

"A METHOD OF REPLENISHING WITH PALLADIUM A PLATING SOLUTION
FOR ELECTRODEPOSITION OF A PALLADIUM-NICKEL ALLOY"

This invention relates to methods of replenishing with
palladium plating solutions for electrodeposition of palladium-
5 nickel alloys.

Heretofore electrodeposition of a palladium-nickel alloy has
been effected using a plating solution which comprises aqueous
ammonia containing 5 to 30 g/l of palladium and 5 to 30 g/l of
nickel using the process disclosed in British Patent Specification
10 No. 1 143 178. This has produced a palladium-nickel alloy deposit
having a palladium content of 30 to 90% by weight and excellent
corrosion resistance. In this plating solution disclosed in British
Patent Specification No. 1 143 178 palladium and nickel form ammine
complex salts and dissolve in the aqueous ammonia. In particular
15 the palladium is dissolved in the aqueous ammonia to form
tetramminepalladium (II) chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ (sometimes known as
tetramminepalladous chloride or palladous ammine chloride).

As electrodeposition proceeds, palladium in the plating
solution is gradually used up. For instance, as shown in Example 1
20 described hereinbelow, when producing a palladium-nickel alloy
deposit using a plating solution comprising aqueous ammonia
containing 20 g/l of palladium and 10 g/l of nickel, about 2 g of
palladium and about 0.5 g of nickel are lost per litre of plating
solution in 3 hours under the conditions described in Example 1.
25 In other words, the palladium concentration in the plating solution

- 2 -

is reduced from the original 20 g/l to 18 g/l after 3 hours.

In order to perform normal electrodeposition, it is desirable to maintain the palladium concentration within the range 18 to 22 g/l and to maintain an adequate standard of electrodeposition it is

- 5 necessary to correct the palladium concentration in the plating solution by replenishing the palladium. This replenishment is achieved

conventionally by intermittently adding a palladium salt to the plating solution after determining the palladium concentration by, for example, quantitative analysis. The palladium salt employed for this replenishment has, heretofore, been for example, 5 a palladousammine complex salt such as dichlorodiamminepalladium ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$) or a salt such as palladium chloride (PdCl_2), an alkalichloropalladite such as potassium chloropalladite (K_2PdCl_4) or ammonium chloropalladite ($(\text{NH}_4)_2\text{PdCl}_4$). These salts are all soluble in aqueous ammonia and chemically react with the 10 ammonia to form tetramminepalladium (II) chloride ($(\text{Pd}(\text{NH}_3)_4\text{Cl}_2)$).

The known salts can be directly added to the plating solution and dissolved therein, but since the ammonia concentration in the plating solution is relatively low, usually about 5 g/l, it takes time for the salt to be dissolved and therefore the plating 15 operation has to be suspended during that time. For example, to dissolve 4 g of dichlorodiamminepalladium which corresponds to 2 g of palladium in 1000 cc of the plating solution of Example 1, takes 30 to 60 minutes even if the plating solution is stirred. With other palladium salts, an even longer time is needed. 20 This impedes the smooth progress of the electrodeposition in a factory.

Alternatively, it is also possible to dissolve these salts 7 in aqueous ammonia prior to addition to the plating solution. This overcomes the necessity to suspend electrodeposition, but the 25 volume of the plating solution gradually increases by repeatedly

replenishing the palladium in this manner, and thus unnecessary plating solution is created. For example, if a solution with a palladium concentration of 150 g/l (the saturated solution at 20°C) is employed, each replenishment of 2 g/l of palladium increases the volume of 1000 cc of plating solution by 13 cc. In other words, under the conditions of Example 1, if a solution of a palladium salt dissolved in aqueous ammonia is employed and even though this solution is a saturated solution, the volume of the plating solution is increased by 13 cc after every three hours of electrodeposition. Thus as the electrodeposition proceeds, the plating solution continues to increase in volume by an amount greater than the loss due to evaporation and this increase in volume becomes a problem in time. To overcome the problem the volume of the plating solution may be kept constant by removing samples and either separately recovering palladium from the samples or heating the samples to evaporate the water to reduce their volume and, where appropriate, returning the samples to the plating solution. Such operations, however, not only increase cost but make the process inconvenient.

The conventionally employed salts for replenishing the plating solution such as dichlorodiamminepalladium $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, palladium chloride PdCl_2 , potassium chloropalladite K_2PdCl_4 , ammonium chloropalladite $(\text{NH}_4)_2\text{PdCl}_4$ etc. are all soluble in aqueous ammonia and chemically react with the ammonia to form an aqueous solution of an ammine complex salt, in which NH_3 is coordinated with the

metallic ion, the complex salt being tetramminepalladium (II) chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$. To overcome these problems the present invention seeks to provide a method of replenishing with palladium a plating solution by addition of crystalline tetramminepalladium (II) chloride to the plating solution.

According to the present invention there is provided a method of replenishing with palladium a plating solution which contains 5 to 30 g/l of nickel and which is used for electrodeposition of a palladium-nickel alloy, the method comprising adding crystalline tetramminepalladium (II) chloride to the plating solution until the content of palladium is 5 to 30 g/l.

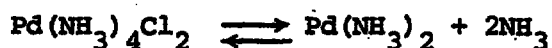
Since crystalline tetramminepalladium (II) chloride is readily soluble not only in water and aqueous ammonia but also in the plating solution itself, the direct addition thereof to a plating solution having a relatively low ammonia concentration can replenish the plating solution without the need to suspend the electrodeposition or cause an increase in volume of the plating solution.

For example, when 5 g of crystalline tetramminepalladium (II) chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ (2 g as palladium) is added to 1000 cc of the plating solution and stirred, it is completely dissolved in 0.5 to 1 minute.

A method according to the present invention can also be applied where the plating solution includes any one or more of an aromatic sulphamide, naphthalene sulphonic acid, an organic acid salt and an inorganic acid salt. Further, the method is also applicable

to a plating solution prepared using dichlorodiamminepalladium or other palladium salts. Still further, the method can be applied regardless of the ammonia concentration and hence the pH of the plating solution. Tetramminepalladium (II) chloride exists in
5 forms having the chemical formulae $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$, either of which is obtained as a white to slightly yellowish crystalline powder.

An aqueous solution of tetramminepalladium (II) chloride exhibits an ammonia alkalinity due to the following chemical
10 equilibrium:



If the ammonia generated escapes into the atmosphere, the equilibrium is shifted to the right and dissolution becomes incomplete. Therefore, in order to maintain an aqueous solution of tetrammine-
15 palladium (II) chloride stable, it is desirable that an excess of ammonia is always present in solution. Since the plating solution already contains aqueous ammonia, tetramminepalladium (II) chloride therein is stable. Since tetramminepalladium (II) chloride is readily soluble in water, aqueous ammonia and the plating solution,
20 the size of the crystalline particles thereof is not critical.

EXAMPLE 1

39.7 g (20 g as palladium) of dichlorodiamminepalladium $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ was dissolved in 700 cc of water and 90 cc of 25% aqueous ammonia. Then 50 g of ammonium sulphate and 45 g (10 g
25 as nickel) of nickel sulphate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were dissolved and the pH was adjusted to 8.5 to 9.0 using dilute sulphuric acid, after which water was added to make up the total volume to 1000 cc. The resulting plating solution had the following composition:

5 $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$: 37.7 g/l (Pd: 20 g/l)
 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$: 45 g/l (Ni: 10 g/l)
 $(\text{NH}_4)_2\text{SO}_4$: 50 g/l
 pH: 8.5 - 9.0
 Temperature: 25°C
 Volume: 1000 cc

and was used to electrodeposit a palladium-nickel alloy under the following conditions:

10 Test piece as cathode Brass plate
 Cathode surface area 0.5 dm²
 Cathode current density: 1 A/dm²
 Anode: Palladium plate
 Anode current density: 1 A/dm²
 Current concentration: 0.5 A/l
 Electrodeposited alloy: 80% Pd and 20% Ni
 Density of the electro- 11.0 g/cm³
 deposited alloy:
 Current efficiency: 99%
 Alloy electrodeposition rate: 0.0141 g/min.
 (Palladium electrodeposition (0.0113 g/min.)
 rate):

20

After every 30 minutes of electrodeposition, the test piece was replaced and whenever the palladium concentration in the plating solution dropped below 18 g/l or the nickel concentration dropped below 9 g/l, a calculated amount of either crystalline tetrammine-
 25 palladium (II) chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ or crystalline nickel

5 sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was added to the plating solution to return the concentration of palladium or nickel respectively to the original initial concentration. The pH adjustment was effected by adding calculated amounts of 25% aqueous ammonia. The electro-
deposition proceeded until the total amount of palladium replenished had reached 40 g/l.

10 It was found that the crystalline tetramminepalladium (II) chloride was completely dissolved in 0.5 to 1 minute, during which electrodeposition was suspended. No abnormalities were observed in the palladium-nickel alloy deposit produced, the adhesion to the test piece and corrosion resistance were good. No substantial increase in volume of the plating solution was observed.

EXAMPLE 2

15 As a brightener 5 g/l of sodium 1,3,6-naphthalenetrisulphonate was added and dissolved in the plating solution of Example 1. Using the plating solution, an experiment was conducted under the same conditions as those in Example 1. The same results were obtained except that the brightness of the palladium-nickel alloy deposit was improved.

EXAMPLE 3

20 19.9 g (10 g as palladium) of dichlorodiamminepalladium $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ was dissolved in 700 cc of water and 30 cc of 25% aqueous ammonia. Then, 50 g of ammonium sulphate and 45 g (10 g as nickel) of nickel sulphate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were dissolved therein and
25 water was then added to make up the total volume to 1000 cc.

The resulting plating solution had the following composition:

	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$:	19.9 g/l (Pd: 10 g/l)
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$:	45 g/l (Ni: 10 g/l)
	$(\text{NH}_4)_2\text{SO}_4$:	50 g/l
5	pH:	7.0 - 7.5
	Temperature:	30°C

and was used to electrodeposit a palladium-nickel alloy under the following conditions:

	Volume:	1000 cc
10	Test piece as cathode:	Brass plate
	Cathode surface area:	0.5 dm ²
	Cathode current density:	1 A/dm ²
	Anode:	Palladium plate
	Anode current density:	1 A/dm ²
15	Current concentration:	0.5 A/l
	Electrodeposited alloy:	55% Pd and 45% Ni
	Density of the electro-deposited alloy:	10.04 g/cm ³
	Current efficiency:	99%
	Alloy electrodeposition rate:	0.0120 g/min.
20	(Palladium electrodeposition rate):	(0.0066 g/min)

After 30 minutes of electrodeposition, the test piece was replaced, and whenever the palladium concentration in the plating solution dropped below 9 g/l or the nickel concentration dropped below 9 g/l, a calculated amount of either crystalline tetrammine-

palladium (II) chloride $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ or crystalline nickel sulphate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were added to the plating solution to return the concentration of palladium or nickel respectively to the original concentration. The electrodeposition proceeded until
5 the total amount of palladium replenished had reached 20 g/l.

It was found that the crystalline tetramminepalladium (II) chloride was completely dissolved in 0.5 to 1 minute during which electrodeposition was not suspended. The palladium-nickel alloy deposit produced was bright, no abnormalities were observed and
10 adhesion to the test piece and corrosion resistance thereof were good. No substantial increase in volume of the plating solution was observed.

As has been described above the plating solution can be replenished simply and without generation of ammonia and this has
15 great practical effect.



- 11 -

CLAIMS

1. A method of replenishing with palladium a plating solution which contains 5 to 30 g/l of nickel and which is used for electrodeposition of a palladium-nickel alloy, the method comprising adding crystalline tetramminepalladium (II) chloride to the plating solution until the content of palladium is 5 to 30 g/l.
2. A method as claimed in claim 1 in which any one or more of an aromatic sulphamide, naphthalene sulphonic acid, an organic acid salt and an inorganic acid salt are added to the aqueous solution.
3. A method as claimed in claim 1 substantially as herein described with reference to Examples 1 to 3.

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