

"HARDENED GOLD PLATING PROCESS"

5. The present invention relates to the electro-deposition of gold on substrates. More particularly, the invention relates to improving the corrosion resistance of cobalt-hardened gold coatings which are electrodeposited on various substrates.

10. It is known in the metallizing art to electro-plate cobalt-hardened gold coatings on substrates. In conventional procedures a deposition bath comprising ions of the metal to be deposited and a suitable electrolyte is provided, the article or object to be plated is immersed in or otherwise contacted with the bath while connected as the cathode to an external current source, and a metal electrode is connected as the anode to the same current source. During electro-
15. plating operations ions of the metal to be deposited are reduced in the bath to zero valent metal which plates out on the workpiece or substrate surface.

20. The use of cobalt to harden gold coatings is described in U.S. Patent No. 2,905,601 which will be discussed below in greater detail.

25. It has been found, however, that such conventional cobalt-hardened gold coatings do not have the high degree of corrosion resistance which is an important property for some commercial purposes. Thus, it would be desirable to provide a system or process for preparing special cobalt-hardened, gold electrodeposits with markedly improved corrosion resistance and cosmetic appearance such as brightness and smoothness. In some instances it has been possible to achieve
30. such desirable results at substantially reduced thicknesses of metal.

In accordance with the present invention it has now been found that cobalt-hardened gold coatings having improved corrosion resistance can be obtained by initially coating the workpiece or substrate with a ductile, low-stress or stress-free nickel deposit.

The necessary nickel coating on the substrate is derived from a specially prepared electroplating bath which, preferably, can be utilized with insoluble anodes. In general, the nickel electroplating baths will contain a nickel salt such as nickel sulphate, as a source of nickel ions, and boric acid or citric acid as the electrolyte. Although other conventional additives may be employed, it has been found essential to use ortho-formyl benzene sulphononic acid as the brightener and preferably to use a blend of potassium perfluoroalkyl sulphonates, sold under the tradename designation of FC 98, as the wetting agent.

Following the electrodepositing of the ductile, stress-free nickel coating the workpiece is subjected to the electrodeposition of the outer coating comprising cobalt-hardened gold.

By practising the foregoing sequential electrodeposition steps, the cobalt-hardened gold coating affords a superior corrosion resistance as compared to the corrosion resistance of the same cobalt-hardened gold coating without the intermediate ductile, stress-free nickel coating. On the other hand, the superior corrosion resistance was not attained even with the intermediate ductile, stress-free nickel coating when the gold was hardened with, for example, iron rather than cobalt.

Corrosion resistance was measured by Western Electric's manufacturing specification WL 2316.

A nickel salt electroplating bath useful in the initial coating step of the present invention may have the following composition:

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

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The preferred sources of the nickel metal 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.

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

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The organic components of the nickel 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 wetting agent may be FC 98, a tradenamed product marketed by the Minnesota Mining & Manufacturing Company.

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For most purposes the pH of the electroplating bath is adjusted to a range of 2 to 5, preferably 2.5 to 4.5.

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The compounds which can be used to effect the pH adjustment include nickel carbonate, sulphuric acid, potassium citrate, or citric acid.

5. The baths of the present invention may be operated at temperatures of about 46 to 57°C and at relatively high current density of up to about 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
10. baths of the present invention.

- Nickel deposited on various substrates when utilizing the baths of this invention are characterised by being semi-bright, ductile, and low-stressed. Furthermore, it is possible to use insoluble anodes in
15. carrying out both the initial and second coating steps. The insoluble anodes which can be employed include, for example, platinized titanium, platinized tantalum, platinized columbium (niobium) as well as a platinum metal anode itself. Additionally, titanium
20. anodes having mixed oxide coatings, such as ruthenium dioxide - titanium dioxide coatings, may also be used.

- The electroplating of hardened gold deposits can be carried out utilizing the baths and the processes described in U.S. Patent No. 2,905,601 Rinker and Duva
25. (1959). Although cobalt-hardened gold outer coatings are preferred, it will be understood that other metal hardeners such as indium, or nickel may also be employed in the practice of the present process which involves the use of a high speed gold treating process
30. following the application of a high speed nickel

treating process to form the initial or intermediate coating on the substrate or workpiece.

5. The electroplating bath useful for the gold plating step will comprise (1) an electrolyte e.g. a weak, stable, organic acid, (2) gold as a cyanide (for example as potassium gold cyanide), and (3) one or more base metal salts soluble in the bath.

10. Examples of acids which may be employed are formic, acetic, citric, tartaric, lactic, kojic, or similar acids and mixtures of these acids. The acid should be present in proportions of 10 to 150 grams per litre and may be partially neutralized with ammonium or alkali metal hydroxide to give a pH of about 3-5. It is this weak organic acid and the procedure of maintaining the bath within a limited pH range that produces the
15. desired effect of a gold alloy deposition.

20. The gold may be added as the double cyanide of gold and an alkali metal, for example as potassium gold cyanide, and may be present in proportions of 8 grams per litre to 26 grams per litre (as gold), preferably 12 grams/litre (as gold).

25. Base metal salts which may be added comprise the sulphates, sulphamates, formates, acetates, citrates, lactates, tartrates, fluoborates, borates, and phosphates, of base metals such as nickel, zinc, cobalt, indium, manganese, antimony, and copper. These metal salts are preferably added in the proportion of from 0.5 to 5 grams per litre. Very satisfactory results are obtained when two such base metal salts are
30. included in the bath. Although the addition of a base

metal salt is necessary, it does not matter which salt or mixture of salts is added as long as the added salts are soluble and compatible with all other bath ingredients.

5. The bath may be operated at a current density of 1 to 100 amperes per square foot (0.1 to 11 amperes per square decimetre (ASD)). Moderate to rapid agitation improves the operation. The bath may be operated at normal room temperature (70°F (21°C)) which is advantageous in that no thermostatic regulation is necessary
10. but higher or lower temperatures of from 50° to 120°F (10 to 49°C) may be employed. The maximum cathode/anode surface area ratio should be about 4:1.

A preferred electroplating bath useful for the second coating step may have the following formulation:

15.	<u>Component</u>	<u>Concentration (g/l)</u>
	Acetic Acid and Sodium Citrate	100 to 300
	Formic Acid	10 to 50 mls/l
	Gold (as potassium gold cyanide)	12 to 26
20.	Cobalt (as sulphate)	0.5 to 1.75
	Water	Remainder

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 Examples.

EXAMPLE 1

A first electrolytic bath was prepared by dissolving the following ingredients in water:

		<u>g/l</u>
30.	Nickel (as sulphate)	75
	Boric Acid	40

O-Formyl Benzene Sulphonic Acid	1.5
FC 98	0.1
Water	Remainder

5. A second electrolytic bath was prepared by dissolving the following ingredients in water:

	<u>g/l</u>
Citric Acid (as potassium citrate)	200
Formic Acid	20 mls/l
Gold (as potassium gold cyanide)	12
10. Cobalt (as sulphate)	1.5
Water	Remainder

The pH of this bath was adjusted to about 4.8 to 5.2 by the addition of an alkali or an acid.

15. The substrate, a commercial copper plated circuit board, was first treated in the nickel electroplating bath to give a semi-bright, ductile, and low-stress or stress-free nickel deposit having a thickness between about 2.5 to 5 microns. The thus coated substrate was then treated in the second or gold electroplating bath
20. to give a bright, smooth, and hard gold deposit. This coating has a thickness of from about 1 to 2 microns. The corrosion resistance of the resulting product, as measured in accordance with Western Electric's manufacturing specification WL 2316, was found to be out-
25. standing.

EXAMPLE 2

30. Example 1 was repeated but with the omission of the step of electrodepositing the nickel coating. The resulting product's corrosion resistance was substantially lower than that of Example 1.



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CLAIMS

1. A process for obtaining on a substrate a gold plating of improved corrosion-resistance which comprises the following sequential plating steps:

(a) electrodepositing a ductile, low-stress or stress-free nickel coating on the said substrate from an electroplating bath containing a nickel salt, an electrolyte and ortho-formyl benzene sulphonic acid; and

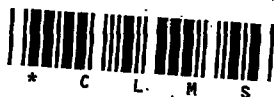
(b) electrodepositing a metal-hardened gold coating on the resulting ductile, low-stress or stress-free nickel plated substrate from an electroplating bath containing a gold salt, an electrolyte and a gold hardener metal salt.

2. A process as claimed in Claim 1 in which the gold hardener metal salt in the electroplating bath of step (b) comprises a cobalt, indium, nickel, or zinc salt or a mixture thereof.

3. A process as claimed in Claim 1 or Claim 2 in which the electrolyte in step (a) comprises boric acid or citric acid or a mixture thereof.

4. A process as claimed in Claim 1, 2 or 3 in which the electroplating bath in step (a) includes as a wetting agent a blend of potassium perfluoroalkyl sulphonates.

5. A process as claimed in Claim 1, 2, 3 or 4 in which the electroplating bath in step (a) incorporates nickel sulphate as the nickel salt and boric acid as the electrolyte.



6. A process as claimed in any one of Claims 1 to 5 in which the electrolyte in the electroplating bath of step (b) comprises a weak stable organic acid.

7. A process for obtaining on a substrate a gold plating of improved corrosion-resistance which comprises the following sequential plating steps:

(a) electrodepositing a ductile, low-stress or stress-free nickel coating on the said substrate from an electroplating bath containing a nickel salt, an electrolyte comprising boric acid or citric acid or a mixture thereof, ortho-formyl benzene sulphonic acid, and as a wetting agent a blend of potassium perfluoro-alkyl sulphonates; and

(b) electrodepositing a base metal-hardened gold coating on the resulting ductile, low-stress or stress-free nickel plated substrate from an electroplating bath containing a gold salt, an electrolyte comprising acetic acid, citric acid or formic acid or a mixture thereof, and a gold hardener metal salt comprising a cobalt, indium, nickel, or zinc salt or a mixture thereof.

8. A process as claimed in any one of Claims 1 to 7 in which the electroplating bath of step (b) is maintained at a pH of 3 to 5.

9. A process as claimed in any one of Claims 1 to 8 in which the gold salt in the electroplating bath of step (b) comprises a gold cyanide salt.



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10. A process as claimed in any one of Claims 1 to 9 in which the electroplating bath of step (a) is operated at a pH of 2 to 5.

11. A process as claimed in any one of Claims 1 to 10 in which the electrodeposition in step (a) is carried out with insoluble anodes.

12. A process as claimed in any one of Claims 1 to 11 in which the electrodeposition in step (b) is carried out with insoluble anodes.

13. A process as claimed in any one of Claims 1 to 12 in which the electrolyte in the electroplating bath of step (b) comprises acetic acid.

14. A process as claimed in any one of Claims 1 to 13 in which the electrolyte in the electroplating bath of step (b) comprises citric acid.

15. A process as claimed in any one of Claims 1 to 14 in which the electrolyte in the electroplating bath of step (b) comprises formic acid and citric acid.

16. A process as claimed in any one of Claims 1 to 15 in which the gold hardener metal salt in the electroplating bath of step (b) is cobalt sulphate.

17. A process as claimed in Claim 1 substantially as specifically described herein with reference to Example 1.

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18. A hardened gold plating whenever prepared by a process as claimed in any one of Claims 1 to 17.

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