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3,458,409

METHOD AND ELECTROLYTE FOR THICK, BRILLIANT PLATING OF PALLADIUM

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3 Claims

ABSTRACT OF THE DISCLOSURE

Palladium is electroplated to give a thick, bright deposit. The aqueous electrolyte comprises ammonia; a palladium salt and an amount of pyridine, pyridine carboxylic acid, or pyridine carboxylic acid amine sufficient to give a bright deposit. A lead salt may also be present in solution to assist in providing a bright deposit.

This invention relates to a plating bath composition for electroplating palladium on metal surfaces.

At present white colored plating on the component parts of weak electric apparatus, jewelry, etc., is usually of silver or nickel. Plating procedures for plating silver and nickel were developed many years ago and nowadays they are popularly adopted for industrial uses. The plated surfaces resulting from utilizing these methods of plating resulted in some drawbacks with respect to corrosion resistance, anti-weathering property, wear resistance, electric properties, color, etc. Many measures had to be taken to counter them. In spite of such inconveniences silver plating and nickel plating are widely adopted because there are no alternatives.

Recently the need for higher quality electroplated apparatus and jewelry has developed. This high quality cannot be obtained by conventional plating procedures. Therefore the need for better plating procedures is getting more and more urgent. We have succeeded in electroplating palladium to eliminate the drawbacks of the surfaces plated by the conventional methods. Palladium plating is superior to the conventional ones in respects of corrosion resistance, anti-weathering property and wear resistance. So it can satisfy the practical necessity of today's requirements.

Although palladium plating is inferior to silver plating in electric properties, e.g. it has a large electric resistance, superior in corrosion resistance and anti-weathering property, and it proves better quality under severe circumstances or after long term usage. Moreover it gives a beautiful color which is durable and different from that of silver or nickel.

There are several kinds of baths introduced since 1930's, though they were seldom used practically. Those baths are largely classified according to the composition as follows:

(1) Those which contain ammonium solution of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ as a principal ingredient: Ex. Keitel, Trans. Electrochem. Soc., 59, 275 (1931).

(2) Those which contain aqueous solution of $\text{K}_2\text{Pd}(\text{NO}_2)_4$ as a principal ingredient: Ex. Wise, U.S.P. 1,970,950 (1934); Raper, U.S.P. 1,993,627 (1935).

(3) Those which contain aqueous solution of K_2PdCl_4 as a principal ingredient: Ex. Wise U.S.P. 2,335,821 (1943); 2,457,021 (1948).

(4) Those which contain aqueous solution of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ as a principal ingredient: Ex. Laister, Metal Ind., 85, 428, (1944); Philpott, Platinun Metals Rev., 4, 12, (1960).

We thoroughly investigated and experimented on above listed baths. As a result it was found that none of those baths could give satisfactory brilliant plating, i.e. with those baths we could not get brilliant surfaces when the thickness of plating was more than 0.5×10^{-4} cm. As the thickness of the plate exceeded this value, plating gradually became dull greyish black. Such a color is very undesirable as to good appearance. Generally, brilliance is indispensable when we plate a merchandise to raise its value. On the other hand sufficient properties of corrosion resistance, anti-weathering, wearing resistance, etc. usually cannot be obtained on the palladium plated surfaces when the thickness of plating layer is only 0.5×10^{-4} cm., the upper limit of thickness which gives brilliance. Here we fall into a dilemma. Buffing may be considered to improve brilliance, but it is not only expensive but also impossible on many weak electric apparatus parts and jewelry.

Thus we had to conclude that the plating baths commonly employed were not practical. So we started developing a new bath suitable for thick brilliant plating. Accordingly the object of the present invention is to provide a bath for electroplating palladium, which can give a plating layer of practically sufficient thickness and brilliance without sacrificing the easiness of operation and the beneficial properties of resultant plating layers.

(a) We composed many baths, each having ammonia solution of one of the various palladium salts as a principal ingredient, to make experiments on the effects of plating. During these experiments we found that we could improve brilliance by adding pyridine. The plated surface had brilliance until the plating grew as thick as about 3×10^{-4} cm. At 5×10^{-4} cm. the surface showed slight milk-white blur, which could easily be mirror polished by buffing. Conventional baths cannot give such plating. The resulting plating of this bath fully satisfies the present practical requirements. We also found that brilliance was maintained until the plating grew as thick as at least 10×10^{-4} cm., if EDTA-Pb (chelate compound made from ethylenediaminetetraacetic acid and lead iron) was added to this bath.

This knowledge constitutes the essential part of this invention. Accordingly the plating solution of this invention contains one of various palladium salts dissolved in ammonium hydroxide, and also EDTA-Pb if required. Aforesaid objects of this invention are achieved when the bath is controlled so that the concentration of palladium salt as metal is 1–50 g./l., concentration of pyridine more than 0.01 mol./l., concentration of EDTA-Pb as Pb 0.05–1 g./l., alkalinity of the solution more than pH 9.5, temperature 10–50° C., and cathode current density 0.1–10 A./dm.².

(b) Palladium concentration of this bath is between 1 g./l. and 50 g./l. considering the purpose of plating and economical requirements, provided that low cathode current density be used for low palladium concentration. Palladium concentration of more than 15 g./l. is usually necessary for cathode current density of 1 A./dm.².

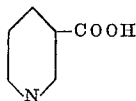
Dichlorodiaminepalladium $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is the most suitable source of palladium, because this material is easily prepared and purified, and also because this material is rapidly dissolved in ammonium hydroxide. As palladium salts are dissolved in ammonium hydroxide, palladium exists in the solution as an ammonium complex salt whatever the kind of original salt might have been.

Ammonium solution of palladium salt is defined as solution in which palladium exists dissolved as ammonium complex salt.

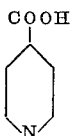
(c) Pyridine is an important ingredient of this bath, but it is inconvenient to use this material because of its of-

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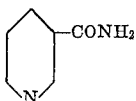
fensive odor. So we tried to use derivatives of pyridine.
Pyridine 3-carboxylic-acid



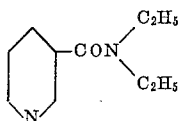
and pyridine 4-carboxylic-acid



brought satisfactory results. Position of the carboxyl radical in the pyridine nucleus has no effect on plating. Nicotinamide

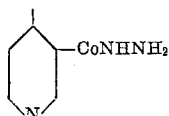


and N-diethyl-3-pyridine-carboxylic-acid-amide



also produced good results.

These materials are oxidized by the anode to change into corresponding pyridine-carboxylic-acids during electroplating process. Then it is understood that the effects provided by these materials are brought because of their pyridine nucleus and that the sort and the position of substituent have no bearing in the process. Of course such derivatives are not suitable that have substituents which are not chemically stable in electrolyzing process. For example 4-pyridine-carboxylic-acid-hydrazide



did not bring good result. The lowest effective concentration of these materials is 0.01 mol./l. and there are no undesirable results even if the concentration is raised higher than this, for example 2 mol./l.

Anyway, plated surfaces produced from the baths which contain pyridine, pyridine-carboxylic-acid, or pyridine-carboxylic-acid-amide are evidently superior to those from conventional baths.

(d) When brilliant plating thicker than 5×10^{-4} cm. is required, good results are obtained by adding EDTA-Pb to the bath. Concentration of EDTA-Pb in the bath should strictly be maintained within 0.05–1 g./l. as Pb. Otherwise EDTA-Pb has no effect or even causes bad results.

As EDTA-Pb is added the plating layer becomes an alloy which contains 1–2% of lead, and accordingly amount of lead in the bath gradually decreases. Then lead must be replenished as EDTA-Pb.

Although it is not explained how EDTA-Pb operates to give brilliance, the concentration of lead in the bath is supposed to have significant influence. We made experiments on the baths to which ions of lead nitrate, lead chloride, etc., or weak organic complex salt such as lead acetate, lead citrate, etc., was added instead of EDTA-Pb. Such baths also gave brilliant plating. But lead concentration in the baths had to be kept very low, i.e., 1–5 mg./l., and as a natural result they did not bring constant effects. So those baths cannot be expected to be practically useful.

On the other hand the baths to which strong chelate compounds such as CyDTA-Pb(1-2-cyclohexylenedinitrilo-tetraacetic lead) and DTPA-Pb (diethylenetriamine-

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pentaacetic lead) were added constantly gave the same brilliant plating as we got from the bath which contains EDTA-Pb when the lead concentration was within 0.05–1 g./l.

Summarizing the above, the primary cause of brilliance is the presence of lead in the bath. Concentration of lead should be kept within a definite range determined by strength of complicating agent.

(e) When the bath of the present invention is utilized, there is interrelation between palladium concentration, temperature of the bath and cathode current density. Cathode current density should be lowered as palladium concentration decreases and bath temperature becomes low. The bath usually gives a good result at palladium concentration of more than 15 g./l., temperature of 30–40° C. and cathode current density of 1 A./dm.².

The plating bath is made alkaline by means of the addition of ammonia. Generally a pH of above 9.5 is desirable.

Plating is nearly mirror-brilliant at the thickness of 3×10^{-4} cm., and at 5×10^{-4} cm. presents slight milk white blur which can easily be buffed off. Addition of EDTA-Pb is necessary for brilliant plating thicker than 5×10^{-4} cm. It is able to give brilliance to the plating at least as thick as 10×10^{-4} cm.

Current efficiency is always 90–95% and troubles which may be caused by hydrogen absorbed, i.e., embrittlement caused by hydrogen, do not arise on the plated surface.

Anode should be metal palladium plate or black lead electrode. As palladium concentration in the bath decreases, palladium salt such as dichlorodiaminepalladium $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ should be added.

Proper pH of the bath should be maintained by adding concentrated ammonium hydroxide. Various inorganic or organic salts may be added to the bath to raise electric conductivity.

Preparatory treatment on the metal to be plated is processed in the same way as usual. There are no restriction as to the kind of the metals on which palladium is plated.

Execution 1

Dichlorodiaminepalladium	g./l.	40
Pyridine	g./l.	5
Ammonium hydroxide (the amount which makes pH of the bath 10)	percent.	25
Cathode current density	A./dm. ²	1
Temperature	° C.	35
Without agitation.		

Under these conditions plating was brilliant until it grew as thick as 3×10^{-4} cm. At the thickness of 5×10^{-4} cm. slight milk white blur appeared, but it was easily buffed off. There was no cracking, and plating well adhered to the base. Current efficiency was 95%.

Execution 2

Dichlorodiaminepalladium	g./l.	40
Pyridine	g./l.	5
Ammonium hydroxide (the amount which makes pH of the bath 10)	percent.	25
Cathode current density	A./dm. ²	0.5
Temperature	° C.	35
Without agitation.		

Same results as Execution 1 were obtained.

Execution 3

Dichlorodiaminepalladium	g./l.	40
Pyridine 3-carboxylic-acid	g./l.	5
Ammonium hydroxide (the amount which makes pH of the bath 10)	percent.	25
Cathode current density	A./dm. ²	1
Temperature	° C.	35
Without agitation.		

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Same results as Execution 1 were obtained. The bath which contained pyridine 4-carboxylic-acid instead of pyridine 3-carboxylic-acid also resulted same plating.

Execution 4

Dichlorodiaminepalladium	-----g./l.	40	5
Nicotinamide	-----g./l.	5	
Ammonium hydroxide (the amount which makes pH of the bath 10)	-----percent.	25	
Cathode current density	-----A./dm. ²	1	10
Temperature	-----° C.	35	
Without agitation.			

Same results as Execution 1 were obtained. The same results were also obtained when more nicotinamide was used to make its concentration 150 g./l.

Execution 5

Dichlorodiaminepalladium	-----g./l.	40	
Nicotinamide	-----g./l.	5	
EDTA (Na salt)	-----g./l.	50	20
Ammonium hydroxide (the amount which makes pH of the bath 10)	-----percent.	25	
EDTA-Pb (as Pb)	-----mg.	400	
Cathode current density	-----A./dm. ²	1	25
Temperature	-----° C.	35	
Without agitation.			

With above bath composition and plating conditions, plating was performed until layer grew as thick as 15×10^{-4} cm. Mirror-like brilliance resulted and no cracking took place. Plating layer well adhered to the base. Current efficiency was 95%. Same results were obtained when potassium chloride was added to the bath in the proportion of 50 g./l. to raise electric conductivity.

We claim:

1. A method for obtaining a thick, brilliant palladium plating comprising electroplating a metal in a diaphragmless electroplating cell which contains an aqueous ammoniacal solution maintained at a pH of above 9.5, comprising ammonia, a palladium salt in an amount sufficient

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to supply a concentration of palladium metal of from 1 to 50 grams per liter, and a brightening agent for brightening the palladium plating selected from the group consisting of pyridine, pyridine carboxylic acid, and pyridine carboxylic acid amides, said agent being present in the bath in an amount of from about 0.01 to 2 mols per liter, maintaining the current density in said bath during said plating, at from 0.5 to 1 A./dm.² and maintaining the bath at a temperature of about 35° C. during said plating.

2. The method in accordance with claim 1 wherein said bath contains a lead complex consisting of lead chelated with an organic chelating agent, said complex being present to provide lead in an amount of from about 0.05 gram to 1 gram per liter.

3. An electroplating bath comprising an aqueous ammoniacal solution containing a palladium salt, said salt being present in an amount sufficient to provide palladium metal in a concentration of from about 1 to 50 grams per liter, a brightening agent selected from the group consisting of pyridine, pyridine carboxylic acid, and pyridine carboxylic acid amide, said agent being present in the bath in an amount of about 0.01 to 2 mols per liter, and a lead complex consisting of lead chelated with an organic chelating agent, said complex being present to provide lead in an amount of from about 0.05 gram to 1 gram per liter.

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