



(11) **EP 2 350 355 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
03.05.2017 Bulletin 2017/18

(21) Application number: **09820962.0**

(22) Date of filing: **28.08.2009**

(51) Int Cl.:
C25D 3/56 (2006.01)

(86) International application number:
PCT/US2009/055317

(87) International publication number:
WO 2010/044957 (22.04.2010 Gazette 2010/16)

(54) **ZINC ALLOY ELECTROPLATING BATHS AND PROCESSES**

ZINNLEGIERUNGSGALVANISIERUNGSBÄDER UND -VERFAHREN

BAINS ET PROCÉDÉS D'ÉLECTROPLACAGE D'ALLIAGE DE ZINC

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK SM TR**

(30) Priority: **17.10.2008 US 253267**

(43) Date of publication of application:
03.08.2011 Bulletin 2011/31

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention relates generally to improvements in the electrodeposition of zinc nickel alloys from aqueous alkaline plating baths and to new additives for use in such electrodeposition processes.

BACKGROUND OF THE INVENTION

10 **[0002]** Electrodeposition of zinc and zinc alloys based on alkaline plating baths has been known for many years. However, it is not possible to produce a commercially acceptable deposit from a simple sodium zincate electrolyte as the deposit is powdery and dendritic. For this reason, various additives have been proposed to provide improved deposition, such as cyanides (which have obvious environmental problems) and polymers of amines and epichlorohydrin which act as grain refining additives. These polymers are limited to usage in baths having relatively low concentrations of zinc because it is not possible to prevent uncontrolled deposition of zinc at higher metal concentrations. Also, electroplating processes using these additives tend to have poor cathode efficiency, a narrow bright range, a narrow operating window, and tend to produce pitted and "burnt" deposits. Plating compositions of this type are described in U.S. Pat. No. 2,080,479 to Hoff and U.S. Pat. No. 4,861,442 to Nishihama and U.S. Pat. No. 4,983,263 to Yasuda et al, the content, each of which is herein incorporated by reference.

20 **[0003]** More recently, additives have been proposed which allow higher zinc concentrations to be used, which have significantly reduced burning and pitting and which allow a wider range of operating parameters. Further, the additives enable an excellent deposit distribution (that is, evenness of the deposit across the article being plated, irrespective of its shape in particular areas). This maximizes the efficiency of zinc usage. These additives are based generally on polyquaternary amine compounds and are described in U.S. Pat. No. 5,435,898 and U.S. Pat. No. 5,405,523, which also provide further discussion of the prior art and the content each of which is herein incorporated by reference.

25 **[0004]** Plating compositions for depositing zinc nickel alloys from alkaline electrolytes are well known and are described in US patents such as US Pat. No. 6,468,411, US Pat. No. 5,417,840, US. Pat. No. 4,861,442, and US. Pat. No. 4,889,602, which also provide further discussion of the prior art and the content each of which is herein incorporated by reference. Plating solutions that provide an alloy composition containing from 12% to 15% nickel are most desirable giving optimal corrosion performance. This alloy is currently utilized by many automotive manufacturers.

30 **[0005]** The zinc to nickel metal concentration ratio of alkaline zinc nickel plating baths of the prior art producing zinc nickel alloys of >12% Ni containing oligomeric or polymeric amine species is of the order 7:1 to 10:1. This is consistent with the ratio of nickel in the desired alloy of 12% to 15% and corresponds to more 'normal deposition.' Unexpectedly it has been found that baths of the present invention producing zinc nickel alloys of 12% to 15% Ni have a zinc to nickel metal concentration ratio of the order 1.5:1 to 2.5:1. Thus the zinc to nickel metal concentration ratio is not consistent with the alloy deposited. This type of deposition is described as 'anomalous deposition' and is generally typical of the acid zinc nickel based electrolytes described in US patents and applications such as US 4,699,696 and US 2003/0085130 A1.

35 **[0006]** Further it is known that in practice used baths of alkaline zinc nickel become contaminated with the anions of the nickel salts such as sulphate introduced into the solution by means of replenishment and with carbonate from solution contact with air. These anions contribute to burning of the deposit in the high current density areas reducing the operable current density range, which can lead to the solution eventually being unusable. This anion contamination is particularly deleterious for plating solutions utilized for rack operation where solution turnover is minimal and the used current density range is wide. Current practice either involves replacement or dilution of the solution to reduce contamination of these anions. For rack plating, precipitation of carbonate and sulfate by cooling a portion of the plating solution is usually insufficient to produce a wide enough operable current density range. Deposits of suitable appearance can be obtained by producing alloys containing greater than 15% nickel, but these are not desirable with regard to corrosion performance. US 6,652,728 describes aqueous alkaline cyanide-free baths for the galvanic deposition of zinc or zinc alloy coatings on a substrate.

40 **[0007]** It is a shortcoming of the prior art in alkaline zinc nickel plating that certain components of the composition, particularly the oligomeric or polymeric amine complexants used in many of the patents referenced above, strongly adsorb on the cathode surface during the plating process and inhibit the effectiveness of the other additives, especially the polyquaternary amine compounds described above.

45 **[0008]** It is accordingly, an object of the present invention to provide an alkaline zinc nickel alloy electroplating bath in which electroplated coatings with even brightness, improved deposit distribution thickness, good resistance to burning, and high cathode efficiency may be obtained in a wide range of current density even in the presence of polluting anions such as carbonate and sulfate.

50 **[0009]** It is another object of the present invention to provide such an electroplating bath which permits electroplating

at a high current density and at a shortened electroplating time.

[0010] Another object of the present invention is to provide an alkaline zinc nickel alloy electroplating bath which may contain a wide range of zinc concentration levels for different plating operations.

[0011] It is also important, and an object of the present invention, that the zinc nickel plating bath be operable in manual, automatic rack and barrel plating operations.

[0012] Other objects and advantages will be apparent from the following descriptions.

SUMMARY OF THE INVENTION

[0013] The present invention is thus concerned with electrodeposition on a variety of electrically conducting substrates in a medium which seeks to provide improved cathode efficiency and/or improved brightness and leveling, and further to provide coatings that are resistant to post-plate "blistering". Suitable substrates include iron and ferrous-based substrates (including both iron alloys and steels), aluminium and its alloys, magnesium and its alloys, copper and its alloys, nickel and its alloys, and zinc and its alloys. Aluminum and its alloys and ferrous-based substrates are particularly preferred substrates, with steels being most preferred.

[0014] The present invention is as described in the appended claims, wherein, there is provided an additive for an alkaline zinc nickel alloy electroplating bath medium, the additive comprising a ureylene quarternary ammonium based polymer. It has been discovered that a zinc nickel alloy electroplating bath containing an effective additive amount of a ureylene quarternary ammonium based polymer accomplishes the objects of the present invention when used in conjunction with non-polymeric complexants. A polymer that is preferred by the present invention because of its effectiveness in enabling the plating bath to plate over a wide range of current densities is Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane]. Another polymer that is preferred is Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane. Others include random copolymers comprising the reaction product of (i) one or more di-tertiary amines, including an amide or thioamide functional group and (ii) one or more second di-tertiary amines including an unsaturated moiety with (iii) one or more first linking agents capable of reacting with said amines (i) and (ii). Such useful random co-polymers are disclosed in U.S. Patent No. 7,109,375, the teaching of which are incorporated herein in their entirety. The molecular weights of these urea based polymers must only be small enough that they are bath soluble. It is not believed that the functionality of the polymer is significantly affected by its molecular weight, assuming that the polymer itself is still sufficiently soluble. Generally, the polymers useful in this invention include at least one urea based polymer of the form of either (a) Urea, N, N'-bis[3-at (dialkylamino) alkyl]-, polymer with 1,4 [2-haloalkane] or (b) Urea, N,N'-bis[3-(dialkylamino)alkyl], polymer with 1,1'-oxybis[2-haloalkane], wherein for (a) or (b) the alkyl functional groups are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, and hexyl and the halogen functional group is selected from the group consisting of chloro, bromo, fluoro, and iodo. Other useful polymers include the random co-polymers described above.

[0015] The bath medium comprises triethanolamine and N,N,N',N' tetrakis-hydroxyisopropylethylenediamine as non polymeric complexants. Non-polymeric complexants that are preferred by the present invention include trimethanolamine, triethanolamine, tripropanolamine, or N,N,N',N' tetrekis-hydroxyisopropylethylenediamine. It is also preferable that at least two of these complexants are concurrently used in the bath.

[0016] The improved baths exhibit many advantages over the baths of the prior art, including even deposit appearance, effective plating at a high current density, uniform plating thickness, and high cathode efficiency. It is particularly advantageous that the improvements of the present invention result in uniform plating thickness because it is a well known deficiency in the prior art that uniform plating thickness is difficult when the objects being plated comprise complex shapes with small ridges and surface variations.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The use of polycationic polymers in zinc plating solutions is well known and has been utilized in zinc plating systems for many years. These polymers are generally able to produce processes that yield metal plating that is resistant to burning and pitting and exhibit a highly uniform metal distribution. Polycationic polymers are also used in the deposition of zinc iron and zinc cobalt deposits where the complexant used to hold the iron or cobalt in solution is typically sodium heptonate, sodium gluconate, or sodium tartrate. Examples of such baths that are able to plate both zinc and zinc alloys are disclosed in U.S. Pat. No. 4,983,263 to Yasuda et al, the content of which is herein incorporated by reference. However, polycationic polymers have not been thought to be effective in zinc nickel plating electrolytes. It is desirable and widely sought throughout the plating industry to produce deposits of zinc nickel alloy containing 12% to 15% nickel. These processes generally suffer from several problems including non-optimal plating uniformity and low brightness and cathode efficiency.

[0018] It has been discovered that the combination of certain amino based complexants and urea based polycationic polymers, rather than the usual oligomeric or polymeric amine complexants and epichlorohydrin based polycationic

polymers, greatly improves the quality of zinc nickel electroplated deposits. Surprisingly, it has been found that solutions that do not contain polymeric or oligomeric complexants, but which utilize the complexants taught by the present invention, are responsive to certain based polymers and result in a greatly improved zinc nickel plating process. Prior to the present invention, the polymeric or oligomeric complexants used in zinc processes interfered with the functioning of the polycationic polymers.

[0019] This improved process gives similar metal thickness distribution characteristics to zinc plating but which can contain the desirable features of a zinc nickel alloy. A similar resistance to burning or pitting between the zinc and zinc nickel processes is also observed even in the presence of interfering anions such as carbonate and sulfate. The final result is that a zinc nickel process utilizing the additives of this invention can be operated to produce zinc nickel alloys containing 12% to 15% nickel still retaining the good deposition characteristics and extended operable current density range which was heretofore only achievable with a pure zinc plate.

[0020] Alkaline zinc electroplating baths, both containing cyanide ions and cyanide free baths, are well known in the art and have been commonly used for years. The basic alkaline zinc electroplating bath contains a zinc compound and an alkali hydroxide. Zinc can be introduced into the aqueous bath by any soluble zinc salt, but zinc oxide is the salt most often and most preferably used. The alkali hydroxide is generally either sodium hydroxide or potassium hydroxide. At high pH ranges, it is generally thought that the zinc ions from the zinc salt are transformed into a zincate ion, and thus zincate ions are generally present in a working alkaline zinc plating bath. It will be appreciated that as used herein, the term "zinc ion" includes zincate or other ionic species containing zinc atoms useful in electroplating baths for electroplating metallic zinc and zinc alloys.

[0021] Zinc alloy electrolytic baths also contain salts of other metals, which are generally nickel, cobalt, or iron. The present invention deals specifically and most preferably with zinc nickel alloy plating. Nickel is introduced into the zinc plating bath by means of any soluble nickel salt. It is most preferable if this salt contains divalent nickel, and therefore the most common and preferable nickel salts for use in the present invention are nickel (II) sulfate or nickel (II) acetate or nickel (II) carbonate.

[0022] The composition of the zinc nickel plating bath generally contains about 5-25 g/L, but can contain up to 50 g/L or more, of zinc ions. This content is calculated on zinc ion concentration and would not be affected by whatever corresponding anion (or cation) is used. Preferably, zinc is present in the solution at a concentration of about 5-20 g/L. The alkaline hydroxide, preferably sodium or potassium hydroxide, is generally present at a concentration of about 50 g/L to 500 g/L or more, and is preferably about 70 to 100 g/L as sodium hydroxide or 100 to 140 g/L as potassium hydroxide. Nickel is generally present in such baths from about 0.25 -10 g/L, but is preferably in the range of 1-6 g/L.

[0023] Depending upon the purpose for which the electroplating is carried out, the zinc nickel bath can be used in widely different concentration ranges. For example, where increased throwing power is important, the desirable zinc concentration is about 5 to 10 g/L, preferably 6 to 8 g/L and about 70 to 140 g/L for the alkali hydroxide. When the current efficiency and operability are important factors such as in barrel plating, the desired concentration of zinc is about 8 to 12 g/L and 80 to 150 g/L alkali hydroxide.

[0024] In zinc nickel alloy baths it is important that the metal ions in appropriate amounts and in appropriate form be present in the bath. One preferred way is to use a chelating agent in the bath in an effective amount to maintain the metals, other than the soluble zinc, in the bath in solution, e.g., to dissolve the required amount of nickel and other alloy ingredients in the bath. The chelating agent used herein should complex the nickel ions to an electrodepositable extent in a strong alkalinity of a pH of above 13 and thus permit their stable dissolution. It is an essential aspect of the present invention that appropriate complexants be used to effectively dissolve the nickel ions into solution. By utilizing the preferred properties of the chelating agents taught in this disclosure, unfavorable interaction between the chelating agents and polycationic polymers can be avoided.

[0025] It has been found that the preferred chelating agents are selected from the group consisting of monoethanolamine, diethanolamine, trimethanolamine, triethanolamine, tripropanolamine, and N,N,N',N' tetrakis-hydroxyisopropylethylenediamine. However, it is believed that the functionality of the present invention can be achieved with any amino alcohol or ethylenediamine based complexing agent provided that it is not polymeric. A combination of triethanolamine and N,N,N',N' tetrakis-hydroxyisopropylethylenediamine will be present as the nickel complexing agent. Typically, the chelating agent should generally only be present in the plating solution at a concentration high enough to ensure the dissolution of the nickel ions. Generally, levels of about 10-150 g/L or more are employed and depend upon the concentration of nickel or other alloying metal in a given bath.

[0026] The second essential aspect of the present invention is the use of particular polycationic polymers which aid in the plating process to produce a better quality zinc nickel alloy plate. The incorporation of these materials gives the process a very high throwing power, which results in a uniform metal distribution, as well as aiding in producing plates that are resistant to burning and pitting. It has been found that the combination of polycationic based polymers with the above chelating agents reduces an interfering effect at the surface of the plating allowing the polymers and other additives to adsorb onto the substrate surface and produce their favorable effect. The polymers that are able to exhibit such a result are uylene quaternary ammonium based polymers, which include as polymers of the form Urea, N,N'-bis[3-(di-

alkylamino)alkyl]-, polymer with 1,4-[2-haloalkane] or Urea, N,N'-bis[3-(dialkylamino)alkyl]-, polymer with 1,1'-oxybis[2-haloalkane] or Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane. Other polymers useful in this invention include random co-polymers comprising the reaction product of (i) one or more di-tertiary amines, including an amide or thioamide functional group and (ii) one or more second di-tertiary amines including an unsaturated moiety, with (iii) one or more first linking agents capable of reacting with said amines (i) and (ii). Such useful random co-polymers are disclosed in U.S. Patent No. 7,109,375, the teachings of which are incorporated herein by reference in their entirety. A polymer that is preferred by the present invention because of its effectiveness in enabling the plating bath to plate over a wide range of current densities is Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane]. Another polymer that is preferred is Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane and others such as Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane and N'-[3-(dimethylamino)propyl]-N,N'-dimethyl-1,3-propanediamine, N-[2-hydroxy-3-(2-propenyloxy)propyl] derivatives. These polymers are preferably incorporated into the bath by preparing a stock aqueous concentrate made up at about 25-300 g/L, however this is optional and it is possible to directly add the polymer to the bath. In the operating zinc nickel alloy plating bath, the urea based polymer is preferably present in an amount of up to about 20 g/L, more preferably 0.01g/L to 7g/L, and most preferably at a concentration of about 0.1-2g/L.

[0027] The zinc nickel alloy electroplating bath of the present invention can be utilized to obtain uniform coatings over a wide range of current densities, which are additionally resistant to burning and pitting. These results are obtainable even if the concentrations of the components change to a reasonable degree. It is the ability to effect a uniformly thick coating of zinc-nickel alloy under different current density that forms one of the primary advantage of the present invention.

[0028] In order to further illustrate the composition and process of the present invention, the following examples are provided. It will be understood that the examples are provided for illustrative purposes and are not intended to be limiting of the scope and the present invention as herein described and is set forth in the claims.

(Example 1)

[0029] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 90 g/L sodium hydroxide, 8g/L zinc ions, 4g/l nickel ions, 68g/L triethanolamine, 30g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine, 12.5g/l sodium silicate, and 400mg/L Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane]. At a temperature 30C a bright steel Hull cell panel was plated for 20 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright with no visible defects. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

(Example 2)

[0030] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 90 g/L sodium hydroxide, 8g/L zinc ions, 4g/l nickel ions, 68g/L triethanolamine, 30g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine, 12.5g/l sodium silicate, and 100mg/L Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane and N'-[3-(dimethylamino)propyl]-N,N'-dimethyl-1,3-propanediamine, N-[2-hydroxy-3-(2-propenyloxy)propyl] derivatives. At a temperature 30C a bright steel Hull cell panel was plated for 30 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright with no visible defects. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

(Example 3)

[0031] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 120 g/L potassium hydroxide, 8g/L zinc ions, 4g/l nickel ions, 68g/L triethanolamine, 30g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine, 12.5g/l sodium silicate, and 100mg/L Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane and N'-[3-(dimethylamino)propyl]-N,N'-dimethyl-1,3-propanediamine, N-[2-hydroxy-3-(2-propenyloxy)propyl] derivatives. At a temperature 30C a bright steel Hull cell panel was plated for 30 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright with no visible defects. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

(Example 4)

[0032] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 90 g/L sodium hy-

droxide, 12g/L zinc ions, 4.5g/l nickel ions, 60g/L triethanolamine, 12.5g/l sodium silicate, and 400mg/L Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane]. At a temperature 30C a bright steel Hull cell panel was plated for 30 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright with no visible defects. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

Comparative Example (Example 5)

[0033] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 110 g/L sodium hydroxide, 8g/L zinc ions, 700mg/l nickel ions, 8g/L tetraethylenepentamine, 2g/l triethanolamine, 15g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine, 4g/l sodium silicate and 50mg/L N-benzyl nicotinamide. At a temperature 30C a bright steel Hull cell panel was plated for 20 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright from the low led to 4asd and beyond 4asd was dull showing a coarse grained deposit. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

Comparative Example (Example 6)

[0034] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 110 g/L sodium hydroxide, 8g/L zinc ions, 700mg/l nickel ions, 8g/L tetraethylenepentamine, 2g/l triethanolamine, 15g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine, 4g/l sodium silicate, 400mg/L Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane] and 50mg/L N-benzyl nicotinamide. At a temperature 30C a bright steel Hull cell panel was plated for 20 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance was uniformly bright with no visible defects. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

Comparative Example (Example 7)

[0035] An aqueous electrolytic bath suitable for plating zinc nickel alloy was prepared containing 90 g/L sodium hydroxide, 8g/L zinc ions, 4g/l nickel ions, 68g/L triethanolamine, 30g/L N,N,N',N' tetrakis-hydroxyisopropylethylenediamine and 12.5g/l sodium silicate. At a temperature 30C a bright steel Hull cell panel was plated for 20 minutes at 1A in a Hull cell using a nickel anode. The plated panel appearance showed three distinct bands. The first band from the HCD region beyond 5asd showed a coarse grained deposit, the second band from 5asd down to about 0.5asd was semi bright to dull and the third band below 0.5asd was bright. The deposit thickness and nickel alloy content shown in Table 1 below was measured at current densities 4A, 2A, 0.5A per square decimeter across the plated panel using a Fischerscope X-ray system XDL-B.

Table 1

Example	Thickness (microns) and alloy % Ni			A:C ratio
	4asd (A)	2asd (B)	0.5asd (C)	
1	3.5um/12.8%	2.5um/12.6%	1.7um/12.8%	2.06:1
2	4.2um/13.2%	3.0um/12.1%	2.0um/13.0%	2.10:1
3	5.3um/13.4%	3.9um/13.3%	2.5um/12.5%	2.12:1
4	6.0um/12.9%	4.7um/12.7%	2.9um/12.2%	2.07:1
5	10.3um/14.1%	6.5um/13.2%	2.9um/13.3%	3.55:1
6	8.9um/15.2%	5.9um/13.6%	2.4um/12.7%	3.71:1
7	11.0um/14.5%	8.0um/15.0%	3.5um/14.4%	3.14:1

[0036] It can be seen from these results that the novel process of the present invention, which is exhibited by examples 1-4, plates zinc nickel alloys with a much improved deposit distribution compared to those baths that do not utilize the combination of a relevant urea based polymer in combination with a non-polymeric and non-oligomeric complexant, which are exhibited by examples 5-7. Example 5 is a bath containing the oligomeric based amine complexant tetraethylenepentamine and Example 6 is the same bath as Example 5 with a polycationic polymer.

Claims

1. An alkaline aqueous electrolytic bath capable of electrodeposition of a zinc-nickel alloy comprising:

- (i) zinc ions;
- (ii) nickel ions;
- (iii) at least one non-polymeric complexing agent capable of complexing the nickel ions and comprising triethanolamine and N,N,N',N' tetrakis-hydroxyisopropylethylenediamine.
- (iv) at least one urea based polymer selected from the group consisting of (a) Urea, N,N'-bis[3-(dialkylamino)alkyl]-, polymer with 1,4-[2-haloalkane], or (b) Urea, N,N'-bis[3-(dialkylamino)alkyl]-, polymer with 1,1'-oxybis[2-haloalkane], wherein for (a) or (b) the alkyl functional groups are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, and hexyl and the halogen functional group is selected from the group consisting of chloro, bromo, fluoro, and iodo, and (c) random co-polymers comprising the reaction product of (1) one or more di-tertiary amines including an amide or thioamide functional group, and (2) one or more second di-tertiary amines including an unsaturated moiety, with (3) one or more first linking agents capable of reaction with said amines (1) and (2); with the proviso that the alkaline aqueous electrolytic bath does not contain polymeric and oligomeric complexants.

2. The alkaline aqueous electrolytic bath according to claim 1 wherein the non-polymeric complexing agent additionally comprises a nonpolymeric complexing agent chosen from the group consisting of monoethanolamine, diethanolamine, trimethanolamine,, and tripropanolamine.

3. The alkaline aqueous electrolytic bath according to claim 1 wherein the urea based polymer comprises Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,1'-oxybis[2-chloroethane].

4. The alkaline aqueous electrolytic bath according to claim 1 wherein the urea based polymer comprises Urea, N,N'-bis[3-(dimethylamino)propyl]-, polymer with 1,4-dichlorobutane.

5. The alkaline aqueous electrolytic bath according to claim 1 wherein sodium hydroxide is present in an amount of about 50 g/L to about 500 g/L.

6. The alkaline aqueous electrolytic bath according to claim 1 wherein zinc ions are present in a concentration of about 2 g/L to about 30 g/L.

7. The alkaline aqueous electrolytic bath according to claim 1 wherein nickel ions are present in a concentration of about 0.25 g/L to about 10 g/L.

8. The alkaline aqueous electrolytic bath according to claim 1 wherein a non-polymeric complexing agent is present in a concentration of about 5 g/L to about 150 g/L.

9. The alkaline aqueous electrolytic bath according to claim 1 wherein the urea based polymer is present in a concentration of about 0.02 g/L to about 20 g/L.

10. The method for the electrodeposition of zinc-nickel alloy on a conductive substrate comprising the steps of:

(a) contacting the conductive substrate with an alkaline aqueous electrolytic bath comprising:

- (i) zinc ions;
- (ii) nickel ions;
- (iii) at least one non-polymeric complexing agent capable of complexing the alloy metal ions and comprising triethanolamine and N,N,N',N' tetrakis-hydroxyisopropylethylenediamine.
- (iv) at least one urea based polymer selected from the group consisting of (a) Urea, N,N'-bis[3-(dialkylamino)alkyl]-, polymer with 1,4-[2-haloalkane] and (b) Urea, N,N'-bis[3-(dialkylamino)alkyl]-, polymer with 1,1'-oxybis[2-haloalkane], wherein for (a) or (b) the alkyl functional groups are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, and hexyl and the halogen functional group is selected from the group consisting of chloro, bromo, fluoro, and iodo, and (c) random co-polymers comprising the reaction product of (1) one or more di-tertiary amines including an amide or thioamide functional group, and (2) one or more second di-tertiary amines including an unsaturated moiety with (3) one or more first linking agent capable

or reacting with said amines (1) and (2);

(b) electrolytically depositing metallic zinc or a metallic zinc alloy onto the surface of the conductive substrate; with the proviso that the alkaline aqueous electrolytic bath does not contain polymeric and oligomeric compl-
exants.

11. The method according to claim 10 wherein the electrolytic metal deposition step occurs when the cathode current density is applied in the range of about 0.1 ampere per square decimeter to about 25 ampere per square decimeter.

12. The method according to claim 11 wherein the alkaline aqueous electrolytic bath comprises the features of any of claims 2 or 3 to 10.

Patentansprüche

1. Alkalisches, wässriges Elektrolysebad, das eine Zink-Nickel-Legierung elektrolytisch ablagern kann und umfasst:

(i) Zinkionen;

(ii) Nickelionen;

(iii) mindestens ein nicht-polymeres Komplexierungsmittel, dass die Nickelionen komplexieren kann und Triethanolamin und N,N,N',N'-Tetrakis-hydroxyisopropylethyldiamin umfasst;

(iv) mindestens ein auf Harnstoff basierendes Polymer ausgewählt aus der Gruppe bestehend aus (a) Harnstoff, N,N'-Bis[3-(dialkylamino)alkyl]-Polymer mit 1,4-[2-Halogenalkan], oder (b) Harnstoff, N,N'-Bis[3-(di-alkylamino)alkyl]-Polymer mit 1,1'-Oxybis[2-halogenalkan], wobei für (a) oder (b) die alkylfunktionellen Gruppen ausgewählt sind aus der Gruppe bestehend aus Methyl, Ethyl, Propyl, Butyl, Pentyl und Hexyl und die halogenfunktionelle Gruppe ausgewählt ist aus der Gruppe bestehend aus Chlor, Brom, Fluor und Iod, und (c) statistischen Copolymeren, die das Reaktionsprodukt von (1) einem oder mehreren di-tertiären Aminen, die eine amid- oder thioamid-funktionelle Gruppe enthalten, und (2) eine oder mehreren sekundären di-tertiären Aminen, die einen ungesättigten Anteil enthalten, mit (3) einem oder mehreren ersten Verbindungsmitteln, die mit den Aminen (1) und (2) reagieren können; mit der Maßgabe, dass das alkalische, wässrige, elektrolytische Bad keine polymeren und oligomeren Komplexierungsmittel enthält.

2. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem das nichtpolymere Komplexierungsmittel zusätzlich ein nicht-polymeres Komplexierungsmittel ausgewählt aus der Gruppe bestehend aus Monoethanolamin, Diethanolamin, Triethanolamin und Tripropanolamin umfasst.

3. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem das auf Harnstoff basierende Polymer Harnstoff, N,N'-Bis[3-(dimethylamino)propyl]-Polymer mit 1,1'-Oxybis[2-chlorethan] umfasst.

4. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem das auf Harnstoff basierende Polymer Harnstoff, N,N'-Bis[3-(dimethylamino)propyl]-Polymer mit 1,4-Dichlorbutan umfasst.

5. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem Natriumhydroxid in einer Menge von etwa 50 g/L bis etwa 500 g/L vorhanden ist.

6. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem Zinkionen in einer Konzentration von etwa 2 g/L bis etwa 30 g/L vorhanden sind.

7. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem Nickelionen in einer Konzentration von etwa 0,25 g/L bis etwa 10 g/L vorhanden sind.

8. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem ein nichtpolymere Komplexierungsmittel in einer Konzentration von etwa 5 g/L bis etwa 150 g/L vorhanden sind.

9. Alkalisches, wässriges Elektrolysebad nach Anspruch 1, bei dem das auf Harnstoff basierende Polymer in einer Konzentration von etwa 0,02 g/L bis etwa 20 g/L vorhanden ist.

10. Verfahren zur elektrolytischen Ablagerung von Zink-Nickel-Legierung auf einem leitfähigen Substrat umfassend die

Schritte:

(a) In-Kontakt-Bringen des leitfähigen Substrats mit einem alkalischen, wässrigen Elektrolysebad, das umfasst:

- 5 (i) Zinkionen;
- (ii) Nickelionen;
- (iii) mindestens ein nicht-polymeres Komplexmierungsmittel, dass die Legierungsmetallionen komplexieren kann und Triethanolamin und N,N,N',N'-Tetrakishydroxyisopropylethylendiamin umfasst;
- 10 (iv) mindestens ein auf Harnstoff basierendes Polymer ausgewählt aus der Gruppe bestehend aus (a) Harnstoff, N,N'-Bis[3-(dialkylamino)-alkyl]-Polymer mit 1,4-[2-Halogenalkan], oder (b) Harnstoff, N,N'-Bis[3-(dialkylamino)alkyl]-Polymer mit 1,1'-Oxybis[2-halogenalkan], wobei für (a) oder (b) die alkylfunktionellen Gruppen ausgewählt sind aus der Gruppe bestehend aus Methyl, Ethyl, Propyl, Butyl, Pentyl und Hexyl und die halogenfunktionelle Gruppe ausgewählt ist aus der Gruppe bestehend aus Chlor, Brom, Fluor und Iod, und (c) statistischen Copolymeren, die das Reaktionsprodukt von (1) einem oder mehreren di-tertiären Aminen, die eine amid- oder thioamid-funktionelle Gruppe enthalten, und (2) einem oder mehreren sekundären di-tertiären Aminen, die einen ungesättigten Anteil enthalten, mit (3) einem oder mehreren ersten Verbindungsmitteln, die mit den Aminen (1) und (2) reagieren können;

20 (b) elektrolytisches Ablagern von metallischem Zink oder metallischer Zinklegierung auf der Oberfläche des leitfähigen Substrats, mit der Maßgabe, dass das alkalische, wässrige, elektrolytische Bad keine polymeren und oligomeren Komplexmierungsmittel enthält.

25 11. Verfahren nach Anspruch 10, bei dem der Schritt der elektrolytischen Metallablagerung erfolgt, wenn die Kathodenstromdichte im Bereich von etwa 0,1 Amper pro Quadratdezimeter bis etwa 25 Amper pro Quadratdezimeter angelegt wird.

12. Verfahren nach Anspruch 11, bei dem das Elektrolysebad die Merkmale einer der Ansprüche 2 oder 3 bis 10 umfasst.

30 Revendications

1. Bain électrolytique aqueux alcalin capable d'une électrodéposition d'un alliage de zinc-nickel comprenant :

- 35 (i) des ions zinc ;
- (ii) des ions nickel ;
- (iii) au moins un agent complexant non polymère capable de complexer les ions nickel et comprenant de la triéthanolamine et de la N,N,N',N'-tétrakis-hydroxyisopropyléthylènediamine ;
- 40 (iv) au moins un polymère à base d'urée choisi dans l'ensemble constitué par (a) un polymère de N,N'-bis[3-(dialkylamino)alkyl]urée avec un 1,4-[2-halogénoalcane], et (b) un polymère de N,N'-bis[3-(dialkylamino)alkyl]urée avec un 1,1'-oxybis[2-halogénoalcane], où, pour (a) ou (b), les groupes fonctionnels alkyle sont choisis dans l'ensemble constitué par méthyle, éthyle, propyle, butyle, pentyle et hexyle, et le groupe fonctionnel halogéno est choisi dans l'ensemble constitué par chloro, bromo, fluoro et iodo, et (c) les copolymères statistiques comprenant le produit de la réaction de (1) une ou plusieurs amine(s) di-tertiaire(s) comprenant un groupe fonctionnel amido ou thioamido, et (2) une ou plusieurs deuxième(s) amine(s) di-tertiaire(s) comprenant un fragment insaturé, avec (3) un ou plusieurs premier(s) agent (s) de liaison capable(s) de réagir avec lesdites amines (1) et (2) ;

sous réserve que le bain électrolytique aqueux alcalin ne contienne pas d'agents complexants polymères et oligomères.

- 50 2. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel l'agent complexant non polymère comprend de plus un agent complexant non polymère choisi dans l'ensemble constitué par la monoéthanolamine, la diéthanolamine, la triméthanolamine, et la tripropanolamine.
3. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel le polymère à base d'urée comprend un polymère de N,N'-bis[3-(diméthylamino)propyl]-urée avec du 1,1'-oxybis[2-chloroéthane].
- 55 4. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel le polymère à base d'urée comprend un polymère de N,N'-bis[3-(diméthylamino)propyl]-urée avec du 1,4-dichlorobutane.

5. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel de l'hydroxyde de sodium est présent en une quantité d'environ 50 g/l à environ 500 g/l.

6. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel les ions zinc sont présents à une concentration d'environ 2 g/l à environ 30 g/l.

7. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel les ions nickel sont présents à une concentration d'environ 0,25 g/l à environ 10 g/l.

8. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel un agent complexant non polymère est présent à une concentration d'environ 5 g/l à environ 150 g/l.

9. Bain électrolytique aqueux alcalin selon la revendication 1, dans lequel le polymère à base d'urée est présent à une concentration d'environ 0,02 g/l à environ 20 g/l.

10. Procédé d'électrodéposition d'un alliage de zinc-nickel sur un substrat conducteur, comprenant les étapes de :

(a) mise en contact du substrat conducteur avec un bain électrolytique aqueux alcalin comprenant :

(i) des ions zinc ;

(ii) des ions nickel ;

(iii) au moins un agent complexant non polymère capable de complexer les ions métalliques de l'alliage et comprenant de la triéthanolamine et de la N,N,N',N'-tétrakis-hydroxyisopropyléthylènediamine ;

(iv) au moins un polymère à base d'urée choisi dans l'ensemble constitué par (a) un polymère de N,N'-bis[3-(dialkylamino)alkyl]urée avec un 1,4-[2-halogénoalcane], et (b) un polymère de N,N'-bis[3-(dialkylamino)alkyl]urée avec un 1,1'-oxybis[2-halogénoalcane], où, pour (a) ou (b), les groupes fonctionnels alkyle sont choisis dans l'ensemble constitué par méthyle, éthyle, propyle, butyle, pentyle et hexyle, et le groupe fonctionnel halogéno est choisi dans l'ensemble constitué par chloro, bromo, fluoro et iodo, et (c) les copolymères statistiques comprenant le produit de la réaction de (1) une ou plusieurs amine(s) di-tertiaire(s) comprenant un groupe fonctionnel amido ou thioamido, et (2) une ou plusieurs deuxième(s) amine(s) di-tertiaire(s) comprenant un fragment insaturé, avec (3) un ou plusieurs premier(s) agent(s) de liaison capable(s) de réagir avec lesdites amines (1) et (2) ;

(b) déposition électrolytique de zinc métallique ou d'un alliage de zinc métallique sur la surface du substrat conducteur ;

sous réserve que le bain électrolytique aqueux alcalin ne contienne pas d'agents complexants polymères et oligomères.

11. Procédé selon la revendication 10, dans lequel l'étape de déposition de métal électrolytique a lieu quand la densité de courant de cathode est appliquée dans la plage allant d'environ 0,1 ampère par décimètre carré à environ 25 ampères par décimètre carré.

12. Procédé selon la revendication 11, dans lequel le bain électrolytique aqueux alcalin comprend les caractéristiques de l'une quelconque des revendications 2 et 3 à 10.

REFERENCES CITED IN THE DESCRIPTION

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