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METHOD OF COATING ZINC SURFACES

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This invention has to do with the treatment of zinc or zinc alloys to provide a corrosion resistant surface coating or film thereon.

More particularly, this invention relates to the treatment of zinc or zinc alloys produced on strip line operations, such as mill, hot galvanized, acid or cyanide zinc plated steel sheets, to protect the sheets from corrosion.

This invention is particularly applicable to zinc or zinc alloys provided with chromate conversion films or coatings, and is especially directed to improved chromate films and methods of improving chromate films on zinc or zinc alloy coated steel sheet materials to improve the corrosion resistance of the zinc or zinc alloy coatings.

It is an object of the present invention to provide improved chromate conversion films on zinc or zinc alloys to prevent corrosion of the metal under humid conditions.

Another object of the present invention is to provide materials and methods for improving the resistance of zinc and zinc alloys to corrosion on a commercial scale.

Still another object of this invention is to provide zinc or zinc alloys with surfaces free of corrosion products which can be subsequently readily processed to provide suitable surfaces for painting or similar treatment.

Zinc or zinc alloys used in strip line operations for milled, hot-galvanized and electro-galvanized sheets and wires have a tendency to discolor when stored under humid conditions, especially when the sheets are stacked one upon the other. This discoloration is due to the formation of white zinc oxide, which is produced by the reaction of the zinc or zinc alloy with water when the metals are stored under humid conditions. This formation of white zinc oxide considerably hampers subsequent processing of the zinc or zinc alloy sheets. Thus, for example, zinc sheets containing the white oxide coating are difficult to paint or similarly treat.

It has been suggested to treat the zinc or zinc alloy sheets with chromate solutions in order to provide a chromate coating on the sheets. In general, such chromate coatings have been found to enhance the corrosion resistance of the zinc or zinc alloys. When zinc or zinc alloy sheets are stacked for storage under very humid conditions, however, it has been discovered that the chromate coatings tend to break down, so that corrosion of the metal continues. Moreover, although chromate coatings by themselves do increase resistance to corrosion, enough corrosion still occurs with such coatings to present many problems.

According to the present invention, it has been discovered that when chromate conversion coatings are treated with a rust inhibiting solution comprising anions selected from the group consisting of molybdate, tungstate, vanadate, phosphate and mixtures of the foregoing, the ability of the chromate coatings to protect the metal substrata from corrosion is greatly increased.

In carrying out the present invention, the zinc or zinc alloy is first provided with a chromate conversion coating, and the resulting coating is then treated with a rust inhibiting solution containing molybdate ions, tungstate ions, vanadate ions, phosphate ions or mixtures of the foregoing.

Although not wishing to be restricted to this explanation, it is believed that the molybdate, tungstate, vanadate and phosphate ions disclosed herein have the intrinsic ability to penetrate the gelatinous chromate film without destroying the adhesion of this film to the metal substrata and without staining or reducing the strength of the chromate film. When the stock treated as indicated here is subjected to moisture, it is believed that the ions of tungstate, molybdate, vanadate and phosphate remain in solution in the chromate film and act as an effective corrosion inhibitor.

In any event, improvements in corrosion resistance of chromate film by as much as 1000 percent or more have been achieved by following the teachings contained herein.

In producing the chromate coating, the zinc or zinc alloy sheet or zinc or zinc alloy coated steel sheet to be treated is sprayed with or immersed in a solution containing chromate ions, e.g., CrO_4, Cr_2O_7, at a temperature of about 70° to 200° F. for short periods of time. Ordinarily, spraying or immersing for between about 0.5 and 60 seconds, and usually between 1 and 30 seconds, is sufficient. The time of contact between the treating solution and the surface to which it is applied is not important in the usual sense providing thorough wetting is obtained. In this connection, any suitable surface active agents or wetting agents may be added to the treating solution to insure proper wetting of the sheets. The required temperatures may be obtained by either preheating the solution and/or preheating the sheet.

Following the chromate coating operation, the resulting sheets are washed with water in order to substantially remove any excess chromate solution present. The quantity of washing water required may be adjusted by regulating the rate of flow of the water to fit into the operating cycle being used.

The resulting sheet, after water washing to remove the excess chromate ions, is sprayed, swabbed with, or immersed in a solution comprising water soluble molybdate ions, tungstate ions, vanadate ions, phosphate ions or mixtures of the foregoing. Illustrative of the water soluble molybdate ions are MoO_4, Mo_2O_7, Mo_3O_{10}, Mo_4O_{13}, Mo_7O_{24}, $Mo_{10}O_{31}$. The water soluble tungstate ions include WO_4 and W_7O_{24}. Water soluble vanadate ions include VO_3 and V_2O_7. Water soluble phosphate ions include PO_4, P_2O_7 and P_3O_{10}.

The solution of tungstate, molybdate vanadate and phosphate ions, as well as mixtures of the foregoing, may have a temperature of between about 70° and 180° F., preferably between about 105° and 125° F. Here again, the desirable temperature may be achieved by heating the solution or the sheets, or both. The preferred temperatures indicated are at approximately the middle of the broad range. At these temperatures, i.e., 105° to 125° F., enough heat is provided to aid in air drying the sheet, and yet the temperature is low enough to avoid any danger of rupturing the chromate film. The time of contact between the sheet and the solution of corrosion inhibiting ions should be sufficient for the chormate film to be thoroughly wetted, thereby insuring adsorption of the corrosion preventing ions. This time of contact will ordinarily be quite short, i.e., between about 0.5 and 60 seconds and usually between about 1 and 30 seconds. Here again, a suitable surface active agent may be employed to insure thorough wetting of the surface being treated.

Chromium compounds suitable for use in preparing the chromate coating baths include chromic acid and the water soluble salts of chromic acid, as, for example, water soluble chromate and dichromate salts of the metals in groups IA and IIA of the periodic table of elements and ammonium, including sodium, potassium, lithium, rubidium, cesium, magnesium, and ammonium. Such chromate coating baths are well known in the art, and may contain such materials as boric acid, sodium fluosilicate, so-

dium chloride, nitric acid and the like. The chromate ion-containing solution should be such that it will provide a clear chromate film. Typical examples of such solutions are as follows.

CHROMATE COATING SOLUTION NO. 1

Material:	Grams per liter
Chromic acid	5 to 15, preferably 10.
Boric acid	5 to 15, preferably 11.
Sodium fluosilicate	1.0 to 5.0, preferably 2.5.

Water to make 1 liter.
pH, 1.0 to 1.5, preferably 1.3.

CHROMATE COATING SOLUTION NO. 2

Material:	Grams per liter
Sodium dichromate	17.0 to 29.0, preferably 22.5.
Boric acid	17.0 to 29.0, preferably 22.5.
Sodium fluosilicate	2.5 to 7.5, preferably 5.0.

Water to make 1 liter.
pH, 3.0 to 4.0, preferably 3.5.

CHROMATE COATING SOLUTION NO. 3

Material:	Grams per liter
Sodium dichromate	17.0 to 29.0, preferably 22.5.
Boric acid	17.0 to 29.0, preferably 22.5.
Sodium fluosilicate	2.5 to 7.5, preferably 5.0.
Nitric acid, 70%	1.8 to 3.8, preferably 2.8.

Water to make 1 liter.
pH, 1.3 to 2.3, preferably 1.8.

CHROMATE COATING SOLUTION NO. 4

Material:	Grams per liter
Chromic acid	4.6 to 10.6, preferably 7.6.
Boric acid	8.2 to 14.2, preferably 11.2.
Sodium fluosilicate	1.5 to 3.5, preferably 2.5.
Nitric acid, 70%	0.3 to 0.9, preferably 0.6.

Water to make 1 liter.
pH, 1.2 to 1.8, preferably 1.8.

CHROMATE COATING SOLUTION NO. 5

Material:	Grams per liter
Sodium dichromate	17.0 to 29.0, preferably 22.5.
Boric acid	17.0 to 29,0, preferably 22.5.
Sodium chloride	2.5 to 7.5, preferably 5.0.

Water to make 1 liter.
pH, 3.4 to 4.4, preferably 3.9.

CHROMATE COATING SOLUTION NO. 6

Material:	Grams per liter
Sodium dichromate	8.25 to 14.25, preferably 11.25.
Boric acid	8.25 to 14.25, preferably 11.25.
Sodium chloride	1.5 to 3.5, preferably 2.5.
Nitric acid 70%	0.4 to 1.0, preferably 0.7.

Water to make 1 liter.
pH, 1.5 to 2.5, preferably 2.0.

Although the above chromate solutions are illustrative of commercially operative embodiments, applicants in no way intend themselves to be restricted to the specific materials or concentrations indicated in the above described solutions. Rather, compositions of other chromate solutions that may be used in carrying out the present invention will be well understood by those skilled in the art.

The corrosion protection solutions described herein may be prepared simply by dissolving water soluble compounds comprising anions of molybdate, tungstate, vanadate, phosphate or mixtures of the foregoing in water. Such solutions may comprise between about 0.0025 and 0.5 gram mole per liter of the indicated anions, and preferably between about 0.005 and 0.30 gram mole per liter. The pH of the corrosion protection solutions may vary, depending upon the particular compounds used. In general, the pH of the solution will vary between about 2.5 and 9.5 and usually between about 4.0 and 8.2. Typical of the molybdate compounds which may be used in the corrosion protection solution are molybdic trioxide, and the water soluble salts of molybdic acid, as for example, the water soluble molybdates of the metals of groups IA and IIA of the periodic table of elements, and ammonium. Preferred for use are sodium molybdate, potassium molybdate, magnesium molybdate, and ammonium molybdate. Typical of the tungstate, phosphate and vanadate compounds which may be mentioned are the water soluble tungstates, vanadates and phosphates of the metals of groups IA and IIA of the periodic table of elements, and ammonium. Preferred for use are the sodium, potassium and ammonium water soluble salts of these anions.

Examples of suitable corrosion protection aqueous solutions for use in the present invention are indicated in Table I:

Table I

CORROSION PROTECTION SOLUTIONS

Material	Grams per liter	pH	Designation
Molybdic trioxide	5.0	2.7	A
Sodium molybdate	2.5	7.5	B
Do	10.0	8.7	C
Do	30.0	9.2	D
Ammonium molybdate	10.0	5.3	E
Sodium tungstate	3.0	7.6	F
Do	11.0	8.7	G
Do	15.0	8.9	H
Magnesium molybdate	10.0	8.2	I
Monoammonium phosphate	3.0	4.0	J
Disodium phosphate	3.0	9.0	K
Ammonium metavanadate	3.0	6.7	L

The nature of the invention will be clear from the following examples, which, although illustrative, are not intended to limit the scope of the invention, except as such limitations may appear in the claims.

In each test, ten 4" x 4" hot zinc galvanized sheets are processed in accordance with the method described herein. The galvanized panels are first cleaned in a weak sodium carbonate solution by immersing the panels electrolytically until free of water breaks after the water rinse. Chromate coating solutions having the preferred concentrations indicated in Formulae 1 to 6 above were used in the tests. The specimens were immersed in the chromate solutions indicated in Table II for a period of about 15 seconds at a temperature of about 120° to 140° F. Following conversion film formation, the coated sheets were rinsed with water until substantially all of the free chromate ions were removed from the sheets. The resulting sheets were then treated with corrosion protection solutions corresponding to the Formulae A to L, inclusive, indicated hereinabove, by immersing the specimens in the corrosion protection solution for about 15 seconds at temperatures of 105° to 125° F. The specimens were then removed from the corrosion protection solutions and air-dried at temperatures of about 150° F.

The ten treated sheets in each test were then placed horizontally one on top of the other with a film of water between each sheet and pressed together with a three-pound weight. The stack was put into a humidity cabinet maintained at 100 percent relative humidity and a temperature of 115° to 120° F. for forty hours. At the end of this period, the stack of metal sheets was opened and inspected for white corrosion formation. The percent area of the sheets which was not corroded is given in the table as percent corrosion protection.

Two controls were set up. In the first control, the zinc plates were merely cleaned with the weak sodium carbonate solution. In the second control, the zinc plates were cleaned with the weak sodium carbonate solution and then treated with the chromate coating solutions indicated in Table II, cold water rinsed, warm water rinsed, and air-dried, at a temperature of 150° F.

The results of tests described are indicated in Table II:

Table II

TREATMENT OF GALVANIZED SHEET

Test No.	Chromate Solution Bath No.	Rust Inhibiting Solution Bath Designation	Results of Stack Test, Percent Corrosion Protection
Control—0		Untreated	0
Control—1	1		7
Control—2	2		8.3
Control—3	3		21.8
Control—4	4		15
Control—5	5		15
Control—6	6		24
7	3	A	40
8	5	B	85
9	6	C	85
10	3	D	89
11	3	E	83
12	4	F	75
13	6	G	88
14	6	H	87
15	6	I	78
16	1	J	65
17	6	K	98
18	2	L	50

As is obvious from the table, the percent corrosion protection for the tests in which the specimens were treated with the corrosion resistant solutions is dramatically greater than the percent corrosion protection of the specimens which were untreated, or which were merely treated with the chromate coating solution.

The invention is in its broader aspects is not limited to the specific mechanisms shown and described but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. In the method of chromate conversion coating zinc and zinc alloys, the improvement which comprises treating the chromate containing coating following formation thereof with a separate aqueous solution having a concentration of betwen about 0.0025 and 0.5 gram mole per liter of a member selected from the group consisting molybdate ions, tungstate ions, vanadate ions, phosphate ions and mixtures of the foregoing.

2. A method for producing an improved corrosion resistant coating on galvanized metal, which comprises treating the galvanized surface with a solution of soluble chromate ions to produce a chromate film on said surface, substantially removing free chromate ions from the treated surface, and treating the resulting surface with a rust inhibiting aqueous solution having a concentration of between about 0.0025 and 0.5 gram mole per liter of a member selected from the group consisting of molybdate ions, tungstate ions, vanadate ions, phosphate ions and mixtures of the foregoing.

3. The method of claim 2 wherein the galvanized metal is dried without rinsing following treatment with the rust inhibiting solution.

4. Improved corrosion resistant zinc and zinc alloy articles having surfaces coated with a chromate containing film having absorbed therein a member selected from the group consisting of water soluble molybdates, vanadates, tungstates, phosphates and mixtures of the foregoing.

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