Immersion Plating of Palladium

AN ECONOMIC PROCESS FOR THE DEPOSITION OF THIN TARNISH-RESISTANT COATINGS

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The advantages gained from the inert properties of electrodeposited coatings of the platinum group metals as a means of providing tarnish protection on silver and base metals have for long been recognised and their use—particularly in the case of rhodium—has become widely established. Electrodeposited platinum and palladium have also been successfully employed in the telecommunications industry and elsewhere.

With the development of printed circuits, however, a need has arisen for a non-electrolytic method of deposition of these metals, more particularly because of the difficulties in making electrical connections to isolated parts of such circuits.

Palladium, with its comparatively low cost per unit weight and relatively low density, is easily the least expensive of the platinum group metals and is only about half as expensive as gold. The immersion palladium plating process described here combines this low cost with the most economic method of obtaining a thin tarnish-resistant coating. This non-electrolytic method merely involves the immersion of the part to be coated in the palladium solution.

The development of an immersion palladium solution followed from the examination of the dinitrito-sulphato complexes of the platinum metals. One of these compounds, designated DNS Platinum, has already been reported to provide a much improved electrolytic platinum plating solution which is now in commercial use. (N. Hopkin and L. F. Wilson, *Platinum Metals Rev.*, 1960, **4**, 56).

The DNS Immersion Palladium bath is based on a solution of the complex dinitrito-sulphato-palladous acid, $H_2Pd(NO_2)_2SO_4$, and patent applications covering solutions of this type have been filed in a number of countries.

The terminology covering metallic deposition from aqueous solutions without the use of an external e.m.f. is not yet clearly defined. The process described here is, however, based on the simple mechanism of chemical replacement. The favourable position in the electrochemical series occupied by the platinum group metals is of particular advantage in a process of this type. Moreover, this type of bath offers a number of advantages: it demands the minimum of chemical control and special skill, deposition ceases once the maximum thickness has been applied, and the risk of a costly error due to the production of inordinately thick deposits is eliminated. Indiscriminate deposition, inevitable with simple chemical reduction techniques, does not occur.

Method of Use

In keeping with the nature of the palladium deposition technique, the pre-treatment processes are all non-electrolytic. As with electrolytic deposition, however, the parts must be clean and free from grease before the immersion coating is applied. With large components, or large numbers of small components, the degreasing stage is best carried out either by immersion in hot trichlorethylene or by suspension in the vapour formed above the boiling solution.

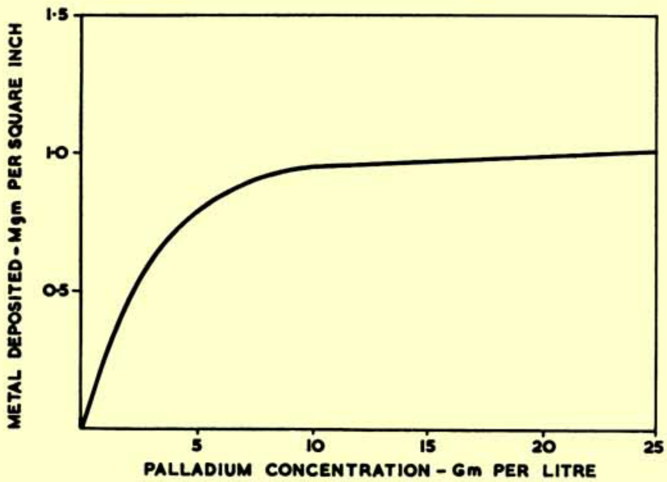

Fig. 1 The rate of deposition of palladium depends in part upon the metal concentration in the solution. An initial concentration of 10 grams per litre is recommended. (Deposition time 30 minutes; temperature 30°C)

This stage is followed by immersion in hot caustic soda and by rinsing in de-ionised water, prior to immersion in the DNS palladium solution. With printed circuits these techniques are generally too drastic, and scouring with white chalk or pumice powder will degrease and remove any oxide film from the copper tracks. Rinsing in de-ionised water is recommended before immersion in the palladium solution, which can be contained in glass or polythene vessels.

When small numbers of intricate parts are to be coated it is advantageous to stir the components with a glass rod to make sure that all surfaces are covered by a film of solution. For larger quantities, the solution is suitable for use in a plating barrel.

Masking of areas that do not require plating can be carried out using a chlorinated rubber paint, but the extra costs involved in this procedure rarely make it economic.

The DNS palladium immersion solution is supplied as a concentrate and needs merely to be diluted with de-ionised water to a concentration of 10 g/l to form the plating bath.

Rate of Deposition

This solution will give thin replacement deposits on many basis metals, but the rate of deposition depends on several factors.

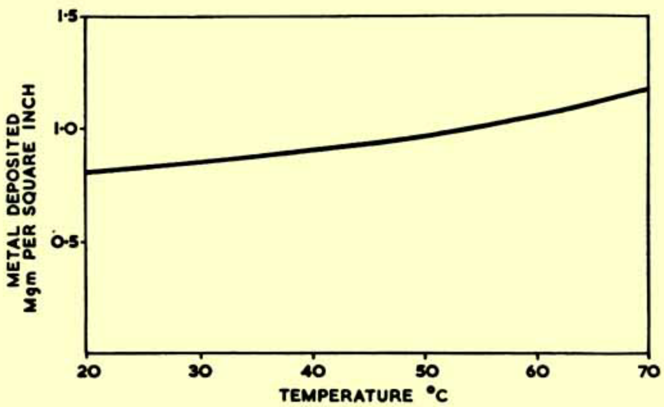

Fig. 2 Rate of deposition is almost independent of the temperature of the solution and the bath can be operated successfully at room temperature. (Deposition time 30 minutes; concentration 10 grams per litre)

The farther the base metal is from palladium in the electrochemical series, the faster will be the deposition rate, as is to be expected from the chemical replacement mechanism. The concentration of palladium in the solution will also affect the deposition rate; this is illustrated in Fig. 1.

Variation of deposition rate with temperature is shown in Fig. 2. It will be seen that the variation over the temperature range 30° to 70°C is not of any significance. In fact for all practical purposes the bath can be worked successfully at room temperature.

As deposition proceeds, less basis metal is exposed and the rate of deposition falls. Thus the rate of deposition is an inverse function of thickness of metal already deposited.

Replenishment of the immersion solution is not worth while because of the inevitable build-up of contaminants while the bath is in operation. The 10 g/l solution can be economically worked until the plating rate has fallen by half, by which time 90 per cent of the palladium has been deposited. The table shows the amount of metal deposited on various basis materials, from a fresh solution, in 30 minutes at room temperature.

Properties of the Deposit

As is typical of replacement deposits, that obtained from DNS electroless palladium is not completely pore-free and cannot therefore be considered to give indefinite protection from corrosion. It does, however, provide a surprisingly high order of tarnish resistance.

Thickness of Palladium Deposited in 30 Minutes

Basis Metal	Thickness of Deposit: mgm per sq. inch	Thickness of Deposit: inch
Copper ..	1.00	0.00005
Beryllium copper	2.02	0.000011
Brass	2.00	0.000011
Phosphor bronze	1.5	0.000008
Fine silver ..	1.15	0.000006
Standard silver	1.3	0.000007
Nickel-silver ..	1.5	0.000008
Mild steel ..	2.6	0.000014

Silver contacts, immersion plated with palladium, have remained untarnished for several months in an atmosphere that produced a tarnish film on unprotected silver within two weeks. The solderability of immersion palladium coated printed circuits was unimpaired after prolonged exposure in a similar atmosphere.

Provided that the basis metal is itself bright, the palladium deposited will also be bright and lustrous. Adhesion of the deposit is excellent.

In producing a deposit by a replacement mechanism no measurable change is observed in the dimensions of the object plated. This is of particular advantage in plating flush-bonded printed circuits. Since the deposit is thin there is insufficient stress built up in it to cause mechanical trouble due to cracking and exfoliation, yet it is sufficiently hard to provide a durable film. Unlike gold, palladium does not exhibit the high rate of diffusion into certain base metals and surface contamination from this cause does not occur.

Applications

Several important applications are envisaged. Because the deposit is readily solderable—even after prolonged storage—it is of considerable interest in the printed circuit field. In this type of application it can be used either as a tarnish-inhibiting process to facilitate soldering after storage or as a means of improving contact performance.

It is also of use as a general tarnish-inhibitor for metal components; because it will deposit readily on silver it may be applied to silver contacts to prevent tarnishing between assembly and commissioning, without the need to remove the deposit when the equipment goes into service. It may also find use on base metal contacts in telecommunications engineering.