

SPECIFICATION

Bath and process for high speed nickel electroplating

5 The present invention relates to a nickel plating bath and to a process for using it. 5

It is known in electrolytic nickel plating systems to use soluble anodes. The use of soluble anodes was prescribed because of the belief that organic additives in the bath would break down in the presence of insoluble anodes. It was also known that the stress of the nickel deposit was adversely affected by insoluble anodes. For various commercial reasons it would be highly desirable to use insoluble anodes in a nickel electroplating system without encountering break down of organic additives or stressed nickel deposits. 10

United States patents relating to nickel plating include U.S. Patents 2,228,991 (Freed); 2,409,119 (Freed); 2,409,120 (Freed et al.); 2,485,149 (Freed et al.); and 2,998,360 (Castellano). As far as can be determined, these patents involve the use of a conventional or modified consumable anode. See, for example, page 2, column 2, lines 53 to 64, of U.S. Patent 2,228,991. 15

The present invention relates to a new and improved electroplating bath for use with insoluble anodes and can be operated at relatively high speeds to produce nickel deposits which are also relatively stress-free. The insoluble anodes which can be employed in the process of this invention are, for example, platinized titanium, platinized tantalum, platinized columbium (niobium) as well as a platinum metal anode itself. Additionally, titanium anodes having mixed oxide coatings, such as ruthenium dioxide—titanium dioxide coatings, may also be used. 20

The electroplating bath of this invention contains certain selected additives which have been found to have markedly increased resistance to breakdown during operations carried out in the presence of insoluble anodes as compared to conventional nickel brighteners. In addition to a conventional nickel source, e.g. nickel, sulphate, and an electrolyte conducting or buffering agent such as boric acid, the electroplating bath will contain ortho-formyl benzene sulphonic acid as the brightener and a blend of potassium perfluoro-alkyl sulphonates sold under the trade name designation of FC 98 as the wetting agent. 25

In general, the electroplating baths of the present invention will be formulated as follows: 30

Component	Concentration (g/l)	
35 Nickel Salt	30 to 105 (as Ni)	35
Electrolyte	20 to 100	
O-formyl benzene sulphonic acid	0.25 to 3.0	
FC 98	0.02 to 0.2	

40 The preferred sources of the nickel metal ions are nickel sulphate, nickel citrate, and nickel carbonate. These salts are preferably employed in an amount of from 135 to 470 g/l to provide the desired nickel metal ion concentration. 40

Electrolytes which are most useful for the present purpose include boric acid and citric acid. 45 The preferred amounts used in preparing the electroplating baths of this invention will range from 22.5 to 45 g/l. The use of boric acid is especially preferred. 45

The organic components of the bath are usually the brighteners and the wetting agents. In formulating the special electroplating bath of this invention the specific brightener employed is ortho-formyl benzene sulphonic acid. The required wetting agent is FC 98, a tradenamed product marketed by the Minnesota Mining & Manufacturing Company. 50

For most purposes the pH of the electroplating bath is adjusted to a range of 2 to 5, preferably 2.5 to 4.5. The compounds which may be used to effect the pH adjustment include nickel carbonate, sulphuric acid, potassium citrate, and citric acid. 50

The baths of the present invention may be operated at temperatures of 46 to 57°C and at a relatively high current density of up to 1000 ASF (110 ASD), and preferably about 100 to 600 ASF (11 to 66 ASD). The ability to use such high current densities is another important advantage of the electroplating baths of the present invention. 55

Nickel deposits on various substrates when utilizing the baths of this invention are characterized by being semi-bright, ductile, and low-stressed. Heretofore such properties could only be obtained by the use of consumable anodes in nickel electroplating systems. 60

The invention may be put into practice in various ways and one specific embodiment will be described to illustrate the invention with reference to the accompanying example. 60

EXAMPLE

An electroplating bath was formulated from the following ingredients:

Components	Concentration g/l	
5 Nickel Sulphate	75 (as Ni)	5
Boric Acid	40	
O-formyl benzene sulphonic acid	1.5	
10 FC 98*	0.1	10

*Blend of potassium perfluoroalkyl sulphonates. Prior to use sufficient nickel carbonate was added to the bath to adjust the pH to about 2.5. The bath was used in a conventional electroplating bath with platinized titanium anodes to coat copper at 55°C and 500 ASF (55 ASD). The resulting nickel deposit was semi-bright and ductile. Further analysis indicated low-stress in the deposit. In utilizing this bath substantially no break down of the organic additives present in the bath was noted.

CLAIMS

- 20 1. A process for electroplating a workpiece having a conductive surface with a semi-bright, ductile, low-stress or stress-free nickel deposit which comprises contacting the workpiece as the cathode with a plating bath comprising a source of nickel ions, an electrolyte, and ortho-formyl benzene sulphonic acid or a salt thereof, and carrying out electroplating using insoluble anodes.
- 25 2. A process as claimed in Claim 1 in which the electrolyte comprises boric acid or citric acid or salts thereof.
3. A process as claimed in Claim 1 or Claim 2 in which the plating bath also contains a wetting agent comprising at least one potassium perfluoroalkyl sulphonate.
4. A process as claimed in Claim 1, 2 or 3 in which the source of nickel ions in the plating bath comprises nickel sulphate.
- 30 5. A process as claimed in Claim 1, 2, 3 or 4 in which the electrolyte is boric acid.
6. A process as claimed in any one of Claims 1 to 5 in which the plating bath has a pH of 2.5 to 4.5.
7. A process as claimed in any one of Claims 1 to 6 in which the electroplating is carried out at a current density of up to 1000 ASF (110 ASD).
- 35 8. A process as claimed in Claim 7 in which the electroplating is carried out at a current density of 100 to 600 ASF (11 to 66 ASD).
9. A process as claimed in Claim 1 substantially as specifically described herein with reference to the Example.
- 40 10. An article whenever provided with a semi-bright, ductile, low-stress or stress-free nickel deposit by a process as claimed in any one of Claims 1 to 9.
11. An electroplating bath suitable for use with insoluble anodes in the electrodeposition of semi-bright, ductile and low-stress or stress-free nickel deposits, the said bath comprising a source of nickel ions; an electrolyte comprising boric acid or citric acid or salts thereof; ortho-formyl benzene sulphonic acid or a salt thereof as a brightener; and a wetting agent comprising
- 45 a blend of potassium perfluoroalkyl sulphonates.
12. An electroplating bath as claimed in Claim 11 in which the source of nickel ions comprises nickel sulphate.
13. An electroplating bath as claimed in Claim 11 or Claim 12 in which the electrolyte is boric acid.
- 50 14. An electroplating bath as claimed in Claim 11, 12 or 13 having a pH of 2.5 to 4.5.
15. An electroplating bath as claimed in Claim 11 substantially as specifically described herein with reference to the Example.

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7. A process as claimed in any one of Claims 1 to 6 in which the electroplating is carried out at a current density of up to 1000 ASF (110 ASD).
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