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CORROSION RESISTANT FERROUS METAL ARTICLES AND METHOD OF PREPARING THE SAME

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ABSTRACT OF THE DISCLOSURE

Corrosion resistant ferrous metal articles are prepared by electroplating thereon a metallic chromium coating having a thickness of 0.1–0.5 microinch, and then electrochemically treating the article as a cathode in an aqueous electrolyte containing a water soluble hexavalent chromium compound to deposit a chromium oxide containing film. The resultant surface is receptive to organic coatings and the invention is especially useful in the manufacture of thin gauge tin free strip or sheet for use as container stock.

This invention broadly relates to corrosion resistant ferrous metal articles and a method for preparing the same. In some of the more specific variants, the invention is concerned with thin gauge tin free steel sheet material which is useful as container stock and a method for its preparation.

Tinplate is widely used at the present time for the manufacture of containers of the type used in the storage and preservation of foods and beverages. However, due to the high cost of tin and the lack of a dependable source of tin in this country, it is desirable to provide low cost corrosion resistant tin free steel strip or sheet for use as container stock.

A number of efforts have been made heretofore to provide satisfactory tin free strip or sheet for use as container stock. Inasmuch as a clean steel surface is subject to rapid corrosion, some type of an initial protective coating must be applied at the time of manufacture. The initially protected steel surface must be receptive to the usual organic coatings that are applied to tinplate such as paints, varnishes, lacquers and enamels to thereby provide relatively permanent protection against corrosion. The steel surface should also be receptive to the organic adhesives which may be used in joining the side seams of containers prepared therefrom. Thus, satisfactory tin free steel sheet material for use as container stock should have a surface which has a combination of desirable characteristics, including the following:

(1) The steel surface must have an initial protective film or coating thereon which retards corrosion, at least from the time of manufacture in the form of thin gauge strip or sheet until it is organically coated and is ready for use in the preparation of containers.

(2) The initially protected steel surface should have a pleasing bright silver to light grey appearance, as distinguished from a dark or discolored appearance, as it is often desirable to apply clear organic protective coatings thereto.

(3) The initially protected steel surface must be receptive to organic protective coatings of the usual types applied to tinplate and must form a good base therefor. For example, the organic coatings must adhere tightly to the steel surface and provide good underfilm corrosion resistance.

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(4) The organically coated steel surface should pass the peel and side seam adhesion tests, as the side seams of tin free containers are often formed by cementing the side edges together with a resinous organic cement. If the overlapped edge portions cannot be tightly adhered together with the organic cement, the side seams separate and the container fails.

This is a highly competitive field and in addition to the above requirements, the initially coated steel strip or sheet must complete in price with other low cost materials.

In fact, the competition is so keen that the method used in initially treating the steel surface must not add appreciably to the overall cost of manufacture of blackplate. A wide variety of methods have been proposed heretofore for protecting the steel surface initially. However, the treatments and/or coatings proposed heretofore have had some disadvantage or deficiency which prevented them from being satisfactory in all respects.

One of the treatments that has been proposed heretofore involves electrodepositing a substantially nonporous layer of metallic chromium on ferrous metal sheet material for the purpose of producing a substrate surface which is sufficiently corrosion resistant, and also receptive to organic finishes. However, relatively thick chromium coatings were required of the order of 2 microinches or thicker to obtain sufficient corrosion protection before the organic coating was applied. This has at least two disadvantages, one being the high cost of applying the chromium plating. As is well known, chromium plating is very inefficient and only a small fraction of the electric current is effective in plating out metallic chromium. Additionally, the relatively thick chromium coatings often are not sufficiently ductile and cracks appear therein when the substrate is subjected to drastic forming, such as in the manufacture of containers therefrom.

It has been discovered that very thin coatings of metallic chromium may be electrodeposited on ferrous metal substrates, and although such initially deposited chromium coatings are porous and are unsatisfactory without further treatment, this problem may be readily overcome by an inexpensive electrochemical treatment of the coated substrate. The resultant substrate is an excellent base for organic coatings, and it is fully equivalent in this respect and in initial corrosion resistance to substrates having the much heavier chromium coatings of the prior art.

It has been further discovered that the very thin layers of metallic chromium which are deposited in accordance with the invention are ductile and formable, and are not subject to cracking during a forming operation on the substrate such as when side seams are formed in the manufacture of containers. Thus, the present invention provides for the first time an entirely satisfactory inexpensive method for the treatment of ferrous metal strip or sheet to provide high quality container stock.

It is an object of the present invention to provide improved corrosion resistant ferrous metal articles and a novel method of preparing the same.

It is a further object to provide a novel method of improving the corrosion resistance of ferrous metal substrates by electroplating a thin layer of chromium thereon, and then electrochemically treating the coated substrate to produce a corrosion resistant surface which is receptive to organic coatings.

It is still a further object to provide improved corrosion resistant container stock which is useful in the manufacture of containers and a novel method of preparing the same including applying an organic coating such as paint, varnish, lacquer or enamel to the initially treated ferrous metal substrates of the invention.

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

In accordance with the present invention, the corrosion resistance of ferrous metal articles is improved by electroplating at least a portion of the surface area thereof with a coating of metallic chromium having a thickness of 0.1–0.5 microinch, and then electrochemically treating the chromium coated surface as a cathode in an aqueous electrolyte containing a water soluble hexavalent chromium compound. Thereafter, the treated ferrous metal surface may be coated with an organic finish to provide relatively permanent protection against corrosion. There are certain preferred variants of the invention which produce superior results, as will be illustrated and described in greater detail hereinafter.

Any suitable prior art chromium plating bath may be used for electrodepositing the metallic chromium layer. As is well known, chromium plating baths usually contain chromic acid or other water soluble chromium compound and a catalyst such as sulfate ion, fluoride ion, silicofluoride ion, or a combination thereof. The catalyst may be added as a free acid providing the desired ion, such as sulfuric acid, or as a water soluble salt such as the alkali metal compounds. The molar ratio of chromic acid to the catalyst is usually about 100:1. The chromic 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 used in prior art chromium plating, such as about 300–2,000 amperes per square foot, and preferably about 500–1,000 amperes per square foot. The bath temperature also may be in accordance with the prior art, such as about 90–150° F., and preferably about 110–130° F. Insoluble anodes are used, and preferably a composite steel anode prepared by applying a lead coating to the side facing the ferrous metal substrate to be plated, and polyvinyl chloride or other inert insulating substances to the opposite side to prevent or reduce stray currents. The substrate surface is scrubbed free of oil, dirt and other surface contaminants by a prior art process prior to electroplating with the metallic chromium.

While the above plating baths and conditions are satisfactory, it is understood that still other prior art chromium plating baths may be used. Examples of other plating baths and conditions are disclosed in U.S. Pat. Nos. 1,942,469; 2,177,392 and 2,415,724, and in the text "Modern Electroplating," edited by Frederick A. Lowenheim, 2nd ed., John Wiley & Sons, Inc., New York, N.Y., 1963. Chapter 5, pages 80–140 and the references cited on pages 128–140 are especially pertinent as this portion of the text is directed to chromium plating. The teachings of this text, and the references cited therein, are incorporated herein by reference.

Regardless of the specific prior art chromium plating bath and conditions which are employed, it is understood that the coating of metallic chromium that is electrodeposited has a thickness of 0.1–0.5 microinch. Unsatisfactory results are achieved due to insufficient metallic chromium at coating thicknesses less than 0.1 microinch, while coatings having thicknesses above 0.5 microinch tend to crack during forming into containers and the like, thereby decreasing the desirable properties of the substrate rather than improving them. Additionally, chromium coatings above 0.5 microinch are expensive and add appreciably to the cost of manufacturing tin free steel for container stock due to the inefficiency of the chromium plating process. Best results are usually achieved by maintaining the metallic chromium coating at a thickness of 0.1–0.3 microinch. A metallic chromium coating having a thickness of 0.1 microinch is satisfactory for container stock to be used in the preparation of containers for the storage and preservation of less corrosive carbonated beverages and foodstuffs, whereas metallic chromium coatings of 0.3 microinch are pre-

ferred when storing and preserving corrosive foodstuffs and carbonated beverages.

Metallic chromium coatings of 0.1–0.5 microinch in thickness have a porosity whereby the ferrous metal surface is subject to corrosion at the pore sites. Thus such metallic chromium coatings do not provide satisfactory initial protection against corrosion of the ferrous metal substrate. As a result, heretofore these extremely thin metallic chromium coatings have not been considered to be useful in the manufacture of high quality container stock.

It has been discovered unexpectedly that metallic chromium coatings having a thickness of 0.1–0.5 microinch may be electrochemically treated to render them satisfactory for container stock. The bath that is used for the electrochemical treatment may contain a water soluble hexavalent chromium compound such as chromic acid, alkali metal dichromate including sodium or potassium dichromate, etc. Chromic acid is often preferred. Satisfactory baths may contain about 50–100, and preferably about 80, grams per liter of chromic acid, or about 2.5–3.5, and preferably about 3 ounces per gallon of sodium or potassium dichromate.

The electrochemical treatment baths may be operated at a temperature of about 90–150° F., and preferably at about 100–130° F. The substrate may be treated cathodically under current conditions to provide about 25–200 amperes per square foot, and preferably about 50–100 amperes per square foot, over a period of time to result in treatment with about 25–500 coulombs per square foot, and preferably about 75–125 coulombs per square foot. The optimum treatment is often at the rate of 50 amperes per square foot for 2 seconds to thereby provide 100 coulombs per square foot, using a bath temperature of about 100° F. The electrochemical treatment bath should not contain more than 20 parts per million by weight of chloride ion in the absence of additives to prevent staining of the electrochemically treated surface. Also, higher levels of chloride ion tend to catalyze chromium oxide formation in the film, which causes inferior peel test values and poor underfilm corrosion test results in some instances.

As a general rule, about 0.6–5.0 milligrams per square foot of chromium should be present in the film that is deposited in the electrochemical treatment. The cathodic electrochemical treatment results in the deposition of a chromium oxide-containing film which also contains metallic chromium. The chromium content of the chromium oxide seems to be largely in the plus three valence state, and may include hydrated Cr_2O_3 in most instances. Preferably, the film should contain about 1–3 milligrams per square foot of total chromium in the metallic chromium and chromium oxide contents of the film and for best results about 1–2 milligrams per square foot.

Surprisingly, the electrochemical treatment markedly reduces the porosity of the initial metallic chromium coating. It is thought that for some as yet unexplained reason the metallic chromium content of the electrochemically deposited film tends to seek out the pores in the initially deposited metallic chromium film, and thereby renders it less porous. In addition to this, the chromium oxide content of the film and the metallic chromium dispersed therein tends to cover and further protect the initial metallic chromium coating where it is continuous to thereby markedly increase the corrosion resistance. At the same time, a surface is produced which is highly receptive to the prior art organic coatings. The organically coated electrochemically treated surface also is an excellent base for the side seam adhesives which are sometimes used in the manufacture of containers, and the peel test and the side seam adhesion test results are far above minimum specifications.

Organic coatings of the types usually applied in the prior art to tin free steel or tinplate to further improve the corrosion resistance, and to provide relatively perma-

nent protection for the initially protected ferrous metal base, may be applied over the electrochemically treated surface to produce corrosion resistant container stock. While the invention is not limited thereto, examples of suitable organic coatings include phenolic, modified phenolic, epoxy, modified epoxy, vinyl resin, Teflon and drying oil based paints, varnishes, lacquers and enamels. The selection of a specific organic coating to be employed in a given instance is within the skill of the art.

The present invention is especially useful in the treatment of blackplate strip or sheet, herein referred to as sheet material or ferrous metal sheet material, of the usual gauges used in tin free steel or tinplate manufacture. Blackplate having a weight of 55-90 pounds per base box is often used for container stock to be used in the preparation of containers for the preservation and storage of foods and carbonated beverages. However, the treatment of the invention may be applied to any ferrous metal surface.

The ferrous metal article to be treated need not be given a special pretreatment prior to deposition of the metallic chromium coating. The surface, however, should be free of rolling oil, rust, dirt, scale and other foreign matter, and it is preferred that the article be cleaned by the usual prior art steps used in the manufacture of chromium plate. In instances where the substrate is blackplate strip, the strip may be passed continuously through an electroplating line at high speed and electrolytically cleaned in a caustic cleaner, such as anodic and cathodic treatment in an Orthosil solution, rinsed with water, thereafter pickled in dilute sulfuric acid or hydrochloric acid, scrubbed and rinsed with water, and then plated with metallic chromium. After plating with the metallic chromium, the strip may be continuously rinsed with water, and then immersed in the electrochemical treatment bath where it receives the chromium oxide-containing film. If desired, the strip entering the plating bath and/or the chemical treating bath may be prewetted with electrolyte by means of sprays or the like arranged above the baths, and/or counter current rinsing may be used to recover dragout electrolyte for recycle, as is disclosed in U.S. Pats. Nos. 2,648,625 and 2,825,681 and British Pat. No. 546,269. Thereafter, the strip may be continuously rinsed with hot or cold water, dried, oiled lightly with dioctylsebacate or other suitable lubricant such as is used in tinplate manufacture, and coiled. The strip may be coated with an organic finish continuously following prior art procedures, and the resultant strip cut into suitable lengths for the manufacture of containers therefrom. Alternatively, the organic coating may be applied to the dried strip following the electrochemical treatment and the oiling step may be eliminated. Also, the electrochemically treated strip may be cut into sheets of a desired size, then organically coated, and containers made therefrom, or containers may be prepared from the electrochemically treated strip, and the completed container coated with the organic finish.

The chromium plated and electrochemically treated ferrous metal substrate produced in accordance with the present invention is not discolored. The treated surface is bright, and varies between grey and silver-grey in appearance. This is of importance as often it is desired to apply clear organic coatings.

The foregoing detailed description and the following specific example are for purposes of illustration only, and are not intended as being limiting to the spirit or scope of the appended claims.

EXAMPLE

Coils of 55 pounds double reduced blackplate are cleaned by a prior art procedure to remove grease, dirt and other foreign matter from the surface. The treatment includes cathodic and anodic electrolytic treatment in a caustic cleaner (Orthosil), rinsing with water, pickling in dilute (2-3%) aqueous sulfuric acid, scrubbing and

rinsing with water and drying. The clean strip is then passed continuously through a series of vessels in a pilot line wherein it is electroplated with metallic chromium, rinsed with water, electrochemically treated, rinsed with water and dried.

The electrolyte for the chromium plating bath contains 250-275 grams per liter of chromic acid, and sulfate and silicofluoride ion as a catalyst in a mole ratio of chromic acid to catalyst of 100:1 to 100:2. The temperature of the electrolyte is maintained at about 120° F., and the current density at about 800-1,000 amperes per square foot. The anodes in the chromium plater are lead coated steel on the surfaces facing the strip, and are coated with polyvinyl chloride on the opposite side thereof so as to eliminate stray currents. The amount of metallic chromium deposited on the strip is varied on different runs to produce coatings having thicknesses of 0.1, 0.2, 0.3, 0.4 and 0.5 microinch.

The metallic chromium plated strip is withdrawn from the chromium plater, rinsed with water, and is then passed into an electrochemical treating vessel filled with an electrolyte containing 80 grams per liter of chromic acid. The electrolyte temperature is maintained at 120° F., and the strip surface is treated cathodically for 2 seconds at 50 amperes per square foot to thereby provide a surface treatment of 100 coulombs per square foot. The strip is passed between steel anodes coated with lead on the surface facing the strip. This treatment results in about 1-2 milligrams per square foot of total chromium in the film deposited on the strip. The chromium is present in the film in the form of a mixture of metallic chromium and chromium oxide in which the chromium has a valence of plus 3. About 1/3 to 1/2 of the total chromium in the film is metallic (Cr⁰).

The treated strip is withdrawn from the electrochemical treating vessel, rinsed in water, dried and coiled. Samples of strip are cut from the various runs for the different metallic chromium coating weights and tested for corrosion resistance by the underfilm corrosion test. A peel adhesion test was also conducted.

The peel adhesion test is based on the relative peel strength of an adhesive bonded between two previously lacquered strips of metal. The metal samples for testing are trimmed to a convenient size (6 x 11 inches), lacquered with epoxy lacquer to provide a dry film weight of 1.5-2.0 milligrams per square inch, and the lacquered panels are cured in an oven for 10 minutes at 400-405° F. The lacquered panels are sheared into 3/4 inch x 5 1/4 inch strips. A film of nylon adhesive having a size of 1/2 inch x 3/4 inch is heat tacked over a hotplate to the ends of lacquered test strips. Another test strip is placed over the adhesive and the specimen is ready for bonding. The test samples are heat bonded on a hydraulic press with platen temperatures set at 450° F. and at a gauge pressure of 8,000 pounds. The bonding cycle for each specimen is maintained for 5 seconds. With each sample, the platens are shimmed to allow a 3 mil adhesive layer to remain between the bonded strips. After the bond is formed, the samples are cooled to room temperature and aged overnight. The specimens are tested using an Instron tensile tester operated at a crosshead speed of 1 inch per minute. The sample pieces are gripped on one end and peeled at 180° over 1/2 inch peel rolls. The results of this test are reported from the values of high and low peel strength obtained with each set of specimens. A minimum and maximum value is reported from the average peel strength values for 12 specimens. This is indicated in pounds of peel strength per 3/4 inch specimen.

Five series of samples having chromium thicknesses of 0.1, 0.2, 0.3, 0.4 and 0.5 microinch had minimum average peel strength values of 39.4-48.9 pounds, and maximum average peel strength values of 61.4-65.1 pounds. Values above 20 pounds are considered to be satisfactory, and thus the products of this example exceeded the mini-

imum specifications by a wide margin. Tests on a prior art sample having a metallic chromium coating thickness of about 2 microinches gave maximum peel strength values of 50–70 pounds, the average of which is 60 pounds, or a little lower than for the products of the invention. Therefore, the products of this example are fully comparable or better than the prior art products with respect to peel strength test values.

In the underfilm corrosion test, a 6 inch x 9 inch panel for each metallic chromium coating weight is coated with 3–4 milligrams per square inch of an epoxy-urea-formaldehyde organic coating. The coated panels are cut into one inch strips and scribed with an "X" through the organic coating using a sharp tool to expose base steel. The entire scribe areas of the strips are immersed in the test medium, which is a lemon-lime carbonated beverage, for 2 weeks at 80° F. The beverage is maintained under a carbon dioxide atmosphere as described in the American Iron and Steel Institute report entitled "Corrosion Resistant Tinplate for Carbonated Beverage Containers" by Mittleman et al., which was presented at the technical meeting on Nov. 18, 1965 and later printed.

After two weeks, the samples are removed from the test medium, rinsed with water, dried and examined under 10, 30 and 60 power magnification for indications of underfilm corrosion. No trace of underfilm corrosion was found on strip samples having metallic chromium coating thicknesses of 0.1, 0.2, 0.3, 0.4 and 0.5 microinch, and thus all samples passed the 2 week underfilm corrosion test with a rating of "excellent." A 2 week underfilm corrosion test on a prior art sample having a chromium coating thickness of about 2 microinches gave no better results, and thus the products of this example are comparable.

What is claimed is:

1. A method of improving the corrosion resistance of ferrous metal strip comprising the steps of continuously introducing the ferrous metal strip into a chromium plating bath and continuously electroplating thereon a coating of metallic chromium having a thickness of 0.1–0.5 microinch, the chromium plating bath comprising 100–400 grams per liter of chromic acid and chromium electroplating catalyst selected from the group consisting of sulfate ion, fluoride ion, silicofluoride ion and mixtures thereof, the chromium coated ferrous metal strip being subject to corrosion in the absence of further treatment, continuously withdrawing the chromium coated ferrous metal strip from the chromium plating bath, thereafter continuously passing the chromium coated ferrous metal strip through an aqueous electrolyte for electrochemically treating the same, and continuously electrochemically treating the chromium coated ferrous metal strip as a cathode at a current density of at least 50 amperes per square foot in said aqueous electrolyte for the electrochemical treatment to deposit a metallic chromium and chromium oxide-containing film thereon and increase the corrosion resistance, said aqueous electro-

lyte for the electrochemical treatment having a temperature of about 90–150° F. and containing less than 100 grams per liter of chromic acid, and said metallic chromium and chromium oxide-containing film containing a total of 0.6–5 milligrams of chromium per square foot.

2. The method of claim 1 wherein the ferrous metal strip is of container stock gauge, and an organic coating is applied over the electrochemically treated ferrous metal strip to provide corrosion-resistant container stock.

3. The method of claim 2 wherein the coating of metallic chromium has a thickness of 0.1–0.3 microninch.

4. The method of claim 3 wherein the metallic chromium coating is porous and metallic chromium is deposited in the pores during the deposition of the metallic chromium and chromium oxide-containing film to thereby reduce the porosity, a total of 1–3 milligrams of chromium per square foot is present in the chromium oxide and the metallic chromium contained in the film, and the organic coating is selected from the group consisting of varnishes, lacquers and enamels.

5. The method of claim 4 wherein the coating of metallic chromium has a thickness of about 0.1 microninch.

6. The container stock prepared by the method of claim 2.

7. The method of claim 1 wherein the metallic chromium coating is porous and metallic chromium is deposited in the pores during the deposition of the metallic chromium and chromium oxide-containing film to thereby reduce the porosity, and a total of 1–3 milligrams of chromium per square foot is present in the chromium oxide and the metallic chromium contained in the film.

8. The corrosion resistant ferrous metal strip prepared by the method of claim 1.

9. The method of claim 1 wherein the coating of metallic chromium has a thickness of 0.1–0.3 microninch.

10. The method of claim 1 wherein the coating of metallic chromium has a thickness of about 0.1 microninch.

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