respect of time of immersion in that prolonged submersion of the articles to be brightened will have no adverse effect upon brightness; however, prolonged immersion can remove excessive zinc or cadmium metal. Articles may be left overnight, for example, in solutions of the invention composition without imparting the bath, as it is quite tolerant to impurities. However optimum results are obtained by dipping the articles in the bath for from 10 seconds to 5 minutes at bath temperatures of from 20° C. to 40° C.

The invention is illustrated by the following examples of certain preferred embodiments. Unless otherwise noted, percentage figures are by weight in all instances.

Example I

A pulverulent composition was prepared for use in making up a bright dip bath for zinc castings, consisting of 65% sodium nitrate, 32% sodium bisulfate, 1.5% sodium bifluoride and 1.5% citric acid. An aqueous solution of this composition was prepared by dissolving it in water to provide a concentration of 1 ounce per gallon of solution. A zinc plated part was immersed in this solution for 30 seconds to 1 minute at ambient or slightly higher temperature (20° to 30° C.), removed, rinsed in plain water and dried.

The zinc surface has a bright, silvery, high-luster finish. This brightening treatment, which does not incorporate a trivalent chromium compound, will not impart much corrosion resistance to the surface. However, further treatment of the surface with a commercial sealer, such as a solution containing from 0.1 to 0.1% by weight of a polyacryamide (American Cyanamid CYANEX P–250) containing sufficient sodium dichromate to provide from 10 to 500 p.p.m. hexavalent chromium ion, will result in a surface that withstands a conventional salt spray test for 72 hours without evidence of corrosion. Such test consists of subjecting the treated casting, while suspended on a rack, to a continuous spray of neutral aqueous salt solution containing 5% sodium chloride maintained at a temperature of 34° C. Further, this supplemental "sealing" operation will render the film heat resistant, i.e. temperatures up to 200° C., without impairing the corrosion resistance.

Example II

A pulverulent composition was prepared for use in making up a bright dip for a zinc electroplated substrate, consisting of 58.7% sodium nitrate, 28.5% sodium bisulfate, 1.4% sodium bifluoride, 1.4% citric acid and 10% chromium potassium sulfate (chrome alum).

This composition was dissolved in water to provide a concentration of 2 ounces per gallon, and the zinc coated part was immersed in it for 30 seconds to 1 minute at ambient temperature. After removing and rinsing the part, and allowing it to dry, the surface exhibited a bright white high-luster which withstood the salt spray test for 6 hours without evidence of corrosion. With further treatment in a sealant such as described in Example I, salt-spray corrosion resistance is increased to 48 to 72 hours.

Example III

A pulverulent composition was prepared for use in making up a blue-bright bath, consisting of 56% sodium nitrate, 27.2% sodium bisulfate, 1.4% sodium bifluoride, 1.4% citric acid, 9.5% chrome alum and 4.5% omega chrome cyanide (Mordant Blue No. 3).

A water solution of this composition was prepared containing 1⅓ ounces per gallon, and a zinc electroplate was immersed in this solution for 20 seconds to 1 minute at ambient temperature. Upon removal and rinsing, the casting exhibited a bright bluish tint which withstood a conventional salt spray test for 6 hours. Again further treatment with a sealant as described above will provide a 48 to 72 hour resistance to salt spray corrosion.

Example IV

A pulverulent composition was prepared consisting of 64.5% sodium nitrate, 32% sulfamic acid, 2% sodium fluoride and 1.5% citric acid. This composition was dissolved in water to provide a solution containing 1 ounce per gallon. A zinc plated part immersed in it for 10 seconds to 1 minute at ambient temperatures produced again a clear, bright, highly lustrous finish.

Example V

A pulverulent composition was prepared consisting of 75% urea nitrate, 13% sodium fluoride and 12% citric acid. No inorganic sulfate or sulfamic acid component was used, but the amounts of sodium fluoride and citric acid were increased substantially as noted to adjust the pH.

A solution of this composition was prepared by dissolving it in water to provide a concentration of 4.0 ounces per gallon. A zinc plate immersed in this solution for 30 seconds to 1 minute at ambient temperature, rinsed and dried, exhibited a high luster.

Example VI

A pulverulent composition was prepared consisting of 87% urea nitrate and 13% sodium fluoride. This composition, when dissolved in water to provide a concentraction of ½ ounce per gallon, produced a good brightness on zinc plates immersed in it for a period of 5 seconds to 1 minute at ambient or slightly higher temperature.

Example VII

A composition consisting of 99.8% by weight of urea nitrate and 0.2% sodium fluoride was dissolved in water to provide a concentration of 1 ounce per gallon. Zinc plate immersed in this solution for 5 seconds to 1 minute at ambient temperature showed noticeable improvement in brightness.

Example VIII

A composition was prepared consisting of 75% urea nitrate, 10% sodium fluoride, 10% citric acid and 5% chrome alum. The composition, when dissolved in water to provide a concentration of 2 ounces per gallon was utilized as a bright dip bath for zinc plate. Such electroplate was immersed for 10 to 30 seconds at ambient temperature and showed corrosion resistance to the salt spray test for periods in excess of 6 hours.

Example IX

A composition was prepared containing 75% urea nitrate, 10% sodium fluoride, 5% citric acid, 5% chrome alum and 5% Mordant Blue No. 3. When dissolved in water to provide a concentration of 2 ounces per gallon. this composition produced a blue-bright dip bath imparting a bluish bright luster to the surface of zinc plate immersed in it. Normal immersion times of 10 seconds to 1 minute were employed at ambient solution temperature and salt spray corrosion resistance in excess of 6 hours was indicated.

Example X

A composition was prepared consisting of 84% sodium nitrate, 15.5% sulfamic acid, 0.25% sodium fluoride and 0.25% citric acid. This composition when dissolved in water to a concentration of 1 ounce per gallon was used as a bright dip for a cadmium plated casting. Such casting was immersed in the solution for a period of 5 seconds to 5 minutes at ambient or slightly higher solution temperatures (up to 40° C.). The casting showed excellent brightness and moderate corrosion resistance without sealing.

The same solution was used for treatment of zinc electroplate castings and gave good results for these as well, although the compositions of Examples I to IV above are preferred for treatment of zinc surfaces. Conversely, the baths described in any of the foregoing Examples will also serve to brighten cadmium surfaces appreciably, although the bath composition described in this Example appears to give best results and is preferred for such surfaces.

The treatment of the zinc or cadmium surfaces by any of the foregoing procedures can be supplemented in various ways, either to produce a higher coloration or greater corrosion resistance where the treated surfaces are to be the final or finished product surfaces. The following are examples.

Example XI

A zinc electroplate subjected to a bright dip solution as described in Example IV above modified to include approximately 2.0% of chrome alum. The resulting finish was a "blue-bright" which exhibited up to 16 hours resistance to the salt spray corrosion tests.

Example XII

A composition was prepared containing 61.0% nitrate, 2.0% sodium fluoride, 31.0% sulfamic acid, 1.5% citric acid, 20% chrome alum and 2.5% Mordant Blue C (conc.). At a concentration of 4.0 ounces per gallon of aqueous solution of this composition, a zinc plated part immersed for 1 minute developed a deeper blue than that of Example XI.

Example XIII

A composition was prepared containing 25% potassium nitrate, 50% sulfamic acid, 6% sodium fluoride and 19% citric acid. When dissolved in water to a concentration of 1.5 ounces per gallon, a very satisfactory bright dip for zinc articles is obtained.

In general, the nitrate may be the potassium or ammonium salts in equivalent amount for the sodium or urea salts named in the examples, or it may be a mixture of such nitrates. Similarly, the acid salt may be the potassium or ammonium equivalents of the sodium bisulfate or sulfamic acid specifically named; and again, mixtures of the salts are satisfactory. Such substitutions are determined primarily by economic considerations rather than operability.

In terms of ounces per gallon of the several components when the compositions are dissolved in water to make up the bright dip solutions, the nitrate (inorganic or urea) salt may range from about 0.045 to 5.98 ozs./gal., the acid salt will range from 0 to about 4.8 ozs./gal., the soluble fluoride from about 0.0007 to 0.9 oz./gal., citric acid from 0 to about 0.9 oz./gal., chrome alum up to about 0.9 oz./gal., and the mordant up to about 0.9 oz./gal. The preferred concentrations are: nitrate salt 0.075 to 1.4 ozs./gal.; acid salt 0.075 to 1.4 oz./gal. if present; soluble fluoride of from 0.001 to 0.08 oz./gal.; and citric acid 0.001 to 0.08 oz./gal. In the alternative where urea nitrate is used without an acid salt, from 0.25 to 3.4 ozs./gal. of urea nitrate are combined with 0.001 to 0.52 oz./gal. of soluble fluoride and 0.001 to 0.4 oz./gal. of citric acid. With either type of formulation, from 0.0025 to 0.4 oz./gal., each of chrome alum and Mordant Blue No. 3, are preferred limits.

What is claimed is:

1. A hexavalent chromium-free pulverulent composition for dissolution in water to provide a bright dip for zinc and cadmium surfaces, said composition consisting essentially of

(a) from 15% to 99.8% by weight of a water-soluble nitrate salt;

(b) up to 80% by weight of an acid salt selected from the group consisting of sodium, potassium and ammonium bisulfates and sulfamic acid;

(c) from .2% to 15% by weight of a water-soluble fluoride salt;

(d) up to 15% by weight of citric acid;

(e) up to 15% by weight of a trivalent chromium compound;

(f) up to 15% by weight of an acid soluble oxidation resistant organic dye;

wherein the amount of acid salt in the composition is always sufficient to produce a pH of from 4.0 to 0.5 upon addition of from 0.3 to 6 ozs. of said composition per gallon of water.

2. A pulverulent composition as defined in claim 1, wherein said nitrate is selected from the group consisting of sodium, potassium, ammonium and urea nitrates.

3. A pulverulent composition as defined in claim 2, wherein the nitrate present is an inorganic nitrate and is present in amount which is the equivalent of about 15% to 85% sodium nitrate.

4. A pulverulent composition as defined in claim 3, wherein said nitrate is sodium or potassium nitrate, and said acid salt is sodium bisulfate in amount of from about 15% to 35%.

5. A pulverulent composition as defined in claim 1, consisting essentially of about 65% sodium or potassium nitrate, about 32% sodium bisulfate or sulfamic acid, the balance being essentially equal amounts of said fluoride and citric acid.

6. A pulverulent composition as defined in claim 1, consisting essentially of about 75% of urea nitrate, about 10% each of soluble fluoride and citric acid, and about 5% of chrome alum.

7. A pulverulent composition as defined in claim 1, consisting essentially of about 75% urea nitrate, 10% soluble fluoride, 5% citric acid, the balance being substantially equal weights of chrome alum and omega chrome cyanide.

8. A pulverulent composition as defined in claim 1, consisting essentially of about 55% to 65% sodium or potassium nitrate, 25% to 30% sodium bisulfate, and about 1% each of sodium bifluoride or fluoride and citric acid, the balance being said trivalent chromium mordant.

9. A pulverulent composition as defined in claim 8, wherein said chrome compound is chrome alum.

10. A pulverulent composition as defined in claim 8, wherein said organic dye is omega chrome cyanide.

11. A pulverulent composition as defined in claim 1, consisting essentially of about 75% sodium or potassium nitrate, 10% sodium fluoride, 10% citric acid and the balance chrome alum.

12. A pulverulent composition as defined in claim 1, consisting essentially of about 84% sodium or potassium nitrate, about 15.5% of said acid salt, and about 0.25% by weight each of said fluoride and citric acid.

13. A method of treating a zinc or cadmium surface to enhance its brightness, which comprises contacting said surface for at least five seconds at a temperature of at least 20° C. with an aqueous solution containing from about 0.045 to 5.98 ozs./gal. of a nitrate selected from

the group consisting of sodium, potassium, ammonium and urea nitrates and mixtures thereof; up to 4.8 ozs./gal. of an acid selected from the group consisting of sodium, potassium and ammonium bisulfates and sulfamic acid sufficient to produce a pH not over 4.0; from about 0.007 to 0.9 oz./gal. of a water soluble fluoride; up to about 0.9 oz./gal. of citric acid; up to about 0.9 oz./gal. of a water soluble trivalent chromium compound; and from about 0.0025 to 0.4 oz./gal. of an acid soluble, oxidation resistant organic dye.

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