

# Bright Palladium Plating

## PRODUCTION OF PORE-FREE DEPOSITS AT ROOM TEMPERATURE

By L. A. Heathcote

Research Laboratories, Johnson Matthey & Co Limited

The advantages of palladium coatings in the field of electrical contacts are now well established. In R. W. Beattie's (1) opinion palladium forms a reliable contact finish for telephone two-motion selector plugs and sockets, while H. C. Angus (2) has found that in the majority of miniature slip ring applications where gold or rhodium is employed, reduced mechanical wear, improved "noise" performance and longer life can be obtained from palladium. J. E. Philpott (3) has described the plating of printed circuit boards, with special reference to the use of the tetrammino-palladous nitrate bath. For all these purposes a bright, pore-free deposit is required.

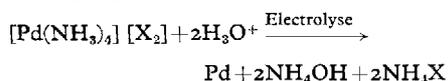
Because of its simplicity and ease of maintenance, the tetrammino-palladous nitrate bath is excellent for producing semi-bright pore-free deposits of 0.0002 inch thickness, where the surface can be improved by scratch brushing or polishing if required. For contact surfaces, however, it is the "as plated" finish that is important, especially when barrel plating, and it is for this reason that a new bright palladium plating bath has been developed in the Johnson Matthey Research Laboratories.

### The Plating Bath

The most widely used palladium plating baths are based on solutions of tetrammino-palladous nitrate  $[\text{Pd}(\text{NH}_3)_4][(\text{NO}_3)_2]$ , tetrammino-palladous chloride  $[\text{Pd}(\text{NH}_3)_4][\text{Cl}_2]$  and tetrammino-palladous nitrite  $[\text{Pd}(\text{NH}_3)_4][(\text{NO}_2)_2]$ . The nitrate bath can be prepared by dissolving the solid salt in water; the chloride and nitrite baths are prepared by

dissolving the diammino-palladous salt  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  or  $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]$  in strong ammonia, and adding certain "conducting" salts. These compounds are sodium or ammonium salts of inorganic acids, such as chloride, sulphamate, sulphate, nitrate, nitrite or carbonate, and may be added singly or in groups. The various bath compositions, some of which have been patented, are given in the literature.

The products of electrolysis of a tetrammino-palladous salt solution are shown by the following equation:

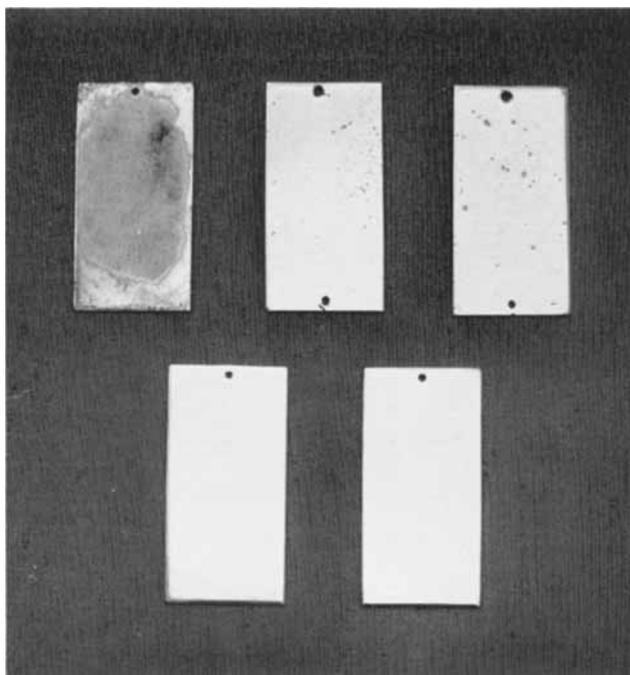


Palladium is anodically insoluble in this bath, and the metal content is maintained by replenishing with the corresponding palladium ammine complex. This practice leads to an accumulation of ammonium salt in the bath, which may have an adverse effect on its performance. In the case of a tetrammino-palladous nitrate bath, when fifteen times the metal concentration had been plated out, the ammonium nitrate produced reduced the pH from 8.0 to 5.0 and the cathode efficiency from 98 per cent to 50 per cent. By operating a divided cell, with a tetrammino-palladous chloride bath, Atkinson and Raper (4) restricted the salt build-up to the anode compartment from which it could be removed, but such a cell is not always convenient to use.

It is claimed that no salt accumulates with tetrammino-palladous nitrite baths, because ammonium nitrite is unstable,



*The results of exposure for twenty-four hours to 1 per cent SO<sub>2</sub> in air at high humidity, followed by four hours in 1 per cent moist H<sub>2</sub>S, of copper panels palladium plated from the new bright bath. The top row from left to right are plated 0.000005, 0.00005 and 0.0001 inch thick, and show increasing corrosion resistance with increase in thickness. In the second row the panel on the left is plated 0.00015 inch thick, that on the right is plated 0.0002 inch thick; both are free of corrosion spots*



but in the author's experience 40 to 50 per cent of the nitrite is oxidised to nitrate at the anode. However, the life of a tetramminopalladous nitrite bath should be double that of the corresponding nitrate bath on this basis.

Initially the pH of ammine baths is usually in the range 8 to 10, and the ammonia produced during electrolysis helps to maintain this. Plating temperatures range from 20 to 90°C, but the lower values are better for ease of control and ease of pH maintenance.

The new palladium plating bath is prepared from tetrammino-palladous nitrite and ammonium salts of organic acids to contain 15 g per litre of palladium. Glass or plastic tanks should be used, the solution being operated at 30°C with a pH of 8 to 9. The metal content is maintained by adding the palladium salt dissolved in ammonia. Anodes of platinum, palladium or platinum on titanium are used.

### **Plating Properties of the Bath**

Mirror bright deposits can be obtained on polished articles in both vat and barrel plating. The current densities suggested are in the range 3 to 18 amp/ft<sup>2</sup> for vat plating,

and for barrel plating 2 amp/ft<sup>2</sup> based upon total cathode area. Deposits of 0.001 inch and over are equally bright.

Gas pitting of the deposited surface is common with cathode efficiencies of less than 100 per cent unless the work is continuously agitated, as with barrel plating, or vibrated to remove the gas bubbles that form.

Thin films of palladium form on the anodes during plating, but these are kept to a minimum by gentle circulation of the electrolyte, such as that provided by continuous filtration apparatus. A remarkable property of this bath is its ability to produce bright deposits at very high current densities even up to 450 amp/ft<sup>2</sup> for example, although with a reduced cathode efficiency. Rapid agitation of the work or electrolyte is necessary and the most likely application is for plating wire or continuous strips of small articles which are separated later. At 120 amp/ft<sup>2</sup>, for example, the cathode efficiency is 20 per cent, and 0.0001 inch is deposited in four minutes.

The throwing power of the bath is 50 per cent, determined with a Haring and Blum cell and calculated from the formula modified

by Field, where 100 per cent would be perfect. This is similar to the throwing power of cyanide copper or silver baths.

### Properties of the Deposit

The function of an electrodeposited noble metal coating is to provide the underlying base metal with a corrosion resistant surface. Pore-free deposits of minimum thicknesses are therefore required, and it is recognised that the smoother the surface the thinner the deposit needed to give complete protection.

Two methods were used to test for porosity in the deposits on polished copper panels, a gas exposure method, and an electrographic technique using cadmium sulphide papers. The electrographic test was carried out by placing the panel on a piece of moistened filter paper impregnated with cadmium sulphide, applying a pressure of 200 lb/in<sup>2</sup> and passing a current of 25 mA/in<sup>2</sup> for 30 seconds, the panel being the anode. Any pores appeared as black spots on the cadmium sulphide paper, and by this method the deposits were found to be pore-free down to a thickness of 0.00002 inch.

The gas test, which is more severe, consisted of exposing the panels to a humid atmosphere containing 1 per cent SO<sub>2</sub> for 24 hours, washing them, drying with filter papers, and exposing to moist 1 per cent H<sub>2</sub>S for four hours. Deposits of 0.0002 inch were completely pore-free by this test and those of 0.00015 inch were substantially pore-free.

The stress in the deposit was found, by spiral contractometer, to be 25,000 to 30,000 lb/in<sup>2</sup>. Semi-bright deposits from tetramino-palladous nitrate baths have a stress of 30,000 to 35,000 lb/in<sup>2</sup>, and fully bright deposits 70,000 lb/in<sup>2</sup>. The hardness of the deposited palladium is 300 to 400 V.P.N.

### References

- 1 R. W. Beattie, Palladium Plating on Telephone Plugs and Sockets, *Platinum Metals Rev.*, 1962, 6, 52
- 2 H. C. Angus, The Performance of Platinum-Metal Electrodeposited Contacts. Paper read at IMF North-West Branch Symposium, March 1964
- 3 J. E. Philpott, Palladium Plating of Printed Circuits, *Platinum Metals Rev.*, 1960, 4, 12
- 4 R. H. Atkinson and A. R. Raper, *J. Electrodepositors' Tech. Soc.*, 1933, 8, 1

## High-Stability Fixed Resistors

### NOBLE METAL FILMS IN GLASS TUBES

A new type of noble metal film resistor, now in quantity production by Siemens and Halske, is described by Werner Kugelstadt (*Siemens Zeitschrift*, 1965, 39, (2), 145-149).

The resistors comprise a thin 80:20 gold-platinum diffusion alloy film applied to the inside of high insulating toughened glass tubes, and helically grooved to obtain the required values.

The alloy film is deposited and fired on to the substrate by a ceramic decorating technique using a solution containing organic compounds of gold and platinum, and small amounts of other metals to promote adhesion, which are controlled to provide a film sufficiently soft to be mechanically grooved without stressing. The thickness of the film is controlled within the range 0.01 to 5.0 μ in which maximum stability is obtained with a specific resistance of about 40 μΩ cm.

Use of the relatively soft elastic noble metal alloy film of stable structure is claimed to eliminate corrosion and irreversible changes in resistance during temperature cycling due to differences in thermal expansion between the film and the substrate. It is also claimed to provide a positive temperature coefficient of resistance of about 300 × 10<sup>-6</sup> per °C constant between -70 and +200°C, and to give exceptionally low noise in operation.

The resistors have a maximum continuous operating temperature of 165°C. Two main types are available, for power loadings of 0.5 and 1.0 watt with values between 1 Ω and 240 KΩ, and 2 Ω and 510 KΩ respectively. The author discusses in detail factors governing the performance of metal film resistors, and gives data on electrical properties, dimensions, and conformity of the resistors to German and United States specifications.