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CORROSION PROTECTED ZINC PRODUCTS AND METHOD OF PRODUCING THEM

Allan E. Chester, Highland Park, Ill., assignor to Poor & Company, Chicago, Ill., a corporation of Delaware

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This invention relates to corrosion protected zinc products and to a method of producing them.

One of the objects of the invention is to provide a new and improved process for treating zinc surfaced articles in order to provide improved corrosion resistance.

Another object of the invention is to provide a new and improved process for producing bronze colored surfaces on zinc articles.

Another object is to provide new and useful coloring and protective film forming compositions for zinc.

Still a further object of the invention is to produce new and useful bronze colored zinc surfaced articles. Other objects will appear hereinafter.

In accomplishing these objects in accordance with the invention it has been found that new and improved results in producing zinc coatings of enhanced corrosion resistance can be obtained by subjecting zinc or a zinc coated article to treatment with a chromic acid solution containing electrolyzed ammonium sulfate, i. e. ammonium persulfate, and trifluoroacetic acid.

Chromic acid aqueous solutions as heretofore used in the art normally produce a yellow brown or greenish brown iridescent stain on zinc, apparently due to the formation of soluble chromium chromates. The same is true of chromic acid aqueous solutions containing electrolyzed ammonium sulfate. It has now been found that chromic acid solutions containing electrolyzed ammonium sulfate and trifluoroacetic acid when applied to zinc surfaced articles form a beautiful uniform bronze film which also provides enhanced corrosion protection for the zinc.

The invention will be illustrated but is not limited by the following example.

Example

(A) A lead lined tank is filled with 250 gallons of hot water (140° F. to 200° F.) and 1904 pounds of chromic acid (CrO_3) are dissolved therein with agitation.

To the chromic acid solution there is added a composition made by dissolving 190 pounds of ammonium sulfate in sufficient water to make 45 gallons and then electrolyzing the resultant solution, using a nickel anode and a graphite cathode and a current of 50 amperes for 34 hours with agitation.

To the above mixture enough cold water is added to make 432 gallons of solution and 1296 cc. (3 cc. per gallon) of trifluoroacetic acid is added.

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The resultant composition is a concentrate which is suitably diluted with water before use.

(B) Zinc is plated onto sheet steel in a conventional fashion from a conventional bath without adding any brightening agents. A typical conventional zinc plating bath has the following composition:

95 to 100 grams sodium cyanide
45 to 55 grams zinc metal (added as the chemically equivalent proportion of zinc oxide)
100 to 120 grams sodium hydroxide and enough water to make 1 liter of solution

2 grams per liter of zinc dust are stirred into this electrolyte and the entire mixture is filtered in order to remove traces of heavy metals.

(C) The concentrate described under (A) is diluted with water, preferably 1 part of said composition to 49 parts by weight of water. The zinc plated article plated from the bath described under (B) is immersed in this diluted treating bath preferably at a temperature of 70° F. to 85° F. for a period of 5 seconds to 3 minutes. It is then removed from the bath and washed with water.

The resultant article contains a beautiful uniform bronze film which is resistant to white corrosion, as compared with the untreated zinc plated article.

The dilution of the treating bath will affect the tightness and color of the coatings formed on the zinc. The range of dilution with respect to the concentrate described under (A) is preferably 1 part of said composition to 19 to 99 parts by weight of water.

The chromic acid concentration of the treating bath preferably varies from 20 to 100 grams per gallon.

The trifluoroacetic acid concentration of the treating bath is preferably within the range of 0.03 to 0.5 gram per gallon (calculated as fluorine (F)).

The weight ratio of trifluoroacetic acid, calculated as fluorine, to chromic acid (CrO_3) in the treating bath is a fraction of a per cent, preferably about 0.5%.

The electrolyzed ammonium sulfate preferably constitutes about 30 to about 55 grams per gallon of the treating bath.

The more concentrated treating solutions tend to produce tighter and darker coatings. The color of the coating can be varied by making other additions to the treating bath. For example, in order to obtain a deep olive drab coating chlorides may be added to the treating bath. Thus, 10 to 100 grams per liter of ammonium

chloride may be employed or the equivalent quantities of other inorganic chlorides such as, for example, sodium chloride and potassium chloride can be used.

In the practice of this invention trifluoroacetic acid appears to have unique properties which are not possessed by other fluorine containing acids, such as fluoboric acid. It is believed that in some unexplained way the trifluoroacetic acid either prevents the formation of soluble chromium chromates or converts them to an insoluble form.

The relative proportions of the ingredients in the concentrate may vary depending upon the dilution desired. Thus, the CrO_3 and electrolyzed ammonium sulfate may each be varied up to 25% by weight either way from the proportions given in the example. The quantity of trifluoroacetic acid is preferably within the range of 1 cc. to 25 cc. per gallon of concentrate.

The "electrolyzed ammonium sulfate" is prepared by electrolyzing ammonium sulfate for 1000 to 2500 ampere hours in an aqueous solution between a nickel anode and a graphite cathode.

The resultant solution contains ammonium persulfate as well as nickel ammonium sulfate and apparently enhances the penetrating effect of the treating bath.

The increased corrosion protection provided by the application of the invention is apparently due to the formation of a tightly adherent chromate film on the zinc surface. Chromic acid solutions have been used before in treating zinc surface articles, but the present invention provides a new and improved way of producing bronze to olive colored zinc surfaced articles which are very uniform in appearance. The invention also provides a simple way of varying the depth of color. The treatment described is particularly applicable to zinc plated articles and has been successfully used in the treatment of articles plated either in alkaline or acid baths.

The expression "zinc surfaced article" is employed herein to cover any article having an exterior surface of zinc regardless of whether the article is made entirely of zinc or whether it merely contains a zinc coating. The expression "zinc plated article" is employed herein to describe a zinc coated article in which the zinc coating has been applied by an electroplating process.

The invention is hereby claimed as follows:

1. A process of coloring zinc and of protecting it against corrosion which comprises treating a zinc surfaced article with an amount of an aqueous solution consisting essentially of chromic acid, ammonium persulfate and trifluoroacetic acid sufficient to form a uniform bronze colored film on said article.

2. A process of coloring zinc and of protecting it against corrosion which comprises treating a zinc surfaced article with an aqueous solution consisting essentially of chromic acid, ammonium persulfate and trifluoroacetic acid, the quantity of chromic acid corresponding to 20 to 100 grams per gallon of solution, the quantity of ammonium persulfate corresponding to 30 to 55 grams per gallon of solution and the quantity of trifluoroacetic acid corresponding to about 0.03 to 0.5 gram per gallon of solution, calculated as fluorine.

3. A coloring and protecting film-forming composition for treating zinc surfaced articles consisting essentially of an amount of an aqueous solution of chromic acid, trifluoroacetic acid and ammonium persulfate sufficient to form a uniform bronze colored film on said article.

4. A coloring and protecting film-forming composition for treating zinc articles consisting essentially of an aqueous solution of chromic acid, trifluoroacetic acid and ammonium persulfate made by electrolyzing ammonium sulfate in water for 1000 to 2500 ampere hours.

5. A protective film-forming composition for treating zinc surfaced articles comprising an aqueous solution consisting essentially of chromic acid, ammonium persulfate and trifluoroacetic acid, the quantity of chromic acid corresponding to 20 to 100 grams per gallon of solution, the quantity of ammonium persulfate corresponding to 30 to 55 grams per gallon of solution and the quantity of trifluoroacetic acid corresponding to about 0.03 to 0.5 gram per gallon of solution, calculated as fluorine.

6. A zinc surfaced article containing a bronze to olive coating formed thereon by reaction with an amount of an aqueous solution of chromic acid, ammonium persulfate and trifluoroacetic acid sufficient to form a uniform bronze colored film on said article.

7. A zinc surfaced article containing a bronze to olive coating formed thereon by reaction with an aqueous solution comprising essentially chromic acid, ammonium persulfate and trifluoroacetic acid, the quantity of chromic acid corresponding to 20 to 100 grams per gallon of solution, the quantity of ammonium persulfate corresponding to 30 to 55 grams per gallon of solution and the quantity of trifluoroacetic acid corresponding to about 0.03 to 0.5 gram per gallon of solution, calculated as fluorine.

ALLAN E. CHESTER.

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