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71 Applicant: THE DOW CHEMICAL COMPANY
Dow Center 2030 Abbott Road Post Office Box 1967
Midland Michigan 48640(US)

72 Inventor: McIntyre, John Mark
319 Petunia
Lake Jackson Texas 77566(US)

74 Representative: Weickmann, Heinrich, Dipl.-Ing. et al,
Patentanwälte Dipl.-Ing. H. Weickmann Dipl.-Phys.Dr. K.
Fincke Dipl.-Ing. F.A. Weickmann Dipl.-Chem. B. Huber
Dr.-Ing. H. Liska Möhlstrasse 22
D-8000 München 86(DE)

54 Process for electroplating metal parts.

57 This invention is an improved method of producing a coated metal part in a process which comprises electroplating a nickel-zinc coating onto an electrically conductive substrate from a bath containing nickel and zinc ions and removing substantially all the zinc from the coating. The improvement comprises supplying nickel and zinc ions to the bath from a plurality of nickel anodes and a plurality of zinc anodes. The total surface area of the zinc anodes, which projects toward the substrate is about twice as large as the total surface area of the nickel anodes which project toward the substrate. The bath composition is maintained at 0.75 to 1.25 molar nickel and 0.75 to 1.25 molar zinc by operating each anode at about the same current density. Electroplating is continued for a time and at a current density sufficient to deposit a 5 to 100 micron thick nickel-zinc coating onto the substrate. The coating is 60 to 70 weight percent zinc and 30 to 40 weight percent nickel.

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PROCESS FOR ELECTROPLATING METAL PARTS

The invention resides in a method for electroplating metal parts. These parts are useful as electrodes which are capable of reducing hydrogen overvoltage that may occur during electrolytic decomposition of water or
5 brine.

More particularly, the invention resides in a process of electroplating a nickel-zinc coating onto a substrate. The substrate to be plated must be a solid, electrically conductive substance. It may be
10 porous or nonporous and may include such substances as iron, nickel, ceramics and other materials well known to those skilled in the art. The substrate may be a substance upon which has been applied a protective coating, such as an iron substrate coated with nickel,
15 prior to the application of the nickel-zinc coating. A particular benefit to the process is the fact that the electroplating bath composition remains relatively constant. No make-up components must be added to the bath and no waste bath must be removed.

20 When a multi-component coating is to be applied onto a substrate by electroplating, it is very

difficult to apply a uniform, chemically consistent coating.

Various approaches have been used to solve the problem. For example, a single inert anode, such as graphite, has been used in an electrolytic cell to coat a cathode. In this procedure, the electrolyte composition is controlled and maintained at a constant concentration of the ions to be plated onto the cathode. However, this procedure requires constant attention and usually results in a poor coating because of the difficulties in maintaining the bath concentration constant.

Another method used involves the use of a single anode which contains one of the metals which is to be used as a coating component. The other metal or metals are added to the bath. The difficulty with this method is similar to that when an inert anode is used; i.e., maintaining the concentration of the bath at a constant level is very difficult.

Another approach which has been taken is the use of an anode containing all the components desired in the coating. However, when a single anode having multiple components is used, the anode does not dissolve uniformly. This causes variations in the bath composition and results in a non-uniform coating on the cathode.

Burns et al. in U.S. Patent 1,837,355 (December 22, 1931) teach a method using dual anodes, each having one component to be coated onto the cathode. They control the composition and concentration of the electrolyte to make the cathode potentials of each coating component substantially equal over the operating

portion of the current density range. However, with this procedure, the coating applied to the end of the cathode nearest one anode is rich in one component, while the coating on the other end of the cathode is
5 rich in the other component.

Coated metal parts formed from substrates coated with a nickel-zinc alloy are known. See U.S. Patents 3,420,754; 4,104,133 and 3,272,728.

This invention resides in a method for producing
10 a coated metal part by electroplating a nickel-zinc alloy coating onto an electrically conductive substrate from a bath containing nickel and zinc ions; and removing substantially all of the zinc from the coating; characterized by the steps of supplying nickel and zinc ions.
15 to the bath from a set of nickel anodes and from a set of zinc anodes, wherein the ratio of the total surface area projected toward the substrate by the zinc anode set, as compared to that projected by the nickel anode set, is about 2 to 1, maintaining the bath at a concentration of from 0.75 to 1.25 molar nickel and from 0.75
20 to 1.25 molar zinc by operating each of the individual anodes in each set at approximately the same current density; and electroplating for a time and at a current density sufficient to deposit a 5 to 100 micron thick
25 nickel-zinc coating onto the substrate, wherein the coating is from 60 to 70 weight percent zinc and 30 to 40 weight percent nickel.

In the electroplating method of the present invention, the substrate to be coated is used as a
30 cathode in an electroplating cell. A plurality of anode sets is provided. Each anode set contains one

component of the coating which is to be electroplated onto the cathode. For example, if a nickel-zinc coating is to be applied to the cathode, one anode set contains nickel, while another anode set contains zinc. Each
5 anode set is located in the electroplating cell parallel to the cathode, i.e., each anode is the same approximate distance from the cathode as is each other anode set. Anode sets may be located on one, or more than one, side of the cathode, depending upon the size and shape
10 of the cathode. An anode set may consist of a single anode or it may be a plurality of anodes.

Each anode set projects a surface area toward the cathode which is proportional to the concentration of that component in the coating. For example, if a
15 coating is desired which has a composition of 34 weight percent nickel and 66 weight percent zinc, the ratio of the projected surface area of the nickel containing anode set as compared to the projected surface area of the zinc containing anode set should be approximately
20 1:2. If one zinc anode and one nickel anode are used, the zinc anode should project a surface area toward the substrate which is twice as large as that projected by the nickel anode to result in a coating that is about 66 weight percent zinc and about 34 weight percent
25 nickel. However, if one nickel anode is used and two zinc anodes are used, each anode should project the same surface area toward the substrate. Since two zinc anodes are used with one nickel anode, the zinc anodes project toward the substrate a surface area twice as
30 large as that projected by the nickel anode. Any numerical combination of anodes may be used so long as the zinc anodes project a surface area twice as large as that of the nickel anodes.

In operation, current is provided to each anode set at a voltage sufficient to cause electroplating to occur. The current is supplied such that each anode has a current density (in amps per square foot of projected surface area) approximately equal to the
5 current density of each other anode.

The current density of each anode should be from 0.1 to 2 amps per square inch (ASI) (0.0155 to 0.31 amp/cm²). If the current density is too low, the
10 alloy composition changes. If, however, the current density is too high, side reactions occur which produce hydrogen and make the plating process less efficient. Preferably, the current density is from 0.2 to 1.0 ASI (0.031 to 0.155 amp/cm²) and most preferably the current
15 density is from 0.4 to 0.6 ASI (0.062 to 0.093 amp/cm²). For example, when nickel and zinc anodes are being used to apply a coating having a composition of 34 percent nickel and 66 percent zinc, the zinc anode set projects toward the cathode a surface two times greater than the
20 surface area projected by the nickel anodes. If the nickel anode set projects 2 square inches (12.9 cm²) of surface area, the zinc anode sets should project 4 square inches (25.8 cm²) of surface area. In operation, two amps of current would be provided to the nickel
25 anode set, while four amps of current would be supplied to the zinc anode set. Thus, each anode set would have a current density of 1 amp per square inch (0.155 amp/cm²) of projected surface area.

The electroplating process should be operated
30 at a bath temperature between 10 and 60°C. Below 10°C the nickel and the zinc will crystallize as salts and precipitate from the plating bath. Above 60°C, a

different alloy is formed having a high nickel concentration. Within the 10 to 60°C temperature range, higher temperatures are preferred because the bath's electrical resistance is lower at higher temperatures.

5 Preferred bath temperatures are from 50 to 55°C.

The plating bath should have a nickel concentration of from 0.1 molar to 2.5 molar. Zinc should also have a concentration in the bath of from 0.1 molar to 2.5 molar. Concentrations below 0.1 molar cause the

10 plating bath to have a high electrical resistance, while concentrations above about 2.5 molar approach the solubility limits of the nickel and zinc salts. Preferably, the nickel concentration and the zinc concentration in the bath are maintained at about 1 molar.

15 The ratio of nickel ions to zinc ions in the bath should be from 2:1 to 1:2. Preferably, the ratio is about 1:1. Nickel to zinc ratios outside this range cause a different alloy to be deposited onto the substrate.

The concentration of the components in the

20 bath and their concentration ratios are maintained by operating each anode at the same current density and by constructing and positioning each anode so that the surface area of the zinc anodes projected toward the substrate is proportional to the concentration of zinc

25 in the coating deposited on the substrate. Likewise, the surface area of the nickel anodes should project a surface area toward the substrate proportional to the concentration of nickel in the substrate coating.

The pH of the bath should be maintained at a

30 pH of from 2 to 5. Below a pH of 2, an excessive

amount of hydrogen gas is generated at the cathode and plating efficiency is reduced. Above a pH of about 5, zinc precipitates. Preferably, the pH should be from 3.5 to 4. The pH may be controlled by adding acid to the bath.

Although the anodes are operated at a constant current density, the voltage applied to each anode is allowed to float. One rectifier may be used for each set of anodes. This will allow the current density of each anode to be set at the desired level. One rectifier is connected to each anode and both are commonly connected to the cathode.

The voltage drawn by each anode primarily depends on four things:

- (1) anode to cathode distance;
- (2) current density;
- (3) bath temperature; and
- (4) bath composition.

The electroplating time depends, inter alia, upon the current density and the desired thickness of the coating. For low overvoltage cathodes, coating thicknesses of from about 5 to 100 microns are beneficial. Below about 5 microns, the coating tends to be non-uniform and provides minimum voltage savings when used as a low overvoltage cathode. When coating thicknesses above about 100 microns are used as low overvoltage cathodes, gas produced at the cathode blinds in the pores and hence the cathode does not operate efficiently. Preferably, the coating should be from 30 to 50 microns and most preferably from 35 to 45 microns.

Optionally, the substrate may be cleaned prior to coating. After the substrate has been coated with the desired coating and to the desired thickness, it may be removed from the electroplating cell and
5 treated in a manner to remove substantially all the zinc from the coating to leave a high surface area nickel coating on the substrates. An alkali solution, such as NaOH, may be used to remove the zinc. Substrates prepared in this manner are useful as low overvoltage
10 cathodes in electrolytic cells. They are especially useful in chlor-alkali electrolytic cells. They are also useful for the electrolysis of water.

Example 1

15 Sheets of perforated mild steel, 2½ ft. by 6 ft., were folded to form a 1½ ft. by 6 ft. envelope which was welded together along the 1½ ft. end sections. Bolts were welded into the open edge of the envelope. The bolts are used in the assembly of these envelopes into a commercial chlorine electrolytic cell cathode.

20 Each part was cleaned by caustic soak degreasing for 15 minutes in a 90°C caustic cleaner solution, rinsed in water, electropolished in a caustic cleaner solution at 90°C for 5 minutes while applying a
25 500 amp electrical current, rinsed in water, acid etched in 18 percent hydrochloric acid at 55°C for 5 minutes, and rinsed in water.

Immediately after cleaning, the parts were nickel electroplated in a typical Watts nickel electroplating bath at a temperature of 55°C and 1080 amps for
30 15 minutes. After rinsing in water a NiZn alloy was electroplated on the parts in a bath containing one

molar nickel chloride, one molar zinc chloride, and 0.5 molar boric acid at a temperature of 55°C. A dual anode was used. Both anodes used titanium mesh baskets, each basket being 6 in. wide x 3 in. thick x 30 in. deep (15.25 cm wide x 7.62 cm thick x 76.2 cm deep), which were suspended into the plating vat by hooks connected to separate buss bars. One anode assembly was filled with nickel chips and the other with zinc balls. Two anode assemblies, 6 ft. long x 3 in. thick x 30 in. deep (1.83 meters long x 7.62 cm thick x 76.2 cm deep), were placed parallel to each other about 1 ft. (30.48 cm) apart and the part was equally spaced between them. The anodes were spaced in an alternating sequence of two baskets of zinc balls, one basket of nickel chips, for a total of eight baskets of zinc and four baskets of nickel in each 6 ft. long anode assembly. All the zinc baskets were hung from a common buss bar attached to the anode side of one rectifier and all nickel baskets were hung from a common buss bar attached to the anode side of another rectifier. The substrate to be electroplated with the alloy was connected to a common buss bar attached to the cathode side of both rectifiers. The substrate was electroplated for 30 minutes by applying 360 amps to the nickel anode assembly, and 720 amps to the zinc anode assembly, with a total of 1080 amps to the cathode part. Thus, each anode was operated at approximately the same current density. After plating, the part was rinsed. After electroplating numerous parts using this dual anode system, the composition of the electrolyte remained approximately identical to the original concentration.

Zinc was removed from the alloy coating by leaching the coated parts in a 10 percent caustic

solution [150 gallons per part, (568 lit/part)] for 8 hours.

Example 2

5 The cathodes produced in Example 1 were
assembled into diaphragm chlorine electrolytic cells.
These cells were compared to cells which contained
conventional steel cathodes. When operating at
approximately 70°C and a cathode current density of 60
amps per square foot (929 cm²) the cells with coated
10 low overvoltage cathodes showed an average voltage
savings of 70 to 85 millivolts during four months of
operation.

1. A method for producing a coated metal part by electroplating a nickel-zinc alloy coating onto an electrically conductive substrate from a bath containing nickel and zinc ions; and removing substantially all of the zinc from the coating; characterized by the steps of supplying nickel and zinc ions to the bath from a set of nickel anodes and from a set of zinc anodes, wherein the ratio of the total surface area projected toward the substrate by the zinc anode set, as compared to that projected by the nickel anode set, is about 2 to 1, maintaining the bath at a concentration of from 0.75 to 1.25 molar nickel and from 0.75 to 1.25 molar zinc by operating each of the individual anodes in each set at approximately the same current density; and electroplating for a time and at a current density sufficient to deposit a 5 to 100 micron thick nickel-zinc coating onto the substrate, wherein the coating is from 60 to 70 weight percent zinc and 30 to 40 weight percent nickel.

2. The method of Claim 1, wherein the ratio of the concentration of nickel ions in the bath to the concentration of zinc ions in the bath is from 2:1 to 1:2.

3. The method of Claim 2, wherein the ratio of the concentration of nickel ions in the bath to the concentration of zinc ions in the bath is about 1 to 1.

4. The method of Claim 1, 2 or 3, wherein the current density of each anode is from 0.1 to 2 amp/cm² (0.0155 to 0.31 am/cm²).

5. The method of Claim 4, wherein the current density is about 0.5 amp per square inch (0.0775 amp/cm²).

6. The method of any one of the preceding Claims, wherein the thickness of the NiZn alloy coating is from 5 to 100 microns.

7. The method of Claim 6, wherein the thickness of the nickel-zinc coating is from 30 to 50 microns.

8. The method of any one of the preceding Claims, wherein the coating contains about 66 weight percent zinc and about 34 weight percent nickel.

9. The method of any one of the preceding Claims, wherein the temperature of the bath is from 10° to 60°C and the pH is from 2 to 5.

10. The method of Claim 1, 2 or 3, wherein the nickel concentration and the zinc concentration in the bath are maintained at about 1 molar.

11. The method of any one of the preceding Claims, wherein the zinc is removed by treating the coated substrate with an alkali solution.

12. The method of any one of the preceding Claims, wherein the number of nickel anodes in the nickel anode set is one half the number of zinc anodes in the zinc anode set.

13. The article produced by the method of any one of the preceding Claims.

14. An electroplating cell for the production of coated metal parts comprising a cathode; two anode sets; a first anode set consisting essentially of nickel and a second anode set consisting essentially of zinc; wherein the second anode set has a surface area facing the cathode which is about twice as large as a surface area of the first set of anodes facing the cathode; means to supply current to each anode in each anode set at a level where each anode has a current density approximately equal to the current density of each other anode; means to maintain a cell bath at a temperature of from 10°C to 60°C; and means to control the pH of the cell bath at from 2 to 5.

15. An electrolytic cell for the production of chlorine and caustic comprising an anode; a cathode; and a separator element located between the anode and the cathode; wherein the cell is characterized by using the article of Claim 13 as the cathode.

16. An electrolytic cell for the electrolysis of water comprising an anode; a cathode; and a separator element located between the anode and the cathode; wherein the cell is characterized by using the article of Claim 13 as a cathode.



European Patent
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EUROPEAN SEARCH REPORT

0100777

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82107250.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	GB - A - 2 059 438 (THOMAS STEEL STRIP CORPORATION) * Totality, especially tables; claims *	1-10, 14	C 25 D 3/56 C 25 D 17/00 C 25 B 1/04 C 25 B 1/46//
D, Y	US - A - 4 104 133 (J.R. BRANNAN et al.) * Example 1; claims *	1, 4, 5, 9, 11, 15	(C 25 D 3/56 C 25 D 3/12 C 25 D 3/22)
X	US - A - 4 313 802 (A. SHIBUYA et al.) * Totality, especially column 3, examples; claims *	1-5, 9, 10	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 25 D C 25 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 24-02-1983	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			