# Reductions in the Thickness of Gold Layers For Connector Applications by Utilizing Undercoats of Electrolytic Nickel Phosphorous Alloys

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Gold plating has usually been the most expensive part of plating a connector. This paper will describe the use of a new electrolytic nickel-phosphorous underlayer that offers opportunities to reduce the gold thickness. Deposition in both high-speed and barrel applications will be described, as well as the properties of the deposits obtained. The use of GDMS (Glow Discharge Mass Spectroscopy) for analysis will be explained.

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# INTRODUCTION.

Gold has been used as a contact material in the electronic market for many years. Its importance and use increased as the electronics market grew with a significant impact on the cost of electronic components as the use of gold coatings grew.

Over this period alternative coatings were looked at, but mostly gold could only be replaced by another precious metal. Sometimes cheaper, sometimes not. E.g. Palladium has been both cheaper and more expensive whereas Platinum and Rhodium have always been more expensive.

As the market continued to grow alternative process methods were introduced to reduce cost by selectively plating only the contacting part of the component or board. These processes and methods led to the techniques for selective plating.

E.g. Rack and Barrel Plating >

- Reel to Reel (Controlled depth immersion) >
- Reel to Reel (Selective partial masking) >
- Reel to Reel (Selective extensive masking).

At the same time process chemistry of the gold processes was improved to give benefits in the deposit. As the chemistry was understood more control of these baths was also improved to give consistent deposits. Benefits were lower porosity levels and improvements in distribution.



Examples of reduction in the gold plated area.

However as can be seen from above limitations have and are being reached regarding the selectivity of gold plating both mechanically within the plant and with solution chemistry.

Work has been carried out through many years to evaluate different underlayers to the gold as well as different surface preparations of the base material. Options looked at have been.

Microetch of copper and copper alloy base substrates.

Chemical polish of copper and copper alloy base substrates.

Silver plating as an undercoat.

Nickel (Sulphate & Sulphamate) plating as an undercoat.

Palladium Nickel as an underlayer (and an alternative).

Low carat golds (Gold/Copper/Cadmium) as an underlayer.

Generally nickel has been found to be the most useful and widely used product and is the current "favourite" for the electronics market.

This paper will describe the use of an alternative nickel based electrolyte, producing a Nickel – Phosphorous layer, as an undercoat. This when used with an acid hard gold to give an optimised deposit can give opportunities for cost saving.

## PREVIOUS WORK

The potential to use electrolytic Nickel Phosphorous alloys has been available for some time. D W Baudrad <sup>(1)</sup> investigated and reported on autocatalytic opportunities in 1981 as an alternative to gold. J.C. Puippe, J.B. Vanhumbeck and G. Ide <sup>(2)</sup> reported in 1989 that deposits of Nickel Phosphorous containing 8.0% Phosphorous could be used in electrical contacts. Only recently, 2001, a paper by H.D.Park, D Chang, K.H.Lee and S.G.Kang <sup>(3)</sup> outlining the internal stresses in these coatings containing up to 14% P

was presented in the journal Plating And Surface Finishing. In 2001 Dr Unruh reported in the "Oberflächentechnik Jahrbuch 2001" <sup>(4)</sup> on the desire for amorphous nickel phosphorous deposits. He reported that the ideal alloy to produce would have between 8.7% and 12.5% in the deposit to achieve an amorphous NiP deposit and therefore optimise the opportunity for the gold layer to deposit uniformly, continuously and thinly. The theory being that the gold would deposit finely from these grain boundaries giving ultimately a fine continuous less porous deposit. With the high corrosion resistance from the nickel phosphorous and the high wear characteristics it was expected that once the gold was overplated, a continuous, corrosion resistant, hard wearing deposit would be obtained. From the information obtained it was therefore perhaps surprising to see that very few products currently available in the market had this nickel phosphorous coating followed by hard acid gold.

# SOLUTION TRIALS.

Initially work was carried out on a number of formulations to establish the optimum formulation for development. In the early stages solutions based on Nickel Sulphate, Nickel Sulphamate, Nickel Chloride and Nickel Fluoride were evaluated.

	Bath A	Bath B	Bath C	Bath D
NiSO <sub>4</sub> .6H <sub>2</sub> O	150 g/l		250 g/l	250 g/l
Ni(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O		200 g/l		
NiCl <sub>2</sub> .6H <sub>2</sub> O	50 g/l	50 g/l	50 g/l	
NiF <sub>2</sub>				20 g/l
H <sub>3</sub> PO <sub>3</sub>	30 g/l	30 g/l	30 g/l	30 g/l
H <sub>3</sub> PO <sub>4</sub>			40 g/l	
H <sub>3</sub> BO <sub>3</sub>	30 g/l	30 g/l		30 g/l

A potential formulation was identified and a Taggucci Experiment was carried out using a  $L_8$  array to determine the effect of parameters on phosphorous content in deposit. Panels were plated at  $5A/dm^2$ .

Parameter	Level 1	Level 2	Effect on P
			content
NiSO <sub>4</sub> .6H <sub>2</sub> O	150 g/l	250 g/l	Low increase
H <sub>3</sub> PO <sub>3</sub>	20 g/l	60 g/l	Medium increase
H <sub>3</sub> PO <sub>4</sub>	0	40 g/l	Low increase
H <sub>3</sub> BO <sub>3</sub>	0	30 g/l	Medium increase
Additive	0	10 mls/l	Low decrease
pН	0.8	1.4	Medium increase
Temperature °C	65	85	Medium increase

From these results the optimum formulation was confirmed.

Nickel Sulphate	250 g/l
Nickel Chloride	50 g/l
Boric Acid	30 g/l
"P" Acid	60 ml/l
Additive	10 ml/l

Current density was found to have the greatest effect on the phosphorous content and pH on the cathode efficiency. In barrel applications a current density range of  $1 \text{ A/dm}^2$  to  $2 \text{ A/dm}^2$  has been achieved and for reel to reel plating current densities of 80 A/dm<sup>2</sup> can be obtained with spot or jet plating.



Under barrel conditions the phosphorous content is reduced from that obtained in rack or vat applications with similar current densities and typically 10-12% phosphorous is obtained.

Deposit properties from trial installations;

### Barrel conditions

% Phosphorous. 10 - 12 % Appearance. Bright deposit, darker than nickel Ductility. Good. Hardness. 600 HV Corrosion resistance. Good.

Reel to Reel conditions

% Phosphorous. 6-8 % Appearance. Bright deposit, darker than nickel Ductility. Good. Hardness. 620 HV Corrosion resistance. Good.

# SUITABILITY AS A CONTACT MATERIAL.

In order to compare nickel phosphorous with nickel as an underplate for gold, coupons were plated in sulphamate nickel and nickel phosphorous and overplated with 0.25 microns of a hard acid gold.

The coupons were made of brass and plated to 0.5, 1.0 and 1.5 microns in pure nickel and nickel phosphorous to give 5, 10 and 20% P in the deposit. This was controlled by adjusting the current density.

Nickel Sulphamate bat	<u>h;</u>	
Nickel Sulphamate Nickel Bromide Boric acid pH Temp. Current density		400 g/l 10 g/l 40 g/l 4.0 65° C 5 A/dm <sup>2</sup>
Nickel Phosphorous ba	<u>ith;</u>	
Nickel Sulphate Nickel Chloride Boric Acid "P" Acid Additive pH Temp. Current density	5%P 10%P 20% P	250 g/l 50 g/l 30 g/l 60 ml/l 10 ml/l 1.4 65°C 5.0A/dm <sup>2</sup> 3.5 A/dm <sup>2</sup>
	20%P	1.0 A/dm <sup>2</sup>

Gold bath;	
Gold	8 g/l
Cobalt	0.9 g/l
pH	4.5
Temp.	35° C
Current density	$1 \text{ A/dm}^2$
Thickness	0.25 microns

#### CORROSION EVALUATION.

The plated coupons were tested for porosity by; electrographic cadmium sulphide test, 24 hr exposure to  $SO_2$  and 2 hr in nitric acid vapour. The amount corrosion products were assessed on an increasing scale of 1 - 5 for porosity to the brass base and A – E for porosity to the underlayer. Hence A1 has very few corrosion products and E5 has a high level of corrosion to the underlayer as well as the base.

Underlayer	Thickness	Corrosion to Base
	microns	
Nickel	0.5	5
Nickel	1	3
Nickel	1.5	1
NiP 5%	0.5	1
NiP 5%	1	1
NiP 5%	1.5	1
NiP 10%	0.5	1
NiP 10%	1	1
NiP 10%	1.5	1
NiP 20%	0.5	1
NiP 20%	1	1
NiP 20%	1.5	1

Electrographic Cadmium Sulphide Test.

Underlayer	Thickness	Corrosion to	Corrosion to
	microns	base	underlayer
Nickel	0.5	5	D
Nickel	1	5	Е
Nickel	1.5	5	Е
NiP 5%	0.5	4	D
NiP 5%	1	2	Е
NiP 5%	1.5	2	В
NiP 10%	0.5	3	D
NiP 10%	1	1	D
NiP 10%	1.5	1	D
NiP 20%	0.5	2	D
NiP 20%	1	1	E
NiP 20%	1.5	1	E

Results of Sulphur Dioxide Test

Underlayer	Thickness	Corrosion to	Corrosion to
	microns	base	underlayer
Nickel	0.5	2	Е
Nickel	1	2	Е
Nickel	1.5	2	Е
NiP 5%	0.5	1	В
NiP 5%	1	1	В
NiP 5%	1.5	1	А
NiP 10%	0.5	1	С
NiP 10%	1	1	А
NiP 10%	1.5	1	А
NiP 20%	0.5	1	С
NiP 20%	1	1	В
NiP 20%	1.5	1	А

Results of Nitric Acid Test

#### CONTACT RESISTANCE.

Contact resistance measurements were carried out at 5 points across the plated coupons in the "as plated" condition and after heat aging at 250°C for 1 hour.

Underlayer	Thickness microns	Contact Res. Before ageing	Contact Res. After ageing
Nickel	0.5	0.2	3.4
Nickel	1	0.2	1.2
Nickel	1.5	0.4	0.2
NiP 5%	0.5	0	0.8
NiP 5%	1	0	2.8
NiP 5%	1.5	0.2	1.6
NiP 10%	0.5	0	0.4
NiP 10%	1	0.2	0.8
NiP 10%	1.5	0.2	0.8
NiP 20%	0.5	1	1.4
NiP 20%	1	1.8	1.4
NiP 20%	1.5	0.8	0.8

Contact resistance measurements.

# EVALUATION OF RESULTS.

The porosity results all show an improvement in the corrosion products formed from the base substrate when a nickel underlayer is replaced by a nickel phosphorous one, and generally 0.5 microns of nickel phosphorous is has a similar rate of pore closure to 1.5 microns of nickel. The deposits containing 10% phosphorous show the best results indicating the formation of an amorphous structure. The corrosion products formed through the gold to the underlayer also show an improvement of nickel phosphorous over nickel. This may be due to improved porosity in the gold deposit by having a better surface to build on, or improved corrosion resistance of the underlayer. In either case the combination of a thin gold deposit over a nickel phosphorous underlayer gives good corrosion resistant finish.

Contact resistance measurements confirm these findings with only a slight increase after ageing.

In order to maximise the amount of samples that could be tested after plating the use of GDMS (Glow Discharge Mass Spectroscopy) was used to analyse for phosphorous in the deposit.

# HIGH RESOLUTION – GLOW DISCHARGE MASS SPECTROSCOPY.

Ionisation is obtained by sputtering solid inorganic samples with ions from argon. The sputtered particles in the argon plasma are afterwards separated according to their mass.

- The GDMS covers all the periodic classification of elements (natural occurring elements).
- This technique permits the measurement of the concentration of elements at a % level until trace (ppb), repeatability between 1% and 20% depending on the element concentration.
- The method of ionisation of the samples is relatively independent of the matrix.
- The technique permits the analysis of conductive and non-conductive substances. The samples are directly analysed in solid form. The best geometry for a sample being a strip 20mm x 2mm x 2mm. Samples can be produced by ourselves. Samples in powder must be compressed into a suitable sample geometry.



Sample in needle form.

Solid Samples.

- High purity metals for Microelectronics; Aluminium, Copper, Silicon etc.
- Alloys used for Aeronautic/Aerospace industries; Super alloys, Cobalt etc.
- Precious Metals; Gold, Platinum, Silver, Palladium, Rhodium etc.

Powder Samples (using a binding material if nonconducting.

Rare Earth, Graphite/Carbon for electronics, Silicon Carbide, Chrome etc.

Samples for Semi – Conductors.

 Gallium Arsenide, Tellurium, Indium Phosphide, Cadmium/Zinc/Tellurium etc.

Samples of Non – Conductors. (used with a median into a paste).

Alumina, Ceramic, Glass, YAG, etc

Samples with low melting points.

Lead, Tin-Lead Solders, Gallium MBE Grade (melting point 29.78 C).

Flat samples can also be analysed using an adapted cell. In this case the plasma is initiated between the body of the cell and the surface of the sample. The material is sputtered layer by layer; the analysis through the layer on a profile is therefore possible. The sputtering rate depends on the material and the condition applied in the plasma. Typically between 0.01 micron and 1.0 micron per minute.



Sample in Plate Form

# DESCRIPTION OF THE TECHNIQUE.

The spectrometer comprises of three parts.

- The source of the process of atomisation and ionisation of the sample.
- The analyser which separates the species according to their mass and charge.
- > The detection system for these species.



Principle of Mass Discharge Plasma Spectrosco

The advantage of using this analytical technique is that samples can be analysed quickly and accurately.

# CONCLUSIONS.

The results so far show that gold thickness can be reduced by the use of this new electrolytic nickel phosphorous underlayer. Opportunities to reduce costs can be undertaken even though the lifetime of this new electrolytic Nickel Phosphorous bath is lower than for a conventional Nickel bath. The cost implication of the Nickel Phosphorous bath can be more than offset by the reduction in gold usage.

Further improvements can be made, in the performance of the overall deposit, by the choice of gold process used. Current developments in gold plating technology would indicate the improvements that can be made and this new gold technology will be the subject of another paper.

## References.

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