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ELECTRODEPOSITION OF PALLADIUM

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ABSTRACT OF THE DISCLOSURE

Electrolysis or electrodeposition is carried out with an aqueous neutral or alkaline bath containing a palladium compound and an ammonium salt of a weak organic acid which does not form an insoluble compound with the palladium compound.

This invention relates to improvements in and relating to the electrodeposition of palladium onto a basis metal.

Palladium is usually deposited from a plating bath or electrolyte which comprises an aqueous solution of a palladium compound and generally also contains ammonia to render the bath slightly alkaline.

For example, palladium plating baths based on palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$ commonly known as the "P" salt or palladium tetrammino-dinitrate, $Pd(NH_3)_4(NO_3)_2$ have been proposed. Such baths are usually operated at a pH of from 5 to 9 and a temperature of from about 50° C. to 95° C.

Deposits of palladium obtained by the use of plating baths as at present known, have, for various reasons, not proved entirely satisfactory and certain disadvantages are inherent in the use of the aforesaid baths.

More recently, it has been proposed to provide a palladium plating bath, particularly suitable for plating printed circuit boards, which comprises an aqueous solution containing in addition to palladium ions, and ammonium ions, also a source of sulphamate ions, for example, the bath may be based on the reaction of the known "P" salt, above referred to, with sulphamic acid or ammonium sulphamate, to form a compound the exact nature of which is not yet definitely known.

The bath is stated to offer advantages over the conventional baths and to be operable at, or near, room temperature.

The object of this invention is to provide a novel palladium plating bath or electrolyte which is stable, can be operated at a low temperature and by means of which substantially pore-free and heavy deposits of palladium can be consistently obtained.

According to one feature of this invention, a plating bath or electrolyte for the electrodeposition of palladium comprises an aqueous neutral or alkaline solution containing a palladium compound and an ammonium salt of a weak organic acid, which does not form an insoluble compound with the palladium compound.

According to another feature of the invention, a method of electrodepositing palladium comprises electrolysing an electrolyte comprising an aqueous neutral or alkaline solution containing a palladium compound and an ammonium salt of a weak organic acid which does not form an insoluble compound with the palladium compound.

According to yet another feature of the invention, a method of electrodepositing palladium on a basis metal comprises depositing on said basis metal palladium metal from a plating bath or electrolyte comprising an aqueous neutral or alkaline solution containing a palladium compound and an ammonium salt of a weak organic acid which does not form an insoluble compound with the palladium compound.

The palladium compound employed in carrying out the invention is preferably palladium-diammino-dinitrite.

$$Pd(NH_3)_2(NO_2)_2$$

but other palladium compounds, such as palladium-tetrammino-nitrate, $Pd(NH_3)_4(NO_3)_2$, or palladium chloride may also be used.

The organic acid salts may advantageously be chosen from the following ammonium salts, namely, ammonium tartrate, ammonium oxalate, ammonium citrate, ammonium formate and an ammonium salt of ethylene diamine tetra-acetic acid. Of these salts, the applicants have found that very satisfactory results are obtained with the use of ammonium formate.

Ammonia is preferably included in the solution to give a pH of from 7 to 10, preferably 8–9, the brightness of the deposit in general increasing with increase in the pH. The solution should, preferably, be free of cyanide ions.

The baths of the invention should preferably be operated at a temperature of 15°–75° C. It will be found advisable, however, in the case of a bath containing ammonium formate, not to operate at a temperature of over 40° C. over a period as, in that event, the palladium is liable to precipitate out and be deposited chemically. The current density at which the baths are operated may vary from 1 amp/sq. ft. to 500 amps/sq. ft.

The following are examples of suitable plating baths in accordance with the invention and operating conditions therefor, it being clearly understood that the invention is in no way limited to, or by, these examples.

In the examples in which the palladium compound used is palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$, the plating bath is made by dissolving the palladium salt in ammonia at the rate of 2 mls. of 0.880 ammonia per gram of palladium (2.175 grams of $Pd(NH_3)_2(NO_2)_2$ correspond to 1 gram of Pd), and an equal amount of water. The organic acid salt is then added and the pH adjusted as required.

EXAMPLE I

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—24 g./l. (representing 11 g./l. of Pd).
Ammonium tartrate—50 g./l.
Water to 1 litre.

This bath should be operated at a current density of 6 amps/sq. ft. at a temperature of 30° C. The pH of the bath was adjusted to 8.5. A bright deposit of palladium was obtained.

EXAMPLE II

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—24 g./l. (=11 g./l. of Pd).
Ammonium oxalate—50 g./l.
Water to 1 litre.

This bath should also be operated at a current density of 6 amps/sq. ft. at a temperature of 30° C. The pH of

the bath was adjusted to 8.5. A bright deposit of palladium was obtained.

EXAMPLE III

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—24 g./l. (=11 g./l. of Pd).
Ammonium citrate—60 g./l.
Water to 1 litre.

The operating conditions for this bath may be the same as those of the previous examples.

EXAMPLE IV

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—24 g./l. (=11 g./l. of Pd).
Ammonium formate—80 g./l.
Water to 1 litre.

This bath should be operated at a current density of 12 amps/sq. ft. and at a temperature of from 20° C. to 40° C., the most satisfactory results being obtained at a temperature of 30° C. The pH of this bath was adjusted to from 8 to 9.

If desired, the palladium content of the above bath may be increased to 15 g./l., in which case, bright deposits of a thickness of 0.0008 inch are obtainable by the use of a current density of 18 amps/sq. ft.

EXAMPLE V

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—21.7 g./l.
Ethylene diamine tetra-acetic acid—80 g./l.
Water to 1 litre.

The ethylene diamine tetra-acetic acid was neutralised with ammonia to form the ammonium salt and the palladium salt dissolved in ammonia. The pH of the bath was adjusted to 8.5.

The bath should be operated at current density of 6 amps/sq. ft. at a temperature of 16° C. The cathode efficiency is 59% and a bright deposit of a thickness of 0.00012 inch is obtainable.

EXAMPLE VI

Palladium diammino-dinitrite $Pd(NH_3)_2(NO_2)_2$—24 g./l.
Ammonium oxalate—50 g./l.
Water to 1 litre.

The pH of this bath was adjusted by addition of ammonia to a value of 8.0.

A bright deposit of a thickness of 0.0001 inch is obtainable with this bath when operated at a current density of 12 amps/sq. ft. and a temperature of 30° C. a cathode efficiency of 53% being obtained. The article being plated should be agitated.

EXAMPLE VII

Potassium palladous tetranitrite $K_2Pd(NO_2)_4$—43 g./l. (=12 g./l. Pd).
Ammonium citrate—70 g./l.
Water to 1 litre.

The pH of this bath was adjusted to 9.0 by addition of ammonia and citric acid.

A bright deposit of a thickness of 0.0001 inch was obtained with this bath when operated at a current density of 6 amps/sq. ft. and a temperature of 30° C. A cathode efficiency of 57% was obtained.

EXAMPLE VIII

Palladium acetate $Pd(CH_3COO)_2$—21.1 g./l. (=10 g./l. Pd).
Ammonium oxalate—50 g./l.
Water to 1 litre.

The palladium acetate was first dissolved, by warming in ammonia to form $Pd(NH_3)_4(CH_3COO)_2$ and the pH of the final solution was adjusted to 8.7 with the addition of ammonia and acetic acid.

This bath produced a dull deposit of a thickness of 0.00019 inch when operated at a current density of 6 amps/sq. ft. and a temperature of 30° C. and gave a cathode efficiency of 94%.

EXAMPLE IX

Potassium palladous dichloride—46 g./l. (=15 g./l. Pd).
Ethylene diamine tetra-acetic acid—80 g./l.
Water to 1 litre.

The ethylene diamine tetra-acetic acid was neutralised with ammonia and the pH of the final solution was adjusted to 9.6 with the addition of ammonia.

The bath gave a dull deposit of a thickness of 0.00018 inch when operated at a current density of 6 amps/sq. ft. and a temperature of 30° C. The cathode efficiency was 90%.

EXAMPLE X

Palladium diammino-chloride $Pd(NH_3)_2Cl_2$—15.9 g./l. (=8 g./l. Pd).
Ammonium formate—100 g./l.
Water to 1 litre.

The palladium diammino-chloride was dissolved in ammonia and the pH of the final solution was adjusted to 9.8.

This bath gave a dull deposit of a thickness of 0.00017 inch when operated at a current density of 6 amps/sq. ft. and a temperature of 30° C. The cathode efficiency of the bath was 86%.

EXAMPLE XI

Palladium tetrammino nitrate $Pd(NH_3)_4(NO_3)_2$—27.8 g./l.
Ethylene diamine tetraacetic acid—40.0 g./l.
Water to 1 litre.

The ethylene diamine tetraacetic acid was neutralised with ammonia and the pH of the final solution was adjusted to 7.5 with dilute nitric acid.

This bath gave a dull deposit of a thickness of 0.00019 inch when operated at a current density of 6 amps/sq. ft. and a temperature of 30° C. The cathode efficiency was 94%.

Bright deposits may also be obtained with baths having the compositions given in the following Examples XII–XXI inclusive and using palladium diammino dinitrite as the palladium compound and ammonium formate NH_4OOCH, as the ammonium salt and when operated under the conditions specified therein.

Example	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI
Palladium in g. per litre	10	14	60	5	12	16	16	14	14	10
Ammonium formate, g./l.	20	50	60	80	70	60	70	60	60	60
pH	9.0	8.0	9.0	8.5	10.0	8.5	9.0	8.5	8.5	8.5
Current density, amps/ft.^{2}	2	18	6	6	12	12	450	120	60	6
Thickness, in	0.0001	0.0005	0.00015	0.00018	0.0002	0.0008	0.0001	0.0001	0.001	0.00015
Cathode efficiency, percent	80	65	73	78	70	70	9	20	30	85
Temperature, ° C.	20	30	30	30	40	30	30	30	30	70
Agitation of the article being plated	NO	NO	NO	NO	NO	NO	YES	YES	YES	NO

1 g. Pd≡2.175 g. $Pd(NH_3)_2(NO_2)_2$

The compositions of further plating baths in accordance with this invention and by means of which bright deposits of thickness of about 0.0001 inch may be obtained are given in the following Examples XXII to

XXVII inclusive together with the operating conditions in respect of each bath.

Example No	XXII	XXIII	XXIV	XXV	XXVI	XXVII
Salt	(1)	(1)	(2)	(2)	(3)	(3)
Grams per litre of salt	80	60	60	80	80	80
Grams per litre of palladium as $Pd(NH_3)_2(NO_2)_2$.	10	14	15	10	10	16
pH	8.5	9.0	8.0	8.6	8.8	8.5
Current density in amps/ft.^{2}	30	6	30	6	3	12
Thickness in inches	0.0001	0.0001	0.00015	0.0001	0.00012	0.00012
Temperature, ° C	30	30	30	32	37	37
Agitation of article being plated.	YES	NO	YES	NO	YES	YES
Cathode efficiency, percent	53	61	66	60	56	61

[1] Ammonium citrate.
[2] Ammonium tartrate.
[3] Ammonium acetate.

Plating baths in accordance with this invention may be used to electrodeposit palladium onto copper, Phosphor-bronze, brass, beryllium-copper, stainless steel, mild steel, nickel or silver or other metals. No particular pre-treatment is necessary, normal cleaning procedures being used.

It will be found that bright deposits up to a thickness of at least 0.001 inch are obtainable with barrel plating, the baths being stable and operable at a low temperature at or near room temperature.

The invention is intended to include within its scope a method of electrodepositing palladium upon a base which comprises immersing the base as a cathode in a plating bath or electrolyte in accordance with the invention and electrolysing the said bath. The invention also includes within its scope any base when plated with palladium by the use of a plating bath or electrolyte in accordance with the invention or by the method of the invention.

What we claim is:

1. A plating bath or electrolyte for the electrodeposition of palladium consisting essentially of water, a palladium compound and an ammonium salt of a weak organic carboxylic acid, the bath containing substantially no ethylene diamine tetraacetic acid and having a pH of between about 7 and about 10.

2. The bath or electrolyte claimed in claim **1** wherein the palladium compound is $Pd(NH_3)_2(NO_2)_2$.

3. The bath or electrolyte claimed in claim **1** wherein the palladium compound is $Pd(NH_3)_4(NO_3)_2$.

4. The bath or electrolyte claimed in claim **1** wherein the ammonium salt is ammonium tartrate, ammonium oxalate, ammonium citrate or ammonium formate.

5. The bath or electrolyte claimed in claim **1** and having a pH from about 8 to about 9.

6. The bath or electrolyte claimed in claim **1** wherein the palladium compound is palladium chloride.

7. A method of electrodepositing palladium which comprises electrolyzing a bath or electrolyte consisting essentially of water, a palladium compound and an ammonium salt of a weak organic carboxylic acid, the bath containing substantially no ethylene diamine tetraacetic acid and having a pH between about 7 and about 10.

8. A method of electrodepositing palladium on a basis metal which comprises electrodepositing the palladium on the basis metal from a bath consisting essentially of water, a palladium compound and an ammonium salt of a weak organic carboxylic acid, said bath containing substantially no ethylene diamine tetraacetic acid and having a pH between about 7 and about 10.

9. The method claimed in claim **8** wherein the palladium compound is $Pd(NH_3)_2(NO_2)_2$.

10. The method claimed in claim **8** wherein the palladium compound is $Pd(NH_3)_4(NO_3)_2$.

11. The method claimed in claim **8** wherein the palladium compound is palladium chloride.

12. The method claimed in claim **8** wherein the ammonium salt is ammonium tartrate, ammonium oxalate, ammonium citrate or ammonium formate.

13. The method claimed in claim **8** wherein the pH is between about 8 and 9.

14. The method claimed in claim **8** wherein the electrodeposition is conducted at a bath temperature of 15–75° C. and a current density of 1 to 500 amps/ft.^{2}.

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