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"ELECTRODEPOSITION OF PALLADIUM AND
PALLADIUM ALLOYS"

The present invention relates to compositions and methods for the electrodeposition of palladium metal or alloys on substrates from baths utilizing palladium in the form of palladium amine compounds such as palladous

5. di-amine chloride, i.e. $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$.

There is a considerable body of prior art dealing with the electrodeposition of palladium metal and its alloys on substrates. This art is represented by the following U.S. Patents:

10. 3,530,050 - Hill et al.
3,580,820 - Yamamura et al.
3,677,909 - Yamamura et al.
4,066,517 - Stevens et al.
4,098,656 - Deuber

15. It is apparent from these references that the palladium metal component of the electroplating bath, whether employed alone or in conjunction with an alloying metal, is advantageously in the form of amine complex salts such as, for example, palladous amine
20. chloride and palladium diamine dinitrite.

The amine palladium and palladium alloy electrolytes or electroplating baths disclosed in the prior art are normally operated at a pH within the range of about 6.5 and 10.0. Unfortunately these baths with
25. use become difficult to operate when heated to temperatures of from about 20° to 70°C because the pH tends to drop to pH 5 or lower. Once the pH drops to these levels premature precipitation of the palladium metal salt as well as the alloying metal salt occurs. It
30. has been suggested previously that this undesirable

drop in pH might be avoided by utilizing buffers such as ammonium or alkali metal phosphates. However, the use of such buffers had the untoward effect of causing undesirable precipitation of these metals as phosphates.

5. Consequently, the main problem associated with use of amine palladium complex electrolytes is the necessity of frequent pH adjustment and premature precipitation of the palladium and/or its alloying metal.

10. This invention aims to provide electroplating baths containing palladium amine complexes alone or with an alloying metal compound which are less liable to an undesirable drop of the pH during operation.

15. This invention also aims to provide a palladium amine complex-containing electroplating bath wherein the tendency to premature precipitation of the palladium or alloying metal salts is lessened.

20. In accordance with the present invention it has now been found that pH stability can be improved, while lessening the tendency to premature precipitation of palladium metal or alloying metal salts, by utilizing a borate buffer in formulating the electroplating bath. The borate buffer is used in an amount sufficient to bring the bath to a pH within the range of 6.5 to 9.5. This pH will not drop to pH 5 or lower under actual operating conditions utilizing conventional
25. palladium metal plating temperatures of from about 20° to 75°C and current densities ranging from about 1 to 1000 ASF (0.1 to 108 ASD), preferably 3 to 50 ASF (0.32 to 5.4 ASD). Consequently, the premature
30. precipitation of palladium or alloying metal salt is

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avoided through the maintenance of the desired pH range in the bath; and, in addition, the special borates employed in the practice of the present invention do not have the tendency to form metal salts

5. which would undesirably precipitate and interfere with the normal functioning of the electroplating bath.

The borates employed for the present purposes are formed by the neutralization of boric acid with an alkali metal, ammonia, ammonium hydroxide, or an amine.

10. The neutralization can be conducted either in situ, i.e. during formation of the bath, or as a separate step with the thus formed borate used as a component of the bath. The neutralization of the boric acid can be carried out, as described above, with the following

15. substances, ammonia; ammonium hydroxide; alkali or alkaline earth metal compounds such as sodium hydroxide or potassium hydroxide; or an amine such as ethylene diamine or diethylene triamine. Preferred borates are sodium tetraborate and ammonium biborate.

20. Preferably the borate is formed in situ where the alkaline reactant is used in an amount not only sufficient to convert the boric acid, usually about 10 to 50 g/l, to the corresponding borate but also sufficient to raise or adjust the initial pH of the

25. newly formulated electroplating bath to about 6.5 to 9.5.

The palladium amine complex can either be the halide, nitrite, nitrate, sulphate, sulphonate or carboxylic acid derivative.

Illustrative complexes include the following

30. Palladous diamine chloride $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$

Palladium diamine dinitrite $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$

Palladium tetramine nitrate $[\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2]$

Palladium diamine sulphate $[\text{Pd}(\text{NH}_3)_2\text{SO}_4]$

Other palladium salts may be utilized for example

5. dichlorodiamine palladium chloride.

The palladium metal in the amine complex is preferably used in an amount ranging from about 1 to 50 g/l, and preferably about 5 to 35 g/l.

10. It is often desirable to plate the workpiece or substrate with a palladium alloy, and alloying metals which may be employed in this invention include copper, cobalt, cadmium, gold, iron, indium, nickel, silver, tin and zinc which conveniently may be added to the bath as amino salts. Illustrative alloying
15. metal components include nickelous amine chloride, aminozinc acetate, ethylene diamine tetracetic acid cobalt complex, and nitrilotriacetic acid nickel complex.

20. The alloying metal component may be present in the electroplating bath in an amount ranging from about 0 to 50 g/l, and when present preferably in amounts of from about 5 to 20 g/l.

25. The bath will also preferably contain from about 5 to 150 g/l, preferably from 10 to 100 g/l, of a conducting salt. The conducting salt may be an ammonium or alkali metal halide, carboxylic acid, sulphate, nitrate, or sulphonate salt. Examples of such salts include ammonium chloride, ammonium citrate, ammonium nitrate, sodium nitrate, ammonium sulphonate, and
30. potassium sulphate, and mixtures thereof. The

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especially preferred conducting salts are ammonium chloride, ammonium citrate, potassium citrate, and mixtures thereof.

5. In formulating the electroplating baths of this invention it is also useful for certain applications to utilize a brightener. The brighteners most useful for the present purposes are aromatic sulphonated amides, aromatic sulphonated imides, alkali metal aromatic sulphonates, and aromatic sulphonic acids and mixtures thereof. Specific preferred brighteners are naphthalene sulphonate sodium salt, saccharin sodium salt, and mixtures thereof. In general, the brighteners will be used in amounts ranging from about 0.1 to 5 g/l, preferably from about 0.5 to 4 g/l.

15. In some instances it is desirable to provide a source of "free" or uncomplexed nitrite ions in the bath. The source of the free nitrite ions is preferably a water soluble inorganic nitrite compound such as an alkali metal nitrite. Especially preferred nitrites are sodium nitrite, potassium nitrite, and ammonium nitrite. The amount of nitrite ions employed may vary widely and is preferably at least about 0.05% by weight relative to the palladium ions in the bath. Initially the concentration of the nitrite ions may range from about 0.1 to about 50% by weight, based on the weight of the palladium ions.

20. The baths of this invention have been used in conjunction with insoluble platinum, platinum clad, tantalum, or columbium anodes. In general, rack plating is employed and the workpieces, e.g. box and

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pin contacts, printed circuit board contacts, or decorative jewelry, have surfaces of metals such as copper, brass, bronze, nickel, silver, or steel. Palladium metal or palladium metal alloy deposits of high quality can be produced.

The invention can be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

10. EXAMPLE I

An aqueous palladium metal electroplating bath was prepared with the following formulation:

<u>Component</u>	<u>g/l</u>
Palladous Diamine Chloride	10 (Pd metal)
15. Ammonium Chloride	50
Boric Acid	30
Ammonium Hydroxide	to pH 8.2
Water	Remainder

The bath was operated at a temperature of from about 20° to 70°C and at a current density of 10 ASF (1.1 ASD). After 4 hours of operation, the pH had not dropped below 7.5.

EXAMPLE II

25. An aqueous palladium metal electroplating bath was prepared with the following formulation:

<u>Component</u>	<u>g/l</u>
Palladium Diamine Dinitrite	10-30 (Pd metal)
Sodium Nitrite	10
Ammonium Nitrate	30
30. Boric Acid	20
Ammonia	to pH 7.5
Water	Remainder

The bath was operated at a temperature of from about 50° to 70°C and at a current density of from 100 to 1000 ASF (11 to 108 ASD). The pH had not dropped below 7.5 after 4 hours of operation.

5. EXAMPLE III

An aqueous, palladium-nickel metal alloy electroplating bath was prepared with the following formulation:

	<u>Component</u>	<u>g/l</u>
10.	Palladous Diamine Chloride	10 (Pd metal)
	Nickelous Amine Chloride	12 (Ni metal)
	Ammonium Chloride	30
	Ammonium Citrate	10
	Boric Acid	15
15.	Ammonium Hydroxide	to pH 9.0
	Water	Remainder

The bath was operated at a temperature of from about 20° to 50°C and at a current density of about 20 ASF (2.2 ASD). After 4 hours of operation the pH had not dropped below 7.5.

EXAMPLES IV A to IV D

Example IV A

Example II was repeated, with the exception that the palladium metal content was reduced to 24 g/l and 5 g/l of silver metal was present in the form of silver dinitrite alkali metal salt. The temperature of the bath was maintained at between 20° and 25°C.

Example IV B

Example II was repeated, with the exception that palladium metal content was reduced to 5 g/l and

alloying zinc metal (1 g/l) was present in the form of amino zinc acetate.

Example IV C

5. Example III was repeated with the exception that 3 g/l of benzaldehyde-o-sodium sulphonate and 0.1 g/l of sodium salt of naphthalene sulphonate were added. This bath was operated at 30°C and between 10 and 50 ASF (1.1 and 5.4 ASD).

Example IV D

10. Example III was repeated, with the exception that from 0.1 to 10 g/l of sodium saccharin were added. This bath was electrolyzed at 35°C and at current densities between 5 and 50 ASF (0.54 and 5.4 ASD) to give low stress nickel-palladium deposits.
15. None of the baths of Example IV A to D showed an excessive pH drop, i.e. from 7.5 to 5 over a 4 hour operating period. On the other hand, when these baths as well as the baths of Examples I through III were operated without the prescribed borate buffer, i.e.
20. alkali metal or ammonium hydroxide neutralized boric acid, or when other buffers such as citrates, phosphates, or tartrates were used in place of the borates, the pH dropped in 4 hours or less to pH 5 undesirably resulting in a concomitant precipitation of the
25. palladium and/or the second or alloying metals.

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CLAIMS

1. An aqueous palladium or palladium alloy electroplating bath containing an ammonium, amine, or alkali metal borate buffer whereby the bath has a pH of from 6.5 to 9.5.

2. An aqueous palladium electroplating bath containing 1 to 50 g/l of palladium metal, 0 to 20 g/l of an alloying metal, 5 to 150 g/l of a conductivity salt, 0 to 5 g/l of a brightener, and 10 to 50 g/l of boric acid neutralized with an alkali metal or ammonium hydroxide, ammonia or an amine whereby the pH of the bath is in the range 6.5 to 9.5.

3. An electroplating bath as claimed in Claim 1 or Claim 2 containing an alloying metal component comprising copper, cobalt, cadmium, gold, iron, indium, nickel, silver, tin or zinc or mixtures thereof.

4. An electroplating bath as claimed in Claim 2 or Claim 3 in which the alloying metal component is present in the bath in the form of an amino complex or salt.

5. An electroplating bath as claimed in Claim 3 in which the alloying metal is present as a nickel amino complex.

6. An electroplating bath as claimed in Claim 3 in which the alloying metal is present as a silver amino complex.



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7. An electroplating bath as claimed in Claim 2 in which the alloying metal is present as a zinc amino complex.

8. An electroplating bath as claimed in any one of Claims 1 to 7 containing a conductivity salt.

9. An electroplating bath as claimed in Claim 8 in which the conductivity salt is a halide, carboxylic acid, sulphate, nitrate or sulphamate salt of ammonium or an alkali metal or a mixture thereof.

10. An electroplating bath as claimed in any one of Claims 1 to 9 containing a brightener.

11. An electroplating bath as claimed in Claim 10 in which the brightener is an aromatic sulphonated imide, an aromatic sulphonated amide, an alkali metal aromatic sulphonate, or an aromatic sulphonic acid, or a mixture thereof.

12. An electroplating bath as claimed in any one of Claims 1 to 11 in which the palladium metal is present as an amine palladium halide, nitrite, nitrate, sulphate, sulphamate, or carboxylic acid derivative.

13. An electroplating bath as claimed in Claim 12 in which the palladium is present as palladous diamine chloride.

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14. An electroplating bath as claimed in Claim 12 in which the palladium is present as palladium diamine dinitrite.

15. An electroplating bath as claimed in any one of Claims 2 to 14 in which the boric acid is neutralized with ammonium hydroxide.

16. An electroplating bath as claimed in any one of Claims 2 to 14 in which the boric acid is neutralized with ammonia.

17. An electroplating bath as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples I to III or IV A to IV D.

18. A method of electrodepositing metallic palladium or palladium alloys on a substrate which comprises passing an electric current between a cathode and an anode through an electroplating bath as claimed in any one of Claims 1 to 17 for a period of time sufficient to deposit the desired thickness of palladium or palladium alloy.

19. A method as claimed in Claim 18 in which the bath is at a temperature of from about 20° to 75°C and the current density of from about 1 to 1000 ASF (0.1 to 108 ASD).



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20. A method as claimed in Claim 18 substantially as specifically described herein with reference to any one of Examples I to III or IV A to IV D.

21. A substrate whenever provided with a palladium or palladium alloy electrodeposit by a method as claimed in Claim 18, 19 or 20.

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