Nanotechnology for Lead-Free PWB Final Finishes with Organic Metal

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ABSTRACT

The use of an Organic Metal finish only a few nano-meters deposited onto copper pads of printed circuit boards provides effective protection against oxidation and preserves solderability. The Nano layer has a thickness of only 50 nm, and contains the Organic Metal (conductive polymer) and a small amount of silver. Being more then 90% (by volume), Organic Metal is the major component of the deposited layer; Ag is present equivalent to a thickness of 4 nm. This Organic Metal – Ag complex final finish performs as well as any of the established surface finishes with a significant reduction in energy and environmental impact.

1. INTRODUCTION

Although being an organic material, an Organic Metal (OM) is a special advanced form of a conductive polymer because it possesses metallic properties. It is synthesized and dispersed in the form of 10 nm size primary particles [1]. It has been published several years ago that the Organic Metal has a strong effect in the prevention of Cu oxidation [2]. The Organic Metal Technology has been in commercial use for almost 10 years in a process for finishing printed circuit boards, ensuring solderability after storage and thermal ageing. Here, the Organic Metal is used as the Cu surface preparation "predip" prior to an immersion Sn deposition [3]. This process has become well established and is widely used in the printed circuit board industry as one of the top quality alternative finishes which are required for successful lead-free electronics manufacturing. In this process the Organic Metal predip is applied as an approximate 80 nm thin adsorbed layer which leads to the selective formation of Cu(+1) and a passivation of Cu. It also takes part as a catalyst in providing electrons for the reduction of Sn (2+) which is subsequently deposited as Sn (0) onto the Cu.

Over the past 10 years it has been the object of Enthone's research to provide a solderable surface finish for PCBs which would mainly contain the Organic Nanometal. The first Organic Metal Universal Nanofinish was proposed to the market 4 years ago [4]. It was already suitable for lead free soldering (but not stable enough against discoloration). Now the new generation Nano finish with the Organic Metal – Ag complex performs as well as any other surface finish with regard to ageing resistance, discoloration and solderability.

2. PROCESS DESCRIPTION AND PERFORMANCE

2.1 Process Flow

The Process starts with a combination of a special acid cleaner and a specially adapted micro etch. A short pre-dip (conditioning 60 sec) prepares the boards for the active bath (OMN 35°C for 60 to 90 sec). A final rinse and a dryer complete the process.

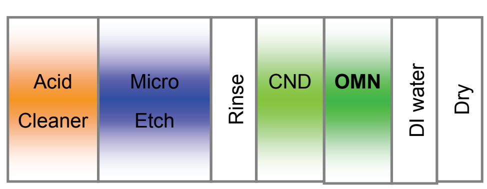


Figure 2.1.1: Process Scheme

2.2 Morphology investigation by SEM and GCM

Figure 2.2.1 shows a scanning electron microscopy (SEM) image of copper pad of a PCB after treatment with the Organic Metal / silver Nano size finish. It shows that the OM-Ag complex is exclusively located on the phase boundaries of the Cu crystallites. Most of the visible area is Cu-surface.

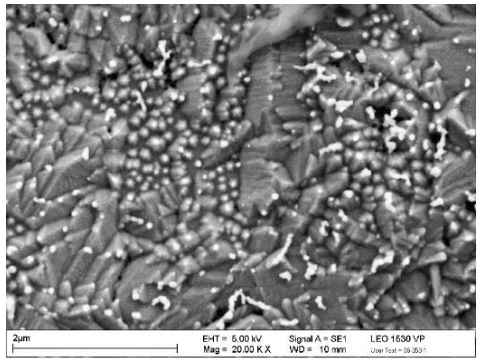


Figure 2.2.1: SEM image of a PCB after treatment with the Organic Metal / silver nano particle finish

2.3 Coulometric Investigation

The electrochemical investigation conducted by a galvanostatic Coulometric measurement (GCM) shows that the Organic Metal Universal Nanofinish has formed a new type of complex (Fig. 2.3.1). The potential at which this complex is oxidized is significantly different from Ag on Cu alone.

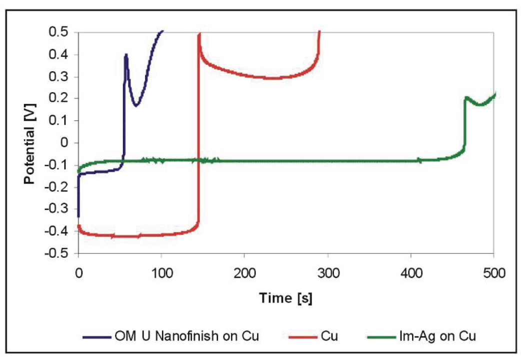


Figure 2.3.1: Potential-time-curves

The finish potentials on the copper surface in relation to the immersion time in the Organic Metal / silver nanoparticle bath are displayed in figure 2.3.2. The potentials indicate that the amount of free copper surface decreases slowly at the beginning of the process, having the highest coverage rate between 40 and 60 s immersion times. After 60 s the rest of the free copper surface is coated slowly, and after about 90 s there is no (electrochemically accessible) free copper detectable.

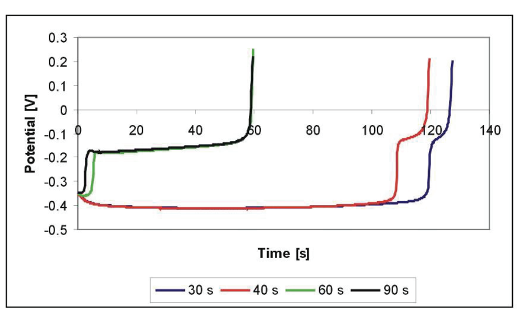


Figure 2.3.2: Potential-time curves for different immersion times

2.4 XPS investigations

XPS depth profiles [5] of copper and silver on the OrmeSTAR ULTRA finished copper surfaces show that the Ag is only detectable nominally to a depth of only 2 – 3 nm, before and after reflow. At the outermost surface the Ag:Cu ratio changes only slightly during the reflow process (becoming smaller), but from a depth of about 2 nm on no change in the ratio could be detected after the reflow process. Hence, no Ag:Cu migration needs to be worried about. The Ag:Cu seems to be immobilized in the complex with the OM.

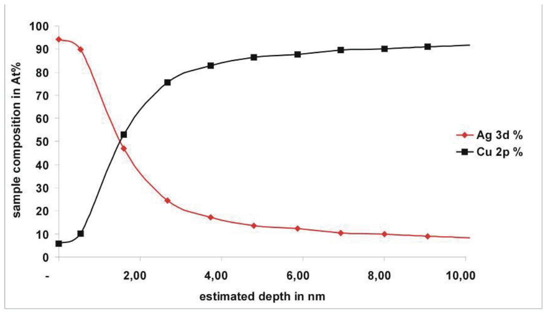


Figure 2.4.1: Distribution of silver and copper in the fresh sample (surface)

Even more interesting is the ratio of metallic to oxidized copper on the surface of the pad before and after reflow as shown in figure 2.4.2. This ratio did not change during the reflow process. This proves the exceptional capability of this new nanofinish in oxidation prevention of Cu.

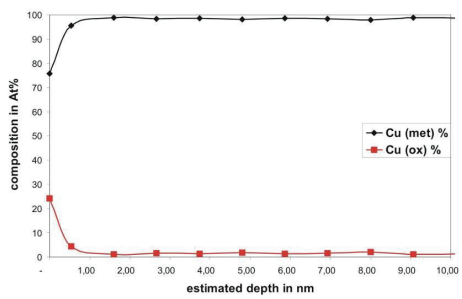


Figure 2.4.2: Ratio of metallic to oxidized copper in the fresh sample (surface)

2.5 Kelvin Potential

The surface potentials of copper, oxidized copper, silver on copper after immersion and Organic Metal / silver nanoparticle finish on copper after immersion were determined using a scanning Kelvin probe (SKP, UBM Messtechnik GmbH). The Kelvin potential is a very reliable indicator of the sensitivity of a surface towards oxidation. Figure 2.5.1 shows a copper surface treated with organic metal / silver nanoparticle finish in the fresh stage after finishing.

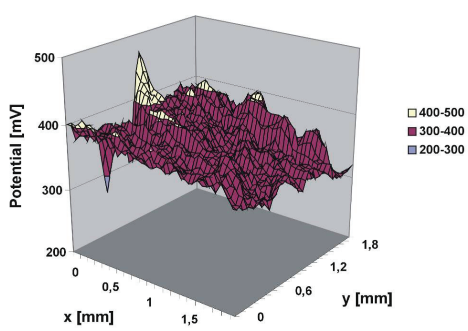


Figure 2.5.1: Copper surface treated with Organic Metal / silver nanoparticle finish

The Kelvin potentials of different treated and untreated copper surfaces are summarized in table 2.5.2.

Table 2.5.2 Kelvin potentials of different surfaces

Surface	**Kelvin potential [mV]**
Cu (pure, unoxidized)	70
Cu oxides	150 - 180
Cu treated with organic metal / silver nanoparticle finish (50 nm layer, containing nominally 4 nm Ag)	320 – 340
Cu treated with immersion silver (500 nm layer)	400

We can see that the new nanofinish composed from an organic metal-Ag nanoparticle size complex reaches almost the same potential as a pure Ag layer which contains over 100 times more silver!

2.6 Microvoids

For some immersion Ag surface processes micro voids may occur due to the galvanic displacement reaction. With the Nanofinish, no micro voids occur because the coating is nearly 100% additive. This deposit results in excellent solder joint strength with ball shear results similar to those found with OSP.

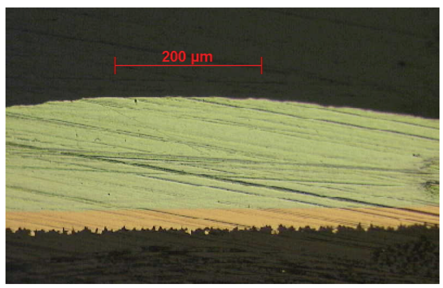


Figure 2.6.1

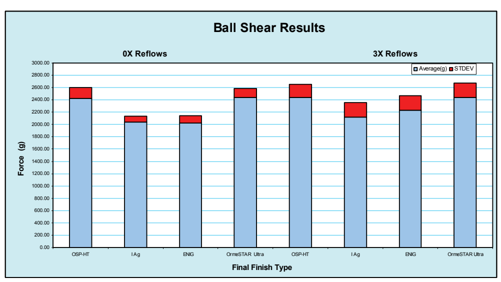


Figure 2.6.2

2.7 Solderability Testing

Wetting balance and wave solder testing were performed to determine solderability after multiply heat cycles. Using a mild rosin bearing flux with SAC 305 solder, test coupons were subjected to multiple reflow simulations with a peak temperature of 260°C. The Organic Metal surface finish performed in a manner similar to OSP-HT and Immersion Silver. Surprisingly, ENIG did not perform well in this testing. Due to the odd result on ENIG, this test was repeated with fresh samples from the same PWB vendor, a different vendor with the same bath, and a third vendor with a completely different system, all with the same results.

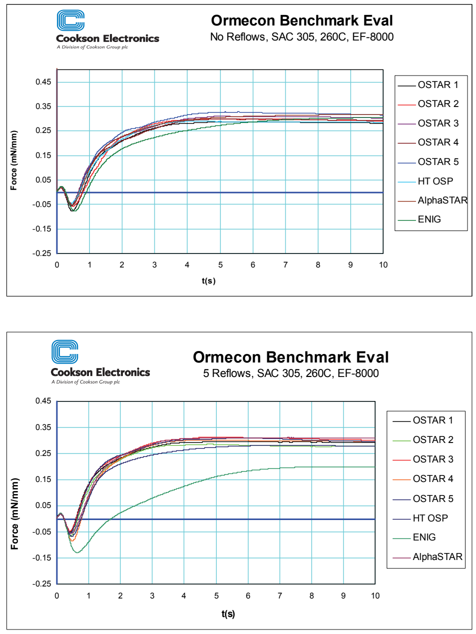


Figure 2.7.1

Wave solder testing was performed on a standard test vehicle with 1200 holes drilled at 10, 20 and 30 mils. The double sided test vehicle uses different pad sizes and shapes with two thicknesses at 0.063 and 0.093 inches.

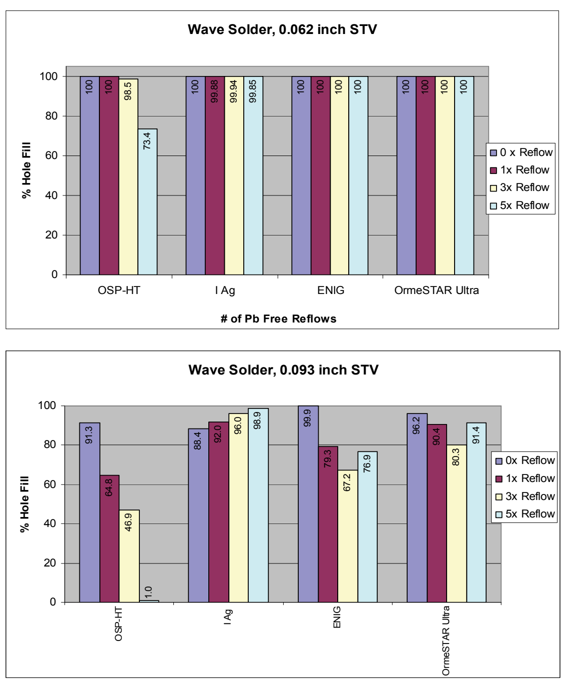


Figure 2.7.2

The wave soldering results show the Organic Metal surface finish solders as well as or better then immersion silver or ENIG.

The Nanofinish does not show any discoloration during reflow. The excellent solderability of the surface was also confirmed in reflow tests. Figure 2.7.3 shows a printed circuit board before treatment, directly after the surface finish with OrmeSTAR Ultra and the surface after treatment and reflow conditioning..

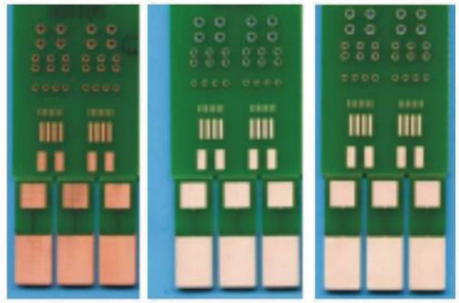


Figure 2.7.3: No discoloration after reflow

Figure 2.7.4 shows a test panel after three lead free reflow steps. First practical tests in PCB manufacturing and in assembly facilities have confirmed these results.

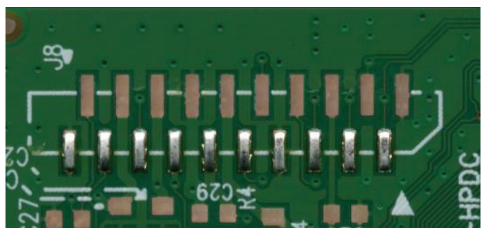


Figure 2.7.4: Excellent wetting after 3 lead free reflow steps

The very good solderability results have been confirmed by an external evaluation of Nanofinish is given in figure 2.8.1

2.8 Solder joints

An external study [6] shows that the lead-free-Sn solder joints (BGA pads) with the Nanofinish are of superior quality without defects compared to those solder joints made on the ENIG surfaces. Signs of wetting failure were not apparent and the Nanofinish solder joints are expected to be more long-term reliable.

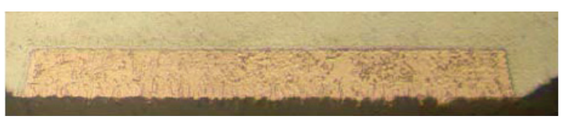


Figure 2.8.1: Perfect solder joint

The ENIG surface showed an increase in P between the ternary phases and the NiP phase, which can lead to cleavage fractures. Critical phase formation was found in all NiP / Au samples. The external analysis concluded that "according to the actual results for lead free tin soldering all PCBs finished with the Nanofinish surface are distinctly superior to PCBs with NiP/Au surfaces, with regard to solderability and in view of forming reliable solder joints. "

3. Summary

The Organic Metal based Nanofinish is the first described example of a nanoparticulate complex between an Organic Metal and Ag. Although it does not form a closed nanolayer, it completely and effectively protects the Cu and prevents it from being oxidized even after four lead free reflow steps. Its aging resistance and wetting (soldering) performance is excellent and equal to or better than other well-established metallic finishes. This finish should be considered by anyone currently struggling with the cost and soldering inconsistencies of ENIG or attempting to use OSP on demanding multilayer PCBs.

REFERENCES

[1] B. Wessling, Handbook of Conducting Polymers (T. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, Eds.). Dekker, New York, (1998)
[2] B. Wessling, Adv. Mater. 6, 3, 226, (1994)
[3] www.ormecon.de (ORMECON CSN, technical information)
[4] N. Arendt, C. Arribas, J. Posdorfer, M. Thun, B. Wessling, OnBoard Technology, 12, (April 2006)
[5] B. Wessling M. Thun, C. Arribas-Sanchez, S. Gleeson, J. Posdorfer, M. Rischka, B. Zeysing, NRL article, (2007)
[6] Dr.-Ing. Manfred Deger, Analytik - Labor – Possendorf, (June 2007)

Additonal internal studies performed by Enthone SAMPL labs.

Nanotechnology for Lead-Free PWB Final Finishes

Presented By: Jim Kenny

APEX 2010

Properties of the Organic Nanometal

- a conductive polymer
- a noble metal – almost as noble as silver
- a nanometal – primary particles 10 nm in size
- a catalyst for

  - oxidation and reduction processes

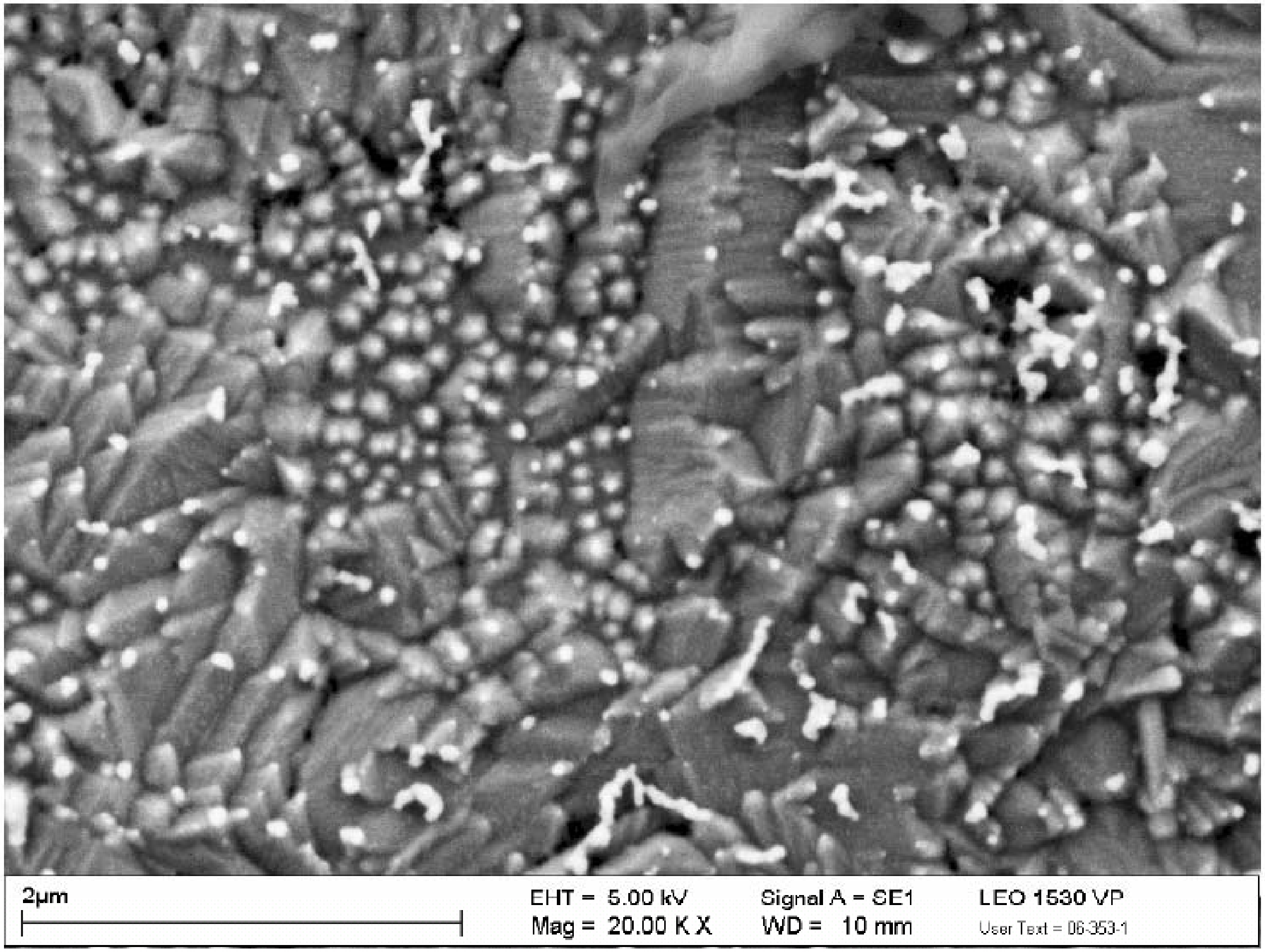
  - passivation of Cu, Fe, ...

  - deposition of Sn on Cu (PCB finish)

  - complexion of Cu and oxidation prevention

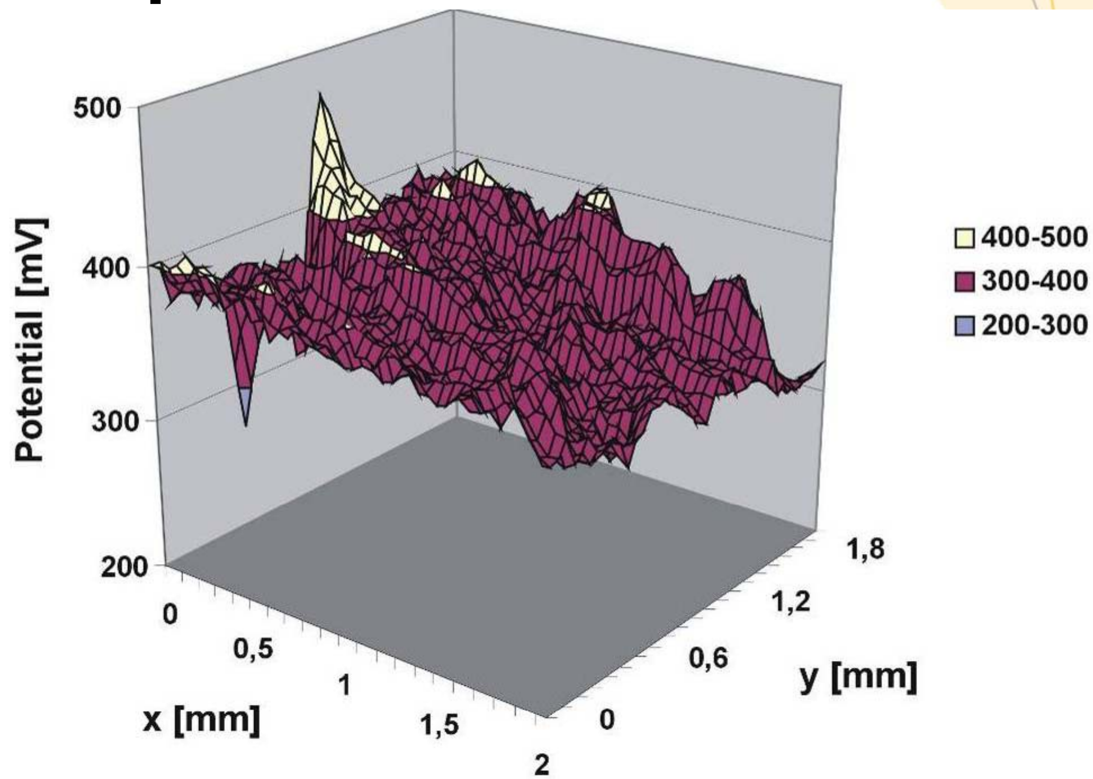
SEM of Nanofinish® layer

- **SEM picture:**
  50 nm particles arranged at the phase boundaries, the active sites
- nominally
  4 nm Ag
- 90% Organic Metal (by volume), 30% by weight



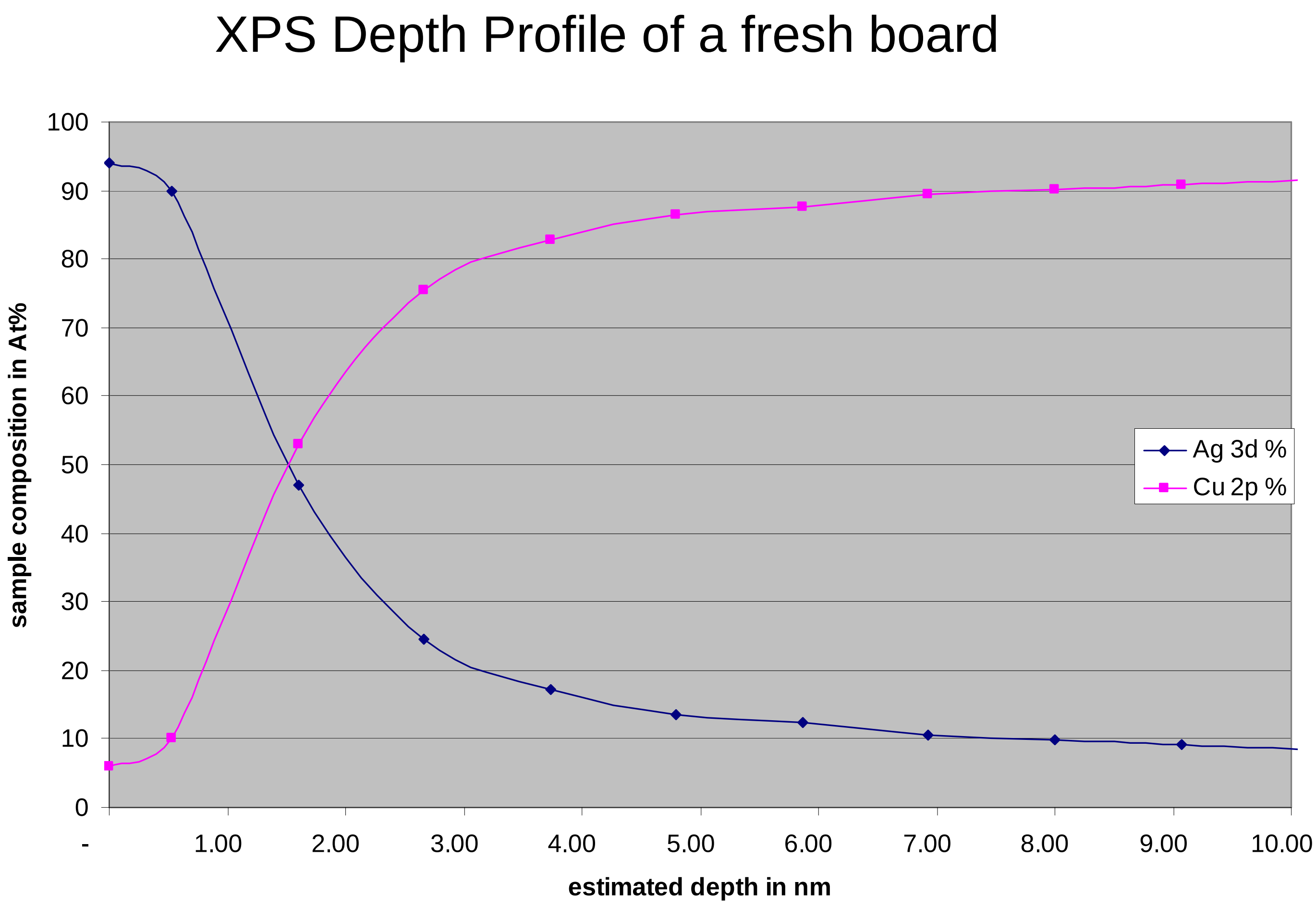
Kelvin potential

- **Kelvin Potential** (a surface potential characterizing ability to remove electrons)



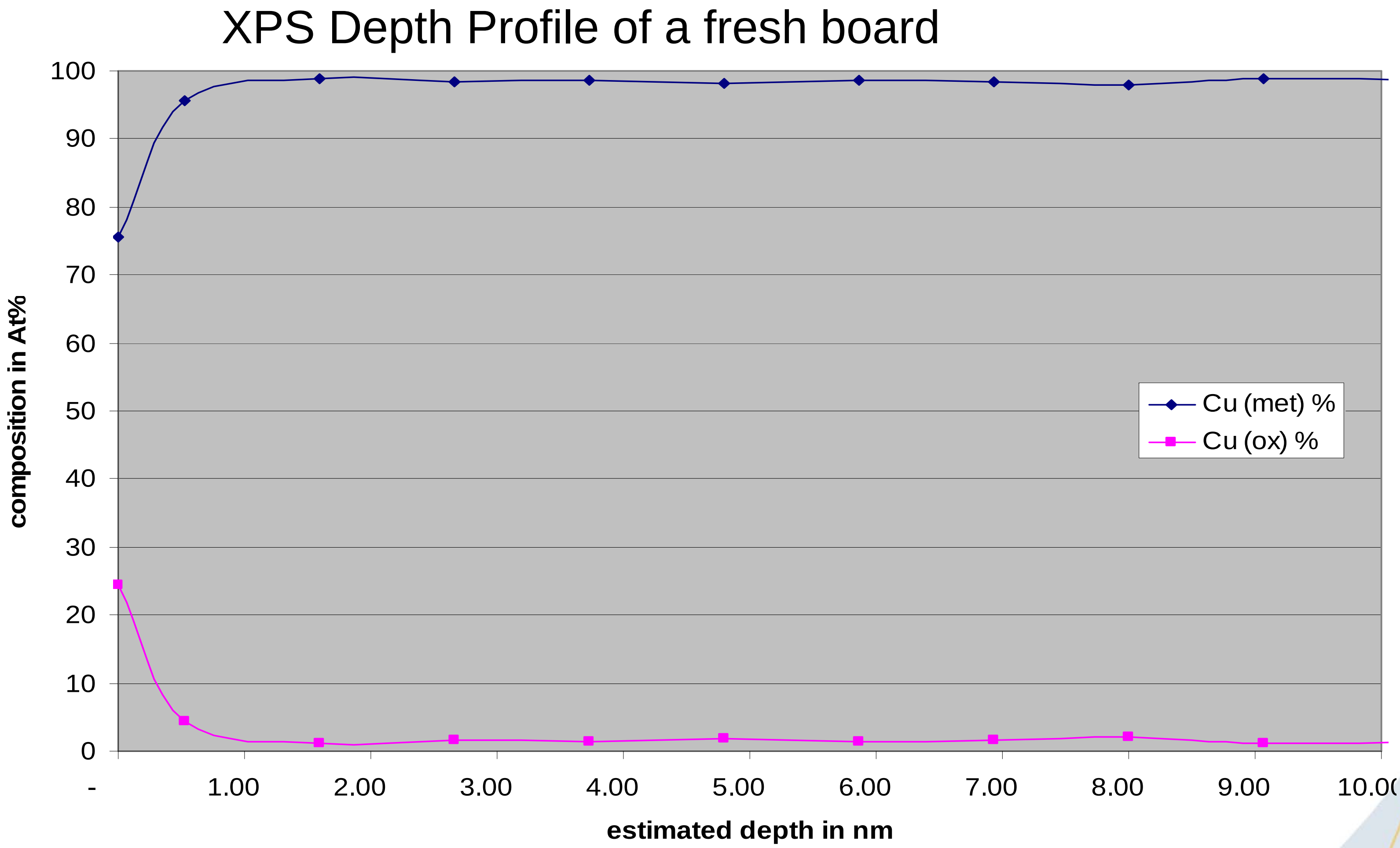
Surface	Kelvin potential [mV]
Cu (pure, unoxidized)	70
Cu oxides	150 - 180
Nanofinish (50 nm layer)	320 – 340

XPS evaluations



Ag can only be found on the outermost surface

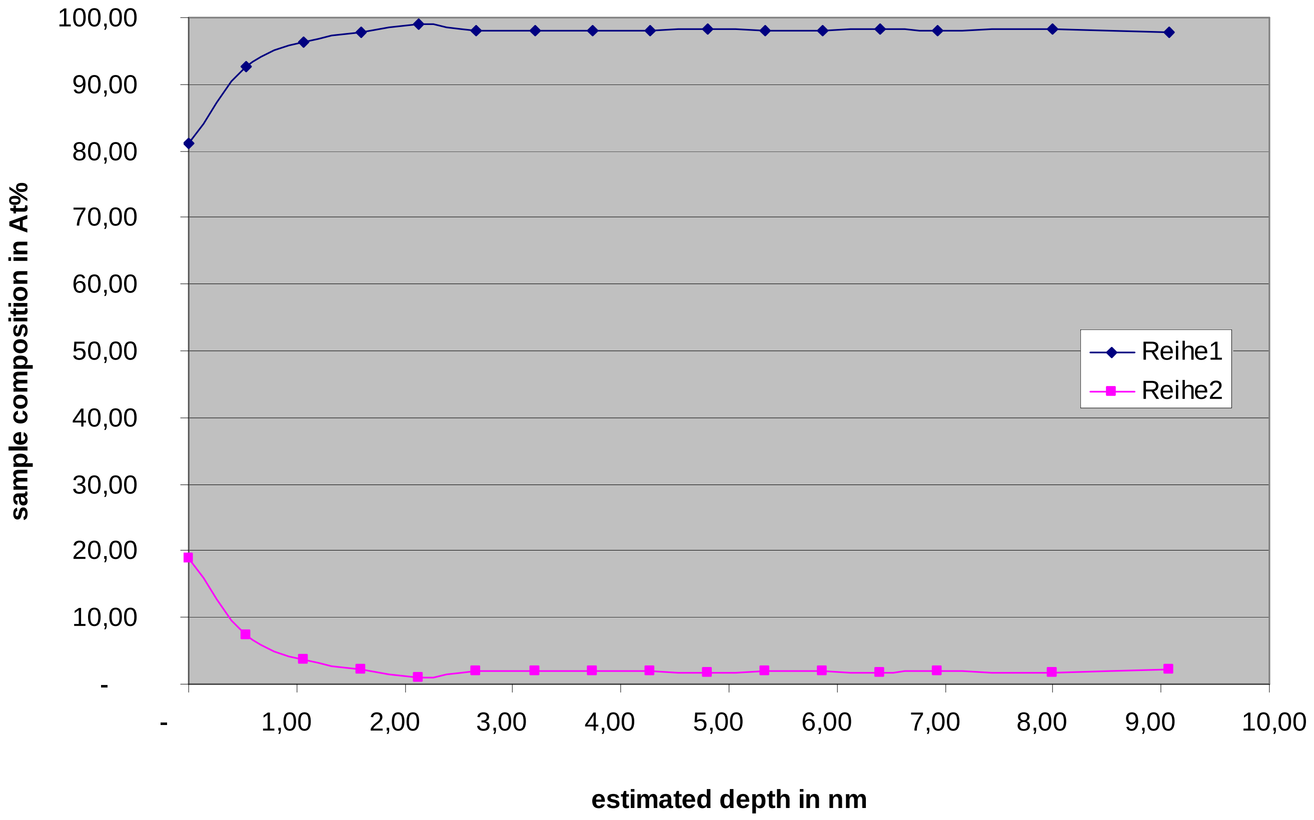
XPS: no oxidation



extremely low oxide content

XPS: no oxidation

XPS Depth Profile after one reflow step



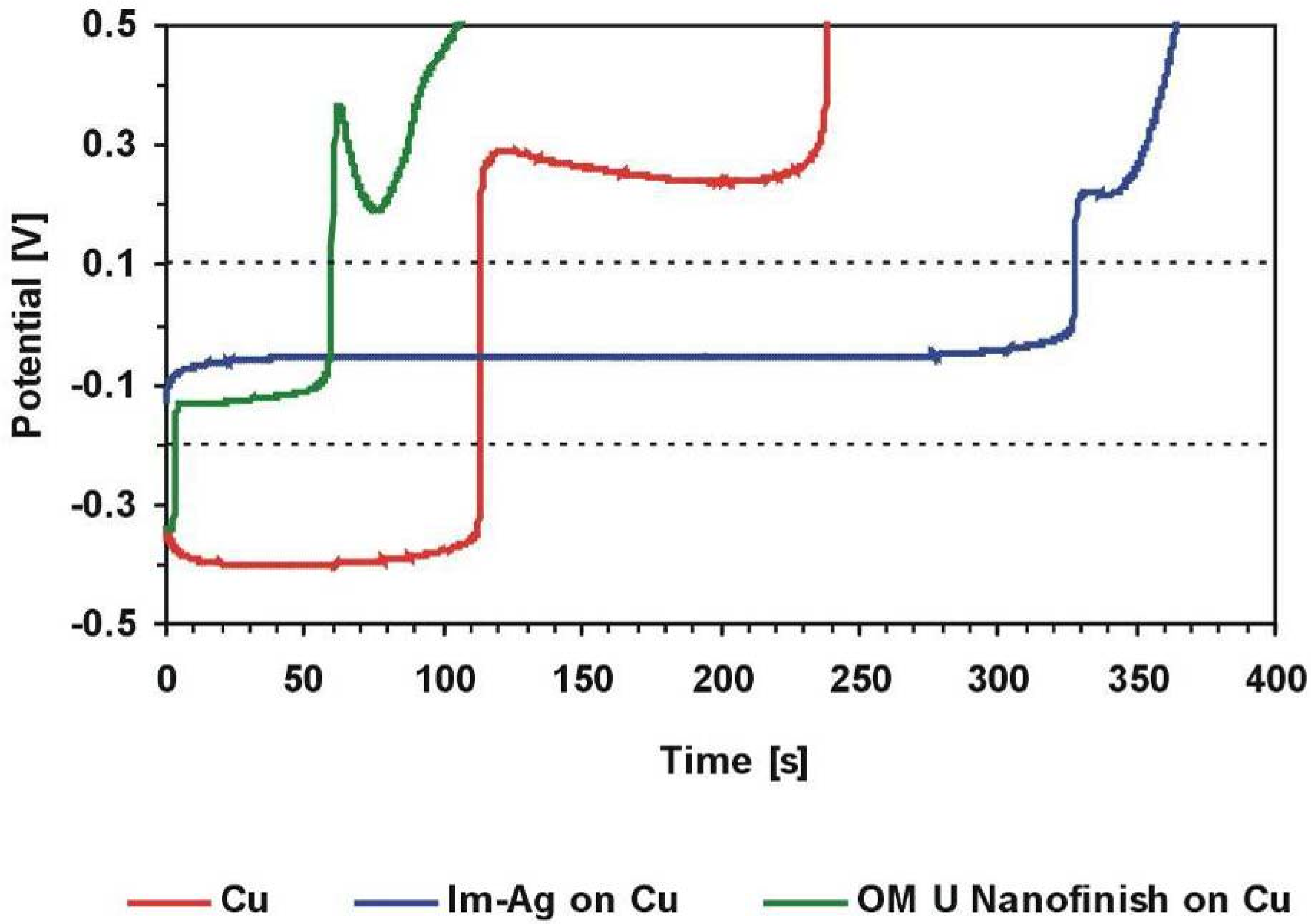
extremely low oxide content, even after 1 reflow

Different electrochemical potentials

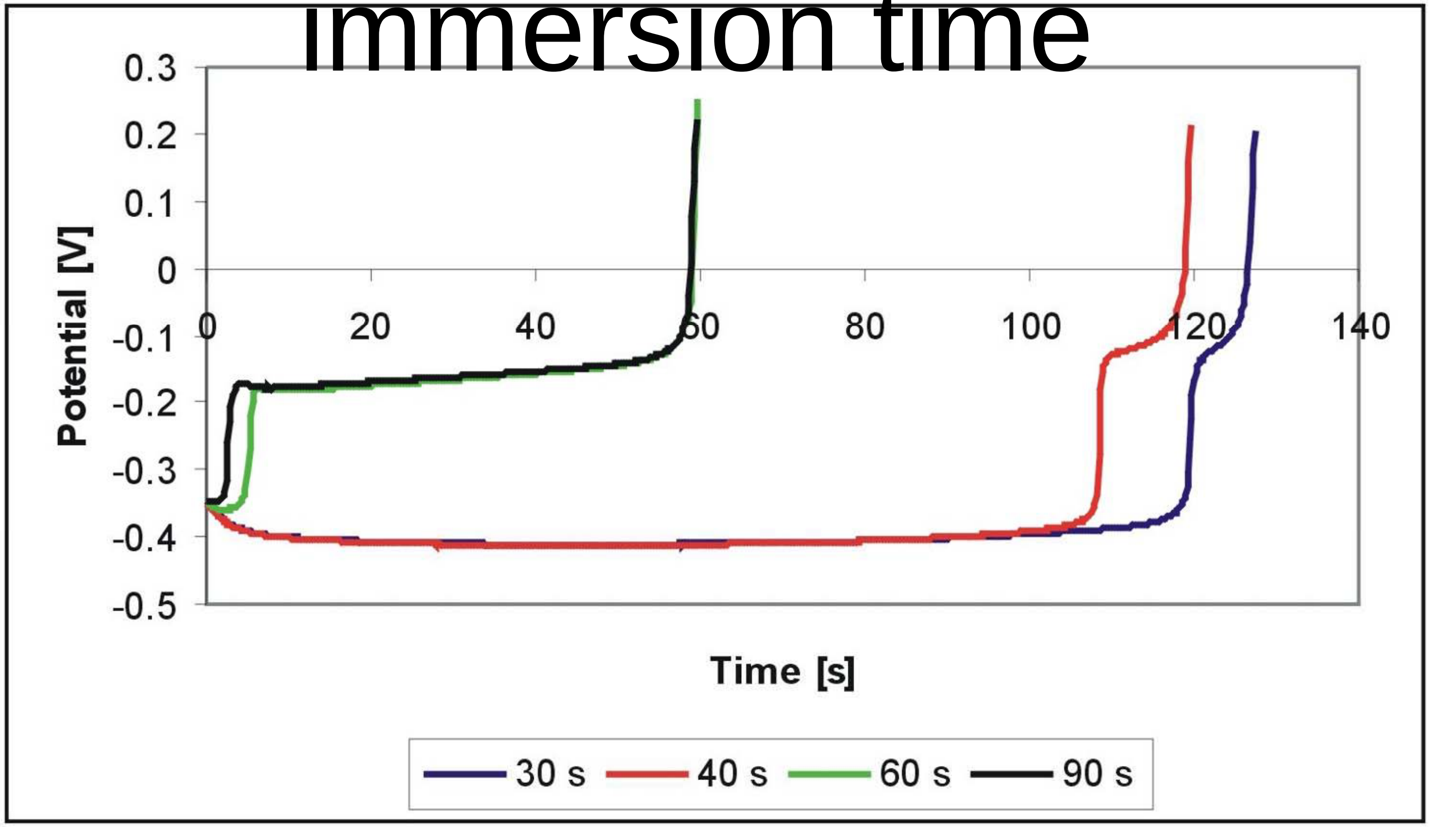
- **GCM** **(electro-chemical measurement)**

  showing 50 nm Ag-Cu-OM complex

  potentials different from Ag and Cu



Results after different immersion time



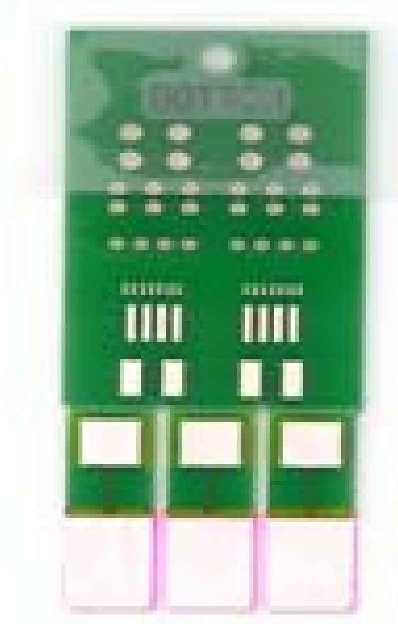
Potential at – 0.4 V shows open Cu area – practically all is covered if > 60 sec immersion time. Then OM-Ag complex layer 50 – 60 nm „thick“.

Process Flow

ACL7002 45 °C - 2'
MET7002 35 °C - 2'20"
Rinse City water RT - 20"
Rinse City water RT - 20"
DI rinse RT - 20"
CND7200 40 °C - 60"
OMN7200 35 °C - 90"
DI rinse RT - 20"
DI rinse RT - 20"
NFR7000, 5 % RT - 45 "
DI rinse RT - 5"
Drying air gun
baking 120 °C - 5'

Simple process flow.

Low temperatures.



No chemical attack of materials.

Benchmark Evaluation Objective

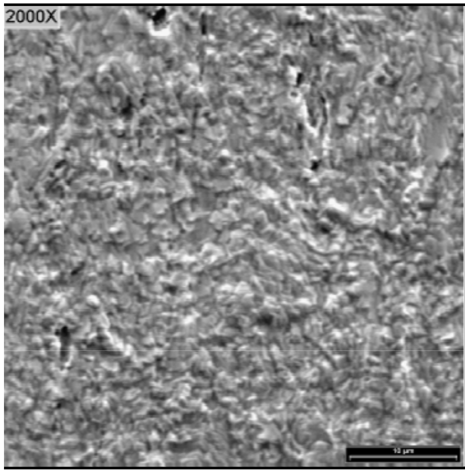
- To evaluate Nanofinish surface finish using standard PWB performance test methods.
- Test Vehicles plated/coated with OSP, Immersion Ag, and ENIG will be tested as controls (3).
- Four (4) surface finishes evaluated in total

Thickness & Appearance
XRF / UV Spec / GCM

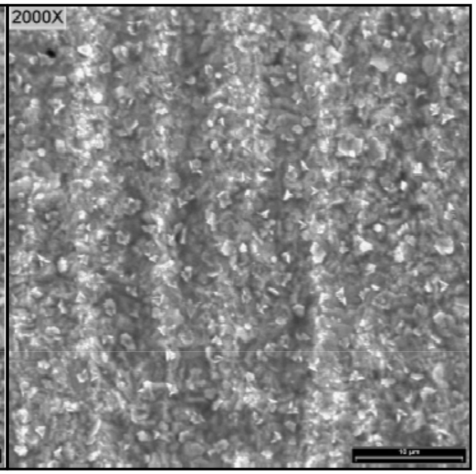
Coating / Plating Thickness-

OSP - (UV Spec)	0.43 micron
Immersion Silver (XRF)	0.23 micron
ENIG- (XRF)	4.3/0.07 micron Ni/Au
Nanofinish (GCM)	0.057 micron

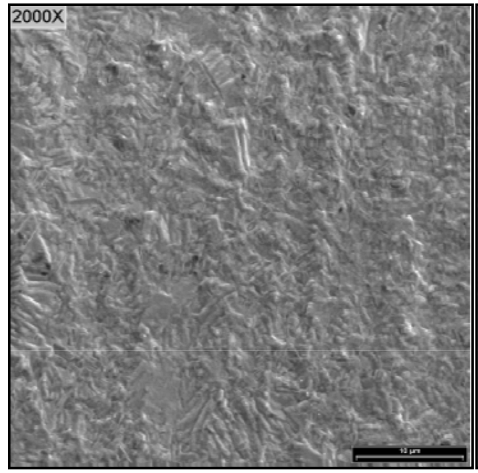
OSP 0x



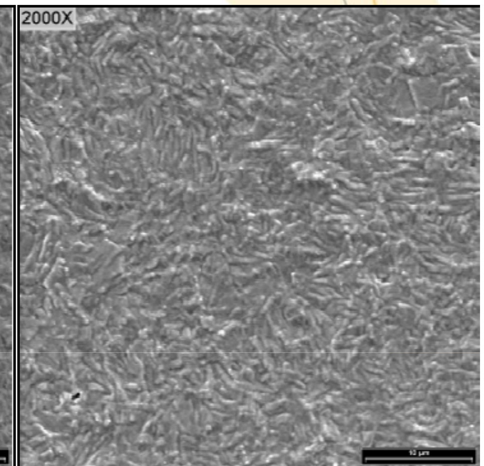
OSP 1x



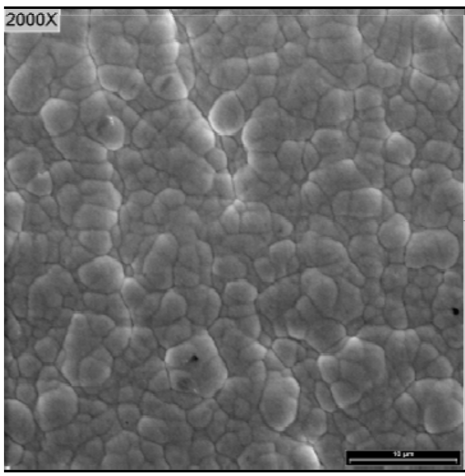
Immersion Silver 0x



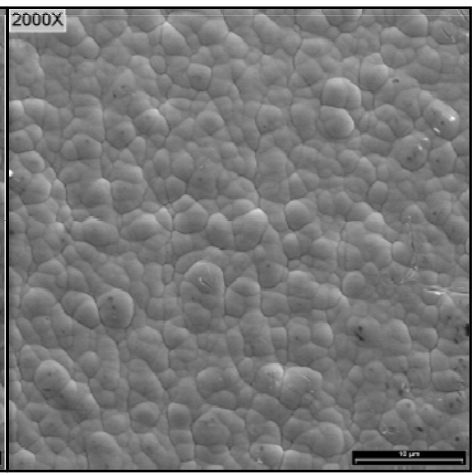
Immersion Silver 1x



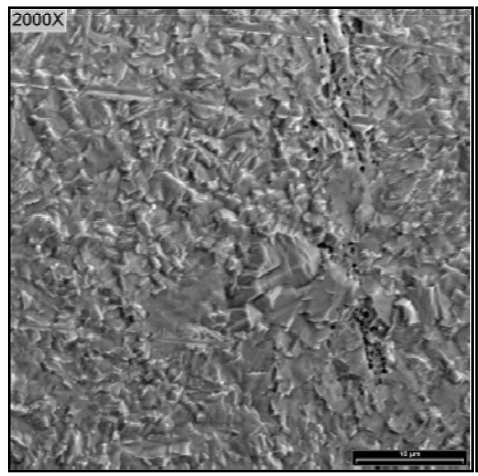
ENIG 0x



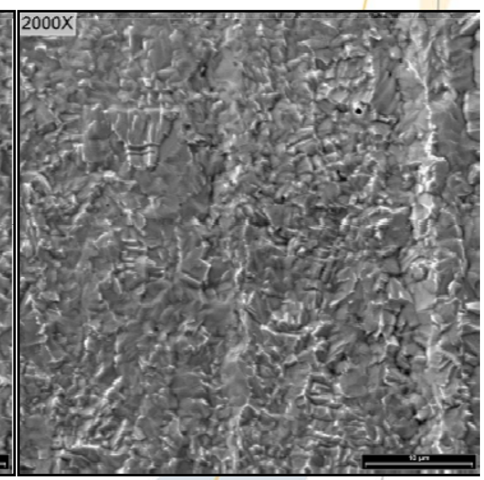
ENIG 1x



Nanofinish 0x



Nanofinish Ultra 1x



Solderability

Wetting Balance Test

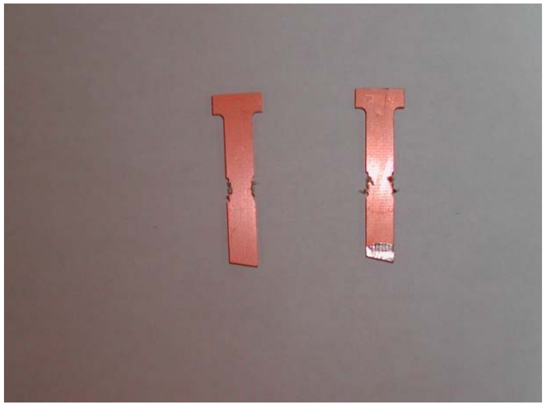
Solder Spread Test

Wave Solder Test

Solderability
Wetting Balance

KWB-1000 Wetting Balance

Wetting Balance Coupon

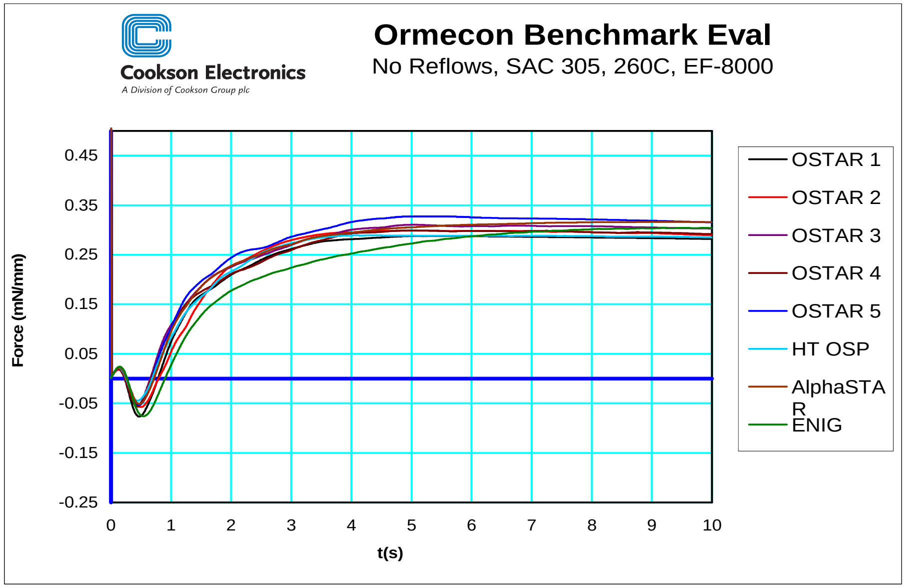


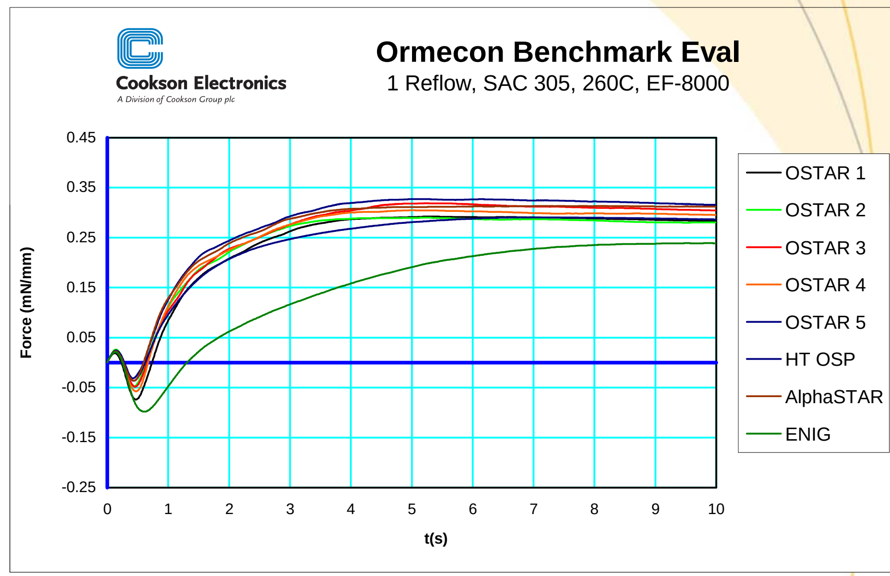
Solderability
Wetting Balance Test Conditions

KWB-1000 Wetting Balance parameters

	Flux	Solder
Insert speed-	1.0 in./sec.	0.5 in./sec.
Extract speed-	1.0 in./sec.	0.5 in./sec.
Dwell time-	5.0 sec.	10.0 sec.
Hang time-	5.0 sec.	20.0 sec.
Hang distance-	n/a	0.05 in.
Flux depth-	0.3 in.	n/a
Solder depth-	n/a	0.062 in.
Solder temperature-	n/a	500°F
T. alarm band-	n/a	9°F
Time unit-	0.01 sec.	0.01 sec.
Gain-	n/a	5.0 grams
Globule block-	n/a	Disabled

Alpha Metals EF-8000 Flux and SAC305 solder used


Cookson Electronics
A Division of Cookson Group plc
Ormecon Benchmark Eval
No Reflows, SAC 305, 260C, EF-8000
Force (mN/mm)
0.45
0.35
0.25
0.15
0.05
-0.05
-0.15
-0.25
0 1 2 3 4 5 6 7 8 9 10
t(s)
OSTAR 1
OSTAR 2
OSTAR 3
OSTAR 4
OSTAR 5
HT OSP
AlphaSTAR
ENIG


Cookson Electronics
A Division of Cookson Group plc
Ormecon Benchmark Eval
1 Reflow, SAC 305, 260C, EF-8000
Force (mN/mm)
0.45
0.35
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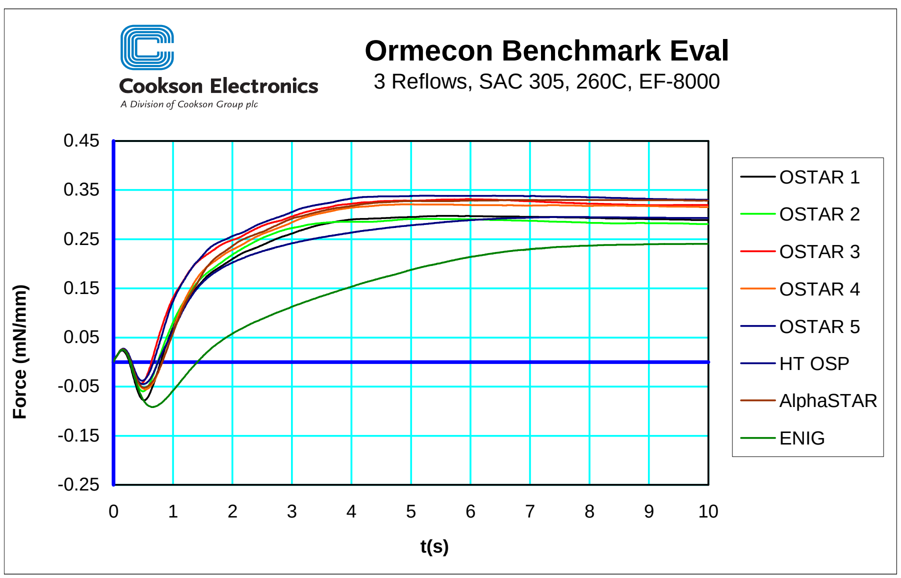
0.05
-0.05
-0.15
-0.25
0 1 2 3 4 5 6 7 8 9 10
t(s)
OSTAR 1
OSTAR 2
OSTAR 3
OSTAR 4
OSTAR 5
HT OSP
AlphaSTAR
ENIG


Cookson Electronics
A Division of Cookson Group plc
Ormecon Benchmark Eval
3 Reflows, SAC 305, 260C, EF-8000
Force (mN/mm)
0.45
0.35
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t(s)
OSTAR 1
OSTAR 2
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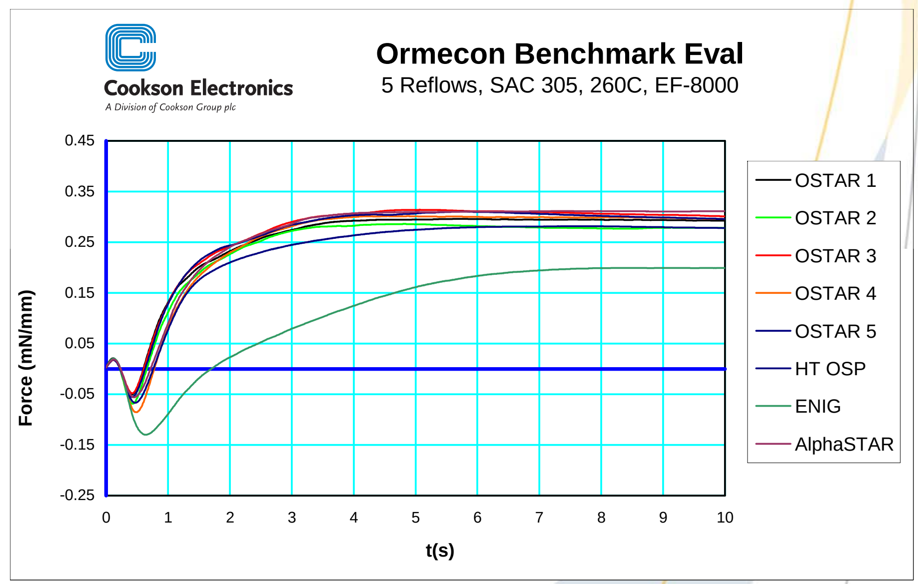
HT OSP
AlphaSTAR
ENIG


Cookson Electronics
A Division of Cookson Group plc
Ormecon Benchmark Eval
5 Reflows, SAC 305, 260C, EF-8000
Force (mN/mm)
0.45
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0.05
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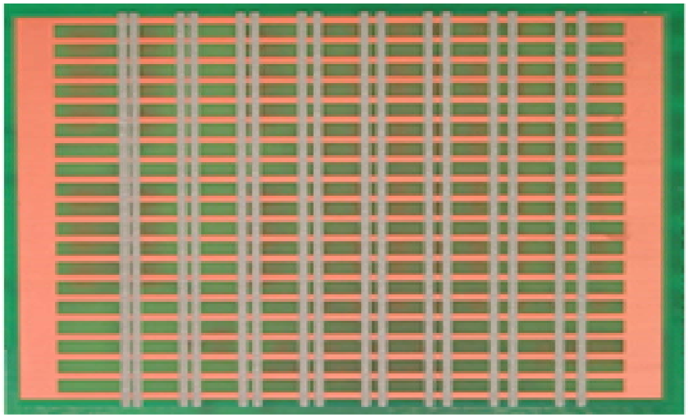
-0.25
0 1 2 3 4 5 6 7 8 9 10
t(s)
OSTAR 1
OSTAR 2
OSTAR 3
OSTAR 4
OSTAR 5
HT OSP
ENIG
AlphaSTAR

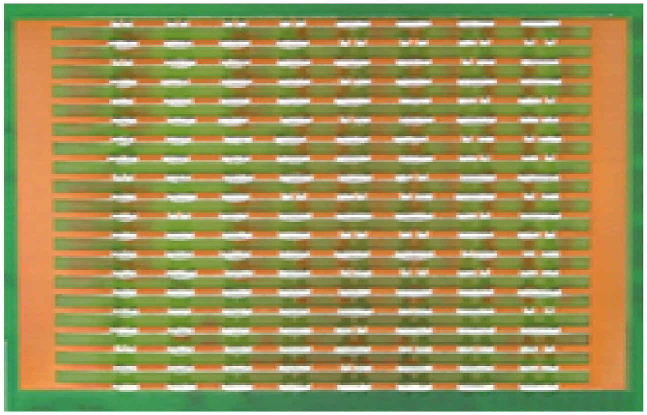
Solderability
Solder Spread

enthone

Solder Spread Test

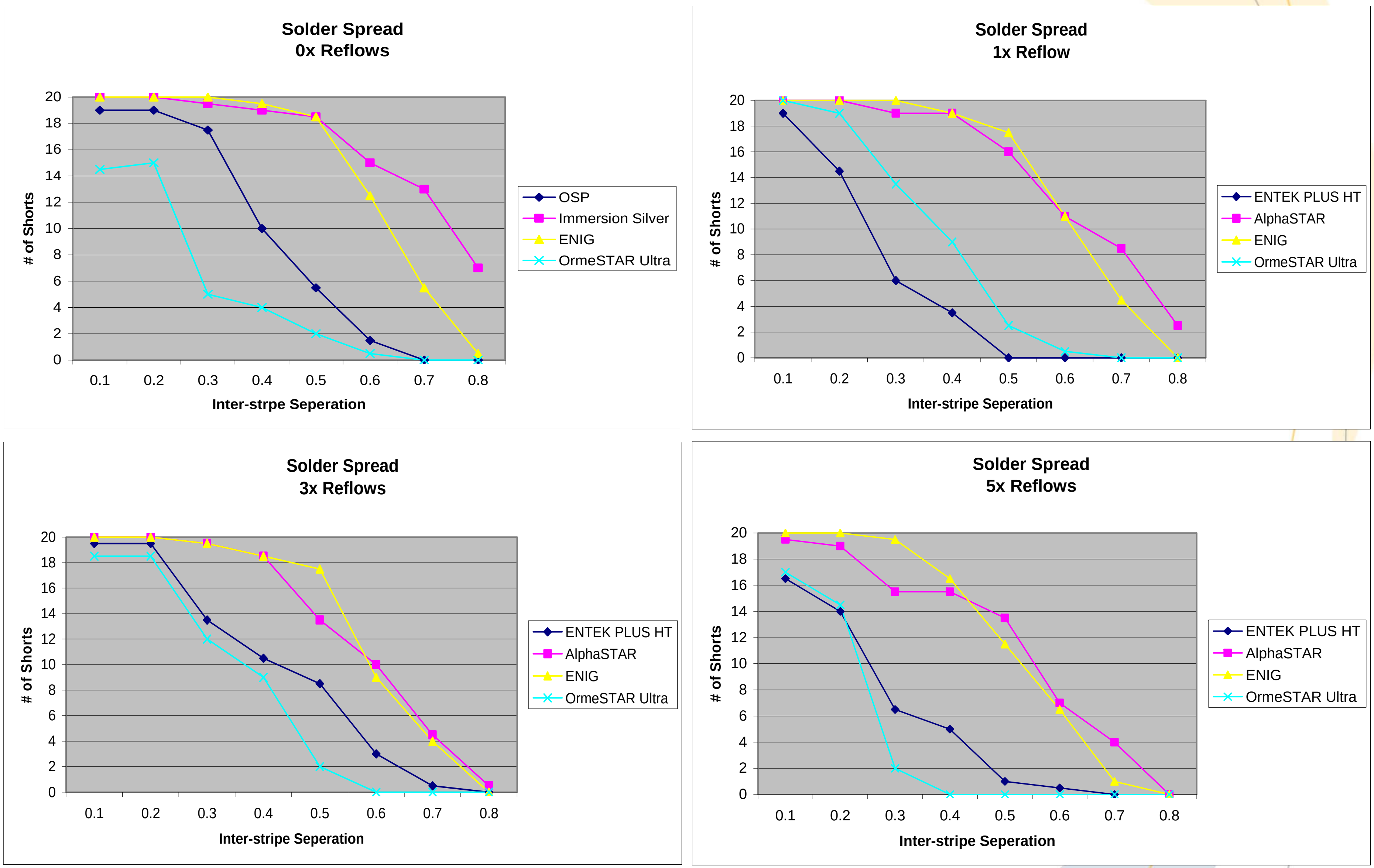


Pre Reflow



Post Reflow

shared intelligence™ Cookson Electronics


Solder Spread
0x Reflows
# of Shorts
Inter-strpe Seperation
OSP
Immersion Silver
ENIG
OrmeSTAR Ultra
Solder Spread
1x Reflow
# of Shorts
Inter-stripe Seperation
ENTEK PLUS HT
AlphaSTAR
ENIG
OrmeSTAR Ultra
Solder Spread
3x Reflows
# of Shorts
Inter-stripe Seperation
ENTEK PLUS HT
AlphaSTAR
ENIG
OrmeSTAR Ultra
Solder Spread
5x Reflows
# of Shorts
Inter-stripe Seperation
ENTEK PLUS HT
AlphaSTAR
ENIG
OrmeSTAR Ultra

Solderability
Wave Solder Test Method

-Alpha Metals Wave solder unit

-Flux type- Alpha Metals EF-8000 Alcohol – Rosin 6% solids no-clean flux.

-Flux application- Spray-fluxer application -1200 to 1300μg/in^2 flux loading (wet weight calculation).

-Solder contact time- 3.5 seconds

-Conveyor angle- 6-7°

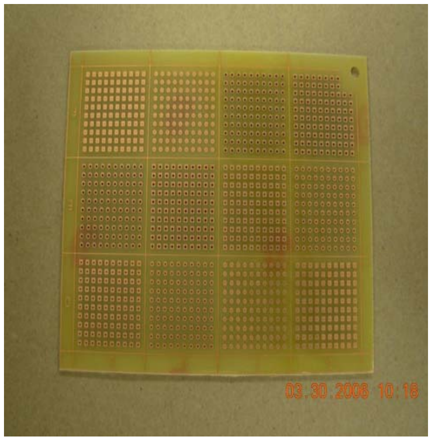
-Pre-heat conditions- Set to achieve 180- 210°F topside measured temperature.

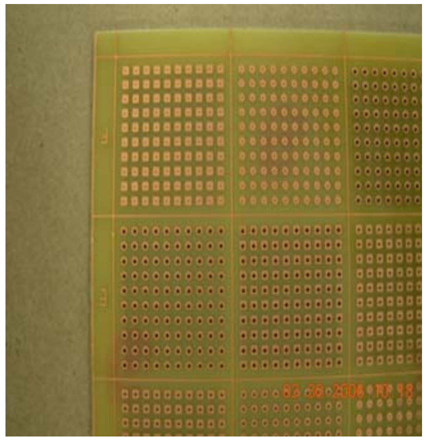
-Chip wave- off

-Air nozzle only, not nitrogen inerted.

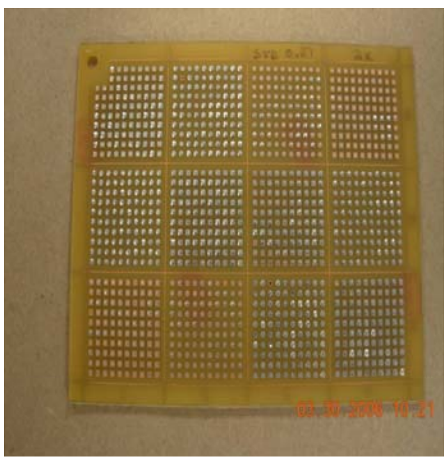
-SACx0307 Solder temperature- 500°F

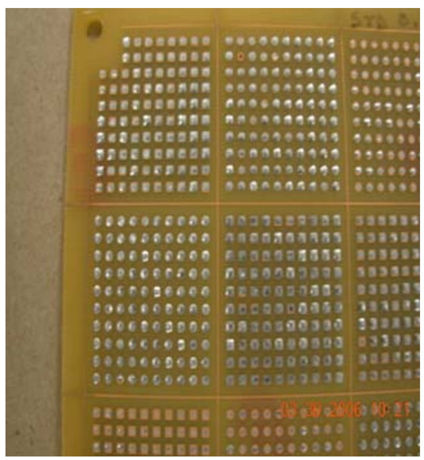
Solderability
Wave Solder
Evaluation





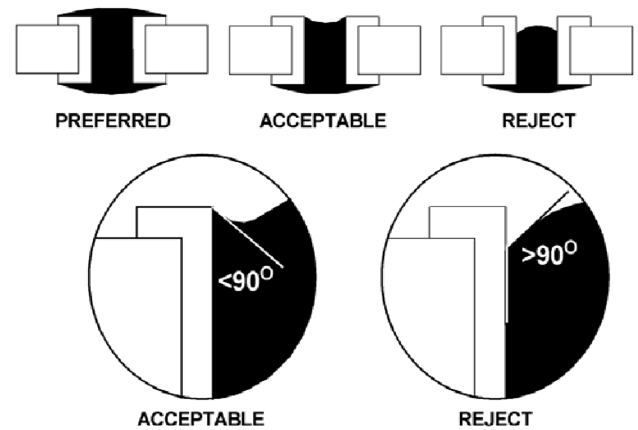
STV Test Vehicle Un-Soldered





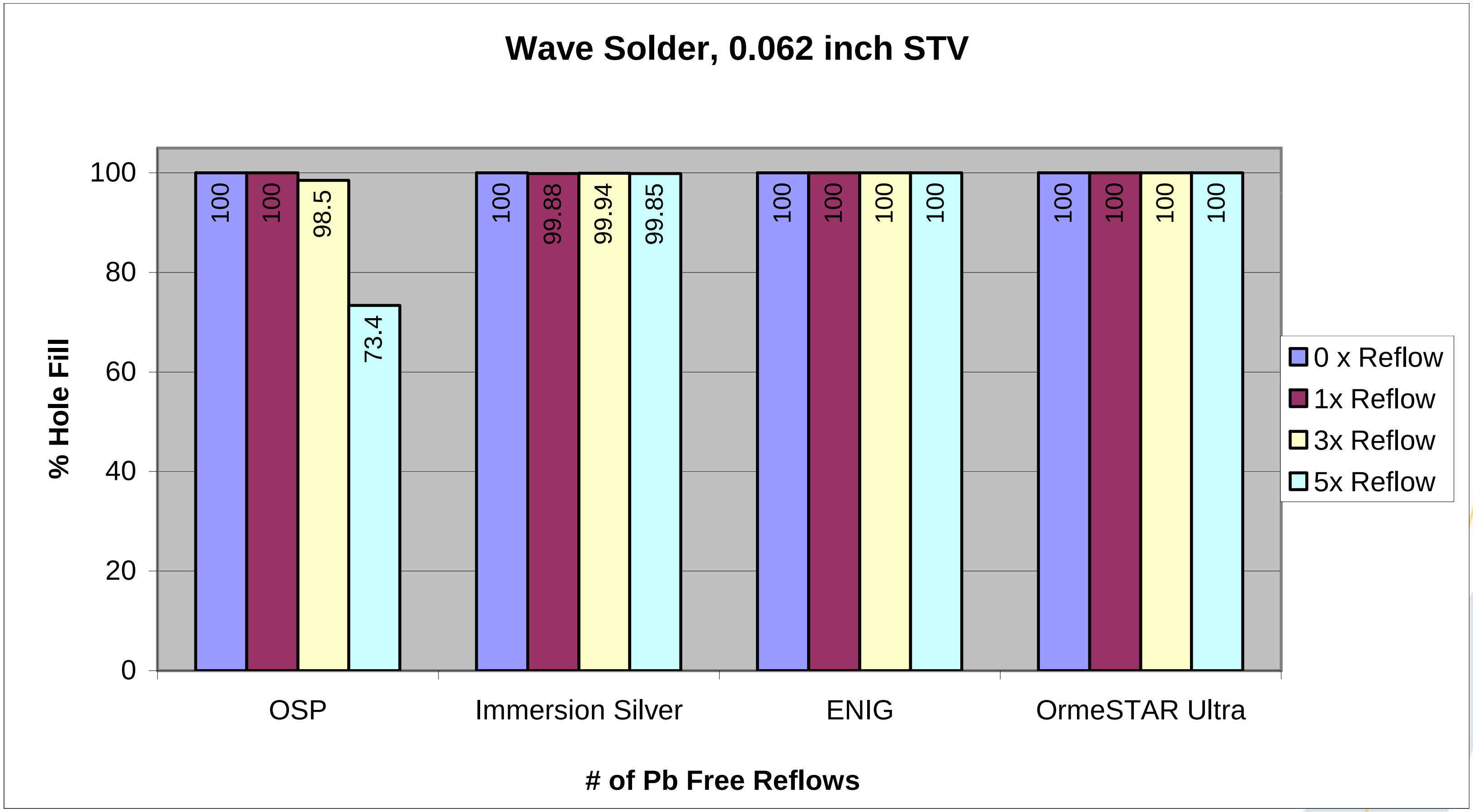
STV Test Vehicle Soldered

Solderability Inspection Criteria
J-STD-003A

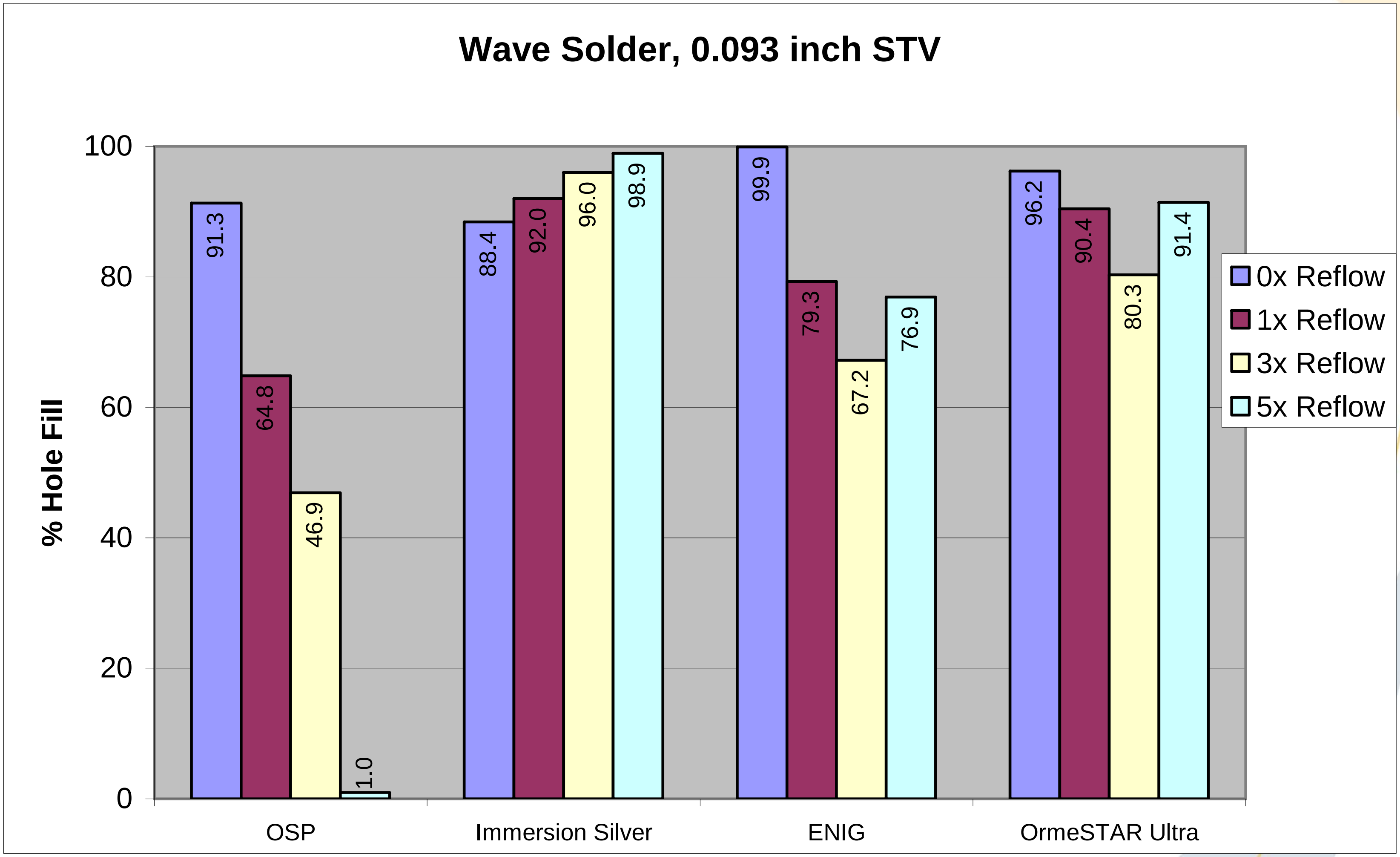


PREPARED BY: BOB GALLANT 8/27/98

Solderability
Wave Solder 0.062 inch STV
Results



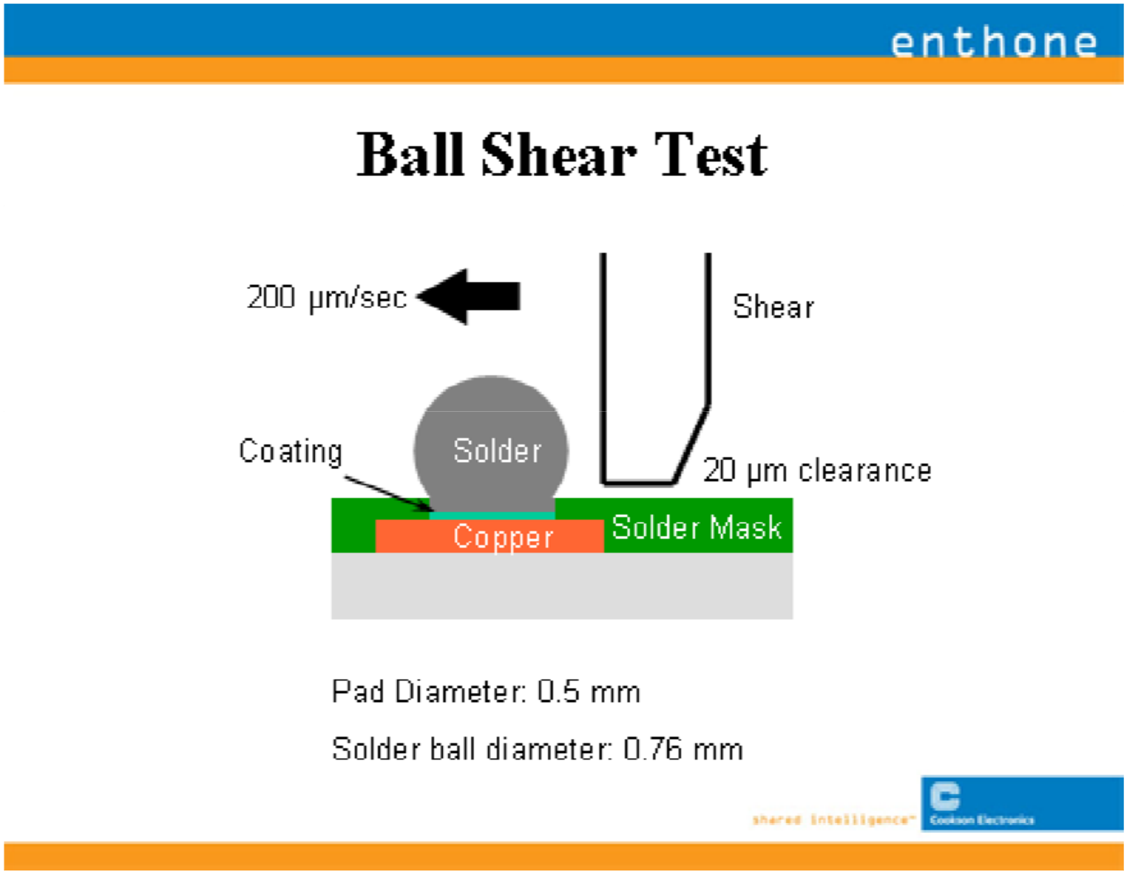
Solderability
Wave Solder 0.093 inch STV
Results

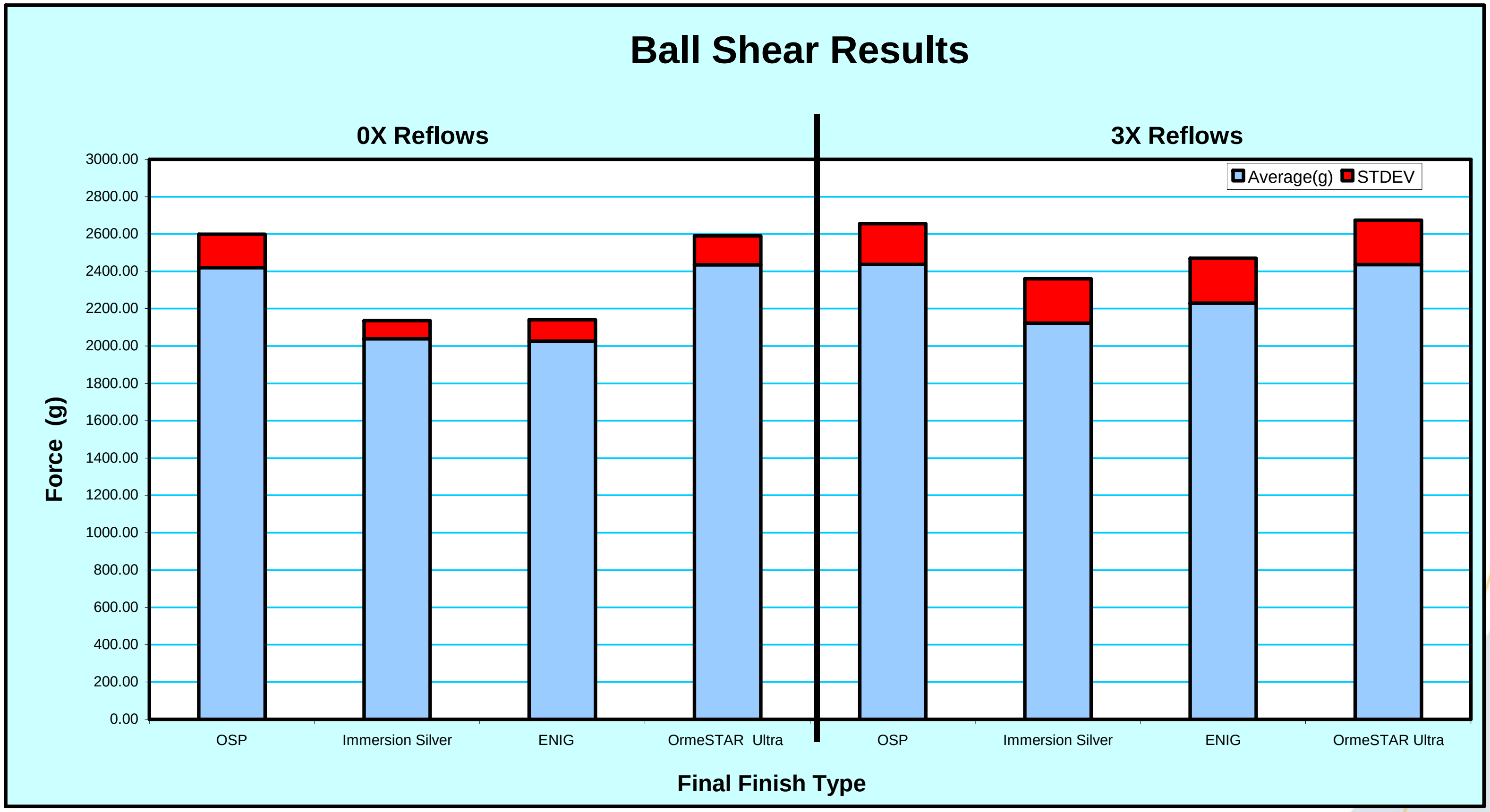


Solder Joint Reliability

Ball Shear

Solder Joint Reliability
Ball Shear Test Method



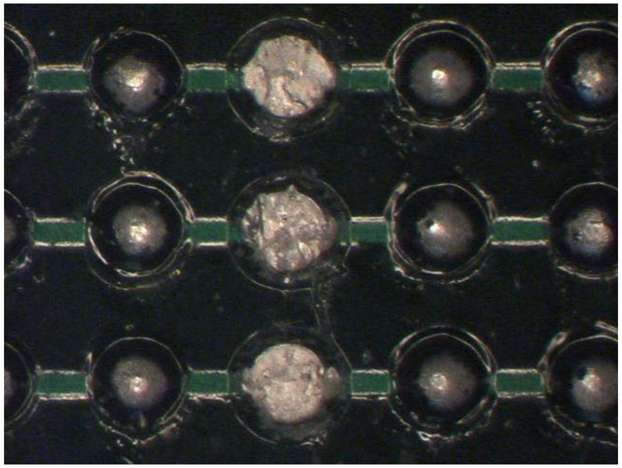

Ball Shear Results
0X Reflows
3X Reflows
Average(g)
STDEV
Force (g)
3000.00
2800.00
2600.00
2400.00
2200.00
2000.00
1800.00
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
OSP
Immersion Silver
ENIG
OrmeSTAR Ultra
OSP
Immersion Silver
ENIG
OrmeSTAR Ultra
Final Finish Type

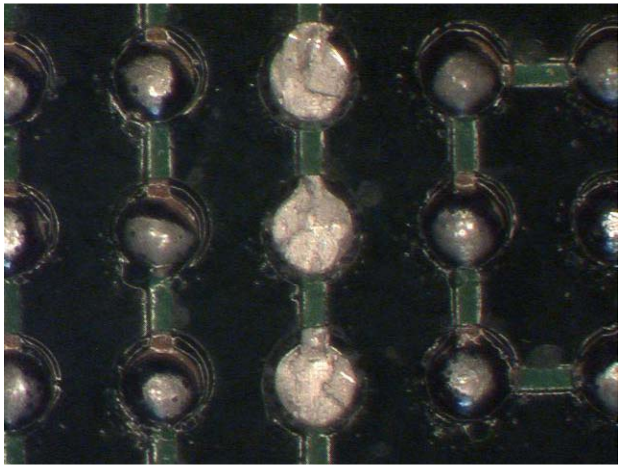
OrmeSTAR Ultra Post Shear

0X

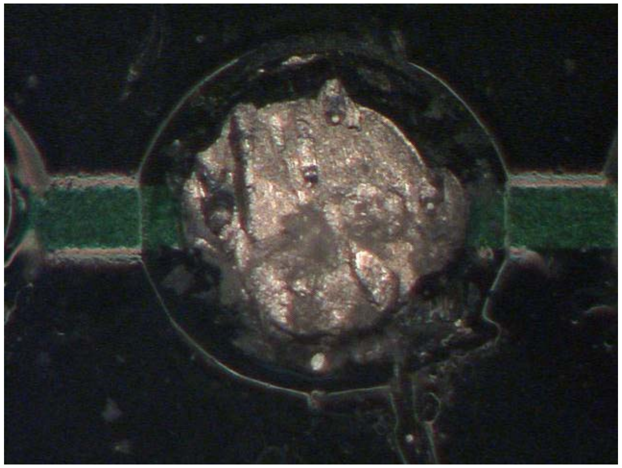
3X

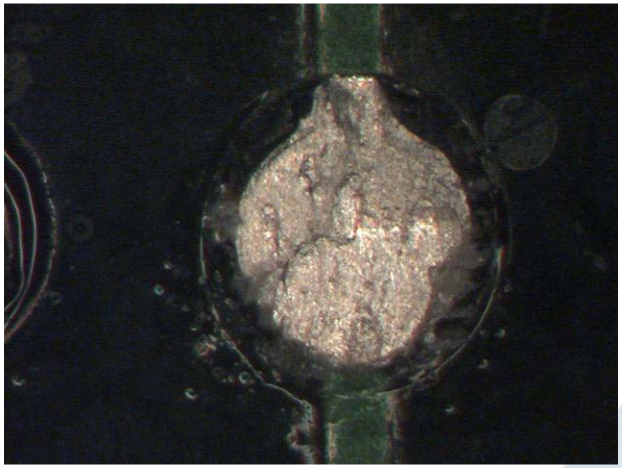
50X





150X





Surface Insulation/Electromigration
Test Method & Evaluation

SIR-

- Test Vehicle- SIR Coupon
- Temperature/Humidity Conditions- 85° C, 85% RH
- Bias- no bias voltage applied
- Test voltage- +100 volts
- Test frequency- 24, 48, 72, and 96 hours
- Pass condition- greater than $1x10^{8}$ ohms

Electromigration

- Temperature/Humidity Conditions- 85° C, 85% RH
- Bias- 10 volts
- Test voltage- +100 volts
- Test frequency- 168, 336, and 504 hours
- Pass condition- Less than one decade change from initial reading.

Surface Insulation/Electromigration Results

- **SIR** – Test Completed.
  - **All test vehicles > 1.0 x 10^8 ohms (Pass Condition)**

- **Electromigration**- Test Completed

- All test vehicles exhibited <1 decade change out to 504 hours **(Pass Condition)**

All Surface Finishes Passed

Ionic Cleanliness

Ionic Cleanliness Results

µg./square inch

	Sample #1	Sample #2	Average
Bare Copper	0.3	0.2	**0.3**
ENTEK PLUS HT	7.4	8.3	**7.9**
AlphaSTAR	4.4	3.5	**4.0**
ENIG	3.7	3.2	**3.5**
OrmeSTAR Ultra	3.5	3.4	**3.5**

Contact Resistance

Contact & Wear Resistance
Contact Resistance

Contact Resistance Test Results					
	No Reflows			1X Reflows	
	mOhms	*mOhms*		*mOhms*	*mOhms*
Surface Finish	**10 g**	**20 g**		**10 g**	**20 g**
OrmeSTAR Ultra Std. (A)	**0.9**	**0.8**		**1.5**	**1.4**
ENIG	**6**	**5.6**		**6**	**5.3**
AlphaSTAR Immersion Ag	**1.5**	**1.2**		**1.6**	**1.2**
ENTEK PLUS HT	**15 - 20**	**25 - 35**		**15**	**150**
Pure Au Standard	**0.9**	**0.6**			

Nanofinish Process & Test Results Summary

- Extremely high ageing and oxidation resistance, therefore very good solderability after storage, ageing, <u>up to 10 reflow</u>
  - can stand 155° C / 4 hrs like metallic finishes.
  - No intermetallic growth over time.
- Excellent wetting force.
- Only slight discoloration during reflow with no impact on solderability.
- No “black pad“ risk, no copper corrosion („broken neck“) risk
- Homogeneous and reliable solder joint, no phase separation
- No negative issues with shear strength, surface resistance or e-corrosion

Nanofinish Process & Test Results Summary

- Excellent light reflection / optical contrast
  - OrmeSTAR coating makes it lighter / silvery
  - optical control will be easier and can be automated
- Electrical tests can be done after finishing
- At assembly, misprinting can be corrected
  - Solder paste can be removed by organic solvents without removing the Nanofinish layer
- Dwell time between assembly steps no problem, no deterioration of solderability
- Significant reduction in energy and raw material demand (details see attachment) – environmental friendly surface finish