United States Patent [19]

Miller

[11] **3,895,969**

[45] * **July 22, 1975**

[54] **COMPOSITION AND PROCESS FOR INHIBITING CORROSION OF NON-FERROUS METAL SURFACED ARTICLES AND PROVIDING SURFACE FOR SYNTHETIC RESIN COATING COMPOSITIONS**

[75] Inventor: **Russell C. Miller,** Chicago, Ill.

[73] Assignee: **J. M. Eltzroth and Associates Inc.,** Schaumberg, Ill.

[*] Notice: The portion of the term of this patent subsequent to Aug. 28, 1990, has been disclaimed.

[22] Filed: **June 13, 1973**

[21] Appl. No.: **369,479**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 137,682, April 26, 1971, Pat. No. 3,755,018.

[52] **U.S. Cl.** **148/6.2;** 148/6.21; 148/6.16

[51] **Int. Cl.** **C23f 7/26**

[58] **Field of Search** 148/6.2, 6.16, 6.21

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Primary Examiner—Ralph S. Kendall
Assistant Examiner—Charles R. Wolfe, Jr.
Attorney, Agent, or Firm—Johnston, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

Compositions and a process are provided for inhibiting corrosion of non-ferrous metal surfaces and for producing a surface to which synthetic resin coating compositions will adhere so that the resultant coatings have satisfactory impact and bending resistance, together with resistance to creeping corrosion between the metal and the dried resin coating.

17 Claims, No Drawings

COMPOSITION AND PROCESS FOR INHIBITING CORROSION OF NON-FERROUS METAL SURFACED ARTICLES AND PROVIDING SURFACE FOR SYNTHETIC RESIN COATING COMPOSITIONS

This application is a continuation-in-part of U.S. application Ser. No. 137,682 filed Apr. 26, 1971, now U.S. Pat. No. 3755018.

BACKGROUND

Non-ferrous metal surfaced articles, for example, aluminized and galvanized iron and steel, aluminum, aluminum-zinc alloys, magnesium, and magnesium-aluminum alloys may suffer surface deterioration by corrosion through contact with the atmosphere or moisture, or both. Chemical passivation treatments are widely used to inhibit or suppress such surface corrosion.

One of the passivating treatments employed for this purpose consists in treating the non-ferrous metal surface with an aqueous solution of chromic acid, or a mixture of chromic acid and dichromate, preferably with a part of the hexavalent chromium reduced to the trivalent state.

While chromic acid based passivating solutions have been widely adopted, they have been by no means effective in preventing corrosion under all conditions, particularly in high speed operations and especially where the treated surface is further coated with a synthetic resin coating composition which dries to form a synthetic resinous film. The manner in which the non-ferrous metal surface is pretreated may make the difference between satisfactory adherence of the resinous film to the substrate and non-adherence as well as satisfactory resistance of the coating or film to impact, bending, and creeping corrosion between the surface of the metal and the resinous film.

It would be desirable, therefore, to provide a process in which corrosion of the non-ferrous metal surface is inhibited and wherein the non-ferrous metal surface is receptive to a synthetic resinous coating composition so that the resultant coated products containing a dried film of the resin have satisfactory impact and bending qualities as well as resistance to creeping corrosion beneath the coating of synthetic resin. It would also be desirable to provide a process in which non-ferrous metal surfaced articles such as aluminized and galvanized sheets, coils, wires, tubes and rods, can be treated at high linear speeds of say 100 to 500 feet per minute or even higher so as to produce a treated article which is corrosion resistant and has a surface which will adhere to synthetic resin coating compositions, thereby producing coated articles having the physical and chemical characteristics previously mentioned.

OBJECTS

One of the objects of the present invention is to provide a new and improved process for making said non-ferrous metal surfaced articles, for example, galvanized iron and steel, with surfaces inhibited against corrosion and adapted to adhere to synthetic resin coating compositions, thereby producing articles coated with a synthetic resinous film having satisfactory impact and bending resistance and resistance to creeping corrosion between the metal and the resinous coating.

Another object of the invention is to provide a process of the type described in which a non-ferrous metal surfaced article is brought into contact at a high rate of speed, for example, at a linear speed of at least 100 feet per minute, with an aqueous solution of a composition which will inhibit corrosion of the surface of said article and at the same time enhance the receptivity of said surface for synthetic resin coating compositions.

A further object of the invention is to produce new and useful compositions for treating non-ferrous metal surfaces which are effective for the purposes previously indicated. Other objects will appear hereinafter.

BRIEF SUMMARY OF THE INVENTION

In accordance with the invention a non-ferrous surfaced article is treated with an aqueous chromate depositing solution containing hexavalent chromium and trivalent chromium, together with fluoboric acid and/or fluosilicic acid and/or hydrofluoric acid in sufficient amount to enhance adherency of the resultant surface to organic film forming polymers which dry to a water resistant coating, with the further proviso that said solution is free from hydrochloric acid, nitric acid, phosphoric acid and phosphates, in any appreciable amount other than that occurring by generation within the chromate depositing solution.

DETAILED DESCRIPTION OF THE INVENTION

The composition of the chromate depositing solution should be such that it will be effective when a non-ferrous metal surfaced article is brought into contact with it at a linear speed of at least 100 feet per minute and preferably 100 to 500 feet per minute at a pH of 1.5 to 2.5, to deposit a minimum amount of chromium of at least 0.2 mg/sq.ft. Thereafter, the resultant surface can be coated or painted with a composition comprising an organic film forming polymer which dries to a water resistant coating. If the coating composition containing the polymer is non-aqueous, the chromate coated non-ferrous metal surface should be rinsed with water and dried to an acceptable degree (depending on the particular organic resin) before the coating composition is applied. Preferably, the final rinse water should be on the acid pH side using a very small amount of the chemical treatment bath itself. The amount used should be minimized, using just enough to produce a pH value of 4.5 to 6.0 (electrometric) in said final rinse.

It is essential for the baked or primer-baked systems (polyvinyl chloride, acrylic, epoxy, melamine, polyester, etc.) to be "laid-down" on a neutral or slightly acidic substrate surface, free of chromic acid, chromate or water spots or stains, or any powdery or loose surface contamination.

Apparently, fluoboric acid and hydrofluoric acid both remove oxide films from the surface of the metal without replacing them with water soluble substances which cause inferior adherence of the synthetic resin coating compositions. Fluosilicic acid has a similar action. On the other hand, strong mineral acids such as nitric acid and hydrochloric acid in any appreciable amount in the chromate depositing solution tend to produce water soluble substances on the surface of the metal which leads to inferior adhesion of synthetic resin coating compositions. This does not occur so readily, however, where radicals such as the borate, fluoborate or fluoride radicals are present in the form

of a metallic salt dispersible in the solution. Boric acid can also be a component of the solution. In addition the solution can contain reducing agents such as, for example, sodium sulfite and/or sodium nitrite, which are added for the purpose of partially reducing hexavalent chromium to trivalent chromium. Phosphoric acid and phosphates are not used because they are reactive with non-ferrous metal surfaces to form phosphates which might interfere with chromate deposition on the surface.

In carrying out the process of the invention the temperature of the chromate depositing solution for use on a non-ferrous metal surfaced article is normally within the range of 80°F. to 210°F. and usually 100°F. to 110°F.

The time of contact between the chromate depositing solution and the non-ferrous metal surfaced article will normally be within the range of one second to sixty seconds. However, in operations where high speed coating is not required the time of contact may be much longer. In the latter case the pH of the solution can also be somewhat higher, but would be within the range of 0.8 to 5.0.

The chromate depositing solution can have a solids content within the range from 0.2 gram per liter to 75.0 grams per liter, the remainder being water, and the chemical composition should be essentially the following:

Ingredients	Grams per Liter
Hexavalent chromium (expressed as Cr)	0.05–50.0
Trivalent chromium (expressed as Cr)	0.03–5.0
Fluoride or bifluoride (expressed as F)	0.03–3.0
Borate (expressed as B_2O_3)	0.01–3.0
Fluoborate (expressed as BF_4)	0.03–10.0
Sulfate (expressed as SO_4)	0.01–3.0
Magnesium (expressed as Mg)	0.01–3.0
Aluminum (expressed as Al)	0.01–3.0
Iron (expressed as Fe)	0.01–0.05
Nickel (expressed as Ni)	0.01–0.05
Optional:	
Acetate (if increased wetting rate is desired)	0.01–0.1
Acid stable surfactant (for increased wetting)	0.01–0.1

In addition where the chromate depositing solution does not initially contain trivalent chromium, sodium nitrite, sodium sulfite, or other reducing agents can be added. The quantity of sodium nitrite and the quantity of sodium sulfite would usually be within the range of 0.05 to 0.2 grams per liter.

The invention will be further illustrated but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

EXAMPLE I

A chromate depositing solution was prepared having the following composition:

Ingredients	Grams per Liter
$Na_2Cr_2O_7.2H_2O$	6.75
CrO_3	1.36
NaF	1.36
H_3BO_3	1.16
$NaHSO_4$	0.89
Na_2SO_3	0.2
$NaNO_2$	0.2
$MgSO_4$	0.67
HBF_4 (50%)	2.73
$NiSO_4$	trace
$FeSO_4$	trace

This composition makes up to a 15 gram per liter chromate depositing solution.

Clean strips of hot-dip galvanized steel were immersed in the above composition at a temperature of 125° F. and agitated manually for a period of 3 to 5 seconds after the pH had been adjusted to a value of 2.0 by adding NaOH.

The resultant strips were then rinsed with cold water, rinsed with hot water, dried, and aged for 72 hours at room temperature after which they were painted with an acrylic resin paint. The resultant product showed excellent paint adherence with resistance to creeping corrosion beneath the paint film.

EXAMPLE II

A chromate depositing solution was prepared having the following composition:

Ingredients	Grams per Liter
$K_2Cr_2O_7$	5.55
CrO_3	2.22
NaF	1.15
H_3BO_3	2.00
$NaHSO_4$	0.90
Na_2SO_3	0.2
$NaNO_2$	0.2
$Al_2(SO_4)_3$	0.70
HBF_4 (50%)	2.50
$NiSO_4$	trace
$FeSO_4$	trace

This composition makes up to approximately a 15 gram per liter chromate depositing solution.

The pH was adjusted to 3.0 by adding NaOH and the temperature was raised to 150° F.

Clean strips of hot dip galvanized steel were immersed in the resultant solution and agitated manually for a period of 3 to 5 seconds.

The resultant strips were then rinsed with cold water, rinsed with hot water, dried, and aged for 72 hours at room temperature after which they were painted with an acrylic resin paint. The product showed excellent paint adherence with resistance to creeping corrosion between the paint film.

EXAMPLE III

A chromate depositing solution was prepared having the following composition:

Ingredients	Grams per Liter
$Na_2Cr_2O_7.2H_2O$	2.88
CrO_3	2.88
$NH_4F.HF$	1.00
H_3BO_3	0.80
$NaHSO_4$	0.66
Na_2SO_3	0.1
$NaNO_2$	0.1
$MgSO_4$	0.50
HBF_4 (50%)	1.66
$NiSO_4$	trace
$FeSO_4$	trace

This composition makes up to approximately a 10 gram per liter chromate depositing solution.

The pH value of the solution was raised to 3.5 by adding NaOH and the temperature was raised to 165° F.

Hot dip galvanized steel was immersed in this solution for 3 to 5 seconds and the resultant product thereafter rinsed, dried, aged and painted as described in Example I with very satisfactory results.

EXAMPLE IV

A chromate depositing solution was prepared having the following composition:

Ingredients	Grams per Liter
$Na_2Cr_2O_7.2H_2O$	1.66
CrO_3	0.33
NaF	0.33
H_3BO_3	0.33
$NaHSO_4$	0.10
Na_2SO_3	0.05
$NaNO_2$	0.05
$MgSO_4$	0.10
HBF_4 (50%)	0.66
$NiSO_4$	trace
$FeSO_4$	trace

This composition makes up to approximately a 3.5 gram per liter solution.

The pH value of the solution was adjusted to 2.0 by adding NaOH. The temperature of the bath was raised to 175° F. and clean aluminum strips were immersed therein for 5 to 10 seconds. The resultant aluminum strips were all cold rinsed and warm rinsed with water. Thereafter they were dried, painted with an acrylic resin paint, baked and aged.

EXAMPLE V

The procedure was the same as in Example I except that the pH of the solution was adjusted to 1.5 by adding HBF_4 and the temperature was raised to 150° F. Clean strips of mill-run aluminum were immersed in the solution with agitation for a period of 5–10 seconds. The resultant aluminum strips were then rinsed with cold water, followed by a warm water rinse and dried. They were thereafter painted with an acrylic resin paint, baked and aged.

EXAMPLE VI

The procedure was the same as in EXAMPLE II except that the pH of the solution was adjusted to 2.0 and the temperature raised to 165° F. Clean aluminum strips were then immersed in the bath and subsequently rinsed, dried and painted as described in Example V.

EXAMPLE VII

The procedure was the same as in Example III except that the pH of the solution was adjusted to 2.0, and clean aluminum strips were immersed in the solution at a temperature of 165° F. for a period of 5–10 seconds with agitation. The resultant strips were subsequently recovered, rinsed, dried and painted as described in Example VI.

EXAMPLE VIII

The chromate depositing solution was made up as described in Example IV. The pH value was adjusted to 1.5 by adding HBF_4. The temperature of the bath was adjusted to 150° F. and clean strips of hot dip galvanized steel were immersed therein and agitated manually for a period of 3 to 5 seconds. Thereafter the resultant strips were rinsed, dried, aged and painted as described in Example I.

The procedure described in Examples IV to VII were also carried out using clean strips of aluminum alloy 3003 and 2024.

The sheet panels produced as described in the examples were coated with primer coats and also with primer coats and finish coats. Various primer coats were used, for example, Lily Varnish Primer 465 and 11 PL Primer 12870. Various finish coats were used, for example, Acrylic JT 411- 3, Duracron Super 610 and Duracron Super 810. The resultant products were subjected to corrosion resistance tests (ASTM-B-117-64). They were also subjected to "pull-away" tests with pressure sensitive adhesive tape (3-M transparent No. 600). They were subjected to various bending tests including "pull-away" tests at the bend. In addition they were subjected to hardness tests and impact tests. The impact tests were made on a Gardner impact tester at pressures of 40–160 pounds per square inch, dependent upon: gauge thickness, temper (hardness); type of basic metal. The products satisfactorily passed these tests.

While acrylic resin coating compositions are especially useful, other organic film forming polymers can be employed, for example, polyvinyl chloride, epoxy resins, mixed epoxy-acrylic resins, polyester resins and polyurethane resins.

In the practice of the invention as will be seen from the foregoing examples, the chromate depositing solution is normally made up first as a solution containing hexavalent chromium compounds, namely, dichromates and chromic acid, together with other additives. In general, the chemical composition of the initial solutions is essentially as follows:

Ingredients	Grams per Liter
Dichromates (e.g., $Na_2C5_2O_7.2H_2O$ or $K_2Cr_2O_7$)	1.66–6.75
Chromic acid	0.33–2.88
Sodium or ammonium fluoride or bifuloride	0.33–1.36
Boric acid	0.33–2.00
Sodium acid sulfate	0.10–0.90
Aluminum sulfate	0–0.70
Magnesium sulfate	0–0.70
Fluorboric acid (50%)	0.66–2.75
Nickel sulfate ($NiSO_4$)	trace
Iron Sulfate ($FeSO_4$)	trace

To this solution the reducing agents are added to generate trivalent chromium in situ. As indicated by the examples, it is preferable to use sodium nitrite and sodium sulfite as reducing agents and the amount used is approximately 1% of each, based on the total weight of all of the materials contained in the concentrated aqueous solution. Other reducing agents can be employed such as, for example, zinc dust, cadmium dust, potassium sulfite, sodium bisulfite, sodium hydrosulfite, and sodium thiosulfate.

Nitrates can also be used in the foregoing compositions and their presence in low concentrations give better coatings and product excellent undercoated surfaces for application of organic coatings, but have the tendency to decrease impact resistance whenever its

percentage composition of the total solute is 2% or over (in these compositions aforementioned).

It will be understood that while the operating pH for high speed production is usually within the range of 1.5 to 2.5, the pH can vary within the broader range of 0.8 to 5.0 under other operating conditions depending upon time of contact of liquid and substrate, temperature, concentration, preliminary preparation, and method of application. It is important that the non-ferrous metal substrate be clean and that all oxide be removed therefrom before treatment with the chromate depositing solution. The time of treatment can vary from one second to five minutes and the solids concentration of the treating chromate depositing solution from 0.5 ounce per gallon to 12 ounces per gallon. The non-ferrous metal surface can be immersed in the chromate depositing solution with or without agitation or the chromate depositing solution can be applied by spraying or by a combination of spraying and immersion.

The presence of trivalent chromium is particularly important where the non-ferrous metal surface is composed of aluminum or aluminum alloy materials. In hot dip galvanized lines trivalent chromium is produced by the action of the acid on zinc and at least a minimum amount of reducing agent should always be present to insure the development of trivalent chromium.

When the chromate depositing solution is in continuous operation it is desirable to maintain certain hexavalent chromium to trivalent chromium ratios to produce chromate coatings which will have high quality standards regarding: physical tests and corrosion resistance tests previously mentioned. Examples:

For aluminum or aluminum alloys:

1. A weight ratio as Cr of 1:1 (hexavalent chromium to trivalent chromium) is desirable for a heavy, uniform chromate conversion coating weight of 30 to 75 micrograms per square inch; time: 5 to 10 seconds; temperature 120–180°F., hot rinse.
2. A weight ratio as Cr of 1:25 (hexavalent chromium to trivalent chromium) can produce a uniform light chromate conversion coating weight of 5 to 15 micrograms per square inch; time: 5 to 10 seconds; temperature 120°–180°F., hot rinse.

For zinc, zinc coated steel, zinc alloys, etc.;

1. A weight ratio as Cr of 1:1 (hexavalent chromium to trivalent chromium) is desirable for a heavy uniform chromate conversion coating weight of 20 to 50 micrograms per square inch; time 2–10 seconds, temperature 100°–150°F., cold rinse, then hot rinse.
2. A weight ratio as Cr of 1:25 (hexavalent chromium to trivalent chromium can produce a uniform light chromate conversion coating of 5 to 20 micrograms per square inch, time 2–10 seconds, temperature 100-150°F. cold rinse, hot rinse.

Now it has been tested, and proven, for both aluminum-type and zinc-type surfaces that weight ratios as Cr of both 1:50 and 1:100 (hexavalent chromium to trivalent chromium) at a pH of 4.4, at 150°F., 7.5 gr. total chromium, in 5 minutes can lay down a chromate conversion coating, but not of high standard of quality. If such metal substrate is clean, and on the neutral or acid side, the impact, bending, etc., will not be impaired or lessened in quality, the corrosion resistance will be drastically degraded.

Further, any attempts to control and adopt as satisfactory such ratios should be a function of: quality standard desired or necessary; economy; method of controlling: total solids (particularly reacted metal salts which decrease chemical activity, etc.) condition of water used in liquid level control, inorganic and organics contained, trivalent chromium content and build up; the concentration of functional and active ingredients, time of solution contact with metal substrate, method of applying such solution; temperature of the chromate depositing solution, pH of such solution—assuming, first, the substrate is chemically clean and free of: oxides, imbedded foreign particles (metallic scale, dross, etc.)

From this description, and from experience in actual production operations, it will be apparent that a careful study and testing of equipment and operational practices is essential for a successful operation in film-forming on a metallic substrate.

Another feature of the invention is based on the discovery that effective operation of the chromate depositing solution can be maintained by adding to the operating solution only hexavalent chromium (preferably chromic acid), fluoborate (preferably fluoboric acid), fluoride (preferably hydrofluoric acid), and certain of the other additives contained in the makeup solution, depending upon the chemistry of the water used for liquid level control, and water to make up for dragout and evaporation. The weight ratio of CrO_3 to HBF_4 is usually within the range of 3:1 to 1:3. The weight ratio of HBF_4 to H_2F_2 is usually within the range of 10:1 to 1:10. For example. a replenishing composition can be made by dissolving 400 parts of chromic acid and 715 parts of 40 to 50% fluoboric acid and 70 parts of (48%) hydrofluoric acid and water to make 3000 parts by weight. This composition is added to the chromate depositing solution in sufficient proportions to give a pH value within the range of 0.8 to 5, preferably 2.0 to 2.5 for galvanized steel; 1.5 to 2.2 for aluminum and to maintain the desired total chromium content and the hexavalent to trivalent chromium ratio. Again, it is mandatory that the linear speed of metal passing through treatment, method of application, chemistry of cleaning, rinsing and conversion coating material, be analyzed and adjustments made.

Further, aluminum in general will furnish the other metallic constituents, e.g., zinc, iron, magnesium, nickel, that seemingly act as surface catalysts. Such metals are eroded and dissolved into the operating bath, and, too, must be controlled by some method. Zinc coated steel, zinc alloys may or may not replenish the "starting" bath due to their presence or absence from the substrate being chemically reacted. In such case, it may be advisable to incorporate small amounts in the replenishing solution, generally in the weight ratio of 0.05 to 1% of total weight of solute dispersed in the water.

Again, too much cannot be demanded in the preparation of the metal before the conversion coating treatment is applied. When all the desired "steps" in this operation are performed, the treated metal will successfully undergo hot water rinsing, 150° to 170°F., without appreciable loss of "coating" and moreover will successfully resist "wipe off" action by handerchief, tissue and dry fingers or hand. This is the desired "hard, uniform coating".

When hard water containing precipitatable salts of calcium, magnesium, iron and/or aluminum is used in the chromate depositing solution, it is sometimes desirable to add sufficient sulfuric acid or other mineral or organic acid or sequestrant either to remove such salts, sequester them or otherwise nullify their adverse effect. This addition is usually added in the replenisher solution. The amount will vary depending on the hardness of the water and is usually within the range of 0.1 to 1% by weight of the replenisher composition.

The amount of chromate deposited, as Cr, is usually at least 10 micrograms per square inch, preferably 45–70 micrograms per square inch, but in some cases 100 micrograms per square inch, or higher. The amount of chromate which it is desirable to deposit can be much greater on one type of surface than another. Thus, ten times as much chromate might be deposited on an aluminum surface as on a hot dip galvanized surface. Testing procedures are recommended as excessive chromate coatings may not be good practice in certain paint applications, e.g., high speed or high temperature operations.

An important feature of the invention resides in the fact that the total chromate coating weight, which is preferably 10 to 25 mg/sq.ft., contains 1.5 to 3 times as much Cr as a chromate conversion coating of the same weight deposited by a conventional method using ferricyanide. Coatings deposited by the ferricyanide method usually contain 20–25% by weight Cr while coatings deposited by the present process contain 30–60% by weight Cr. Hence, there is more Cr per unit of coating weight. The net result is a superior coating. Thus, coatings produced by the present process will hold paint for 1000 hours of salt spray (ASTM test B117-64).

In general, the weight ratio of trivalent chromium as Cr to hexavalent chromium as Cr in the chromate depositing solution should be at least 1:100 but no more than 200:1, preferably 1:1 to 2:1 and not more than 5:1 for the optimum operating conditions.

Non-ferrous metals such as zinc and aluminum contain substances such as magnesium, iron and/or nickel which can be introduced into the chromate depositing solutions by erosion during the time that aluminum and/or zinc surfaced articles are in the solution even though the time of treatment is usually only 1 to 30 seconds. This may account for the fact that such substances may not have to be replenished in the chromate depositing solution.

An important feature of the invention resides in the fact that both aluminum and zinc surfaced articles can be processed out of the same tank.

The replenisher solution is an important aspect of the invention in that once the original bath is put into operation, it can be kept going continuously for a long period of time merely by adding a replenisher composition consisting of a few ingredients, viz., chromic acid (CrO_3) and a substance from the group consisting of fluoboric acid, hydrofluoric acid, water and mixtures thereof. Although it is desirable in most cases to use a replenisher solution containing all of said ingredients, under some conditions only the chromic acid and one other acidic ingredient of the type described is necessary. For example, a suitable replenisher might contain 500 parts by weight of chromic acid and 740 parts by weight of fluoboric acid or 400 parts by weight of chromic acid and 715 parts by weight of fluoboric acid. The replenisher ingredients can be added to the bath separately or simultaneously but are preferably pre-mixed with water. The amount of water added will depend to some extent upon operating conditions including evaporation and drag-out.

While the invention has been described particularly with respect to zinc and aluminum surfaces, especially aluminum, aluminum alloys and aluminized and galvanized iron and steel, it is also applicable to other non-ferrous metal surfaces including magnesium, magnesium-aluminum alloys, copper and copper alloys, and copper-clad phenolic sheets.

The invention makes it possible to provide non-ferrous metal surfaced articles which are inhibited against corrosion and adapted to adhere to synthetic resin coating compositions thereby producing articles coated with a synthetic resinous film having satisfactory impact and bending resistance and resistance to creeping corrosion between the metal and the resinous coating.

The invention is hereby claimed as follows:

1. A process for treating non-ferrous metal surfaced articles to improve corrosion resistance and receptivity to synthetic resin coatings which comprises bringing said articles into contact with a chromate depositing solution containing as essential components hexavalent chromium and trivalent chromium together with an acid from the group consisting of fluoboric acid, fluosilicic acid, hydrofluoric acid and mixtures thereof in sufficient amount to enhance adherency of the resultant surface to organic film forming polymers which dry to a water resistant coating, said chromate depositing solution having a solids content within the range from 0.2 gram per liter to 75.0 grams per liter, the remainder being water, and consisting essentially of the following:

Ingredients	Grams per Liter
Hexavalent chromium (expressed as Cr)	0.05–50.0
Trivalent chromium (expressed as Cr)	0.03–5.0
Fluoride or bifluoride (expressed as F)	0.03–3.0
Borate (expressed as B_2O_3)	0.01–3.0
Fluoborate (expressed as BF_4)	0.03–10.0
Sulfate (expressed as SO_4)	0.01–3.0
Magnesium (expressed as Mg)	0.01–3.0
Aluminum (expressed as Al)	0.01–3.0
Iron (expressed as Fe)	0.01–0.05
Nickel (expressed as Ni)	0.01–0.05
Acetate (as acetate radical)	0.0–0.1

with the further proviso that the weight ratio of trivalent chromium as Cr to hexavalent chromium as Cr is at least 1:100 but no more than 200:1, and the pH of said solution is between 0.8 and 5.0.

2. A process as claimed in claim **1** in which said non-ferrous metal surfaced articles are in the form of sheets, coils, wires, tubes or rods which are brought into contact with said chromate depositing solution at a linear speed of at least 100 feet per minute and the pH of said solution is within the range of 1.5 to 2.5, the said solution being effective to deposit at least 0.2 mg/sq.ft. of chromate as chromium.

3. A process as claimed in claim **1** in which said non-ferrous metal surfaced articles are from the group consisting of zinc, aluminum, magnesium, aluminized and galvanized iron and steel, zinc-aluminum alloys, magnesium-aluminum alloys, copper and copper alloys.

4. A process as claimed in claim 1 in which the weight ratio of trivalent chromium as Cr to hexavalent chromium as Cr does not exceed 50:1.

5. A process as claimed in claim 1 in which the resultant non-ferrous metal surfaced article is coated with a coating containing an organic film forming polymer which dries to a water resistant coating.

6. A process as claimed in claim 4 in which said polymer is an arcylic resin.

7. A process as claimed in claim 1 in which said chromate depositing composition consists essentially of an aqueous solution of the following:

Ingredients	Grams per Liter
Dichromates	1.66–6.75
Chromic acid	0.33–2.88
Sodium or ammonium fluoride or bifluoride	0.33–1.36
Boric acid	0.33–2.00
Sodium acid sulfate	0.10–0.90
Aluminum sulfate	0–0.70
Magnesium sulfate	0–0.70
Fluoboric acid (50%)	0.66–2.75
Nickel sulfate ($NiSO_4$)	trace
Iron sulfate ($FeSO_4$)	trace

and a sufficient amount of a reducing agent to convert a part of the hexavalent chromium to trivalent chromium so that the ratio of trivalent chromium as Cr to hexavalent chromium as Cr is no more than 5:1 but at least 1:100.

8. A process as claimed in claim 7 in which said reducing agent consists essentially of sodium sulfite and sodium nitrite each in proportions of 0.05 to 0.2 gram per liter.

9. A process as claimed in claim 1 in which the treatment of metal surfaced articles is carried out for a period of from 1 to 30 seconds.

10. A process as claimed in claim 1 in which the weight ratio of trivalent chromium as Cr to hexavalent chromium as Cr in the chromate depositing solution is within the range of approximately 1:1 to 2:1.

11. A process as claimed in claim 1 in which said process is carried out continuously and said solution is replenished periodically by adding chromic acid and a substance from the group consisting of fluoboric acid, hydrofluoric acid, water and mixtures thereof.

12. A process as claimed in claim 1 in which said process is carried out continuously and said solution is replenished periodically by adding chromic acid, and a substance from the group consisting of fluoboric acid, hydrofluoric acid, water and mixtures thereof, the weight ratio of chromic acid to fluoboric acid added being within the range of 3:1 to 1:3, and the ratio of fluoboric acid to hydrofluoric acid being in the range of 10:1 to 1:10.

13. A process as claimed in claim 1 wherein said chromate depositing solution contains hard water including precipitatable salts and a sufficeint amount of an additive to nullify the adverse effect of such salts.

14. A process as claimed in claim 13 in which said additive is sulfuric acid.

15. A process as claimed in claim 1 in which the applied chromate conversion coating contains 30 to 60% by weight Cr.

16. A non-ferrous metal surfaced article resulting from the process of claim 1.

17. An article as claimed in claim 16 containing a paint coating, said article being capable of withstanding 1000 hours of salt spray under ASTM B117-64 test conditions.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,895,969

DATED : July 22, 1975

INVENTOR(S) : RUSSELL C. MILLER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

COLUMN 6, line 41, in the table, "$Na_2C5_2O_7.2H_2O$" should read: --$Na_2Cr_2O_7.2H_2O$--.

Column 12, line 22, "sufficeint" should read --sufficient--.

Signed and Sealed this

twentieth Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks