ENEPIG and Nickel Corrosion

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Abstract:

Nickel corrosion in ENEPIG deposits has been reported on multiple occasions. It was originally observed in cases where the desired gold thickness was in excess of 2.0 µins (0.05 µm). The boards were left in the gold bath for an extended dwell time until the desired gold thickness was achieved. In those cases, the gold ion reaches through micro-pores and micro cracks that are common in thinner palladium deposits below the palladium substrate to the underlying nickel and continues to deposit, corroding the nickel.

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

Introduction:

Nickel corrosion, also referred to as “Black Pad” has been associated with the ENIG (electroless nickel/immersion gold) surface finish. Nickel corrosion occurs during immersion gold deposition. It occurs when the nickel deposit is compromised (uneven with deep crevices) in combination with an extended dwell time in an aggressive (low in gold content, high in acidity) immersion gold bath.

The expectation with ENEPIG is that these conditions would not exist due to the presence of the electroless palladium layer. However, nickel corrosion was observed in some instances with ENEPIG. Excessive nickel corrosion in an ENEPIG compromises the solderability of the surface finish and would give rise to wire bond lifts at the nickel interface.

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 is a list of metals whose order indicates the relative tendency to be oxidized, or to surrender electrons. The electromotive series begins with the metal most easily oxidized, i.e., the metal with the greatest electron-donating tendency, and ends with the metal least easily oxidized. The tendency to be oxidized, is called the oxidation potential and is expressed in volts. The more negative the oxidation potential, the more readily oxidation takes place. The series is also called the replacement series, since it indicates which metals replace, or are replaced by, other metals. In general, a metal will replace any other metal lower in the series and will be replaced by any metal higher in the series.

The tendency to be oxidized is not absolute; it can only be compared with the tendency of other substances to be oxidized. In practice, it is measured relative to a standard hydrogen electrode, which is arbitrarily assigned an oxidation potential of zero. Table 1 shows select common metals and their oxidation potential, which is a measure of their tendency to undergo the half reaction; $M \rightarrow M^{+n} + n\,e^-$ to occur, in which some metal M loses *n* electrons, e^-, and acquires a positive charge of M^+.

Table 1. Select metals and their oxidation potential

Metal-Metal ion Equilibrium	Electrode Potential (v) vs Hydrogen
Au – Au^{+2}	+ 1.498
Pd – Pd^{+2}	+ 0.987
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

The driving force for the reaction is the difference between the 2 half reactions:

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).

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 is impervious to the gold ions. If the Pd layer is thin (1 – 4 µin/0.025 – 0.1µm)), it is not totally impervious, and the gold ions may have access to the underlying nickel, offering an easier path to immersion gold deposition. Nickel corrosion would occur. A thicker Pd layer (6–8 µin/0.15 – 0.2 µm), would go a long way in preventing nickel corrosion.

The effect of the following attributes in creating nickel corrosion were investigated:

- Thickness of the electroless palladium layer
- Type of electroless palladium (phos vs non-phos)
- Type of immersion gold (standard immersion vs Reduction Assisted immersion gold).

Experimental Design:

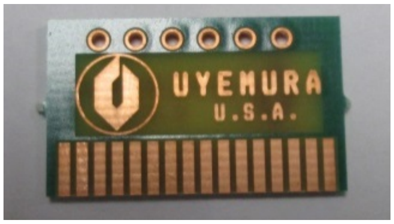

Fig 1 Test Vehicle (2.4 X 1.5 cm)

The test vehicle (fig 1) used in this study consisted of a 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. The nickel deposit (7 -8 % phosphorous) was a single source 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 an acidic pH of ~5.5 at a temperature of 180°F; the second gold bath was a "Reduction Assisted immersion gold" bath also known as a "Mixed Reaction" bath. All the plating was done using plating chemicals commercially available from C. Uyemura & Co.

The thickness of the Pd deposit was varied by changing the dwell time in the baths. The rate of deposition over time was recorded. The different thickness Pd layers were individually placed in the immersion gold bath for an exaggerated dwell time of 30 minutes. The exaggerated dwell in the gold bath was by design, to ensure that some level of Ni corrosion would occur and there would be a way to evaluate the difference that the thickness of the Pd layer would play in Ni corrosion.

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 section thru the ENEPIG layer at different palladium thickness were evaluated for Ni corrosion using SEM magnification.

Table 2. Process Sequence

Process	TEST #1	TEST #2	TEST #3
Cleaner	O	O	O
Microetch	O	O	O
Activator	O	O	O
E'less Ni	O	O	O
E'less P-Pd(1)	O	X	O
E'less Pd(2)	X	O	X

IG Standard(3)	O	O	X
IG Mixed Rxn(4)	X	X	O

(1) Electroless Phos palladium
(2) Electroless Non-phos palladium
(3) Standard Immersion Gold
(4) Reduction Assisted Immersion Gold

Test #1 Phos palladium / immersion gold

Test #1 followed the process sequence outline in Table 2.

Six solder test coupons were plated in electroless nickel to fixed dwell time and nickel thickness. This was followed by Electroless Phos-Palladium. The coupons' dwell time in the EP bath was 1,2,4,6,8 and 10 minutes; giving rise to EP thickness that varied from 2 – 10 µin (0.05 – 0.25 µm) of palladium. All six samples were then immersed into the immersion gold bath for 30 minutes at 180°F.

The holes from each coupon were then cross sectioned. Using the SEM, twenty corners were evaluated for nickel corrosion at 5000 and 1000X.

Minutes In EP bath	EN µin/µm	EP µin/µm	IG µin/µm
1	272/6.8	2/0.05	4/1.0
2	272/6.8	3.2/0.08	3.2/0.08
4	272/6.8	4.8/1.2	2.8/0.07
6	272/6.8	5.2/0.13	2.4/0.06
8	272/6.8	6.4/0.16	2/0,05
10	272/6.8	8.8/0.22	2/0.05

Table 3. Palladium thickness at different dwell times and the corresponding thickness of immersion gold
Fig 2 is a graphic presentation of the data from Table 2.

The data shows that the gold thickness at the lower EP thickness was as high as 4.0 µin (0.1µm.) It diminished as the thickness of the EP increased and was limited to 2 µin (0.05 µm), when the thickness of the EP was 8 µin (0.20 µm) or greater. The explanation is that the gold ions, at the lower EP thickness, had access to the underlying nickel and deposited at an accelerated rate, producing nickel corrosion.

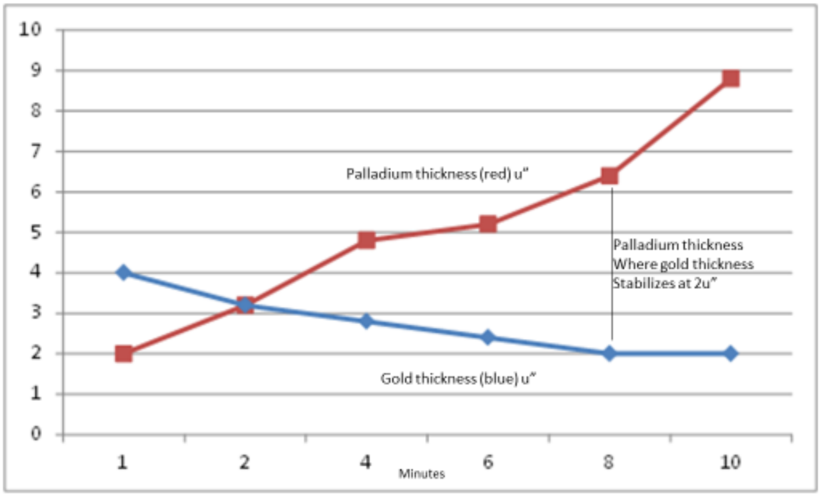

Fig 2. Chart of Phos-Palladium and Gold thicknesses vs time in the palladium bath

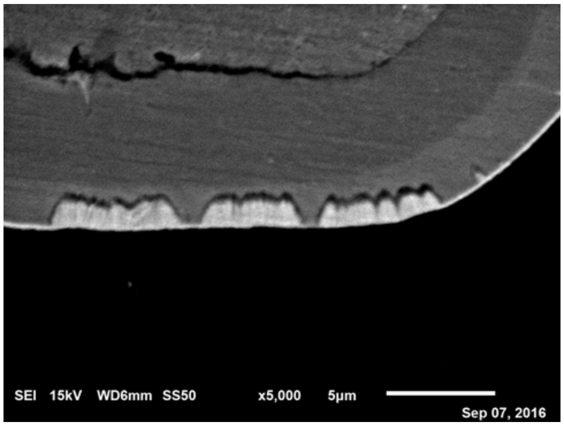

Fig 2 Ni Corrosion at 2 µin (0.05µm) of EP

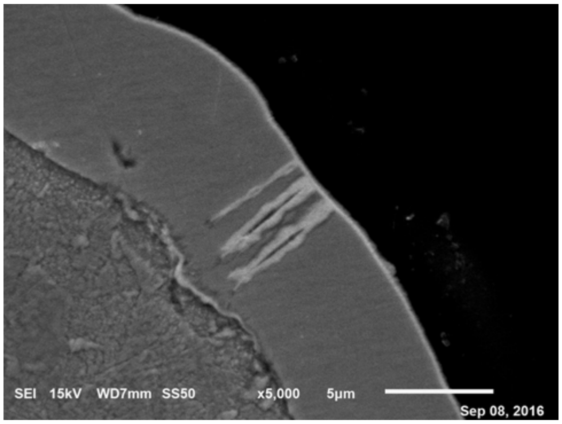

Fig 3 Ni Corrosion at 4.8 µin (0.12 µm) of EP

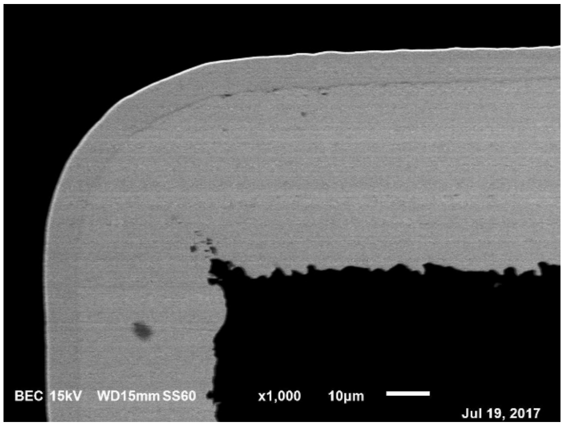

Fig 4. No Corrosion at 8.8 µin (0.22 µm) of EP

Test # 2 Non-phos palladium / immersion gold

Test #2 followed the process sequence outline in Table 2.
Six solder test coupons were plated in electroless nickel to fixed dwell time and nickel thickness. This was followed by electroless non phos palladium. The coupons' dwell time in the EP bath was 1,2,4,6,8 and 10 minutes, giving rise to EP thickness that varied from 2 – 10 µin (0.05 – 0.25 µm) of palladium. All six samples were then immersed into the immersion gold bath for 30 minutes at 180^{o}F.

The holes from each coupon were then cross sectioned. Using the SEM, twenty corners were evaluated for nickel corrosion at 5000 and 1000X.

Table 4 Non-phos EP

Minutes in Non-Phos Palladium	EN µin/µm	EP µin/µm	IG µin/µm
1	27/6.8	1.6/0.04	3.2/0.06
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

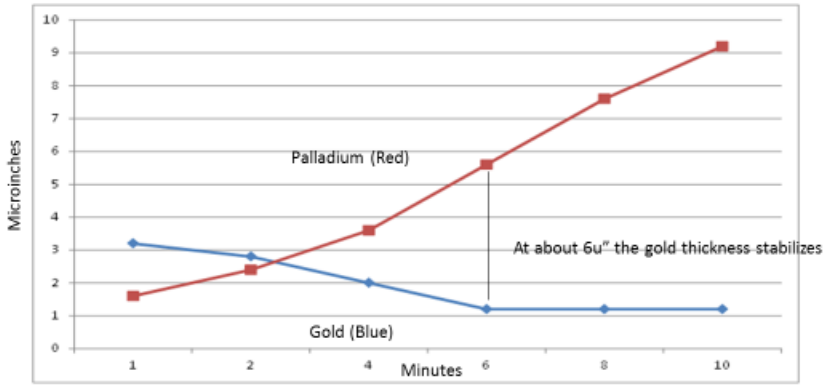

Fig 6 Chart of Nonphos-Palladium and Gold thicknesses vs time in the palladium bath

Under the conditions of the test (the 30 minutes extended dwell time in the gold bath) the data from the non-phos EP shows trends similar to the phos-EP data. At the lower EP thickness, corrosion of the nickel will occur, and at an EP thickness greater than 6.0 µin (0.15µm) no corrosion occurs and the gold thickness is limited to 1.2 µin (0.03µm).

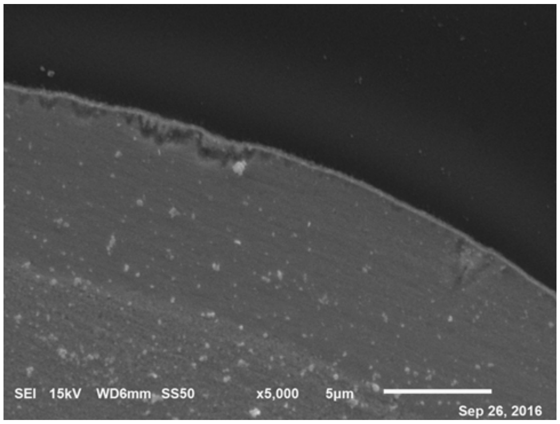

Fig 7. EP at 1.6 µin (0.04 µm)

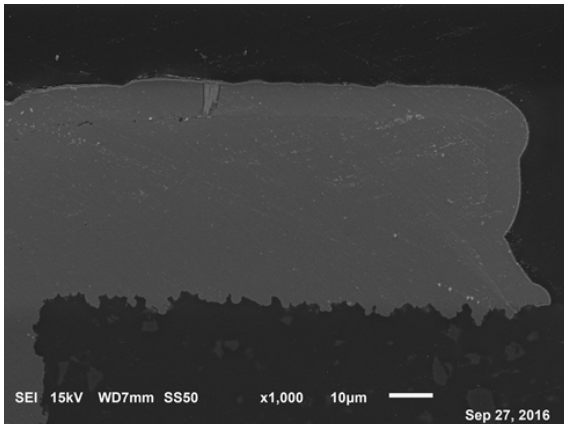

Fig 8. EP at 3.6 µin (0.09 µm)

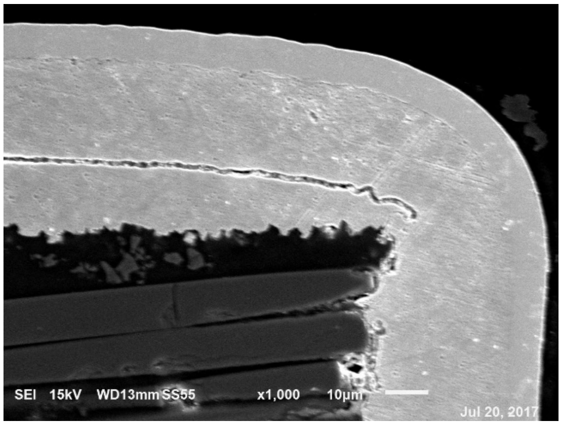

Fig 9. EP at 7.6 µin (0.19 µm)

Table 5.

Phos-Pd with Reduction Assisted Immersion gold

Minutes in Non-Phos Palladium	EN µin/µm	EP µin/µm	IG µin/µm
1	255/6.4	1.47/0.04	8.73/0/22
2	255/6.4	2.10/0.05	8.05/0.20
4	255/6.4	3.56/0.09	7.28/0.18
6	255/6.4	4.92/0.12	7.24/0.18
8	255/6.4	6.50/0.17	7.30/0.18
10	255/6.4	7.70/0.19	6.96/0.17

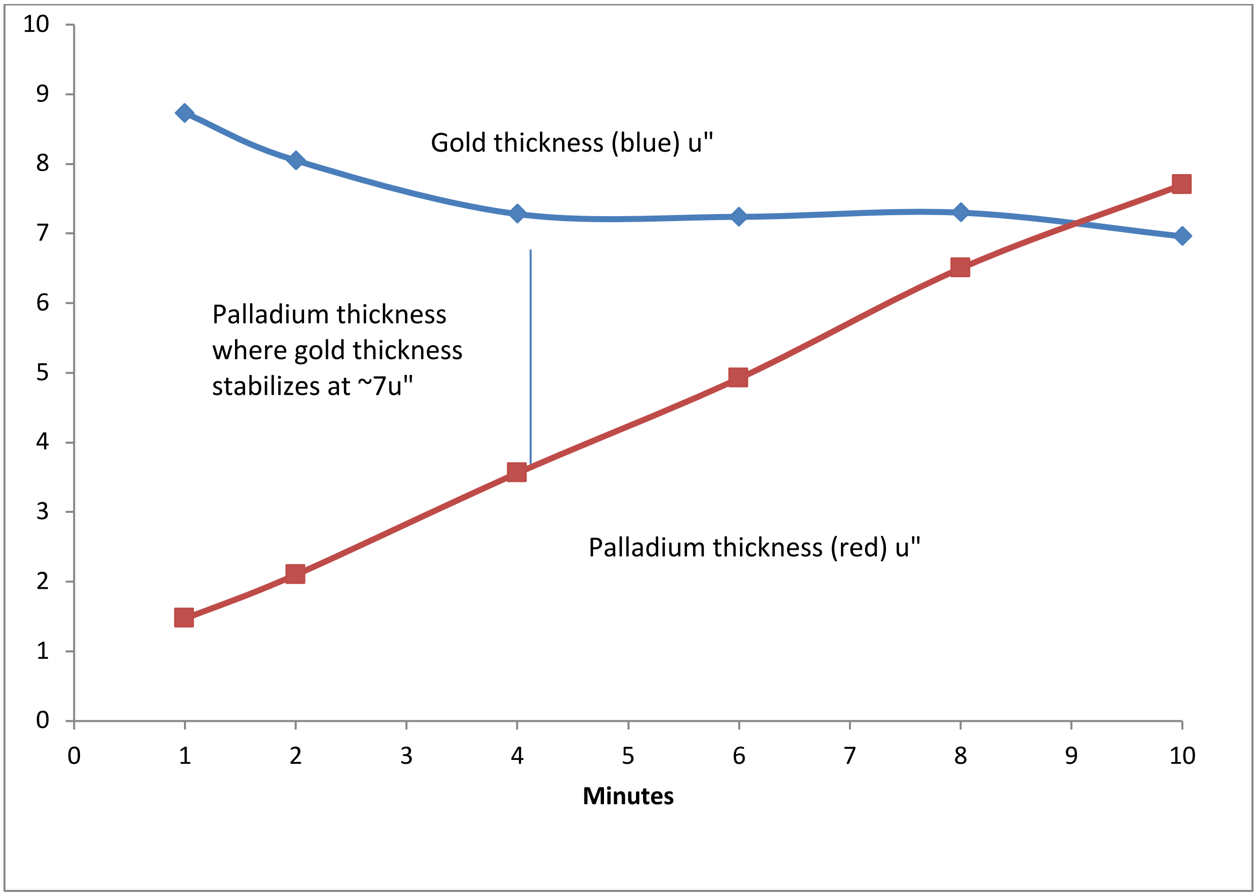

Fig 10. Chart of Phos palladium with Reduction Assisted immersion gold vs time in the palladium bath

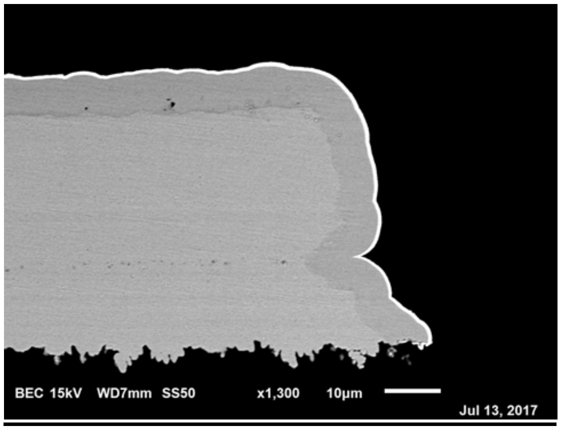

Fig 11. Phos palladium with Reduction Assisted Immersion gold

Mitigation of Nickel Corrosion:

The data clearly indicates that increasing the thickness of the EP layer in the range of 6 -8 uins would go a long way toward minimizing nickel corrosion in ENEPIG. Presently the IPC-4556 Specification for ENEPIG specifies 2–12 µin (0.05 – 0.3 µm) the for the EP layer and 1.2 -2.0 µin (0.03 – 0.05 µm for IG. The authors of this paper recommend increasing the lower limit of EP thickness to 7 µin (0.18 µm)

The increased dwell time in the immersion gold bath, in an attempt to achieve higher thickness of the IG, will create a level of Ni corrosion, particularly at the lower EP thickness. IG gold bath should be run per vendor specification regarding 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, “Reduction Assisted” immersion gold should be substituted for traditional immersion gold. This type of gold bath will deposit gold up to 8 µin (0.2 µm) without any Ni corrosion.

EPIG is an alternative finish to ENEPIG. This finish will eliminate the EN layer, thus mitigating any Ni corrosion.

Click here for information on EPIG, ENIG, ENEPIG and other products from Uyemura, *the global leader in PCB final finishes.*