

Study of the mechanism responsible for “Black pad” defect on PWB’s using electroless nickel / immersion gold as final finish.

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Introduction

Over the past several years there has been consistent growth in the use of electroless nickel/immersion gold (ENIG) as a final finish. The finish is now frequently being used for PBGA, CSP, QFP and COB and more recently gathered considerable interest as a low cost under-bump metallurgy for flip chip bumping application.

One of the largest users for this finish has been the telecommunication industry, where millions of square meters of PCBs with ENIG have been successfully used. The finish offers advantages such as co-planarity, Al-wire bondability and the ability to survive multiple soldering cycles (up to 3 reflows). In addition to these advantages the nickel layer allows multiple hand reworks without copper dissolution being a factor. The nickel also acts like a rivet to improve through-hole thermal integrity.

The assembly industry over several years has experienced various defects associated with surface finishes. A defect known as “Black pad” has been reported. The exact definition of “black pad” varies from chemical vendor / board manufacturer / assembler and OEM. This adds to the confusion. The defect is quite often mistaken for other defects such as de-wetting due to contaminated ENIG surface, BGA interfacial fracture due to mismatch of thermal expansion coefficient differences between materials or associated with miss registration of soldermask, excessive gold thickness >5 microinches and insufficient or no under fill used. Due to the fact that both defects result in a failed or open solder joint, when the joint is de-soldered the underlying nickel appears black. The “black pad” defect is generally at very low ppm level, due to this low level and the number of variables involved, the root cause has been difficult to find.

In addition to the papers referenced several chemical manufactures / PWB fabricators / Contract manufactures / OEM’s have investigated the defect, to give a possible insight to the mechanism.

Below is a summary of some of their observations on “black pad” defect.

1. On examination of the defective solder joints, the pads appear black/ dark gray due to light refraction and the metal surface oxidized from the thermal excursion of soldering.

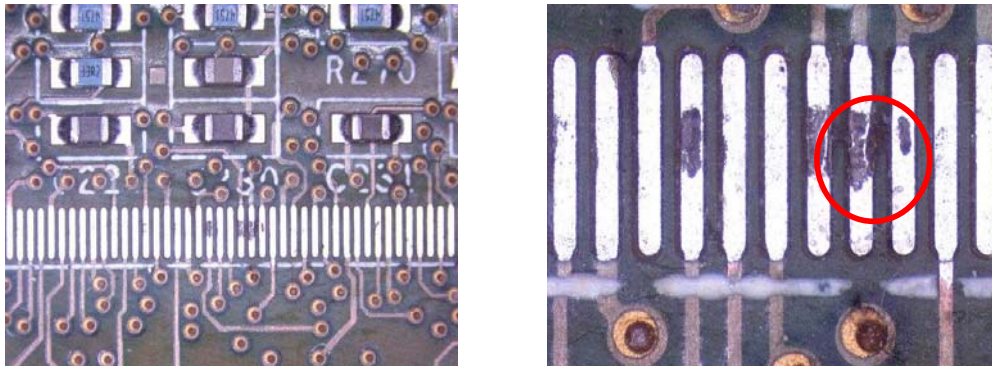


Fig 1 shows QFP defective solder joint assembled with ENIG PWB surface finish.

- Cyanide stripped ENIG shows “mud crack” topography of the electroless nickel surface. Using SEM at X1000 magnification (Scanning electron microscopy). The level of mud cracking has not been correlated, to when a solder joint is defective.

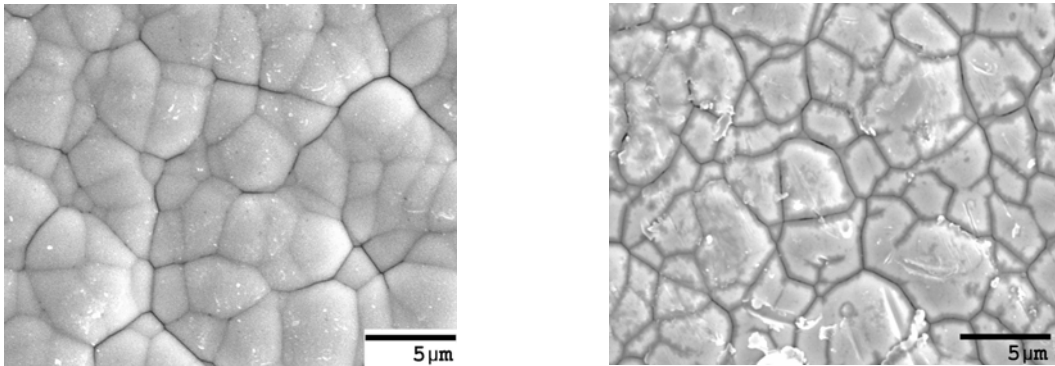
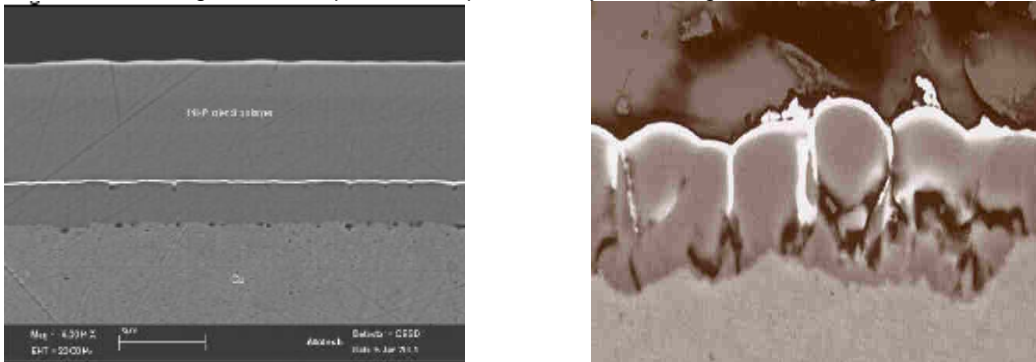


Fig 2 shows with / without “mud cracks” at X1000 mag on the top surface of Electroless nickel after immersion gold cyanide stripped

- Cross-section of through hole/surface mount pad with a reinforced layer on top of the ENIG showing the “tooth decay” effect, deep corrosion of the electroless nickel layer penetrating down to copper level. This is best examined by electroplating a nickel protective layer over the ENIG to prevent gold smear and electroless nickel layer fracturing. It is expected to have a certain amount of gold penetrating into the nickel surface. Ideally this should not be greater than 30% of the total thickness.

Fig 3 SEM X10,000 mag after electroplated nickel protective layer, showing no immersion gold corrosion into the



electroless nickel layer and high levels of corrosion.

- Cyanide strip of immersion gold and examination of the surface reveals light and dark areas. Dark areas representing corrosion / uneven electroless nickel surface morphology.

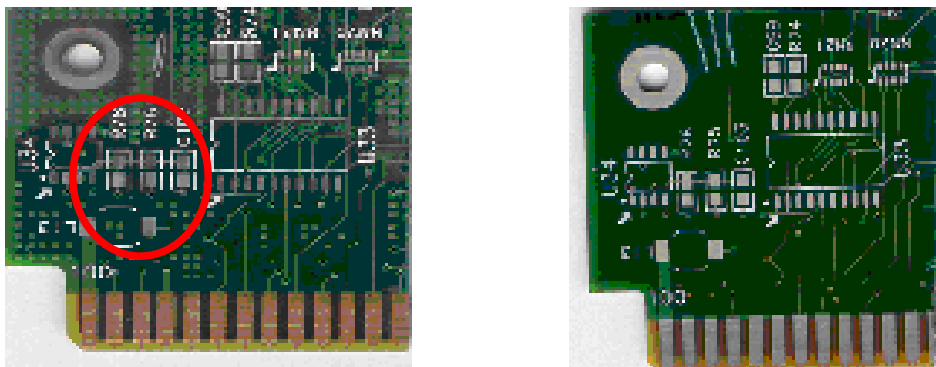


Fig 4 Shows uneven electroless nickel after gold stripping.

- Uncontrolled immersion gold displacement resulting in unsuitable structure on the deposited electroless nickel causing peeling/blistering of the gold layer. Should not be mixed with contaminated or oxidized nickel surface prior to immersion gold deposition.

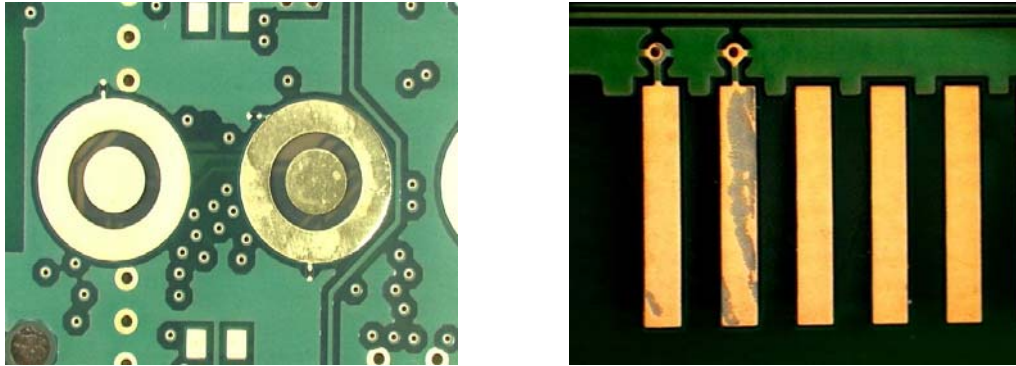


Fig 5 Peeling/ Blistering immersion gold on electroless nickel plating as result of accelerated deposition

Summary of several studies have shown many factors can increase / decrease the “black pad”.

- A minimum electroless nickel thickness of 160 microinches is recommended. Lower thicknesses will produce a more nodular surface morphology giving rise to higher penetration of immersion gold.^{1,2,3,8}

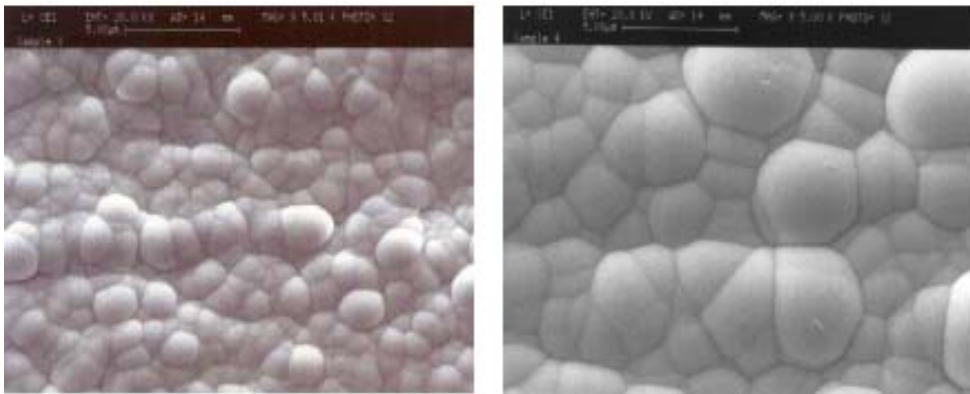


Fig 6 shows low nickel thickness, <100 microinches more nodular surface and normal thickness 200 microinches (+/- 25)

- Deposition rate of the electroless nickel can substantially change both chemical and physical properties of the deposited nickel. This includes internal stress, mechanical and electrical properties and more importantly the phosphorous content co-deposited. As a general rule the faster the rate the lower the P content. Hence a controlled and consistent electroless nickel deposition rate is needed.^{1,2,8}
- Phosphorous content in the electroless nickel has been studied by many and several have made correlations to indicate 7-11%wt is better than 4-6%wt.^{1,2,8,10}
- Immersion gold thickness has clearly shown a strong link to “black pad” defect. The industry is recommending 2-5 microinches. Higher thickness of immersion gold, 6-9 microinches, will result in higher attack of the electroless nickel layer. The impact of high gold will be magnified if the thickness of the electroless nickel is below 120 microinches.^{1,3,8,9}

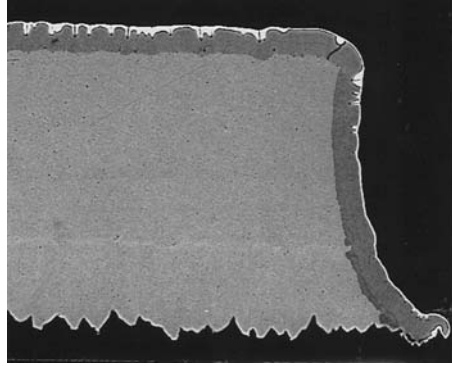


Fig 7 Shows excessive gold penetration into electroless nickel.

Control of your ENIG process is essential, as variation in key process parameters can lead to variability in the ENIG surface that can lead to negative impact on the yield at the assembler.^{5,8} Since the knowledge base from both the PWB manufacturer and chemical supplier has greatly increased over the past 2 years so called “best practices” have been adopted. This has considerably reduced the incidences of “black pad” or other types of defects associated with ENIG.

This study investigated the possible mechanisms that could lead to “black pad” created due to the design of the circuit board.

There remain several unanswered questions regarding the impact of the circuit board design on the creation of “black pad” in certain areas of the board. Examination of defective boards has shown that cyanide stripping the immersion gold and visual examination of the underlying electroless nickel surface for any noticeable darkening would indicate the presence of high corrosion and lead to defective assembly.

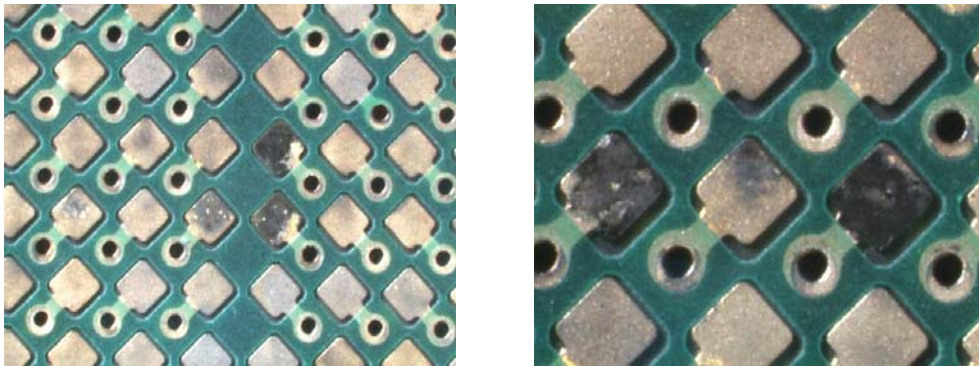


Fig 8 shows after cyanide stripping “black pad” which would result in poor solder joint formation.

The following were investigated:

1. Accelerated deposition of immersion gold onto the electroless nickel layer, caused by a galvanic effect from copper and nickel insitu, electrically connected in the gold bath.
2. Impact of having a different quality of electroless nickel that is electrically connected and then exposed to the immersion gold bath and then varying the exposed surface area of the electroless nickel to the immersion gold bath.
3. Impact of the complexing agents used in the immersion gold bath on the attack of the underlying electroless nickel surface and influence on deposition speed.

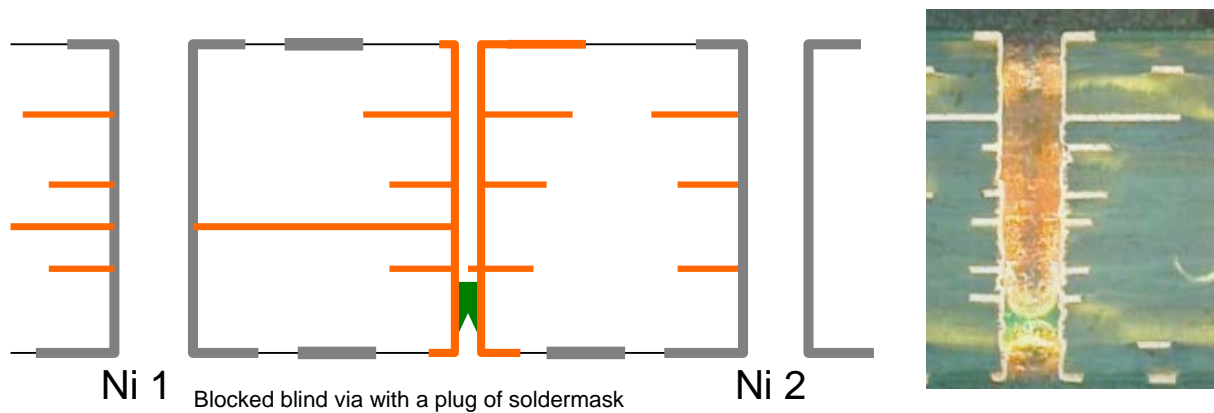
Testing

1. Accelerated deposition of immersion gold onto the electroless nickel layer, caused by a galvanic effect from copper and nickel insitu and electrically connected in the immersion gold bath.

Principle:

A situation could exist where an electroless nickel plated pad that is electrically connected to a hole that is has exposed copper (small via hole) that did not get coated with electroless nickel (skip area) is then exposed to the immersion gold bath chemistry. As complexity is increasing this situation can become more possible, a blind via partially plugged with soldermask electrically connected to several circuits.

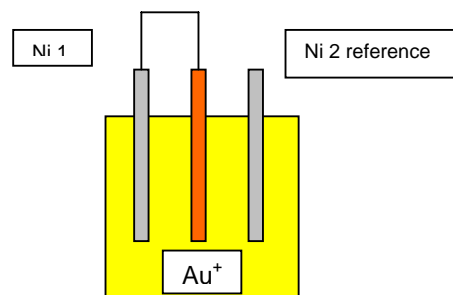
Area were nickel and copper are electrically connected, then exposed to immersion gold bath



Assuming there is a Cu/Ni galvanic element set-up in the immersion gold bath, it is possible that a range of possible mixed metal exposed area ratios could exist. On a standard PWB a hole 0.4 mm in diameter and 2.2 mm in height, hence a copper surface area of 2.75 mm². The pad on the other hand could be 200 μm wide and 1 mm long, so the nickel surface area of 0.2 mm². This is an area ratio of 1:14. Starting on this assumption, we tried several exposed surface area ratios of 36:1 to 1:36 of Ni/Cu galvanic element in the immersion gold bath.

All samples were plated under standard conditions in the immersion gold bath and then samples were gold stripped and surface examined for "black pad" appearance.

Test design:



The simulation of the system Cu/NiP in the immersion gold bath is shown above. An electroless nickel-plated strip (Ni1) was connected to a strip of copper clad board, both with the same surface areas in the immersion gold bath. In addition to this a similar sample of electroless nickel-plated strip (Ni2) for reference was also immersed into the gold bath simultaneously. Using this step we expected to show a gold thickness variation between the electroless nickel-plated strip (Ni1) and the reference (Ni2). The gold thickness of the (Ni1) connected to Cu was 0.82 microns and the reference sample (Ni2) was 0.75 microns, no real variation in gold thickness was observed, the small variation can be contributed to XRF measurement accuracy. Both samples appearance was good before and after stripping. Hence the exposed surface area ratio examined in this case showed no impact

Varying Ni/Cu ratio's

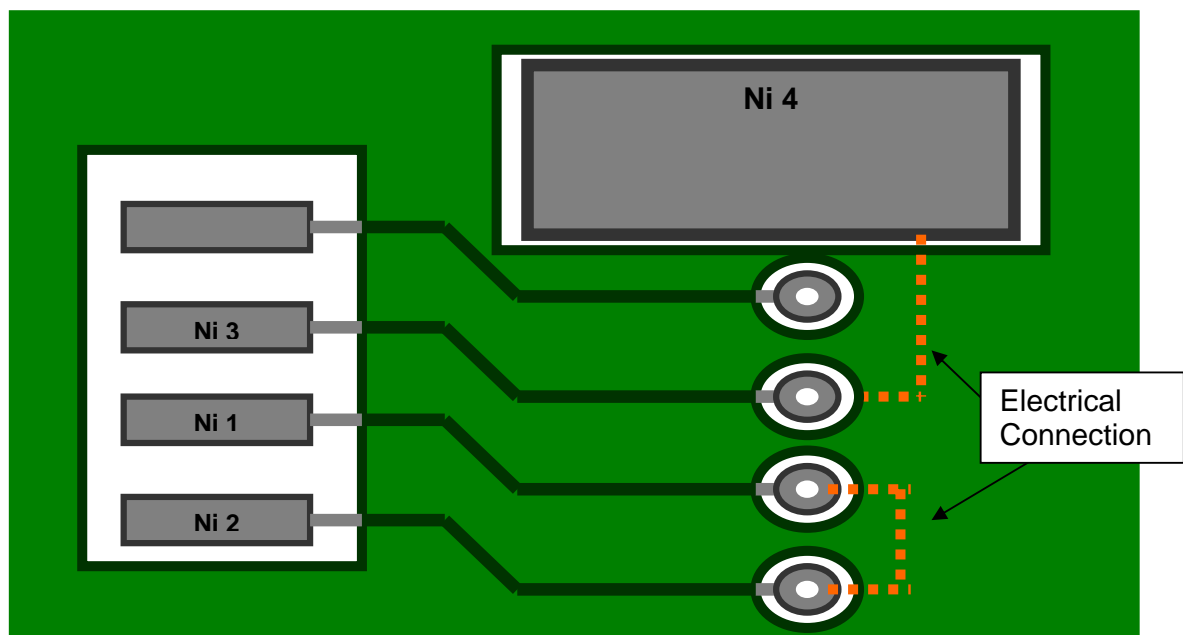
Test No.	Ratio Cu/Ni	Ni [μm] Ni 1	Au [μm]	Time in Gold bath [min]	Ni [μm] Ni 2	Au [μm]	Appearance of Ni After Au stripping Connected / reference (Ni 1 / Ni 2)
1	1 : 1	6,3	0,08	10	5,3	0,08	Grey / -grey
2	8 : 1	4,6	0,10	10	4,7	0,09	Grey / -grey
3	16 : 1	4,4	0,13	10	4,6	0,10	Black / -grey
4	36 : 1	3,8	0,14	10	4,2	0,09	Black / -grey
5	36 : 1	3,7	0,10	10	4,7	0,12	Black / -grey
6	1 : 8	4,2	0,09	10	4,9	0,08	Grey / -grey
7	1 : 16	3,8	0,10	10	3,8	0,10	Grey / -grey
8	1 : 36	3,1	0,08	10	4,4	0,08	Grey / -grey
9	1 : 36	3,6	0,09	10	4,9	0,10	Grey / -grey

The above data shows that as the ratio of exposed copper area to nickel in the immersion gold bath increases to above 8:1 then there is the potential to produce a darker electroless nickel surface as compared to the control, however if the nickel surface area to copper is increased no darkening of the nickel surface after gold stripping was observed.

2. **Impact of having a different quality of electroless nickel that is electrically connected and then exposed to the immersion gold bath and then varying the exposed surface area of the electroless nickel electrically connected in the immersion gold bath.**

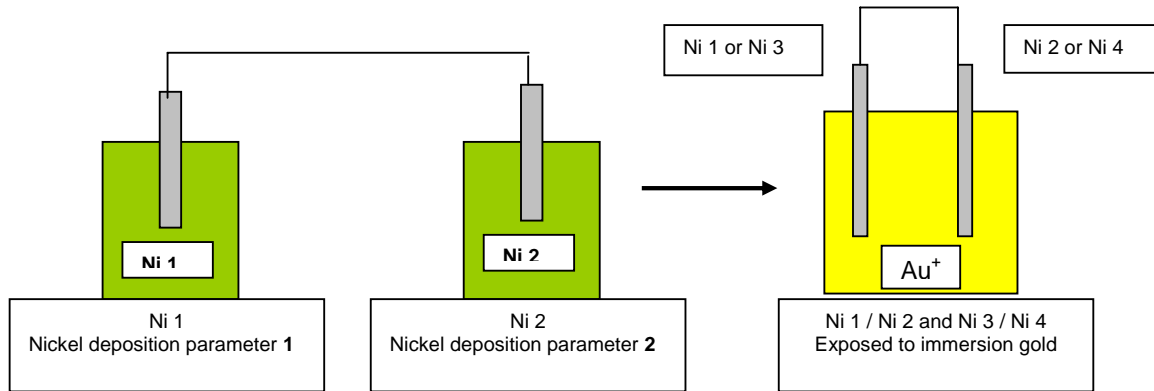
Principle:

Creating different nickel qualities by changing deposition parameters, to built up a Ni-P/Ni-P galvanic element. Checking for "black pad" and then altering the ratio of exposed electroless nickel at different qualities.



In the illustration above there exists two potentials for NiP/NiP galvanic element. Ni 1 and Ni 2 have similar exposed area to the immersion gold bath but may plate in the electroless nickel bath at different rates. It is also assumed that these two pads have a common electrical connection. (for illustration purposes these pads were shown next to each other). The second situation is where Ni 3 and Ni 4 are electrically connected but have a difference in surface area ratio.

Test design:



To simulate a different nickel quality, electroless nickel bath parameters were altered.

Standard Test conditions:

- Nickel bath: Atotech Aurotech CNN nickel
- Nickel make up: 60ml/l Part A / 150 ml/l Make up
- Nickel bath agitation: mechanically
- Dummy plating: 10 min with 0,5 dm²/l
- Gold bath: Aurotech SF plus, 2 g/l Au
- Gold bath parameter: pH 4,8 / T = 80- 85 °C
- Gold thickness: 0,09 to 0,11 µm in 10-15 min

Variation of speed in the electroless nickel bath.:

Test No.	Variable Parameter:		Plating area:		0,5 dm ² /l	
No air	Ni 1	Ni 2	Au Thickness Ni 1	Au Thickness Ni 2	Appearance after Au stripping Ni 1	Appearance after Au stripping Ni 2
5A 1	85°C/pH 5,0	80°C/pH 4,8	0.11	0.11	good	good
5A 2	85°C/pH 5,0	90°C/pH 5,3	0.08	0.08	good	good
5A 3	80°C/pH 4,8	90°C/pH 5,3	0.09	0.09	good	good

In this test maintaining the exposed surface area of electroless nickel but altering electroless nickel bath parameters to obtain a different quality of the plated electroless nickel had no impact. The parameters varied were considered to represent maximum/minimum in normal production environment in temperature and pH variations, caused by localized heating and pH dosing effect in a production condition. On measuring the P content on varying the above parameters the change was +/- 1% (8-9%) this condition may not been sufficient to show variance in nickel appearance. The variation in parameters was considered possible extremes in a normal production environment for the Aurotech™ ENIG process.

Variation in plating rate to alter electroless nickel quality, then exposing different surface area ratio of electroless nickel to the immersion gold bath.

No.	Area ratio	Ni 3	Ni 3 area [dm ²]	Thickness		Appearance after stripping	Ni 4	Ni 4 area [dm ²]	Thickness		Appearance after stripping
				Au	Ni				Au	Ni	
1	20	pH5.3/9 0°C	0.4	0.09	8.82	good	pH4.8/8 0°C	0.02	0.09	4.68	good
2	0.05	pH5.3/9 0°C	0.02	0.09	8.24	good	pH4.8/8 0°C	0.4	0.09	4.32	good
3	20	pH4.8/8 5°C	0.4	0.08	5.86	good	pH4.8/8 5°C	0.02	0.10	6.16	good
4	20	pH5.3/9 0°C	0.4	0.08	8.68	good	pH5.3/9 0°C	0.02	0.10	9.93	good
5	20	pH4.8/8 0°C	0.4	0.11	4.46	good	pH4.8/8 0°C	0.02	0.13	4.42	good
6	200	pH5.3/9 0°C	2	0.09	9.94	good	pH4.8/8 0°C	0.01	0.12	4.57	good
7	0.005	pH5.3/9 0°C	0.01	0.09	8.1	good	pH4.8/8 0°C	2	0.08	4.23	good

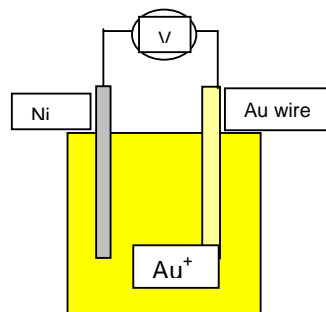
As would be expected we did result in varying the electroless nickel thickness between Ni 3 / Ni 4, due to bath loading impact but generally the gold thickness remained fairly constant. No darkening of the electroless nickel was observed. Hence no impact of Ni/Ni galvanic or area to ratio was observed.

3. Impact of the complexing agents used in the immersion gold bath on the attack of the underlying electroless nickel surface.

Principle:

Many investigations have shown higher gold thickness, > 0.125 microns, can result in a higher level of corrosion on the surface of electroless nickel. The gold deposition rate is dependent on several parameters from the immersion gold bath. In addition to these parameters the underlying electroless nickel surface morphology and percent weight of phosphorous co-deposited can impact gold thickness. In this investigation we looked at the impact of the type of complexors employed in the immersion gold as a function of deposition thickness versus time and the mixed potential of electroless nickel against a gold electrode immersed in the different complexing agents employed in immersion gold baths. Complexors are used in the electrolyte to enable the base metal (Ni) once removed by the displacement reaction to prevent formation of insoluble Ni salts. At the same time the complexor can also affect the attack rate of the base material (Ni) as this must be controlled otherwise a too vigorous displacement would occur resulting in unsuitable structure on the depositing metal. (Peeling of the gold layer).

Test design:



Test No.	Gold bath	Nickel bath Parameters	Ni Au Thickness [microns]	Appearance after Au stripping Ni
1	Complexing agent 1 K[Au(CN) ₂] 2g/l Au / pH 4,8	85°C/pH 5,0	0.12	Good
2	Complexing agent 2 K[Au(CN) ₂] 2g/l Au / pH 4,2	85°C/pH 5,0	0.10	Good
3	Complexing agent 3 K[Au(CN) ₂] 2g/l Au / pH 4,8	85°C/pH 5,0	0.06	Good
4	No Complexing agent K[Au(CN) ₂] 2g/l Au/pH 4,8	85°C/pH 5,0	0.0	Very little plating

The deposition (mixed metal) potentials measured changed as the complexing agent was changed while maintaining other parameters such as gold content, temperature, agitation, immersion time and pH. The data indicates that having no complexing agent has the most electronegative potential.

Deposition versus immersion time in gold bath against different complexing agents

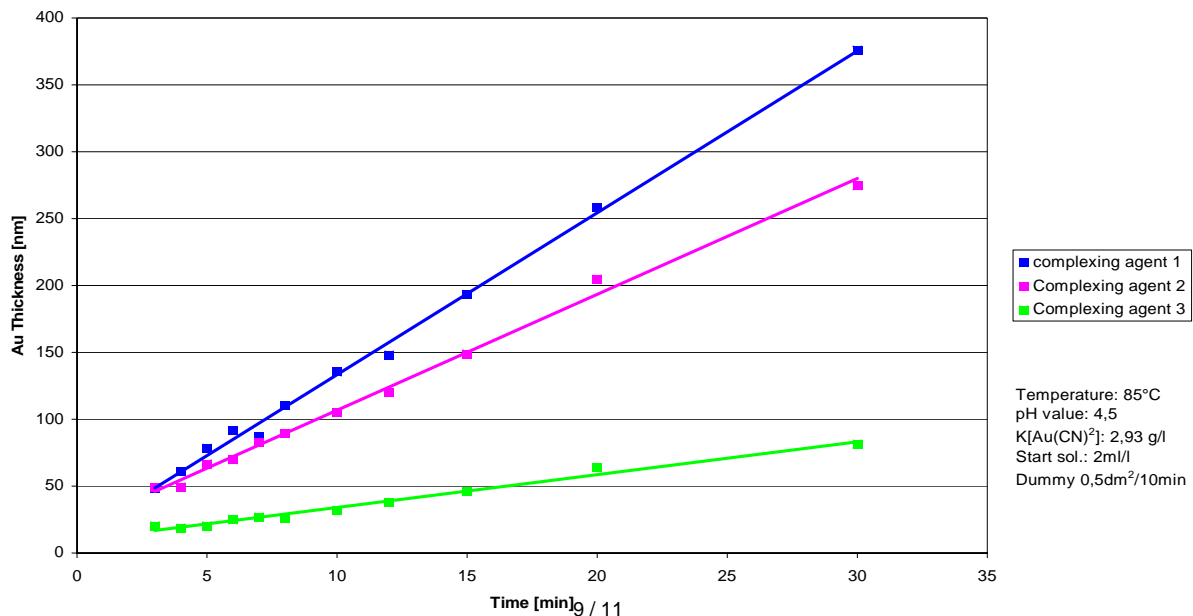
Minutes	Complexing agent 1 [nm]	Complexing agent 2 [nm]	Complexing agent 3 [nm]
3	48	49	20
4	61	49	19
5	78	67	20
6	91	70	25
7	87	83	27
8	110	89	26
10	135	105	32
12	148	120	38
15	193	149	46
20	258	205	64
30	376	275	81

The deposition time of the different samples was 3, 4, 5, 6, 7, 8, 10, 12, 15, 20 and 30 minutes. Gold baths with complexing agents 1, 2 and 3 were used.

Electroless nickel parameters used in the above tests: 4.5 pH and 85 °C. 25 minutes

Deposition rate of NiP/Au inside different Gold baths:

Deposition rate Vs time for different complexing agents used in Immersion Au baths



The testing was able to establish that the type of complexing agent can alter the rate of deposition. In addition to this the complexing agent can act as a “stripper” for the electroless nickel (anodic dissolution) by enhancing the normal displacement reaction in which gold ions are displacing nickel metal. The test proved that the deposition rate is dependent on complexing agent. Examination of panels with greater than 0.13 microns showed darkening of the electroless nickel with complexor 1 more than complexor 2, but both showed a darkening of the nickel once gold thickness of > 0.15 microns was plated. However complexor 3 showed no darkening but also only had a maximum gold thickness of 0.08 microns after 30 minutes, unsuitable for production.

Conclusions:

As many chemical suppliers/board manufacturers have improved or use “best practises” this has greatly reduced this defect. Key factors that have proven to be beneficial are electroless nickel thickness > 4 microns and maintaining a constant deposition rate in both the electroless nickel and immersion gold bath. This is done by process/equipment control and finally ensuring that the mean thickness of the gold deposit is kept in the range of 0.08-0.09 microns. In this investigation we tried to examine the impact of the circuit boards on ENIG chemistry.

1. Accelerated deposition of immersion gold onto the electroless nickel layer, caused by a galvanic effect from copper and nickel electrically connected insitu, in the immersion gold bath. The data revealed that as the level of copper to nickel exposed surface area in the immersion gold bath increases to above 8:1 ratio then there is the potential to produce a dark electroless nickel surface as compared to the control, however the opposite was not the case. On increasing the ratio of nickel to copper no effect was seen.
2. Impact of having a different quality of electroless nickel which is electrically connected and exposed to the immersion gold bath simultaneously. In this test maintaining the exposed surface area of electroless nickel but altering electroless nickel bath parameters to obtain a different quality of the plated electroless nickel had no impact. The parameters varied were considered to represent maximum temperature and pH variations caused by localized heating and pH dosing effect in a production condition. Altering the exposed area of electroless nickel did not affect the surface appearance even at a ratio of 20:1.
3. Impact of the complexing agents used in the immersion gold bath on the attack of the underlying electroless nickel surface revealed that the complexing agent had a considerable impact on the deposition speed. However there is a stronger impact on the thickness of immersion gold deposited than the type of complexor used. The impact may have been greater if a lower phosphorous content electroless nickel bath was used (5-7 %). All complexors selected showed a linear relationship to deposition against time. The question is how steep should the curve be in the given operating range?
4. It should be noted that the results obtained in this study were as result of using the Atotech Aurotech™ ENIG process and should not be summarised to be the case with all other ENIG process.

This investigation into the mechanism responsible for “Black pad” defect on electroless nickel / immersion gold on PWB’s has shown that a galvanic cell between Cu/Ni could exist and result in an accelerated immersion gold deposition resulting in higher nickel corrosion and “black pad” defect. Future studies will continue to look at how the black nickel is impacted by the growth of nickel-tin Intermetallic during soldering and how this impacts joint integrity.

Acknowledgements:

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