

Bright Platinum Plating

A NEW ELECTROLYTE YIELDING HEAVY DEPOSITS

By N. Hopkin, B.Sc., and L. F. Wilson, Ph.D.

This article, a communication from the Johnson Matthey Research Laboratories, describes the development of a stable platinum plating bath capable of producing heavy and bright deposits on a wide range of base metals. This bath has been given the name DNS Platinum Plating Solution.

About thirty years ago a great deal of interest was being taken in platinum plating, and a number of papers and patent specifications appeared describing improved electrolytes and their methods of operation. Two of these baths have since been employed to a limited extent, although it has been well understood that both suffered from shortcomings of one kind or another. Very little work has been done in the intervening years to improve this situation.

A factor of much importance in diverting attention away from platinum as an electrodeposit was the introduction, shortly after the development of the newer electrolytes, of a successful rhodium plating process. Rhodium seemed to offer all the desirable properties of platinum—complete freedom from tarnish and good reflectivity—while it could be readily plated from a stable bath which yielded an exceptionally hard and wear-resistant deposit. Rhodium plating therefore became firmly established, more particularly in electronic applications where a reliable and stable contact surface is essential.

None the less platinum still has considerable usefulness in electrodeposited form, and during the last year or two it has again attracted attention. In the first place, the greatly increased use of electrodeposited noble metals in light duty contact applications has brought about a re-examination of the properties and relative merits of gold, rhodium, palladium and platinum that affect

contact performance. Secondly, platinum deposited electrolytically on to metals such as titanium and tantalum has been found to provide a particularly valuable material for use as electrodes, both in cathodic protection and in electrochemical production methods.

It was felt that existing electrolytes were inadequate to meet the needs of these newer developments, and the authors therefore undertook an investigation designed if possible to provide a more reliable platinum bath from which heavy, coherent deposits could be obtained, preferably bright at all thicknesses. Such an electrolyte has in fact been developed, and found to be satisfactory in prolonged laboratory and plating shop tests.

Disadvantages of Existing Electrolytes

The two baths hitherto operated on a commercial scale are based respectively on diammino-dinitrito-platinum and sodium hexahydroxy-platinate.

The diammino-dinitrito platinum bath, introduced by Keitel and Zschiegner (1), comprises this compound, $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, sometimes referred to as platinum "P" salt, together with ammonium nitrate and sodium nitrite, in a dilute solution of ammonia. It suffers from several disadvantages. It is operated at a high temperature, around 95°C, and frequent additions of ammonia are necessary to replace losses due to evaporation. The concentration of nitrite ions tends to

rise, suppressing the dissociation of the platinum complex and causing a decrease in current efficiency. At times, in fact, the current efficiency may fall to zero, and treatment with ammonium nitrate, followed by vigorous boiling, is necessary to restore normal operation. Further, only "flash" deposits can be produced readily; if thicker deposits are required the work must be removed and scratch brushed at intervals, and the resulting deposits are not bright.

The Powell and Scott bath (2) consists of sodium hexahydroxy platinate, $\text{Na}_2\text{Pt}(\text{OH})_6$, $2\text{H}_2\text{O}$, dissolved in dilute sodium hydroxide. It too has disadvantages. As the bath is alkaline it absorbs carbon dioxide from the atmosphere; caustic soda must therefore be added from time to time, with a consequent build-up of sodium carbonate in the bath. It is sometimes difficult to obtain consistent results from this bath, and very careful control of plating conditions is always necessary. It is suitable only for deposits up to about 0.0001 inch in thickness, heavier deposits tending to be rough and dull and liable to chip away from the base metal.

The only other platinum bath that has been described in recent years is that developed by Atkinson (3) consisting of chlorplatinic acid, H_2PtCl_6 , dissolved in hydrochloric acid. This bath, on account of its unusually high acid content, is suitable only for the deposition of platinum on to noble metals, while its high temperature of operation and the serious difficulty of controlling agitation have so far precluded its use on a commercial scale.

Deposition from Complex Nitritoplatinites

Early in the investigation attempts were made to produce electrodeposits from a wide range of platinum compounds. The only promising results were obtained from solutions of complex nitritoplatinites, of general formula $\text{K}_2\text{Pt}(\text{NO}_2)_a\text{X}_{4-a}$ where X represents an anion, e.g. chloride, sulphate.

Little is known of the preparation and properties of complex nitritoplatinites and an

extensive study was begun of the chemistry of these compounds. A large number of compounds of this general type were prepared, including:

$\text{K}_2\text{Pt}(\text{NO}_2)_3\text{Cl}$	Potassium chloro-trinitroplatinite
$\text{K}_2\text{Pt}(\text{NO}_2)_2\text{Cl}_2$	Potassium dichloro-dinitroplatinite
$\text{K}_2\text{Pt}(\text{NO}_2)\text{Cl}_3$	Potassium trichloro-nitroplatinite
$\text{K}_2\text{Pt}(\text{NO}_2)_2\text{SO}_4$	Potassium sulphato-dinitroplatinite

The corresponding perchlorato-nitritoplatinites were also prepared, as were the sulphato-dinitritoplatinites of sodium, ammonium, lithium, magnesium, aluminium, nickel, and zinc. Further compounds prepared and studied were the potassium dinitritoplatinite salts with acetate, borate, tartrate, citrate, fluoborate, phosphate, sulphate and sulphonilate radicals.

Practically all of these compounds in solution yielded electrodeposits of good quality on a laboratory scale, with cathode efficiencies of the order of 10 to 15 per cent. Plating tests were carried out on 1 inch square copper specimens, degreased in trichlorethylene and electrolytically cleaned in an alkali phosphate solution. Operating conditions were 5 amp/sq. ft. and 40°C ; the platinum concentration was 10 g/l and platinum anodes were used. The pH of all solutions was adjusted to below 2 with sulphuric acid.

Extended plating tests were then carried out to establish the working life of the solutions, the platinum concentration being maintained by daily addition of a concentrated solution of the platinum compound. In a number of cases the solutions darkened rapidly during use, and after a time either cracked, or rough and powdery deposits were produced. In other cases, however, plating was continued until a turnover of more than 500 per cent of the initial platinum content had been achieved.

Of all the compounds investigated it was found that while sodium and potassium sulphato-dinitritoplatinites gave good results a solution containing sulphato-dinitritoplatinous acid, $\text{H}_2\text{Pt}(\text{NO}_2)_2\text{SO}_4$ gave optimum

results. A solution of this compound has now been prepared for commercial use under the name DNS Platinum Plating Solution and patent applications covering baths of this type have been filed in a number of countries.

Plating Conditions

Good deposits are obtained from the new bath with a platinum concentration above 4 g/l. Below this figure the plates are uneven and dark in appearance. The concentration recommended for general use is 5 g/l. Platinum anodes, which are completely insoluble, are used and the concentration of platinum in solution is maintained by addition of a concentrated solution of DNS as necessary.

The pH of the solution has a marked effect on the plating properties. Above pH=2, black powdery deposits are obtained and there is heavy gassing at the cathode. Below this value satisfactory deposits are produced and variation of the pH below 2 leads to only slight changes in current efficiency.

Bright plates are produced with current densities up to 25 amp/sq. ft., but cracking occurs above about 20 amp/sq. ft. At 10 amp/sq. ft. there is no evidence of cracking, but a current density of 5 amp/sq. ft. is recommended for building up heavy deposits.

If the temperature of the bath is below 25°C the deposits may be rough and have a "frosted" appearance, but in the range 30° to 70° the smooth bright character of the deposits remains unchanged. The deposition rate at 50°C is 0.0001 inch in 2 hours at 5 amp/sq.ft., which is ideal for general use, though for fast plating this time can be reduced to 30 minutes using a 15 g/l bath at 20 amp/sq. ft.

Despite the low cathode efficiency of the bath no gassing occurs, making agitation unnecessary and removing the danger of porosity due to gas pitting. There is a tend-

ency for a slight precipitate to form in a new bath and after a few days' operation the solution may need to be filtered. During use the bath gradually darkens to an orange-red colour but this has no effect on plating.

Platinum from DNS solution can be deposited successfully on to copper, brass, silver, nickel, lead and titanium. Owing to the acidity of the bath it cannot be used to plate directly on to iron, tin, zinc, or cadmium, and with these metals an undercoat of nickel or silver is needed.

Character of Deposits

The deposits from the new bath are exceptionally bright and lustrous at all thicknesses. Electrographic tests have shown that deposits up to 0.0005 inch on polished copper are free from porosity, but that above 0.001 inch deposits are liable to show cracking. However, on etched copper surfaces, deposits in the range 0.001 to 0.002 inch can be prepared in which the cracking is much less severe than corresponding deposits on highly polished surfaces. Microhardness tests on deposits give values of 400 to 450 V.P.N.

Plates 0.0001 and 0.0003-inch in thickness, on polished copper, corrosion tested in 25 per cent nitric acid, remain unattacked for four and sixteen hours respectively. Similar plates exposed over a 5 per cent sodium sulphide solution for one week remain unattacked.

The advantages of the DNS bath may be summarised as follows:

1. The deposits are bright and smooth and no polishing is necessary.
2. Deposits may readily be obtained up to 0.001 inch in thickness.
3. The bath is stable, gives consistent results, and does not deteriorate on standing.
4. The bath can be used for plating on base metals.

References

- | | | |
|---|--------------------------------------|--|
| 1 | C. W. Keitel and H. E. Zschiegner .. | <i>Trans. Electrochem. Soc.</i> , 1931, 59, 273 |
| 2 | A. R. Powell and A. W. Scott .. | B.P. 363, 569, 1931 |
| 3 | R. H. Atkinson | <i>Trans. Inst. Met. Finishing</i> , 1958, 36, 7 |