The present invention relates to an aqueous zinc-nickel electroplating bath, including water; nickel ion; zinc ion; at least one complexing agent; and at least one non-ionogenic, surface active polyoxyalkylene compound, wherein the bath has an alkaline pH. In one embodiment, the zinc ion, the nickel ion and the non-ionogenic surface active polyoxyalkylene compound are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a substantially gamma phase.

Publication Classification

(51) Int. Cl. 7 .................................................. C25D 3/56
(52) U.S. Cl. .................................................. 205/246; 106/1.29

ABSTRACT
ALKALINE ZINC-NICKEL ALLOY PLATING COMPOSITIONS, PROCESSES AND ARTICLES THEREFROM

BACKGROUND OF THE INVENTION

[0001] For many years, attempts have been made and processes have been employed for electroplating a bright, level zinc-nickel alloy on a substrate such as a metal. Most of the processes have employed alkaline baths. A great variety of additives have been used to enhance the brightness, levelness, ductility, strength and nickel content of the deposited zinc-nickel alloys. Non-ionogenic, surface active polyoxyalkylene compounds have been used in acidic zinc-nickel baths, but it has been common knowledge in the art for many years that non-ionogenic, surface active polyoxyalkylene compounds are not effective brightening, leveling or ductilizing agents in alkaline electroplating baths for depositing zinc-nickel alloys having desirable characteristics.

[0002] A continuing and long-felt need has existed in the art for zinc-nickel alloys having enhanced brightness, levelness, ductility, strength and nickel content.

SUMMARY OF THE INVENTION

[0003] In one embodiment, the present invention relates to an aqueous zinc-nickel electroplating bath, including water; nickel ion; zinc ion; at least one complexing agent; and at least one non-ionogenic, surface active polyoxyalkylene compound, wherein the bath has an alkaline pH.

[0004] In another embodiment, the present invention relates to an aqueous alkaline plating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which comprises (A) from about 1 to about 100 g/l of zinc ions; (B) from about 0.1 to about 50 g/l of nickel ions; (C) at least one complexing agent at a concentration sufficient to maintain the nickel ion in solution; and (D) from about 0.1 to about 50 g/l of at least one non-ionogenic, surface active polyoxyalkylene compound.

[0005] In one embodiment, the present invention relates to an aqueous alkaline electroplating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which includes: (A) from about 1 to about 100 g/l of zinc ion; (B) from about 0.1 to about 50 g/l of nickel ion; (C) at least one complexing agent at a concentration sufficient to maintain the nickel ion in solution; and (D) from about 0.1 to about 50 g/l of at least one non-ionogenic, surface active polyoxyalkylene compound, in which the zinc ion, the nickel ion and the non-ionogenic surface active polyoxyalkylene compound are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a substantially gamma phase.

[0006] In one embodiment, the present invention relates to a process for electroplating a zinc-nickel alloy on a substrate, comprising electroplating the substrate with the aqueous alkaline electroplating bath described herein. In another embodiment, the present invention further relates to an article comprising a substrate electroplated to the process described herein.

[0007] The present inventors have discovered that, contrary to accepted teachings in the art, the presence in the zinc-nickel bath of the non-ionogenic surface active polyoxyalkylene compound produces a zinc-nickel coating that is one or more of smooth, adherent, ductile, leveling, and fine-grained, over a wide range of plating conditions and cathode current densities. Use of the composition of the invention can increase the efficiency of the electroplating process and increases the ductility of the deposit. Increasing the efficiency of the process translates into decreasing processing time for the plating operation and increasing its competitive advantage. Increasing the ductility of the deposit enables the alloy, which is already known to have superior corrosion resistance properties, to be used in many more applications where bending of the plated object is required. Examples of uses where bending is required include tubing for fuel lines or air conditioning use; wire for various usages; sheet steel for appliances or automotive surfaces. Thus, a long-felt need has been met by the present invention.

DETAILED DESCRIPTION

[0008] The improved zinc-nickel alloy electroplating baths of the present invention comprise an aqueous alkaline solution containing zinc ions, nickel ions and at least one non-ionogenic, surface active polyoxyalkylene compound as described more fully below. The alkaline plating baths are free of added cyanide.

[0009] As used herein, the term “non-ionogenic surface active polyoxyalkylene” refers to both (1) materials having a substantially non-ionic character, such as materials referred to in the chemical arts as nonionic surfactants, and (2) derivatives and reaction products of polyoxyalkylenes that have a limited degree of ionic character, but which are substantially non-ionic in character, such as a polyoxyalkylene with a terminal group such as, for example, a sulfonate, phosphonate, amine or halide group. Many such compounds are known in the art.

[0010] In one embodiment, the plating baths of the present invention include at least one non-ionogenic, surface active polyoxyalkylene compound present in an amount effective to provide grain refinement of a zinc-nickel alloy electroplated with the bath. Grain refinement means that the electrodeposited material has reduced roughness and/or reduced dendritic character, and more uniform coverage of the substrate on which the electrodeposited material is applied. A grain refining addition agent is one which improves the electrodeposited by reducing and, in one embodiment, eliminating, rough and dendritic deposits in areas in which the applied current density is relatively high, and by extending coverage of the electrodeposited into areas in which the applied current density is relatively low. As is known in the art, when applying current in an electrodeposition process, distance or length of the cathodic substrate from the anode (current source) is inversely related to applied current density, so that parts of a cathodic substrate closer to the anode are exposed to a relatively higher current density and parts of a cathodic substrate further away from the anode are exposed to a relatively lower current density. In the absence of a grain refining agent, parts of a cathodic substrate exposed to a high current density may have a rough and/or dendritic electrodeposited material while, on the other hand, parts of the cathodic substrate exposed to low current density may be poorly covered by the electrodeposited material. The grain refining addition agent of the present invention may smooth
and balance the process so that the electrodeposited material is smoother, more evenly distributed, and/or is free of dendritic deposits.

[0011] The plating baths of the invention contain an inorganic alkali component in sufficient quantity to provide the bath with the desired pH. In one embodiment, the amount of the alkali component contained in the plating bath is an amount sufficient to provide a bath having the desired pH of at least 10, and in one embodiment, an amount sufficient to provide a bath having a pH of at least about 11 or, in one embodiment, a pH of about 14. In one embodiment, an amount from about 50 to about 220 grams of alkali component per liter of plating bath are utilized, and in another embodiment, the amount is from about 90 to about 110 grams per liter. In one embodiment, the alkali component is an alkali metal derivative such as sodium or potassium hydroxide, sodium or potassium carbonate, and sodium or potassium bicarbonate, etc., and mixtures thereof.

[0012] Zinc Ion

[0013] The alkaline plating baths of the present invention generally will contain zinc ion at concentrations ranging from about 0.1 to about 100 g/l. In one embodiment, the concentration of zinc ion ranges from about 1 to about 50 g/l, and in another embodiment, from about 5 to about 20 g/l. The zinc ion may be present in the bath in the form of a soluble salt such as zinc oxide, zinc sulfate, zinc carbonate, zinc acetate, zinc sulfate, zinc sulfamate, zinc hydroxide, zinc tartrate, etc. In one embodiment, the zinc ion is obtained from one or more of ZnO, Zn(OH)₂, ZnCl₂, ZnSO₄, ZnCO₃, Zn(SO₄)₂·N₃H₂, Zn(OCOC₂H₅)₂, Zn(BF₄)₂ and zinc methane sulfonate.

[0014] Here, as in all of the specification and claims, the numerical limits of the disclosed ranges and ratios may be combined.

[0015] Nickel Ion

[0016] The alkaline plating baths of the present invention further comprise from about 0.1 to about 50 g/l of nickel ions, and in one embodiment, the bath contains from about 0.5 to about 20 g/l of nickel ions. Sources of nickel ions which can be used in the plating baths include sources of nickel such as one or more of nickel hydroxide, inorganic salts of nickel, and organic acid salts of nickel. In one embodiment, the nickel source includes one or more of nickel hydroxide, nickel sulfate, nickel carbonate, ammonium nickel sulfate, nickel sulfamate, nickel acetate, nickel formate, nickel bromide, nickel chloride, etc. The nickel and zinc sources which may be used in the invention may comprise one or more of the above-described sources and one or more of the above-described sources. In one embodiment, the nickel ion is obtained from one or more of NiSO₄, Ni(OH)₂·6H₂O, NiCO₃, Ni(SO₄)·N₃H₂, Ni(OCOC₂H₅)₂, (NH₄)₂Ni(SO₄)·6H₂O, Ni(OOCCH₃)₂, a Ni complex, Ni(BF₄)₂ and nickel methane sulfonate.

[0017] In one embodiment, the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy having a substantially gamma crystallographic phase. As is known in the art, a zinc-nickel alloy having a substantially gamma crystallographic phase is more resistant to corrosion, particularly chloride- or salt-derived corrosion, than is an alloy having a phase other than the substantially gamma phase.

[0018] Complexing Agent

[0019] The plating baths of the invention further comprise at least one complexing agent. The at least one complexing agent may be any complexing agent known in the art. In one embodiment, the at least one complexing agent is a complexing agent suitable for nickel ion. In one embodiment, the at least one complexing agent may be one or more of the complexing agents described below. In another embodiment, the at least one complexing agent may be an amine such as ethylenediamine, diethylenetriamine, and/or higher polyamines such as those described below.

[0020] In one embodiment, the at least one complexing agent comprises at least one polymer of an aliphatic amine. In one embodiment, the amount of the polymer of an aliphatic amine contained in the aqueous alkaline plating baths of the present invention ranges from about 1 to about 150 g/l and in another embodiment, ranges from about 5 to about 50 g/l.

[0021] Typical aliphatic amines which may be used to form such polymers of aliphatic amines include 1,2-alkyleneimines, monoethanolamine, diethanolamine, triethanolamine, ethylenediamine, diethylenetriamine, imino-bis-propylamine, polyethyleneimine, triethylenetetramine, tetraethylpentamine, hexamethylenediamine, etc.

[0022] In one embodiment, polymers derived from 1,2-alkyleneimines are used, in which the alkyleneimines may be represented by the general formula (IV):

\[
\text{H} \quad \begin{array}{c}
\text{N} \\
\text{A} \\
\text{B} \\
\text{CH}_2 \\
\end{array} 
\]

[0023] wherein A and B are each independently hydrogen or alkyl groups containing from 1 to about 3 carbon atoms. Where A and B are hydrogen, the compound is ethyleneimine. Compounds wherein either or both A and B are alkyl groups are referred to herein generically as alkyleneimines although such compounds have been referred to also as ethyleneimine derivatives.

[0024] Examples of poly(alkyleneimines) which are useful as a complexing agent in the present invention include polymers obtained from ethyleneimine, 1,2-propyleneimine, 1,2-butyleneimine and 1,1-dimethylethyleneimine. The poly(alkyleneimines) useful in the present invention may have molecular weights of from about 100 to about 100,000 or more although the higher molecular weight polymers are not generally as useful since they have a tendency to be insoluble in the zinc plating baths of the invention. In one embodiment, the molecular weight will be within the range of from about 100 to about 60,000 and in another embodi-
ment, from about 150 to about 2000. In one embodiment, the poly(ethylenimine)s have molecular weights of from about 150 to about 2000. Useful polyethyleneimines are available commercially from, for example, BASF under the designations Lugalan® G-15 (molecular weight 150), Lugalan® G-20 (molecular weight 200) and Lugalan® G-35 (molecular weight 1400).

[0025] The poly(alkyleneimines) may be used per se or may be reacted with a cyclic carbonate consisting of carbon, hydrogen and oxygen atoms. A description of the preparation of examples of such reaction products is found in U.S. Pat. Nos. 2,824,857 and 4,162,947, which disclosures are incorporated herein by reference. The cyclic carbonates further are defined as containing ring oxygen atoms adjacent to the carbonyl groupings which are each bonded to a ring carbon atom, and the ring containing said oxygen and carbon atoms has only 3 carbon atoms and no carbon-to-carbon unsaturation.

[0026] In one embodiment, the at least one complexing agent which can be incorporated into the aqueous alkaline plating baths of the present invention include carboxylic acids such as citric acid, tartaric acid, gluconic acid, alpha-hydroxybutyric acid, sodium or potassium salts of said carboxylic acids; polyamines such as ethylenediamine, triethylenetetramine; amino alcohols such as N-(2-aminoethyl)ethanolamine, 2-hydroxyethylaminomethylamine, N-(2-hydroxyethyl)diaminomethylamine; etc. When included in the baths of the invention, the amount of metal complexing agent may range from 5 to about 100 g/l, and more often the amount will be in the range of from about 10 to about 30 g/l.

[0027] In one embodiment, the at least one complexing agent useful in the aqueous alkaline electroplating baths of the present invention comprise compounds represented by the formula:

$$R^1(R^8)^{—}N—R^4(N^3R^6)^{—}N(R^8)^{—}R^3$$

(V)

[0028] wherein R1, R8, R9 and R10 are each independently alkyl or hydroxyalkyl groups provided that at least one of R1—R3 is a hydroxy alkyl group, and R8 is a hydroxycarbylene group containing up to about 10 carbon atoms. In one embodiment, the groups R1—R10 may be alkyl groups containing from 1 to 10 carbon atoms, or in another embodiment, the groups R1—R10 may be hydroxyalkyl groups containing from 1 to 5 carbon atoms, or in another embodiment, the groups R1—R10 may be hydroxyalkyl groups containing from 1 to 10 carbon atoms, or in another embodiment, from 1 to 5 carbon atoms. The hydroxyalkyl groups may contain one or more hydroxyl groups, and in one embodiment, at least one of the hydroxyl groups present in the hydroxyalkyl groups is a terminal group. In one embodiment, each of R1, R8, R9 and R10 is a hydroxyalkyl group as defined above.

[0029] Specific examples of complexing agents characterized by Formula (V) include N-(2-hydroxyethyl)-N,N',N'-triethylenediamine; N,N'-di(2-hydroxyethyl)N,N'-diethyl ethylenediamine; N,N'-di(2-hydroxyethyl)-N,N'-diethyl ethylenediamine; N,N',N,N'-tetrais(2-hydroxyethyl)ethylenediamine; N,N',N,N'-tetrais(2-hydroxyethyl)propylene diamine; N,N,N',N'-tetraakis(2,3-dihydroxypropyl)ethylenediamine; N,N,N',N'-tetraakis(2,3-dihydroxypropyl)propylene diamine; N,N,N',N'-tetraakis(2-hydroxypropyl)ethylenediamine; N,N,N',N'-tetraakis(2-hydroxyethyl)1,4-diaminobutane; etc. An example of a useful commercially available metal complexing agent is Quadrol from BASF. Quadrol is N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine.

[0030] Non-Iogenic, Surface Active Polyoxyalkylene Compound

[0031] The plating baths of the invention further comprise at least one non-ionic, surface active polyoxyalkylene compound. The presence in the zinc-nickel bath of the non-ionic surface active polyoxyalkylene compound produces a zinc-nickel coating that is more or more of 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. A wide variety of non-ionic, surface active polyoxyalkylene compounds may be suitable for practice of this aspect of the present invention.

[0032] In one embodiment, the non-ionic, surface active polyoxyalkylene compound is a nonionic surfactant. Suitable nonionic surfactants are described in McCutcheon's Volume 1: Emulsifiers & Detergents, North American Edition, 1995. The disclosure of the nonionic surfactants in McCutcheon's is incorporated by reference herein for its teachings relating to such compounds.

[0033] In one embodiment, the non-ionic, surface active polyoxyalkylene compounds which can be utilized in the present invention include the condensation products of ethylene oxide and/or propylene oxide with compounds containing a hydroxy, mercapto or amino group containing at least one O—H, N—H and/or S—H bond, i.e., an active hydrogen atom. Examples of materials containing hydroxyl groups include alkyl phenols, styrenated phenols, fatty alcohols, fatty acids, polyalkylene glycols, etc. Examples of materials containing amino groups include amines and polyamines, fatty acid amides, etc. Examples of materials containing a mercapto group include alkyl mercaptans, aromatic mercaptans, and include those containing more than one —SH group per molecule, e.g., dithiols, trithiols, etc.

[0034] In one embodiment, the non-ionic, surface active polyoxyalkylene compounds useful in the plating baths of the invention include a polyoxyalkylene compound having the formula (Ia), (lb) or (lc):

$$\begin{align*}
R^1-O-([CH_2]_x)SO_\frac{1}{2}H \\
R^1-O-([CH_2]_x)SH \\
R^1-O-([CH_2]_x)OH
\end{align*}$$

or

[0035] wherein R1 is a substituted or unsubstituted aryl, alkyl, alkenyl or alkynyl group containing up to about 24 carbon atoms, wherein the substitution may be aryl or alkyl or both, R2 is an alkyl group containing from 1 to about 4 carbon atoms, n is 2 or 3, and x is an integer between 2 and about 100. Such compounds are produced generally by treating alkyl, aryl or fatty alcohols or alkyl or alkoxy-substituted phenols or naphthals with excess ethylene oxide or propylene oxide.

[0036] In one embodiment, when R3 is an alkyl carbon chain, it may contain from about 14 to 24 carbon atoms and may be derived from a long chain fatty alcohol such as oleyl alcohol or stearyl alcohol.
Nonionic polyoxyethylene compounds are described, for example, in U.S. Pat. No. 3,855,085. Such polyoxyethylene compounds are available commercially under the general trade designations Surfynol® by Air Products and Chemicals, Inc. of Wayne, Pa., and under the designation Pluronic® or Tetronic® by BASF Wyandotte Corp. of Wyandotte, Mich. Examples of specific polyoxyethylene condensation products useful in the invention include Surfynol® 465 which is a product obtained by reacting about 10 moles of ethylene oxide with 1 mole of tetramethyldicyclosiloxane. Surfynol® 485 is the product obtained by reacting 30 moles of ethylene oxide with tetramethyldicyclosiloxane. "Pluronic® L35" is a product obtained by reacting 22 moles of ethylene oxide with polypropylene glycol obtained by the condensation of 16 moles of propylene oxide. BASF Tetronic® 90R4 is an ethylene oxide/propylene oxide ethylene diamine copolymer. BASF Pluronic® L62 is a propylene oxide/ethylene oxide block copolymer (ethylene oxide 20%, propylene oxide 80%). Surfynol 465 is a PEG10 tetramethyl decyndiol. Pluronic® 1085 is an ethylene oxide/propylene oxide block polymer (ethylene oxide 50%, propylene oxide 50%). BASF Pluronic® 25R2 is an ethylene oxide/propylene oxide block polymer (ethylene oxide 20%, propylene oxide 80%). Tomadex 91-6 is a linear alcohol (C10,11)-ethylene oxide (6 moles). Igepal® CO 710 is a nonylphenoxyl ethoxylate. Lugalvan® HS-1000 is a trihydroxylic ethoxylate. PluroFac® C-17 is an ethoxylated alkyl alcohol.

Alkoxylated amine, long chain fatty amine, long chain fatty acid, alkanol amines, diamines, amides, alkanol amides and polyglycol-type surfactants known in the art are also useful. One type of amine surfactant found particularly useful in the plating bath is the compound obtained by the addition of a mixture of propylene oxide and ethylene oxide to diamines. More specifically, compounds formed by the addition of propylene oxide to ethylene diamine followed by the addition of ethylene oxide are useful and are available commercially from BASF under the general trade designation Tetronic®.

In one embodiment, the non-ionogenic, surface active polyoxyalkylene compound is a Carbowax®-type surfactant, available from Union Carbide. Carbowax®-type surfactants which are polyethylene glycols having a range of different molecular weights may be useful. As is known in the art, the number designation of the Carbowax® compounds corresponds approximately to the average molecular weight of the compounds. For example, Carbowax® 600 is an ethylene oxide polymer with a molecular weight about 600. Carbowax® 1000 has a molecular weight range of from about 950 to 1050 and contains from 20 to 24 ethoxy units per molecule. Carbowax® 2000 is an ethylene oxide polymer with a molecular weight of about 2000. Carbowax® 4000 has a molecular weight range of from about 3000 to 3700 and contains from 68 to 85 ethoxy units per molecule. Although higher molecular weight materials may be used, at some point the compound separates from the aqueous bath. Other known nonionic glycol derivatives such as polyalkylene glycol ethers and methoxy polyethylene glycols which are available commercially can be utilized as the non-ionogenic, surface active polyoxyalkylene compound in the compositions of the invention.

In one embodiment, the non-ionogenic, surface active polyoxyalkylene compound is an ethylene oxide condensation product. Ethylene oxide condensation products with fatty acids also are useful nonionic surfactants. Many of these are available commercially such as under the general tradenames Ethosulf® from Armak Ind. Examples include condensates of coco acids, oleic acid, etc. Ethylene oxide condensates of fatty acid amides, e.g., oleamide, also are available from Armak Inc.

In some of the baths, improved results are obtained when polyoxyalkylated glycols, phenols and/or naphthols are included. For example, in one embodiment, ethylene oxide and propylene oxide condensates with aliphatic alcohols, sorbitan alkyl esters, alkyl, alkyloxy and styrenated phenols and naphthols are useful additives. In one embodiment, about 6 to about 40 moles of the oxide may be condensed with the above-identified compounds. Many of these condensates are available commercially under such tradenames as Tween® from ICI America, Triton® from Rohm & Haas Co., Tergitol® from Union Carbide, and Igepal® from Rhone-Poulenc.

In one embodiment, the non-ionogenic, surface active polyoxyalkylene compound is a low molecular weight polyoxyalkylene glycol based on 2 to about 4 carbon atom alkylene oxides, which may comprise a homopolymer or copolymer having a molecular weight of from about 400 to about 5000, and in one embodiment an average molecular weight from about 600 to about 2500. In one embodiment, the homopolymers or copolymers are primarily based on ethylene oxide, and in one embodiment are homopolymers based on ethylene oxide.

In one embodiment, the bath comprises a low molecular weight polyoxyalkylene glycol based on 3 to about 4 carbon atom alkylene oxides, and includes the homopolymers or copolymers thereof with each other and/or with ethylene oxide. The low molecular weight polyoxyalkylene glycol is one that has a molecular weight up to about 2500 and in one embodiment, from about 300 to about 2000, and in another embodiment from about 600 to about 1500. In one embodiment, the homopolymers and copolymers are primarily based on propylene oxide, and in one embodiment, are homopolymers based on propylene oxide, such as for example, polypropylene glycol.

The copolymers may be random or block copolymers, where the repeating units of the block copolymers are block or heteric or the various combinations of these repeating units known in the art.

In one embodiment, the polyoxyalkylene compounds may be polyoxyalkylene glycol ether all-block, block-heteric, heteric-block or heteric-heteric block copolymers where as noted, the alkylene units have from 2 to about 4 carbon atoms and may comprise surfactants which contain hydrophobic and hydrophilic blocks where each block is based on at least oxyethylene groups or oxypropylene groups or mixtures of these groups. Mixtures of homopolymers and copolymers may also be used, especially the 2 or 3 component mixtures.

The most common method of obtaining these materials is by reacting an alkylene oxide such as ethylene oxide with a material that contains at least one reactive hydrogen. Alternative routes include the reaction of the active hydrogen material with a preformed polyglycol or the use of ethylene chlorohydrin instead of an alkylene oxide. A wide variety of such compounds are commercially available, as noted above, for example.
[0047] In one embodiment, the at least one non-ionogenic, surface active polyoxyalkylene compound includes one or more of alkoxylated alkyl phenols, alkoxylated alkyl naphthols, alkoxylated aliphatic monohydric alcohols, alkoxylated polyoxypropylene glycols, alkoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol. In one embodiment, polyethoxylated alkyl phenols are used. In one embodiment, the polyethoxylated alkyl phenol surfactant is a commercially available ethoxylated nonyl phenol sold under the trade name Tergitol® NP-15 by Union Carbide Corporation and under the trade name Igepal® CO-730 by Rhone-Poulenc Surfactants and Specialties. The latter surfactant is believed to contain approximately 15 repeating ethyleneoxy units in the hydrophilic portion of the molecule. Another suitable nonionic surfactants include Igepal® CA-887 from Rhone-Poulenc.

[0048] In one embodiment, the one or more non-ionogenic, surface active polyoxyalkylene compound may include, for example, alkoxylated alkyl phenols, e.g., nonylphenol; alkyl naphthols; aliphatic monohydric alcohols; aliphatic polyhydric alcohols, e.g., polyoxypropylene glycol. Exemplary alkoxylated compounds within the above classes which are commercially available include Igepal® CA 630, trade name for an ethoxylated octyl phenol, available from Rhone-Poulenc; Brij® 98, trade name for an ethoxylated octyl alcohol available from ICI America, Inc.; Pluronic® F68, trade name for a polyoxyethylene polyoxypropylene glycol available from BASF; and Surlyn® 485, a trade name for ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol available from Air Products and Chemicals, Inc. Other grades of these trade name non-ionogenic, surface active polyoxyalkylene compounds may also be useful.

[0049] In one embodiment, the at least one non-ionogenic, surface active polyoxyalkylene compound comprises a polyhydroxy compound which has been treated with an alkylic oxide in an alkylation reaction. In one embodiment, the polyhydroxy compound may include suitable water soluble compounds such as diols, triols, polyols and larger molecules such as mono- or polysaccharides. In one embodiment, such materials include, without limitation, aditols, aditols, aldonic acids, uldaric acids, uronic acids, aldolactones, amylloses, soluble celluloses, and the like. In one embodiment, the polyhydroxy compounds may include one or more of sorbitol, glucose, methyl glucose, gluconoic acid, glucaric acid, mannitol, fructose, glycerin, ethylene glycol, diethylene glycol (diglyme), triethylene glycol (triglyme), higher glycols, trimethyl propane, pentacyrtritol, trihydroxy butane, trihydroxy butanone, trihydroxy hexane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, tri(hydroxymethyl)ethane, or mixtures thereof.

[0050] In one embodiment, the at least one non-ionogenic, surface active polyoxyalkylene compound comprises at least one compound having a formula:

$$R^3-O-\{R^4-O-L\}_n-X$$  \hspace{1cm} (Ia)

or

$$R^3-O-\{R^4-O-L\}_n-Y$$  \hspace{1cm} (Ib)

[0051] wherein $R^3$, $R^4$, $R^5$, $R^6$, and $R^7$ are C$_1$-C$_8$ branched or unbranched alkyl, alkylene or alkynyl group, or phenyl-$O-\{R^5-O-\}_m-CH_2-\ldots$, in which $m=0-100$ and $R^5$ is a C$_1$-C$_8$ branched or unbranched alkylene; $R^7=\text{C}_1-\text{C}_8$ branched or unbranched alkylene; $X=\text{H}, -\text{SO}_2\text{Z}, -\text{SO}_3\text{Z}, -\text{SO}_2\text{Z}, -\text{PO}_2\text{Z}_2$, $-\text{PO}_3\text{Z}_2$ (wherein $Z$ independently may be $H$, an alkali metal ion, or $Z$ may be an alkaline earth metal ion), $-\text{NH}_2$, $-\text{Cl}$ or $-\text{Br}$; $Y$ is an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and is equal to or less than the number of active hydrogens in OH, $-\text{NH}$, $\text{NH}_2$ or $-\text{SH}$ groups in the $Y$ component. The $Y$ component may be any of the polyhydroxy, amine, polyamine or mercaptan compounds defined herein.

[0052] In one embodiment, the polyhydroxy compound $Y$ in formula (Ia) is a higher glycol, such as one having a general formula

$$\text{HO-(}R^8-O-\{R^9-O-\}_n-\text{H)}$$  \hspace{1cm} (III)

[0053] wherein $R^8$, $R^9$=C$_1$-C$_8$ alkylene, or a C$_1$-C$_9$ alkylene substituted with one or more additional hydroxyl groups, or a mixture of such $R^9$ groups.

[0054] In one embodiment, one or more of the oxygen atoms in the polyhydroxy compound may be replaced by a sulfur atom. Thus, for example, in one embodiment, the polyhydroxy compound is thioglycol (2,2-thiodiethanol). In one embodiment, the polyhydroxy compound is mercaptoethanol. In one embodiment, the number of sulfur atoms substituted for oxygen is limited to the number which provides a water soluble non-ionogenic, surface active polyoxyalkylene compound. As will be recognized, in general the greater the number of sulfur atoms replacing oxygen atoms, the lower the solubility of the non-ionogenic, surface active polyoxyalkylene compound.

[0055] In one embodiment, the one or more non-ionogenic surface active polyoxyalkylene compound comprises alkoxylated thioglycol. In one embodiment, the non-ionogenic surface active polyoxyalkylene compound comprises alkoxylated mercaptoethanol. In one embodiment, the alkoxylolation of these sulfur-containing moieties is ethoxylation. In one embodiment, the bath includes a thioglycol ethoxylate available from BASF as Legulvan® HS-1000.

[0056] In one embodiment, the alkylene oxide used to treat a polyhydroxy compound in preparing the non-ionogenic, surface active polyoxyalkylene compounds of the invention comprises from 2 to about 4 carbon atoms, and thus may be ethylene oxide, propylene oxide, 1-butylene oxide, 1-iso-butylene oxide, 2-butylene oxide. In another embodiment, the oxalkylene group comprises from 2 to about 6 carbon atoms.

[0057] In one embodiment, the number of moles of oxalkylene groups per mole of polyhydroxy compound ranges from about 2 to about 120. In another embodiment, the number of moles of oxalkylene groups per mole of polyhydroxy compound ranges from 12 to 40 moles per mole of additive.

[0058] In one embodiment, the at least one non-ionogenic, surface active polyoxyalkylene compound comprises a bath soluble terminal substituted polyoxyalkylene compound derived from the sulfation, amination, phosphating, chlorination, bromination, phosphorylation and sulfonation, as well as combinations thereof, of either or both of:

[0059] (a) the product of polymerization of alkenyloxides including ethylene oxide, propylene oxide, glycidol, butylene oxide and mixtures thereof; or

[0060] (b) the product of alkylation of mono and polyhydroxy compounds including hydroxyl-con-
taining alkyl, alkenyl, alkynyl or aryl groups, as well as mixtures thereof. Thus, in one embodiment, one or more terminal hydroxy group is converted to —SO₂Z, —SO₃Z, —SO₃⁻Z —PO₃Z⁻, —PO₃⁻Z⁻ (wherein Z independently may be H, an alkali metal ion, or Z may be an alkaline earth metal ion) —NH₂, —Cl or —Br or combinations thereof. It will be appreciated that the compound may contain one or more such terminal group on the molecule depending upon the degree of substitution and the number of reactive hydroxy groups on the molecule.

[0061] In one embodiment, the molecular weight of the one or more non-ionogenic, surface active polyoxyalkylene compound thereof is controlled to render the compound soluble in the bath at the concentration desired. The one or more non-ionogenic, surface active polyoxyalkylene compound of the present invention should be water soluble at usual operating temperatures.

[0062] In one embodiment, the at least one non-ionogenic, surface active polyoxyalkylene compound is present in the bath in an amount ranging from about 0.1 to about 50 grams per liter of electrolyte, in another embodiment, from about 5 to about 20 grams per liter and in another embodiment, from about 1 to about 10 grams per liter. In one embodiment, the amount of the at least one non-ionogenic, surface active polyoxyalkylene compound is effective to provide grain refinement of a zinc-nickel alloy electroplated with the bath. In another embodiment, the amount of the at least one non-ionogenic, surface active polyoxyalkylene compound is effective to provide a zinc-nickel alloy which is one or more of bright, level, and corrosion resistant. In another embodiment, the amount of the at least one non-ionogenic, surface active polyoxyalkylene compound is effective to enhance the ductility of the zinc-nickel alloy. In one embodiment, the amount of the non-ionogenic, surface active polyoxyalkylene compound, together with the amounts of zinc and nickel in the plating bath, is effective to result in the deposition of a zinc-nickel alloy having a substantially gamma phase crystal structure.

[0063] Auxiliary Brightening Agents

[0064] In one embodiment, an auxiliary brightening agent is added to the aqueous alkaline electroplating bath. Many brightening agents are known in the art and may be suitably selected by those of ordinary skill.

[0065] In one embodiment, one or more of the following auxiliary brightening agents may be added: the condensation product of piperazine, guanidine, formaldehyde, and epichlorohydrin, as defined in U.S. Pat. No. 4,188,271 (described in more detail below, and incorporated by reference herein); polyethylene imine; pyridinium propyl sulfonate; N-benzyl-3-carboxy pyridinium chloride; trigonelline; Golpanol® PS (sodium propargyl sulphonate); propargyl alcohol; ethylenglycolpropargyl alcohol ether; BEO (ethoxylated butyne diol); Aerosol AY65 (sodium diamylsulphosuccininate); NN,N-bis(3-dimethylaminopropyl)urea, polymer with 1,3-dichloropropene—see U.S. Pat. No. 6,652,726 B1; carboxyethylisothiuronium betaine; Rewopol® EHS (ethyl hexyl sulfate); benzoates; Lithien® A-APS (a proprietary anionic surfactant from BASF); Lugalvan® BPC 34 (a 34 wt % aqueous solution of N-benzyl nicotinate); benzyl-2-methylimidazole; Tamol NN (a formaldehyde condensate of 2-naphthalene sulfonate); methyl naphthyl ketone; benzoic acid; Lutensit® CS40 (40% cumene sulfonate); Golpanol® VS (sodium vinyl sulfonate); benzoazolium-2-[4-(dimethylamino)phenyl]-3,6-dimethyl chloride; DPS (N,N-dimethyl-dithiocarbamyl propyl sulfonic acid sodium salt); MPS (3-mercapto-1-propanesulfonic acid, sodium salt); OPS (O-ethylidihydrocarbamo-S-(3-sulfopropyl)-ester, potassium salt; SPS (bis-(3-sulfopropyl)-disulfide, disodium salt; UPS (3-S-isothiouronium propyl sulfonate); ZPS (3-(benzothiazolyl-2-mercapto)-propyl-sulfonic acid, sodium salt) (DPS, MPS, OPS, SPS, UPS and ZPS are available from Raschig GmbH); N-(polyacrylamide); safranin; crystal violet and derivatives thereof; phenazinium dyes and derivatives thereof; Lugalvan® HT (thiodiglycol ethoxide); sodium citrate; sodium lauryl sulfate; Dequest® (1-hydroxyethylben-1,1-diphosphonic acid); Lugalvan® BNO (ethoxylated beta naphthol); Lugalvan® SES (sodium salt of a sulphonated allylphenol ethoxylate); sulfurized benzene sulfonic acid; butyndiol dihydroxypropyl sulfonate; sodium saccharin; MPSA (3-mercapto-1-propanesulfonic acid, sodium salt); the formaldehyde condensate of 1-naphthenyl sulfonic acid; benzotriazole; tartaric acid; EDTA (ethylenediaminetetraacetic acid); sodium benzoate; the aqueous reaction product of 2-aminoipyridine with epichlorohydrin; Mirapel® A15 (ureylene quaternary ammonium polymer); the aqueous reaction product of imidazole and epichlorohydrin; vanillin; anisaldehyde; Heliotrop (piperonal); thiourea; polyvinyl alcohol; reduced polyvinyl alcohol; o-chlorobenzaldehyde; α-naphthaldehyde; condensed naphthalene sulfonate; nicain; pyridine; 3-hydroxypropionate sulfonate; allyl pyridinium chloride; dibenznesulfonamide; pyridinium butane sulfonate; sodium allyl sulfonate; sodium vinyl sulfonate; naphthalene trisulfonic acid; cumene sulfonate; CMP (carboxymethyl pyridinium chloride); Golpanol® 9531 (propargyl hydroxypropyl ether sulfonate); o-sulfobenzaldehyde; Lugalvan® ES-9751 (aqueous reaction product of imidazole and epichlorohydrin); mercapto thio ether; PVP (polyvinylpyrrolidone); sodium adipate; chloral hydrate; sodium gluconate; sodium salicylate; manganese sulfate; cadmium sulfate; sodium tellurite; and glycine. The foregoing list is not exhaustive and is exemplary only. Any other known brightener useful in electroplating zinc and/or nickel may be useful herein.

[0066] In one embodiment, the auxiliary brightener is a material disclosed and claimed in U.S. Pat. No. 6,652,728 B1, the disclosure of which is incorporated by reference herein for its teachings relating to the polymer of general formula A and the use thereof in alkaline zinc or zinc alloy electroplating baths. U.S. Pat. No. 6,652,728 B1 discloses an aqueous alkaline cyanide-free bath for the galvanic deposition of zinc or zinc alloy coatings on substrate surfaces, which is characterized in that the bath contains:

[0067] (a) a source of zinc ions and optionally a source of further metal ions,

[0068] (b) hydroxide ions, and

[0069] (c) a polymer soluble in the bath and having the general formula A:

\[
A = \begin{cases} 
R_1 & \text{if } n = 1 \\
R_2 & \text{if } n = 2 \\
R_3 & \text{if } n = 3 \\
R_4 & \text{if } n = 4 \\
R_5 & \text{if } n = 5 \\
\vdots & \text{if } n = k 
\end{cases}
\]
[0070] wherein m has the value 2 or 3, n has a value of at least 2, R₁, R₂, R₃ and R₄, which may be the same or different, each independently denote methyl, ethyl or hydroxyethyl, p has a value in the range from 3 to 12, and \( X^- \) denotes \( \text{Cl}^- \), \( \text{Br}^- \) and/or \( \text{I}^- \). In one embodiment, in the above formula A, each of R₁, R₂, R₃ and R₄ are methyl, both m and p=3, \( X^- \) is \( \text{Cl}^- \) and n is in the range from 2 to about 80. The amount of this additive may range, in one embodiment, from about 0.1 g/l to about 50 g/l, and in one embodiment, from about 0.25 to about 10 g/l.

[0071] In one embodiment, in addition to any of the above brighteners, and in one embodiment, in addition to the material defined in U.S. Pat. No. 6,652,728 B1, there is also included in the bath a further additive which as a quaternary derivative of a pyridine-3-carboxylic acid of the formula B and/or a quaternary derivative of a pyridine-3-carboxylic acid of the formula C:

![Diagram of molecular structures](image)

[0072] wherein R₆ denotes a saturated or unsaturated, aliphatic, aromatic or araliphatic hydrocarbon radical with 1 to 12 carbon atoms. The amount of this additional additive may range from about 0.005 to about 0.5 g/l, and in one embodiment, from about 0.01 to about 0.2 g/l.

[0073] The quaternary derivatives of a pyridine-3-carboxylic acid of the formula B or C that may be used in one embodiment as a further additive in the bath according to the invention are compounds known and described, for example, in DE 40 38 721. Similar materials are also disclosed in U.S. Pat. No. 3,296,105. These derivatives are generally prepared by reacting nicotinic acid with aliphatic, aromatic or arylaliphatic halogenated hydrocarbons.

[0074] In one embodiment, the alkaline aqueous electropolishing bath may include one or more aldehydes as a brightener and/or to further improve gloss and leveling. Examples of aldehydes which may be included in the plating baths include one or more aromatic aldehydes such as anisaldehyde, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 1,3-benzodioxole-5-carboxaldehyde (piperonal), veratraldehyde, p-tolualdehyde, benzaldehyde, m-chlorobenzaldehyde, 2,3-dimethoxybenzaldehyde, salicylaldehyde, cinnamaldehyde, adducts of cinnamaldehyde with sodium sulfitre, etc. The amount of aldehyde which may be included in the plating baths may range from about 0.01 to about 2 g/l.

[0075] The foregoing lists of brighteners are exemplary and are not intended to be either exhaustive or limiting of the scope of auxiliary brighteners which may be useful together with the present invention. Additional or alternative brighteners may be suitably selected by those of ordinary skill in the art.

[0076] Additional Components

[0077] In one embodiment, the alkaline plating baths of the present invention include one or more additional components to provide further improved and stable plating baths and to provide for further improved zinc-nickel alloys. For example, alkaline plating baths may contain additional metal-complexing agents, aromatic aldehydes to improve the gloss or brightness of the alloy, polymers of aliphatic amines, surface-active agents, etc.

[0078] In one embodiment, the bath may further comprise an additive comprising a reaction product of one or more piperazines, at least one additional nitrogen-containing compound selected from the group consisting of ammonia or aliphatic acyclic compounds containing at least one primary amine group, formaldehyde, and an epichlorohydrin or a glycerol halohydrin or mixtures thereof. Such reaction products are disclosed in U.S. Pat. No. 4,188,271, the disclosure of which relating to such reaction products is incorporated herein by reference. In one embodiment, the reaction product is obtained by the process of

(a) preparing an intermediate product by reacting formaldehyde with a mixture of

(i) one or more piperazines having the formula

![Diagram of molecular structure](image)

[0079] wherein R¹ and R¹ are each independently hydrogen or lower alkyl groups, and

(ii) at least one additional nitrogen-containing compound from the group consisting of ammonia or aliphatic, acyclic compounds containing at least one primary amine group, and

[0080] (b) reacting said intermediate product with an epichlorohydrin or glycerol halohydrin or mixtures thereof at a temperature within the range of from room temperature to the reflux temperature of the mixture. In one embodiment, the molar ratio of the piperazine(s), additional nitrogen-containing compound, formaldehyde and epichlorohydrin or glycerol halohydrin is in the range of from about 1:1:2:1 to about 1:1:4:5:1.

[0081] In one embodiment, the additional nitrogen-containing compound is an aliphatic acyclic amine having at least two primary amine groups. In one embodiment, the epichlorohydrin is epichlorohydrin. In one embodiment, the additional nitrogen-containing compound is ammonia, guanidine, one or more lower alkyl amines, one or more
alkylene diamines or mixtures thereof. In one embodiment, the product is the condensation product of piperazine, guanidine, formalin, and epichlorohydrin, as defined in U.S. Pat. No. 4,188,271. When present, this reaction product may be added to the bath in a concentration in the range from about 0.1 g/l to about 5 g/l, and in one embodiment at a concentration in the range from about 0.3 g/l to about 1 g/l, and in one embodiment, at a concentration of about 0.4 g/l.

[0085] In one embodiment, the bath according to the invention may further contain additives such as 3-mercaptopropyl, 1,2,4-triazole and/or thiourea. The concentration of these additives is the normal concentration for use of such additives in zinc baths, and ranges for example from 0.01 to 0.50 g/l.

[0086] In one embodiment, the bath according to the invention may also contain a water softener. In one embodiment, the sensitivity of the bath to foreign metal ions, in particular calcium and magnesium ions from tap water, is reduced by the use of such additives. Examples of such water-softener are EDTA, sodium silicates and tartaric acid.

[0087] Conditions of pH, Temperature, Time, Current Density

[0088] The aqueous alkaline plating baths of the invention can be prepared by conventional methods, for example, by adding the specific amounts of the above-described components to water. The amount of the alkali metal base compound such as sodium hydroxide which is included in the mixture should be sufficient to provide the bath with a pH of at least about 10 and in one embodiment, sufficient to provide a pH above 11. In one embodiment, the pH is greater than 12, and in one embodiment, a pH of about 14.

[0089] By use of the bath according to the invention, in one embodiment, electrically conducting substrates of metal may be provided with a bright, level, highly ductile and corrosion resistant coating of zinc-nickel alloy or other appropriate alloy.

[0090] The present invention accordingly relates to a process for the electroplating or electrodeposition of zinc-nickel alloy coatings on conventional substrates, which is characterized in that a bath having the above-described composition may be used as an electroplating bath. The aqueous alkaline plating baths of the present invention deposit a bright, level and ductile zinc-nickel alloy on substrates. In the process according to the invention, in one embodiment, the deposition of the coatings is carried out at a current density in the range from about 0.01 to about 150 A/dm², in one embodiment, from about 0.5 to about 25 A/dm² and in one embodiment, from about 1 to about 10 A/dm². The process conveniently may be carried out at room temperature, or at a lower or higher temperature. In one embodiment, the process may be carried out at a temperature, in one embodiment, in the range from about 10° C. to about 45° C., and in one embodiment, from about 15° C. to about 45° C., and in one embodiment, from about 25° C. to about 40° C. The disclosed higher temperatures may be useful, e.g., for inducing evaporation of water from the electrolyte.

[0091] In one embodiment, the process according to the invention may be carried out as a drum electroplating process when used for mass parts, and as a frame galvanizing process for deposition on larger workpieces. In this connection anodes are used that may be soluble, such as for example zinc anodes, which at the same time serve as a source of zinc ions so that the zinc deposited on the cathode is recovered by dissolution of zinc at the anode. Alternatively insoluble anodes such as for example nickel or iron anodes may also be used, in which case the zinc ions removed from the electrolyte would have to be replenished in another way, for example by using a zinc dissolving tank. In one embodiment, when the anodes are iron anodes, or another such metal, the anode is isolated by a suitable membrane or other divider, from the cathode and the remainder of the bath.

[0092] In one embodiment, the bath of the present invention may be used in an electroplating bath comprising a divider separating the anode or the anode and anodic chamber from the cathodic chamber. In one embodiment, the divider comprises at least one of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic such as used in a Daniel cell. Suitable dividers are disclosed in commonly assigned, copending U.S. patent Ser. No.10/731,648, filed Dec. 9, 2003, which claims priority to U.S. Provisional Application No. 60/508,673, filed Oct. 3, 2003, both entitled “APPARATUS AND METHOD FOR TREATMENT OF METAL SURFACES BY INORGANIC ELECTROPHORETIC PASSIVATION”. The disclosures of both applications are incorporated herein by reference for their teachings relating to dividers, separators and membranes for electroplating baths.

[0093] As is usual in electrodeposition, the process according to the invention may also be operated with appropriate gas injection or electrodes to provide agitation of the electrolyte and with or without movement of the articles being coated (e.g., cathode rod agitation or barrel rotation), without having any deleterious effects on the resultant coatings.

[0094] The plating baths of the invention may be operated on a continuous or intermittent basis, and from time to time, the components of the bath may have to be replenished. The various components may be added singularly as required or may be added in combination. The amounts of the various compositions to be added to the plating bath may be varied over a wide range depending on the nature and the performance of the zinc-nickel plating baths to which the composition is added. Such amounts can be determined readily by one of ordinary skill in the art.

[0095] The aqueous alkaline plating baths of the invention can be used over substantially all kinds of substrates on which a zinc-nickel alloy can be deposited. Examples of useful substrates include those of mild steel, spring steel, chrome steel, chrome-molybdenum steel, copper, copper-zinc alloys, etc., including such substrates which have an initial electroplated strike or barrier layer applied thereto prior to application of the zinc-metal alloy in accordance with the present invention. As is known, a strike layer is one which may make the substrate more receptive to subsequently applied layers, such as the present zinc-nickel alloy layer, and a barrier layer is one which hinders diffusion or migration of atoms between layers, such as between the substrate and the present zinc-nickel alloy layer. The strike layer may be, for example, an acidic zinc layer, an acidic zinc-nickel alloy layer or an acidic nickel layer.

[0096] Thus, as described above, in one embodiment, the present invention relates to a process for electroplating a
zinc-nickel alloy on a substrate, comprising electroplating the substrate with the aqueous alkaline electroplating bath described herein. The present invention further relates to an article comprising a substrate electroplated to the process described herein.

[0097] Test Methods

[0098] Composition and thickness of the electrodeposited alloy is determined by using x-ray fluorescence (XRF) to examine panels prepared using a Hull cell. Efficiency is determined by comparing thickness at various currents or by comparing the weight gain of a panel prior to and subsequent to electrodeposition for panels that have similar total amp seconds of applied current and comparing that to the theoretical thickness or weight gain using Faraday’s law. Throwing power is determined by measuring the relative coating weight gains for two cathodes placed on either side of a central anode but at varying distances (e.g., by use of a Haring Blum cell). Crystallographic phase and preferred orientation is determined by using an x-ray powder diffractometer (XRPD) preferably equipped with multiple axis capability. Bendability is measured both as elongation and as compressive decohesion. Elongation is determined by use of a cylindrical mandrel test (e.g., ISO 8401 paragraph 4.4), focuses upon effects of bending on the alloy coating on the outside of the bend, and is generally expressed as percent elongation. Compressive decohesion also is determined by use of a cylindrical mandrel test, but focuses upon effects of bending on the alloy coating on the inside of the bend, and is carried out according to the method described in Hu, M. S. and Evans, A. G., “The cracking and decohesion of thin films on ductile substrates”, Acta Metal. 37, 3 (917-925) 1989. Residual stress is determined by use of a XRPD to measure peak broadening and incorporating Poisson’s ratio into a calculation. Poisson’s ratio is estimated by determining the reduced modulus using nanoindentation (Hysitron). Brightness is determined by visual observation. Smoothness is determined by measuring the root mean square (RMS) vertical deflection of the deposit with an atomic force microscope (AFM).

[0099] Elemental composition of the coating may be determined with EDS and/or proton induced x-ray emission (PIXE) spectroscopy. X-ray photoelectron spectroscopy (XPS) may be used to determine oxidation state of deposited elements. Morphology, especially of the initial nucleate stages of deposition, may be examined using a cold cathode field emission SEM. Grain size variations of the coatings may be observed by preparing polished metallographic cross sections and subjecting them to ion bombardment using an argon ion beam while the samples are uniformly rotated in a vacuum chamber (Zalar rotation). The resulting argon ion etched cross sections are examined using the cold cathode field emission SEM.

[0100] Haring Blum panels, uniform current density coupons, and Hull cell panels may be used to evaluate the composition and properties of coatings obtained from various electrolytes with and without addition agents. Haring Blum panels (e.g., at 2.5 A current for 30 minutes) may be used to obtain information on throwing power and relative deposition efficiency. Constant current density (28 ASF for 20 minutes) coupons may be subjected to bendability and compressive decohesion testing, micro-hardness and modulus determination testing and in many cases X-ray diffraction. Haring Blum, constant current density and Hull Cell panels may be used to determine elemental composition and morphology.

[0101] All of the important material properties are generally thought to be dependent upon the arrangement of atoms within the deposited ZnNi alloy. The study of the atomic arrangement of atoms is facilitated by uses of electron or x-ray diffraction techniques. X-ray diffraction, in particular, is easy to implement and provides a great deal of information about a deposit, particularly an alloy. The use of an X-ray powder diffractometer in reflectance mode can provide information on the phases present in a crystallized alloy, the preferred orientation of the crystals (which is commonly a fiber orientation with electrodeposits), and the texture of the deposit. For zinc nickel alloys a variety of phases are possible. A hexagonal zinc phase (ICDD 87-0713), a cubic gamma phase (ICDD 06-0653, nominal composition Ni$_x$Zn$_{1-x}$) and a tetragonal delta phase (ICDD 10-0209 nominal composition Ni$_x$Zn$_{1-x}$) have all been reported in the literature on electrodeposited ZnNi.

[0102] The use of a Haring Blum cell is reviewed by McCormick and Kuhn (Metal Finish., 72 (2), (74) 1993) and by Gabe in the Metal Finishing Guidebook and Directory (1998, pp. 566). With this apparatus two cathodic panels are simultaneously plated using a single anode, usually made from a mesh material, placed between the two cathodes. The resulting geometry produces two separate cells with very similar symmetric current and potential distribution. The three electrodes are arranged so that differents lengths between the anode and the two cathodes are present. Various formulae may be used to calculate throwing power. All the formulae have in common the use of the ratio of the mass gain of the two cathodic panels and the ratio of the length between the two cathodic panels and the anode. In one embodiment, the Haring formula for throwing power may be used, which is % TP=100 (L-B) / L, where L is the far-to-near cathode distance ratio and R is the ratio of the weights gained by the cathodic panels.

[0103] In one embodiment, the sum of the weight gain from the two coupons may be used to compare deposition efficiency, at similar current densities, between electrolytes. By recording the current and time used to plate the Haring Blum panels, measuring the resulting alloy composition, and calculating the theoretical mass gain for an alloy of identical composition we can obtain an estimate of plating efficiency by the ratio observed mass gain to theoretical mass gain. The theoretical mass gain is calculated from a formula such as $M_{theo}=\frac{14}{60}\times SA_{cath}$, where I is the current, t is plating time in minutes, $A_i$ is the atomic percentage of element i in the resulting deposit, $g_i$ is the electrochemical equivalent of the specific element in grams of element i that can be deposited in one amp hour, derived from Faraday’s law, and tabulated in numerous references such as Schlesinger and Pannovic, Modern Electroplating, 4th ed., Appendix Table 4 (2000). For example, a 15 atomic percent nickel balance zinc deposit obtained by plating Haring Blum cathodes for 2 A and 30 minutes has a theoretical mass of 1.204 g/Ah and 1.095 g/Ah electrochemical equivalents for nickel and zinc respectively. If the combined weight gain of the two panel is 0.6 grams, the calculated efficiency is 0.6/1.204*100% or ~ 50%.

[0104] Bendability testing is done in accordance with the procedure described in International Standard 8401 “Metal-
lic coatings—Review of methods of measurement of ductility, chapter 4.4, Cylindrical Mandrel Testing. Essentially this consists of bending 2.5×10 cm coupons, with electroplated surfaces toward the exterior of the bend, around cylindrical mandrels of varying diameter and noting the diameter at which cracking is observed at 10× magnification. By use of the equation \( E = \frac{T_{\text{tot}}}{d+T_{\text{tot}}} \times 100 \) the percent elongation of the coating is determined (where \( T_{\text{tot}} \) is the thickness of the substrate plus the thickness of the coating and \( d \) is the diameter of the mandrel) and recorded. Compressive decohesion is observed by bending similar coupons, in this case with the plated surface toward the cylindrical mandrel, around varying diameters of cylindrical mandrels and again observing cracking. For compressive decohesion an easy to use equation is not available but the observation of the type of compressive decohesion may be made. If there are a multiplicity of cracks with no evidence of delamination from the substrate the observation of a diffuse microcracking at the observed diameter is made. If there are only a few cracks and it is evident that some of the coating is not adhering to substrate the observation of concentrated decohesion at the observed diameter is made. This latter observation should be considered a significant failure of the coating at the observed bend radius.

**EXAMPLES**

**[0105]** The following examples illustrate the aqueous alkaline plating baths of the invention. The amounts of the components in the following examples are in grams/liter. Unless otherwise indicated in the specification and claims, all parts and percentages are by weight, temperatures are in degrees centigrade, and pressures are at or near atmospheric pressure. In the following examples, the source of zinc ions is zinc oxide in caustic soda, and the source of nickel ions is nickel sulfate.

**[0106]** Electrolytes:

**[0107]** In the examples, five different alkaline electrolytes and two acid electrolytes are prepared. These electrolytes are used with various combinations of grain refiners in accordance with the invention, or without such grain refiners or in the acid electrolytes, in comparative examples.

<table>
<thead>
<tr>
<th>Electrolyte one (E1):</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>Triethanolamine</td>
</tr>
<tr>
<td>Tetraethylenepentamine</td>
</tr>
<tr>
<td>Nickel ion from nickel sulfate</td>
</tr>
<tr>
<td>Quadrol</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
</tbody>
</table>

**[0108]**

<table>
<thead>
<tr>
<th>Electrolyte two (E2):</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>Triethanolamine</td>
</tr>
<tr>
<td>Tetraethylenepentamine</td>
</tr>
</tbody>
</table>

**[0109]**

<table>
<thead>
<tr>
<th>Electrolyte three (E3):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrol</td>
</tr>
<tr>
<td>1,2-ethanediamine,N-(2-aminoethyl)-(DETA)</td>
</tr>
<tr>
<td>Triethanolamine</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
</tbody>
</table>

**[0110]**

<table>
<thead>
<tr>
<th>Electrolyte four (E4):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrol</td>
</tr>
<tr>
<td>1,2-ethanediamine,N-(2-aminoethyl)-(DETA)</td>
</tr>
<tr>
<td>Triethanolamine</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
</tbody>
</table>

**[0111]**

<table>
<thead>
<tr>
<th>Electrolyte five (E5):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymin Ⓡ G-35</td>
</tr>
<tr>
<td>Triethanolamine</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
</tbody>
</table>

**[0112]** Electrolyte Six (E6):

**[0113]** Atotech Ni 75, a proprietary zinc-nickel alkaline electrolyte which contains no non-ionogenic, surface active polyoxyalkylene compound.

<table>
<thead>
<tr>
<th>Electrolyte seven (acid 1) (E7):</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
</tr>
<tr>
<td>NiSO₄</td>
</tr>
<tr>
<td>NH₄Cl</td>
</tr>
<tr>
<td>Sodium xylene sulfonate</td>
</tr>
<tr>
<td>2-ethylhexylsulfate</td>
</tr>
<tr>
<td>ethoxylated chloridoglycol (mw=1200)</td>
</tr>
<tr>
<td>Bisace N</td>
</tr>
<tr>
<td>Sodium benzate</td>
</tr>
<tr>
<td>NH₄OH</td>
</tr>
</tbody>
</table>
Exemplary Non-Ionogenic Surface Active Polyoxyalkylene Compounds

Non-ionogenic surface active polyoxyalkylenes from the following table were tested in the Examples. However, there are a large variety of such compounds, and some included in these Examples are exemplary and are not intended to limit the invention in any way. Those of ordinary skill in the art can identify similar non-ionic surface active polyoxyalkylenes from or in addition to those identified in the following list and those identified elsewhere in the application.

<table>
<thead>
<tr>
<th>Additive code</th>
<th>Additive name</th>
<th>General description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA1</td>
<td>Carbowax 600:</td>
<td>EO polymer with molecular weight ~600</td>
</tr>
<tr>
<td>AA2</td>
<td>BASF Tetronic 90R4:</td>
<td>EO poly ethylene diamine copolymer</td>
</tr>
<tr>
<td>AA3</td>
<td>Carbowax 2000:</td>
<td>EO polymer with MW of ~2000</td>
</tr>
<tr>
<td>AA4</td>
<td>BASF Pluronic L62:</td>
<td>EO poly block copolymer (EO 20%, PO 80%)</td>
</tr>
<tr>
<td>AA5</td>
<td>Surlyn 465:</td>
<td>PEG10 tetramethyl decylenediol</td>
</tr>
<tr>
<td>AA6</td>
<td>Pluronic 10R5:</td>
<td>EO poly block polymer (EO 50%, PO 50%)</td>
</tr>
<tr>
<td>AA7</td>
<td>BASF Pluronic 25R2:</td>
<td>EO poly block polymer (PO 20%, PO 80%)</td>
</tr>
<tr>
<td>AA8</td>
<td>Terminol 91-6:</td>
<td>linear alcohol (C10+) + EO (6 moles)</td>
</tr>
<tr>
<td>AA9</td>
<td>Igepal CO 710:</td>
<td>nonylphenoxyl ethyl alcohol</td>
</tr>
<tr>
<td>AA10</td>
<td>Lupasol HS-1000:</td>
<td>thiodiglycol ethylene oxide</td>
</tr>
<tr>
<td>AA11</td>
<td>Pluronic C-17:</td>
<td>ethoxylated alkyl alcohol</td>
</tr>
</tbody>
</table>

Examples 1-34

The following table provides examples of the present invention and of several comparative examples. In the table, the following headings have the following meanings:

E’lyte” is the electrolyte used, selected from E1-E8 as defined above.

“% E” is the percent elongation, may also be referred to as “bendability” and is determined by use of a cylindrical mandrel test (e.g., ISO 8401, paragraph 4.4).

“D. of comp. Decoh.” is the diameter of a cylindrical mandrel at which a sample bent around the mandrel forms cracks observable by use of a 10x magnifying loop, as a result of compressive decohesion, as described above.

“Throwing power” is determined by use of a Haring Blum cell, in which two cathodic panels are simultaneously plated using a single anode. The two cathodic panels are set at different lengths or distances from the anode. The % throwing power is determined from the equation % TP=100(L-R)/L, where L is the far-to-near cathode distance ratio and R is the far-to-near ratio of the weights gained by the respective cathodic panels.

“Current efficiency” is determined by weighing a panel before and after plating and carefully measuring the total current consumed, in amp-hours. Then, the nickel concentration is measured by x-ray fluorescence. Then, the theoretical mass of the deposit is calculated using Faraday’s law.

“Nano hardness Reduced modulus RA” is a measurement of hardness using a very small tip similar to an atomic force microscope. This is measured by impressing a very small hardened tip into the surface of the material and very carefully measuring the depth of penetration and the force needed to move the tip. The reduced modulus is a relationship obtained by examining the loading and unloading of the needle tip as a function of depth and it is related to the elastic modulus (or Young’s modulus) through Poisson’s ratio, which is a measure of necking in a sample.

“Major phases by XRD” relates to the crystal phase of the ZnNi alloy, determined by using an x-ray powder diffractometer (XRPD), which may have a multiple axis capability. Generally, the gamma phase is preferred, relative to the delta phase.
"Preferred orientations" relates to the crystallographic orientation of x-rays reflected from the crystal planes of the ZnNi alloy, determined by using an x-ray powder diffractometer (XRPD), which may have a multiple axis capability. The "600" orientation has been associated with improved corrosion resistance.

<table>
<thead>
<tr>
<th>Ex. E’lyte</th>
<th>Additional grain refiner</th>
<th>Concentrations</th>
<th>Anode</th>
<th>Ni</th>
<th>Appearance</th>
<th>D of comp. % E Decoh.</th>
<th>Throwing Power</th>
<th>Current eff.</th>
<th>Nano hardness</th>
<th>Reduced modulus</th>
<th>RA Major phases by XRD</th>
<th>Preferred orientations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 E1 Comp</td>
<td>None</td>
<td>Ni</td>
<td>12–14%</td>
<td>Matte</td>
<td>3%</td>
<td>16</td>
<td>60%</td>
<td>45%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 E1</td>
<td>AA2</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Hazy</td>
<td>&gt;20%</td>
<td>11</td>
<td>Nd</td>
<td>75%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>3 E1</td>
<td>AA1</td>
<td>0.0007 mol/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>&gt;20%</td>
<td>11</td>
<td>90%</td>
<td>82%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>4 E1</td>
<td>AA1</td>
<td>0.0007 mol/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Bright</td>
<td>&gt;20%</td>
<td>11</td>
<td>97%</td>
<td>75%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>5 E1</td>
<td>AA1</td>
<td>0.0007 mol/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Bright</td>
<td>&lt;3%</td>
<td>11</td>
<td>97%</td>
<td>75%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>6 E1</td>
<td>AA1</td>
<td>0.0007 mol/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Bright</td>
<td>20%</td>
<td>75%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 E1</td>
<td>AA3</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>9–12%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 E1</td>
<td>AA3</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 E1</td>
<td>AA4</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>8–9%</td>
<td>Non-uniform metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 E2</td>
<td>AA4</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>13%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 E1</td>
<td>AA5</td>
<td>0.04 g/dm³</td>
<td>Ni</td>
<td>7–13%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 E1</td>
<td>AA6</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>8–10%</td>
<td>Matte</td>
<td>&gt;20%</td>
<td></td>
<td></td>
<td>zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 E2</td>
<td>AA6</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>10–13%</td>
<td>Smooth metallic</td>
<td>15%</td>
<td></td>
<td></td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 E1</td>
<td>AA7</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>7–9%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>nickel; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 E2</td>
<td>AA7</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>13–15%</td>
<td>Smooth metallic</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 E1</td>
<td>AA8</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>9–10%</td>
<td>Matte</td>
<td>&gt;25%</td>
<td></td>
<td></td>
<td>nickel; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 E2</td>
<td>AA8</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>11–14%</td>
<td>Smooth metallic</td>
<td>&gt;20%</td>
<td></td>
<td></td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18 E1</td>
<td>AA9</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>9–11%</td>
<td>Matte</td>
<td>&gt;15%</td>
<td></td>
<td></td>
<td>nickel; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19 E1</td>
<td>AA9</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>11–14%</td>
<td>Smooth metallic</td>
<td>8%</td>
<td></td>
<td></td>
<td>nickel; zinc; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 E1</td>
<td>AA10</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>&gt;26%</td>
<td>9</td>
<td>73%</td>
<td>gamma; nickel</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21 E1</td>
<td>AA11</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>8–10%</td>
<td>Matte</td>
<td>&gt;25%</td>
<td>9</td>
<td></td>
<td>nickel; zinc</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 E1</td>
<td>AA11</td>
<td>0.4 g/dm³</td>
<td>Ni</td>
<td>11–14%</td>
<td>Smooth metallic</td>
<td>&gt;25%</td>
<td>9</td>
<td></td>
<td>nickel; zinc</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 E3 Comp</td>
<td>BA3</td>
<td>0.12 g/dm³</td>
<td>Ni</td>
<td>12–14%</td>
<td>Bright</td>
<td>3%</td>
<td>32 mm</td>
<td>95%</td>
<td>35%</td>
<td>6.1 GPa</td>
<td>140 GPa 3.2</td>
<td>gamma; zinc; nickel</td>
</tr>
<tr>
<td>24 E4 Comp</td>
<td>BA3</td>
<td>0.12 g/dm³</td>
<td>Isolated Fe</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>7%</td>
<td>12 mm</td>
<td>80%</td>
<td>25%</td>
<td>5.8 GPa</td>
<td>140 GPa 2.1</td>
<td>gamma; zinc; nickel</td>
</tr>
<tr>
<td>25 E4 Comp</td>
<td>BA3</td>
<td>0.12 g/dm³</td>
<td>Isolated Fe</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>14%</td>
<td>9 mm</td>
<td>90%</td>
<td>50%</td>
<td>gamma; zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>26 E5 Comp</td>
<td>BA3</td>
<td>0.12 g/dm³</td>
<td>Isolated Fe</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>3%</td>
<td>15 mm</td>
<td>85%</td>
<td>30%</td>
<td>zinc; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>27 E6 Comp</td>
<td>BA4</td>
<td>0.3 g/dm³</td>
<td>Ni</td>
<td>11–13%</td>
<td>Smooth metallic</td>
<td>3%</td>
<td>15 mm</td>
<td>90%</td>
<td>45%</td>
<td>gamma; nickel</td>
<td>330; 112</td>
<td></td>
</tr>
<tr>
<td>28 E5</td>
<td>BA5</td>
<td>Ni</td>
<td>12–14%</td>
<td>Smooth metallic</td>
<td>9%</td>
<td>12 mm</td>
<td>57%</td>
<td></td>
<td>nickel; zinc</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29 E5 Comp</td>
<td>BA2</td>
<td>12–15%</td>
<td>Smooth metallic</td>
<td>&lt;3%</td>
<td>&gt;24 mm</td>
<td></td>
<td></td>
<td></td>
<td>nickel; zinc</td>
<td>330; 112</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
[0127] While the invention has been explained in relation to various of its embodiments, it is to be understood that other modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

1. An aqueous zinc-nickel electroplating bath, comprising water;
   zinc ion;
   nickel ion;
   at least one complexing agent; and
   at least one non-ionogenic, surface active polyoxyalkylene compound, wherein the bath has an alkaline pH.

2. The bath of claim 1, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 3 wt % to about 25 wt % of the alloy.

3. The bath of claim 1, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 8 wt % to about 22 wt % of the alloy.

4. The bath of claim 1, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy having a substantially gamma crystallographic phase.

5. The bath of claim 1, wherein the at least one non-ionogenic, surface active polyoxyalkylene compound comprises at least one compound having a formula:

\[ R^3-O-[R^4-O]_m-X \]  
(Ila)

or

\[ (R^3-O-[R^4-O]_m)-Y \]  
(IIb)

wherein \( R^3 \) is an aryl or alkyl group containing up to about 24 carbon atoms, \( R^4 \) is an alkyl group containing from 1 to about 4 carbon atoms, \( n \) is 2 or 3, and \( x \) is an integer between 2 and about 100.

6. The bath of claim 1, wherein the at least one non-ionogenic, surface active polyoxyalkylene compound comprises at least one compound having a formula:

\[ R^3-O-[R^4-O]_m-X \]  
(IIa)

or

\[ (R^3-O-[R^4-O]_m)-Y \]  
(IIb)

wherein \( R^3 \) is a \( C_1-C_{10} \) branched or unbranched alkyl, alkenyl or alkynyl group, or phenyl-\( \{R^3-O\}_{m} \)-CH\(_2\)-, in which \( m=0-100 \) and \( R^4 \) is a \( C_1-C_4 \) branched or unbranched alkylene; \( R^4= \) \( C_4-C_6 \), branched or unbranched alkylene; \( X=H, -SO_2Z, -SO_3Z, -SO_2Z-PO_2Z, -PO_2Z \) (wherein \( Z \) independently may be \( H \), an alkali metal ion, or \( Z \) may be an alkaline earth metal ion); \( -NH_2, -Cl \) or \( -Br; Y \) is an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and is equal to or less than the number of active hydrogens in \( -OH, -NH, -NH_2 \) or \( -SH \) groups on the \( Y \) component.

7. The bath of claim 6, wherein the \( Y \) group is a glycol having a general formula:

\[ HO-[R^3-O-L]_m-H \]  
(III)

wherein \( R^3= \) \( C_1-C_4 \) alkylene, or a \( C_1-C_4 \) alkylene substituted with one or more additional hydroxyl groups, or a mixture of such \( R^3 \) groups.

8. The bath of claim 1, wherein the at least one non-ionogenic, surface active polyoxyalkylene compound is present in an amount effective to provide grain refinement of a zinc-nickel alloy electroplated with the bath.

9. The bath of claim 1, wherein the complexing agent comprises at least one aliphatic amine.

10. The bath of claim 1, wherein the complexing agent comprises at least one polymer of an aliphatic amine.
11. The bath of claim 10, wherein the polymer is a poly(alkyleneimine).

12. The bath of claim 10, wherein the polymer is a polyethyleneimine.

13. The bath of claim 1, wherein the complexing agent comprises at least one compound represented by the formula

\[ R^2(NH)_{(R''R') R''}^{-1} \]

wherein \( R^2 \), \( R'' \) and \( R^{10} \) are each independently alkyl or hydroxyalkyl groups provided that at least one of \( R'' \) is a hydroxy alkyl group, and \( R^{10} \) is a hydrocarbylene group containing up to about 10 carbon atoms.

14. The bath of claim 13, wherein the hydrocarbylene group \( R^{10} \) is an alkylene group containing from 1 to about 10 carbon atoms.

15. The bath of claim 13, wherein \( R^7 \), \( R^8 \), \( R^9 \) and \( R^{10} \) in Formula (V) are hydroxyalkyl groups.

16. The bath of claim 1, wherein the bath further comprises a reaction product obtained by the process of

(i) preparing an intermediate product by reacting formaldehyde with a mixture of

(ii) one or more piperazines having the formula

\[ (V) \]

wherein \( R^{12} \) and \( R^{13} \) are each independently hydrogen or lower alkyl groups, and

(iii) at least one additional nitrogen-containing compound from the group consisting of ammonia or aliphatic, acyclic compounds containing at least one primary amine group, and

(b) reacting said intermediate product with an epihalohydrin or glycerol halolohydrin or mixtures thereof at a temperature within the range of from room temperature to the reflux temperature of the mixture.

17. The bath of claim 1, wherein the bath further comprises one or more auxiliary brightener.

18. An aqueous alkaline electroplating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which comprises

(A) from about 1 to about 100 g/l of zinc ion;

(B) from about 0.1 to about 50 g/l of nickel ion;

(C) at least one complexing agent at a concentration sufficient to maintain the nickel ion in solution; and

(D) from about 0.1 to about 50 g/l of at least one non-ionogenic, surface active polyoxyalkylene compound.

19. The bath of claim 18, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 3 wt % to about 25 wt % of the alloy.

20. The bath of claim 18, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a nickel content from about 8 wt % to about 22 wt % of the alloy.

21. The bath of claim 18, wherein the zinc ion and the nickel ion are present at concentrations sufficient to deposit a zinc-nickel alloy having a substantially gamma crystallographic phase.

22. The bath of claim 18, wherein the at least one non-ionogenic, surface active polyoxyalkylene compound comprises at least one compound having a formula:

\[ \text{(Ia)} \]

or

\[ \text{(Ib)} \]

or

\[ \text{(Ic)} \]

wherein \( R^7 \) is an aryl or alkyl group containing up to about 24 carbon atoms, \( R^8 \) is an alkylene group containing from 1 to about 4 carbon atoms, \( n \) is 2 or 3, and \( x \) is an integer between 2 and about 100.

23. The bath of claim 18, wherein the at least one non-ionogenic, surface active polyoxyalkylene compound comprises at least one compound having a formula:

\[ \text{(IIa)} \]

or

\[ \text{(IIb)} \]

\[ \text{(IIc)} \]

wherein \( R^5 \) is \( C_{1-16} \) branched or unbranched alkyl, alkylene or alkenyl group, or phenyl-\( O - \left( CH_2 \right)_m \), in which \( m = 0-100 \) and \( R^7 \) is a \( C_1-C_4 \) branched or unbranched alkylene; \( R^8 = C_{1-16} \) branched or unbranched alkylene; \( X = \text{H, SO}_2 Z, \text{SO}_2 Z_2, \text{PO}_2 Z_2, \text{PO}_2 Z_2 \); wherein \( Z \) independently may be H, an alkal metal ion, or \( Z_2 \) may be an alkaline earth metal ion) -NH_2, -Cl or -Br; \( Y \) is an aliphatic polyhydroxy group, an amine group, a polyamine group or a mercaptan group, and is equal to or less than the number of active hydrogens in \( OH, -NH, \text{NH}_2, \text{SH} \) groups on the \( Y \) component.

24. The bath of claim 23, wherein the \( Y \) group is a glycol having a general formula:

\[ \text{(IIIa)} \]

wherein \( R^5 = C_{1-4} \) alkylene, or a \( C_1-C_4 \) alkylene substituted with one or more additional hydroxy groups, or a mixture of such \( R^5 \) groups.

25. The bath of claim 18, wherein the complexing agent comprises at least one aliphatic amine.

26. The bath of claim 18, wherein the complexing agent comprises at least one polymer of an aliphatic amine.

27. The bath of claim 26, wherein the polymer comprises a poly(alkyleneimine).

28. The bath of claim 26, wherein the polymer comprises a polyethyleneimine.

29. The bath of claim 18, wherein the complexing agent comprises at least one compound represented by the formula

\[ R^7(NH)_{(R''R') R''}^{-1} \]

wherein \( R^7 \), \( R^8 \), \( R^9 \) and \( R^{10} \) are each independently alkyl or hydroxyalkyl groups provided that at least one of \( R^{10} \) is a hydroxy alkyl group, and \( R^{12} \) is a hydrocarbylene group containing up to about 10 carbon atoms.
30. The bath of claim 29, wherein the hydrocarbylene group \( R'^{11} \) is an alkylene group containing from 1 to about 10 carbon atoms.

31. The bath of claim 29, wherein \( R^7, R^8, R^9 \) and \( R^{10} \) in Formula (V) are hydroxyalkyl groups.

32. The bath of claim 18, wherein the bath further comprises a reaction product obtained by the process of

(a) preparing an intermediate product by reacting formaldehyde with a mixture of

(i) one or more piperazines having the formula

\[
\text{(VI)}
\]

wherein \( R^2 \) and \( R^{13} \) are each independently hydrogen or lower alkyl groups, and

(ii) at least one additional nitrogen-containing compound from the group consisting of ammonia or aliphatic, acyclic compounds containing at least one primary amine group, and

(b) reacting said intermediate product with an epihalohydrin or glycerol halohydrin or mixtures thereof at a temperature within the range of from room temperature to the reflux temperature of the mixture.

33. The bath of claim 18, wherein the bath further comprises one or more auxiliary brightener.

34. An aqueous alkaline electroplating bath for the electrodeposition of a zinc-nickel alloy coating on a substrate which comprises

(A) from about 1 to about 100 g/l of zinc ion;

(B) from about 0.1 to about 50 g/l of nickel ion;

(C) at least one complexing agent at a concentration sufficient to maintain the nickel ion in solution; and

(D) from about 0.1 to about 50 g/l of at least one non-ionogenic, surface active polyoxyalkylene compound,

wherein the zinc ion, the nickel ion and the non-ionogenic surface active polyoxyalkylene compound are present at concentrations sufficient to deposit a zinc-nickel alloy comprising a substantially gamma phase.

35. The bath of claim 34, wherein the bath further comprises one or more auxiliary brightener.

36. A process for electroplating a zinc-nickel alloy on a substrate, comprising electroplating the substrate with the bath of claim 1.

37. A process for electroplating a zinc-nickel alloy on a substrate, comprising electroplating the substrate with the bath of claim 18.

38. A process for electroplating a zinc-nickel alloy on a substrate, comprising electroplating the substrate with the bath of claim 34.

39. An article comprising a substrate electroplated according to the process of claim 36.

40. An article comprising a substrate electroplated according to the process of claim 37.

41. An article comprising a substrate electroplated according to the process of claim 38.