

[54] **METHOD OF IMPROVING THE CORROSION RESISTANCE OF ZINC COATED FERROUS METAL SUBSTRATES AND THE CORROSION RESISTANT SUBSTRATES THUS PRODUCED**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 818,096, April 21, 1969, abandoned.

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[51] **Int. Cl.**..... **B21b**

[58] **Field of Search**..... 204/41, 28, 38 B, 29, 38 R, 204/36, 38 E, 183.5, 194, 195, 196.5

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[57]

ABSTRACT

The corrosion resistance of zinc coated ferrous metal substrates is increased markedly by electroplating at least a portion of the zinc surface thereof with a coating of metallic chromium having a thickness of about 0.1–0.5 microinch, and thereafter electrochemically treating the resultant metallic chromium coated substrate as a cathode in an aqueous electrolyte containing a water soluble hexavalent chromium compound to deposit a metallic chromium and chromium oxide containing film thereon. In one preferred variant, the zinc surface is brightened prior to the electrodeposition of the metallic chromium coating to thereby increase the brightness of the final product and to render it more pleasing in appearance. The chromium plated and electrochemically treated zinc coated ferrous metal substrate is an excellent base for protective organic coatings, and protective organic coatings may be applied thereto to further increase the corrosion resistance and/or for decorative purposes. The method of the invention is easily adapted to high speed electroplating lines operating at strip speeds of at least 500 feet per minute and costs may be reduced substantially. The invention also provides the corrosion resistant substrates prepared by the method of the invention.

29 Claims, No Drawings

METHOD OF IMPROVING THE CORROSION RESISTANCE OF ZINC COATED FERROUS METAL SUBSTRATES AND THE CORROSION RESISTANT SUBSTRATES THUS PRODUCED

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 818,096, filed Apr. 21, 1969, now abandoned, for METHOD OF IMPROVING THE CORROSION RESISTANCE OF SUBSTRATES HAVING ZINC SURFACES AND THE CORROSION RESISTANT SUBSTRATES THUS PRODUCED.

BACKGROUND OF THE INVENTION

A bright untreated zinc coated ferrous metal article exposed to the atmosphere soon develops a surface film composed of corrosion products which are produced by the reaction therewith of atmospheric substances such as carbon dioxide, oxygen and/or moisture. The article may be, for example, hot dipped galvanized steel, electrogalvanized steel, or other forms of zinc coated ferrous metal articles. As the corrosion proceeds, in some instances the layer of corrosion products is dark or olive in color, and in still other instances a white deposit of corrosion products is produced. The corrosion products render the appearance of the article less pleasing to the eye.

The term "white rust" is used to refer to a specific form of corrosion. It is a relatively thick white deposit of corrosion products which is composed largely of zinc hydroxide and/or basic zinc carbonate, and it forms on unprotected zinc surfaced articles exposed to the air and an excessive amount of moisture. White rust forms very rapidly when moisture is confined against a zinc surface by an overlying member, and it is especially severe where bright untreated zinc coated sheets and other shapes are arranged during storage or shipment so that water or moisture can accumulate between adjacent surfaces. The initial pleasing appearance of galvanized steel and other zinc surfaces is destroyed by white rust.

Zinc surfaced articles are subject to still other types of corrosion. For example, solid zinc articles are subject to surface pitting when exposed to corrosive environments. Zinc coated articles having corrodible basis metals, such as galvanized steel, are subject to "red rust" formation and pitting on surface areas where sacrificial protection has been lost due to conversion of the metallic zinc coating to corrosion products. Thus, in addition to producing a less pleasing appearance, the corrosion also damages the underlying substrate surface.

The prior art has long sought a suitable process for treating zinc surfaced articles to effectively inhibit the formation of white rust and the other types of corrosion referred to above. In general, most prior art processes involve the application of a relatively thick protective coating such as oil, wax, varnish or paint, or a chemical treatment in which a thin chromate coating or other thin protective coating or film is deposited which is integral with the zinc surface. These prior art processes have not been entirely satisfactory due to, among other reasons, their being ineffective in inhibiting the formation of undesirable corrosion products for long periods of time, too expensive, or too time consuming to apply in high speed continuous lines. In some instances, the

protective coatings thus produced has to be removed prior to use of the articles or the coating substances discolored or destroyed the initial bright zinc finish.

The widely used prior art chromate chemical treatments have several disadvantages. For example, they require careful control of operating conditions such as concentrations of ingredients, bath temperature, and time of treatment as there is a pronounced tendency towards the formation of undesirable colored chromate films. In most instances, it is not possible to apply a sufficiently thick chromate film to provide optimum protection without discoloration. Nevertheless, chromate chemical treatments are used extensively due to the lack of a suitable alternative process.

Another prior art process for inhibiting the undesirable corrosion of zinc surfaced articles involves the electrodeposition thereon of relatively heavy metallic chromium coatings. The electrodeposition of metallic chromium coatings one microinch or more in thickness also has not proved to be entirely satisfactory. For instance, electroplating metallic chromium is very inefficient in current usage and it is not possible to achieve an efficiency of more than about 20-25 percent. Heavy electrical equipment must be used to provide the large amount of current that is required for electroplating thick metallic chromium coatings and expensive cooling apparatus is necessary to maintain a suitable bath temperature. Even when employing heavy electrical equipment and extensive cooling capacity, it is possible to achieve only relatively slow line speeds as otherwise the current and cooling capacity requirements are too great. Thus, the protection of zinc surfaces by application of metallic chromium films in high speed electroplating lines has not met with commercial success prior to the present invention due to the deficiencies of the process and the limitations of the equipment presently available.

When metallic chromium coatings having thicknesses greater than one microinch are electrodeposited on zinc substrates by the prior art processes, the heavy coatings thus produced tend to be highly stressed and to become microcracked on the flat surface, and fail to protect the underlying zinc at sites of the cracks. Additionally, the heavy metallic chromium coatings are milky or cloudy and the bright appearance of the initial zinc surface is lost. Thus, the heavier metallic chromium coatings of the prior art also were not entirely satisfactory in appearance and in the protection afforded the underlying zinc surface.

Prior to the present invention an entirely satisfactory process was not available for protecting zinc surfaced articles by the electrodeposition thereon of metallic chromium coatings whereby the prior art operating problems are overcome during the electrodeposition step, and whereby satisfactory protection against corrosion is obtained without detracting from the appearance of the initially bright zinc surface.

It is an object of the present invention to provide a novel method of improving the corrosion resistance of zinc coated ferrous metal substrates which overcomes the above mentioned disadvantages of the prior art and which may be easily adapted to high speed electroplating lines.

It is a further object to provide a novel method of improving the corrosion resistance of zinc coated ferrous metal substrates wherein the zinc surface thereof is

electroplated with a thin coating of metallic chromium and then electrochemically treated.

It is still a further object to provide a novel method of increasing the brightness of the electrodeposited metallic chromium coatings of the present invention.

It is still a further object to apply a protective and/or decorative organic coating on the chromium plated and electrochemically treated product produced by the method of the invention.

It is still a further object to provide the products produced in accordance with the method of the invention.

Still other objects of the invention and the advantages thereof will be apparent to those skilled in the art upon reference to the following detailed description and the examples.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED VARIANTS THEREOF

In accordance with one important variant of the present invention, the corrosion resistance of zinc coated ferrous metal substrates is improved by electroplating on the zinc surface thereof a thin coating of metallic chromium, and thereafter electrochemically treating the metallic chromium electroplated substrate as a cathode in an aqueous electrolyte containing a hexavalent chromium compound to deposit thereon a film or coating containing a mixture of metallic chromium and chromium oxide.

Any suitable prior art chromium plating bath may be used for electrodepositing the flash metallic chromium coating. As is well understood in the chromium plating art, chromium plating baths usually contain chromic acid or other suitable water soluble hexavalent chromium compounds and a catalyst therefor such as sulfate ion or admixtures thereof with fluoride ion and/or silicofluoride ion. The chromium compound may be added to the plating bath as chromic acid or as an alkali metal chromate such as sodium chromate, sodium dichromate, potassium chromate or potassium dichromate. The catalyst may be added to the plating bath as the free acid or as a water soluble salt thereof providing the desired ion, such as sulfuric acid or water soluble alkali metal sulfates, fluorides and/or silicofluorides.

The preferred chromium compound is chromic acid in many instances. The mole ratio of chromic acid to the catalyst is usually about 100:1, but other ratios conventional in the art may be employed such as about 50:1-200:1. The chromium acid content of the bath may range from about 100 to 400 grams per liter, and is preferably about 150-300 grams per liter. The current density may be the same as is used in prior art chromium plating such as about 300-2000 amperes per square foot and is preferably about 500-1000 amperes per square foot. The bath temperature also may be in accordance with the prior art, and may be about 90°-150°F. and is preferably about 100°-130°F.

Insoluble anodes are usually used. A composite steel anode prepared by applying a lead coating to the side facing the substrate to be plated and polyvinyl chloride or other inert insulating substance to the opposite side to reduce stray currents is often preferred. The substrate surface to be electroplated with the flash chromium coating is preferably free of contaminants such as oil, dirt and other substances. When contaminants are present, the substrate surface may be scrubbed free of the same in an aqueous bath, but preferably an

acidic or alkaline bath which will attack the zinc surface to an undesirable extent is not used. Examples of still other chromium plating baths and operating conditions are disclosed in U.S. Pat. Nos. 1,942,469, 2,177,392, and 2,415,724, and in the text *Modern Electroplating* by Frederick A. Lowenheim, 2nd Edition, John Wiley and Sons, Inc., New York, New York (1963), the teachings of which are incorporated herein by reference. Chapter 5, pages 80-140, and the references cited on pages 128-140 of *Modern Electroplating* are especially pertinent.

Regardless of the specific prior art chromium plating bath and operating conditions which are employed, the thin coating of metallic chromium that is electrodeposited on the zinc surface has a thickness of about 0.1-0.5 microinch. Unsatisfactory results are usually obtained due to insufficient metallic chromium in the coating at thicknesses less than about 0.1 microinch. Metallic chromium coatings having thicknesses above 0.5 microinch do not result in an appreciable increase in the degree of corrosion protection that is produced in the synergistic combination, and sometimes tend to be cloudy or milky which detracts from the appearance. Also, heavy metallic chromium coatings tend to be highly stressed and are often microcracked on the surface, and the substrate surface is subject to corrosion at the sites of the cracks. Additionally, coatings above 0.5 microinch are expensive to apply and markedly increase the cost of producing the composite coatings. Metallic chromium coatings having a thickness of 0.2-0.5 microinch and preferably 0.3-0.4 microinch are very satisfactory. Preferred results are obtained in many instances with very thin metallic chromium coatings having a thickness of about 0.1-0.3 microinch.

The metallic chromium coated substrate is electrochemically treated as a cathode in an aqueous electrolyte containing a water soluble hexavalent chromium compound to deposit thereon a film or coating containing a combination or mixture of metallic chromium and chromium oxide. The bath that is used for the electrochemical treatment may contain the same ingredients that were employed in the metallic chromium plating bath but in much lower concentrations. For example, the metallic chromium plating bath may be diluted with about 3-7 volumes and preferably about 5 volumes of water to prepare a satisfactory electrochemical treatment bath. The electrochemical treatment bath may contain a water soluble hexavalent chromium compound such as chromic acid, alkali metal chromates including sodium and potassium chromate, alkali metal dichromates including sodium and potassium dichromate, and other hexavalent water soluble chromium compounds, and a water soluble catalyst such as the sulfate compounds and admixtures thereof with fluoride and silicofluoride compounds as previously described for the plating bath. Chromic acid is usually preferred as the hexavalent chromium compound and satisfactory electrochemical treatment baths may contain about 20-50 grams and preferably about 35 grams per liter of chromic acid, or about 1-2 ounces and preferably about 1.5 ounces per gallon of potassium dichromate. Sulfate ion may be present in an amount of about 0.05-0.2 gram per liter and preferably about 0.10 gram per liter, and silicofluoride ion in an amount of about 0.1-1.0 gram per liter and preferably about 0.3-0.5 gram per liter, and for still better results about 0.4 gram per liter.

The electrochemical treatment may be at a temperature of about 90°–150°F. and is preferably at about 100°–130°F. The metallic chromium coated substrate is treated cathodically under current conditions providing about 25–400 amperes per square foot and preferably about 100–300 amperes per square foot over a period of time sufficient to result in treatment with about 25–500 coulombs per square foot of current, and preferably about 75–125 coulombs per square foot. The optimum treatment is often at a bath temperature of 100°F. and at a rate of about 200–300 amperes per square foot for a sufficient period of time to provide approximately 100 coulombs per square foot of current, e.g., about 0.3–0.5 second.

As a general rule, the film deposited during the electrochemical treatment should contain about 0.6–5 mg per square foot of total chromium present in the metallic chromium and in the chromium oxide. The cathodic electrochemical treatment results in the deposition of a mixture of chromium oxide and metallic chromium, and the total chromium is the amount present in both of these substances. The chromium in the chromium oxide portion of the film seems to be largely in the plus 3 valence state, and it is thought to be hydrated Cr_2O_3 in many instances. Preferably, the film should contain about 1–3 mg per square foot of total chromium in the metallic chromium and chromium oxide contents of the film, and for still better results about 0.8–1.5 mgs of total chromium per square foot.

The electrochemically treated metallic chromium coating of the invention is tightly adherent and it is an excellent base for organic protective coatings. Prior art organic coatings of the types usually applied to galvanized steel, tinplate or blackplate may be applied directly to the flash chromium electroplated surface or to the electrochemically treated surface. Examples of suitable organic coatings include phenolic, modified phenolic, epoxy, modified epoxy, polyester, modified polyester, vinyl resin, Teflon, and drying oil-based paints, varnishes, lacquers and enamels. Silicone modified polyester enamels give exceptionally good results in many instances. The organic coatings may be applied to the electrochemically treated metallic chromium plated substrate by prior art techniques such as spraying, brushing, roller coating and electrostatic deposition.

The present invention is especially useful in producing synergistic composite coatings or blackplate strip or sheet of the usual gauges employed in the manufacture of galvanized steel and tinplate. For instance, blackplate having a weight of 55–90 pounds per base box may be used in practicing the present invention, but heavier or lighter weights may be used.

The ferrous metal substrate to be provided with the composite coating need not be given a special pretreatment prior to applying the initial coating of zinc provided the surface is free of contaminants. However, in most instances contaminants are present and the ferrous metal substrate should be subjected to the usual prior art pretreatment or cleaning steps used in the manufacture of galvanized steel. The clean ferrous metal substrate may be coated with zinc by hot dipping, electrogalvanizing, vapor deposition under vacuum, electrostatic or electrophoretic deposition of powdered zinc followed by roll compacting or fusion, or by other suitable known processes. The zinc coated substrate is then passed through a prior art chromium plating bath

and about 0.1–0.5 microinch of metallic chromium is electrodeposited over the zinc coating. Thereafter, if desired the substrate with the composite zinc-chromium coating may be electrochemically treated to deposit a film containing metallic chromium and chromium oxide. The final product may be washed, dried, oiled, and coiled, or it may be given an organic coating.

The present invention may be combined with prior art electrogalvanizing lines or with hot dip galvanizing lines. Thus, the ability to electrodeposit the thin chromium coatings described herein in a high speed line is of importance in commercial operations as the composite coating may be produced by adding the chromium electrodeposition step of the invention to existing high speed electrogalvanizing lines or hot dip galvanizing lines.

The composite coatings are not discolored and the chromium plates surface remains bright in appearance. The brightness of the composite coating may be further improved by subjecting the zinc surfaced substrate to a brushing or rolling step, or to other suitable methods designed to provide a bright fresh zinc surface, prior to electrodepositing the metallic chromium coating. The rolling step need not be drastic, and it may be a skin pass wherein the substrate is reduced about 1–2 percent in thickness to thereby produce a fresh, bright, smooth zinc surface for receiving the flash coating of metallic chromium. The brushing or prerolling step is especially important in instances where it is desired to apply a clear organic coating, or for other purposes where maximum brightness of the final product is desired.

The composite coating of the present invention exceeds the combined individual corrosion resistances of the initial zinc coating, the metallic chromium coating, and the coating produced by the electrochemical treatment, by several fold when measured by standard ASTM corrosion tests, such as the salt fog test and/or the water immersion test. As a general rule the composite coating will increase the corrosion resistance of the initial zinc coating by about five fold or more. Surprisingly, the electrochemically treated 0.1–0.5 microinch metallic chromium coatings described herein are as effective as metallic chromium coatings 10 to 50 times as thick which have not received the electrochemical treatment of the invention.

The term "zinc coated ferrous metal substrates", as used in the specification and claims, is intended to embrace ferrous metal articles in general having a surface subject to corrosion which is composed of zinc or predominantly of zinc. Examples of zinc coated ferrous metal substrates include ferrous metal material or articles provided with a decorative or protective coating of zinc or alloys containing predominantly zinc, and especially hot dip galvanized steel and electrogalvanized steel. In instances where zinc alloys are used, the alloy should contain more than 50 percent by weight of zinc and the remainder prior art alloying elements for zinc and incidental impurities. For instance, small amounts of aluminum and other metals are often added to the molten zinc bath in hot dip galvanizing lines.

The zinc coatings that are applied to ferrous metal and other substrates may be in accordance with prior art practice. For example, the zinc coating may have a thickness comparable to zinc coatings produced in the manufacture of galvanized steel by the electrolytic and

hot dip methods. Electrogalvanized steel usually has a zinc coating weight of about 0.05–0.5 ounce per square foot, and hot dip galvanized steel usually has a zinc coating weight of about 0.25–1.5 ounce per square foot. These coating weights are for purposes of illustration only as heavier or lighter zinc coatings may be used, but better results are usually obtained when the zinc coating is at least 80 microinches in thickness. The corrosion resistance of electrogalvanized steel having a zinc coating weight of only 0.05–0.1 ounce per square foot per side is increased remarkably by the method of the invention.

EXAMPLE I

A coil of electrogalvanized blackplate strip 0.02 inch in thickness and having 0.1 ounce per square foot of electrolytically deposited zinc thereon (80 microinches) was used in this example. The electrogalvanized strip was produced by a prior art process and after plating and withdrawing from the zinc plating bath, it was washed in water, dried and coiled without oiling. The freshly plated zinc surface was free of contaminants such as dirt, oil and grease, and it was not necessary to scrub the surface prior to electroplating with a flash coating of chromium.

The above electrogalvanized blackplate strip is electroplated with 0.3 microinch of metallic chromium using a chromium plating bath containing 150 grams of chromic acid, sodium sulfate in an amount to provide 1–1.1 gram per liter of sulfate ion, and sodium silicofluoride in an amount to provide 1.8–2.0 grams per liter of silicofluoride ion. The temperature of the electrolyte is 120°F., and the current density is 800–1000 amperes per square foot. The electrogalvanized strip is passed through the plater at a speed of 400 feet per minute. The electrogalvanized strip is not pretreated prior to passing into the chromium plater with the exception of wetting it in water.

The blackplate strip withdrawn from the plater has a composite coating thereon which consists of 80 microinches of electroplated zinc in contact with the steel basis metal, and 0.3 microinch of metallic chromium over the zinc coating. The strip is washed to remove the electrolyte, and then dried and coiled without oiling. Samples of the blackplate strip having the composite coating thereon are tested by the standard ASTM salt fog corrosion test (ASTM method B-117) until 5 percent red rust is apparent. Samples of the electrogalvanized blackplate strip prior to the electrodeposition of the chromium coating and blackplate strip electroplated with 0.3 microinch of metallic chromium by a prior art process are tested by the same salt fog test procedure to provide comparative data. The results thus obtained are as follows:

Zinc, oz./sq. ft.	Cr ^o microinches	Hours to 5% red rust
None	0.3 microinch	2 hrs.
0.1 oz./sq. ft.	None	54 hrs.
0.1 oz./sq. ft.	0.3 microinch	312 hrs.

The above data show that the blackplate strip with 0.3 microinch of metallic chromium flash plated thereon has a salt fog test life of only 2 hours to 5% red rust, and blackplate strip with 0.1 ounce of zinc per square foot has a salt fog test life of 54 hours to 5 percent red rust. The life of the zinc coating alone plus the life of the chromium plating alone to 5 percent red rust

is a total of only 56 hours; however, when the two coatings are combined, the composite coating has a salt fog test life to 5 percent red rust of 312 hours, or approximately five times as long. Thus, there is a marked synergistic effect.

The adhesion of the metallic chromium was excellent as shown by deformation tests. Also, organic protective coatings could be applied without further treatment.

EXAMPLE II

The procedure of Example I is followed with the exception of subjecting the electrogalvanized blackplate strip to a skin rolling step prior to passing it into the chromium plater. The reduction in thickness is 1–2 percent, and the rolled electrogalvanized strip is much brighter than the original matte finish. The rolled electrogalvanized strip having a fresh, bright, zinc surface thereon is electroplated with chromium as in Example I, and all subsequent steps are the same as in Example I.

The composite coating is much brighter than that of Example I, and there is no substantial difference in the two products with respect to corrosion resistance. The greatly improved surface brightness is of advantage in instances where appearance and maximum brilliance are of importance.

EXAMPLE III

The procedure of this example is the same as that of Example I with the exception of using an electrogalvanized blackplate strip having 0.2 ounce of zinc per square foot electroplated thereon.

The salt fog test life of the product of this example is 600 hours to 5 percent red rust, or approximately twice that of Example I, and the initial electrogalvanized blackplate strip has a corrosion life of 112 hours. The flash chromium coatings of the present invention also greatly increase the corrosion life of heavier zinc coatings, and the increase is of substantially the same magnitude as that for the lighter zinc coatings i.e., approximately five fold.

EXAMPLE IV

The metallic chromium plated electrogalvanized blackplate strips produced in accordance with Example I and Example III are given an electrochemical treatment in this example in which a film containing a mixture of metallic chromium and chromium oxide is deposited thereon.

The metallic chromium plated strip produced in Examples I and III is passed into an electrochemical treating vessel filled with an electrolyte containing 40 grams per liter of chromic acid, about 0.1 gram per liter of sulfate ion, and about 0.4 gram per liter of silicofluoride ion. The electrolyte temperature is maintained at 120°F. and the strip surface is treated cathodically at 250 amperes per square foot for a period of time to provide a surface treatment of 100 coulombs per square foot, i.e., about 0.4 second. This treatment deposits a film on the strip which contains 1–2 mgs per square foot of total chromium.

The strip is withdrawn from the electrochemical treating vessel, rinsed with water, dried, and coiled. Samples of the strip are tested for corrosion resistance following the procedure of Example I. The test results indicate that the corrosion resistance of the product produced in accordance with Example I is increased by

about 50–60 hours to 5 percent red rust formation, and the product produced in accordance with Example III is increased in corrosion resistance by approximately 125–135 hours to 5 percent red rust formation. Thus, the electrochemical treatment further increases the corrosion resistance of the composite coating.

EXAMPLE V

Hot dipped galvanized steel strip coated with 1.25 ounces of zinc per square foot is electroplated with metallic chromium in a series of runs following the general chromium plating procedure of Example I. The metallic chromium coating weights varied between 0.1 microinch and 5.0 microinches. Thereafter a portion of each of the metallic chromium plated products thus produced is electrochemically treated to deposit thereon a film containing a mixture of metallic chromium and chromium oxide following the general procedure of Example IV.

Samples of each of the metallic chromium plated products (no electrochemical treatment) and of each of the electrochemically treated metallic chromium plated products are subjected to the standard water immersion test for a period of 100 hours and then observed for white rust formation. The results thus obtained are recorded below in Table 1.

Table 1

Microinches of Metallic Chromium	Electrochemical Treatment	Visible White Rust (%)
0.1	No	5
0.1	Yes	2
0.3	No	25
0.3	Yes	4
0.5	No	20
0.5	Yes	4
0.7	No	7
0.7	Yes	3
0.9	No	6
0.9	Yes	3
1.0	No	6
1.0	Yes	2
3.0	No	4
3.0	Yes	2
5.0	No	3
5.0	Yes	3

The above data show that for a given metallic chromium coating weight, the sample receiving an electrochemical treatment is much more corrosion resistant than the corresponding sample which did not receive an electrochemical treatment.

Surprisingly, the electrochemically treated samples having metallic chromium coating weights of 0.1–0.5 microinch are as corrosion resistant as the nonelectrochemically treated sample having a metallic chromium coating weight of 5.0 microinches.

We claim:

1. A method of improving the corrosion resistance of zinc coated ferrous metal substrates having a zinc surface comprising electroplating at least a portion of the surface area thereof with a coating of metallic chromium having a thickness of about 0.1–0.5 microinch, and thereafter electrochemically treating the resulting metallic chromium coated substrate as a cathode in an aqueous electrolyte containing a water soluble hexavalent chromium compound to deposit a metallic chromium and chromium oxide containing film thereon.

2. The method of claim 1 wherein the zinc coated ferrous metal substrate is steel electroplated with a coat-

ing of metallic zinc, the substrate being substantially free of an iron-zinc alloy layer between the steel base and the electroplated coating of zinc.

3. The method of claim 1 wherein the metallic chromium coating has a thickness of about 0.2–0.5 microinch.

4. The method of claim 1 wherein the metallic chromium coating has a thickness of about 0.1–0.3 microinch.

5. The method of claim 1 wherein the said metallic chromium and chromium oxide containing film contains a total of 0.6–5 milligrams of chromium per square foot.

6. The method of claim 1 wherein the metallic chromium coating has a thickness of about 0.1–0.3 microinch and the said metallic chromium and chromium oxide containing film contains a total of about 0.8–1.5 milligrams of chromium per square foot.

7. The method of claim 1 wherein the zinc surface of the zinc coated steel substrate is brightened prior to electroplating the metallic chromium coating thereon.

8. The method of claim 1 wherein a protective organic coating is applied on the electrochemically treated metallic chromium coated substrate.

9. The method of claim 1 wherein the zinc coating on the zinc coated ferrous metal substrate contains 0.05–0.5 ounce of zinc per square foot.

10. The method of claim 1 wherein the zinc coated ferrous metal substrate is prepared by a hot dip galvanizing process.

11. The method of claim 10 wherein the metallic chromium coating has a thickness of about 0.2–0.5 microinch.

12. The method of claim 10 wherein the metallic chromium coating has a thickness of about 0.1–0.3 microinch.

13. The method of claim 10 wherein the said metallic chromium and chromium oxide containing film contains a total of 0.6–5 milligrams of chromium per square foot.

14. The method of claim 10 wherein the metallic chromium coating has a thickness of about 0.1–0.3 microinch and the said metallic chromium and chromium oxide containing film contains a total of about 0.8–1.5 milligrams of chromium per square foot.

15. The method of claim 10 wherein the zinc surface of the zinc coated ferrous metal substrate is brightened prior to electroplating the metallic chromium coating thereon.

16. The method of claim 10 wherein a protective organic coating is applied on the electrochemically treated metallic chromium coated substrate.

17. The method of claim 1 wherein the zinc coated ferrous metal substrate is zinc coated ferrous metal strip, the metallic chromium coating is electroplated thereon while passing through a high speed electroplating line at a strip speed of at least 500 feet per minute, and thereafter the metallic chromium coated substrate is electrochemically treated at a strip speed of at least 500 feet per minute.

18. The method of claim 17 wherein the said high speed electroplating line also includes a zinc electroplating zone and the zinc coating is electroplated on the steel strip as it is passing therethrough, the metallic chromium coating is electroplated on the zinc electro-

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plated strip, and thereafter the metallic chromium coated strip is electrochemically treated.

19. The method of claim 18 wherein the zinc coating on the zinc coated ferrous metal substrate contains 0.05-0.5 ounce of zinc per square foot.

20. The method of claim 19 wherein a protective organic coating is applied on the electrochemically treated metallic chromium coated substrate.

21. The method of claim 17 wherein the zinc coated strip is rolled under pressure to brighten the surface prior to electroplating the said metallic chromium coating thereon.

22. The method of claim 1 wherein a protective organic coating is applied on the electrochemically treated metallic chromium coated substrate.

23. The corrosion resistant substrate prepared by the method of claim 22.

24. The corrosion resistant substrate prepared by the method of claim 1.

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25. The method of claim 1 wherein the metallic chromium coating has a thickness of about 0.2-0.5 microinch.

26. The method of claim 1 wherein the metallic chromium coating has a thickness of about 0.1-0.3 microinch.

27. The method of claim 1 wherein the said metallic chromium and chromium oxide containing film contains a total of 0.6-5 miligrams of chromium per square foot.

28. The method of claim 1 wherein the zinc surface of the zinc coated ferrous metal substrate is brightened prior to the electrodeposition of the metallic chromium coating thereon.

29. The method of claim 1 wherein the zinc coating on the zinc coated ferrous metal substrate contains 0.05-0.5 ounce of zinc per square foot.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,082 Dated June 11, 1974

Inventor(s) L. W. Austin, L. C. Beale, Jr., E. J. Smith

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

Claim 6, line 1, change "1" to -- 2 --.

Claim 7, line 1, change "1" to -- 2 --.

Claim 22, line 1, change "1" to -- 2 --.

Claim 25, line 1, change "1" to -- 2 --.

Claim 26, line 1, change "1" to -- 2 --.

Claim 27, line 1, change "1" to -- 2 --.

Claim 29, line 1, change "1" to -- 2 --.

Signed and sealed this 1st day of July 1975.

(SEAL)

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