

12

1.

2133041

BATH AND PROCESS FOR HIGH
SPEED ELECTROPLATING OF
PALLADIUM

The present invention relates to electroplating baths and methods for the high speed electrodeposition of ductile palladium metal on substrates from baths formulated from a particular combination of components.

5. A considerable body of patent literature exists over a period of many years relating to the electrodeposition of palladium metal. This prior art is represented by the following U.S. Patents:

- | | | | |
|-----|-----------|---|----------------------|
| | 330,149 | - | Pilet et al. |
| 10. | 1,921,941 | - | Powell et al. |
| | 1,993,623 | - | Raper |
| | 2,207,358 | - | Powell et al. |
| | 2,451,340 | - | Jernstedt |
| | 3,150,065 | - | Fatzer |
| 15. | 3,206,382 | - | Wilson |
| | 3,458,409 | - | Hayashi |
| | 3,480,523 | - | Tyrrell |
| | 3,530,050 | - | Ickenham et al. |
| | 3,544,435 | - | Angus et al. |
| | 3,580,820 | - | Yamamura et al. |
| 20. | 3,933,602 | - | Henzi et al |
| | 4,076,599 | - | Caricchio, Jr. et al |
| | 4,092,225 | - | Davis |
| | 4,098,656 | - | Deuber |
| | 4,144,141 | - | Schuster et al |

- The problems usually encountered in the known
25. palladium metal electroplating baths, including limited deposition rates and brittleness due to hydrogen embrittlement were recently set forth in several papers presented at The Second AES Symposium On Economic Use of And Substitution For Precious Metals in The
30. Electronics Industry held on October 5th and 6th, 1982 at Danvers, Mass. The papers were by J.A.Abys
- "A Unique Palladium Electrochemistry Characteristics

and Film Properties" and by H.S. Trop and A.V. Siaweleski "Application of BTL Pd Technology to Barrel Plating."

5. It is apparent therefore that there is a need for commercial palladium metal baths which will efficiently operate at high speeds over a wide range of current densities to produce a ductile palladium deposit on a variety of substrates.

10. This invention enables the provision of means for overcoming or at least mitigating problems associated with using the prior palladium metal electroplating baths.

15. The invention also enables the provision of electroplating baths with the right combination of components to permit the efficient deposition of palladium metal on various substrates.

20. This invention further enables the provision of palladium amine complex-containing electroplating baths wherein high speed deposition of ductile palladium metal is readily achievable.

25. This invention still further enables the provision of an improved method for plating ductile palladium metal on a variety of substrates with high tolerance to metallic impurities such as copper using these special electroplating baths.

These and other facets of the present invention will become more readily apparent from the following description of the features thereof.

30. In accordance with the present invention it has now been found that the efficient high speed deposition of ductile palladium metal can be achieved by using, as a source of the palladium in the bath, a palladium amine complex in combination with at least

four other bath components. These other bath components include ammonium sulphate, ammonium halide salt, an alkali metal pyrophosphate, and a stress reducing agent. The electroplating baths of this invention

5. will generally be operated under slight basic conditions, preferably at a pH of from about 7 to 9.

The temperature of the bath may range from about 50 to 80 degrees C, while current densities as high as 3000 ASF (330 ASD) may be effectively used in the

10. practice of the present invention. In another feature of the invention, the electroplating bath may also contain a surfactant, preferably an alkali metal fluorochemical sulphonate, to minimize or avoid a pitting problem that may be encountered.

15. As set forth above, one of the principal ingredients of the electroplating baths is the palladium amine complex which can be a halide, nitrite, nitrate, sulphate, or sulphonate.

Illustrative complexes include the following:

20. Palladous diamine chloride - $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
 Palladous diamine dinitrite $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$
 Palladous tetramine nitrate $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$
 Palladous diamine sulphate $\text{Pd}(\text{NH}_3)_2\text{SO}_4$

The above chloride and dinitrite complexes
 25. are preferred for the present purposes.

Other palladium salts which may be used are dichlorodiamine palladium and the like.

The palladium metal in the bath may be used in amounts ranging from about 10 to 80 g/l,
 30. and preferably about 40 to 70 g/l.

The other four essential electroplating bath components are ammonium sulphate, ammonium halide, an alkali metal pyrophosphate, and a stress reducing agent. Although the amounts of these components used
 35. in the baths may vary over a wide range, the presence of each of these components is essential in order to

attain the desired results. It will be understood that three of these components are known conducting salts or electrolytes.

5. Ammonium sulphate may be used in amounts ranging from about 20 to 60 g/l, and preferably from about 30 to 50 g/l.

- The ammonium halide may be ammonium chloride, ammonium bromide, or ammonium fluoride. However, the use of ammonium chloride is especially preferred.
10. Amounts of the ammonium halide in the bath may vary from about 10 to 80 g/l, and preferably from about 20 to 30 g/l.

- Tetrapotassium pyrophosphate is the preferred alkali metal pyrophosphate which can be employed in
15. formulating the electroplating baths of this invention. Nevertheless other tetra alkali metal pyrophosphates such as tetrasodium pyrophosphate, ammonium pyrophosphate, and the like may be used. The tetra alkali metal pyrophosphate may be used in amounts ranging from about
20. 20 to 150 g/l, and preferably from about 80 to 100 g/l, expressed as the trihydrated salt. The use of electroplating baths containing palladous diamine dinitrite and tetrapotassium pyrophosphate is described in the U.S. Patent 4,092,225 to Davis, but it has a
25. current density limitation of about 50 ASF (5.5 ASD).

- The fifth essential component of the palladium electroplating baths of this invention is a stress reducing agent. Preferably, the stress reducing agent is a derivative of benzene sulphonic acid; and the
30. use of o-formyl benzene sulphonic (OFB) was found to be particularly useful in many operations.

Other stress reducing agents which may be employed in the present invention include, for example, saccharin and 2-butene-1,4-dione. In general, the amount of stress reducing agent usually employed will range from about 1 to 10 g/l, and preferably from about 3 to 5 g/l.

The electroplating baths of this invention may also contain other ingredients useful in this art, provided that they do not have any deleterious results on the formation of ductile palladium or the high rate of deposition that can be achieved herein. As previously mentioned, one of these other ingredients is a surfactant which can minimize or eliminate any metal pitting problem that may occur in the practice of this invention. Minor amounts of an anionic fluorochemical wetting agent or surfactant such as a blend of potassium perfluoroalkyl sulphonates, sold under the trade marks FC-98 and FC-95 by the Minnesota Mining and Manufacturing Company, may be employed to prevent pitting. The amount of wetting agent or surfactant will generally range from about 5 to 20 ml/l, preferably from about 7 to 15 ml/l for the present purposes.

FC-95 and FC-98 are potassium perfluoroalkyl sulphonates, and their use is generally preferred. Both FC-95 and FC-98 decompose at 390 degrees C. In a 0.1% aqueous solution FC-95 has a pH of 7-8, while FC-98 has a pH of 6-8. FC-98, which is potassium perfluorocyclohexyl sulphonate, is slightly less surface active and is capable of producing foam that is less dense and less stable. Both types have outstanding chemical and thermal stability, especially in acidic and oxidizing systems. The

6.

method of preparing these perfluoroalkyl sulphonates is disclosed in U.S. Patent 2,519,983 to Simons; while a prior art use of such surfactants in electroplating is illustrated by U.S. Patent 2,750,334 to Brown.

5. The teachings of these patents are incorporated herein by reference.

10. The pH of the electroplating baths will be from about 7 to 9, preferably from about 7 to 8; and the baths will be operated at temperatures of from about 30 to 80 degrees C., preferably from about 60 to 70 degrees C. Although the tank current densities which can be effectively used with the baths of this invention may range from about 10 to 200 ASF (1.1 to 22 ASD), somewhat higher current densities are preferred, 15. i.e. from about 180 up to about 200 ASF (19.8 to 22 ASD). However, in contrast, a current density range of from about 200-3,000 ASF (22 to 330 ASD) can be attained by the practice of the present invention in high speed plating systems. Under the preferred 20. operating conditions of the present invention the rate of ductile palladium metal deposition on the substrate may be as high as 6 microns per minute, with ranges of from about 1 to 25 being readily attained.

25. The baths of this invention can be used in conjunction with insoluble platinum, platinum clad, tantalum, or columbium anodes. In general, rack plating is employed and workpieces, e.g. box and pin contacts, printed circuit board contacts, decorative jewellery, etc, have surfaces of metals such as copper, brass, 30. bronze, nickel, silver, steel, etc. The palladium metal, or when desired, palladium metal alloy ductile deposits are of high quality.

7.

Electroplating baths preferred in the present invention have the following composition:

	<u>Component</u>	<u>Concentration g/l</u>
5.		
	(a) Pd metal complex	40 to 80
	(b) $(\text{NH}_4)_2\text{SO}_4$	30 to 60
	(c) NH_4Cl	10 to 80
	(d) OFB	1 to 10
10.	(e) $\text{K}_4\text{P}_2\text{O}_7$	20 to 150
	(f) FC-98	5 to 20 ml
	(g) NH_4OH	up to pH 8
	(h) Water	Remainder

15. The invention will be more fully understood by reference to the following illustrative embodiments wherein concentrations are given in grams per litre (g/l) unless otherwise indicated.

20.

EXAMPLE I

A series of runs were carried out with electroplating baths having the formulations set forth in Table A. All plating was carried out in a tank at current density of 200 ASF (22 ASD), temperature of 70 degrees C., pH 8, with rapid agitation and a constant anode/cathode ratio. The substrate used was copper, and the palladium metal complex was palladosamine chloride, $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. The pH was adjusted with NH_4OH .

TABLE A

FORMULATION	RUN A	RUN B	RUN C	RUN D	RUN E
Pd metal complex, as Pd metal	60	60	60	60	60
$(\text{NH}_4)_2\text{SO}_4$	50	50	50	-	50
NH_4Cl	30	30	30	30	30
OFFB (1)	5	5	-	5	0
$\text{K}_4\text{P}_2\text{O}_7$	100	-	100	100	0
FC-98 (1 g/l sol'n)	10 ml	10 ml	10 ml	10 ml	10 ml
Results	200 ASF (22 ASD) CD was achieved; the deposit was smooth and ductile; 6% elongation	Deposit burned at 200 ASF (22 ASD) maximum CD was 40 ASF (4.4 ASD); deposit was ductile	200 ASF (22 ASD) CD was achieved cracks were observed when bend testing the deposit; thickness could not be built up	Deposit was (22 ASD); maximum CD was 120 ASF (13.2 ASD); deposit was ductile	Deposit burned at 200 ASF (22 ASD); maximum CD was 40 ASF (4.4 ASD) deposit cracked during the bend test; thickness could not be built up
(current density = CD)					

(1) Ortho-formyl benzene sulphonic acid

The above data indicate that in addition to the palladium metal complex and ammonium the electroplating baths had to contain ammonium sulphate, a stress reducing agent, and tetra-potassium pyrophosphate in order to achieve the desired results. Run A, which was formulated in accordance with the present invention, gave excellent results: a high speed, ductile palladium metal deposit. In contrast, the other Runs which did not use electroplating with all of the necessary components failed to give satisfactory results.

EXAMPLE II

A palladium electroplating bath was prepared by dissolving the following ingredients in water:

	Components	Concentration g/l
20.	Pd, as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	70
	$(\text{NH}_4)_2\text{SO}_4$	50
	NH_4Cl	30
	$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	100
	OFB	10
25.	FC-98 (1 g/l sol'n)	10 mil

The bath was operated at a pH of 9, 70-75 degrees C., and at an achieved current density in the order of 195 ASF (21.45 ASD). High speed ductile palladium foils of up to 75 microns were plated on a copper substrate at a rate of 6 microns per minute. The foils could be rolled into a cylinder and deformed into a square.

10.

EXAMPLE III

Another electroplating bath was prepared by dissolving the following ingredients in water:

5.	Components	Concentration g/l
	Pd, as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	60
	$(\text{NH}_4)_2\text{SO}_4$	50
10.	NH_4Cl	30
	$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	100
	OFB	5
	FC-98 (1 g/l sol'n)	10 ml

15. This bath was also operated at a pH of 8 and a temperature of about 70-75 degrees C. Spot cell tests were done with this bath, and current densities up to 3000 ASF (330 ASD) were achieved. Good ductile deposits with a deposition rate up to 25 microns/minute were obtained.
- 20.

EXAMPLE IV

	<u>Components</u>	<u>Concentration g/l</u>
	Pd, as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	60
	$(\text{NH}_4)_2\text{SO}_4$	50
	NH_4Cl	30
5.	$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	100
	OFB	5
	FC-98 (1 g/l sol'n)	10 ml
	Cu, as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	2

10. The bath was operated at a pH of 7.5, 70°C., current density of 200 ASF (22 ASD). A ductile foil of 25 microns thick was obtained with no codeposition of copper.

15. The foregoing data reveal that the palladium electroplating baths of this invention permit the high speed deposition of ductile palladium metal at high current densities, i.e. up to about 200 ASF (22 ASD) in a tank and 3000 ASF (330 ASD) or higher in a spot cell. In addition, the data show that the bath
20. is highly tolerant to copper, nickel, iron and gold.

CLAIMS :

1. A high speed bath for the electro-deposition of ductile palladium metal comprising palladium metal in the form of a palladium amine complex, ammonium sulphate, ammonium halide, an alkali metal pyrophosphate and a stress reducing agent.
5. 2. A bath as claimed in Claim 1 comprising from 40 to 80 g/l palladium metal.
10. 3. A bath as claimed in Claim 1 or 2 comprising from 20 to 90 g/l ammonium sulphate.
15. 4. A bath as claimed in Claim 1, 2 or 3 comprising from 10 to 70 g/l ammonium halide.
5. 5. A bath as claimed in any one of Claims 1 to 4 comprising from 20 to 150 g/l alkali metal pyrophosphate.
20. 6. A bath as claimed in any one of Claims 1 to 5 which also contains a minor amount of an anionic fluorochemical surfactant.
25. 7. A bath as claimed in any one of Claims 1 to 6 wherein the surfactant is an alkali metal perfluoro-alkyl sulphonate.
30. 8. A bath as claimed in any one of Claims 1 to 7 wherein the ammonium halide is ammonium chloride.
9. A bath as claimed in any one of Claims 1 to 8 wherein the palladium amine complex is palladium diamine chloride.



10. A bath as claimed in any one of Claims 1 to 9, wherein the stress reducing agent is a derivative of benzene sulphonic acid.

5. 11. A bath as claimed in any one of Claims 1 to 10 wherein the benzene sulphonic acid derivative is o-formyl benzene sulphonic acid.

10. 12. A method of electrodepositing high speed ductile palladium on a metallic substrate which comprises immersing the substrate in an electroplating bath as claimed in any one of claims 1 to 11 and passing current between the substrate and a bath electrode.

15. 13. A method as claimed in Claim 12, wherein the bath is at a pH of from 7 to 9.

20. 14. A method as claimed in Claim 12 or 13, wherein the bath is at a temperature of from 50 to 80°C.

25. 15. A method as claimed in Claim 12, 13 or 14, wherein the bath is operated at a current density of from 10 to 3000 ASF (1.1 to 330 ASD).

30. 16. A method for electrodepositing high speed ductile palladium on a metallic substrate which comprises immersing the substrate in an electroplating bath operated at a pH within the range of from 7 to 9, a temperature of from 50 to 80 degrees C., and a current density of from 10 to 3000 ASF (1.1 to 330 ASD); the electroplating bath comprising an aqueous



solution having the following components:

Components	Concentration g/l
5.	
(a) Palladium metal, as the palladous amino complex	40 to 60
(b) $(\text{NH}_4)_2\text{SO}_4$	30 to 50
(c) NH_4Cl	20 to 30
(d) alkali metal pyrophosphate	80 to 100
10.	
(e) stress reducing agent	3 to 5

17. A method as claimed in any one of Claims 12 to 16 wherein the pH of the electroplating bath is from 7 to 9.

15. 18. A method as claimed in any one of Claims 12 to 17, wherein the temperature of the bath is from about 60 to 70°C.

20. 19. A method as claimed in any one of Claims 12 to 18, wherein the current density is from 180 3000 ASF (19.8 to 330 ASD).

25. 20. A method as claimed in any one of Claims 12 to 19, wherein the substrate is selected from copper, nickel, brass, iron, gold, and alloys thereof.

21. A method as claimed in Claim 16, wherein the palladous amine complex is palladous amine chloride.

30. 22. A method as claimed in Claim 16 or 21, wherein the palladous amine complex is palladous amine nitrite.

35. 23. A method as claimed in Claim 16, 21 or 22, wherein the stress reducing agent is a derivative

(26)



15.

of benzene sulphonic acid.

5. 24. A method as claimed in Claim 16, 21, 22 or 23 wherein the benzene sulphonic acid derivative is o-formyl-benzene sulphonic acid.

10. 25. A method as claimed in Claim 16 or any one of Claims 21 to 24 wherein the bath also contains a minor, anti-pitting amount of an anionic fluoro-chemical surfactant.

15. 26. A method as claimed in Claim 16 or any one of Claims 21 to 26, wherein the alkali metal pyrophosphate is tetrapotassium pyrophosphate.

28. An electroplating bath substantially as herein described with reference to any one of Examples IA, II, III and IV.

20. 29. A method of electroplating substantially as herein described with reference to any one of Examples IA, II, III and IV.

25. 30. An article whenever electroplated by a bath as claimed in any one of Claims 1 to 15 and 28 and/or by a method as claimed in any one of Claims 16 to 27 and 29.
