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54 **ZINC-NICKEL ELECTROPLATED ARTICLE AND METHOD FOR PRODUCING THE SAME.**

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Description

The present invention relates to a method for producing a corrosion-resistant article exhibiting low hydrogen embrittlement characteristics.

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 with an acid, or most importantly, by cathodically discharging hydrogen at the surface of the steel. Since most high-strength steels have corrosion-resistant coatings that are applied by less than 100 percent efficient 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.

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, however, the cadmium-titanium alloy plating bath contains both cadmium and cyanide, which create disposal problems unless expensive waste treatment equipment is employed.

Zinc-nickel alloys have been suggested for electroplating onto steels to render them corrosion-resistant. The plating parameters of a zinc-nickel alloy plating bath are much easier to control and maintain than a cadmium-titanium bath. Additionally, 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. Most prior zinc-nickel baths have, however, been suggested only for high-speed plating. High-speed plating techniques are unsatisfactory for rack plating of larger metal parts. Although it has been suggested that a zinc-nickel bath can be plated at low and medium current densities by employing an ammonium chloride electrolyte, prior attempts at plating low current densities have led to pitted and spongy deposits that do not provide good corrosion resistance. In addition, these prior attempts to produce a zinc-nickel corrosion-resistant coating at low current densities have led to a relatively high degree of hydrogen embrittlement in plated high-strength steel parts to which the coating has been applied.

US-A-4 285 802 describes an aqueous bath for producing a bright zinc-nickel alloy electroplated deposit. The bath includes a soluble zinc-contain-

ing compound, a soluble nickel salt, an ammoniated electrolyte, a non-ammoniated electrolyte, a nonionic polyoxyalkylated surfactant and an aromatic carbonyl compound. This document furthermore describes a method for producing corrosion-resistant zinc-nickel coated articles by electroplating with said electroplating baths as well as substrates having a nickel-zinc alloy electrodeposit thereon.

The present invention provides a method for producing a corrosion-resistant article, such as a high-strength steel, by applying a corrosion-resistant coating of a zinc-nickel alloy with electroplating techniques. A high-strength steel article coated in accordance with the present invention exhibits low hydrogen embrittlement characteristics. The hydrogen embrittlement of the article is maintained at a relatively low level by electroplating the zinc-nickel coating on the article in an aqueous acidic plating solution containing zinc and nickel ions, an electrolyte in the form of a soluble ammonium salt, and a polyoxyalkylated nonionic surfactant. These zinc-nickel alloys are electroplated from a bath containing: from 3.0 to 75.0 g of zinc ions, e.g. selected from the group consisting of zinc chloride, zinc sulfate, zinc fluoborate, zinc acetate and mixtures thereof; from 3.0 to 75.0 g of nickel ions, e.g. selected from the group consisting of nickel chloride, nickel sulfate, nickel sulfamate, nickel fluoborate, nickel acetate, and mixtures thereof; from 3.0 to 100 g of ammonium ions, e.g. in the form of a soluble ammonium salt of hydrochloric acid, sulfuric acid, fluoboric acid, acetic acid, or mixtures thereof; and from 0.5 to 20 g/l of a nonionic polyoxyalkylated surfactant. The bath must also contain at least about 15 g of an anion selected from the group consisting of chloride, fluoborate, and mixtures thereof. In addition, acid anions selected from chloride, sulfate, fluoborate, acetate, sulfamate, and mixtures thereof must be present in a molar amount at least equal to the combined molar amount of zinc, nickel, and ammonium ions present in the bath. The bath can also contain a boric acid buffer, an anionic surfactant, and a brightener if desired. The bath is effectively operated at a pH of from 3.0 to 7.0 and at a temperature ranging from 15°C to 45°C. The potential applied across the anode and the cathode workpiece is sufficient to provide current densities of 0.05 to 200 amperes per square decimeter at the cathode workpiece surface, although current densities below about 12.0 amperes per square decimeter are preferred to produce low hydrogen embrittlement characteristics.

The electroplating bath described above is free of cadmium ions, cyanides, and chelating agents. Yet the bath has a high cathode efficiency, and produces smooth adherent, ductile leveling and fine-grained, zinc-nickel alloy deposits over a wide range of plating conditions and cathode current density. Furthermore, an article plated with the zinc-nickel alloy exhibits lower hydrogen embrittlement and substantially greater corrosion

resistance than an article coated with zinc or zinc-nickel alloys of the prior art. The process can also be utilized to provide zinc-nickel alloy deposits on other substrates, both metallic and nonmetallic, as long as the substrate is conductive. For example, the process can be employed to provide a zinc-nickel alloy deposit on a graphite-epoxy composite structure. Additionally, the bath is very stable, is easy to control, has a high conductivity, while requiring only simple waste treatment procedures.

A zinc-nickel alloy can be electrodeposited onto a variety of electrically conductive substrates in accordance with the present invention. For example, a zinc-nickel alloy can be electrodeposited onto a graphite-epoxy article for the purpose of making that article corrosion-resistant. 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 titanium-cadmium corrosion-resistant coatings.

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 and vapor-degreased in accordance with conventional procedures normally employed in the plating arts. After cleaning and degreasing, the article is completely dried and then cleaned with an abrasive blast. Within a relatively short period of time after the abrasive cleaning, the article is rinsed in cold water for one-half to five minutes. The part is then activated by immersing it in an acid solution for from five to 30 seconds. Within two minutes from the time the part is retrieved from the acid solution, it is rinsed with cold water for a minimum of 30 seconds up to approximately six minutes maximum. Within two minutes after the completion of the cold water rinse, the part can be immersed in the zinc-nickel plating bath as described below.

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 ammonium salt, along with a nonionic polyoxyalkylated surfactant. The 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 acid anions, and that at least a portion of the acid anions comprise chloride or fluoborate. The addition of a buffer such as boric acid, an anionic surfactant, and brighteners are optional, but preferred for the commercial plating embodiment of the present invention.

The zinc cations can be provided by a variety of water-soluble zinc compounds. These compounds can include zinc oxide, which is capable of forming a zinc salt in the presence of acid

anions, such as chloride ions that are normally present in an aqueous bath prepared in accordance with the present invention. The water-soluble compounds also include zinc salts such as zinc chloride, zinc sulfate, zinc fluoborate, zinc acetate and, of course, the various combinations and mixtures thereof. Concentration of the zinc salt is sufficient to provide from about 3.0 to about 75.0 g of zinc ion per liter of solution. Preferably, the zinc ions should be present in an amount ranging from 6.0 to 30.0 g per liter of solution.

The nickel salts can be provided from a variety of water-soluble nickel salts, including nickel chloride, nickel sulfate, nickel sulfamate, nickel fluoborate, nickel acetate, and the various mixtures and combinations thereof. The nickel salt is present in an amount to provide from about 3.0 to about 75.0 g of nickel ion per liter of solution. It is preferred that about 3.0 to about 30.0 g of nickel ion per liter of solution be employed. The nickel to zinc ratio can be varied from 0.4:1 to 4:1, while still obtaining a satisfactory coating. At low nickel/zinc ratios hydrogen embrittlement is minimized. At low ratios, hydrogen reembrittlement tends to be aggravated. For a plated coating exhibiting optimum corrosion resistance, it is preferred that the weight ratio of nickel ion to zinc ion be on the order of 1:1 to 2:1.

The conductivity of the electroplating bath is increased by the presence of the electrolyte. The preferred electrolytes include soluble ammonium salts of hydrochloric acid, sulfuric acid, fluoboric acid, acetic acid, and the various mixtures and combinations thereof. The ammonium salt is present in the bath in an amount sufficient to provide from 3.0 to 100 g of ammonium ion per liter of solution. Preferably, the ammonium ion is present in the weight range of from 50.0 to 90.0 g per liter of solution. While any of the aforementioned ammonium salts can be employed as the electrolyte, it is most preferred that either ammonium chloride or ammonium fluoborate be employed as the salt from which the ammonium ion is derived. These salts provide relatively uniform plating results over a wider range of current densities. The bath contains at least 15.0 g of chloride or fluoborate anions or mixtures thereof per liter of solution. The acid anions, including chloride, sulfate, fluoborate, acetate, sulfamate and mixtures thereof are present in a molar amount at least equal to the combined molar amount of zinc, nickel and ammonium present in the solution. It is preferred that the acid anions be present in the range of from 15.0 to 200 g per liter of solution while 120 to 200 g of acid anions per liter of solution are preferred. Of the acid anions, the chloride anion is most preferred. Consequently, the most preferred bath is one composed primarily of zinc chloride, nickel chloride, and ammonium chloride.

The presence of a nonionic polyoxyalkylated surfactant in the zinc-nickel plating bath is critical to producing a corrosion-resistant, coated high-strength steel that has low hydrogen embrittlement. The presence of the nonionic polyoxyalky-

lated surfactant produces a zinc-nickel coating that is smooth, adherent, ductile, leveling, and fine-grained, over a wide range of plating conditions and cathode current densities. A wide variety of surface-active polyoxyalkylated compounds can be employed in accordance with the present invention as long as they are soluble in the aqueous bath. The following are representative examples of broad classes of compounds that can be employed in accordance with the present invention: alkoxyated alkyl phenols, alkoxyated alkyl naphthols, alkoxyated aliphatic monohydric alcohols, alkoxyated polyoxypropylene glycols, alkoxyated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, alkoxyated ethylene diamine, alkoxyated fatty acids, alkoxyated amides and alkoxyated esters. The polyethoxylated alkyl phenols, however, have been found to be particularly effective in producing corrosion-resistant coated substrates having a low hydrogen embrittlement in accordance with the present invention. Particular polyethoxylated alkyl phenol surfactants that are commercially available include ethoxylated nonyl phenol sold under the trade name "Tergitol NP-15[®]" by Union Carbide Corporation and under the trade name "Igepal CO-730[®]" by GAF Corporation. The latter surfactant contains approximately 15 repeating ethyleneoxy units in the hydrophilic portion of the molecule. Other suitable nonionic surfactants include "Igepal CO-887[®]" from GAF Corporation and "Nentronyx 656[®]" from Millmaster Onyx Corporation. The nonionic surfactant must be present in the bath in accordance with the present invention in an amount ranging from 0.5 to 20.0 g per liter of solution. It is most preferred, however, that from 1.0 to 5.0 g per liter of solution be employed.

Although the presence of the nonionic polyoxyalkylated surfactant in combination with the zinc, nickel and ammonium cations, and chloride and/or fluoborate anions are required to produce a corrosion-resistant coated high-strength steel substrate in accordance with the present invention, other materials can be added to enhance desirable characteristics in the plating process as well as in the final product. For example, boric acid may be advantageously included in the bath to function as a buffer. Boric acid can be present in the range of from 1.0 g per liter of solution up to saturation of boric acid in the bath.

An anionic surfactant is preferably added to the bath to increase the high end of the cathode current density range and to further improve the low hydrogen embrittlement characteristics of the final product. Although anionic surfactants in general tend to be insoluble in plating baths, the nonionic polyoxyalkylated surfactants function as a solubilizer for the anionic surfactants. Numerous anionic surfactants function as a solubilizer for the anionic surfactants. Numerous anionic surfactants can be employed in accordance with the present invention. However, the alcohol sulfates and the alkyl aryl sulfonates are found to be particularly successful. A suitable alcohol sulfate includes the sodium lauryl sulfate commercially

available from E.I. du Pont de Nemours and Company, Inc. under the trade name "Duponol ME Dry[®]". A suitable alkyl aryl sulfonate is the sodium dodecylbenzene sulfonate available from Stepan Chemical Company under the trade name "Nacconol 90F[®]". The anionic surfactant can be present in the bath in amounts ranging from 0.2 to 7.5 g per liter of solution, although from 0.4 to 2.0 g per liter of the anionic surfactant are preferred. It is also to be noted that the foregoing list of anionic surfactants is not intended to be exclusive. Other anionic surfactants that are soluble in the system otherwise formulated in accordance with the present invention and that do not detract from the superior results obtained by the present invention can be employed.

Organic brighteners can also be employed to provide bright, specular deposits over the useful cathode current density ranges, that is, from 0.3 to 4.5 amperes per square decimeter. Suitable organic brighteners include the ring-halogenated aryl aldehydes and aryl olefinic ketones. Examples of the ring-halogenated aryl aldehydes include ortho-chlorobenzaldehyde, para-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, and 2,6-dichlorobenzaldehyde. An example of a suitable aryl olefinic ketone is benzylidene acetone. Other known organic brighteners such as aryl ketones, aryl aldehydes, ring-halogenated aryl ketones, heterocyclic ketones and aldehydes, as well as aryl olefinic aldehydes can be employed. The most preferred brighteners are ortho-chlorobenzaldehyde and benzylidene acetone. These brighteners can be employed in the bath in amounts ranging from 0.02 to 2.0 g per liter of solution. The most preferred range includes the brighteners in amounts ranging from 0.05 to 1.0 g per liter of solution.

The zinc-nickel plating process is carried out in the above described pH, temperature, and current density ranges. When carried out with a preferred solution as outlined above and within the preferred operating ranges set forth below, an alloy containing, for example, from 80 to 95 percent by weight of zinc with the balance being nickel is produced. This coating will provide excellent corrosion resistance as well as sufficient porosity to allow hydrogen embrittlement to be relieved.

The bath is effectively operated in a pH range of from 3.0 to 7.0 while a pH range from 5.5 to 6.5 is preferred. It is preferred that the pH of the bath be adjusted by the addition of ammonium hydroxide or hydrochloric acid as the need may be, so as to avoid 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 occurs over a broad temperature range of from 15°C to 45°C while the narrower range of from 20°C to 32°C is preferred. The cathode current densities range from 0.05 to 200 amperes per square decimeter, preferably 0.05 to 12.0 amperes per square decimeter and still yield a satisfactory corrosion-resistant coating and article having a relatively low hydrogen

embrittlement. However, current densities in the range of from 2.0 to 4.0 amperes per square decimeter are preferred.

Although not necessary, a chromate or phosphate treatment of the part can follow the zinc-nickel plating step. In any event, within eight hours of completion of the plating step, the part is baked to relieve hydrogen embrittlement. Most steels except carburized steel and 440 steels can be baked at temperatures on the order of 176.7°C to 204.4°C for a minimum of 12 hours. Carburized steels and 440 steels, however, should be baked at a lower temperature of from 121.1°C to 148.9°C for only five to eight hours. If desired, the part can be chromate or phosphate treated subsequent to the hydrogen embrittlement bake.

Examples

The following examples are included to assist one of ordinary skill in making and using the invention. Examples I, II, IV, V are comparison examples; example IX shows two embodiments, one of which is also a comparative example.

All parts and percentages referred to in the following examples are by weight unless otherwise indicated. Additionally, when the Hull cell is mentioned, testing was undertaken utilizing a conventional 267 ml Hull cell employing three amperes of current for three minutes. The bath was not agitated. The pH adjustments were made as necessary by utilizing appropriate acids or ammonium hydroxide.

Example I

An aqueous electroplating bath containing no surfactant was prepared containing per liter of solution, 15 grams of zinc oxide, 47.5 grams of nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 250 grams of ammonium chloride and 20 grams of boric acid. The pH of the bath was 5.7 and was maintained at a temperature of 40°C. Only zinc was employed as an anode. A Hull cell panel was prepared with current densities of up to 8.0 amperes per square decimeter. At a current density of up to 1.5 amperes per square decimeter, the zinc-nickel alloy deposit was semi-bright with a blue tint, indicating a satisfactory deposit. At current densities ranging from 1.5 to 4.0 amperes per square decimeter, the deposit was pitted. The pitting, of course, is an undesirable characteristic in a corrosion-resistant coating. At current densities from 4.0 to 8.0 amperes per square decimeter the deposit was grey, indicating a satisfactory deposit. However, above eight amperes per square decimeter, the deposit was dark grey and slightly spongy. Spongy deposits are undesirable.

Example II

The procedure of Example I was repeated, with the exception that 0.375 gram per liter of solution of an anionic surfactant, "DuPont ME Dry", was added. The temperature of the bath was about 31°C. The bath was cloudy. A Hull cell panel was prepared. The panel generally appeared blotchy.

At a current density of up to 0.7 amperes per square decimeter, the zinc-nickel alloy deposit was cloudy. At a current density of from 0.7 to 2.0 amperes per square decimeter, the deposit was bright; however, the deposit was pitted at current density up to 1.5 amperes per square decimeter. At current densities ranging from 2.0 to 9.0 amperes per square decimeter, the deposit was cloudy. Above 9.0 amperes per square decimeter, the deposit was a blue-black.

Example III

The procedure of Example II was again repeated, but this time adding 3.0 grams per liter of "Tergitol NP-15", a nonionic surfactant, to the plating bath. A Hull cell panel was prepared. There was no blotchy deposit on the panel. At a current density up to 6.0 amperes per square decimeter, the zinc-nickel alloy deposit was bluish bright. At current densities ranging from 6.0 to 12.0 amperes per square decimeter, the deposit was grey. Above 12.0 amperes per square decimeter, a blue-black deposit was obtained. No spongy deposit was noted. Both the coverage of the plating bath and the throwing power of the plating were better in the presence of the nonionic surfactant when compared with the baths of both Example I and Example II.

Example IV

An aqueous electroplating bath was prepared containing per liter of solution: 47 grams of zinc chloride, 61 grams of nickel chloride; 250 grams of ammonium chloride; 20 grams of boric acid. The pH of the bath was adjusted to 5.9 by the addition of ammonium hydroxide. The temperature of the bath was 24°C. Notched tensile specimens manufactured and tested in accordance with ASTM F-519, Type Ia, were plated in the bath. Two nickel and two zinc rods having similar area were used as anodes and arranged symmetrically about the specimens. The specimens were plated at preselected current densities for preselected times. After plating, the specimens were baked for 12 hours at 190°C. The specimens were then tested by static tensile loading at 75 percent of established notch ultimate tensile strength. The specimens were loaded continuously for at least 150 hours or until failure. The specimens that withstand the loading for more than 150 hours exhibit satisfactory low hydrogen embrittlement characteristics.

Two specimens were plated at an average cathode current density of 1.0 ampere per square decimeter for 30 minutes. One specimen failed the static tensile test 12.7 hours after loading. The other specimen passed the loading test and was removed from the test device after 167 hours. Another specimen was plated at 2.0 amperes per square decimeter for 15 minutes. This specimen also passed the loading test and was removed from the test apparatus after 167 hours; however, a fourth specimen plated at two amperes per square decimeter for 30 minutes failed 36.5 hours after loading. The plated deposit for specimens

coated at both 1.0 and 2.0 amperes per square decimeter was found to contain about 85 percent zinc and 15 percent by weight nickel.

Example V

An aqueous electroplating bath was prepared containing per liter of solution: 17.8 grams of zinc oxide; 35.6 ml of hydrochloric acid (38 percent by weight HCl); 24 grams of nickel chloride; 220 grams of ammonium chloride; 20 grams of boric acid; approximately 8 ml of ammonium hydroxide (29 percent by weight NH_3). The pH of the bath was 6.2. The temperature of the bath was 24°C. Notched tensile specimens were prepared in accordance with the standards set forth in the previous Example. Three specimens were plated at 1.5 amperes per square decimeter for 20 minutes and three specimens were plated at 3.0 amperes per square decimeter for ten minutes. The zinc-nickel deposited on the specimens was dull with heavy pitting and therefore unsatisfactory from the corrosion-resistance standpoint. All of the specimens were tested by loading them in accordance with the procedure set forth in Example IV, with the exception that the specimens were loaded for 200 hours. All specimens passed the 200-hour loading test.

Example VI

The procedure of Example V was repeated with the exception that the pH of the bath was adjusted to 5.8 and 2.25 grams per liter of solution of a nonionic polyoxyalkylated surfactant ("Tergitol NP-15") were added. Five notched tensile specimens were plated at 30 amperes per square decimeter for 7.5 minutes. The deposit was satisfactory. The fractured cross-section had a grainy look when viewed under magnification. All specimens passed the 200-hour loading test.

Example VII

The procedure of Example VI was repeated with the exception that 0.75 gram per liter of an anionic surfactant ("Duponol ME Dry") was also added to the bath. Three notched tensile specimens were plated at 3.0 amperes per square decimeter for 7.5 minutes. When viewed under magnification, an improvement in the ductile nature of the deposits was observed. All specimens passed a 200-hour loading test.

Example VIII

The procedure of Example VII was repeated with the exception that the pH of the bath was adjusted to 6.2 by the addition of ammonium hydroxide. Two notched tensile specimens were plated at 3.0 amperes per square decimeter for 7.5 minutes. The ductile appearance of the deposits was observed under magnification. All specimens passed the 200-hour loading test.

Example IX

An aqueous electroplating bath was prepared containing per liter of solution: 50 grams of zinc oxide; 100 ml of hydrochloric acid; 167 grams of

nickel chloride; 90 grams of ammonium chloride; 20 grams of boric acid; approximately 75 ml of ammonium hydroxide. The pH of the bath was 5.9. The temperature of the bath was about 28°C. A copper wire was plated at a current density of approximately 100 amperes per square decimeter for approximately 20 seconds at a linear speed of 98 feet per minute. The deposit was dark grey and grainy. Another copper wire was plated at the same condition as before, with the exception that 2.25 grams per liter of solution of a nonionic polyoxyalkylated surfactant ("Igepal CO-730") and 0.75 grams per liter of an anion surfactant ("Duponol ME Dry") were also added to the bath. Now the deposit was light grey and fine grained.

Conclusion

In summary, the zinc-nickel coating plated in accordance with the present invention not only provides excellent corrosion resistance to steel articles but also yields an end product that, when baked, has very low hydrogen embrittlement characteristics.

Although the primary use of the present invention is currently producing a corrosion-resistant coating on steel parts that results in low hydrogen embrittlement of the steel, the invention can also be employed to plate metal strips and wires, as well as other articles. Electroplating of steel parts to produce a product exhibiting low hydrogen embrittlement is generally performed at relatively low current densities. It is, however, generally desirable to plate metal strips and wires at high current densities while still producing a good corrosion-resistant coating. For example, a plating solution containing an ammonium chloride electrolyte and a nonionic surfactant can be employed to plate at current densities up to about 200 amperes per square decimeter. At such high current densities, it is preferable to agitate the solution during plating and also to increase the zinc and nickel content in the solution over that normally used at low current densities.

The present invention has been described in relation to a preferred embodiment thereof and several alternatives thereto. One of ordinary skill, after reading the foregoing specification, will be able to effect various changes, substitutions of equivalents and other alterations without departing from the broad concepts disclosed herein. It is therefore intended that the scope of Letters Patent granted hereon be limited only by the definition contained in the appended claims and equivalents thereof.

Claims

1. A method for producing a corrosion-resistant article said article being conductive, said method comprising:

electroplating a zinc-nickel coating on said article in an aqueous, acidic plating solution containing zinc and nickel ions, an electrolyte in the form of a soluble ammonium salt, and a polyoxyalkylated nonionic surfactant, the bath

containing 3.0 to 75.0 g/l zinc ions, 3.0 to 75.0 g/l nickel ions, 3.0 to 100 g/l ammonium ions, 0.5 to 20 g/l of a nonionic polyoxyalkylated surfactant, at least 15 g/l of an anion selected from chloride, fluoborate, and mixtures thereof and, in addition, acid anions selected from chloride, fluoborate, and mixtures thereof and, in addition, acid anions selected from chloride, sulfate, fluoborate, acetate, sulfamate, and mixtures thereof in a molar amount of at least equal to the combined molar amount of zinc, nickel, and ammonium ions present in the bath, the weight ratio of nickel to zinc in said solution being in the range of from 0.4 to 1.0 to 4.0 to 1.0, the bath being operated in a pH range of from 3.0 to 7.0, at a temperature of 15°C to 45°C and a current density in the range of from 0.05 to 200 amperes per square decimeter, and said coating comprising from 80 to 95% by weight zinc, the balance being nickel.

2. The method of Claim 1 wherein said article comprises high-strength steel and said article being plated at a current density of from 0.5 to 12.0 amperes per square decimeter.

3. The method of Claim 1 wherein said zinc is present in the form of zinc oxide, zinc chloride, zinc sulfate, zinc fluoborate, zinc acetate and mixtures thereof; wherein said nickel is present in the form of nickel chloride, nickel sulfate, nickel sulfamate, nickel fluoborate, nickel acetate and mixtures thereof; and wherein said electrolyte is present in the form of a soluble salt of hydrochloric acid, sulfuric acid, fluoboric acid, acetic acid and mixtures thereof.

4. The method of Claim 1 wherein said nonionic, polyoxyalkylated surfactant is selected from the group consisting of alkoxyated alkyl phenols, alkoxyated alkyl naphthols, alkoxyated aliphatic monohydric alcohols, alkoxyated polyoxypropylene glycols, alkoxyated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, alkoxyated ethylene diamine, alkoxyated fatty acids, alkoxyated amides and alkoxyated esters.

5. The method of Claim 4 wherein said nonionic surfactant comprises a polyethoxylated alkyl phenol.

6. The method of Claim 1 wherein said acid anions are present in a molar amount at least equal to the combined molar amount of nickel, zinc and ammonium ions, the sum total of said acid anions being present in said solution in the range of from 15.0 to 200 grams per liter.

7. The method of Claim 1 wherein said nonionic surfactant is present in an amount ranging from 0.5 to 20.0 grams per liter of solution.

8. The method of Claim 7 wherein said nonionic surfactant is present in an amount ranging from 1.0 to 5.0 grams per liter of solution.

9. The method of Claim 1 wherein said bath further contains boric acid in an amount ranging from about 1.0 gram per liter of solution to saturation in said solution.

10. The method of Claim 1 wherein said bath further contains an anionic surfactant in an amount ranging from 0.2 to 7.5 grams per liter of solution.

11. The method of Claim 10 wherein said anionic surfactant comprises an alcohol sulfate, an alkyl aryl sulfonate, or mixtures thereof.

12. The method of Claim 10 wherein said anionic surfactant is present in an amount ranging from 0.4 to 2.0 grams per liter of solution.

13. The method of Claim 1 wherein said bath further contains a brightener in an amount ranging from 0.02 to 2.0 grams per liter of solution.

14. The method of Claim 13 wherein said brightener is present in said bath in an amount ranging from 0.05 to 1.0 gram per liter of solution.

15. An electroplating bath for producing a conductive corrosion-resistant article comprising 3.0 to 75.0 g/l zinc ions, 3.0 to 75.0 g/l nickel ions, 3.0 to 100 g/l ammonium ions, 0.5 to 20 g/l of a nonionic polyoxyalkylated surfactant, at least 15 g/l of an anion selected from chloride, fluoborate, and mixtures thereof and, in addition, acid anions selected from chloride, sulfate, fluoborate, acetate, sulfamate, and mixtures thereof in a molar amount at least equal to the combined molar amount of zinc, nickel, and ammonium ions present in the bath, the weight ratio of nickel to zinc in said solution being in the range of from 0.4 to 1.0 to 4.0 to 1.0.

16. The bath of Claim 15 wherein said zinc is present in the form of zinc oxide, zinc chloride, zinc sulfate, zinc fluoborate, zinc acetate and mixtures thereof; wherein said nickel is present in the form of nickel chloride, nickel sulfate, nickel sulfamate, nickel fluoborate, nickel acetate, and mixtures thereof; and wherein said electrolyte is present in the form of a soluble salt of hydrochloric acid, sulfuric acid, fluoboric acid, acetic acid and mixtures thereof.

17. The bath of Claim 15 wherein said nonionic, polyoxyalkylated surfactant is selected from the group consisting of alkoxyated alkyl phenols, alkoxyated alkyl naphthols, alkoxyated aliphatic monohydric alcohols, alkoxyated polyoxypropylene glycols, alkoxyated 2,4,7,9-tetramethyl-5-decyne-4,7-diol, alkoxyated ethylene diamine, alkoxyated fatty acids, alkoxyated amides and alkoxyated esters.

18. The bath of Claim 17 wherein said nonionic surfactant comprises a polyethoxylated alkyl phenol.

19. The bath of Claim 17 wherein said acid anions are present in a molar amount at least equal to the combined molar amount of nickel, zinc and ammonium ions, the sum total of said acid anions being present in said solution in the range of from 15.0 to 200 grams per liter.

20. The bath of Claim 15 wherein said nonionic surfactant is present in an amount ranging from 0.5 to 20.0 grams per liter of solution.

21. The bath of Claim 15 wherein said acid anions are present in said solution in an amount ranging from 120 to 200 grams per liter of solution.

22. The bath of Claim 15 wherein said nonionic surfactant is present in an amount ranging from 1.0 to 5.0 grams per liter of solution.

23. The bath of Claim 15 wherein said bath

further contains boric acid in an amount ranging from about 1.0 gram per liter of solution to saturation in said solution.

24. The bath of Claim 15 wherein said bath further contains an anionic surfactant in an amount ranging from 0.2 to 7.5 grams per liter of solution.

25. The bath of Claim 24 wherein said anionic surfactant comprises an alcohol sulfate, an alkyl aryl sulfonate, or mixtures thereof.

26. The bath of Claim 15 wherein said bath further contains a brightener in an amount ranging from 0.02 to 2.0 grams per liter of solution.

27. The bath of Claim 26 wherein said brightener is present in said bath in an amount ranging from 0.05 to 1.0 gram per liter of solution.

Patentansprüche

1. Verfahren zur Herstellung eines korrosionsbeständigen Gegenstandes, der leitfähig ist, dadurch gekennzeichnet, daß:

ein Zink-Nickel-Überzug auf diesen Gegenstand elektroplattiert wird in einer wäßrigensaurigen Plattierungslösung, die Zink- und Nickelionen, einen Elektrolyten in Form eines löslichen Ammoniumsalzes und ein polyoxyalkyliertes, nichtionisches grenzflächenaktives Mittel enthält, wobei das Bad 3,0 bis 75,0 g/l Zinkionen, 3,0 bis 75,0 g/l Nickelionen, 3,0 bis 100 g/l Ammoniumionen, 0,5 bis 20 g/l eines nichtionischen, polyoxyalkylierten grenzflächenaktiven Mittels, mindestens 15 g/l eines Anions, ausgewählt aus Chlorid, Fluoborat und Gemischen davon, sowie zusätzlich Säureanionen, ausgewählt aus Chloridsulfat, Fluoborat, Acetat, Sulfamat und Gemischen davon, enthält, in einer Molmenge, die mindestens gleich ist der kombinierten Molmenge von Zink-, Nickel- und Ammoniumionen, die im Bad vorhanden sind, daß das Gewichtsverhältnis von Nickel zu Zink in der Lösung im Bereich von 0,4 bis 1,0 bis 4,0 bis 1,0 liegt, das Bad in einem pH-Bereich von 3,0 bis 7,0 bei einer Temperatur von 15 bis 45°C und einer Stromdichte im Bereich von 0,05 bis 200 A/dm² betrieben wird und der Überzug 80 bis 95 Gew.-% Zink, Rest Nickel, enthält.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Gegenstand hochfesten Stahl umfaßt und bei einer Stromdichte von 0,5 bis 12,0 A/dm² plattiert wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Zink in Form von Zinkoxid, Zinkchlorid, Zinksulfat, Zinkfluoborat, Zinkacetat oder Gemischen davon vorhanden ist, daß das Nickel in Form von Nickelchlorid, Nickelsulfat, Nickelsulfamat, Nickelfluoborat, Nickelacetat und Gemischen davon vorhanden ist und daß der Elektrolyt in Form eines löslichen Salzes der Salzsäure, Schwefelsäure, Fluoborsäure, Essigsäure und Gemischen davon vorhanden ist.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das nichtionische, polyoxyalkylierte grenzflächenaktive Mittel ausgewählt wird aus der Gruppe bestehend aus alkoxylierten Alkylphenolen, alkoxylierten Alkyl-naphtholen, alkoxylier-

ten aliphatischen einwertigen Alkoholen, alkoxylierten Polyoxypropylenglykolen, alkoxyliertem 2,4,7,9-Tetramethyl-5-decin-4,7-diol, alkoxyliertem Ethylendiamin, alkoxylierten Fettsäuren, alkoxylierten Amiden und alkoxylierten Estern.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel ein polyethoxyliertes Alkylphenol umfaßt.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Säureanionen in einer Molmenge vorhanden sind, die mindestens gleich ist der kombinierten Molmenge von Nickel-, Zink- und Ammoniumionen, wobei die Gesamtmenge der Säureanionen in der Lösung im Bereich von 15,0 bis 200 g/l liegt.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel in einer Menge von 0,5 bis 20,0 g/l Lösung vorhanden ist.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel in einer Menge von 1,0 bis 5,0 g/l Lösung vorhanden ist.

9. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Bad zusätzlich Borsäure in einer Menge von etwa 1,0 g/l Lösung bis zur Sättigung der Lösung enthält.

10. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Bad zusätzlich ein anionisches grenzflächenaktives Mittel in einer Menge von 0,2 bis 7,5 g/l Lösung enthält.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das anionische grenzflächenaktive Mittel ein Alkoholsulfat, Alkylarylsulfonat oder Gemische davon enthält.

12. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das anionische grenzflächenaktive Mittel in einer Menge von 0,4 bis 2,0 g/l Lösung vorhanden ist.

13. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Bad zusätzlich ein Glanzmittel in einer Menge von 0,02 bis 2,0 g/l Lösung enthält.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Glanzmittel in dem Bad in einer Menge von 0,05 bis 1,0 g/l Lösung vorhanden ist.

15. Elektroplattierungsbad für die Herstellung eines leitfähigen, korrosionsbeständigen Gegenstandes, enthaltend 3,0 bis 75,0 g/l Zinkionen, 3,0 bis 75,0 g/l Nickelionen, 3,0 bis 100 g/l Ammoniumionen, 0,5 bis 20 g/l eines nichtionischen polyoxyalkylierten grenzflächenaktiven Mittels, mindestens 15 g/l eines Anions, ausgewählt aus Chlorid, Fluoborat und Gemischen davon, und zusätzlich Säureanionen, ausgewählt aus Chlorid, Sulfat, Fluoborat, Acetat, Sulfamat und Gemischen davon, in einer Molmenge, die mindestens gleich ist der kombinierten Molmenge von Zink-, Nickel- und Ammoniumionen, die im Bad vorhanden sind, wobei das Gewichtsverhältnis von Nickel zu Zink in der Lösung im Bereich von 0,4 bis 1,0 bis 4,0 bis 1,0 liegt.

16. Bad nach Anspruch 15, dadurch gekennzeichnet,

zeichnet, daß das Zink in Form von Zinkoxid, Zinkchlorid, Zinksulfat, Zinkfluorborat, Zinkacetat oder Gemischen davon vorhanden ist, daß das Nickel in Form von Nickelchlorid, Nickelsulfat, Nickelsulfamat, Nickelfluorborat, Nickelacetat und Gemischen davon vorhanden ist und daß der Elektrolyt in Gegenwart eines löslichen Salzes der Salzsäure, Schwefelsäure, Fluoborsäure, Essigsäure und Gemischen davon vorhanden ist.

7. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das nichtionische, polyoxyalkylierte grenzflächenaktive Mittel ausgewählt wird aus der Gruppe bestehend aus alkoxylierten Alkylphenolen, alkoxylierten Alkyl-naphtholen, alkoxylierten aliphatischen einwertigen Alkoholen, alkoxylierten Polyoxypropylenglykolen, alkoxyliertem 2,4,7,9-Tetramethyl-5-decin-4, 7-diol, alkoxyliertem Ethylendiamin, alkoxylierten Fettsäuren, alkoxylierten Amiden und alkoxylierten Estern.

18. Bad nach Anspruch 17, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel ein polyethoxyliertes Alkylphenol umfaßt.

19. Bad nach Anspruch 17, dadurch gekennzeichnet, daß die Säureanionen in einer Molmenge vorhanden sind, die mindestens gleich ist der kombinierten Molmenge von Nickel-, Zink und Ammoniumionen, wobei die Gesamtmenge der Säureanionen in der Lösung im Bereich von 15,0 bis 200 g/l liegt.

20. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel in einer Menge von 0,5 bis 20,0 g/l Lösung vorhanden ist.

21. Bad nach Anspruch 15, dadurch gekennzeichnet, daß die Säureanionen in der Lösung in einer Menge von 120 bis 200 g/l Lösung vorhanden sind.

22. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das nichtionische grenzflächenaktive Mittel in einer Menge von 1,0 bis 5,0 g/l Lösung vorhanden ist.

23. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das Bad zusätzlich Borsäure in einer Menge von etwa 1,0 g/l Lösung bis zur Sättigung der Lösung enthält.

24. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das Bad zusätzlich ein anionisches grenzflächenaktives Mittel in einer Menge von 0,2 bis 7,5 g/l Lösung enthält.

25. Bad nach Anspruch 24, dadurch gekennzeichnet, daß das anionische grenzflächenaktive Mittel ein Alkoholsulfat, Alkylarylsulfonat oder Gemische davon enthält.

26. Bad nach Anspruch 15, dadurch gekennzeichnet, daß das Bad zusätzlich ein Glanzmittel in einer Menge von 0,02 bis 2,0 g/l Lösung enthält.

27. Bad nach Anspruch 26, dadurch gekennzeichnet, daß das Glanzmittel in dem Bad in einer Menge von 0,05 bis 1,0 g/l Lösung vorhanden ist.

Revendications

1. Un procédé pour produire un article résistant à la corrosion, ledit article étant conducteur, ledit procédé consistant:

à déposer par électrolyse un revêtement de zinc-nickel sur ledit article dans une solution de dépôt électrolytique acide, aqueuse, contenant des ions zinc et nickel, un électrolyte sous la forme d'un sel d'ammonium soluble et un tensioactif non ionique polyoxyalkylé, le bain contenant 3,0 à 75,0 g/l d'ions zinc, 3,0 à 75,0 g/l d'ions nickel, 3,0 à 100 g/l d'ions ammonium, 0,5 à 20 g/l d'un tensioactif polyoxyalkylé non ionique, au moins 15 g/l d'un anion choisi parmi les anions chlorure, fluoroborate et leurs mélanges et en outre des anions d'acides choisis parmi les anions chlorure, sulfate, fluoroborate, acétate, sulfamate et leurs mélanges, en quantité molaire au moins égale à la quantité molaire combinée des ions zinc, nickel et ammonium présents dans le bain, le rapport pondéral du nickel au zinc dans ladite solution étant dans la gamme de 0,4 : 1,0 à 4,0 : 1,0, le bain fonctionnant dans une gamme de pH de 3,0 à 7,0, à une température de 15 à 45°C et à une densité de courant dans la gamme de 0,05 à 200 A/dm² et ledit revêtement comprenant de 80 à 95 % en poids de zinc, le solde étant du nickel.

2. Le procédé selon la revendication 1, dans lequel ledit article consiste en acier à résistance élevée et ledit article étant soumis au dépôt électrolytique à une densité de courant de 0,5 à 12,0 A/dm².

3. Le procédé selon la revendication 1, dans lequel ledit zinc est présent sous la forme d'oxyde de zinc, de chlorure de zinc, de sulfate de zinc, de fluoroborate de zinc, d'acétate de zinc et leurs mélanges; dans lequel ledit nickel est présent sous la forme de chlorure de nickel, de sulfate de nickel, de sulfamate de nickel, de fluoroborate de nickel, d'acétate de nickel et leurs mélanges; et dans lequel ledit électrolyte est présent sous la forme d'un sel soluble d'acide chlorhydrique, d'acide sulfurique, d'acide fluoroborique, d'acide acétique et leurs mélanges.

4. Le procédé selon la revendication 1, dans lequel ledit tensioactif polyoxyalkylé non ionique est choisi parmi les alkyphénols alcoylés, les alkylnaphtols alcoylés, les monoalcools aliphatiques alcoylés, les polyoxypropyléneglycols alcoylés, les 2,4,7,9-tétraméthyl-5-décyne-4,7-diols alcoylés, les éthylènediamines alcoylées, les acides gras alcoylés, les amides alcoylés et les esters alcoylés.

5. Le procédé selon la revendication 4, dans lequel ledit tensioactif non ionique comprend un alkyphénol polyéthoxylé.

6. Le procédé selon la revendication 1, dans lequel lesdits anions d'acides sont présents en quantité molaire au moins égale à la quantité molaire combinée des ions nickel, zinc et ammonium, la somme totale desdits anions d'acides étant présente dans ladite solution dans la gamme de 15,0 à 200 g/l.

7. Le procédé selon la revendication 1, dans lequel ledit tensioactif non ionique est présent en quantité de 0,5 à 20,0 g/l de solution.

8. Le procédé selon la revendication 7, dans lequel ledit tensioactif non ionique est présent en quantité de 1,0 à 5,0 g/l de solution.

9. Le procédé selon la revendication 1, dans lequel ledit bain contient en outre de l'acide borique en quantité d'environ 1,0 g/l de solution à la saturation dans ladite solution.

10. Le procédé selon la revendication 1, dans lequel ledit bain contient en outre un tensioactif anionique en quantité de 0,2 à 7,5 g/l de solution.

11. Le procédé selon la revendication 10, dans lequel ledit tensioactif anionique comprend un sulfate d'alcool, un alkylarylsulfonate ou leurs mélanges.

12. Le procédé selon la revendication 10, dans lequel ledit tensioactif anionique est présent en quantité de 0,4 à 2,0 g/l de solution.

13. Le procédé selon la revendication 1, dans lequel ledit bain contient en outre un brillanteur en quantité de 0,02 à 2,0 g/l de solution.

14. Le procédé selon la revendication 13, dans lequel ledit brillanteur est présent dans ledit bain en quantité de 0,05 à 1,0 g/l de solution.

15. Un bain de dépôt électrolytique pour la production d'un article conducteur résistant à la corrosion, comprenant 3,0 à 75,0 g/l d'ions zinc, 3,0 à 75,0 g/l d'ions nickel, 3,0 à 100 g/l d'ions ammonium, 0,5 à 20 g/l d'un tensioactif polyoxyalkylé non ionique, au moins 15 g/l d'un anion choisi parmi les anions chlorure, fluoborate et leurs mélanges et en outre des anions d'acides choisis parmi les anions chlorure, sulfate, fluoborate, acétate, sulfamate et leurs mélanges en quantité molaire au moins égale à la quantité molaire combinée des ions zinc, nickel et ammonium présents dans le bain, le rapport pondéral du nickel au zinc dans ladite solution étant dans la gamme de 0,4 : 1,0 à 4,0 : 1,0.

16. Le bain selon la revendication 15, dans lequel ledit zinc est présent sous la forme d'oxyde de zinc, de chlorure de zinc, de sulfate de zinc, de fluoborate de zinc, d'acétate de zinc et leurs mélanges; dans lequel ledit nickel est présent sous la forme de chlorure de nickel, de sulfate de nickel, de sulfamate de nickel, de fluoborate de nickel, d'acétate de nickel et leurs mélanges; et dans lequel ledit électrolyte est présent sous la

forme d'un sel soluble d'acide chlorhydrique, d'acide sulfurique, d'acide fluoborique, d'acide acétique et leurs mélanges.

17. Le bain selon la revendication 15, dans lequel ledit tensioactif polyoxyalkylé non ionique est choisi parmi les alkylphénols alcoxylés, les alkylnaphtols alcoxylés, les monoalcools aliphatiques alcoxylés, les polyoxypropylèneglycols alcoxylés, les 2,4,7,9-tétraméthyl-5-décyne-4,7-diols alcoxylés, les éthylène-diamines alcoxylées, les acides gras alcoxylés, les amides alcoxylés et les esters alcoxylés.

18. Le bain selon la revendication 17, dans lequel ledit tensioactif non ionique comprend un alkylphénol polyéthoxylé.

19. Le bain selon la revendication 17, dans lequel lesdits anions d'acides sont présents en quantité molaire au moins égale à la quantité molaire combinée des ions nickel, zinc et ammonium, la somme totale desdits anions d'acides étant présente dans ladite solution dans la gamme de 15,0 à 200 g/l.

20. Le bain selon la revendication 15, dans lequel ledit tensioactif non ionique est présent en quantité de 0,5 à 20,0 g/l de solution.

21. Le bain selon la revendication 15, dans lequel lesdits anions d'acides sont présents dans ladite solution en quantité de 120 à 200 g/l de solution.

22. Le bain selon la revendication 15, dans lequel ledit tensioactif non ionique est présent en quantité de 1,0 à 5,0 g/l de solution.

23. Le bain selon la revendication 15, dans lequel ledit bain contient en outre de l'acide borique en quantité d'environ 1,0 g/l de solution à la saturation dans ladite solution.

24. Le bain selon la revendication 15, dans lequel ledit bain contient en outre un tensioactif anionique en quantité de 0,2 à 7,5 g/l de solution.

25. Le bain selon la revendication 24, dans lequel ledit tensioactif anionique comprend un sulfate d'alcool, un alkylarylsulfonate ou leurs mélanges.

26. Le bain selon la revendication 15, dans lequel ledit bain contient en outre un brillanteur en quantité de 0,02 à 2,0 g/l de solution.

27. Le bain selon la revendication 26, dans lequel ledit brillanteur est présent dans ledit bain en quantité de 0,05 à 1,0 g/l de solution.

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