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3,795,591

ELECTRODEPOSITION OF BRIGHT NICKEL IRON DEPOSITS EMPLOYING A COMPOUND CONTAINING A SULFIDE AND A SULFONATE

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U.S. Cl. 204—43 T 31 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous bath suitable for the electrodeposition of a bright iron nickel electrodeposit onto a substrate susceptible to corrosion comprising iron ions, nickel ions, a bath soluble primary nickel brightener, an effective amount of a bath soluble complexing agent containing at least two complexing groups, said groups being independently selected from the group consisting of carboxy and hydroxy, provided at least one group is a carboxy group; the bath having a pH from 2.5 to about 5.5 and an ion of the formula:

$$^{-}O_3S—R—S—A$$

wherein A may be hydrogen, $—R_1—SO_3—$,

$$—S—R_2—SO_3^{-} \text{ or } R_3;$$

R, R_1 or R_2 may be a saturated alkylene, arylene, or aralkylene; and
R_3 may be alkyl, aryl or aralkyl.

BACKGROUND OF THE INVENTION

For many years, electrodeposited nickel has been employed as a substrate for the subsequent electrodeposition of chromium in order to impart satisfactory corrosion resistant properties to a metallic surface. Attempts have been made to obtain various alloys of nickel in order to decrease the cost of obtaining a satisfactory decorative finish. Iron nickel deposits have been used previously for the electrodeposition of electromagnetic films. These films are usually extremely thin surfaces and normally are not decorative in character or exposed to corrosive environments. Application Ser. No. 268,348, entitled Electrodeposition of Bright Nickel Iron Deposits, filed on even date herewith and now abandoned, describes a means of obtaining bright nickel iron electrodeposits.

SUMMARY OF THE INVENTION

It has been found that satisfactory bright iron nickel alloy deposits can be obtained which are comparable to 100% nickel deposits in brightness, leveling and ductility with good corrosion resistant properties as a substrate for chromium electrodeposition. The iron nickel alloy bath contains ions of iron and ions of nickel, and an iron complexing agent containing complexing groups such as carboxy and hydroxy and a compound, which extends the current density of the iron nickel bath, containing a sulfide and a sulfonate.

DESCRIPTION OF PREFERRED EMBODIMENTS

Applicant's invention is directed to the electrodeposition of a bright iron-nickel alloy deposit of from 5 to about 50% by weight iron preferably about 15 to about

35% by weight which can be used as the basis for subsequent electrodeposition of chromium in order to impart desirable decorative and/or corrosion resistant properties to substrates, such as metallic substrates.

The bath and process of the present invention can also be used in the electrodeposition of a nickel-iron alloy for plastics. Normally the plastic substrate such as, acrylonitrile-butadiene-styrene, polyethylene, polypropylene, polyvinyl chloride, phenol-formaldehyde polymers is pretreated by applying a conductive metallic deposit onto the plastic substrate such as, nickel or copper. The iron-nickel deposit may then be used as a subsequent coating onto the conductive metallic deposit.

The bath that may be employed in the present invention utilizes one or more salts of nickel, one or more salts of iron, a complexing agent and a bath soluble compound of the formula having up to 14 carbon atoms, preferably up to 6 carbon atoms;

(I) $^{-}O_3S—R—S—A$

wherein A may be hydrogen, $—R_1—SO_3—$,

$$—S—R_2—SO_3— \text{ or } —R_3;$$

R, R_1 or R_2 may be a saturated alkylene, arylene or aralkylene; and R_3 may be alkyl, aryl or aralkyl.

The alkyl, aryl or aralkyl groups may have included within their definition substitution such as, alkyl of 1 to 4 carbon atoms, halogen such as, chloro, bromo or fluoro or a water solubilizing group. By "water solubilizing group" is meant any polar group which will assist in its solubilization of the molecule in the aqueous electrolyte. Preferred groups are hydroxyl, ether, such as, alkoxy of up to 12 carbon atoms, polyoxyalkylene, such as, polyoxyethylene of up to 1,000 repeating units or polyoxypropylene of up to 50 repeating units, sulfonic, sulfate, nitro, carboxy acid or its alkyl esters of 1 to 6 carbon atoms.

The compounds included within Compound I may be prepared as follows.

When A is hydrogen, that is, compound of the formula:

(II) $^{-}O_3—S—R—SH$

these compounds are prepared by reacting a sultone with sodium sulfide (Na_2S).

When A is $—R_1—SO_3^{-}$ that is, compounds of the formula:

(III) $^{-}O_3S—R—S—R_1—SO_3^{-}$

these compounds may be prepared by reacting the compound of Formula No. II with a sultone.

When A is $—S—R_2—SO_3—$, that is, compound of the formula:

(IV) $^{-}O_3S—R—S—S—R_2—SO_3—$

these compounds are prepared by reacting a compound of Formula II with a mild oxidizing agent such as hydrogen peroxide.

When A is R_3, that is, compound of the formula:

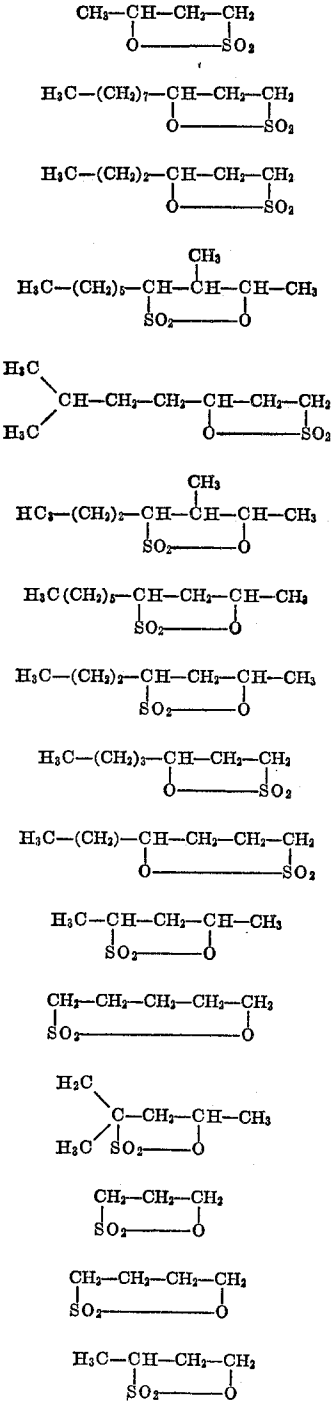
(V) $^{-}O_3S—R—S—R_3$

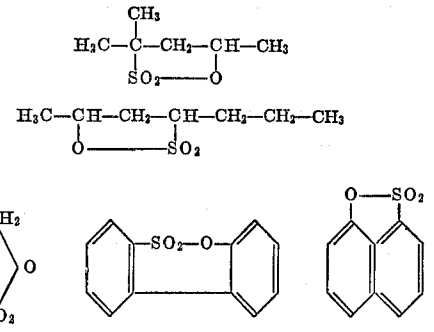
these compounds may be prepared by reacting the sodium salt of a mercapto containing compound with a sultone.

Examples of the mercapto containing compound are an alkyl mercapto that is an alkyl group from 1 to 12 carbon atoms, preferably 1 to 6, such as, methylmercaptan, propylmercaptan, butyl mercaptan, hexylmercaptan, octylmercaptan, decylmercaptan, dodecylmercaptan arylmercapto compounds such as, benzenethiol, naphthylmercapto or aralkylmercapto, such as, benzylmercaptan, 2-phenyl ethylmercaptan; 4-butylmercaptan and the like.

It is to be appreciated that the grouping $—SO_3^-$ is meant to include the acid and all bath soluble salts such as, the alkali metal salt, such as, sodium, potassium and the like.

The sultones that may be employed in the above described reactions are one of the following structures;





As can be seen, the groups R, R_1 and R_2 are the residual portions of the reaction with a sultone and the compounds mentioned above.

The organic sulfide of the present invention is used in the nickel-iron bath in a concentration ranging from about .001 to .020, preferably 0.001 to 0.005 grams/liter.

In order to introduce iron and nickel ions into the bath, any bath soluble iron and nickel containing compound may be employed providing the corresponding anion is not detrimental to the bath. Preferably inorganic nickel salts may be employed such as, nickel sulfate, nickel chloride, and the like as well as other nickel materials such as, nickel sulfamate and the like. When nickel sulfate salts are used they are normally present in amounts ranging from 40 to 300 grams/liter (calculated as nickel sulfate $6H_2O$); nickel chloride may also be used and is present in an amount ranging from about 80 to 250 grams/liter. The chloride or halide ions are employed in order to obtain satisfactory conductivity of the solution and at the same time to obtain satisfactory corrosion properties of the soluble anodes.

Preferably the inorganic salts of iron are employed, such as, ferrous salts, such as, ferrous sulfate, ferrous chloride, and the like. These salts are present in an amount ranging from about 3 to 60 grams/liter. Other bath soluble iron salts that may be employed, such as, soluble ferrous fluoborate, or sulfamate, and the like.

The iron complexing agent that is employed in the present invention is one that is bath soluble and contains complexing groups independently selected from the group consisting of carboxy and hydroxy providing at least 1 of the complexing groups is a carboxy group and further providing that there are at least two complexing groups. The complexing agent that may be employed is present in amount ranging from about 10 to about 100 grams/liter. Suitable complexing agents are hydroxy substituted lower aliphatic carboxylic acids having from 2 to 8 carbon atoms, from 1 to 6 hydroxyl groups and from 1 to 3 carboxyl groups such as, ascorbic acid, isoascorbic acid, citric acid, malic acid, gluteric acid, gluconic acid, muconic, glutamic, gluheptonate, glycollic acid, aspartic acid and the like as well as amine containing complexing agents, such as nitrilotriacetic acid, ethylene diamine tetraacetic acid, as well as the water soluble salts thereof such as ammonium and the alkali metal salts such as potassium, sodium, lithium, and the like. It can also be appreciated that the iron may be introduced into the bath as a salt of the complexing agent.

By "carboxy" is meant the group —COOH. However, it is to be appreciated that in solution, the proton disassociates from the carboxy group and therefore this group is to be included in the meaning of carboxy.

The purpose of the complexing agent is to keep the metal ions, in particular, the ferrous and ferric ions in solution. It has been found that as the pH of a normal Watts nickel plating bath increases above a pH of 3.0, ferric ions tend to precipitate as ferric hydroxide. The complexing agent will prevent the precipitation from taking place and therefore makes the iron and nickel ions available for electrodeposition from the complexing agent.

Because of the operating parameters employing the complexing agent, the pH of the bath preferably ranges from about 2.5 to about 5.5 and even more preferably about 3 to about 3.5.

The temperature of the bath may range from about 120° F. to about 180° F. preferably about 160° F.

The average cathode current density may range from about 10 to about 70 amps sq. ft. preferably about 45 amps sq. ft.

It is preferred that the complexing agent concentration should be at least three times the total iron ion concentration in the bath. The complexing agent concentration ratio to total iron ion concentration may range from 3 to 50:1.

The bath may also contain various buffers such as boric acid and sodium acetate and the like ranging in amounts from about 30 to 60 grams/liter, preferably 40 grams/liter. The ratio of nickel ions to iron ions ranges from about 5 to about 50 to 1.

While the bath may be operated without agitation, various means of agitation may be employed such as mechanical agitation, air agitation, cathode rod movement and the like.

It has been found that various nickel brightening additives may be employed to impart brightness, ductility and leveling to the iron nickel deposits. Suitable additives are the sulfo oxygen compounds as are disclosed as brighteners of the first class described in Modern Electroplating, published by John Wiley and Sons, second edition, page 272.

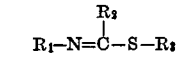
The amount of sulfo-oxygen compounds employed in the present invention ranges from about 0.5 to about 10 g./l. It has been found that saccharin may be used in amounts ranging from 0.5 to about 5 g./l. resulting in a bright ductile deposit. When other sulfo-oxygen compounds are employed, such as, naphthalenetrisulfonic, sulfobenzaldehyde, dibenzenesulfonamide, good brightness is obtained but the ductility is not as good as with saccharin. In addition to the above sulfo-oxygen compounds that may be used, others are sodium allyl sulfonate, benzene sulfinates, vinyl sulfonate, beta-styrene sulfonate, cyano alkane sulfonates (having from 1 to 5 carbon atoms).

The bath soluble sulfo-oxygen compounds that may be used in the present invention are those such as the unsaturated aliphatic sulfonic acids, mononuclear and binuclear aromatic sulfonic acids, mononuclear aromatic sulfinic acids, mononuclear aromatic sulfonamides and sulfonimides, and the like.

It has also been found that acetylenic nickel brighteners may also be used in amounts ranging from about 10 to about 500 mg./l. Suitable compounds are the acetylenic sulfo-oxygen compounds mentioned in U.S. 2,800,440. These nickel brighteners are the oxygen containing acetylenic sulfo-oxygen compounds. Other acetylenic nickel brighteners are those described in U.S. 3,366,557 such as the polyethers resulting from the condensation reaction of acetylenic alcohols and diols such as, propargyl alcohol, butyndiol, and the like and lower alkylene oxides such as, epichlorohydrin, ethylene oxide, propylene oxide and the like.

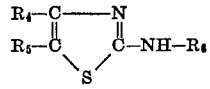
It has also been found that nitrogen heterocyclic quaternary or betaine nickel brighteners may also be used in amounts ranging from about 1 to about 50 mg./l. Suitable compounds are those nickel brighteners described in U.S. 2,647,866 and the nitrogen heterocyclic sulfonates described in U.S. 3,023,151. Preferred compounds described therein are the pyridine quaternaries or betaines or the pyridine sulfobetaines. Suitable quaternaries that may be employed are quinaldine propane sultone, quinaldine dimethyl sulfate, quinaldine allyl bromide, pyridine allyl bromide, isoquinaldine propane sultone, isoquinaldine dimethyl sulfate, isoquinaldine allyl bromide, and the like.

At times the low current density areas are not fully bright. To extend the current density range of the iron-nickel bath of the present invention other organic sulfide nickel brighteners are employed in amounts ranging from about 0.5 to about 40 mg./l. of the electroplating bath composition. These organic sulfides are of the formula:

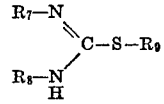


where R_1 is hydrogen or a carbon atom of an organic radical, R_2 is nitrogen or a carbon atom of an organic radical and R_3 is a carbon atom of an organic radical. R_1 and R_2 or R_3 may be linked together through a single organic radical.

More specifically, the bath soluble organic sulfide compounds used are 2-amino thiazoles and isothioureas having the formulae:

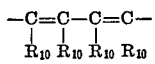


and

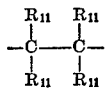


wherein

R_6 is selected from H, lower alkyl sulfonic acid groups, aryl sulfonic acid groups, lower alkoxy aryl sulfonic acid groups and the salts thereof; R_4 and R_5 are selected from H, halogen, lower alkyl groups and the bivalent radical



in which the R_{10} groups are selected from H, halogen and lower alkyl groups; R_9 is selected from the lower alkyl sulfonic acid groups and lower alkyl carboxy acid groups and the salts thereof; and R_7 and R_8 are selected from H, halogen, lower alkyl groups and the bivalent radical

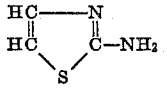
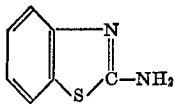
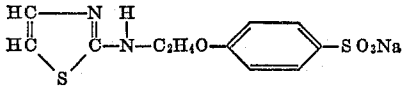
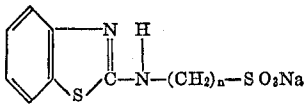
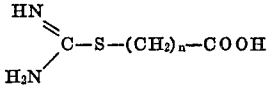
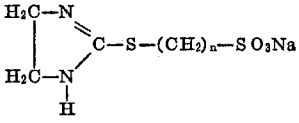


in which the R_{11} groups are selected from H, halogen and lower alkyl groups.

It is to be appreciated that in referring to halogens, it is intended to include chlorine, bromine, fluorine and iodine, although chlorine is generally preferred. Moreover, where reference is made to lower alkyl or alkoxy groups, it is intended to include groups containing from about 1 to 6 carbon atoms in a straight or branched chain, with from about 1 to 4 carbon atoms being preferred. Additionally, in referring to the sulfonic or carboxy acids and their salts, it is intended to include those sulfonic and carboxy acids which have halogen substituents on their alkyl, alkoxy or aryl groups and wherein the salts are exemplified by the alkali metal salts, sodium, potassium, lithium, cesium and rubidium, particularly sodium. In referring to the bivalent radicals above, a six membered ring is formed when R_4 and R_5 are joined and a five membered ring is formed when R_7 and R_8 are joined.

Suitable compounds are those of the formula:

TABLE I

	Concentration range (grams/liter)
(1) 	0.001–0.005
(2) 	0.001–0.02
(3) 	0.001–0.06
(4)  n=1–4	0.001–0.02
(5)  n=1–2	0.001–0.01
(6)  n=1–4	0.001–0.015

Compound 1, 2-aminothiazole and Compound 2, 2-aminobenzothiazole can be reacted with bromoethane sulfonate, propane sultone, benzyl chloride, dimethylsulfate, diethyl sulfate, methyl bromide, propargyl bromide, ethylene dibromide, allyl bromide, methyl chloro acetate, sulfophenoxyethylene bromide, the latter, for example, can be reacted with Compound 1 to give Compound 3, etc., to form compounds that give even improved results over Compounds 1 and 2. Also, substituted 2-aminothiazoles and 2-aminobenzothiazoles, such as 2-amino-5-chlorothiazole, 2-amino-4-methylthiazole, etc., can be used instead of Compounds 1 and 2. To form compounds such as 5 and 6, thiourea can be reacted with propiolactone, butyrolactone, chloroacetic acid, chloropropionic acid, propane sultone, dimethyl sulfate, etc. Also, phenyl thiourea, methyl thiourea, allyl thiourea and other similar substituted thioureas may be used in the reactions to form compounds similar to types 5 and 6.

It is to be appreciated that the above nickel brighteners must be soluble in the electroplating bath and may be introduced into the bath, when an acid is involved, as the acid itself or as a salt having bath soluble cations, such as ammonium ions or the alkali metal ion, such as, lithium, potassium, sodium, and the like.

It has been found that the use of bright nickel iron deposits of about 20 to 45% iron content function as well or better than bright nickel deposits in certain composite electroplate systems.

In particular, relatively thin coatings of bright nickel iron having less than about 0.5 mil thickness (such as 0.1 mil thickness) with an alloy content of about 20 to 45% iron, function more effectively than an equivalent bright nickel coating when copper or brass undercoats are employed. In particular, if the iron content is about 35% or more, the alloy deposits corrode more preferentially to copper or brass undercoats than does bright nickel. This action delays penetration to the basis metal.

These bright nickel iron coatings also function well as the thin top coat on semi-bright sulfur free nickel deposits. The bright nickel iron is very effective in such a composite electroplate when overplated with micro discontinuous chromium coatings such as that described in U.S. Pats. 3,563,864 and 3,151,971–3. The microdiscontinuous chromium coatings may be achieved by thin nickel deposits which induce micro-porosity or microcracking in the chromium or by plating the chromium deposit from a specific solution which deposits a microcracked chromium.

It can be appreciated that the nickel salts may be substituted with minor amounts up to 50% of the nickel salts with cobalt salts in order to achieve different corrosion behavior.

A suitable composition that may be employed in the present invention is as follows:

Material	Concentration range	Preferred concentration
Nickel sulfate $6H_2O$	40 to 300 grams/liter	50 grams/liter.
Nickel chloride.$6H_2O$	80 to 250 grams/liter	100 grams/liter.
Ferrous sulfate $7H_2O$	5 to 40 grams/liter	15 grams/liter.
Complexing agent	10 to 100 grams/liter	20 grams/liter.
Boric acid	30 to 60 grams/liter	45 grams/liter.
Cathode current density, avg	25 to 55 amps sq. ft.	
Anode current density	10–20 ASF	
Temperature	140° F. to 160° F.	
pH	2.5 to 5.5	3.0–4.2.
Agitation	Air to rod	
Brightener	See above	

It is to be appreciated that various other additives may be employed to effect desirable results such as surface active agents to overcome any undesirable problems that may occur in particular situations such as pitting.

When signficant amounts of iron are being introduced into the system, it has been found that soluble iron anodes or nickel-iron alloy anodes should be employed. The ratio of nickel to iron in the anode area should be maintained at approximately 4 to 1. Preferably dual (nickel and iron) anodes are used and the iron anodes should be insulated and connected to the anode rail through a highly electrically resistant device such as a nickel-chrome wire or controlled by a separate rheostat to maintain a total current to the iron anodes of about 8 to about 30% preferably about 10% to 25% of the total anode current. Anode bags, filter bags, hoses, tank linings etc. should be those which are generally employed in other bright nickel processes.

EXAMPLE #1

A bright iron nickel bath was formulated as follows:

Nickel sulfate hexahydrate	50 g./l.
Nickel chloride hexahydrate	100 g./l.
Ferrous sulfate heptahydrate	15 g./l.
Ammonium hydrogen citrate	26 g./l.
Boric acid	60 g./l.
pH	4.0.
Temp.	150° F.
Agitation	Rod.
Saccharin	4.5 g./l.
Allyl sulfonate	3.75 g./l.
Butyne diol ethylene oxide (ratio 1.8 moles oxide: 1 mole diol)	200 mg./l.
Quinaldine propane sultone	10 mg./l.

Rolled steel panels were plated at 45 ASF and gave full bright lustrous ductile deposits containing 15–20% iron.

EXAMPLE #2

Following the procedure of Example #1 but containing: 7.5–75 g./l. glycine instead of citrate resulted in the formation of an insoluble complex. No acceptable nickel-iron deposit was obtained.

EXAMPLE #3

Another nickel-iron bath was formulated as follows:

Nickel sulfate hexahydrate	75 g./l.
Nickel chloride hexahydrate	75 g./l.
Ferrous sulfate heptahydrate	15 g./l.
Sodium gluconate	40 g./l.
Boric acid	40 g./l.
pH	3.0
Temp.	150° F.
Agitation	Air.
Saccharin	2.5 g./l.
Allyl sulfonate	6.0 g./l.
Glycerol ether of butyne diol (adduct of 1.8 moles ethylene oxide: 1 mole diol)	50 mg./l.
Glycerol ether of butyne diol sulfonated (same as above adduct except product is sulfonated)	50 mg./l.
Adduct of 1.8 moles epichlorohydrin:1 mole propargyl alcohol; product is sulfonated	15 mg./l.
Thiourea-S-acetic acid	2.5 mg./l.

A test panel (J-steel) plated from this bath gave a bright level deposit with excellent ductility and clean recess areas.

The iron content of the plated deposit was approximately 20–25%.

EXAMPLE #4

A nickel-iron plating bath having a high iron concentration was tested in a pilot plating laboratory. The composition of the bath was as follows:

Ni^{+2}	42.0 g./l.
$NiCl_2.6H_2O$	100.5 g./l.
$NiSO_4.6H_2O$	76.6 g./l.
H_3BO_3	36.0 g./l.
Na Gluconate	65.0 g./l.
Fe total	5.8 g./l.
Saccharin	2.5 g./l.
Allyl sulfonate	6.0 g./l.
Glycerol ether of butyne diol (see Example #3)	0.05 g./l.
Glycerol ether of butyne diol sulfonated (see Example #3)	0.05 g./l.
Adduct of ethylene oxide and propargyl alcohol	0.012 g./l.
pH	3.0
Temp.	155° F.

A J-type steel panel plated at 50 ASF was overall bright, leveled, very ductile, with a part skipped recess area.

0.002 g./l. of dithio dipropane sulfonate was added to the bath and another panel was plated. The resulting deposit was again overall bright, leveled and ductile; however, now the recess areas were clean, covered and bright.

The iron included in these deposits was approximately 38–47%.

EXAMPLE #5

A bath was formulated as follows:

Fe total	3.11 g./l.
Fe^{+2}	2.83 g./l.
Fe^{+3}	0.28 g./l.
Allyl sulfonate	4.5 g./l.
Saccharin	3 g./l.
Butynediol ethylene oxide adduct (1:1.8 mole ratio)	200 mg./l.
Quinaldine propane sultone	10 mg./l.
$NiCl_2.6H_2O$	101.8 g./l.
$NiSO_4.6H_2O$	122.7 g./l.
Ni^{++}	52.6 g./l.
Boric acid	59.1 g./l.
pH	4.0
Temp.	150° F.
Agitation	Cathode or rod.

A J-shaped panel was plated at 40 ASF and obtained was a full bright lustrous deposit in the high current density area and a low current density cloud.

Addition of only 50 mg./l. of benzene sulfinate removed the recess cloud completely. The deposits contained 17.5% Fe.

EXAMPLE #6

Two nickel-iron plating solutions were prepared having the following compositions.

(A)

$NiCl_2.6H_2O$	75 g./l.
$NiSO_4.6H_2O$	75 g./l.
$FeSO_4$	15 g./l.
H_3BO_3	40 g./l.
Na gluconate	12.5 g./l.
Na citrate	12.5 g./l.
Saccharin	3.0 g./l.
Allyl sulfonate	6.0 g./l.
Adduct of butyne diol and epichlorohydrin (1.2 moles hydrin: 1 mole diol); product hydrolyzed	0.06 g./l.
Adduct of butyne diol and epichlorohydrin (1.2 moles hydrin: 1 mole diol); product sulfonated	0.06 g./l.
Adduct of propargyl alcohol and epichlorohydrin (1:1 mole ratio); product sulfonated	0.02 g./l.
Dithiodipropane sulfonate	0.002 g./l.
Temp.	160° F.
Agitation	Air.

(B)

$NiCl_2.6H_2O$	75 g./l.
$NiSO_4.6H_2O$	75 g./l.
$FeSO_4.7H_2O$	15 g./l.
H_3BO_3	40 g./l.
Na gluconate	12.5 g./l.
NH_4 citrate	12.5 g./l.
Saccharin	3.0 g./l.
Allyl sulfonate	6.0 g./l.
Adduct of butyne diol and epichlorohydrin (1.2 moles hydrin: 1 mole diol); product hydrolyzed	0.06 g./l.
Adduct of butyne diol and epichlorohydrin (1.2 moles hydrin: 1 mole diol); product sulfonated	0.06 g./l.
Adduct of propargyl alcohol and epichlorohydrin (1:1 mole ratio); product sulfonated	0.02 g./l.
Dithiodipropane sulfonate	0.002 g./l.
Temp.	160° F.
Agitation	Air.

Test panels were plated from each solution for 10 minutes at 45 ASF. Results showed both deposits to be overall bright with clean recess areas, with panel A having better leveling than panel B. Both panels had excellent ductility.

As can be seen in Example #6 a plurality of complexing agents may be used to obtain desirable results. It has also been determined that the gluconate complexing agent tends after long periods of electrolysis to form insoluble materials such as nickel salt of a gluconate degradation product. To continue to obtain desirable results a combination of complexing agents may be employed, such as, citrate and gluconate.

What is claimed is:

1. An aqueous bath suitable for the electrodeposition of a bright iron-nickel electrodeposit onto a substrate susceptible to corrosion comprising an amount of nickel ion equivalent to that provided by at least about 40 g./l. nickel sulfate hexahydrate and sufficient iron ions to provide a ratio of nickel ions to ferric and ferrous ions of about 5 to about 50 to 1 about 0.5 to about 10 g./l. of a bath soluble organic primary nickel brightener of the

first class containing a sulfo-oxygen group, an amount of a bath soluble complexing agent effective to keep substantially all of the ferric and ferrous ions in solution and containing at least two complexing groups, said groups being independently selected from the group consisting of carboxy and hydroxy, provided at least one group is a carboxy group; the bath having a pH from about 2.5 to 5.5 and an ion at a concentration of about 0.001 to 0.020 gram per liter having the formula:

$$-O_3S-R-S-A$$

wherein A may be hydrogen, $-R_1SO_3$, $-S-R_2-SO_3$ or R_3; R, R_1 or R_2 may be alkylene, arylene or aralkylene; and R_3 may be alkyl, aryl or aralkyl.

2. The bath of claim 1 wherein A is hydrogen.

3. The bath of claim 1 wherein A is $-R_1-SO_3^-$.

4. The bath of claim 1 wherein A is $-S-R_2-SO_3^-$.

5. The bath of claim 1 wherein A is R_3.

6. The bath of claim 1 wherein the ratio of nickel ions to iron ions in the bath ranges from about 5 to about 50 to 1; and the ratio of complexing agent to iron ion concentration ranges in the bath from about 3 to about 50 to 1.

7. The bath of claim 1 wherein the total iron ions are present in an amount ranging from about 5 to 40 g./l. calculated as $FeSO_4.7H_2O$; nickel sulfate present in an amount ranging from about 40 to 300 g./l., calculated as nickel sulfate.$6H_2O$; nickel chloride present in an amount from about 80 to 250 g./l. and the complexing agent is present in an amount from about 10 to 100 g./l.

8. The bath of claim 1 wherein the complexing agent is an aliphatic carboxylic acid having from 1 to 3 carboxyl groups, 2 to 8 carbon atoms, and 1 to 6 hydroxyl groups.

9. The bath of claim 1 wherein the complexing agent contains an amino group.

10. The bath of claim 1 wherein the complexing agent is citric acid.

11. The bath of claim 1 wherein the complexing agent is gluconic acid.

12. The bath of claim 1 wherein the sulfo-oxygen brightener is saccharin.

13. The bath of claim 1 further comprising an acetylenic nickel brightener present in an amount ranging from about 10 to 500 mg./l.

14. The bath of claim 1 further comprising a quaternary nitrogen heterocyclic nickel brightener present in an amount ranging from about 1 to about 50 mg./l.

15. The bath of claim 1 wherein the sulfide compound is an ion of the formula:

$$-O_3S-(CH_2)_3-S-S-(CH_2)_3-SO_3^-$$

16. The bath of claim 1 wherein the sulfide compound is an ion of the formula:

$$HS-(CH_2)_3-SO_3^-$$

17. A process for producing a bright iron-nickel alloy electrodeposit comprising passing a current through the bath of claim 1 and electrodepositing an iron nickel alloy onto a cathodic surface.

18. The process of claim 17 wherein A is hydrogen.

19. The process of claim 17 wherein A is $-R_1-SO_3^-$.

20. The process of claim 17 wherein A is

$$-S-R_2-SO_3^-$$

21. The process of claim 17 wherein A is R_3.

22. The process of claim 17 wherein the ratio of nickel ions to iron ions in the bath ranges from about 5 to about 50 to 1; and the ratio of complexing agent to iron ion concentration ranges in the bath from about 3 to about 50 to 1.

23. The process of claim 17 wherein the total iron ions are present in an amount ranging from about 5 to 40 g./l., calculated as $FeSO_4.7H_2O$; nickel sulfate present in an amount ranging from about 40 to 300 g./l., calculated as nickel sulfate.$6H_2O$; nickel chloride present in an amount from about 80 to 250 g./l. and the complexing agent is present in an amount from about 10 to 100 g./l.

24. The process of claim 17 wherein the complexing agent is an aliphatic carboxylic acid having from 1 to 3 carboxyl groups, 2 to 8 carbon atoms, and 1 to 6 hydroxyl groups.

25. The process of claim 17 wherein the complexing agent contains an amino group.

26. The process of claim 17 wherein the complexing agent is citric acid.

27. The process of claim 17 wherein the complexing agent is gluconic acid.

28. The process of claim 17 further comprising an acetylenic nickel brightener present in an amount ranging from about 10 to 500 mg./l.

29. The process of claim 17 further comprising a quaternary nitrogen heterocyclic nickel brightener present in an amount ranging from about 1 to about 50 mg./l.

30. The process of claim 17 wherein the sulfide compound is an ion of the formula:

$$-SO_3(CH_2)_3-S-S-(CH_2)_3SO_3^-$$

31. The process of claim 17 wherein the sulfide compound is an ion of the formula:

$$HS-(CH_2)_3-SO_3^-$$

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