LOW HYDROGEN EMBRITTLEMENT (LHE) ZINC-NICKEL PLATING FOR HIGH STRENGTH STEELS (HSS)

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ABSTRACT
The invention provides a method for producing a corrosion-resistant article, where the article is conductive and subject to hydrogen uptake during electroplating of a coating. The method comprises electroplating a zinc-nickel coating on the article in an aqueous basic plating solution containing zinc and nickel ions. The method uses an electrolyte in the form of a soluble hydroxide salt with the weight ratio of zinc ions to nickel ions in the solution being sufficient to provide the coating comprising from about 85% to about 95% by weight zinc, and about 5% to about 15% by weight nickel. The plating solution is substantially free of brightening agents which retard hydrogen bake-out.
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FIELD OF THE INVENTION

[0001] The present invention relates to electroplating an article with a zinc-nickel alloy.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to zinc-nickel electroplated articles exhibiting corrosion resistance and low hydrogen embrittlement.

[0003] High-strength steels are subject to delayed, brittle failures at relatively low stresses. Such failures have been attributed to the presence of hydrogen in the steel microstructure. The hydrogen can be introduced into the microstructure by reaction with water or aqueous solution, or, by electrochemically discharging hydrogen at the surface of the steel. Since high-strength steels have corrosion-resistant coatings that are applied by electroplating techniques, hydrogen is discharged onto the steel surface along with the corrosion-resistant coating. Therefore, the quantity of hydrogen deposited at the coating-steel interface must be carefully monitored and controlled.

[0004] Currently, a cadmium-titanium alloy is electroplated onto high-strength steels under carefully controlled conditions. The resulting plated product is then heat treated at elevated temperatures to achieve an acceptable low hydrogen embrittlement level. It is believed that the porosity of the electroplated cadmium-titanium alloy is the key to the removal of the hydrogen during a subsequent heat treatment operation; however, the cadmium-titanium plating bath is very sensitive to contamination, which can cause embrittlement characteristics in coated high-strength steel substrates. More importantly, the cadmium-titanium alloy plating bath contains both cadmium and cyanide, which create disposal problems unless expensive waste treatment equipment is employed.

[0005] Zinc-nickel alloys have been suggested for electroplating onto steels to render the corrosion-resistant. The plating parameters of a zinc-nickel alloy acidic plating bath are described in U.S. Pat. No. 4,765,871 assigned to the assignee of the present invention.

[0006] The zinc-nickel bath is cadmium and cyanide free and contains components that are relatively nontoxic compared to those in a cadmium-titanium plating bath.

[0007] There continues to be a need for an improved coated product having corrosion resistance, low hydrogen embrittlement and which is nontoxic.

SUMMARY OF THE INVENTION

[0008] The invention provides a method for producing a corrosion-resistant article, where the article is conductive and subject to hydrogen uptake during electroplating of a coating. The method comprises electroplating a zinc-nickel coating on the article in an aqueous, basic plating solution containing zinc and nickel ions. The method uses an electrolyte in the form of a soluble hydroxide salt with the weight ratio of zinc ions to nickel ions in the solution being sufficient to provide the coating comprising from about 85% to about 95% by weight zinc, and about 5% to about 15% by weight nickel. The plating solution is substantially free of brightening agents which retard hydrogen bake-out. Thus, the plating solution is substantially free of brightening agents, which retard, prevent or at least inhibit release of hydrogen from the article. The release of previously-absorbed hydrogen is achieved by various methods whereby hydrogen diffuses within the material and is outgassed from the material. The release of hydrogen via bake-out occurs typically at elevated temperature over a period of time.

[0009] Further areas of applicability of the present invention will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description and specific examples, while indicating the preferred embodiment of the invention, are intended for purposes of illustration only and are not intended to limit the scope of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] The following description of the preferred embodiment(s) is merely exemplary in nature and is in no way intended to limit the invention, its application, or uses.

[0011] A zinc-nickel alloy is electrodeposited onto a variety of electrically conductive substrates in accordance with the present invention. The zinc-nickel alloy deposited in accordance with the present invention is especially efficacious, however, when applied to high-strength steel articles. Not only is the steel article rendered corrosion resistant, it also exhibits little or no hydrogen embrittlement after the electroplating process. Accordingly, the present invention provides a viable and effective substitute for prior cadmium-titanium corrosion-resistant coatings.

[0012] The plating bath formed in accordance with the present invention is an aqueous solution containing zinc, nickel and an electrolyte in the form of a soluble hydroxide salt, preferably along with a nickel complexing agent. The metal cations are placed in an aqueous solution of a solubilized oxide or salt of the cation. It is preferred, as will be discussed in more detail below, that the solution contain hydroxide ions. Brighteners are not included in the solution.

[0013] The zinc cations can be provided by a variety of water-soluble zinc compounds. The water-soluble compounds include zinc hydroxide and other zinc salts such as zinc sulfate, zinc oxide and, of course, the various combinations and mixtures thereof. Zinc content is achieved and also replenished by a variety of means. Concentration of the zinc salt should be sufficient to provide at least about one ounce of zinc per gallon of solution. Preferably, the zinc ions should be present in an amount ranging from about 1.1 to about 1.5 ounces per gallon of solution, and more preferably from about 1.17 to about 1.45 ounces per gallon.

[0014] The nickel cations can be provided from a variety of water-soluble nickel salts, including nickel sulfate, nickel fluoride, nickel acetate, and the various mixtures and combinations thereof. Nickel sulfate is preferred. The nickel salt should be present in an amount sufficient to provide at least about 0.1 ounces of nickel ion per gallon of solution. It is preferably about 0.1 to about 0.2 of nickel ion, and more preferably about 0.12 to about 0.15 ounces per gallon.

[0015] For a plated coating exhibiting optimum corrosion resistance and low hydrogen embrittlement and reembrittle-
ment characteristics, it is preferred that the weight ratio of zinc ion to nickel ion in the solution be in the range of from 10:1 to 11:1.

[0016] The conductivity of the electroplating bath is increased by the presence of the electrolyte. The preferred electrolytes include soluble hydroxide salts of metals, preferably Group I alkali metals and most preferably, sodium hydroxide. Various mixtures and combinations of metal hydroxides may be used. The sodium hydroxide should be present in the bath in an amount sufficient to provide from about 15 to about 25 ounces of sodium hydroxide per gallon of solution, preferably from about 17.4 to about 21.2 ounces per gallon of solution. The solution pH is adjusted to a basic range, preferably pH greater than 12 and less than 14.

[0017] Conventional brightening agents, such as organic brighteners, are not included in the solution. Conventional brighteners, and particularly organic brighteners are employed in the art to provide bright, specular deposits. However, the present invention avoids brighteners. By the present invention, it has been determined that such brighteners retard the hydrogen bake-out.

[0018] The zinc-nickel plating process is carried out in the pH, temperature, and current density ranges, suitable as described herein. When carried out with a preferred solution as outlined above and within the preferred operating ranges set forth herein, an alloy containing from 85 to 95 percent by weight zinc and 5 to 15 percent nickel is produced. This coating will provide excellent corrosion resistance as well as resist hydrogen embrittlement. It is most preferred that the coating consist of about 90 weight percent zinc and about 10 weight percent nickel. Here, corrosion resistance is maximized and hydrogen embrittlement is minimized.

[0019] The bath can effectively be operated in a basic pH range, preferably from about 12 to about 13.5. It is preferred that the pH of the bath be adjusted as the need may be, while avoiding the introduction of undesirable ions into the solution. The zinc-nickel alloy can be plated in accordance with the present invention over a wide variety of temperatures and current densities. The electrodeposition can occur over a broad temperature range of about 65 degrees F. to about 85 degrees F., preferably at room temperature from 70 degrees F. to 80 degrees F.

[0020] The cathode current densities preferably range from about 30 to about 68 amperes per square foot to yield a satisfactory corrosion-resistant coating and also achieve low hydrogen embrittlement.

[0021] At a current density that is too low on the order of 20 to 24 ASF, there is not good coverage of the substrate with the coating. At high current density, on the order of over 70 amperes per square foot, for example, the metal is deposited rapidly; the coating appears rough or relatively graney and yields unsatisfactory results.

[0022] The anode of the system is preferably nickel. The part being treated is the cathode. The resulting product has nickel distributed through-out the zinc coating. At the typical 36 amperes per square foot the deposition preferably occurs over a period of time of 15 to 30 minutes of plating depending on the thickness requirement. The 30 minute plating rate (PR) for this process is approximately 0.8 mil (thousand of an inch) at 30 ampere-per-square-foot (ASF), 1.5 mils at 45 ASF and 1.9 mils at 68 ASF, although plating rate can significantly vary depending on combined operating condition and parameters.

[0023] The complexing agent (chelating agent) plays a role in giving sufficient nickel ion concentration and distribution, even at a low concentration. Thus, the complexing agent facilitates distributing the nickel co-precipitation with zinc in a uniform ratio. One exemplary complexing agent is an organic amino compound, such as ethylenediamine (EDA), ethylenetetramine, polyethylenepolyamines such as diethylenetriamine (DETA), triethylenetetramine (TETA), N-hydroxyethylenediamine (HEDDA), etc., and alkaliol amines such as diethanolamine (DEA), triethanolamine (TEA), N-methylenolamine, 2-aminopropanol, etc. The DETA is preferred. The complexing agent may include aminocarboxylic acid salts such as nitritotriacetate, ethylenediamine-tetraacetate, etc., oxycarboxylic acid salts such as citrate, tartarate, gluconate, glycolate, etc., polyhydric alcohols such as sorbitol, mannitol, pentaerythritol, etc. Complexing agents may also include inorganic agents.

[0024] Prior to deposition of the zinc-nickel alloy, the article to be plated is preferably cleaned and activated for electrodeposition in accordance with the following procedure. The article to be plated is first manually solvent cleaned or vapor degreased in accordance with conventional procedures normally employed in the plating arts. After cleaning or degreasing, the article is dried and optional cleaned with an abrasive blast. Within a relatively short period of time after the optional abrasive cleaning, the article is rinsed in cold water for several minutes, activated by immersing it in an acid or other solution for a desired time, rinsed with cold water, transferred, immersed and plated electrolytically in the zinc-nickel plating bath as described below.

[0025] A chromate treatment of the part can follow the zinc-nickel plating step; this is not only preferred, it is also necessary to increase the corrosion protection for zinc-nickel plating and to provide a good adherent base for paint. Conventional chromating and other optional post-treatment steps are utilized as desired. The example below includes a chromating step.

[0026] Chromate is applied from a known process, basically a dip process, non-electrodeposition. The chromate is delivered from various sources. Any chromate can be used and various chromate solutions can be used, for example, chromic acid with sulphuric acid; a di-chromate and sulphuric acid, or di-chromic acid with hydrochloric acid.

[0027] Conventional pre and post treatment methods are described in U.S. Pat. No. 4,765,871, assigned to Boeing and incorporated by reference herein in its entirety.

[0028] Table I summarizes the alloy ranges, bath composition and operating parameters set forth above.

<p>| TABLE I |
|---|---|---|
| Exemplary Values | MATERIAL/CONDITION | BROAD | PREFERRED |
| | Alloy composition | Zn: 85 to 95 | — |
| | (weight percent) | Ni: 5 to 15 | — |
| | Zinc Metal Content | 1.17 to 1.45 cpg | 1.4 cpg |</p>
<table>
<thead>
<tr>
<th>MATERIAL/CONDITION</th>
<th>BROAD</th>
<th>PREFERRED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Metal Content</td>
<td>0.12 to 0.15 opg</td>
<td>0.13 opg</td>
</tr>
<tr>
<td>Zinc to Nickel Weight</td>
<td>10:1 to 11:1</td>
<td></td>
</tr>
<tr>
<td>Ratio (no unit)</td>
<td>Vary as needed</td>
<td></td>
</tr>
<tr>
<td>Nickel Complexing Agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>17.4 to 21.2 opg</td>
<td>18 opg</td>
</tr>
<tr>
<td>pH</td>
<td>12 to 13.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Use NaOH to raise</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Use H₂SO₄ to lower</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Less than 8 opg</td>
<td></td>
</tr>
<tr>
<td>Agitation/Filtration</td>
<td>Mechanical (2 to 3 volume turnover per hour)</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>70 to 80 °F</td>
<td>75 °F</td>
</tr>
<tr>
<td>Anode</td>
<td>Main (primary): Nickel slab</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Auxiliary (secondary): Nickel, nickel plated, platinum plated</td>
<td></td>
</tr>
<tr>
<td>Anode to Cathode Area</td>
<td>Minimum 2:1</td>
<td>Maximize</td>
</tr>
<tr>
<td>Ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode Current Density</td>
<td>30—68 ASF</td>
<td>45 ASF</td>
</tr>
</tbody>
</table>

Legend: opg ounce per gallon
F. degree Fahrenheit
ASF amperes-per-square-foot
Note: For the Anode, do not use Nickel balls in Titanium baskets

**EXAMPLE I**

**[0029]** If the Ni-complexing agent is omitted from the plating solution, but the other operational parameters of the present invention are maintained within ranges defined below, a zinc-nickel coating exhibiting good corrosion resistance and low hydrogen embrittlement is still achieved. The nickel distribution in the coating is not, however, as good as when the Ni-complexing agent is present in the plating solution. In order to achieve this result, the plating bath composition is as per the Examples below. Brighteners are not included and preferably the only organic compound in the bath is the Ni-complexing agent.

**EXAMPLE II**

**[0030]** An aqueous electroplating bath containing no brightener was prepared containing per gallon of solution, 1.17 to 1.45 ounces of zinc, 0.12 to 0.15 ounces of nickel, 17.4 to 21.2 ounces of sodium-hydroxide and a minor amount of Ni-complexing agent. The pH of the bath was 12 to 13.5 and was maintained at about room temperature of 70 to 80 degrees F. Only nickel was employed as an anode. Test panels were prepared with current densities of about 30 to 68 ASF, and more specifically, deposition was conducted at 30 ASF, 36 ASF, 45 ASF and 68 ASF. At a current density of about 30 to 68 amperes per square foot, the zinc-nickel alloy deposit was well-coated on the high strength steel.

**EXAMPLE III**

**[0031]** An acceptable source of zinc metal is available from Atotech and sold under the trade name Reflectalloy and Reflectalloy ZNA. A zinc-metal solution having the designation ZNA ZS supplies zinc and caustic soda to the bath; and the zinc compound has CAS no. 12179-14-5 designation and is present at up to about 10 wt % in the ZNA ZS and the sodium hydroxide has CAS no. 1310-73-2 designation and is present in the ZNA ZS at up to about 30 wt %. Product designation ZNA-92 Ni—C supplies nickel to the bath; and the nickel sulfate has CAS no. 7786-81-4 designation and is present in the ZNA-92 Ni—C at up to about 40-70 wt %. Product designation ZNA-C9300 carrier is used along with the 92 Ni—C to facilitate delivery of nickel; and product ZNA-C9300 carrier is a mixture of diethylene triamine, CAS no. 111-40-0 designation, up to 30 wt % and triethanolamine, CAS no. 102-71-6 designation, up to 10 wt % in the C9300 carrier. Product ZNA-C9400 carrier also adjusts the nickel delivery, and C9400 carrier has characteristics similar to the C9300 carrier. Further characteristics of each of the ZNA ZS, ZNA-92 Ni—C, the C9300 and the C9400 are included in the MSDS and Atotech product literature for each, incorporated herein by reference as a teaching tool. Thus, it can be seen that the plating solution essentially comprises a source of zinc, a source of nickel, a source of caustic soda and a source of complexing or chelating agents to facilitate the deposition of appropriate amounts of nickel with respect to zinc.

**[0032]** The solution in accordance with this present example contains the following quantities to provide 100 gallons of suitable electroplating solution using commercially available starting materials. Supply zinc and caustic soda to the bath via 35 gallons of Reflectalloy ZNA ZS. Supply nickel to the bath using 0.75 gallons Reflectalloy ZNA-92 Ni—C which is a nickel containing component that is used for the initial bath, and to replenish nickel in an operating bath; and it is used in cooperation with the ZNA-C9300 which is supplied in the amount of 4.5 gallons to adjust the amount and rate of nickel deposit and Reflectalloy ZNA-C9400 in an amount of 5.4 gallons to also adjust the rate of nickel deposit. In a typical protocol Rayon grade sodium hydroxide 50% in liquid form provides bath conductivity and assists in dissolution of the zinc. In a typical protocol, the steps are as follows: First fill the plating tank equipped with preferred chiller and agitator to 25 percent of its desired final volume. Second, while agitating, add the ZNA-C9300. Next, add the required amount of the Reflectalloy ZNA-92 Ni—C. Then the required amount of Rayon grade sodium hydroxide is added followed by the addition of the zinc solution. Next, stirring is continued while the required amount of the Reflectalloy ZNA-C9400 carrier is added. Sufficient water to bring the solution to its final desired volume and composition is added. Next, the solution is stirred and the nominal composition is within the ranges as shown in Table 1 and as described in this example with preferably the composition being near the mid-range of the values given in Table 1. Coating was conducted at 36 ASF, 45 ASF and 68 ASF.

**[0033]** The high strength steel specimens were tested by static tensile loading at 75 percent of established notch ultimate tensile strength (dry test). The specimens were loaded continuously for at least 200 hours. The specimens withstood the loading for more than 200 hours and exhibit satisfactory low hydrogen embrittlement characteristics. Best results occurred at 45 ASF, giving a good coating distribution, good resistance to corrosion and good resistance to hydrogen embrittlement. Specimens at 36 ASF and 68 ASF also showed good results in all categories, but the specimen at 68 ASF showed slight corrosion.

**[0034]** High-strength steels are generally those steels having a tensile strength, as a result of alloys being heat-treated, to a tensile strength of about 200 ksi or higher, and more
particularly 220 ksi. The invention is particularly advantageous to high strength steels having the stated tensile strength or higher. However, the invention is also useful for other steels and metals, such as copper, which are susceptible to hydrogen embrittlement during electro-deposition in a solution which liberates hydrogen. The invention is also useful for coating other conductive substrates such as graphite. The invention is an alternative to corrosive acid bath plating, and plating baths containing agents which facilitate hydrogen embrittlement.

[0035] In summary, in the past, there was an attempt to achieve corrosion protection of high strength steels while avoiding hydrogen embrittlement through cadmium plating. Cadmium is a known carcinogen and air pollutant. The process also uses cyanide and special precautions are needed to avoid releasing this as a harmful gas. An acid zinc-nickel plating process that is used for lower strength steels poses problems with hydrogen embrittlement, particularly for higher strength steels.

[0036] The present invention is a more environmentally acceptable plating process for high strength steels that does not introduce hydrogen embrittlement problems, or at least minimizing such problems. The low hydrogen embrittlement zinc-nickel plating process of the invention is alkaline in nature and utilizes commercially available chemicals for plating bath preparation and replenishment. The deposited coating is primarily 85 to 95 percent zinc by weight and 5 to 15 percent nickel by weight, and will have a dull appearance, over a wide range of current density, an effective range of 30 to 68 ampere-per-square-foot. The engineering properties of this coating are low embrittlement, good corrosion resistance, excellent paint base and lubricity. This process can be used on steels heat-treated at 220 ksi tensile strength or higher, replacing low hydrogen embrittlement cadmium and low hydrogen embrittlement cadmium-titanium plating.

[0037] The description of the invention is merely exemplary in nature and, thus, variations that do not depart from the gist of the invention are intended to be within the scope of the invention. Such variations are not to be regarded as a departure from the spirit and scope of the invention.

What is claimed is:

1. A method for producing a corrosion-resistant article, said article being conductive and subject to hydrogen uptake during electroplating of a coating, said method comprising:
   electroplating a zinc-nickel coating on said article in an aqueous, basic plating solution containing zinc ions and nickel ions, an electrolyte in the form of a soluble hydroxide salt, the weight ratio of zinc ions to nickel ions in said solution being sufficient to provide said coating comprising from about 85% to about 95% by weight zinc, and about 5% to about 15% by weight nickel, provided that said plating solution is substantially free of brightening agents.

2. The method of claim 1, wherein said plating solution is substantially free of said brightening agents which retard hydrogen bake-out.

3. The method of claim 1, wherein said article when coated is dull in appearance relative to an article coated in the presence of the brightening agents.

4. The method of claim 1, wherein the article comprises high-strength steel and the article when coated has low hydrogen embrittlement.

5. The method of claim 1, wherein the article when coated has low hydrogen embrittlement being low relative to an article coated in the presence of brighteners.

6. The method of claim 1, wherein the article is plated at a current density of at least about 25 amperes per square foot.

7. The method of claim 1, wherein the article is coated at a current density of less than 75 amperes per square foot.

8. The method of claim 1, wherein the article is coated at a current density of about 30 amperes per square foot up to about 70 amperes per square foot.

9. The method of claim 1, wherein the current density is about 30 to about 68 amperes per square foot.

10. The method of claim 1, wherein the zinc ions of said solution are provided by a precursor zinc compound.

11. The method of claim 1, wherein the nickel ions of said solution are provided by a precursor nickel compound.

12. The method of claim 1, wherein the hydroxide salt contains a group one alkali metal.

13. The method of claim 1, wherein the hydroxide salt is sodium hydroxide.

14. The method of claim 1, wherein the plating solution comprises a nickel complexing agent.

15. The method of claim 14, wherein the nickel complexing agent is diethylene triamine.

16. The method of claim 1, wherein the plating solution is at a pH in a range of at least about 12 and less than 14.

17. The method of claim 1, wherein the zinc ion is present in an amount ranging from about 1.17 to about 1.45 ounces per gallon; the nickel ion is present in an amount ranging from about 0.12 to about 0.15 ounces per gallon and the sodium hydroxide is present in an amount ranging from about 17.4 to about 21.2 ounces per gallon.

18. The method of claim 1, wherein the weight ratio of zinc to nickel is in a range of about 10:1 to about 11:1.

19. An aqueous composition for the electrodeposition of zinc-nickel alloys which comprises:
   at least one ounce per gallon zinc, at least 0.1 ounce per gallon nickel, at least 15 ounces per gallon sodium hydroxide, a weight ratio of zinc/nickel of at least 10:1, a pH of at least 12 and less than 14, and being substantially free of brightening agents.

20. An aqueous composition for the electrodeposition of zinc-nickel alloys which consists essentially of:
   at least one ounce per gallon zinc, at least 0.1 ounce per gallon nickel, at least 15 ounces per gallon sodium hydroxide, a weight ratio of zinc/nickel of at least 10:1, a pH of at least 12 and less than 14, and being substantially free of organics except for nickel-complexing agents.

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