

# Tin-Palladium Catalysts for Electroless Plating

## THEIR WIDESPREAD USE DURING THE COATING OF NON-CONDUCTING SUBSTRATES

By Gerald A. Krulik

Enthone Incorporated, Bridgeview, Illinois

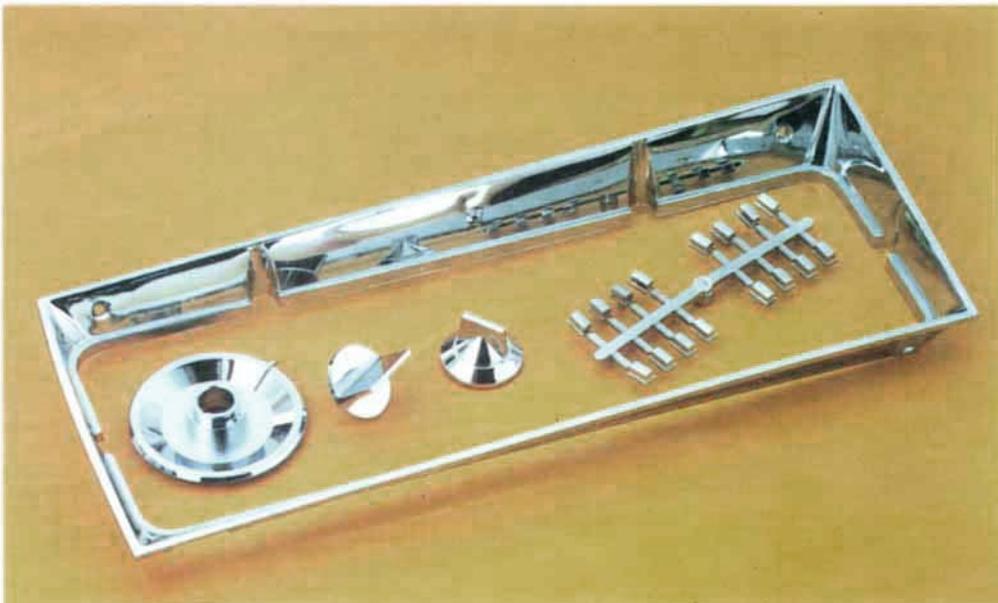
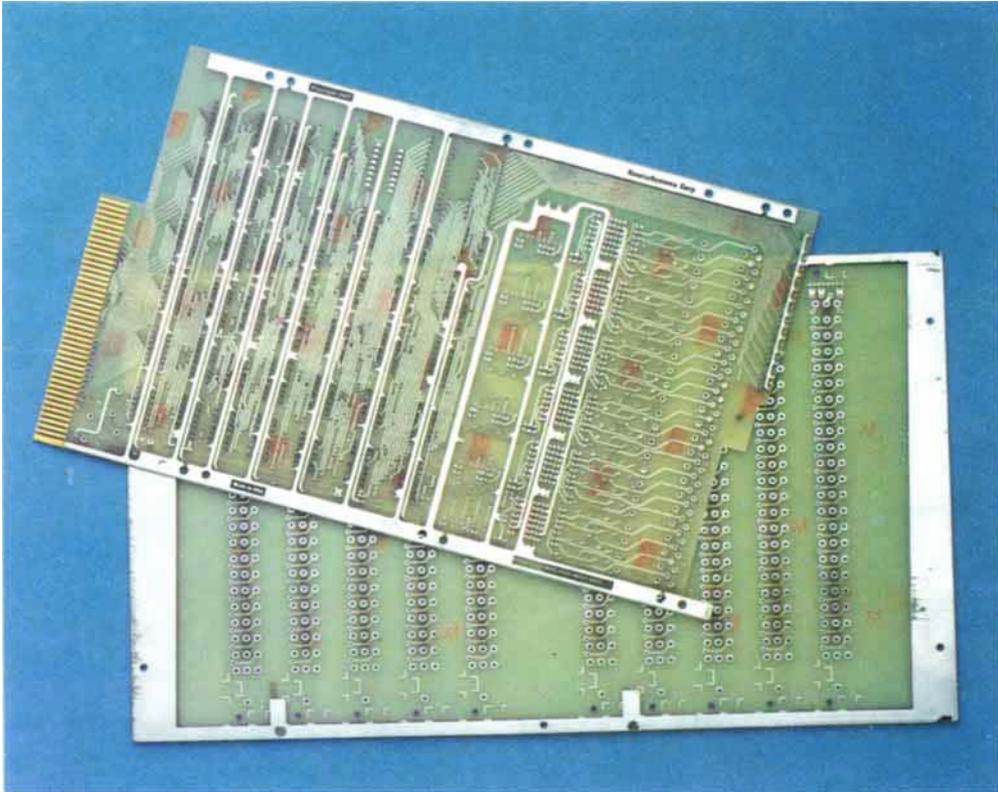
*The application of electroless plating as a surface coating technique for producing both functional and decorative finishes has increased substantially with the growth in the requirement for printed circuit boards, and with the widespread use of plastics for so many purposes. During the plating process a thin layer of catalyst is applied to the dielectric surface and a layer of metal, generally copper or nickel, is then electrolessly plated on top. The versatility and cost-effectiveness of tin-palladium catalysts have resulted in their almost universal use.*

Electroless plating, as a surface finishing technique, has been known for more than a century (1), but only in the last 20 to 30 years have practical commercial processes been developed for plating on a large scale. It is a distinct metal finishing process which has some of the features of both electroplating and immersion plating. However, electroless plating differs from conventional plating because a free electron source is not used to reduce the metal ions to a metal coating. Likewise, it differs from immersion coating in which a dissolved metal ion replaces a surface metal atom through an oxidation/reduction reaction with a metal object placed in the solution. Electroless plating uses instead a dissolved reducing agent to reduce the metal ions to the metallic state on the object to be coated. This reduction takes place only at a solid/liquid catalytic interface.

No dissolution of the object nor use of electric current is necessary. This means that electrical non-conductors or dielectric surfaces can be metal coated at ambient temperatures using simple aqueous solutions.

Until the 1950s the materials used for electroless deposition were mainly silver and copper. They were used mostly for making silver mirrors and for bronzing baby shoes and other decorative objects. In more recent years, practical electroless nickel and copper baths have been developed and used on a large scale. The use of electroless plating has increased concurrently with the growth of the printed circuit market and the growth of the use of plastics in modern life. The process is the only practical method of producing complex electrical circuits on plastic printed circuit boards. In addition electroless plating on plastics allows further coating with decorative electroplating processes to simulate the appearance of metal at lower cost and weight. Plastic parts which have been catalysed, electrolessly plated, and electrolytically plated are illustrated in Figure 1.

For the purpose of this paper, we will concentrate on electroless deposition on non-metallic substrates. Electroless deposition on metals is mainly confined to electroless nickel coatings used for functional applications. It normally proceeds without too much of a problem, at temperatures of 70 to 95°C, although a catalyst is needed on some metals. For example, when electroless nickel is plated on copper or brass, the part must be dipped in a dilute solution of palladium chloride. The palladium chloride is reduced to palladium metal which then acts as a catalyst to initiate



**Fig. 1** Epoxy-glass laminate printed circuit boards which have been catalysed, electroless copper plated, and further processed (above). Acrylonitrile-butadiene-styrene plastic parts which were catalysed, electroless nickel plated, and electrolytically plated with copper, nickel, and chromium for decorative purposes (below). The large part is an automobile headlight housing

Table I					
Comparison of Catalytic Activity of Selected Metals					
Metal	$-\log i_0^*$ (A/cm <sup>2</sup> )	Relative** H <sub>2</sub> evolution	Cost,*** U.S.\$/mole	Relative cost/mole	Relative cost/ unit H <sub>2</sub> evolution
Palladium	3.0	1.0	355	1.0	1.0
Platinum	3.1	0.78	2600	7.3	9.4
Rhodium	3.6	0.23	2060	5.8	25.2
Iridium	3.7	0.19	5125	14.4	75.8
Nickel	5.2	$5.1 \times 10^{-3}$	0.45	$1.3 \times 10^{-3}$	0.25
Gold	5.4	$4.1 \times 10^{-3}$	2625	7.4	1800
Silver	5.9	$1.3 \times 10^{-3}$	36	0.1	76.9
Copper	6.3	$4.1 \times 10^{-4}$	0.14	$3.7 \times 10^{-4}$	0.9

\* Exchange current density for the hydrogen evolution reaction

\*\* For a monolayer of metal

\*\*\*Based on the following prices (U.S. \$ per ounce): Palladium 100; Platinum 400; Rhodium 600; Iridium 800; Nickel 0.22; Gold 400; Silver 10; Copper 0.06

the deposition of the electroless nickel. The electroless nickel itself then functions as a continuously renewed autocatalytic film and the process of electroless nickel deposition continues until the part is removed from the solution.

Typical electroless copper solutions consist of copper sulphate, a chelating agent, sodium hydroxide and formaldehyde, plus various stabilisers and addition agents, and operate at 20 to 55°C. Room temperature (20 to 40°C) electroless nickel solutions, consist of nickel salts, chelators, ammonia or caustic, and sodium hypophosphite, together with various addition agents and stabilisers. They are used to plate on dielectrics, instead of hot (70 to 95°C) nickel solutions.

Electroless metal formulations can be prepared which will deposit metal on any dielectric, whether catalysed or not. However, such formulations merely encapsulate the whole object and rarely give good adherent deposits. Such processes also encapsulate everything they are contained in, and being very unstable, they rapidly break down, so are expensive to use and to maintain.

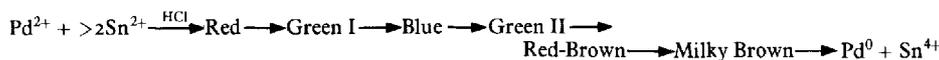
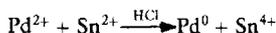
Modern electroless plating solutions are much more stable and will not break down to

any extent in the absence of a catalyst. Electroless plating depends on the integrated processes of cleaning and/or etching, neutralising, catalysing, activating, and electroless plating the dielectric surface (2). In principle, any dielectric can be coated with electroless metal. In practice, the majority of materials plated are acrylonitrile-butadiene-styrene (ABS), polyphenylenoxide-butadiene-styrene, ABS-polycarbonate, epoxy-glass laminates, polysulphone-glass laminates, ceramics, diamonds, and a few other dielectric materials.

Different processes are needed for each substrate material. However, they all share in common the need for a good catalyst. During the process of plating, a thin layer of the electroless plating catalyst is applied to the part. The part is then immersed in the electroless plating solution and a layer of nickel or copper plates out on the surface of the catalyst. The catalyst is thus used only once to initiate the plating and is then covered by the continuous build-up of the electroless metal film. This is a rare example of a throw-away metal catalyst, because the catalyst cannot be recovered unless the plated component is scrapped.

Many metals other than palladium have been used or proposed in the patent literature, these

**The Reduction of Palladium (II) is Greatly Retarded  
in the Presence of Excess Tin (II)**



include, for example, platinum, rhodium, iridium, osmium, ruthenium, copper, nickel and silver (3 a-c). The most reactive catalysts seem to be the ones that are most active for dehydrogenation reactions. Electroless plating can be viewed as a dehydrogenation reaction since hydrogen is evolved simultaneously with metal reduction. The material of choice for most present day commercial catalysts is palladium.

Table I shows a listing of various catalytic metals. They are ranked in order of their exchange current density for the hydrogen gas evolution reaction (4), and palladium is by far the most active of the metals listed. When ranked in order of their cost, it is found that palladium is much more cost effective than any metal except copper and nickel. These latter two metals are rarely used because much greater amounts are needed to get the same catalytic effect, and neither gives as stable a catalytic coating as palladium.

Palladium chloride cannot be used by itself on dielectric surfaces because only palladium metal is catalytic for electroless plating. However stannous chloride is an excellent reducing agent for palladium and has long been used when coating non-conductive items.

The original two-step catalyst process used the combination of a soak in a hydrochloric acid-stannous chloride solution followed by a soak in a palladium chloride-hydrochloric acid solution. The stannous chloride served to wet the surface with a uniform layer of a reducing agent. An intermediate water rinse converted it to an insoluble, hydrous stannous oxychloride coating. Upon dipping in the palladium chloride solution, the palladium chloride was reduced to metallic palladium and bound to the surface.

Around 1960 it was discovered that a stable,

one step catalyst bath could be prepared by combining the stannous and palladium chlorides in specific ratios (5). This single step, tin-palladium catalyst is now almost universally used. The major users are the plating on plastics and the printed circuit industries. In the U.S. the plating on plastics industry coated approximately  $10^7$  square metres and the printed circuit industry processed about  $7 \times 10^6$  square metres, in the year 1977 (2).

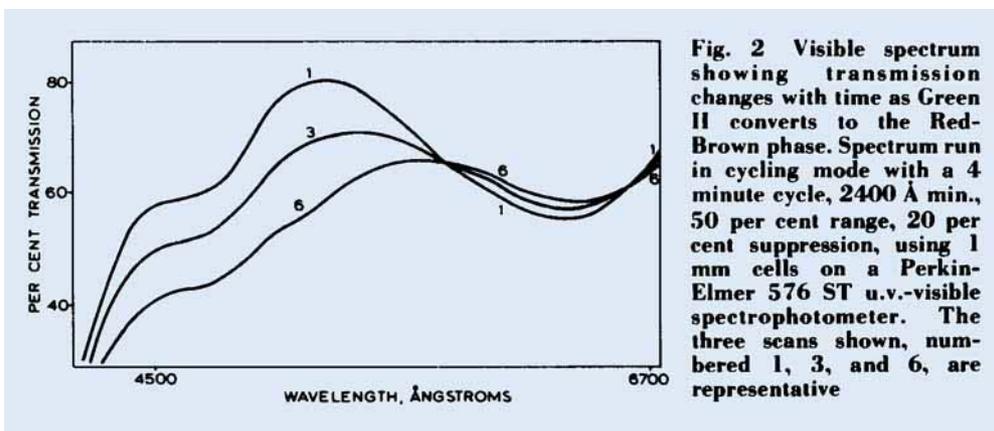
The actual working catalyst concentration on a dielectric is about 1 to  $5 \times 10^{-6}$  g/cm<sup>2</sup> of palladium and 5 to  $20 \times 10^{-6}$  g/cm<sup>2</sup> of tin. Total usage in the U.S.A. is estimated to be at least 250 kilograms of palladium and 10,000 kilograms of tin per year.

### Tin-Palladium Chemistry

The tin-palladium catalyst is quite complex and has been the subject of extensive research and study. The classical reaction is the equimolar reduction of palladium(II) by tin(II) in hydrochloric acid. Shipley first discovered that a large excess of the stannous chloride reducing agent had the unexpected property of producing a stable catalytic solution instead of accelerating the reductive precipitation of palladium (5). The Scheme above shows the successive colour phases obtainable with appropriate ratios of tin to palladium.

Commercial catalysts consist of the stabilised red-brown phase. All of the other coloured solutions are only partially stable and are indifferent catalysts.

The precise identity of the coloured phases is still debatable. Palladium-tin complexes are so labile that few have been isolated. The analogous platinum(II)-tin(II) system has been well studied (6). Here different complexes are



**Fig. 2** Visible spectrum showing transmission changes with time as Green II converts to the Red-Brown phase. Spectrum run in cycling mode with a 4 minute cycle, 2400 Å min., 50 per cent range, 20 per cent suppression, using 1 mm cells on a Perkin-Elmer 576 ST u.v.-visible spectrophotometer. The three scans shown, numbered 1, 3, and 6, are representative

formed by successive substitution and isomerisation of  $\text{SnCl}_3^-$  ligands onto  $\text{PtCl}_4^{2-}$ . An actual direct comparison with palladium cannot be made due to the large number of discrete platinum complexes reported. These range from  $\text{PtCl}_3(\text{SnCl}_3)^{2-}$  to  $\text{Pt}_3(\text{SnCl}_3)_8^{2-}$ .

As noted above, commercial catalysts consist of the red-brown coloured phase, stabilised by various means. In general, high ratios of tin(II) retard the precipitation of palladium(o). Commercial formulations have a range of 20 to 125 molar excess of tin over palladium. The tin-palladium complex rapidly decomposes to palladium(o) and tin(IV) whenever attempts are made to isolate the active catalyst by removing the excess tin. The lack of stability combined with the extremely high optical density of the solution at low palladium concentrations has led to a number of theories. The catalyst has been claimed to be a complex, a hetero-nuclear absorption-transfer complex, a colloid, and even a "semi-colloid". Various formulas have been proposed for the complex. The colloid has been said to be palladium(o), palladium(o) surrounded by a shell of tin(IV), a palladium-tin alloy, and so forth.

Representative spectral curves for the transition from the Green II to red-brown palladium-tin species are shown in Figure 2. This is illustrative of the lability of the palladium-tin species. Most methods of analytical chemistry have been employed to study the catalyst. These have included electrochemistry, electron

spectroscopy for chemical analysis, Mössbauer spectroscopy, Rutherford scattering, X-ray diffraction, light scattering, u.v.-visible spectroscopy, scanning electron microscopy, and transmission electron microscopy. The best current opinion is that the catalyst is a palladium metal colloid of very small particle size, stabilised against precipitation and agglomeration by excess tin on its surface (7).

### Catalyst Preparation

It is relatively easy to make an electroless plating catalyst. It is much less easy to make an optimised, high activity catalyst which will be stable for long periods during commercial use. Some of the factors which have to be considered are listed in Table II.

Very little information on catalyst synthesis is available except in the patent literature. The first U.S. patent, to C. R. Shipley in 1961, has been followed by close to three dozen additional patents (7). Most catalysts are produced by reaction in concentrated hydrochloric acid although a newer synthesis method employs a hydrous stannous chloride melt.

The most basic objective is to make the red-brown active catalyst. A typical concentrate may have a tin:palladium ratio of 50:1. Upon mixing a  $\text{PdCl}_2$  solution with the  $\text{SnCl}_2$  solution, the reaction proceeds very rapidly to the Green II stage. Further reaction to the red-brown stage is slow unless the solution is heated, typically to 60 to 90°C. However this is

not the best method since long heating times are needed which cause partial reduction to continue to the inactive colloidal (milky brown) stage.

A better method is the two step procedure. The object is to form the active catalyst as rapidly as possible, and then stop the reaction at that stage. A typical example would be to use an initial tin:palladium ratio of 10:1. The active catalyst forms rapidly even at 60°C. After all of the Green II species is converted, and before an appreciable amount of inactive material forms, the reaction is quenched by adding the rest of the stannous chloride.

A large number of additives have been used to modify various properties of the catalyst such as activity and air stability (3, a-c). All of these syntheses have been based on hydrochloric acid; use of other acids such as sulphuric acid has given poor catalysts.

The newer method of production is based on a melt of stannous chloride dihydrate rather than an aqueous acid solution (7).  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is not normally thought of as a solvent, but at 37.7°C. it dissolves in its own water of crystallisation. The clear hydrous melt is an excellent, highly acidic solvent for many organic and inorganic compounds. This procedure allows a much broader scope for modifying the catalyst itself in the form of a concentrate. The reacted material can merely be allowed to cool to room temperature to give a stable solid. The concentrate can be easily dissolved in hydrochloric acid to give the equivalent of a normal acid synthesis solution. It can also be dissolved in a wide variety of aqueous chloride, organic acid, mixed acid, or even polar organic liquids to make catalysts for special uses.

The reactions of  $\text{PdCl}_2$  in a hydrous stannous chloride melt are generally similar to those in acidic solution. The same series of colour phases occur. The speed of reaction is much greater due to the highly concentrated nature of the melt. The tin concentration is 12 molar or above, compared to 2 molar or less in hydrochloric acid solution. There is the same preference for a two step synthesis rather than a

Table II  
**Practical Problems in  
Plating Catalyst Optimisation**

Synthesis procedure
Concentrate stability
Palladium film or precipitate formation
Stannous oxidation
Activity changes
Working bath stability
Working bath activity
Polymer absorption
Acceleration behaviour
Electroless deposition activity

one step synthesis. However, a poor catalyst is formed when only  $\text{PdCl}_2$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  are used. It was found that an additional amount of some other halide salt must be added in a minimum quantity of twice the molarity of the palladium.

Extensive work has been done using  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{MgCl}_2$ ,  $\text{LaCl}_3$ ,  $\text{CrCl}_3$ , etc. as the moderating salt. Even better results occur when a double salt of palladium is used as the starting material,  $\text{K}_2\text{PdCl}_4$  being one preferred compound. A much more active catalyst results when  $\text{K}_2\text{PdCl}_4$  is added to a  $\text{KCl-SnCl}_2 \cdot 2\text{H}_2\text{O}$  melt than when  $\text{PdCl}_2$  is added to the same melt. This phenomenon is also seen, but to a much lesser extent, in aqueous syntheses. It seems to be due to a competition between direct reduction of  $\text{PdCl}_2$  by  $\text{SnCl}_3^-$  and the addition of chloride ion to form  $\text{PdCl}_4^{2-}$  followed by attack by  $\text{SnCl}_3^-$ .

The basic hydrous melt catalyst will cool to a highly supercooled, room temperature solution before it finally nucleates and crystallises. The major phase consists of transparent crystals of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{KSnCl}_3 \cdot \text{H}_2\text{O}$ . Interspersed is a highly concentrated dark liquid or solid containing the palladium. This catalyst is highly stable in the absence of air oxidation. The concentrate can be formed as a liquid, paste, hard or soft solid by appropriate additions of anhydrous  $\text{SnCl}_2$ , other halides, sodium acetate, and other compounds. The major direct function of these materials is to control the amount

of free water and thus the ratio of liquid and solid phases.

## Catalyst Operation

Dielectric parts are processed through different cleaning, etching, and conditioning cycles dependent upon the type of plastic used (2). The processing cycles for plating on plastics are very different from those for printed circuits although the actual catalyst solutions can be the same regardless of the material to be plated.

A catalyst bath consists of a suitable dilution of a tin-palladium concentrate in hydrochloric acid in which the objects are simply immersed. The trend has been towards use of lower palladium concentrations, higher operating temperatures, and reduced acidities. Typical conditions of the mid 1960s were 250 mg/l of palladium in 3N hydrochloric acid at room temperature. More active, more stable modern catalysts can operate at palladium concentrations of 25 mg/l, up to temperatures of 48°C, at 0.25N hydrochloric acid.

The total chloride concentration is maintained near 3N by use of sodium chloride to retard oxidation and hydrolysis of the tin(II). The lower acidity baths are less aggressive towards copper clad printed circuit boards and towards copper oxide bonded multilayer circuit boards. A 1 to 5 minute immersion time is sufficient.

The catalysed parts are next immersed in an accelerator solution. This is a warm acidic or basic solution in which tin is soluble. It removes excess inhibitory tin, exposes the catalytic palladium metal nuclei, and may promote the reduction of any residual ionic palladium. Any weakly absorbed palladium is removed at this stage, and this helps prolong the life of the electroless plating solution.

Liquid catalyst concentrates are only used with hydrochloric acid or hydrochloric acid/sodium chloride working baths. Hydrous melt catalysts are much more versatile. Experimental catalyst baths have been prepared in pure organic solvents such as methyl ethyl ketone for use on difficult to catalyse substrates.

Excellent catalysts have been made in organic acid solutions such as lactic and glycolic. Many other special formulations are feasible.

## Conclusions

Electroless plating catalysts are still undergoing modification and improvement. While there has been some commercial testing of copper and nickel based catalysts, none have yet matched the versatility and cost-effectiveness of tin-palladium catalysts.

It is expected that the market for tin-palladium catalysts will continue to expand due to world-wide growth in electronics applications using flexible, double sided and multilayer printed circuit boards. New board materials are being developed with pretreatment processes based on them, but the catalysts employed are the same.

The plating-on-plastics industry continues actively to pursue growth through new applications such as electromagnetic interference/radio frequency interference/shielding, and through development of new and improved pretreatment processes for nylon, polysulphones, and many other less plated polymers. This should help to ensure that despite changes in the amounts of decorative and automotive plated plastics applications, the total market for these catalysts should continue to increase.

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