

A New Ruthenium Plating Bath

By C. W. Bradford, B.Sc., M. J. Cleare, B.Sc., D.I.C., and H. Middleton

Research Laboratories, Johnson Matthey & Co Limited

A new ruthenium plating bath has been developed which gives bright, adherent and pore-free deposits at high cathode efficiencies. Electrodeposited ruthenium has considerable potential applications in the field of light duty electrical contacts where mechanical wear is a problem, particularly for sliding surfaces such as slip rings.

The possible advantages of a good ruthenium plating bath in electrical contact applications have been appreciated for some time. Electrodeposited ruthenium not only has properties comparable with those of rhodium, but is considerably cheaper. The use of these two metals for slip ring surfaces has been discussed by H. C. Angus (1), who concluded that ruthenium should provide as good or even a better electrodeposit for this purpose by comparison with rhodium.

A number of ruthenium plating baths have been described in the past. Most of these were either unstable in use or had very low cathode efficiencies. F. H. Reid and J. C. Blake (2) found that a ruthenium nitrosyl sulphamate bath gave good deposits at reasonable cathode efficiencies (10 to 20 per cent) but reproducibility was a problem.

A new electrolyte based on an interesting ruthenium complex, $K_3[Ru_2NCl_8(H_2O)_2]$ has been developed in the Johnson Matthey Research Laboratories. Under optimum conditions cathode efficiencies of over 90 per cent are obtained. The deposits are mirror-bright, adherent, very hard and pore-free.

The Plating Salt

During investigations into the chemistry of ruthenium nitrosyl complexes, somewhat surprising reduction products were obtained, the nitrosyl group being converted both to ammonia and a nitride complex of Ru^{IV} . The original work in this field had been carried out at the turn of the century by the French

chemist L. Brizard (3). Following his method, $K_3Ru(NO)Cl_5$ was reacted with stannous chloride in hydrochloric acid solution and a deep red crystalline product obtained.

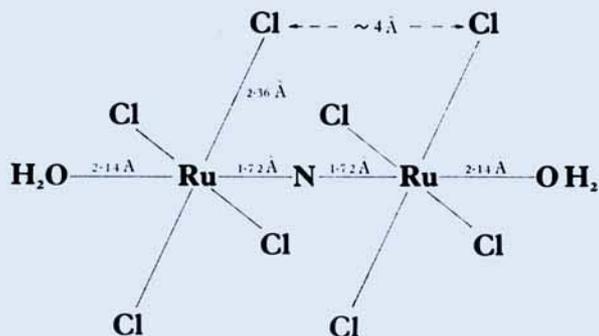
On the basis of chemical analysis, infra-red and Raman spectra, and its diamagnetism, the compound was formulated as $K_3[Ru_2^{IV}NCl_8(H_2O)_2]$, the anion containing a linear Ru-N-Ru group (4) as shown in the diagram.

The infra-red spectrum showed a strong band at 1078 cm^{-1} which was absent in the Raman spectrum. The immobility of this band when the water in the molecule was replaced by D_2O , and its downward shift by 32 cm^{-1} when the nitrogen was replaced by ^{15}N suggested that it was associated with the linear bridging nitrogen group. The proposed structure has subsequently been confirmed by an X-ray crystallographic structural determination (5). The preparation of the salt has been carried out on a 1 Kg scale, yields of 60 per cent being obtained.

The Plating Bath

The plating bath, for which a provisional patent application has been filed (6), was prepared by dissolving sufficient of the salt to give a solution containing 10 g/l Ru, adjusting the pH to 1.3 and adding 10 g/l ammonium formate.

The addition of the formate was found to be necessary to prevent the formation of ruthenium tetroxide at the anode. Other



Structure of the $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$ Anion

This structure of the anion forming the basis of the new ruthenium plating bath was proposed from infra-red, Raman and magnetic susceptibility studies and was confirmed by three-dimensional x-ray crystallography. The ruthenium atoms are slightly displaced away from the planes of the chlorine atoms and towards the bridging nitrogen atom. The ruthenium-nitrogen distance is shorter than that for a single ruthenium-nitrogen bond

mild reducing agents such as ammonium sulphamate were tried and found to be satisfactory in this respect, but the formate had the advantages of giving thicker non-porous and crack-free deposits.

The plating trials were carried out using 150 ml of electrolyte, gold-flashed copper cathodes (2 inch by 1 inch) and platinised titanium anodes (2 inch by $1\frac{1}{4}$ inch).

Optimum Plating Conditions

The best results were obtained when the bath was operated at 7.5 A/ft^2 and at 70°C . The variations of the cathode efficiency with current density and temperature were as shown in Fig. 2, the efficiencies being calculated with respect to Ru^{IV} . The appearance of the deposits deteriorated at current densities greater than 10 A/ft^2 and the efficiency of the bath fell.

During use the pH of the electrolyte decreased and was re-adjusted with ammonium hydroxide. The variation of

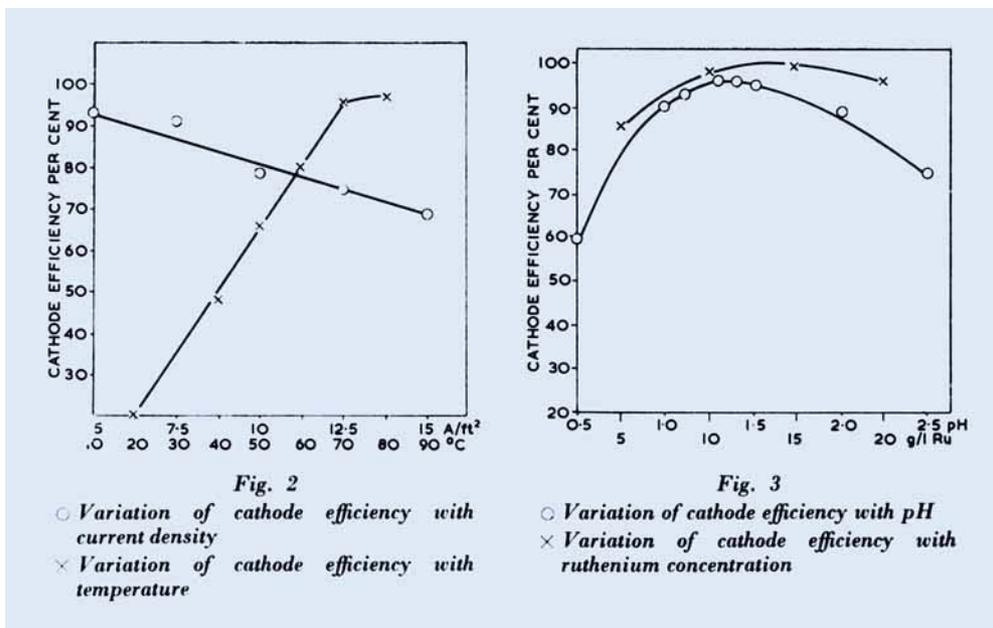
cathode efficiency with pH is shown in Fig. 3, together with the effect of changes in the ruthenium concentration. A maximum efficiency was obtained at pH 1.3, and the deposits began to darken above pH 2.

Apart from the variable under investigation, the optimum conditions were used in obtaining the results shown in Figs. 2 and 3.

A five times turn-over trial was conducted at 70°C , pH 1.0 to 1.5 and 7.5 A/ft^2 . The ruthenium concentration was adjusted by addition of further salt when it had fallen to 9 g/l . A further 1 g of ammonium formate was added for every gram of ruthenium deposited. The properties of deposits remained the same during the turn-over trial, although the cathode efficiency of the bath gradually fell to 65 per cent.

Properties of Deposits

The deposits obtained were mirror bright and adherent up to thicknesses of 0.00025 inch at current densities less than 10 A/ft^2



and when the pH of the electrolyte was between 1.0 and 1.5. The hardness was in the range 750 to 850 V.P.N., similar to the hardness of electrodeposited rhodium.

Under optimum conditions, pore-free and uncracked deposits were obtained up to thicknesses of 0.0001 inch. The porosities were tested by an electrographic technique; the panels were placed on a piece of moistened filter paper impregnated with cadmium sulphide, a pressure of 200 lb/in² applied and a current of 50 mA/in² passed for 30 seconds, the panel being the anode. Any pores appeared as black spots on the cadmium sulphide paper.

The panels were also subjected to a more vicious gas test. This consisted of exposing them to a humid atmosphere containing 1 per cent SO₂ for 24 hours, washing, drying with filter papers and exposing to moist 1 per cent H₂S for 24 hours. Only deposits up to thicknesses of 0.00006 inch withstood this treatment, being unaffected except at the edges.

Stress measurements were made using a spiral contractometer. Values varying from 100,000 to 120,000 lb/in² were obtained

over a pH range of 1.0 to 1.5. The stress was found to increase as the pH of the electrolyte decreased.

A number of other complexes containing ruthenium-nitrogen bonds are at present being investigated as possible plating salts.

While this article was in the press a paper on ruthenium plating by G. S. Reddy and P. Taimsalu was presented at the Institute of Metal Finishing Annual Technical Conference at Scarborough. The plating bath described was based on the ammonium salt of the same ruthenium anion as that detailed here, and ammonium sulphamate was used as the addition agent instead of ammonium formate.

References

- 1 H. C. Angus, Electrodeposition of Rhodium and Ruthenium for Slip-Ring Surfaces, *Trans. Inst. Metal Finish.*, 1965, **43**, 135
- 2 F. H. Reid and J. C. Blake, Electrodeposition of Ruthenium, *Trans. Inst. Metal Finish.*, 1961, **38**, 45
- 3 L. Brizard, *Compt. rend.*, 1896, **123**, 182; *Ann. Chim. Phys.*, 1900, **21**, (7), 311
- 4 M. J. Cleare and W. P. Griffith, Binuclear Nitrido-complexes of Ruthenium, *Chem. Commun.*, 1968, 1302
- 5 A. C. Skapski et al., *Chem. Commun.*, 1969, in the press
- 6 Johnson Matthey British Patent Appln 56634/68