

SPECIFICATION

Electroplating bath and process for producing bright nickel iron electrodeposits

- 5 The present invention is directed to an improved electroplating bath composition and process for producing exceptionally bright and level nickel-iron deposits on electrically conductive substrates which can be utilized as a base for subsequent electrodeposition of chromium in order to impart desirable decorative and/or corrosion resistant properties to the substrate. While the composition and process is primarily applicable for applying plating deposits on metallic substrates, it is also contemplated that the invention can be applied to
- 10 plastic substrates which have been subjected to a suitable pretreatment in accordance with well known techniques to provide an electrically conductive coating thereover such as nickel or copper rendering the plastic substrate receptive to the nickel-iron alloy electroplating operation. A variety of plastic materials can thus be electroplated of which ABS, polyolefin, polyvinyl chloride and phenol-formaldehyde polymers are typical.
- 15 A variety of aqueous electroplating bath compositions and processes for electrodepositing a nickel-iron alloy on electrically conductive substrates are known in the art and are in widespread commercial use. Nickel-iron electrodeposits because of their excellent corrosion resistance are particularly useful for providing decorative finishes on corrosion susceptible substrates over which a subsequent electrodeposition of chromium is applied. In order to achieve satisfactory nickel-iron deposits for decorative purposes it is
- 20 extremely important that such electrodeposits are characterised by high-levelling properties, brightness and good ductility and that uniformity in these beneficial characteristics are achieved over the entire area of the electrodeposit.
- While certain of the known nickel-iron plating bath compositions have provided for satisfactory electrodeposits for use in decorative applications, there has been a continuing need for improved bath
- 25 compositions which provide for still further improvements in the levelling characteristics and brightness of the deposit formed. The use of selected primary and secondary brighteners and combination of brighteners of the types heretofore known in such electroplating baths have enhanced the brightness of the deposit obtained but their effectiveness tends to peak out before an electrodeposit of superior brightness and levelling can be obtained.
- 30 The choice of complexing agents used to stabilize the iron has also been recognized as an important factor in the brightness and levelling of the electrodeposits obtained. For example, a citrate complexing agent not only complexes the iron ions present but also the nickel ions in the bath. Because of the presence of the nickel citrate complex, the resultant brightness and levelling of the electrodeposits does not rise to high levels. The use of gluconates as the complexing agent provides the advantage that it does not complex
- 35 nickel and therefore somewhat better levelling is obtained. However, the iron gluconate complex possesses characteristics which somewhat restrict the degree of levelling of the electrodeposit which is obtained.
- Attempts to increase the operating pH of the bath have resulted in some improvement in the levelling and brightness of the electrodeposit obtained. However, at such higher pH levels, an increase in the ferric ion concentration occurs rendering the operating bath very sensitive to high iron concentrations and too the
- 40 organic addition agents present detract from efficient use and simple control of the operating bath.
- We have found that the use of reducing saccharides in combination with selected complexing agents (such as those disclosed in United States Patent 3,974,044) results in good levelling and brightness of the nickel-iron alloy deposit with low sensitivity to high iron concentrations and the presence of organic
- 45 additives, such as secondary brightener additives. We have also found that the use of tartrates instead of the complexing agents disclosed in U.S. 3,974,044, results in significantly improved levelling and brightness of the nickel-iron alloy deposit but there is a marked increase in the sensitivity of such baths to iron and organic additives. A further problem is evidenced by an apparent interference of such compositions with the buffering additives employed causing the pH of the bath to rise very rapidly during use requiring constant pH
- 50 adjustment and the associated expense and difficulty of such control to maintain the bath within satisfactory operating parameters.
- The present invention provides for a further improvement in nickel-iron electroplating bath compositions and processes by overcoming many of the problems and disadvantages associated with prior art compositions and techniques while at the same time producing nickel-iron electrodeposits which are
- 55 characterised by their extremely high-levelling and brightness characteristics. The bath composition and process of the present invention is further characterised by its ability to achieve superior brightness and levelling over a broader pH range than previously possible even when depositing nickel-iron alloys containing 35% iron and higher while simultaneously providing a bath of reduced sensitivity to iron concentration and to the presence of high concentrations of secondary organic addition agents (brighteners).
- The present invention is based on the discovery of a nickel-iron electroplating bath containing controlled
- 60 effective amounts of a combination of specific constituents which provide for a synergistic effect and achieves superior brightness and levelling of the nickel-iron deposit while at the same time providing a relatively stable operating bath which is tolerant of relatively high iron contents and organic addition agents and which is simple to control and of versatile use. Thus according to the present invention an aqueous bath suitable for the deposition of bright nickel-iron electrodeposits contains as its essential constituents, an
- 65 effective amount of nickel and iron ions sufficient to produce a nickel-iron alloy deposit of the desired

composition. In addition, the bath contains a tartrate complexing agent; a reducing saccharide; about 0.5 to about 3 grams/litre (g/l) of ascorbic acid, isoascorbic acid, the bath soluble salts thereof, and mixtures thereof; a controlled amount of a buffering agent such as boric acid and/or sodium acetate; and a primary or carrier brightener preferably comprising sulpho-oxygen and/or sulphur bearing compounds, in further combination with a secondary brightener agent. The bath further contains a hydrogen ion concentration to provide an operating pH of from about 2.6 to about 4.5, preferably 3.0 to 3.6.

In accordance with the process aspects of the present invention, substrates to be electroplated are immersed in the electroplating bath while cathodically charged and are electroplated at average current densities of 5 up to 100 ASF (0.5 to 10 amperes per square decimetre (ASD)), preferably 30 to 60 ASF (3 to 6 ASD), for periods of time to provide the desired plating thickness. Usually plating thicknesses for decorative purposes range from 0.1 mils to 2 mils (0.0025 to 0.05 mms) with thicknesses of 0.2 to 0.5 mils (0.005 to 0.013 mms) being typical. The operating bath is usually maintained at a temperature ranging from 105°F up to 180°F (41 to 82°C) with temperatures of 130°F to 140°F (54 to 77°C) being preferred. Plating durations of from 5 minutes to 30 minutes are usually satisfactory in consideration of the specific current density employed and the thickness of the plating deposits desired. Agitation of the bath during electroplating is not necessary but it is preferred to employ conventional agitation means such as mechanical agitation, or air agitation.

The nickel and iron ions are preferably introduced into the bath as bath soluble and compatible nickel and iron compounds. Preferably, inorganic nickel salts are employed such as nickel sulphate, or nickel chloride, as well as other nickel materials such as nickel sulphamate. When nickel sulphate, or sulphamate salts are used they are conventionally employed in amounts ranging from 40 up to about 300 g/l (calculated as nickel sulphate hexahydrate). Nickel chloride can also be used and is normally employed in an amount ranging from 40 to 250 g/l. The chloride or halide ions introduced provide for satisfactory conductivity of the bath and also provide satisfactory corrosion properties of the soluble anodes.

The iron compounds preferably comprise inorganic ferrous salts such as ferrous sulphate, or ferrous chloride. Such ferrous salts are usually employed in amounts ranging from 2 up to 60 g/l. Additionally, other bath soluble compatible iron salts can be employed such as soluble ferrous fluoborate, or sulphamate.

The concentration of nickel and iron ions in the bath is usually controlled to provide a weight ratio of nickel to iron ranging from 5:1 up to 50:1.

As mentioned above the aqueous bath contains a complexing agent for the iron constituent consisting of tartaric acid, bath soluble salts thereof, such as nickel, iron, mono and/or di-alkali metal salts, and mixtures thereof. The term "alkali metal salts" is used herein in its broad sense to include the alkali metals, sodium, potassium and lithium as well as ammonium (NH₄). The complexing agent can be conveniently introduced in the form of Rochelle salts comprising potassium-sodium tartrate of L⁺ tartaric acid. The complexing agent is employed in amounts of 5 up to 100 g/l with amounts of 15 to 30 g/l being preferred. Generally, concentrations of the complexing agent above 50 g/l are unnecessary and in some instances may be undesirable due to the formation of insoluble degradation products over prolonged operating periods of the plating bath. The use of such higher concentrations may also be undesirable from an economic standpoint.

The ratio of the complexing agent relative to the iron ion concentration present is preferably within the range of from 1:1 up to 20:1. At ratios below 1:1, the iron constituent may precipitate out while at ratios above 20:1 excessive concentrations of complexing agent may be present, providing the disadvantages and potential problems as hereinabove set forth.

In addition to the nickel and iron ions and complexing agent, the bath further contains as an essential constituent, a controlled amount of a reducing saccharide. The reducing saccharide or mixture of saccharides which can satisfactorily be employed in accordance with the present invention can be either a monosaccharide or a disaccharide. The monosaccharides are preferably polyhydroxyaldehydes or polyhydroxyketones with at least three aliphatically bound carbon atoms. The simplest monosaccharides are glyceraldehyde (generally termed aldose) and dihydroxyacetone (generally termed ketose). Other suitable monosaccharides useful in the practice of the present invention include dextrose, sorbose, fructose, xylose, erythrose and arabinose. Disaccharides are glucoside-type derivatives of monosaccharides, in which one sugar forms a glucoside with an -OH group of some other sugar. Disaccharides suitable for use in the practice of the present invention include lactose, maltose and turanose. Other disaccharides in which the second monosaccharide may, at least momentarily, possess a free carbonyl group, may also be utilized.

The reducing saccharide is employed in amounts ranging from 1 to 50 g/l with amounts of 2 to 5 g/l being preferred. The reducing saccharide functions as a mild reducing agent for ferric ions present but additionally provides for exceptional brightness and levelling of the nickel-iron electrodeposit in combination with the tartrate-type complexing agents and primary and secondary brighteners providing a synergistic effect which is not completely understood at the present time.

A further essential constituent of the bath comprises ascorbic acid and/or isoascorbic acid, the bath soluble salts, such as the alkali metal salts, thereof, as well as mixtures thereof. This constituent is employed in amounts ranging from 0.5 up to 3 g/l with amounts of 1 to 2 g/l being preferred. Amounts of this constituent above about 3 g/l are undesirable because of a reduction in the brightness and levelling obtained in comparison to that achieved when amounts less than 3 g/l are used. Additionally, amounts of this constituent in excess of about 3 g/l also results in the formation of bath insoluble degradation products over prolonged periods of use of the bath causing excessive sludging of the bath and associated equipment. The use of the ascorbic and/or isoascorbic constituent in combination with the remaining bath constituents

prevents a rapid rise in the pH of the bath during use and further reduces the sensitivity of the bath to high iron concentrations and sensitivity to high concentrations of organic compounds such as secondary brighteners which heretofore has resulted in the formation of dark recesses on substrates being plated, and poor adhesion of the electrodeposit as well as high stress in the plating.

5 The electroplating bath further contains as an essential constituent, a buffering agent, such as boric acid and/or sodium acetate, which is present in an amount of 30 up to 60 g/l with amounts of 40 to 50 g/l being preferred. Of the various buffering agents that can be satisfactorily employed, boric acid comprises the preferred material. 5

The bath further contains as essential constituents, controlled amounts of primary or so-called carrier brighteners in combination with secondary brighteners to attain the exceptional brightness and high-levelling of the nickel-iron deposit. The primary brighteners are employed in amounts ranging from 0.5 to 20 g/l with amounts of 2 to 8 g/l being preferred. The secondary brighteners are employed in amounts of 0.25 mg/l up to 1 g/l. The primary and secondary brighteners, when an acid is involved, can be introduced into the bath in the form of the acid itself or as a salt having bath soluble cations such as the alkali metal ions or ammonium. 10 15

The primary brighteners suitable for use include those described in United States Patent No. 3,974,044, as sulpho-oxygen compounds, or sulphur-bearing compounds as further described in "Modern Electroplating" published by John Wiley and Sons, second edition, page 272.

Examples of such brighteners are:

- 20 Benzene sulphonamide 20
- Toluene sulphonamides (o- and p-)
- o-Benzoyl sulphimide
- N-Benzoyl benzene sulphonimide
- p-Toluene sulphonchloramide
- 25 p-Brom benzene sulphonamide 25
- 6-Chloro-benzoyl sulphimide
- m-Aldehydo benzene sulphonamide
- Sulphomethyl benzene sulphonamide
- Benzene sulphonamide m-carboxylic amide
- 30 7-Aldehydo o-benzoyl sulphimide 30
- N-acetyl benzene sulphonimide
- Methoxy benzene sulphonamides
- Hydroxymethyl benzene sulphonamide
- Allyl sulphonamide
- 35 Benzene sulphonic acids (mono-, di-, and tri-) 35
- p-Brom benzene sulphonic acid
- Benzaldehyde sulphonic acids (o, m, p)
- Diphenyl sulphone sulphonic acid
- Naphthalene sulphonic acids (mono-, di-, and tri-)
- 40 Benzene sulphohydroxamic acid 40
- p-Chlor benzene sulphonic acid
- Diphenyl sulphonic acid
- m-Diphenyl benzene sulphonic acid
- 2-Chloro-5-sulphobenzaldehyde
- 45 m-Benzene disulphonamide 45
- Allyl sulphonic acid
- Dichlorobenzene sulphonic acids
- Di-benzene sulphonimide
- Di-toluene sulphonimide
- 50 2-Butyne-1,4-disulphonic acid 50
- 4-Hydroxy-2-butyne-1-sulphonic acid
- 2-Butyne-1-sulphonic acid
- 3-Chloro-2-propyne-1-sulphonic acid
- 2-butene-1,4-disulphonic acid
- 55 2-chloro butene-4-sulphonic acid 55
- 2-chloro propene sulphonic acid
- Cinnamyl sulphonic acid
- 3-Phenyl-2-propyne-1-sulphonic acid.

Preferred sulpho-oxygen primary brighteners are saccharin, naphthalenetrisulphonic acid, sulphobenzaldehyde, dibenzenesulphonamide, sodium allyl sulphonate, benzene sulphinates, vinyl sulphonate, beta-styrene sulphonate, and cyano alkane sulphonates (having from 1 to 5 carbon atoms). 60

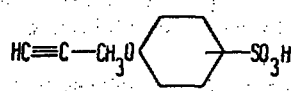
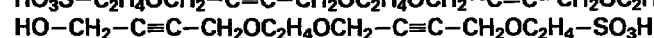
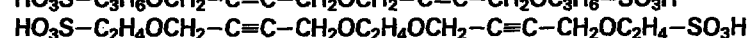
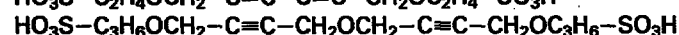
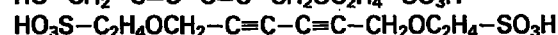
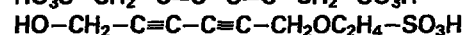
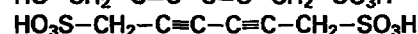
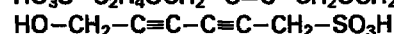
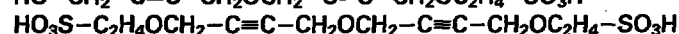
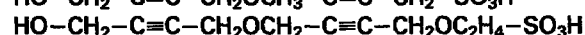
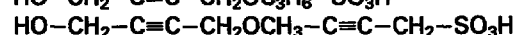
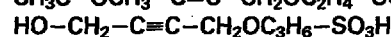
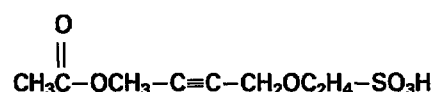
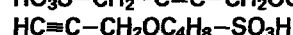
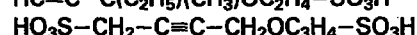
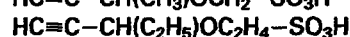
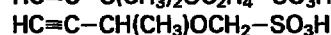
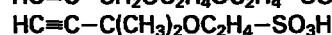
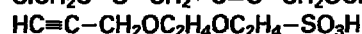
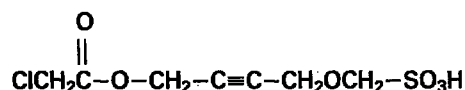
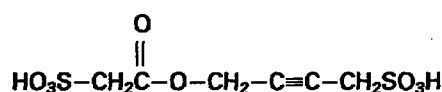
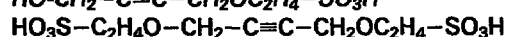
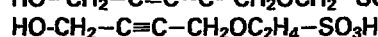
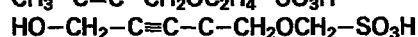
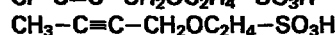
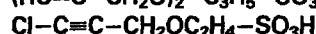
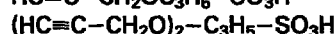
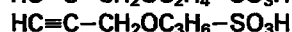
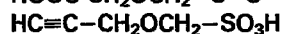
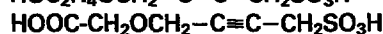
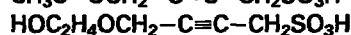
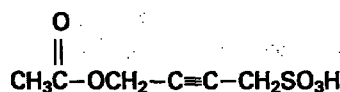
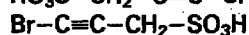
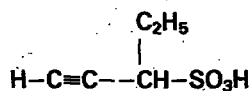
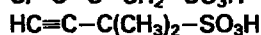
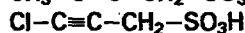
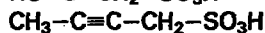
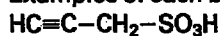
Other bath soluble sulpho-oxygen compounds are those such as the unsaturated aliphatic sulphonic acids, mononuclear and binuclear aromatic sulphonic acids, mononuclear aromatic sulphinic acids, and mononuclear aromatic sulphonamides and sulphonimides. Of the foregoing, saccharin itself or saccharin in combination with allyl sulphonate and/or vinyl sulphonate comprises a preferred primary brightener. 65

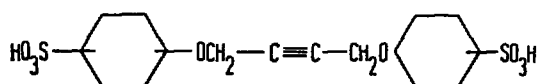
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Suitable secondary brighteners include acetylenic nickel brighteners such as the acetylenic sulpho-oxygen compounds described in United States Patent No. 2,800,440.

These nickel brighteners are the oxygen containing acetylenic sulpho-oxygen compounds.

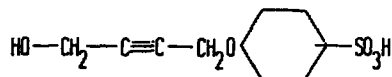
Examples of such brighteners are:





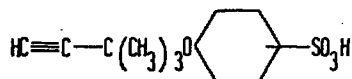
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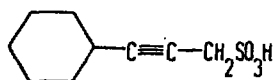
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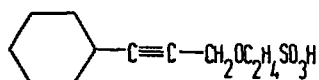
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Other acetylenic nickel brighteners are those described in U.S. Patent No. 3,366,557 such as the polyethers resulting from the condensation reaction of acetylenic alcohols and diols such as, propargyl alcohol, or butyndiol, and lower alkylene oxides such as, epichlorohydrin, ethylene oxide, and propylene oxide.

Additional secondary brighteners that are suitable include nitrogen heterocyclic quaternary or betaine nickel brighteners which are usually employed in amounts of 1 to 150 mg/l. Suitable compounds of this type are those described in U.S. 2,647,866 and the nitrogen heterocyclic sulphonates described in U.S. 3,023,151.

Examples of such brighteners are:

N-allyl pyridinium bromide

N-allyl quinolinium bromide

N-allyl isoquinolinium bromide

N-(β-hydroxy ethyl) pyridinium chloride

N-(β-hydroxy ethyl)-α-chloro-pyridinium chloride

N-ethyl pyridinium sulphate

N-propyl pyridinium iodide

N-ethyl-2,4-dimethyl pyridinium sulphate

N-ethyl-2-bromo pyridinium iodide

N-methyl quinolinium sulphate

N-ethyl quinolinium bromide

N-ethyl-2-methyl quinolinium bromide

N-(β-hydroxy ethyl) quinolinium chloride

N-propanol quinolinium chloride

N-allyl-2,6-dimethyl quinolinium bromide

N-ethyl-2-methyl quinolinium chloride

N-allyl-2-bromo quinolinium bromide

N-allyl-6-bromo quinolinium bromide

N-(β-hydroxy-ethyl) isoquinolinium chloride

N-ethyl isoquinolinium bromide

N-methyl acetate quinolinium chloride

N-allyl-2-methyl pyridinium bromide

N-allyl-4-bromo pyridinium chloride

N-allyl-2,4-dimethyl quinolinium bromide

N-allyl-2,4-dichloro quinolinium bromide

N-allyl-4-ethyl pyridinium bromide

N-allyl-2,8-dimethyl quinolinium chloride

N-allyl-5,8-dimethyl quinolinium bromide

N-allyl-3-ethyl pyridinium bromide

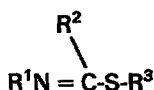
N-allyl-1,3-dimethyl isoquinolinium bromide

N-allyl-3-methyl pyridinium chloride

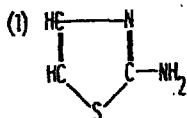
N-allyl-2-methyl-4-ethyl pyridinium chloride

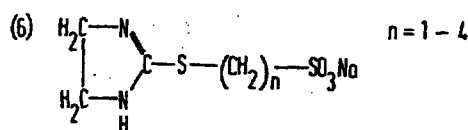
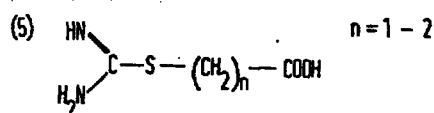
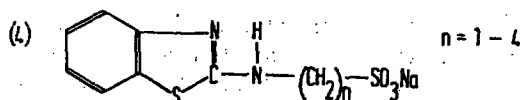
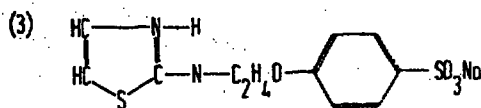
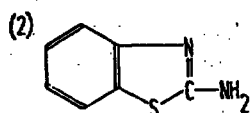
N-allyl-2-methyl-4-ethyl pyridinium bromide

- N-allyl-8-methyl quinolinium chloride
 N-allyl-2,4-dimethyl pyridinium bromide
 N-allyl-3-chloro-2-methyl quinolinium chloride
 N-allyl-3-bromo-2-methyl quinolinium bromide
 5 N-methylpyridinium bromide 5
 N-methylquinolinium bromide
 N-methylpyridinium chloride
 N-methylquinolinium chloride
 N-methylisoquinolinium chloride
 10 N-methyl-2-methyl pyridinium chloride 10
 N-allyl-3-bromo pyridinium bromide
 N-allyl-2-chloro pyridinium bromide
 N-allyl-3-methyl isoquinolinium bromide
 N-allyl-8-methyl quinolinium bromide
 15 N-ethyl acetate-2-methyl quinolinium chloride 15
 N-butyl quinolinium chloride
 N-butyl-2-methyl pyridinium chloride
 N-4-tert butyl pyridinium bromide
 N-4-tert butyl quinolinium bromide
 20 N-butyl-2-methyl quinolinium chloride 20
 N-butyl-8-methyl quinolinium chloride
 N-butyl isoquinolinium chloride
 N-butyl-3-methyl isoquinolinium bromide
 N-allyl-2-methyl quinolinium bromide
 25 N-methyl acetate 2-methyl pyridinium chloride 25
 N-ethyl acetate pyridinium chloride
 N-methyl acetate pyridinium chloride
 Preferred compounds described therein are the pyridine quaternaries or betaines or the pyridine
 sulphobetaines. Suitable quaternaries that may be employed are quinaldine propane sultone, quinaldine
 30 dimethyl sulphate, quinaldine allyl bromide, pyridine allyl bromide, isoquinaldine propane sultone, 30
 isoquinaldine dimethyl sulphate, and isoquinaldine allyl bromide.
 In addition, secondary brighteners further include the reaction product of a polyamine-type brightener
 which has a molecular weight ranging from 300 to about 24,000, and an alkylating agent of the type
 described in U.S. Patent 4,002,543 the substance of which is incorporated herein by reference. Exemplary
 35 alkylating agents are dimethyl sulphate, chloroacetic acid, allyl bromide, propane sultone, benzyl chloride or 35
 propargyl bromide. The polyamine brightener may be sulphonated utilizing as exemplary compounds
 sulphamic acid, or chloro sulphonic acid. The ratio of polyamine to alkylating agent or to the sulphonating
 agent can be varied so that every amino group need not be alkylated or sulphonated as the case may be.
 In addition to the essential primary and secondary brighteners and other bath constituents, an optional
 40 addition agent comprises special carrier agents of the type described in U.S. Patent 3,806,429, the substance 40
 of which is incorporated herein by reference. Such optional special additives are not required in achieving
 the exceptional brightness and high levelling in accordance with the present invention but their inclusion in
 the bath is usually preferred to assure bright nickel-iron deposits over the entire surface of the substrate,
 even those exposed to very low current densities. Such specialty additives comprise organic sulphide
 45 compounds which are normally employed in amounts ranging from 0.5 to 40 mg/l and are of the formula: 45



- 50 where R^1 represents a hydrogen or a carbon atom or an organic group, R^2 represents a nitrogen or a carbon 50
 atom of an organic group and R^3 represents a carbon atom of an organic group. R^1 and R^2 or R^3 may be
 linked together through a single organic radical.
 Typically, the bath soluble organic sulphide compounds can be 2-amino thiazoles and isothiureas.
 55 Examples of such compounds include: 55





Compound (1), 2-aminothiazole and compound (2), 2-aminobenzothiazole can be reacted with bromethane sulphonate, propane sultone, benzyl chloride, dimethyl-sulphate, diethyl sulphate, methyl bromide, propargyl bromide, ethylene dibromide, allyl bromide, methyl chloro-acetate, sulphophenoxy-ethylene bromide, to form compounds suitable for use in this invention. Substituted 2-aminothiazoles and 2-aminobenzothiazoles, such as 2-amino-5-chlorothiazole, or 2-amino-4-methylthiazole, can also be employed. To form compounds such as (5) and (6) thiourea can be reacted with propiolactone, butyrolactone, chloroacetic acid, chloropropionic acid, propane sultone, or dimethyl sulphate. Also, phenyl thiourea, methyl thiourea, allyl thiourea and other similar substituted thioureas can also be used to form suitable reacted compounds.

The maintenance of an appropriate operating pH in the bath can be achieved by employing conventional acids used in nickel-iron plating baths and sulphuric acid and hydrochloric acid are preferred.

The invention can be put into practice in various ways and a number of specific examples will be given to illustrate the invention.

Examples 5 and 6 are in accordance with the invention, the remaining examples are for comparison.

Example 1

An aqueous nickel-iron plating bath was prepared having the following composition:

NiSO ₄ 6H ₂ O	150 g/l
NiCl ₂ 6H ₂ O	75 g/l
FeSO ₄ 7H ₂ O	15 g/l
H ₃ BO ₃	45 g/l
Sodium Gluconate	20 g/l
Saccharin	2.5 g/l
Sodium Allyl Sulphonate	3 g/l
Propargyl Alcohol Ethylene Oxide	23 mg/l
pH	3.3
Temperature	135°F/57°C)
Agitation	Air

A polished steel panel having 180 grit polishing lines was plated at 30 ASF (3 ASD) for 15 minutes. The resulting deposit was overall bright and its levelling when rated on a scale of 1-10 was 5 on the front side and 4 on the back.

5 Example 2

A bath with a composition identical to that of Example 1 was prepared except that the sodium gluconate was replaced by 15 g/l of sodium tartrate. A polished steel panel as in Example 1 was again plated for 15 minutes at 30 ASF (3 ASD). The pH was carefully monitored during electrolysis and maintained at 3.2. The resulting deposit was overall bright and the levelling rates on a scale of 1-10, was 5.5 on the front side and 4.0 on the back.

Example 3

5 g/l of dextrose was added to bath described in Example 2. All other bath components, as well as the pH and temperature, were maintained at exactly the same levels as in Example 2. A polished steel panel as in Example 1 was again plated at 30 ASF (3 ASD) for 15 minutes. The pH was again carefully monitored during electrolysis and maintained at 3.2. The resulting deposit was overall bright and the levelling on a scale of 1-10 was 7.0 on the front and 6 on the back.

Example 4

20 An aqueous nickel-iron plating bath was prepared having the following composition: 20

	NiSO ₄ 6H ₂ O	150 g/l	
	NiCl ₂ 6H ₂ O	75 g/l	
	FeSO ₄ 7H ₂ O	15 g/l	
25	Rochelle Salts	18 g/l	25
	Lactose	5 g/l	
	H ₃ BO ₃	45 g/l	
	Saccharin	2.5 g/l	
	Sodium Allyl Sulphonate	3 g/l	
30	Propargyl Alcohol		30
	Ethylene Oxide	25-mg/l	
	pH	3.2	
	Temperature	140°F (77°C)	
35	Agitation	Air	35

A polished steel panel, which was rolled up at the end and had a 180 grit finish, was plated for 15 minutes at 30 ASF (3 ASD). The resulting deposit was very bright with exceptional levelling (7.0 average) but the pH of the bath had risen from 3.2 to 3.8. As a result, the deposit had dark recess areas, with some gray-white blotchiness, and exfoliated upon bending.

Example 5

0.75 g/l of isoascorbic (erythorbic) acid was added to the plating solution of Example 4. A polished steel panel as in Example 4 was plated using conditions identical to those described in Example 4. The resulting deposit was overall bright, ductile with excellent recess areas and good adhesion. The levelling was comparable and the pH had risen to only 3.25.

Example 6

The process described in Example 5, was repeated, but this time 1.5 g/l of ascorbic acid was used in place of the isoascorbic (erythorbic) acid. The results were identical.

Example 7A

An aqueous nickel-iron plating bath was prepared having a composition as described in Example 5, except that 2 g/l of sodium citrate was added to the bath in place of the isoascorbic acid. A polished steel panel as in Example 4 was plated, again using the same conditions described in Example 5. The resulting deposit was overall bright, with some darkness in the recess, and had some exfoliation upon bending. The levelling was slightly poorer (6.5 average) and the pH rose from 3.2 to 3.5.

Example 7B

The sodium citrate was increased to 5 g/l and Example 7A repeated. Now the deposit was overall bright with a good recess and excellent adhesion. The pH only rose to 3.25, but the levelling was dramatically reduced (4.5 average).

Examples 8A and 8B

65 Examples 7A and 7B were repeated using sodium gluconate in place of sodium citrate. Panels were plated 65

at 2 and at 5 g/l concentrations of sodium gluconate. Results were similar to those obtained with citrate in that the gluconate improved the physical properties and maintained relatively consistent pH, (3.2-3.35). However, the loss of levelling, while not as dramatic as with the citrate, was still substantial the average levelling value being 5.0.

5 The results obtained in accordance with Examples 1 to 8 as hereinbefore described clearly substantiate the benefits attainable in accordance with the practice of the present invention. In accordance with Example 1, only average brightness and levelling is attained employing sodium gluconate as the complexing agent. In Example 2, in which sodium tartrate is substituted for the sodium gluconate constituent, substantially similar results are obtained as were obtained in Example 1. According to Example 3, the addition of a reducing
10 saccharide to the bath of Example 2 provided outstanding levelling and brightness but required a constant monitoring of the pH of the bath by acid addition to maintain the bath at a proper pH level. Such constant monitoring is often commercially impractical.

According to Example 4, a bath similar to that of Example 3 but in which lactose was substituted for dextrose as the reducing saccharide, and without monitoring the pH, an inferior deposit was obtained
15 accompanied by a relatively significant rise in pH during the course of the electroplating operation. By the controlled addition of a small but effective amount of isoascorbic acid (also called erythorbic acid), in Example 5, exceptionally bright and level deposits were attained over the entire surface area which were of good adhesion and mechanical properties. These excellent results were obtained with only a relatively insignificant increase in the pH of the bath. Similarly, in accordance with Example 6, ascorbic acid provides
20 substantially identical excellent results to those obtained employing isoascorbic acid pursuant to Example 5.

Examples 7 and 8 are indicative of the significant reduction in brightness and levelling obtained in a bath of Example 4 by the addition of sodium citrate or sodium gluconate, respectively, in an effort to reduce the rapid rise in pH through a buffering action. While some reduction in pH increase was obtained, the reduction in levelling and brightness of the electrodeposit was significant.

25 These results clearly substantiate the criticality and synergistic effect of the plating bath composition of the present invention in achieving exceptional brightness and high-levelling of nickel-iron alloy electrodeposits as typified by the results obtained in Example 5 and Example 6, while at the same time providing a bath which is relatively stable and simple to control.

30 CLAIMS

1. An aqueous bath suitable for the electrodeposition of bright, nickel-iron electrodeposits comprising nickel ions and iron ions, from 5 to 100 g/l of a complexing agent consisting of tartaric acid, bath soluble salts thereof and mixtures thereof, from 1 to 50 g/l of a reducing saccharide, from 0.5 to 3 g/l of ascorbic acid, or
35 isoascorbic acid or bath soluble salts thereof or mixtures thereof, from 30 to 60 g/l of a buffering agent, from 0.5 to 20 g/l of a bath soluble primary brightener, from 0.25 mg/l to 1 g/l of a secondary brightener, and hydrogen ions to provide a pH in the range from 2.6 to 4.5.
2. A bath as claimed in Claim 1 in which the weight ratio of nickel ions to iron ions is in the range from 5:1 up to 50:1.
- 40 3. A bath as claimed in Claim 1 or Claim 2 in which the said complexing agent is present in an amount of 15 to 30 g/l.
4. A bath as claimed in Claim 1, 2 or 3 in which the said complexing agent is present in an amount such as to provide a weight ratio of complexing agent to iron ions of 20:1 to 1:1.
5. A bath as claimed in Claim 1, 2, 3 or 4 in which the said reducing saccharide is a monosaccharide, or a
45 disaccharide or a mixture thereof.
6. A bath as claimed in Claim 1, 2, 3, 4 or 5 in which the said reducing saccharide is present in an amount of 2 to 5 g/l.
7. A bath as claimed in Claim 1, 2, 3, 4, 5 or 6 in which the ascorbic or isoascorbic acid or salt thereof is present in an amount of 1 to 2 g/l.
- 50 8. A bath as claimed in Claim 1, 2, 3, 4, 5, 6 or 7 in which the said buffering agent is present in an amount of 40 to 50 g/l.
9. A bath as claimed in any one of Claims 1 to 8 in which the said primary brightener is present in an amount of 2 to 8 g/l.
10. A bath as claimed in any one of Claims 1 to 9 in which the said primary brightener comprises
55 saccharin.
11. A bath as claimed in any one of Claims 1 to 9 in which the said primary brightener comprises saccharin in combination with sodium allyl sulphonate, or vinyl sulphonate or mixtures thereof.
12. A bath as claimed in any one of Claims 1 to 11 in which the said hydrogen ions are present to provide a pH of 3.0 to 3.6.
- 60 13. A bath as claimed in any one of Claims 1 to 12 in which the said buffering agent comprises boric acid, the said primary brightener comprises a mixture of saccharin and an alkali metal allyl sulphonate, the said secondary brightener comprises propargyl alcohol ethylene oxide and the said hydrogen ions are present to provide a pH of 3.0 to 3.6.
14. A bath as claimed in Claim 1 substantially as specifically described herein with reference to Example
65 5 or Example 6.



at 2 and at 5 g/l concentrations of sodium gluconate. Results were similar to those obtained with citrate in that the gluconate improved the physical properties and maintained relatively consistent pH, (3.2-3.35). However, the loss of levelling, while not as dramatic as with the citrate, was still substantial the average levelling value being 5.0.

- 5 The results obtained in accordance with Examples 1 to 8 as hereinbefore described clearly substantiate the benefits attainable in accordance with the practice of the present invention. In accordance with Example 1, only average brightness and levelling is attained employing sodium gluconate as the complexing agent. In Example 2, in which sodium tartrate is substituted for the sodium gluconate constituent, substantially similar results are obtained as were obtained in Example 1. According to Example 3, the addition of a reducing
10 saccharide to the bath of Example 2 provided outstanding levelling and brightness but required a constant monitoring of the pH of the bath by acid addition to maintain the bath at a proper pH level. Such constant monitoring is often commercially impractical.

- According to Example 4, a bath similar to that of Example 3 but in which lactose was substituted for dextrose as the reducing saccharide, and without monitoring the pH, an inferior deposit was obtained
15 accompanied by a relatively significant rise in pH during the course of the electroplating operation. By the controlled addition of a small but effective amount of isoascorbic acid (also called erythorbic acid), in Example 5, exceptionally bright and level deposits were attained over the entire surface area which were of good adhesion and mechanical properties. These excellent results were obtained with only a relatively insignificant increase in the pH of the bath. Similarly, in accordance with Example 6, ascorbic acid provides
20 substantially identical excellent results to those obtained employing isoascorbic acid pursuant to Example 5.

- Examples 7 and 8 are indicative of the significant reduction in brightness and levelling obtained in a bath of Example 4 by the addition of sodium citrate or sodium gluconate, respectively, in an effort to reduce the rapid rise in pH through a buffering action. While some reduction in pH increase was obtained, the reduction in levelling and brightness of the electrodeposit was significant.

- 25 These results clearly substantiate the criticality and synergistic effect of the plating bath composition of the present invention in achieving exceptional brightness and high-levelling of nickel-iron alloy electrodeposits as typified by the results obtained in Example 5 and Example 6, while at the same time providing a bath which is relatively stable and simple to control.

30 CLAIMS

1. An aqueous bath suitable for the electrodeposition of bright, nickel-iron electrodeposits comprising nickel ions and iron ions, from 5 to 100 g/l of a complexing agent consisting of tartaric acid, bath soluble salts thereof and mixtures thereof, from 1 to 50 g/l of a reducing saccharide, from 0.5 to 3 g/l of ascorbic acid, or
35 isoascorbic acid or bath soluble salts thereof or mixtures thereof, from 30 to 60 g/l of a buffering agent, from 0.5 to 20 g/l of a bath soluble primary brightener, from 0.25 mg/l to 1 g/l of a secondary brightener, and hydrogen ions to provide a pH in the range from 2.6 to 4.5.
2. A bath as claimed in Claim 1 in which the weight ratio of nickel ions to iron ions is in the range from 5:1 up to 50:1.
- 40 3. A bath as claimed in Claim 1 or Claim 2 in which the said complexing agent is present in an amount of 15 to 30 g/l.
4. A bath as claimed in Claim 1, 2 or 3 in which the said complexing agent is present in an amount such as to provide a weight ratio of complexing agent to iron ions of 20:1 to 1:1.
5. A bath as claimed in Claim 1, 2, 3 or 4 in which the said reducing saccharide is a monosaccharide, or a
45 disaccharide or a mixture thereof.
6. A bath as claimed in Claim 1, 2, 3, 4 or 5 in which the said reducing saccharide is present in an amount of 2 to 5 g/l.
7. A bath as claimed in Claim 1, 2, 3, 4, 5 or 6 in which the ascorbic or isoascorbic acid or salt thereof is present in an amount of 1 to 2 g/l.
- 50 8. A bath as claimed in Claim 1, 2, 3, 4, 5, 6 or 7 in which the said buffering agent is present in an amount of 40 to 50 g/l.
9. A bath as claimed in any one of Claims 1 to 8 in which the said primary brightener is present in an amount of 2 to 8 g/l.
10. A bath as claimed in any one of Claims 1 to 9 in which the said primary brightener comprises
55 saccharin.
11. A bath as claimed in any one of Claims 1 to 9 in which the said primary brightener comprises saccharin in combination with sodium allyl sulphonate, or vinyl sulphonate or mixtures thereof.
12. A bath as claimed in any one of Claims 1 to 11 in which the said hydrogen ions are present to provide a pH of 3.0 to 3.6.
- 60 13. A bath as claimed in any one of Claims 1 to 12 in which the said buffering agent comprises boric acid, the said primary brightener comprises a mixture of saccharin and an alkali metal allyl sulphonate, the said secondary brightener comprises propargyl alcohol ethylene oxide and the said hydrogen ions are present to provide a pH of 3.0 to 3.6.
14. A bath as claimed in Claim 1 substantially as specifically described herein with reference to Example
65 5 or Example 6.



15. A process for electrodeposition of a bright, nickel-iron deposit on an electrically conductive surface of a substrate including the steps of immersing the substrate in an aqueous bath as claimed in any one of Claims 1 to 14, applying a cathodic charge to the said substrate surface to effect a progressive deposition of a nickel-iron electrodeposit thereon, controlling the bath at a temperature of 105°F to 180°F (41 to 82°C), and
5 continuing the electrodeposition of said nickel-iron electrodeposition until desired thickness is obtained.

16. A process as claimed in Claim 15 substantially as specifically described herein with reference to Example 5 or Example 6.

17. An article whenever provided with a bright nickel-iron electrodeposition by a process as claimed in Claim 15 to Claim 16.

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