SUR/FIN®

CLEVELAND, OH | JUNE 4-6, 2018

Where Finishing Connects

Mechanism and Mitigation of Nickel Corrosion in ENEPIG Deposits

George Milad, Jon Bengston, Don Gudeczauskas & Richard DePoto
Uyemura International Corporation
Southington CT

UYEMURA USA

June 2018 Cleveland, OH

Introduction

Nickel corrosion in ENEPIG (Electroless Nickel/Electroless Palladium/Immersion Gold) deposits has been reported in multiple occasions and multiple applications.

This was originally observed in cases where the desired gold thickness was in excess of 2.0 µins (0.05 µm). Normally this is the result of boards which were left in the gold bath for an extended dwell time or the result of electrolyte contamination (Cu, Ni).

In those cases, the gold ion reaches through micro-pores (porosity) that are common in thinner palladium deposits. The gold ions are able to reach the underlying nickel and continue to deposit by corroding the underlying nickel.

This paper is an attempt to reproduce the defect, and to determine the necessary "mitigation action" to avoid / minimize nickel corrosion in the ENEPIG finish.

ENEPIG Attributes: Why is ENEPIG of value?

- A planar solderable finish
- Good shelf life (12 month min).
- Does not tarnish
- Precious metal electrical contact surface
- Al & Gold wire bondable
- The Nickel strengthens the PTH
- The Nickel barrier prevents copper dissolution to solder joints during assmembly & rework

IPC ENEPIG Specification 4556

Amended 4556 Specification 2015

Electroless Ni EN: 120 to 240 µins

Electroless Pd EP: 2 µins minimum at - 4 σ from the process mean to 12 µins maximum at + 4 σ from the process mean

Immersion Gold IG: 1.2 µins minimum at - 4 σ from the process mean to 2.8 µins.

As measured on a 60 X 60 mil pad or equivalent.

The Immersion Gold Reaction

$$2Au^{+} + 2e^{-} \longrightarrow 2Au$$

$$Pd \longrightarrow Pd^{2+} + 2e^{-}$$

$$Ni \longrightarrow Ni^{2+} + 2e^{-}$$

- The immersion gold reaction is an exchange reaction between the gold ions in solution and the substrate basis metal.
- The substrate metal (Ni or Pd) is oxidized to the respective metal ion giving up electrons.
- The gold ion picks up electrons and is reduced to the gold metal.
- The driving force for these reactions follows the electromotive series.

The Electromotive Series

Metal-Metal ion Equilibrium	Electrode Potential (v) vs Hydrogen
$Au - Au^{+2}$	+ 1.498
$Pd - Pd^{+2}$	+ 0.98
$Ag - Ag^{+}$	+ 0.799
$Cu - Cu^{+2}$	+ 0.337
$H_2 - H^{+}$	0.000
$Ni - Ni^{+2}$	- 0.250
$Fe - Fe^{+2}$	- 0.440
$Zn - Zn^{+2}$	- 0.763
$Al - Al^{+3}$	- 1.662

Select metals and their oxidation potential
The driving force for the reaction is the difference between the 2 half reactions:

The Immersion Gold Reaction

Immersion Gold on Nickel:

$Ni \rightarrow Ni^{+2} + 2e$ - 0.250 v

$Au^{+2} + 2e \rightarrow Au$ + 1.498v

Driving force = 0.250 v – (+1.498) = - 1.740 v

Immersion Gold on Palladium:

$Pd \rightarrow Pd^{+2} + 2e$ + 0.987v

$Au^{+2} + 2e \rightarrow Au$ + 1.498v

Driving force = +0.987 v – (+1.498) = - 0.511 v

The immersion gold reaction on nickel proceeds at a much faster rate than on palladium. The immersion gold reaction on palladium proceeds at a lower rate and can only achieve limited gold thickness. Immersion gold thickness on palladium is in the order of 1.2 – 2.0 µin (0.03 - 0.05 µm).

Experimental Design

- The expectation is that nickel corrosion would not occur in ENEPIG as the gold ions have no direct access to the nickel. This would be true if the Pd layer was non-porous and therefore impervious to the gold ions.

- If the Pd layer is thinner (< 4 µin/ 0.1µm), we know that the Pd layer is not totally impervious and the gold ions have access to the underlying nickel thereby proceeding with the preferred and faster reaction path to immersion gold deposition.

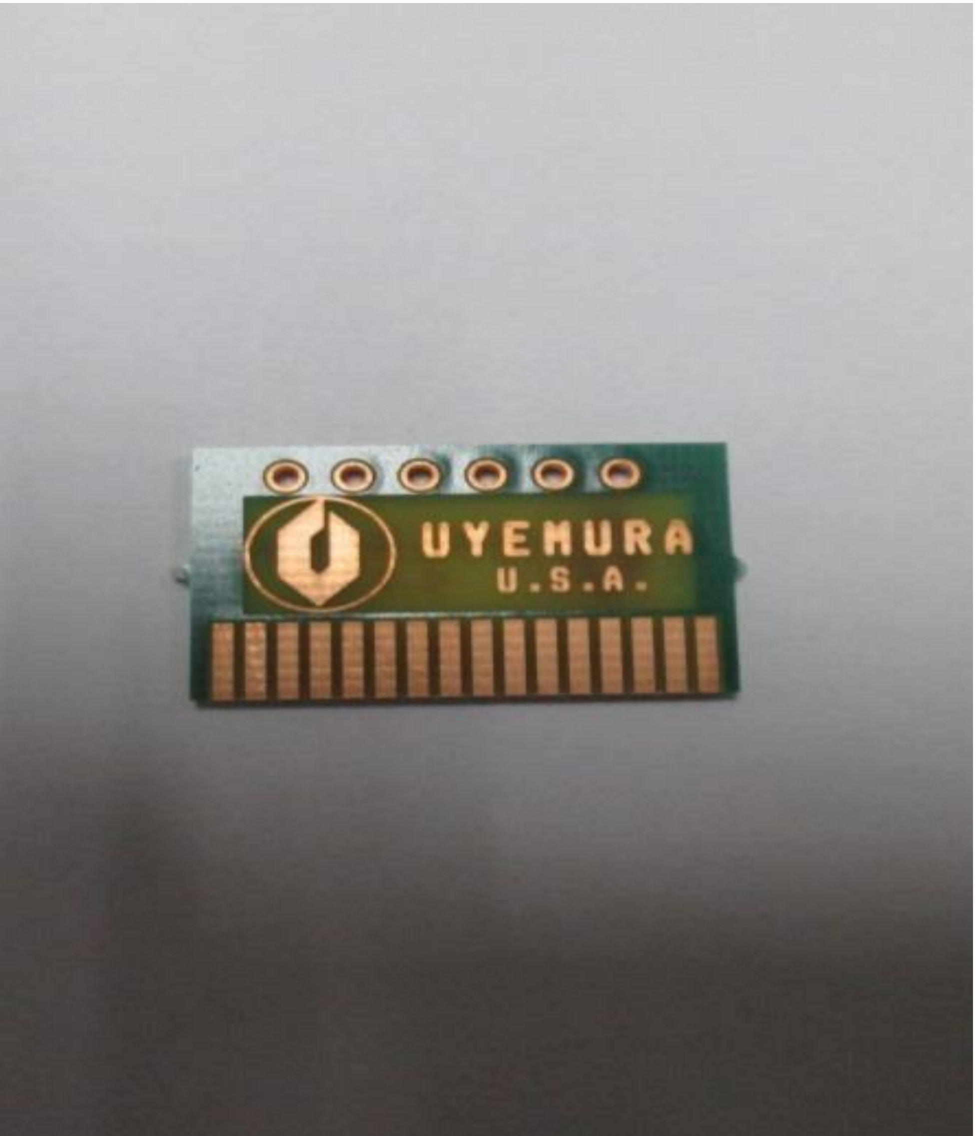
- Nickel corrosion therefore would occur, and the gold would be deposited on the Palladium top layer

Experimental Design

The effect of the following attributes in allowing nickel corrosion to occur were investigated:

- **Thickness of the electroless palladium layer** required to limit / minimize the corrosion of Ni
- The **effectiveness of different types of electroless palladium** (phos vs non-phos) formulations
- The **type of immersion gold (standard immersion vs "Reduction Assisted" immersion gold)** that was used .

Experimental Design



TV & Experimental setup

- The Test Vehicle (fig 1), used in this study consisted of a **double sided, copper clad laminated substrate which was copper plated to a thickness of 20 µm** using an acid copper electroplating process.

- ENEPIG was deposited on the test vehicle using **2 different types of electroless palladium with two different types of gold.**

Nickel Corrosion in ENEPIG

Experimental Design

- The Nickel deposit (7 -8 % Phosphorous) was **a single source and bath type** and was deposited at a **fixed thickness of 225 -275** µin (5.6 – 6.9 µm).

- The electroless palladiums, were, a **phos Pd with ~ 4.0% P** in the deposit and a **non-phos Pd (0% P).**

- Two different gold baths were chosen for this investigation; the first was a standard immersion gold bath that ran at a mildly acidic pH of ~5.5 at a temperature of 180^{o}F.

- the second gold bath was a "Reduction Assisted" immersion gold bath also known as a "Mixed Reaction" bath.

Reduction Assisted Immersion Gold

The bath is combines both an immersion and an autocatalytic (electroless) bath reaction in one electrolyte. The bath composition includes a reducing agent for the autocatalytic reaction.

The deposition of gold in the (RAIG) reaction does not depend on the substrate immersion reaction oxidation alone.

All the plating was done using plating chemicals commercially available from C. Uyemura & Co.

Experimental Design

- The thickness of **the Pd deposit** was varied by **changing the dwell time** in each of the two baths.
- The **rate of deposition was recorded overtime**.
- The samples at different layer thicknesses of Ni-Pd layers were placed in the immersion gold bath for **exaggerated dwell times of 30 minutes**
- The exaggerated dwell in the gold bath was **designed to ensure that some level of Ni corrosion would occur** and that we would be able to see the relationship that the thickness of the Pd layer plays in mitigating Ni corrosion.

Experimental Design

- TEST #1

  Varying Thickness of **phos** palladium with standard immersion gold.

- TEST #2

  Varying Thickness of **non-phos** palladium with standard immersion gold

- TEST #3

  Varying Thickness of **phos** palladium with "Reduction Assisted" immersion gold

- After each test, cross sections of the ENEPIG layer, at different palladium thickness were evaluated for Ni corrosion.

Note: thickness was measured, using a Seiko SEA-5120 Element Monitor MX XRF. The cross section images of the pads of the thru hole were observed using a JEOL JSM-6010LA SEM.

Nickel Corrosion in ENEPIG

Process Sequence

Process Step	Dwell Time minutes	Test #1	Test #2	Test #3
Cleaner	5	5	5	5
Microetch	1	1	1	1
Activator	2	2	2	2
E'less Ni	20	20	20	20
E'less P-Pd[(1)]	1,2,4,5,6,10	X	-	X
E'less Pd[(2)]	1,2,4,5,6,10	-	X	-
IG Standard[(3)]	30	X	X	-
IG Mixed Rxn[(4)]	30	-	-	X

Process Sequence

1. Electroless Phos Palladium
2. Electroless Non-phos Palladium
3. Standard Immersion Gold
4. Reduction Assisted Immersion Gold

TEST #1 Deposit Thickness Phos Pd

TEST #1
Phos-palladium thickness at different dwell times and the corresponding thickness of immersion gold for the different coupons.

Minutes In EP bath	EN µin/µm	EP µin/µm	IG µin/µm 30 mins
1	**272/6.8**	**2.0/0.05**	**4.0/0.1**
2	**272/6.8**	**3.2/0.08**	**3.2/0.08**
4	**272/6.8**	**4.8/0.12**	**2.8/0.07**
6	**272/6.8**	**5.2/0.13**	**2.4/0.06**
8	**272/6.8**	**6.4/0.16**	**2.0/0.05**
10	**272/6.8**	**8.8/0.22**	**2.0/0.05**

TEST #1 Deposit Thickness Graph

TEST 1

Phos-Pd and Gold thickness in µin, vs time in the EP bath.

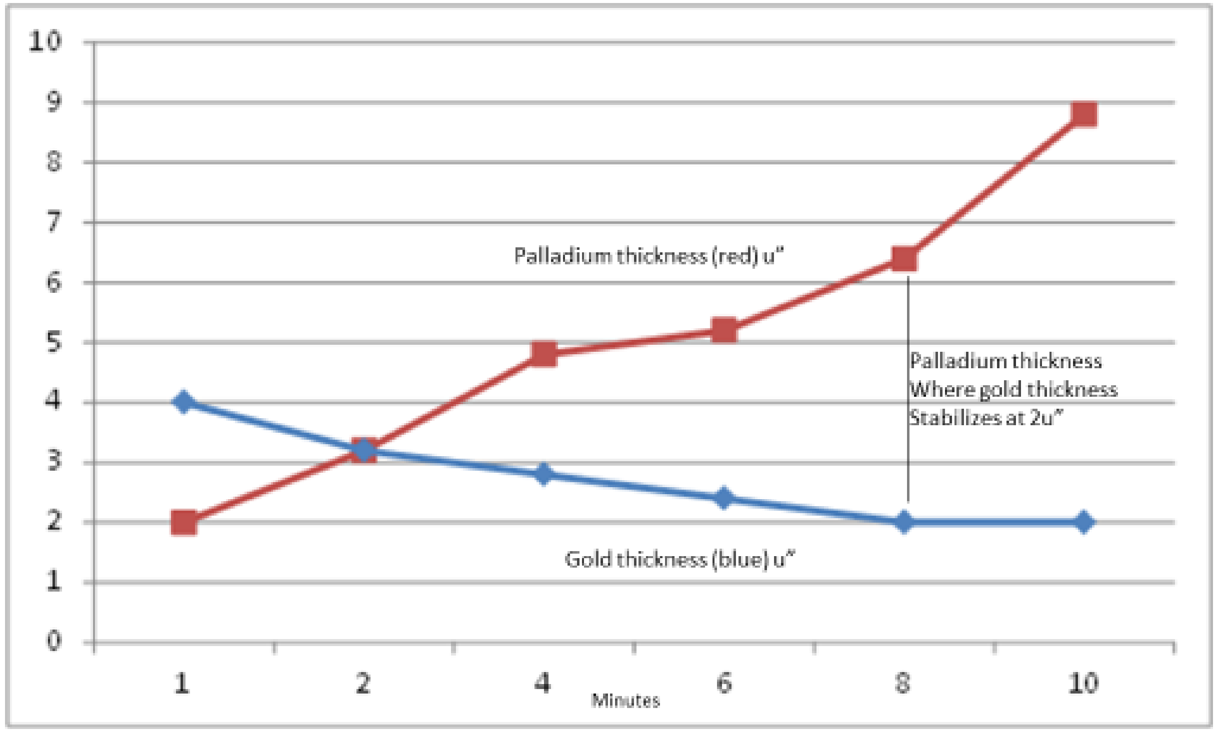
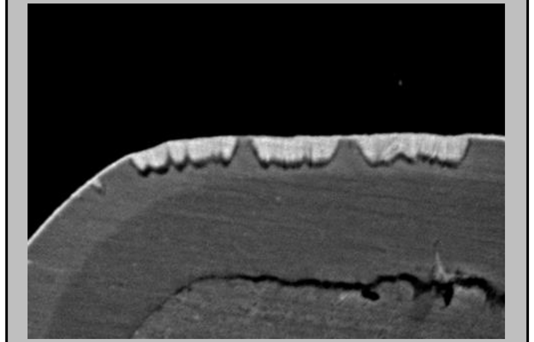


Fig 2. Chart of Phos-Palladium and Gold thicknesses vs time in the palladium bath

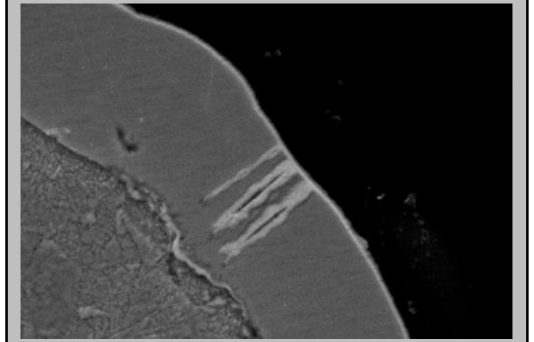
Nickel Corrosion in ENEPIG

TEST #1 Ni Corrosion SEM

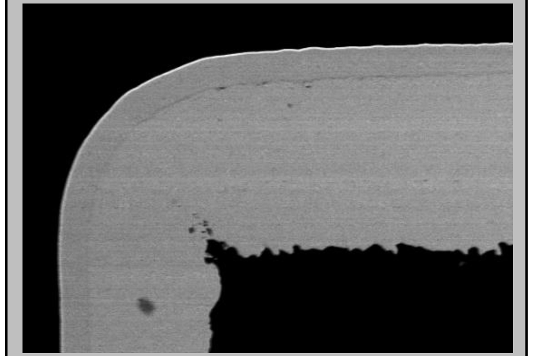
Phos Palladium/Immersion Gold



Ni Corrosion at **2 µin** (0.05µm) of Phos Palladium. Corrosion was extensive and shallow.



Ni Corrosion at **4.8 µin** (0.12 µm) of Phos Palladium. Few intermittent deep corrosion spikes



No Corrosion at **8.8 µin** (0.22 µm) of Phos Palladium. No corrosion was found.

Unacceptable Corrosion

No Corrosion

TEST #2 Deposit Thickness Non Phos Pd

TEST #2
Non-phos palladium thickness at different dwell times and the corresponding thickness of immersion gold for the different coupons.

Minutes in Non-Phos Palladium	EN µin/µm	EP µin/µm	IG µin/µm 30 mins
1	272/6.8	1.6/0.04	3.2/0.08
2	272/6.8	2.4/0.06	2.8/0.07
4	272/6.8	3.6/0.09	2.0/0.05
6	272/6.8	5.6/0.14	1.2/0.03
8	272/6.8	7.6/0.19	1.2/0.03
10	272/6.8	9.2/0.23	1.2/0.03

TEST #2 Deposit Thickness Graph

TEST #2

Non-phos-Pd and Gold thickness in µin, vs time in the EP bath.

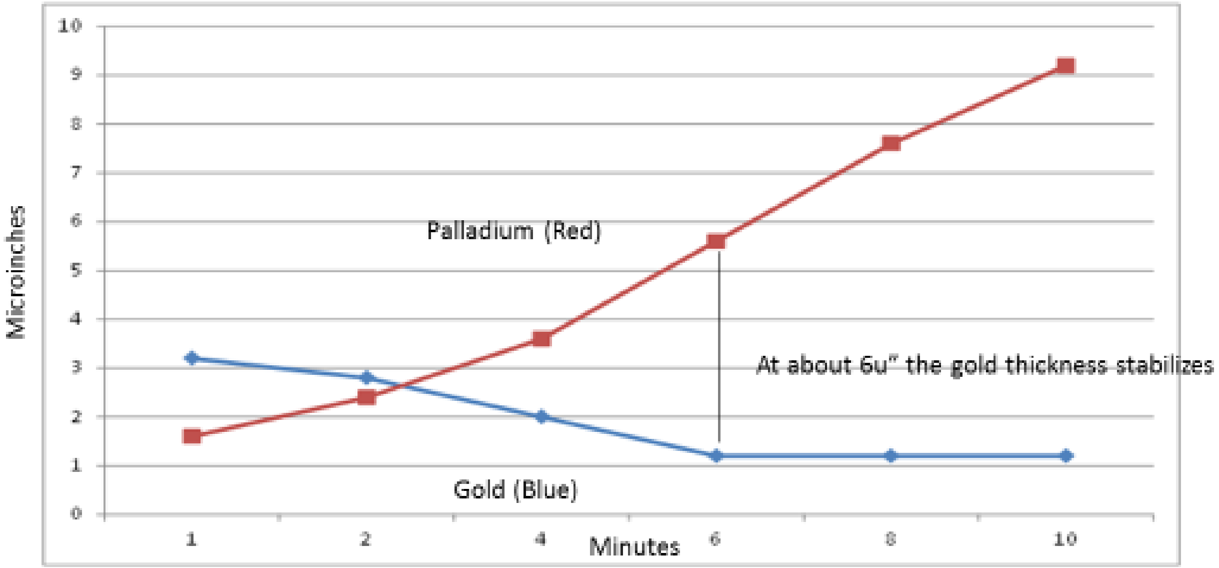
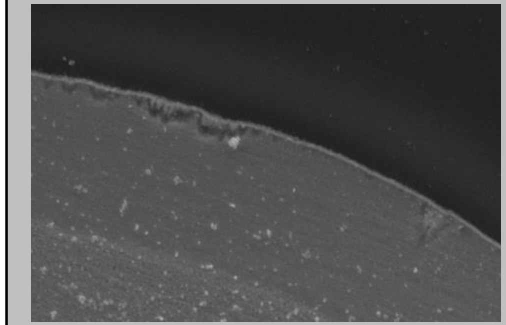


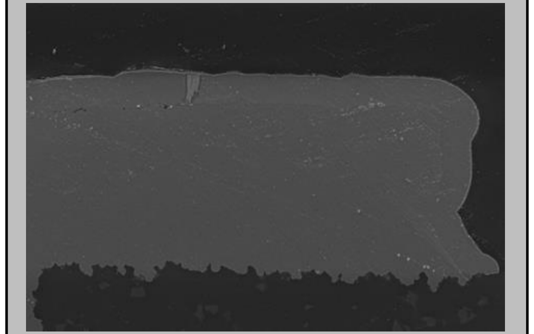
Fig 6 Chart of Nonphos-Palladium and Gold thicknesses vs time in the palladium bath

TEST #2 Ni Corrosion SEM

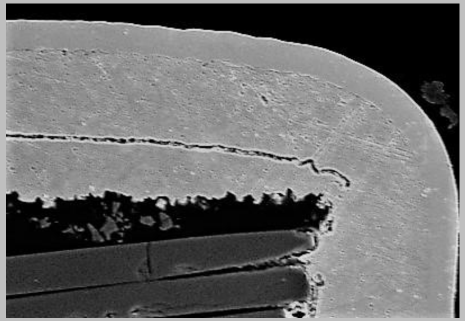
Non-Phos Palladium/Immersion Gold



Ni Corrosion at **1.6 µin** (0.04µm) of Phos Palladium. Corrosion was extensive and shallow.



Ni Corrosion at **3.6 µin** (0.9 µm) of Phos Palladium. Few intermittent deep corrosion spikes



No Corrosion at **7.6 µin** (0.19 µm) of Phos Palladium. No corrosion was found.

Unacceptable Corrosion

No Corrosion

Nickel Corrosion in ENEPIG

TEST #3 Deposit Thickness Phos Pd with RAIG

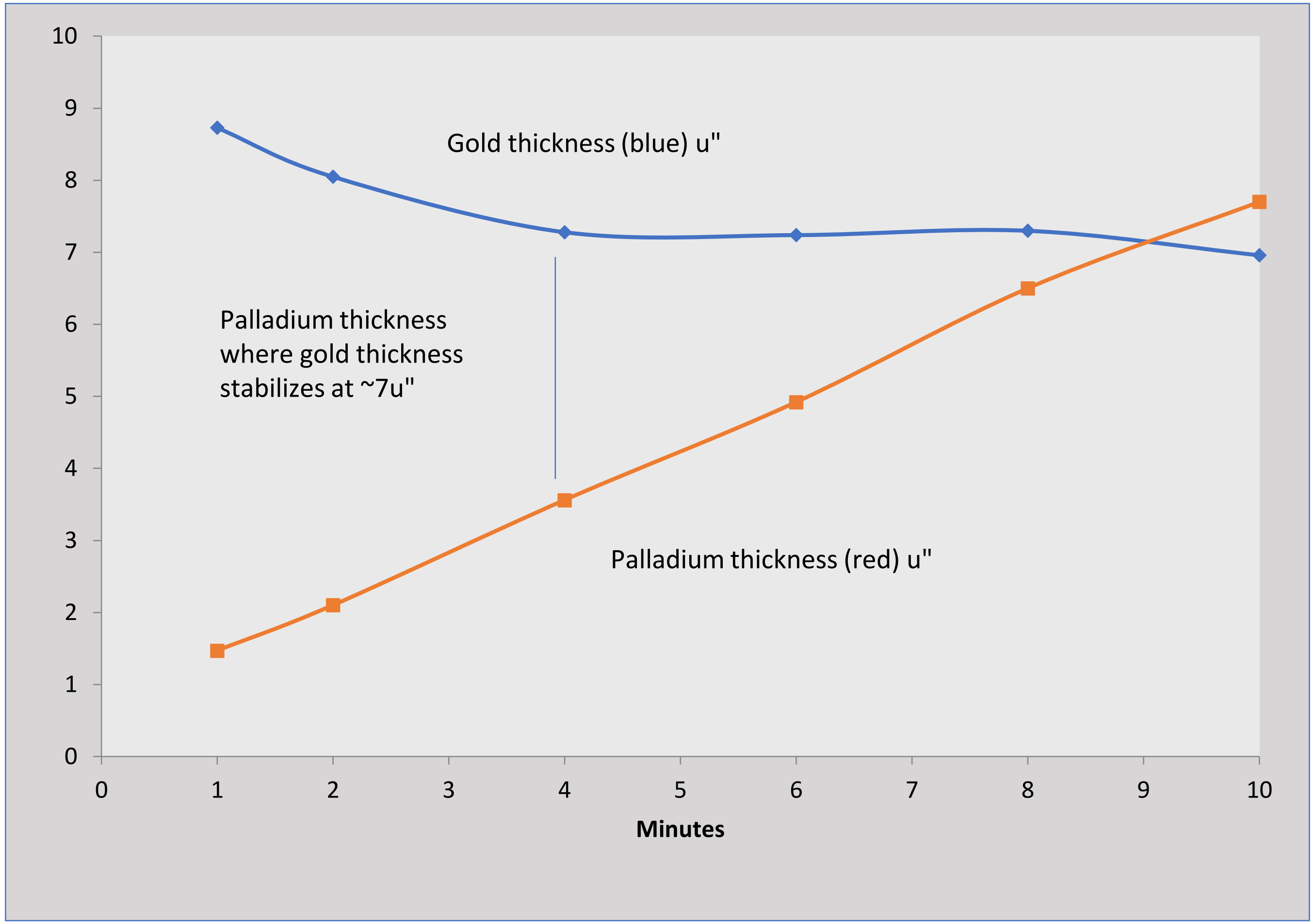
TEST #3
Phos palladium thickness at different dwell times and the corresponding thickness of “Reduction Assisted” immersion gold for the different coupons for Test #3

Minutes in Non-Phos Palladium	EN µin/µm	EP µin/µm	IG µin/µm 30 mins
1	255/6.4	1.5/0.04	8.73/0.22
2	255/6.4	2.1/0.05	8.05/0.20
4	255/6.4	3.6/0.09	7.28/0.18
6	255/6.4	4.9/0.12	7.24/0.18
8	255/6.4	6.5/0.17	7.30/0.18
10	255/6.4	7.7/0.19	6.96/0.17

TEST #3 Deposit Thickness Graph

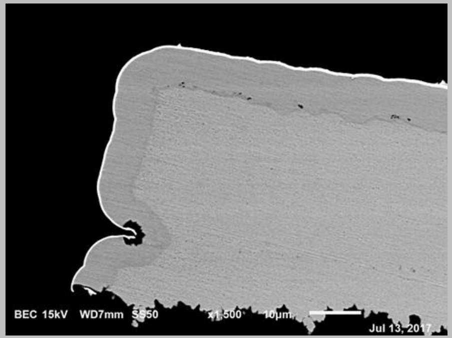
TEST #3

Phos-Pd and Gold thickness in µin, vs time in the EP bath.



TEST #3 Ni Corrosion SEM

Phos Palladium /Reduction Assisted Immersion Gold



Ni Corrosion at **2.0 µin** (0.04µm) of Phos Palladium. Corrosion anomaly due to substrate irregularity

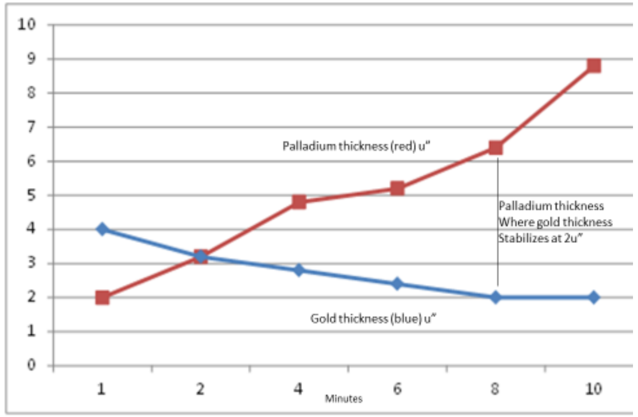
Acceptable Corrosion

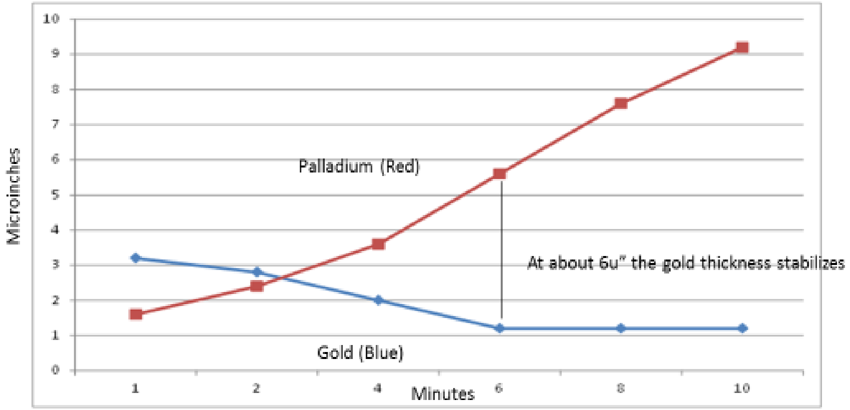
No Corrosion at **6.4 µin** (0.19 µm) of Phos Palladium. No corrosion was found.

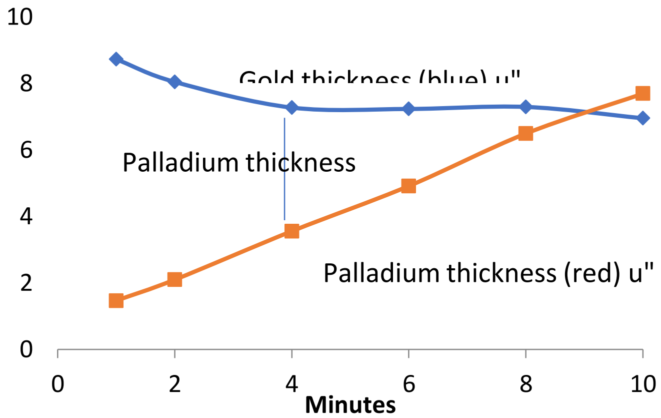
No Corrosion

Nickel Corrosion in ENEPIG

TEST Comparison







TEST #1
Phos Pd/Immersion Gold

TEST #2
Non-phos Pd/Immersion Gold

TEST #3
Non-phos Pd /Reduction Assisted Immersion Gold

The Phos-Pd and the Non-phos Pd show similar trends, with “Standard” immersion gold.

Mitigation

The **data clearly indicates that increasing the thickness** of the **palladium layer** in the **range of 6 -8 uins** would go a long way towards **minimizing nickel corrosion in ENEPIG.**

Presently the **IPC-4556 Specification for ENEPIG specifies for 2 – 12** µin (0.05 – 0.3 µm) the **for the EP layer** and **1.2 -2.8 µin** (0.03 – 0.07) µm for IG.

The authors of this paper recommend increasing the lower limit of EP thickness to 7 µin (0.18 µm).

Mitigation

The increased dwell time in the immersion gold bath is designed to **achieve higher thicknesses of the IG**, which in turn will **create a level of nickel corrosion**, particularly at the lower EP thickness.

IG gold baths should always be run per vendor specification as far as gold concentration, temperature, pH, dwell time and age of bath or MTOs (Metal Turn Overs).

If a thicker layer of immersion gold is a design criteria, immersion gold should be substituted for "Reduction Assisted" immersion gold. This type of gold bath will deposit gold up to **8 µin (0.2 µm)** with no significant Ni corrosion in the ENEPIG deposit.

Conclusion

Nickel corrosion in ENEPIG was reproduced using exaggerated dwell time in the immersion gold bath.

Nickel corrosion will occur at the manufacturing site if there is an attempt to plate thicker (>2.8 µin (0.07 µm) gold with standard immersion gold chemistry.

A different gold bath specifically “Assisted Reduction” Immersion Gold was shown to be capable of depositing higher thickness of gold without compromising the nickel substrate.

SUR/FIN®

CLEVELAND, OH | JUNE 4-6, 2018

Where Finishing Connects

Thank you !!

rdepoto@uyemura.com

UYEMURA USA

Uyemura International Corporation
Southington CT

June 2018 Cleveland OH