Acid Gold Plating and Palladium Nickel in Electronic Applications
An Update

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This paper will provide a technology update on the state of the art processes for both Palladium Nickel and Acid Gold, it will explore the technical aspects and also the financial implications as a result of changing metal prices.
Data will be presented giving performance data on Porosity, Contact Resistance and Corrosion related to thickness reduction.
Newly developed processes will be highlighted and their features and benefits explored.
New applications and trends in Connector, Semi Conductor Lead Frame and Microelectronics will presented.

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Introduction

Precious Metal prices are again at the forefront of our minds with ever changing, and often increasing, prices continuing to give challenges to our technology needs.

In our daily lives we ask for faster, lighter, smaller, smarter and cheaper electronics in our personal electronic items whether they be mobile phones, organizers, cameras, computers, plasma televisions, cars or digital music players, the list is endless.

We want cheaper air travel, more reliable cars with increased features, navigation systems, in-car DVD, climate control, computer controlled ignition and fuel economy systems.

We want medical instruments to enable a better and more complete patient diagnosis, instruments that offer increased capability with more features.

We want advanced military defence systems to protect our families, telecommunications and information technology to increase our ability to expand our knowledge and skills.

We need Smart cards for our financial management. ATM`s that enable us to settle instantly, our credit card, utility charges, traffic offence bills, and so on, and of course to provide us with cash at the push of a button.

All of these things we want at low cost ; yet we still demand instant responses and faultless reliability in any electronic interface that we meet.

We have become an impatient society, but also a very efficient and active society, the pace of life and the number of technological breakthroughs have both increased more dramatically, within the past twenty years, than at any other time in the history of mankind.

We want all of these high technology items to be produced at the “lowest cost possible” and in a “green” and “environmentally acceptable” way to preserve our natural resources and maintain our planet for future generations. The majority of these electronic devices utilise Precious Metals somewhere within their interconnect systems and within the micro-electronic devices they employ.

The increasing price of Precious Metals is a paradox when we need cheaper electronic devices with the challenges of no decrease in features and more importantly no decrease in performance and reliability.

So how do we meet these challenges?

This paper explores new process developments in precious metal plating technology that have enabled and will continue to enable the production of reliable low cost electronic devices and connectors without compromising quality.

Technology breakthroughs in electroplating chemistry have optimized performance and maximized the efficient use of precious metals in electronic components to minimize cost without compromising quality.

Discussion

Precious metals have been used in the creation of electronic devices from the first high voltage connections through the evolution of the Printed Circuit Board and Electronic Connectors into the smaller faster lighter world of microelectronics.

Precious metals have primarily been selected as a result of their Noble Metal, inert properties that can confer corrosion resistance to the critical surface of the device, enabling constant performance, even after prolonged aging or exposure to adverse atmospheres.

This can be of particular significance in military and telecommunications fields where the need for fail safe operation is an essential part of the performance requirement. These industries have been and are likely to remain significant users of precious metal.

Reducing thickness and minimizing plated areas does not need to compromise quality. Process developments optimization have already made significant inroads into improving Precious Metal utilization.[1]

Precious Metal Prices

Of course this is a very significant issue as at the time of writing the gold price has risen to a 25 year high and exceeded USD 700 / troy ounce.

Most metals are seeing a significant increase as the commodity market is experiencing an interesting period of price volatility. The precious metal price increases have the most significant impact on producers of electronic components that utilize the materials for contact and bonding surfaces.

Gold for example has seen an increase of 250% (from USD 290 to > USD 700 per troy ounce) in the 5 years up to May 2006.[2]

This makes life for the producer or supplier of precious metal commodities or precious metal plated components a very turbulent experience.The graphs below show the price changes from 1989 to present for both Gold and Palladium; two very significant metals utilized in electronic interconnect systems.

***Fig 1** : Gold Price 1989 -2006 (USD per troy ounce)* [*www.thebulliondesk.com*](http://www.thebulliondesk.com)

***Fig 2** : Palladium Price 1989 -2006 (USD per troy Ounce)*
[*www.thebulliondesk.com*](http://www.thebulliondesk.com)

What everyone remembers is the very rapid price surge of Palladium in 2000 when it climbed to USD 1100 per troy ounce, a price that had never been seen before in the entire history of Palladium.

What everyone forgets is the same rapid decline of the Palladium price in 2001 with the price reducing significantly and hovering for the past five years in the range USD 150 - 400 per troy ounce offering significant savings compared to gold.[3.4]

Gold over the same period has escalated from USD 290 to over USD 700 per troy ounce and the attractiveness of utilizing Palladium and its alloys, as a very viable alternative to Gold, is again being utilized.

Many electronic connector manufacturers are now reverting to Palladium and Palladium alloy deposits on their connectors to gain competitive advantage from the cost savings achieved.

The use of Palladium and its alloys will be discussed in more detail later in this paper particularly emphasizing and explaining the attractive cost benefits but, in addition, outlining the new novel and patented Non-Ammonia systems that provide an improved and safer working environment to compliment and further enhance the cost savings achieved.

Acid Gold Plating Technology

There have been many papers well documenting the technological development history of Acid Hard Gold [5,6,7,8,9] , so it is not our intention to repeat the history here except to summarise the key milestones.

The 1950`s saw the first Acid Gold processes and the current market leading processes have evolved by dynamic development focusing on optimizing the thickness distribution , increasing the current density and reducing the gold concentrations without detracting from the deposit performance.

A key milestone was the introduction of stable organic additives in the late 1980s and early 1990s and from this stable base the present processes have evolved and a full range of processes are currently available tailored to meet all equipment and application needs.

The major application, in terms of volume for Acid Hard Gold is in reel to reel plating of electronic connectors with processes specifically tailored to operate in each design of reel to reel equipment

eg Dip Selective, Spot and Stripe , Wheel plating , Moving mask , Brush (Static and Rotating),Vibratory ..etc.

All of these systems operate successfully in production environments with many years and economical operation maximized use selectivity of the gold plating area to minimize cost and enhance quality.

Despite all of these successes our job in Research and Development is to seek continuous improvement of technology.

Porosity and Rapid Pore Closure Additives

The escalating gold metal price has led all connector manufacturers to look at how they can reduce costs in gold plating; an obvious way is to seek the same performance at reduced thickness.

Naturally such a strategy puts increased demands onto the performance characteristics of the gold plating chemistry as the relationship between thickness porosity is clearly understood for many years ; simply stated the thicker the deposit the lower the porosity.

Initial trials porosity was evaluated on market leading processes by electrographic porosity test *(Instrument : Fischer Poroprint , using the Cadmium Sulphide defined in BS 4025 alternative can beASTM Test B-741-90)* measuring porosity through to copper utilizing a Cadmium Sulphide test paper .

Values can be reduced and optimized by improving surface morphology and by applying a Nickel underplate, but these test results are simply to provide a comparative measure of pore closure ability of the respective processes related to thickness. The substrate utilized for all tests represented here was a simple polished brass material. *(Standard pre- polished Hull Cell Brass : Ex Schloetter)*

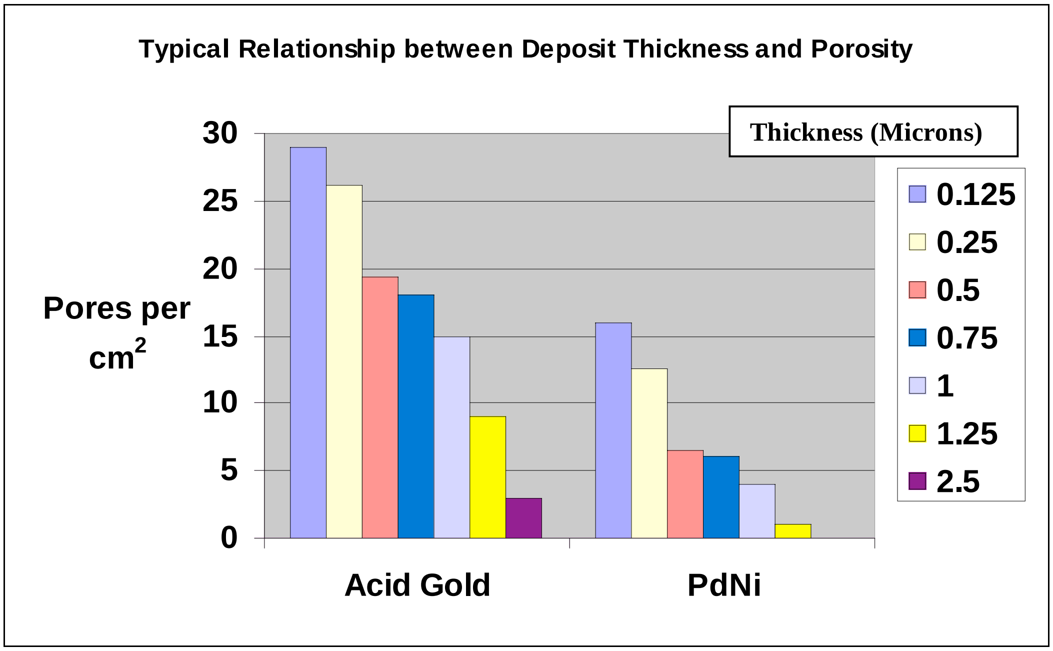

***Fig 3** : Acid Gold and Palladium Nickel : Deposit Thickness vs Porosity*

This is a very logical situation, but what can be done to improve the situation and enable production of good electrodeposits with reduced porosity at lower gold thickness?

- How can I achieve a “Pore free” deposit ?
- What is the minimum thickness to achieve a “Pore Free” deposit

These are questions often asked and whilst it is a simple question the answer is often quite complex as there are a significant number of variables that can influence the path which leads to “Pore Free” deposits.

Factors influencing the Degree of Porosity

Porosity is a significant factor in any electroplated deposit, in Acid Gold plating “Pore Free” usually means in reality less than 10 pores /cm2 when measured on a flat coupon of area greater than 1cm2.
Achievement of this standard will usually mean that a finished connector will conform to the desired porosity specification often expressed as a function of pores per significant surface on a given number of connector pins.

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 porosity 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.

Pretreatment and cleaning

Surface defects can be induced in an otherwise good surface; by the cleaning sequence that is designed to improve the surface to be plated.

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 seen in finished connectors.

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 can arise from mechanical damage to the part or by poorly maintained and controlled equipment, during the connector forming operation or raw material processing.

Entrapped chemicals from preceding stages or poor cleaning / rinsing prior to the initial plating stage can also contribute.

A good way to avoid some of these defects is to use an Electro-polish .
Electro-polishing will removing any “burrs” from stamping operations and also reducing and rounding any sharp peaks to give an overall smoother surface for subsequent electroplating.

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 engrained into the surface layer 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 Micro-etches can be utilized successfully, but are often too slow for Reel to reel connector lines .These etches were originally developed for the printed circuit industry; mixtures are usually based on ammonium persulphate with a dilute sulphuric acid and selected inhibitors to reduce chemical attack.

In connector lines sometimes, but less frequently as a result of health and safety concerns, use aggressive Nitric Acid based etches. If used they should be monitored very carefully to avoid over etching and crater formation in alloy materials in particular where `weaker` area may be selectively attacked by such bright dips.

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. The brightener utilized in Acid Copper provides greater leveling than the additive systems 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.

Thie thickness of such plated layers of course will also have a significant effect and generally a range of 1 up to 5 microns of Nickel is employed, with typically around 2 microns being sufficient for most applications.

Gold Plating Bath : Process Control and Contamination

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 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 pososity 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 it`s 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.

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.

Finally good housekeeping of the process line and cleanliness of the operation line are essential.

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.

New Technology : Rapid Pore Closure Additives

An novel and innovative development in 2006 in Gold Plating technology is **R**apid **P**ore **C**losure (RPC ™) Additives[10] that can be utilized to further enhance the pore closure performance of the market leading Acid Gold process.

The use of RPC™ additives in an already production proven process enables thinner deposits to be utilized with reduced porosity and improved corrosion properties.

This innovation more than meets the needs of connector manufacturers and end users as it becomes a possibility to achieve the exceptionally low porosity values at significantly reduced thicknesses.

The impact of RPC™ Additive on porosity in Acid Gold is very dramatic and you can see a very significant reduction in the pores observed

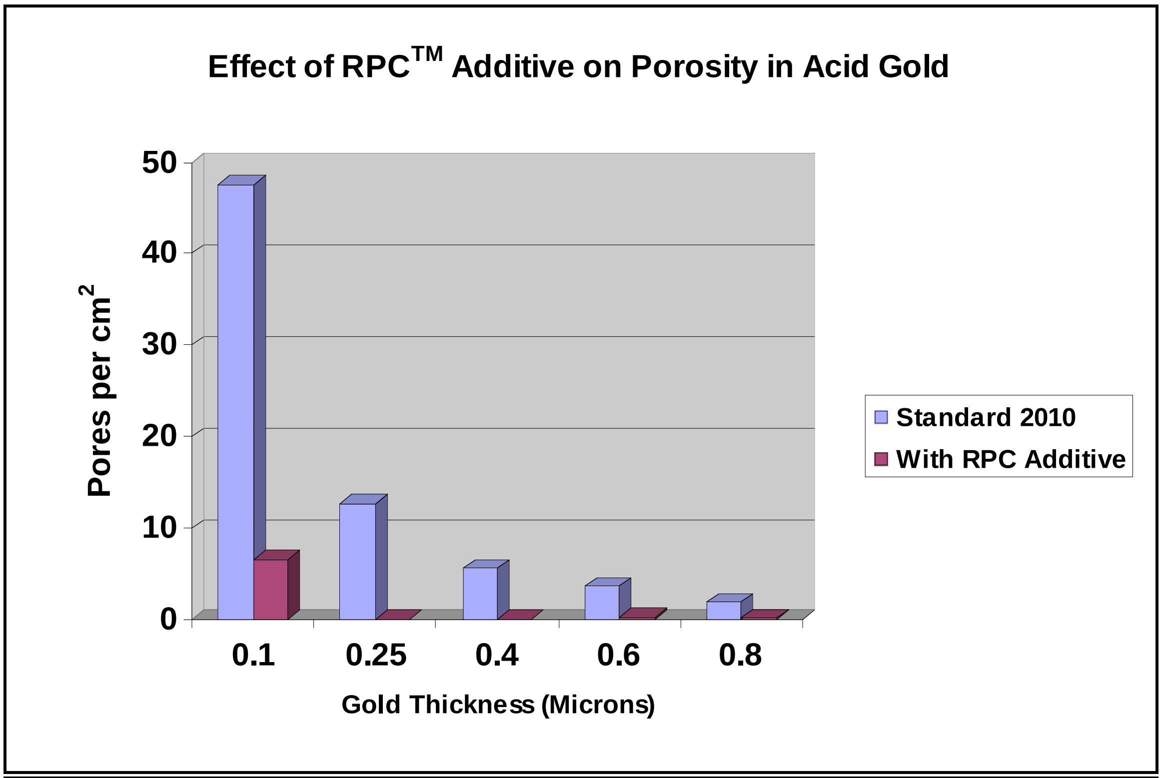

***Fig 4** : Effect of RPC™ Additive on Acid Gold Porosity at various Thicknesses*

Pore Sealant and Self assembled monolayers

An alternative strategy is to utilize a post dip that acts as a pore sealant in a gold plated deposit
There are many types commercially available and appear to be successful in decreasing porosity and improve resultant corrosion performance.
Many of these are also referred to as “lubricants” as they confer some increase in the sliding wear capability.

Finally a self assembled mono layer (SAM) can be applied on the gold deposit.[11]
This can be a way good to seal pores on even the thinnest coating.

ALTERNATIVES TO GOLD PLATING

Palladium Nickel

The technical value of a palladium and its alloys has been well documented elsewhere.[12,13,14]

A few key points to note are :

- The use of Palladium and its alloys in electronics is not new.
  Palladium and Palladium Nickel has been utilized very successfully on reel to reel plating of electronic connectors for more than 20 years.

- For alloy plating the use of Palladium Nickel is well understood and is covered by international specifications (eg ASTM B867-95). Most plating companies have already approved the use of Palladium Nickel as an alternative surface finish to gold.

- Palladium Nickel is the process of choice for alloy plating with more than 200 successful installations in electronic connector reel to reel.

- Palladium Nickel has a significant advantage over other Palladium alloys as it is very tolerant to Nickel contamination which on a reel to reel line is usually the biggest potential contaminant.

For Palladium Nickel chemistry number of evolutionary and breakthrough developments have taken place in the past years…Non-Ammonia being the most recent advance.

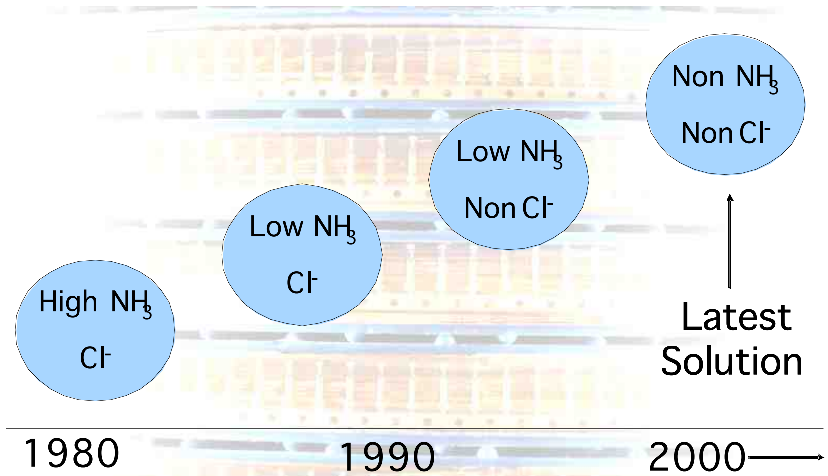

Fig 5 – *Various generations of Palladium Nickel plating chemistries.*

At time of writing Non-Ammonia Palladium Nickel processes have been in production operation for more than three years with no bath replacement needed on a reel to reel line
This is an added advantage of Non Ammonia system : Extended bath life

Technical Performance of Palladium and its Alloys

Property	Unit	Acid Hard Gold	Palladium Nickel (Gold Flashed)
Hardness	**Hv (50g)**	150-200	450 - 550
Solderability	-	Poor	Good
Wear Resistance	-	Good	Good
Corrosion Resistance	-	Good	Good (Except HNO3)
Contact Resistance	**mOhms**	4 - 5	4 - 7
Structure	-	Usually Columnar	Laminar
Ductility	-	Moderate	Excellent

Porosity	-	Moderate	Excellent
Deposit Density	g/cc	16 - 17.5	10.5 - 11.0
Cost	-	Expensive	Lowest …. **(~80% Saving vs Gold)**
Electrolyte Basis (Safety)	-	Cyanide (Gold Potassium Cyanide)	Non-Ammonia Non-Chloride
Electrolyte Property (Environment)		Toxic	Zero Smell and Significantly Reduced Corrosion

Of course in current climate the cost benefits of Palladium Nickel cannot be understated .
A saving of around 80% of the Gold plating cost is still achieved at todays metal prices
(Charts below are based on May 2006 Metal prices Au = 700 USD / troy ounce and Pd= 375 USD per Troy ounce)

Table showing cost for precious metal used in plating a connector to a thickness of 0.75 microns (30 Micro-inches)

Cost per Square Metre Plated (USD)	
Pure Gold	**325.8**
Acid Hard Gold	**290.0**
Pure Palladium	**105.8**
Palladium Nickel	**79.2**

Thickness	**0.75**	**Micron**
Palladium Price	**375**	**USD /Troy Oz**
Gold Price	**700**	**USD /Troy Oz**
Nickel	**70**	**USD / 100g**

***Fig 6** : Pure Gold vs Acid Gold vs Palladium Nickel vs Palladium Cost comparison*

Summary

- Gold plating on electronic connectors continues to be the leading surface finish

- As precious metal prices increase the use of Palladium Nickel is again taking prominence as the cost savings become very significant.

- Palladium Nickel is still only around 20% the cost of gold and as the prices of both metals increase the real dollar value of this percentage saving becomes bigger proportionally

- As prices of Gold escalate the reduction of thickness is an economic reality ; the use of RPC™ Additives to reduce porosity at low thickness is a significant advantage.

- Research and Development will continue to innovate and enhance the benefits of electroplating processes. As we focus more and more onto environmental issues, the next challenge will become the removal of cyanide from our working environment.

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