Observations on Porosity in Precious Metal Plating

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The demand to minimise porosity is of increased interest as precious metal prices increase and the pressure to reduce thickness increases; of course without loss of performance and deposit integrity.

Particular attention will be focussed on electronic connector applications for both Palladium-Nickel plating and Acid Hard Gold plating where some innovative developments and suggestions to minimise porosity are presented.

Standard methods and specifications for evaluating and detecting porosity are outlined and discussed.

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Introduction

This paper will focus on the root causes of porosity in Precious Metal Plating and will discuss techniques and innovations to minimise porosity.
The demand to minimise porosity is of increased interest as precious metal prices increase and the pressure to reduce thickness increases[1]; of course without loss of performance and deposit integrity.
Standard methods and specifications for evaluating and detecting porosity are outlined and discussed. Particular attention will be focussed on electronic connector applications for both Palladium-Nickel plating and Acid Hard Gold plating where some innovative developments and suggestions to minimise porosity will be presented.

Discussion

Porosity is a significant factor in any electroplated deposit.
As thickness specifications decrease, the demands placed on any plated layer increase and the process control required to achieve acceptable results becomes more intense.

There are many ways in which the plater can improve techniques and process sequence to increase the likelihood of successful results.
It should be remembered however that no matter how good the process sequence or plating processes selected the substrate material quality will ultimately have a significant effect on the final plated quality.
A poor standard substrate will invariably give poor results in porosity tests; this is particularly true as thickness specifications decrease.

Substrate Quality

This always generates a lot of discussion, but undoubtedly the substrate quality will have a significant effect on the degree of porosity of a plated layer.
Normally surface defects such as pits, craters and scratches will be underlying causes for pore sites in the finished product.
It should be noted that bright and dull surfaces may both in fact be suitable for plating pore free, but if either have significant surface defects they will fail subsequent porosity tests.

Surface defects can be induced in an otherwise `Good` surface; by the cleaning sequence that is designed to improve the surface to be plated.
Mechanical polishing generates localised heat within the crystal structure of the part, this leads to a change in the crystal lattice and subsequently `Crystallographic ` porosity, originating from lattice defects in grain boundaries of the crystal structure.

Similarly, over aggressive chemical etches can destroy a good surface by etching either too deep or too inconsistently, this can be noticed particularly with Copper alloys of Beryllium or Phosphorus; when an inconsistency in the alloy composition may lead to a localised

over etching of the copper from the matrix, creating isolated craters and corrosion pits in an otherwise good surface.
These defects can result in the sometimes random porosity often encountered in finished electroplated parts.

It should also be noted that a scratched surface does not necessarily mean that it will fail in porosity tests; what matters is how these scratches were introduced.

If they are smooth uniform scratches, with a sinusoidal wave form, with smooth walls produced from a well controlled and lubricated brushing during the forming of the part; this will not present any significant problems.
However an uneven rough edged scratch with uneven side wall texture will invariably be the site of pores often detected in straight lines; on either electrographic or chemical porosity tests.
These scratches often arise from mechanical damage to the part or by poorly maintained and controlled brushing equipment, during the connector forming operation or raw material processing.
In the Printed Circuit industry this is often traced to mechanical brushes present on many TAB plating machines, if the brushes are not `dressed` regularly then a rapid increase in porosity can often be seen.
Maintaining the brushes in a preventative maintenance schedule eliminates this problem

Pores on such badly scratched and damaged surfaces can be the result of entrapped chemicals from preceding stages or poor cleaning / rinsing prior to the initial plating stage.

A good way to avoid some of these defects is to use an inhibited electro-polish. These electro-polishing chemicals will improve the surface topography, by reducing and rounding any sharp peaks to give an overall smoother surface for subsequent electroplating without inducing any crystallographic distortion.
Generally electro-polishing will also avoid localised over-etching of the copper based material.

Poor quality of the surface finish on the base metal originates from a number of sources, but rough die segments and poor die maintenance are the principal culprits. Another common problem area is mechanical scratching from the plating line, or handling or assembly equipment.

Rinses employed to prevent contamination from process to process along the line, should be regularly observed to determine their effectiveness. Contaminated rinses will increase the likelihood of contamination, whilst spray rinses that are improperly aligned will be less effective in providing adequate rinsing.

As thickness of Gold deposits decrease so the need for close control of Surface Condition and Surface Preparation increases.

Increasing thickness of Copper, Nickel or Gold plated layers will usually improve porosity on even a poor surface.
In achieving `Pore Free` deposits at low Gold thickness the Surface Condition of the substrate material and its subsequent preparation prior to plating can be very significant.

Cleaning

Substrate preparation cannot in itself fully prepare a poor surface to enable a pore free deposit. Certain factors can however reduce the likelihood of porosity.

Mechanical cleaning should be avoided, almost all types of mechanical abrasion will increase the likelihood of pore sites developing, these can be either generated by residual polishing compound being engrained into the surface layer or not removed by subsequent electro cleaning, or by abrasive damage and crystallographic defect formation.

An effective degrease stage should always be employed on any machined parts to remove cutting oils and lubricants used in the cutting or stamping operations.
An ultrasonic clean is an added benefit and should be used where possible in particular in parts with poor rinsing / draining properties as a result of blind holes and recesses in the component design.

Chemical or Electrochemical polishes may be used effectively to enhance the surface condition by removing sharp edges and burrs from stamped parts and rounding off sharp peaks from brushed or damaged parts.
Chemical etches should be monitored carefully to avoid over etching and crater formation in alloy materials in particular where `weaker` area may be selectively attacked by the often aggressive chemicals used in such bright dips (Typically concentrated Nitric and Sulphuric Acid mixes)

In some cases for copper and copper alloys a less aggressive etches can be used to condition the surface for plating .These etches originally developed for the Printed Circuit industry can prove effective on reel to reel connector lines.

These, often proprietary, mixtures are usually based on persulphates with selected inhibitors to retard excessive chemical attack. It should be noted that the surface appearance of the copper alloy is often dulled by such chemicals, however this is usually restored when the part is subsequently Copper or Nickel Plated.

Plated Layers

Generally it can be said that any plated layer that levels out surface imperfections will reduce subsequent porosity. Typically Copper or Nickel plated layers are employed.
Nickel serves the additional function of providing a barrier layer to reduce diffusion of

Copper from the substrate material and as a result improves the service life of the finished part.

Acid Copper however has been shown to provide a better reduction in porosity than Nickel on a typical connector finish. This is thought to be because additive systems in Bright Acid Copper provide greater levelling than the additive systems employed in a typical Sulphamate Nickel used in Electronic Connectors.

To achieve the best compromise some manufacturers use a combination of Acid Copper and Sulphamate Nickel, to improve the surface finish of lower quality base materials and reduce subsequent porosity.

The Acid Copper improving the surface topography, whilst the Nickel provides the barrier layer to prevent diffusion.

Plating Bath Maintenance : e.g. Gold Plating

The condition of the Gold plating bath and process control can contribute to increased porosity. Generally speaking any form of contamination will increase the likelihood of porosity.

Organic contamination in the form of oils or grease are a prime cause as they adsorb onto the surface and produce surface defects around which pores grow , the organic material is often then entrapped in the deposit and ruptures on aging or heating.
This form of porosity is more common in Nickel plating, but often is only being noticed at the Gold Plating stage. It is important therefore when considering porosity to look at the whole system to determine the cause and effect; remembering a Nickel Plating problem can appear to be a Gold Plating problem.

Metallic contamination, Iron and Nickel in particular will increase porosity, excess of these materials increases the internal stress of the Gold deposit; this leads to the possibility of increased Stress cracking along grain boundaries with resultant porosity along these surface defects.

Current density and general operating conditions also can contribute to porosity.
Ideally a gold Plating bath should be operated not at its maximum possible Current density, but within the `safe` middle current density range.
Operating always close to the maximum Current density will mean any slight change in performance can lead to burnt deposits ,with a coarse grain size observed as `Burning / dullness` in the finished deposit.
These coarse grained deposits will have large grain boundary defects and be inherently porous.

Additive and Brightener systems employed in a modern Acid gold process will usually be sufficient to provide the best performance in terms of pore closure; but to achieve this they need to be maintained at optimum concentration.
Analytical control of the Gold Plating bath will be the obvious first step in achieving a successful product consistently.

As with any plating bath adequate filtration to remove any particulate matter from the plating line will improve porosity; debris in any plating or rinse stage will adhere to the cathode face and become the origin of a pore site.

More recent developments of Rapid Pore Closure (RPC) Additives [2] have significantly reduced the pore count at any given thickness. The action of RPC additives is explored later in this paper.

Analytical Data and Porosity

Very often corroded contacts are analysed chemically to determine the cause of porosity [3].

This analysis of course includes a microscopic "Visual" analysis that can be very helpful but additionally includes SEM (or other surface analysis methods) to generate quantitative data on chemical elements that are detected within the gold deposit.

This analysis often gives alarming results with materials such as Sodium, Sulphur, Chlorine, Silicon being common elements detected in addition to expected materials such materials as Copper , Nickel, Cobalt , Palladium, Carbon and of course Gold .
Investigations often reveal that in fact these materials (Sodium, Sulphur, Chlorine, and Silicon) are not dispersed throughout the Gold deposit nor are they "surface contaminants" as are often deduced.
In fact they originate from liquid residual material "trapped" in the deposit from earlier treatment processes at a pore site cavity that has been plated over and has "erupted" during the accelerated corrosion test to yield surface corrosion products of contamination material.
This trapped material can be electro-cleaner (often utilising Sodium Metasilicates), Nickel plating solution or Palladium Nickel electrolyte , dependent on the chemistry selected many of the elements detected can be traced to the pre-treatment line and its chemical processes.
So it seems porosity is not always as simple as a "hole" in the deposit; it can be the cause of a latent "volcano" that erupts during accelerated aging tests or, if quality control is not sufficient, porosity related issues will only become apparent in service life when a component fails.

Summary of discussion on porosity

Many factors will influence the porosity of a Gold Plated layer [4]. All of these factors will have a significant bearing on the result achieved.

Particular care should be taken in controlling,

- Substrate Quality
- Cleaning and Pretreatment
- Plated substrate layers , Cu , Ni , Au or Pd Strike
- Palladium-Nickel plating
- Gold plating
- Good housekeeping and cleanliness of the operation line are essential.

Porosity Testing

There are many different tests used to detect porosity, which range from specific "porosity tests", usually Electrographic, to less specific "corrosion" tests which are designed to expose pores by generating corrosion sites.
Corrosion tests often involve exposure to varying concentrations of Acid, Alkaline and /or corrosive fumes. (e.g. Nitric acid vapour, Sulphurous acid, Sodium Hypochlorite or Ammonia vapour) and are usually referred to as "Gas Tests".
These are defined by such bodies as ASTM[5], MIL[6] Specifications and as is becoming more prevalent a customer specific derivative designed to suit a particular technical need or service requirement. Often these are based around the ASTM and MIL Specifications.

Basically, there are two types of porosity tests; utilised electrographic testing and gas testing; these tests are detailed in the following sections…

Electrographic Testing

From the ASTM viewpoint this method is now largely obsolete with the ASTM procedure B741-95(2000) *"Standard Test Method for Porosity in Gold Coatings on Metal Substrates by Paper Electrography"* being withdrawn in 2005.
The test method covered equipment and techniques for determining porosity in gold coatings, particularly electrodeposits and clad metals used on electrical contacts.
The test method was designed to show whether the porosity level is less or greater than some value which by experience is considered by the user to be acceptable for the intended application.

The test method was suitable for flat surfaces, or with appropriate fixtures, for gently curved surfaces only and this is largely the reason why it was withdrawn, as seldom are connectors neither flat , nor of big enough area for the test to be applied sensibly.

The equipment used was usually a similar design to the *Poroprint SD Porosity Tester* supplied by Fischer Instruments, which detected porosity in a variety of coatings through to either Copper or Nickel undercoats.

It is a Paper Electrographic method and two test papers were usually utilised:

(i) Cadmium Sulphide : Specific for Copper undercoats
(ii) Nioxime : Specific for Nickel undercoats

In addition the apparatus may be used for Electrographic testing using ***Dye transfer*** also in accordance with ASTM Test B-741-90.
It is most common in Printed Circuit companies and using Cadmium Sulphide or Nioxime test (BS 4025) as it is very suitable for gold coatings (0.1 -1.25 Microns) on flat surfaces typically seen in this application.

Limitations of method

The ***substrate must be flat and Conductive***, the method is a direct contact method involving compression between two electrodes.

Benefits of electrographic test

- Fast ,easy to use
- Reproducible and reliable
- Produce an Electrograph which can be retained for reference / proof of QC testing.

The Electrographic method is still utilised as a very helpful laboratory tool where flat panels of large area are easily designed for experimental research purpose
It has been invaluable in the development of **Rapid Pore Closure (RPC)** Additives utilised in Gold Plating electrolytes.

A variation on the Paper Electrographic test is B798-95(2005) Standard Test Method for Porosity in Gold or Palladium Coatings on Metal Substrates by Gel-Bulk Electrography

This test method covers equipment and techniques for determining porosity in noble metal coatings, particularly electrodeposits and clad metals used on electrical contacts.

The test method is designed to show whether the porosity level is less or greater than some value which by experience is considered by the user to be acceptable for the intended application. Other porosity testing methods are outlined in Guide B765. Detailed critical reviews of porosity testing are also available. Other porosity test methods are B735, B741, B799, and B809.

Gas Tests utilised for detecting porosity

Gas tests usually involve exposure of the plated connector to a given atmosphere for a fixed period of time followed by a visual evaluation of any corrosion products formed during the test period.

There are many gas tests specified and the method used is decided to suit a specific application, many ASTM specifications exist and are the best reference from which to build a customer specific specification.

Some examples

B 735 – 06Standard Test Method for Porosity in Gold Coatings on Metal Substrates by Nitric Acid Vapor

This is the most common test utilized and the method covers equipment and procedures for using nitric acid vapor for determining porosity in gold coatings, greater than 0.6 m (25 in.) in thickness, particularly electrodeposits and clad metals used on electrical contacts.

The test method is designed to show whether the porosity level is less or greater than some value that, by experience, is considered by the user to be acceptable for the intended application.

Usually the exposure time in one hour, but in some instances the exposure time is increased to 2 hours and this often results in failures as the test is a vigorous severe test to detect porosity or weaknesses in the plated layer.

Palladium Nickel and Gold Porosity testing

It is clear that this is an area with many difficulties facing the connector manufacturer and the end user. There are often discussions that hinge around success of failure of the deposit in the Nitric Acid Vapour test. It should be remembered that ASTM have made the following revisions based on these concerns.

Revision of B735-05 Standard Test Method for Porosity in Gold Coatings on Metal Substrates by Nitric Acid Vapor

Amendment Initiated: 10-05-2006

The nitric acid vapour test is too severe to be used for gold coatings 0.6µm (25µin.) or less in thickness. It is also not suitable for coatings than that are less noble than gold or platinum, such as palladium and its alloys, or gold-flashed palladium and its alloys.

Gold-flashed is defined as a plated thickness of gold between 3 and 5µin

Note: It should be remembered that the Nitric Acid vapour test should NOT be used on Palladium Nickel deposits that may be attacked by oxidizing Acids.

Palladium Nickel compared to Acid Gold: Some facts

Reduced Porosity

Palladium Nickel deposits exhibit **less porosity** than a typical Acid Gold at any given thickness.
This is due to the laminar structure of Palladium Nickel [7,8,9] versus the columnar structure of an Acid Gold deposit. Porosity often occurs along grain boundaries and giving rise to greater porosity.

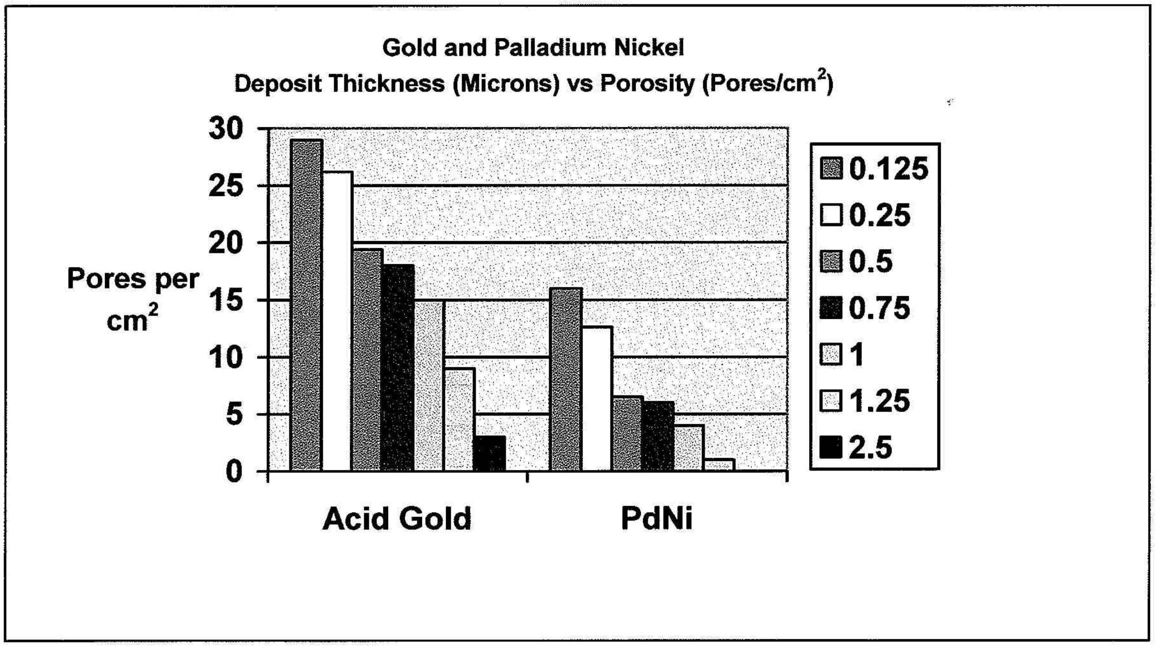


Fig 1 : Comparison of Porosity in Acid Gold vs Palladium Nickel showing superior performance of Palladium Nickel at all thicknesses.

Micro-sections of electro-deposits produced with Palladium Nickel baths together and appropriate additives have clearly demonstrated the laminar structure that can be achieved with Palladium-Nickel.

Increased Ductility

The laminar structure also explains the enhanced ductility, despite its increased hardness, of Palladium-Nickel that is noted when compared to a considerably softer Acid Gold deposit of equivalent thickness.

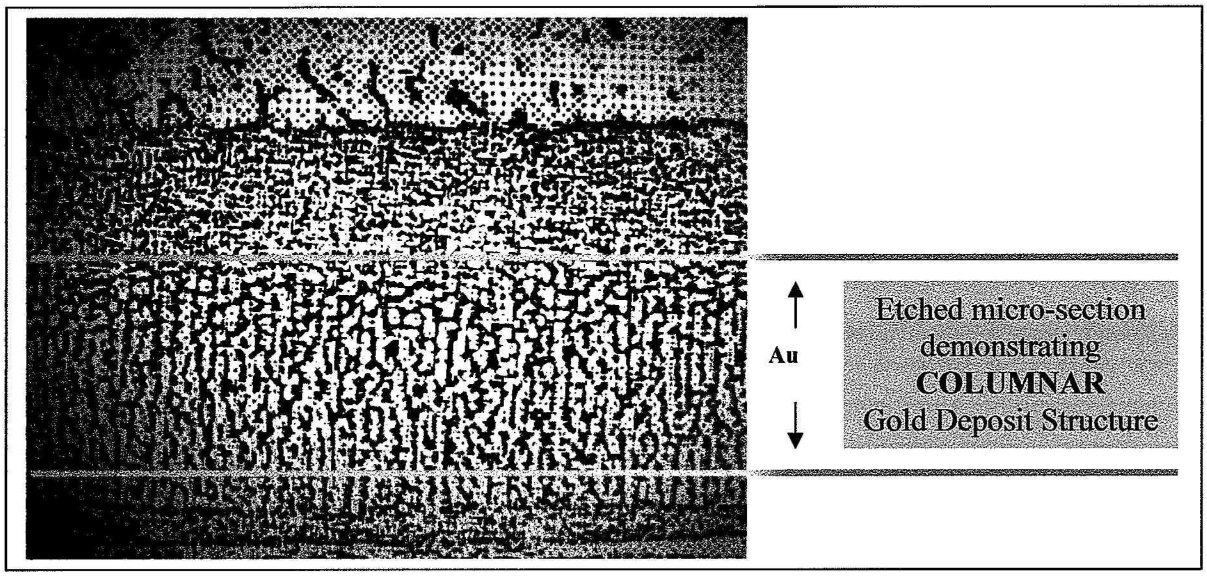


Fig 2 ***Gold Structure:***
Columnar with Grain Boundaries that are, predominantly, in the ***vertical*** *plane.*

Columnar structure invites increased porosity though its vertical grain boundaries and also this porosity is increased when any bending of the connector is carried out as the grain boundaries represent weaknesses in the deposit.

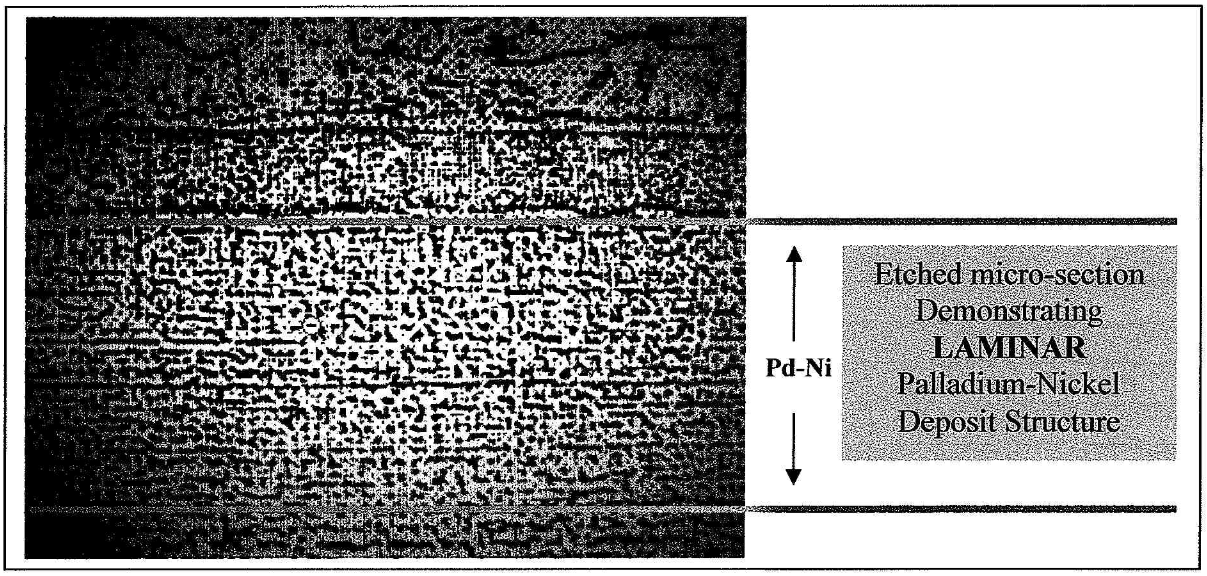


Fig 3 ***Palladium-Nickel Structure:***
Laminar structure with Grain Boundaries that are predominantly in the ***horizontal*** *plane.*

Mixed Flowing Gas Tests

Finally there are tests available that utilize a mixture of corrosive elements designed to expose porosity, these are generally under the heading of mixed gas tests, or more commonly mixed flowing gas (MFG) tests.

A MFG test will usually be applied to higher specification connectors or those which are expected to be exposed to a harsher environment, such as military or automotive connectors

B845-97(2003) Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts

The techniques described in this guide pertain to mixed flowing gas (MFG) tests containing species that are applied to evaluate devices containing electrical contacts such as slip rings, separable connectors, electromechanical relays or switch contacts.

The MFG tests described in this guide are designed to accelerate corrosive degradation processes. Connectors and contacts within closed electronic cabinets may be affected by an environment of different severity than the environment on the outside of such cabinets.

B827-05 Standard Practice for Conducting Mixed Flowing Gas (MFG) Environmental Tests

This practice provides procedures for conducting environmental tests involving exposures to controlled quantities of corrosive gas mixtures.

This practice provides for the required equipment and methods for gas, temperature, and humidity control which enable tests to be conducted in a reproducible manner.

Reproducibility is measured through the use of control coupons whose corrosion films are evaluated by mass gain, coulometry, or by various electron and X-ray beam analysis techniques.

Reproducibility can also be measured by in situ corrosion rate monitors using electrical resistance or mass/frequency change methods.

B 845 – Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts.

Other Mixed flowing gas tests to note include ANSI/EIA-364-65A and IEC 60068-2-60

In addition to make-up air and water vapor, three or four corrosive gases are typically used in MFG testing.

These pre-diluted gases are fed through mass flow meters into a mixing chamber prior to introduction into the MFG exposure chamber. The concentration of each gas can be controlled to the part per billion levels using these mass flow meters.

The gases used in the test are chlorine (Cl_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2).

The relative humidity of the gas mixture is usually maintained between 70 – 75%, sometimes as high as 95%, and the temperature between 25 - 40° C (77 - 104° F).

The duration of the test is variable, but is usually in the range of 500 hours.

Correlations need to be drawn between accelerated test exposed and long-term field exposed samples and components.

Discussion

It is the opinion of the author that, in many instances, the tests applied to electrical connectors are far too severe for the service life expectancy of the connector plated.
This is especially true for consumer goods that are never exposed to any significantly harsher environment than an air-conditioned office or home.
The biggest threat to the "in service life" of the connector is often humidity and temperature rather than exposure to a corrosive gas environment and for this reason it is felt that greater emphasis should be placed an humidity and thermal cycling as a performance or accelerated aging test.

Existing tests using corrosive gasses should be used to **detect pores,** but not directly correlated to service life prediction.

Importantly the test selected should be suitable for the coating under test and care should be taken to ensure conclusions drawn are truly valid.
This is of particular importance with the Nitric Acid test and Palladium Nickel plating where often failures are not "porosity" but simply the intact Palladium Nickel layer being "dissolved" by the Nitric Acid vapour.

Gold Plating Specifications

In addition to the testing specifications for Gold plating porosity of course there are Standards that are in place for specifying the requirements of plated layers applied [10,11].
Some basic guidelines can be seen in the specifications detailed below.

It is interesting to note that the specification most commonly quoted [12,13] is in fact an obsolete MIL-G-45204C (1993) specification that ceased to be current on 7th April 1998.

"MIL-G-45204C, dated 7 June 1983, and AMENDMENT 3, dated 9 June 1993, are hereby canceled. Users may consult the appropriate portions of AMS 2422, "Plating, Gold" and/or ASTM B488 "Electrodeposited Coatings of Gold for Engineering Uses" as possible replacements. Users are cautioned to evaluate AMS 2422 and ASTM B488 for their particular application before citing them as replacement documents".

The ASTM B488 specification that is highlighted follows very closely the original guidelines used in MIL-G-45204C

B488-01(2006) Standard Specification for Electrodeposited Coatings of Gold for Engineering Uses
This specification covers requirements for electrodeposited gold coatings that contain not less than 99.00 mass % gold and that are used for engineering applications.

Standards for Palladium Nickel

As Palladium Nickel is often utilized as a replacement for Gold plating on connectors [11,12,13] it is not uncommon to see the same tests applied to this material.

However this shows a fundamental problem in that Palladium Nickel is a very different material to Gold and it is important that specifiers understand that tests that are perfectly valid for detecting porosity in gold are grossly unfair if applied to Palladium Nickel.

It cannot be overstated that the function of the test is to expose porosity and NOT to attack perfectly good plated layers ;for this reason tests are outlined for Palladium Nickel and are defined in the relevant ASTM specification.

The tests are designed to detect porosity in Palladium Nickel deposits and the Nitric acid test is not utilized.

B 867 – 95 (Re-approved 2003) Standard Specification for Electrodeposited Coatings of Palladium-Nickel for Engineering Use.
This specification covers requirements for electrodeposited palladium-nickel coatings containing between 70 and 95 mass % of palladium metal. Composite coatings consisting of palladium-nickel and a thin gold over plate for applications involving electrical contacts are also covered.

Palladium is the lightest and least noble of the platinum group metals. Palladium-nickel is a solid solution alloy of palladium and nickel. Electroplated palladium-nickel alloys have a density between 10 and 11.5, which is substantially less than electroplated gold (17.0 to 19.3) and comparable to electroplated pure palladium (10.5 to 11.8). This yields a greater volume or thickness of coating per unit mass and, consequently, some saving of metal weight [19]. The hardness range of electrodeposited palladium-nickel compares favorably with electroplated noble metals and their alloys.

Porosity and micro cracks shall be determined by Test Methods B 741, B 798, B 799, or B 809 unless otherwise specified.

ASTM B 867–95 specifically mentions that Nitric Acid vapour tests should NOT be used for Palladium Nickel.
Despite this knowledge there are still many existing customer specifications that demand the use of Nitric acid vapour on Palladium Nickel plated connectors. This is of course

resulting in many difficult situations for connector manufacturers who often see failures despite excellent plating practices being employed.
The successes achieved are usually a result of the quality of the Gold flash plated layer[14] on top of the Palladium Nickel rather than the Palladium Nickel itself.

Some of the other tests can be used on Palladium Nickel such as the Sodium Hypochlorite vapour test, Sulphurous acid and Sulphur or Poly-sulphide based tests outlined below.

B920-01(2006) Standard Practice for Porosity in Gold and Palladium Alloy Coatings on Metal Substrates by Vapours of Sodium Hypochlorite Solution
This test practice covers equipment and methods for revealing the porosity of gold and palladium coatings, particularly electrodeposits and clad metals used on electrical contacts.
The test is suitable for coatings containing gold or 75 % by mass of palladium on substrates of copper, nickel, and their alloys, which are commonly used in electrical contacts.

B799-95(2005) Standard Test Method for Porosity in Gold and Palladium Coatings by Sulfurous Acid/Sulfur-Dioxide Vapor
This test method is designed to show whether the porosity level is less or greater than some value which by experience is considered by the user to be acceptable for the intended application.

B866-95(2003) Standard Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by Polysulfide Immersion
The test method covers equipment and methods for detecting gross defects and mechanical damage (including wear-through) in metallic coatings where the breaks in the coating penetrate down to a copper or copper alloy substrate. The method is suitable for coatings consisting of single or combined layers of any coating that does not significantly tarnish in an alkaline polysulfide solution. e.g.: gold, nickel, tin, tin-lead, and palladium, or their alloys.
B809-95(2003) Standard Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor (Flowers-of-Sulfur)
This standard covers equipment and test methods for determining the porosity of metallic coatings, where the pores penetrate down to a silver, copper, or copper-alloy substrate.
The test method is suitable for coatings consisting of single or combined layers of any coating that does not significantly tarnish in a reduced sulfur atmosphere, such as gold, nickel, tin, tin-lead, and palladium, or their alloys.

Rapid Pore Closure (RPC) Additives

A key issue in the reliability of an electrical contact is the integrity of the plated surface.

If there are breaks in the surface, such as pores, then corrosive elements can attack the substrate or the base material. If there are enough pores, corrosion can creep across the surface of the contact with resultant increased contact resistance and other disastrous consequences.
Usually two to five years of reliable operation is now the norm for many consumer products, exceptions are some telecommunications, as well as the military and other connectors designed to work in less than ideal environments.

As precious metal and indeed specifically gold prices increase the tendency has been to reduce the gold thickness of connectors in order to reduce cost [15,16].

While some porosity in gold plated surfaces is the norm, it can be reduced to an acceptably low level by paying proper attention to design and manufacturing practices, however reduced thickness generally means increased porosity and at some point, reliability will be compromised [18,19].

Rapid Pore Closure (RPC) additives have been developed to speed up the rate of pore closure and enable a reduced porosity regardless of gold thickness specified.

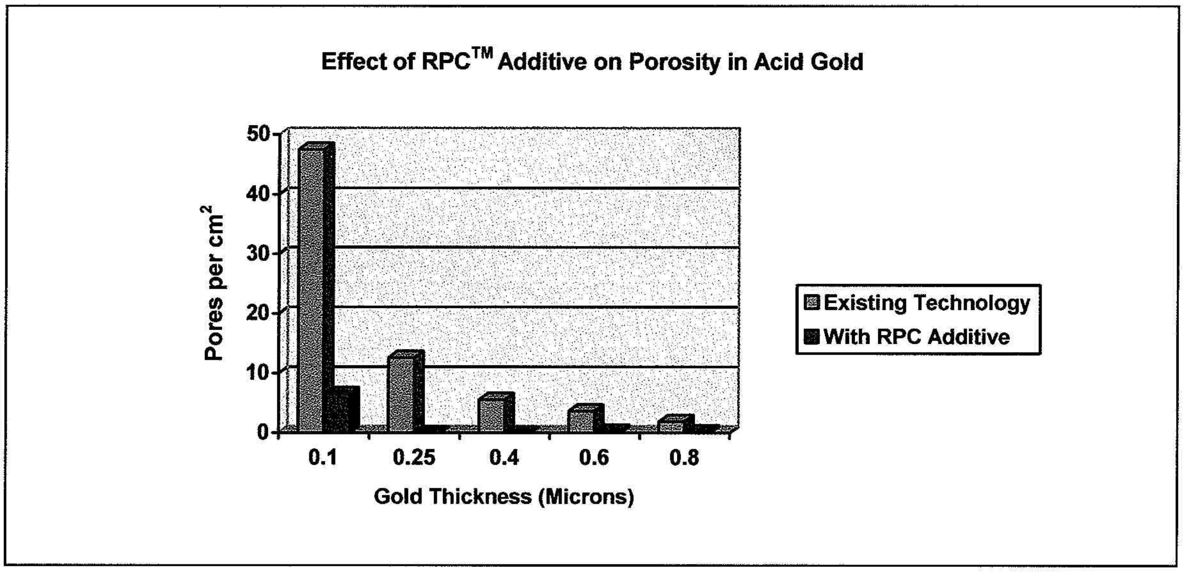


Fig 4 : Effect of ***RPC Additive*** *on Porosity of a High Speed Cobalt Brightened Acid Hard Gold*

Research work has clearly demonstrated that at any given thickness gold plating porosity will be reduced when compared to the same connector produced without the use of RPC additives.

The RPC additives utilise the considerable forces of interfacial tension generated within the Helmholtz double layer during the deposition process to the advantage of pore closure. They work by reducing the electrolyte surface tension enabling a faster wetting of the surface to be plated achieving a faster closure of potential pore.

Selection and choice of RPC additive is, of course, of paramount importance to ensure full compatibility of the RPC additive with the gold plating chemistry to ensure that solving one problem does not create another.

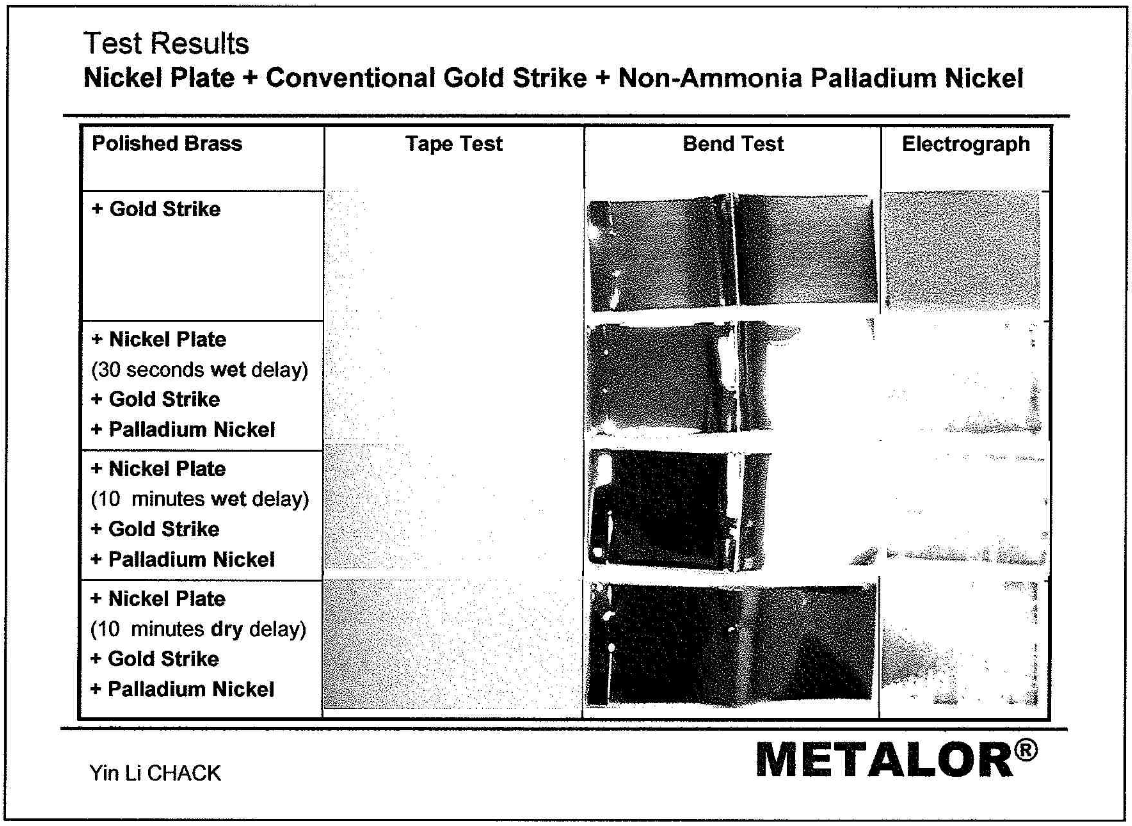
Pre-treatment and Strike plating

One common recommendation for reducing porosity is to include a gold strike between nickel and gold plating. Of course this is good practice and improves the service life of the main gold bath [17] by protecting it from drag in of contaminants from the nickel plating bath. This also maximises adhesion and minimises any immersion coating on the Nickel layer.
Time delays between Nickel and any gold (or palladium alloy) coating should be minimised to avoid nickel passivation and resultant adhesion failures.

A Pure Palladium strike can be significant in reducing porosity not only of Palladium alloys [20,] but also of subsequent gold plating.
Newly developed Non-Ammonia Palladium strikes seem to be ideal in achieving this improved porosity [21,22.]

The following photographs of electrographic test results compare a Non-Ammonia Palladium strike vs. a conventional Gold Potassium Cyanide based Gold Strike as a pre-treatment prior to Palladium Nickel the results clearly show that the Non Ammonia Palladium Strike is significantly better than the Gold strike as an under layer in minimising porosity.

The pink spots on the electrograph represent nickel detected from the under-layer exposed through porosity in the coating it is clearly significantly higher with the use of a gold strike compared to the use of a Non Ammonia Pure Palladium.
Possible explanations for this are the more aggressive nature of the cyanide based strike on the surface of the Nickel layer. Non-ammonia Pure Palladium systems have no tendency to form immersion coatings and will simply deposit onto the nickel layer ,whereas a cyanide gold will explore lattice defects located in the nickel layer structure to create pores sites which are subsequently exposed in the electrographic test.
Alternatives theories point to inadequate rinsing between the gold potassium cyanide based gold strike and the non-ammonia palladium nickel, but this was disproved by processing samples that had been thoroughly rinsed and even dried and in all cases the Pure Palladium strike out performed the gold strike significantly.
It is possible also that a Gold Strike could disrupt the initial growth pattern of the laminar Palladium Nickel layer whereas a Palladium Strike does not, however tests have not supported this theory.



Test Results

Nickel Plate + Conventional Gold Strike + Non-Ammonia Palladium Nickel

Polished Brass	Tape Test	Bend Test	Electrograph
+ Gold Strike			
+ Nickel Plate (30 seconds wet delay) + Gold Strike + Palladium Nickel			
+ Nickel Plate (10 minutes wet delay) + Gold Strike + Palladium Nickel			
+ Nickel Plate (10 minutes dry delay) + Gold Strike + Palladium Nickel			

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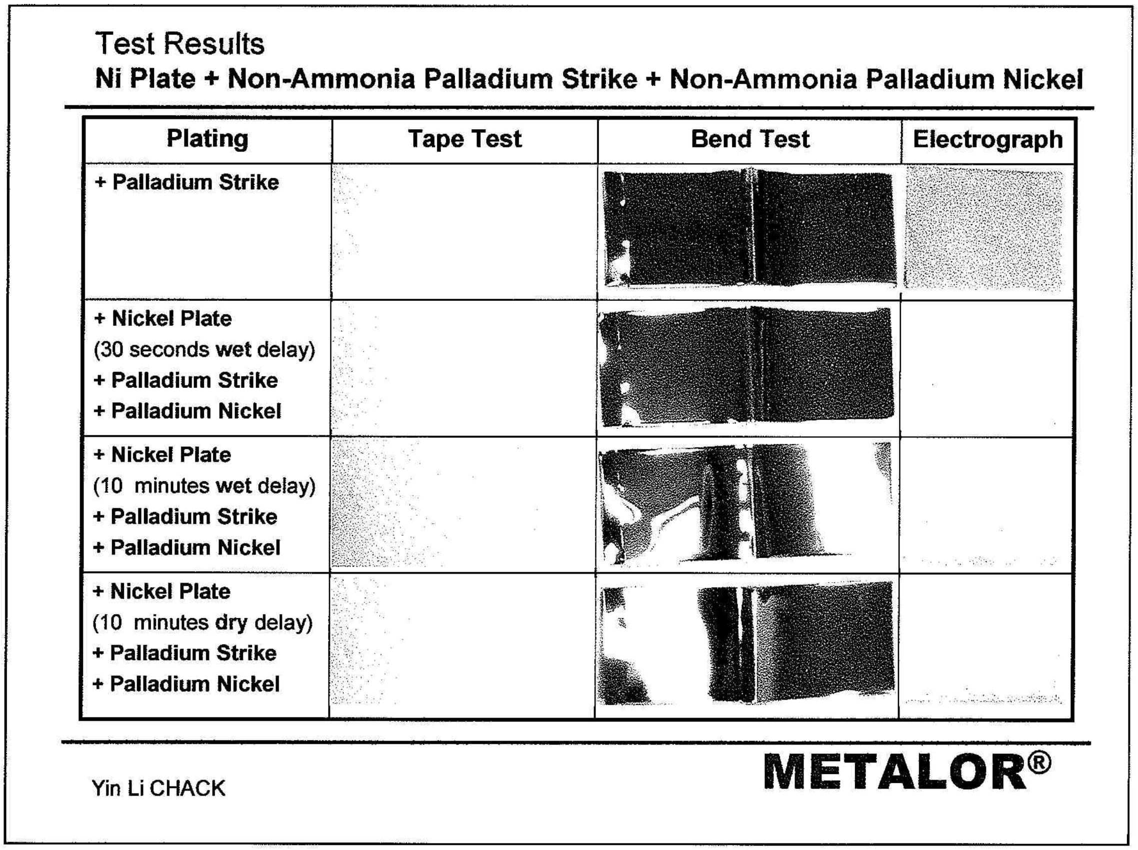
Fig 5 : Conventional Gold Strike applied prior to Palladium-Nickel showing ***significant*** *porosity*



Test Results

Ni Plate + Non-Ammonia Palladium Strike + Non-Ammonia Palladium Nickel

Plating	Tape Test	Bend Test	Electrograph
+ Palladium Strike			
+ Nickel Plate (30 seconds wet delay) + Palladium Strike + Palladium Nickel			
+ Nickel Plate (10 minutes wet delay) + Palladium Strike + Palladium Nickel			
+ Nickel Plate (10 minutes dry delay) + Palladium Strike + Palladium Nickel			

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Fig 6 : Non ammonia Palladium Strike applied prior to Palladium-Nickel showing ZERO porosity

Precious metal process recommendations to minimise porosity

- Minimise surface defects by maximising raw material quality
- Eliminate any stamping and handling issues prior to and during plating
- Optimise pre-treatment line for surface preparation and plating
- Maintain good housekeeping and cleanliness to minimise contamination
- Operate plating baths well within specified plating range (not always at maximum)
- Maintain all processes parameters within guidelines of operation
- Use a Non-Ammonia Pure Palladium Strike , in preference to a Gold Strike
- Use a Non-Ammonia Palladium-Nickel
- Use RPC Additives in the Gold Plating Process

Conclusions

- Escalating precious metal prices coupled with thickness reductions have focussed attention clearly on porosity as a key issue in precious metal plating.

- Substrate quality , pre-treatment and good housekeeping are of paramount importance in reducing porosity.

- Specifications, standards and tests selected to **detect porosity** are often misapplied and are utilised **not** to detect porosity, but to measure the corrosion resistance of a coating to a harsh acid environment.

  An example of this is the use of Nitric acid vapour test on Palladium Nickel plated connectors where Nitric acid is clearly known to attack Palladium Nickel deposits, even if it is pore free, meaning that perfectly good "Pore free" Palladium Nickel plated connectors are often wrongly rejected.
  It is important to consider very carefully the purpose of tests applied to ensure conclusions reached are valid and meaningful for the component under test.
  Tests specified for gold are not always "interchangeable" for tests on palladium nickel, this is clearly explained in ASTM specifications and standards, yet still not fully understood nor implemented throughout our industry.

- Rapid Pore Closure (RPC) additives are available and are utilised in gold plating to minimise porosity by reducing the time and thickness necessary to close potential pore sites. This is achieved by utilising interfacial tension forces to the advantage of deposition maximising the covering power of electrolytes into recessed areas on a micro scale leading to rapid pore closure.

- Non-ammonia Pure Palladium strikes have been shown to give minimum porosity in comparison to traditional gold potassium cyanide based gold strikes when utilised prior to palladium nickel or gold electrodeposits on connectors.

References

1. Stewart J Hemsley , C Dullaghan, S.Burling The Use of Palladium and its Alloys in Electronic Applications: an update of Performance, Environmental and Cost Benefits. Proc ISF 2006 Mumbai India (2006)

2. Metgold 2010 RPC : Rapid Pore Closure
Metalor Technologies Pte Ltd Singapore Hemsley, Priscilla Hong
Email : Stewart.Hemsley@Metalor.com (2006)

3. The Anatomy of a Pore in Gold Plated Contacts by Robert A. Michelson, APEX Electrical Interconnection Consultants, LLC , 2408C Park Drive Harrisburg, PA 17110, www.connectorconsultants.com

4. Acid Gold Plating and Palladium Nickel in Electronic Applications
An Update S J Hemsley, Y L Chack, P Hong *Proc .SUR/FIN® 2006 NASF*
(2006)A New Technology:

5. American Society for Testing and Materials (ASTM) , 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

6. Defence Supply Centre Columbus (DSCC) P. O. BOX 3990
COLUMBUS, OH 43218-3990 http://www.dscc.dla.mil

7. Applications of Palladium and Palladium Alloys; Stewart J Hemsley
Singapore Surface Finishing Seminar : October 2005

8. Modern Trends & Developments in Plating with Platinum Group Metals.
Steven Burling; Metalor Technologies, Birmingham, United Kingdom.
Proc. SUR/FIN® St Louis (2005)

9. Palladium Nickel Ammonia Free.S.A. Burling, L. Chalumeau, J. Gonzalez, C. Leclere, M. Limayrac, S. J. Hemsley, *Proc. SUR/FIN® 2001* Nashville, USA (2001)

10 Stewart J.Hemsley, K.Shiokawa.
Further Developments in Gold Plating Technology for microelectronics.
Proc SURFIN 1999 p 239-248 (1999)

11 Stewart J Hemsley , C Dullaghan, S.Burling The Use of Palladium and its Alloys in Electronic Applications: an update of Performance, Environmental and Cost Benefits.Proc ISF 2006 Mumbai India (2006)

12 Hemsley, Dullaghan , Burling, Gonzalez and Daniels.The Use of Palladium and its Alloys in Electronics Applications Proc Singapore Surface Finishing Seminar October 2006 (2006)

13 S.J.Hemsley Advances in Gold Plating Technology
Proc Asia Pacific Interfinish (Singapore) Nov page 27.1 -27.15 . (1990)

14 S.J.Hemsley Finishing Science (Taiwan) The use of organic additives in Acid Gold plating technology May **135** p135-144 ISSN 1016-7382 (1991)

15 S Burling , C Dullaghan , S. Daniels and S J Hemsley Optimising Reel to Reel plating *Proc. SUR/FIN® 2004* (2004)

16 Hemsley, Shiokawa Further Developments in Gold Plating for Microelectronics
Proc "Surface Mount into the New Millenium" 2^{nd} SMTA Conference
Singapore (1999)

17 Hemsley, Shiokawa Precious metal applications in microelectronics
Proc. Shanghai Microelectronics NEPCON Shanghai (1999)

18 J Abys Keynote speech : Electrodeposition for Electronics Trends and Challenges
Proc Singapore Surface Finishing Society (SSFS) : October 2005 (2005)

19 Dullaghan, Daniels, Burling ,Gonzalez and Hemsley
Palladium and its alloys : A Revival *Proc. SUR/FIN® 2005 (2005)*

20 J.A. Abys et al., *Trans. of the Institute of Metal Finishing*, (July 1999), E.J. Kudrak et al., *Proc. 32nd IICIT*, Anaheim, CA, (Sept. 1999), I.E. Cottington, *Platinum Met. Rev.*, **35** (3), *141-151* (1991) and references therein.

21 Gonzalez.,Hemsley,LeClere et Al
Développement et application d'un nouveau procède de PdNi sans ammoniaque,
Swiss Electroplating Association (2005).

22 Stewart J Hemsley, Yin Li Chack, Palladium Nickel : Solution sans ammoniaques, Oberflashen Polysurfaces 2/07 Galvanotechnik (2007)