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METHOD FOR COATING ZINC AND ZINC ALLOY SHEETS

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This invention relates to the treatment of zinc or alloys thereof and is used for coating purposes on strip line operations such as mill-galvanized or acid-zinc sheets.

The principal object of the invention is to impart a clear protective surface or film, having improved corrosion resistance, on zinc or zinc alloy used in strip line operation by subjecting the surface of the strip being treated to immersion in a filming bath.

Another and more specific object of the invention is to provide a clear protective film on a zinc or zinc alloy coating used for mill-galvanized and acid-zinc sheets thus preventing discoloring, e. g., white bloom, which normally forms during storage by the highly corrosive action of the zinc or zinc alloy under moisture conditions, particularly when sheets are stacked one on another.

Another object of the invention is to provide a treating solution and method which will enable the above mentioned results to be uniformly obtained on a commercial scale.

An additional object of my invention is to provide a composition for use in aqueous acidic solution to impart a clear protective coating to zinc and zinc alloy coated mill-galvanized sheets comprising at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one boric compound selected from the group consisting of boric acid and water soluble salts thereof, at least one alkali metal salt of fluosilicic acid and an acid of sufficient strength and in sufficient quantity to adjust the pH of the resulting solution to between about 0.8 to 4.

Still another object of my invention is to provide a composition as set forth heretofore wherein said chromic compound is in amount equivalent to from about 0.5 to 50 grams of sodium bichromate per liter of solution, the boric compound is in amount equivalent to from about 0.25 to 50 grams of boric acid per liter of solution, the alkali metal salt of fluosilicic acid is in amount equivalent to from about 0.1 to 10 grams of sodium fluosilicate per liter of solution, and the acid is in amount sufficient to maintain a pH of solution of about 0.8 to 4.

The following preferred formulation has been found to eliminate discoloring, e. g., white bloom, during normal storage and, in addition, imparts desirable resistance to corrosion produced by a salt atmosphere and as observed by standard test on salt spray testing apparatus:

Sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$)	g./l.	22.5
Boric acid (H_3BO_3)	g./l.	22.5
Sodium fluosilicate (Na_2SiF_6)	g./l.	5
Glacial acetic acid (CH_3COOH)	ml./l.	100

(Mineral acid, e. g., nitric acid, phosphoric, sulfuric acid and hydrochloric acid, may be substituted for the acetic acid.)

In preparing the mixes of the foregoing example, where possible, the chemicals other than the acid, are preferably supplied in a dry or concentrated form. The acid, being liquid, is preferably added to the formulation at

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the time and place of make-up. As will be appreciated, this affords a substantial saving in shipping since the amount of water will be much less than that indicated above for the actual working solution. The proportions of the mixture set forth in the above formulation may vary between about 0.5 to 50 g./l. of solution sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$); about 0.25 to 50 g./l. of solution boric acid (H_3BO_3); about 0.1 to 10 g./l. of solution sodium silico fluoride (Na_2SiF_6); and the glacial acetic acid (CH_3COOH) may be from about 5 to 50 ml./l. of solution.

Referring to the acetic acid concentration, since the prime function of the acid addition is to control the hydrogen ion concentration so as to maintain a pH of about 0.8 to approximately 4, the volume of the mineral acid to be added to control the pH level will be dependent on the chemical and physical properties of the mineral acid to be employed. Thus, using pH desired as a basis the amount of particular acid used can easily be determined.

With respect to the foregoing formulation, it should be noted that chromic acid and other soluble salts thereof, e. g. potassium bichromate, can be substituted for the sodium bichromate. In addition, the water soluble salts of boric acid and other alkali metal salts of fluosilicic acid can be substituted for the boric acid and sodium fluosilicate respectively.

Of course, the proportion ranges noted heretofore with respect to the preferred formulation would not be applicable as such to the use of chromic acid and other soluble salts thereof, to the use of soluble salts of boric acid, or to the use of other alkali metal salts of fluosilicic acid. However, applicable proportion ranges are easily calculated therefrom. In other words, the calculations should be such that the same molecular amount of hexavalent chromium, borate, or fluosilicate is realized in the mixture being formed.

As noted heretofore, the optimum pH range for the operating solution is about pH 0.8 to pH 4 and a preferred pH is pH 2.6. The immersion time may range from one second to fifteen minutes and the temperature range is from 60° F. to 212° F.

To further illustrate the invention, the following examples are set forth. These examples are directed to some of the varied salts that can be substituted for the sodium bichromate, boric acid, and sodium fluosilicate of the preferred formulation noted heretofore.

Example I

Chromic acid	g./l.	10
Boric acid	g./l.	11.2
Sodium fluosilicate	g./l.	2.5
Glacial acetic acid	ml./l.	40

This formula will produce a bath having a pH of 2.6. It is to be operated at a temperature of about 180° F. with an immersion time of 2 seconds to 60 seconds depending on the surface treated.

Example II

Sodium bichromate	g./l.	10
Boric acid	g./l.	10
Sodium fluosilicate	g./l.	2
Glacial acetic acid	ml./l.	40

pH 2.6—Operation as for Example I.

Example III

Potassium bichromate	g./l.	10
Boric acid	g./l.	10
Potassium fluosilicate	g./l.	2
Glacial acetic acid	ml./l.	40

pH 2.6—Operation as for Example I.

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Example IV

Sodium bichromate	-----g./l.	22.5
Boric acid	-----g./l.	22.5
Sodium fluosilicate	-----g./l.	5
Nitric acid, 60%	-----ml./l.	2.3

pH 1.8—Operation as for Example I.

Example V

Chromic acid	-----g./l.	15.1
Boric acid	-----g./l.	22.5
Potassium fluosilicate	-----g./l.	5
Glacial acetic acid	-----ml./l.	10

pH 1.1—Operation as for Example I.

Example VI

Chromic acid	-----g./l.	7.6
Boric acid	-----g./l.	11.2
Sodium fluosilicate	-----g./l.	2.5
Nitric acid, 60%	-----ml./l.	0.5

pH 1.5—Operation as for Example I.

Example VII

Chromic acid	-----g./l.	5
Sodium borate	-----g./l.	8
Sodium fluosilicate	-----g./l.	2
Nitric acid, 60%	-----ml./l.	4

pH 1.5—Operation as for Example I.

Example VIII

Sodium bichromate	-----g./l.	10
Boric acid	-----g./l.	2
Sodium fluosilicate	-----g./l.	2
Hydrochloric acid, 34%	-----ml./l.	1.5

pH 2.0—Operation as for Example I.

As previously stated, the object of this formulation is to use it directly in the strip line. No pre-cleaning is necessary. The strip preferably enters the solution hot at between 180° and 200° F. Preferably immersion time ranges from two seconds to fifteen seconds although, as noted above, a sheet can be held in solution for fifteen minutes or more without adverse effect. This is helpful when it is necessary to attach an additional strip to the line or if a breakdown in the line occurs.

After immersion, a cold or hot water rinse followed by cold or hot air dry are utilized.

It is preferred to immerse the galvanized sheet in a bath since a continuous immersion process may then be utilized, but the treatment may, in some cases, be carried out by other means, as, for example, by spraying the aqueous solution upon the surface to be treated.

Articles treated with this solution in the manner above set forth, as by immersion or spraying, exhibit considerably enhanced resistance to white corrosion and staining.

In the appended claims, the expression "mill-galvanized sheets" is intended to cover zinc, zinc coated or alloy sheets as well as sheets in which other metals are present in substantial amounts.

The novel principles of this invention are broader than the specific embodiments recited above and rather than unduly extend this disclosure by attempting to list all of the numerous modifications which have been conceived and reduced to practice during the course of this development, these novel features are defined in the following claims.

I claim:

1. A method of treating zinc and zinc alloy mill-galvanized sheets to produce thereon a clear protective coating which comprises subjecting the same to an aqueous acidic solution comprising water, at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one boric compound selected from the group consisting of boric acid and water soluble salts thereof, at least one alkali

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metal salt of fluosilicic acid and an acid of sufficient strength and in sufficient amount to adjust the pH of the resulting solution to between about 0.8 to 4.

2. A method as claimed in claim 1 wherein the chromic compound is in amount equivalent to from about 0.5 to 50 grams of sodium bichromate per liter of solution, said boric compound is in amount equivalent to from about 0.25 to 50 grams of boric acid per liter of solution, and the alkali metal salt of fluosilicic acid is in amount equivalent to from about 0.1 to 10 grams of sodium fluosilicate per liter of solution.

3. A method of treating zinc and zinc alloy mill-galvanized sheets to produce thereon a clear protective coating comprising immersing a hot mill-galvanized strip in an aqueous acidic solution comprising water, a chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one boric compound selected from the group consisting of boric acid and water soluble salts thereof, at least one alkali metal salt of fluosilicic acid and an acid of sufficient strength and in sufficient amount to adjust the pH of the resulting solution to between about 0.8 to 4 holding said strip in the immersed condition for a time of one second to fifteen minutes and passing the coated strip through a water rinse bath.

4. A method as claimed in claim 3 wherein the immersion time ranges from two to fifteen seconds.

5. A method as claimed in claim 3 wherein the treatment is conducted with the solution at a temperature of about 60° F. to 212° F.

6. The method according to claim 1 wherein said pH adjusting acid is nitric acid.

7. The method according to claim 1 wherein said pH adjusting acid is glacial acetic acid.

8. The method according to claim 1 wherein said pH adjusting acid is a mineral acid.

9. The method according to claim 1 wherein said aqueous acidic solution contains sodium bichromate in amount of about 22.5 grams per liter, boric acid in amount of about 22.5 grams per liter, sodium fluosilicate in amount of about 5 grams per liter and the said pH adjusting acid is glacial acetic acid.

10. The method according to claim 1 wherein said aqueous acidic solution contains sodium bichromate in amount of about 22.5 grams per liter, boric acid in amount of about 22.5 grams per liter, sodium fluosilicate in amount of about 5 grams per liter and the said pH adjusting acid is nitric acid.

11. A method of treating zinc and zinc alloy mill-galvanized sheets to produce thereon a clear protective coating which comprises subjecting the same to an aqueous acidic solution consisting essentially of water, at least one chromic compound selected from the group consisting of chromic acid and water soluble salts thereof, at least one boric compound selected from the group consisting of boric acid and water soluble salts thereof, at least one alkali metal salt of fluosilicic acid and an acid of sufficient strength and in sufficient amount to adjust the pH of the resulting solution to between about 0.8 to 4.

12. A method as claimed in claim 11 wherein the chromic compound is in amount equivalent to from about 0.5 to 50 grams of sodium bichromate per liter of solution, said boric compound in amount equivalent to from about 0.25 to 50 grams of boric acid per liter of solution, and the alkali metal salt of fluosilicic acid is in amount equivalent to from about 0.1 to 10 grams of sodium fluosilicate per liter of solution.

13. A method of treating zinc and zinc alloy mill-galvanized sheets to produce thereon a clear protective coating comprising immersing a hot mill-galvanized strip in an aqueous acidic solution consisting essentially of water, a chromic compound selected from the group consisting of chromic acid and water soluble salts

thereof, at least one boric compound selected from the group consisting of boric acid and water soluble salts thereof, at least one alkali metal salt of fluosilicic acid and an acid of sufficient strength and in sufficient amount to adjust the pH of the resulting solution to between about 0.8 to 4, holding said strip in the immersed condition for a time of one second to fifteen minutes and passing the coated strip through a water rinse bath.

14. A method as claimed in claim 13 wherein the immersion time ranges from 2 to 15 seconds.

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