ELECTROLESS NICKEL/IMMERSION SILVER – A NEW SURFACE FINISH FOR PCB APPLICATIONS

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ABSTRACT
Electroless nickel/immersion gold (ENIG) has been the primary, high performance surface finish used in the PCB industry for some decades now. Market research confirms that in terms of processed surface area per year, ENIG useage is second only to Organic Solderability Preservatives (OSP) [1]. ENIG is typically described as a surface finish which is labor intensive to work with at the fabrication level, but its high performance characteristics mitigates this fact to a great extent. Electroless nickel/immersion gold is designed to deliver a highly corrosion resistant and superior solderable surface. This finish is also commonly used for aluminum wire bond applications.

With significant volatility in precious metal pricing and the constant demand for better products at cheaper prices, Original Equipment Manufacturers (OEM's) are being driven to search for ways to reduce cost whilst not sacrificing quality. The layer of gold metal on an ENIG treated surface, although thin, adds a prohibitively high premium to the cost of this finish.

MacDermid has developed an electroless nickel/immersion silver (ENImAg) process that delivers the performance characteristics afforded by ENIG and eliminates the concern associated with the use of a high priced metal, such as gold. This change, from using gold to silver, also has the added benefit of eliminating a cyanide containing process from the fabrication house. Applying, qualifying for and maintaining a cyanide license is a cost adder for the ENIG process.

This paper expands on the work conducted in the 2010, "A New Surface Finish for the Electronics Industry [2]." Process flow and the associated chemical steps will be discussed to alleviate concerns of fabrication difficulties. This work will detail additional performance characterization and discuss the surface finish performance on a production scale. The test data presented will include solderability, tarnish and corrosion resistance, aluminum wire bonding and contact performance.

INTRODUCTION
As the demands of the electronics industry change, the expectations put on the fabrication of the PCB become greater. This encompasses the operating cost of each chemical process, the environmental impact and the ultimate performance throughout end use life. These are not only driven by OEMs and consumers but also by the regulations placed on the industry as a whole.

OEMs request that fabricators provide a 10-15% cost reduction year to year. So, as consumers receive technology that is more advanced than the previous year the Original Equipment Manufacturers expect to pay less for the components used to make that product. It is this mentality that pushes chemical suppliers to constantly design and formulate products that offer greater performance at a lower operating cost. In line with this is the need to preserve our environment by abiding to environmental regulations and develop products that have high performance with low environmental impact. Marrying these two concepts makes the use of MacDermid's electroless nickel/immersion silver a perfect solution.

The benefits of ENIG are well understood. It maintains superior solderability even after environmental exposure and resists corrosion. But just like every surface finish, ENIG has its shortcomings. There are three main issues commonly associated with ENIG that are considered negative. The first that comes readily to mind in today's price sensitive market is the high cost of gold metal. The second is associated to the chemical makeup of the plating baths and the use of cyanide whose limitations will be discussed in the next few paragraphs. The last is a solder joint defect known as black line nickel which will be expanded upon in the performance characteristics section of the paper.

For years investors have watched the stock markets plummet and precious metal prices rise. This morning's gold prices dropped to a recent low of about 1600USD/troy oz, having been above 1800USD a month ago. Five years ago gold prices were down around 600USD/troy oz [3]. Yes, silver prices have also been volatile in recent years but when comparing the cost ratio of gold to silver, the former is typically found to be on the order of 30 to 60 times more expensive than silver. This difference in cost translates to bath make up, drag out, replenishment, and the cost of the plated metal. A quick comparison of plated metal price alone shows how significantly large the difference between the two is.

For comparison, we will compare plating 2 microinches of gold to 25 microinches of silver on 1000 panel square feet of circuit board at 15% metal area. Using a gold price of 1600USD and 30USD for silver, the price of the gold plated parts are almost 8 times greater than the silver plated parts.

Figure 1: 5 Year Metal Price for Gold

Figure 2: 5 Year Metal Price for Silver

One may also reasonably suspect that gold thickness is being pushed to the low end of industry specifications and possibly, on occasion, outside of specification to reduce costs. Plating thinner gold deposits, naturally, has some performance related consequences. Will a thin gold deposit be able to maintain the corrosion resistance expected of a high reliability finish? The IPC has set up a committee which is evaluating reducing the gold thickness specification [4] and determining its performance effects. The performance section of this paper will touch lightly on the use of reduced gold thickness. More thorough experimentation and investigations will be conducted by the IPC group.

Since 2001, a great portion of the US based electronics manufacturing industry has moved to China. In recent history, China itself has experienced an industrial migration of sorts, with the Chinese government providing incentives for industry to move further inland. For example, in May of 2010, "30 suppliers signed contracts with the Chongqing government which, like many inland governments is welcoming companies willing to abandon China's wealthier coastal provinces" [5]. Companies were hoping to find reductions in labor cost which did not necessarily come to fruition but also questions were raised about environmental and government policy. The migration has the potential for increased pollution on the Yangtze River. To mitigate this pollution, the central government required more stringent regulations to be upheld [5,6]. Thoughts also moved to water reduction and more waste treatment practices which require the removal of strong chelators, such as cyanide. Using immersion silver to replace the immersion gold step in ENIG production eliminates the use of cyanide entirely. It should be noted that there are cyanide free immersion gold baths available on the market, however their use is not wide spread at this time because of their lack of robustness in a true production setting.

Process Flow

Directly comparing the new electroless nickel/immersion silver process to conventional ENIG demonstrates clearly that the two are very similar in process flow up to the electroless nickel stage. Though the conditions used for the electroless nickel appear the same, the chemistry applied is different, offering benefits over those processes currently on the market for ENIG applications. Advances made during the formulation of the electroless nickel bath for the immersion silver process have resulted in a medium (6-9%) phosphorous containing EN that has low working temperature and that does not require the use of dummy plating either on make up or after a sustained period of idle time. It does not require periodic over the side additions of proprietary components to keep the bath functioning properly. Overall, the system is extremely stable and does not fall subject to the chemical swings that sometimes have been experienced with EN processes historically. This unique formulation not only promotes more corrosion resistance for both the galvanic reactions occurring during plating but also resists corrosive environments generally. The bath is easier to run on the fabrication level due to its chemical component stability.

After the EN deposit has been rinsed, the parts are immersed in a silver pre-dip solution. This step does not contain any silver ions but readies the nickel surface for silver plating. This step will also remove any passivation which may have occurred during nickel rinsing. It wets the nickel surface uniformly prior to silver plating. The pre-dip is a low temperature process step, typically not higher than 50°C and with a dwell time no longer than 2 minutes. After this step, the parts move directly to the immersion silver plating solution. This bath operates at low pH and also, low temperature (figure 4). The acidity of the bath and the lower operating temperature make it much less aggressive on the PCB substrate materials when compared to the higher pH and high temperature (typically, 85 to 90°C) immersion gold plating bath (figure 3).

The final rinsing stage can vary from fabricator to fabricator depending on the quality of the water employed and the temperature of the environment. As with all surface finishing, the use of good clean rinsing is always best and the addition of hot water in the last stage will help improve ionic cleanliness. One difference between ENIG and ENImAg that should be stated is all ENIG lines contain a drag out rinse. After gold plating, parts must first be immersed in a stagnant drag out rinse. This serves two purposes; one is to contain the cyanide, thereby protecting the waste water stream from cyanide contamination, and the other is to enable the reclamation of any residual gold dragout in this stagnant rinse once its concentration rises to an appreciable concentration. Depending on the level of production throughput, this practice can prove to be an important cost saving exercise.

Chemical Bath	Working Temp (°C)	Estimated Dwell Time
Electroless Nickel	80-88	15-25
Rinse	Ambient	2
Immersion Gold	85-90	8-12
Drag out Rinse	Ambient	0.5 – 1
Cascading Rinse	Ambient	3
Hot Rinse	Ambient	1
Dry		

Figure 3: Partial Process Flow for ENIG

Chemical Bath	Working Temp (°C)	Estimated Dwell Time
Electroless Nickel	80-84	15-20
Rinse	Ambient	2
Silver Predip	50	1-2
Immersion Silver	40	4-8
Cascading Rinse	Ambient	3
Hot Rinse	Ambient	1
Dry		

Figure 4: Partial Process Flow for ENImAg

The following sections compare the functional performance capabilities of electroless nickel/immersion silver to the incumbent ENIG process.

FUNCTIONAL PERFORMANCE

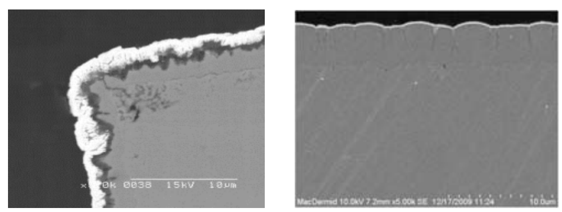
Nickel Corrosion

It is widely accepted that the most concerning performance defect for ENIG is the propensity or potential for black line nickel [7]. Black line nickel is a corrosion defect that is initiated in the immersion gold plating bath and which is exacerbated during the assembly process. Heavy corrosion of the EN deposit results in a phosphorous rich layer being produced. This layer is very difficult to subsequently solder to. If a solder joint is made, it is weak and can result in components falling off the PCBA. After the gold is plated on the PCB (unassembled) the defect cannot be detected without destruction to the circuit board which means the defect frequently goes undetected until the board has already been through the assembly process. Sometimes it may not be apparent until accelerated performance testing is conducted.

IPC 4553 (3.7) states that chemical resistance testing of an ENIG finish is not applicable [4] but there is a fabrication level method that has been used in various forms to test an electroless nickel surface's ability to resist corrosion. This type of corrosion test is used as an indicator of resistance to black line nickel and the corrosivity of the immersion gold bath. As the test is used at different conditions from fabricator to fabricator or chemical supplier to chemical supplier, it is not an industry standardized method. The foundation of the test was adopted from an ASTM method (B735) as pass/fail criteria for high phosphorous electroless nickel deposits. Parts are immersed in concentrated nitric acid for 30 seconds at room temperature. If the part turns black it is considered a failure [8]. Unfortunately, the test is inconsistent and extremely subjective when performed on medium phosphorous nickel deposits which are the norm for ENIG PCB plating. There are also factors within the plating baths themselves that affect the outcome of the test. These include but are not limited to the level of phosphorous in the EN deposit, the level of sulfur in the deposit and the type of sulfur included in the deposit. Typically, as the phosphorous content increases in the EN deposit, the greater the resistance to nitric acid results. Likewise, the lower the sulfur concentration in the EN deposit, greater resistance to nitric acid is achieved. In the interest of presenting a more valid assessment of solder joint quality through solderability, this paper investigates the comparison of ball shear data after JECEC thermal cycling exposure.

Effect of BLN on Solderability

To marry the relationship of nickel corrosion resistance to solder joint reliability, one must first expand on the concept of black line nickel. The term black line nickel directly relates to a black line found along the solder joint to nickel interface. It can run horizontally across the solder joint (figure 5a) or it can present itself as black hair line cracks (figure 5b) in the nickel deposit penetrating from the outer layer of the nickel toward the underlying copper substrate. Both are forms of nickel attack and have a detrimental effect on the solder joint reliability.



(a) **(b)**

Figure 5: Cross Sectional SEM of Black Line Nickel (a) Horizontally Across the Metal Layers (b) Penetrating into the EN

As the solder is no longer bonding to the nickel layer it is now bonding to a phosphorous rich layer which has been produced by the corrosive action of the immersion gold process. This tin/phosphorous joint is not a reliable bond. Depending on the level of phosphorous, the solder joint can crack readily or will crack with thermal conditioning (figure 6).

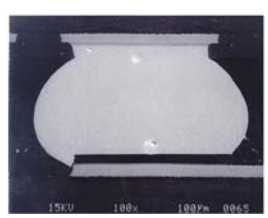


Figure 6: Cracked Solder Joint Resulting From Black Line Nickel Corrosion

Solderability Test

Test panels containing 25mil diameter metal defined and soldermask defined BGA pads were plated through ENIG and ENImAg in production scale tanks. The ENImAg parts were plated at two silver thickness levels; 6 to 8 microinches over the BGA pads on one set and 14 to 16 microinches as measured on the BGA pads for the second set. For ENIG, the gold was plated to 2 microinches thick. All process conditions were kept the same up to and including the electroless nickel step to ensure a true comparison. After silver or gold plating, the parts were rinsed and dried under the same conditions. The only difference being the addition of 30 seconds in the gold drag out rinse for the ENIG parts, as is typically applied in a production setting.

For the assembly, parts were pasted with Kester EM907 SAC 305 using an 8-mil stencil. Using a second stencil, 6-mil thick, SAC305 solder spheres were placed over the entire BGA design which includes 400 pads. The circuit boards were then passed through a Vitrons convection reflow oven with peak temperature of 245°C. Figure 7 displays the reflow profile for multiple pads sizes across the test vehicle.

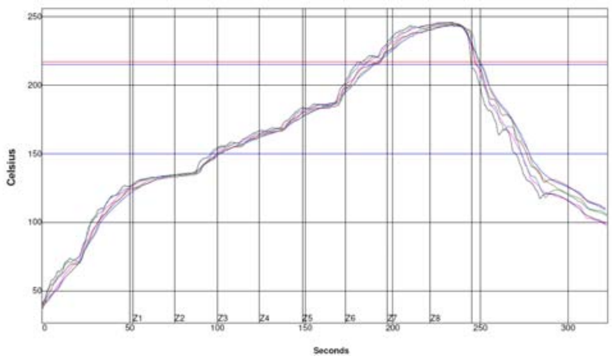


Figure 7: Lead Free Reflow Profile

Ball shear testing was conducted on a Xytec Bond Tester (figure 8) on the original samples. This established a baseline of shear strengths before thermal cycling. Parts were then sent to a third party test house for the thermal cycle exposure. The parts were subjected to two styles of thermal cycling, both detailed in the JEDEC Standard 5.2 [9]. Conditioning included Method G and J for 100 cycle exposure each. Method G cycles from -40°C to +125°C and Method J cycles from 0°C to 100°C. The samples were returned to MacDermid for ball shear post conditioning.

Tester Conditions	Units
Speed	500µm/s
Load	50g
Land Speed	0g
Shear Height	1500µm/s
Over travel	100µm

Figure 8: Xytec Bond Tester Parameters

For any surface finish the required minimum shear strength is 1.5kg. This was achieved on all finishes tested. Overall the performance of ENImAg was comparable to ENIG for all conditions (figure 9). Increasing the silver thickness did not have a detrimental effect on the solder joint reliability.

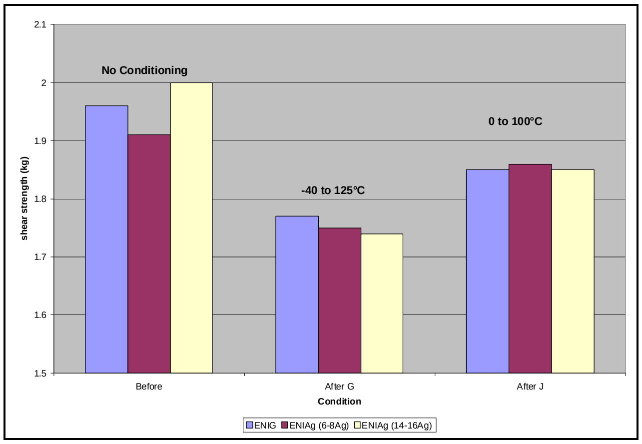


Figure 9: Solder Ball Shear Strengths

Failure modes:

1. Removal of pad from substrate = cratering
2. Fracture at IMC layer
3. Fracture in the solder joint
4. Fracture in the bulk solder.

The location of the fracture can also indicate the quality of the solder joint. In this instance when an undesirable fracture occurs at the intermetallic layer, the reason maybe a function of the solubility properties of a given metal. Many currently working with or transitioning to ENEPIG, understand that the thickness of the palladium layer has a dramatic effect on the solderability. The solubility of palladium into a solder joint is very slow. During the assembly process if the palladium is too thick the metal cannot readily solubilize and leaves a tin/palladium IMC which is not strong. The palladium rich solder joint results in very low solder shear strengths and fracturing at the IMC instead of in the bulk solder. This is not the case for metals such as gold and silver, both solubilize very readily into the solder joint. Though it was not expected, increasing the silver thickness was conducted to see if it had any effect on solder joint reliability, in a similar vein to ENEPIG finishes, such was not the case for silver.

For this experiment, all failure modes for every finish with and without conditioning resulted in “die breaks.” This failure indicates a strong solder joint with failure found in the bulk of the solder. This test was also repeated a number of times to understand consistency. In the second test, electroless nickel/electroless palladium/immersion gold was also run for comparison. Electroless palladium thickness levels were varied to determine the effect on shear strength and failure mode. Thickness targets were 6, 12, and 30 microinches for the palladium layer. Again the ENIG and ENImAg resulted in shear strengths above 1.5kg force, both as plated and after thermal cycling. Again, all resulted in die breaks excluding two soldermask defined pads which formed die shears. It was later determined that these pads had poor solder mask registration which was likely a significant factor in the failure mode. It was found, unsurprisingly, that as the palladium thickness increased on the ENEPIG samples the failure modes transitioned from die break in the bulk solder to dies shears.

CORROSION RESISTANCE

The above section gives an indication of the nickel's resistance to corrosion caused by the top layer plating bath. This next section reviews the finish's resistance to environmental conditioning

For this set of testing the ENImAg was compared to ENIG at two gold thickness, 1 and greater than 2 microinches. As reducing gold thickness is a concern for overall performance this test would help demonstrate if the porosity of a lower gold thickness is such that it degrades with environmental exposure.

Expanding on the work of the 2010 paper discussing the same subject the effect of 85°C/85%RH was tested more extensively. Subjecting the finishes to temperature and humidity will also give a strong indication of robustness of the finish. The following was a comparison of ENIG and ENImAg after a 24 hour exposure to 85°C/85% RH. Visual observation of all parts showed no change in appearance after the temperature and humidity exposure. After conditioning and visual inspection, parts were soldered using wetting balance testing and solder spread testing conducted in accordance with IPC J-std 003.

To introduce a more challenging aspect to the wetting balance test, lead free SAC 305 solder globules were used with Kester 959-T No Clean solder flux. The choice to veer from the exact specification was driven in part due to a preference to use of a flux more typically employed in routine, everyday assembly. The instrument used was a MUST III wetting balance with globule [4]. Each finish was tested in triplicate. One test board per panel contains six pads for solderability testing. The charts below are a representative of the surface wetting on all twenty-four runs. The results show that the ENIG degrades after the 85°C/85% RH exposure, as demonstrated by the significant reduction in wetting forces measured. Though the majority of the pads tested maintained passing forces, an increased propensity for solderability issues was observed and should be considered. The ENImAg maintains fast soldering with high wetting forces even after conditioning.

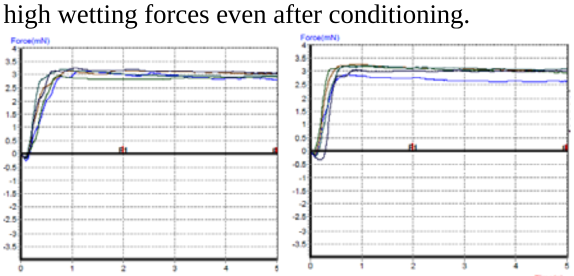


Figure 10: Wetting Balance results for ENImAg (Ag 6-8u-in) and ENImAg (Ag 14-16u-in) after 24 hours at 85°C/85%RH (respectively)

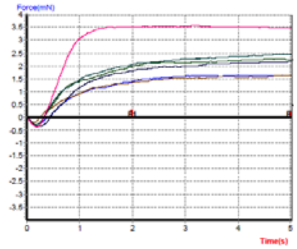


Figure 11: Wetting Balance Results for ENIG (Au 1µ-in) after 24 hours at 85°C/85%RH

The ENIG degradation was not observed on the solder spread test. It seems the act of placing the solder paste on the pad was not sensitive enough to show differences between the finishes when the parts were pasted in a one to one paste to pad ratio. Uniform solder to the edge of all pads was observed on both the ENIG and ENImAg.

Steam Age Exposure

The sister sets of the above coupons were exposed to steam age for 8 hours. Typically, it is not recommended to expose ENIG to steam age as it is well known that this will show degradation, however, this test was to determine whether ENImAg could withstand steam age, as does its forerunner, immersion silver on copper. If deposit degradation does occur it will also be evident in the solder spread data. On the unconditioned parts, regardless of the gold thickness applied, there is uniform full solder coverage of the surface pads. Such is also true for the unconditioned ENImAg. Visual observation indicated that there was degradation of the ENIG, the gold displays oxidation in the form or non-uniform appearance as light and dark gold. This was the same for both gold thickness levels. The ENImAg did not show a cosmetic change after steam age exposure.

After the temperature and humidity exposure, the silver deposit maintains full uniform spread as does only the thicker gold deposit. Degradation in spread is observed on the thinner plated gold deposit. The thin gold deposits showed moderate pull away from the pad edges, such was not the case of the thicker gold deposit which spread uniformly to the pad edges. This type of gold response was expected. All immersion plating baths result in some degree of porosity and though some will say the formulation can dictate the packing or density of the plated immersion deposit, very thin layers will always retain some degree of porosity, this is clearly displayed by the ENIG results obtained. Though the ENImAg finish purposefully involves the use of a thicker layer of metal, the lower silver metal cost and the less aggressive nature of the chemistry used facilitates this well.

As expected none of the finishes passed the wetting balance test according to IPC specification. The thin gold ENIG finish would not wet at all. On the thicker gold ENIG set, 50% of the pads tested did not accept solder. The globule made contact with the pad surface but would not adhere. Therefore, the curves do not pass the buoyancy line. The other 50% were slow to wet with low forces. Surprisingly, but in line with the solder spread testing, the ENImAg samples all accepted solder. Though the parts were slow to wet with lower forces, each pad exited the test with solder adhered to the board surface. Future testing will investigate the effects of more active flux types.

ELECTRICAL PROPERTIES

Contact Resistance

Though not normally an issue with ENIG many OEMs are concerned about the fall out of parts due to poor contact resistance testing. This is a characteristic that plagues organic solderability preservatives and other organic coatings on metal surfaces. During probing for electrical connectivity, the organic materials used transfers onto the probe tip. This in turn alters the resistance readings. The industry has sought the introduction of new probe styles which twist as they test to penetrate the nonconductive organic surface finish. Silver metal, naturally, is highly conductive and will not transfer to probe tips. It maintains high contact resistance performance. Figure 12 below compares the contact resistance of four surface finishes both as plated and after two lead free reflow excursions. Parts were probed five hundred times. Each number is an average of the resistance reading taken every 25 hits. The tip style used was a traditional 30° gold plated conical tip with 8 ounces of force. This probe style is not sharp enough to penetrate through organic layers without transfer being observed, such is the reason for the poor performance of the OSP. It should be noted that the ENIG resistance was compromised by the reflow excursions.

Surface Finish	8 oz As Plated	8oz After 2x Reflow
OSP	11.5	776.5
Immersion Ag	4.1	4.4
ENIG	3.9	5.0
ENImAg	4.0	4.0

Figure 12: Contact Resistance Comparison of Various Surface Finishes

The change in contact resistance observed on the ENIG part was somewhat unexpected. It may be attributed to the thin layer of gold being unable to properly protect the underlying nickel from oxidation during the reflow excursions. Results may be different with a higher thickness of gold on the surface.

Aluminum Wire Bonding

Though currently the percentages may be small, there are an increasing number of end-users specifying ENIG for Aluminum wire bond applications. Aluminum wire bonding is performed differently than gold wire bonding. Aluminum wire bonds are created ultrasonically at room temperature and are described as wedge bonds (figure 13). Gold wire bonding uses a combination of heat, pressure and ultrasonics to form two bond styles known and ball bonds and stitch bonds (figure 14).

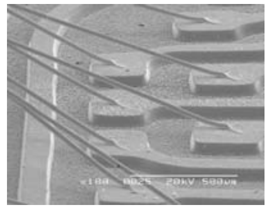


Figure 13: SEM Image of Aluminum Wedge Bond

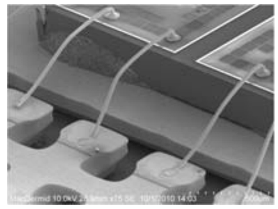


Figure 14: SEM Image of Gold Ball Bond to Lower Stitch Bond

The following expands on the ability to successfully Al wire bond to the new ENImAg finish. Wire pull strength requirements vary from customer to customer and are based on conditioning the parts may see in end use. The following test was conducted as plated with no conditioning and after a 3 hour dry bake at 180°C to simulate die attach and curing steps. Immersion silver on electroless nickel was tested at multiple silver thickness ranges to understand the effect of increased silver thickness on performance. Wire bonding and pull testing was conducted at a third party facility.

Testing was conducted on an ASM wire bonder with a 0.9mil Al wire according to MIL-STD-883. The test was conducted without any cleaning process prior to the bonding operation, with 133 wires being bonded. The resulting wire bonds were pulled on a K&S 1470 machine and resulted in all averages above 8 gram force with and without conditioning for each finish (figure 15). A total of 25 bonds per finish were pulled. The thickness of the silver may play a role in the standard deviation of the pull strength recorded.

	Average No Conditioning	Std Dev No Conditioning	Average 3hr bake@180°C	Std Dev 3hr bake @180°C
4-6μ-in	8.110	0.809	8.427	0.567
4-6μ-in	8.034	0.822	8.557	0.403
8-10μ-in	8.220	0.527	8.102	0.873
8-10μ-in	8.230	0.463	8.436	0.747
12-14μ-in	8.387	0.542	8.347	0.503
12-14μ-in	8.290	0.438	8.486	0.512

Figure 15: Average Aluminum Wire Pull Strengths

CONCLUSION

The benefits of gold surface finishes are well understood and just like every surface finish, it has positives and negatives. One surface finish is not suited for every application. ENIG has a strong hold of market share but as great pressure continues to be applied on the electronics industry both financially and environmentally, one must consider alternatives to this now prohibitively expensive finish. The adoption of MacDermid's electroless nickel/immersion silver finish proves to be high performing and economically viable alternative to the high cost ENIG incumbent. ENImAg can hold up to all the conditioning which ENIG proves to be successful at. Though ENIG has superior unconditioned solderability silver on nickel displays a more consistent wetting performance even after extreme conditioning being applied. ENImAg proves to maintain superior contact resistance as expected from a silver finish and displays superior aluminum wire bond performance. Though the immersion silver finish tested in this research involved a thicker layer of metal than the incumbent ENIG, the lower metal cost of silver and less aggressive nature of the chemistry allows for this on the ENImAg finish and proves the benefits as such.

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