Abstract
Innovation within the electronics industry drives a constant demand for advancement and change within its supply chain. Approximately 10 years ago, the value of immersion silver as a final solderable finish became clearly apparent within a portion of the electronics assembly industry. In subsequent years, immersion silver was widely adopted as a preferred finish for high volume, surface mount printed circuit board assemblies. Today, immersion silver can be categorized as one of the most popular finish options in this space. Its most noteworthy benefits include ease of use at the PCB manufacturing and assembly levels, predictably high yields, excellent electrical characteristics, and low cost relative to most alternatives. These attributes, particularly in an environment characterized by high precious metals costs, make silver an attractive consideration in expanded applications.

This paper describes further development with silver as a final finish, establishing its value to new and broader segments of the electronic materials and assemblies market. More specifically, this work describes a new silver final finish process, and describes its key attributes including and beyond solderability preservation, delivered from a non-electrolytic process cycle. Detailed performance results relating to corrosion and environmental resistance, durability of light reflection, and robust wire bond performance are given. With these and associated attributes, the suitability of silver as a preferred finish for evolving applications such as advanced PCB, LED, and semiconductor packaging is described.

Introduction
In an earlier presentation we discussed the advantages of a nickel undercoat for chemically plated silver for PCB applications [1]. In this paper we will discuss the advantages of the nickel undercoat for wire bonding applications. When considering wire bond applications the industry focuses on electrolytic nickel/electrolytic gold or electroless nickel/electroless palladium/immersion gold. Today's precious metal prices make these finishes extremely costly. The current price of gold is currently over 1400 USD/troy oz. Palladium is at 762USD/troy oz and silver though at an all time high of 40USD/troy oz is still less only 5% the price of the palladium and less than 3% of the cost of the gold [2].

Recently, the boundaries between chip packaging and PCB substrates have disappeared and more applications require both wire bonding and soldering capability. The latest improvement to the chemically plated silver process enables silver to compete in these applications both functionally and financially.

Functional Performance
There are specific functional performance criteria
needed to branch outside of standard PCB surface finishing. A few of the characteristics will remain the same such as solderability and corrosion resistance but the two important characteristics for electronic packaging and LED applications are wire bonding and reflectivity. Wire bonding requires a unique approach to preventing metal surface degradation. Attention needs to be paid to the effects preconditioning may have on the surface finish. This includes metal migration and surface oxidation. The standard organic topcoats traditionally used to protect silver surfaces in PCB applications are not compatible with the wire bond process [3].

**Wire Bonding**

Traditional wire bond finishes include electrolytic nickel followed by electrolytic silver or gold, electroless nickel/immersion gold (ENIG) and the newer electroless nickel/electroless palladium/immersion gold (ENEPIG). In general newer technology packages are favoring chemical plated finishes due to the advantages of more uniform plating at higher density without having to use bussing and waste substrate area. Silver offers the advantages of chemical plating, has excellent properties for wire bonding and all this comes at a lower cost. Immersion silver, however, has not been widely accepted due to the issue of copper migration thru the silver layer and subsequent copper oxidation during the die attach process.

MacDermid used the follow test procedure to assess the wire bondability of using a nickel barrier to prevent copper migration. All parts were processed through immersion silver and the new electroless Ni/Ag process for comparison. Panels were wire bonded using a K&S4524A gold wire bonder with a 1 mil wire and a bonding temperature of 150°C. Each panel was fitted with 20 wire bonds. After performing pull strengths, the parts were exposed to a one hour bake at 180°C. This bake is used to simulate a die attach step. The parts were again gold wire bonded and checked for pull strength.

<table>
<thead>
<tr>
<th>Surface Finish</th>
<th>Conditioning</th>
<th>Pull Strength (gf)</th>
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<tr>
<td>CuAg</td>
<td>As Plated</td>
<td>7.9</td>
</tr>
<tr>
<td>CuAg</td>
<td>Bake</td>
<td>3.2</td>
</tr>
<tr>
<td>NiAg</td>
<td>As Plated</td>
<td>8.5</td>
</tr>
<tr>
<td>NiAg</td>
<td>Bake</td>
<td>6.1</td>
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**Figure 2: Wire Bond Pull Strength Comparison**

Figure 2 shows strong pull strengths for both immersion silver and the new NiAg process when the finishes are freshly coated. In both cases the silver thickness was between 0.3-0.4 microns. After the conditioning bake, the immersion silver finish loses pull strength. It is believed that this is a result of copper migration through the silver deposit as discussed in earlier studies [1] and shown in Figure 3. This topic will be further discussed in the tarnish and corrosion resistance section of this paper.

**Figure 3: EDS of Plated Coupons After Bake**

A) Immersion Silver Only After Bake

B) Electroless Nickel-silver After Bake
Depending on the temperature of the bake and the cleanliness of the oven, the migration of the copper through the immersion silver deposit can vary. Including contamination in the bake such as sulfur will accelerate the extrusion of the copper from under the silver deposit. Very thick silver deposits, on the order of 2 microns would also reduce the copper migration but the only industry accepted way to achieve this thickness would through the use of electrolytic silver thicknesses which as discussed put design constraints on the package or PCB.

Subsequently parts have been wire bonded in a production assembly environment following a DOE on standard process parameters including die attach and cure. The table in figure 4 shows the pull in grams and break mode of several trials. Of course an end user will specify minimum pull strength required in gram forces but for additional information regarding the surface finish quality, close attention should be paid to the mode of failure.

<table>
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<tr>
<th>No</th>
<th>[g]</th>
<th>Mode</th>
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<th>[g]</th>
<th>Mode</th>
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<td>10</td>
<td>8.5</td>
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</table>

As shown in Figure 4, wire pull results were all above minimum 6g and wire breaks were in acceptable mode except for two pulls in trial 3.

The best mode of failure is a wire break, this is represented by a break any where along "C" in figure 5. This indicates that the bonds between the wire and the plated surface are so strong the wire is forced to break. A break mode E at the stitch bond usually indicates issues with the plated surface wire bond compatibility. This failure mode can indicate that the bond is weak and the quality of the surface finish is the reason for the poor wire adhesion.

Figure 5: Wire Break Mode Descriptions

**Pad Space Resolution**

Another requirement for today’s technology is finer space resolution. Again, when comparing to the known surface finishes for this market, there is electrolytic nickel/gold and ENEPIG. Both can require very high thickness to enable wire bonding. The electrolytic deposit adds many concerns for design constraints as discussed earlier. Some ENEPIG requirements call for 200 microinches of nickel, 12 to 30 microinches of palladium followed by 2-4 microinches of gold. The proposed NiAg finish would require 160 microinches of nickel followed by 12 to 15 microinches of silver. As the thickness of a surface finish increases the control
over encroachment into fine spacing gets more difficult. Also the introduction of more chemical plating baths that rely on autocatalytic reactions make extraneous plating a greater reality an cause for concern when working with very fine spacing. The current limit for the new silver process is shown below at 60 microns but additional work is underway to test even finer spacing.

**Tarnish and Corrosion Resistance**

As designs criteria and performance expectations change in the electronics industry corrosion has been a topic of concern. Smaller footprints force assemblers to use reduces solder printing. This is to eliminate bridging of the solder between closely spaced features. The down side is that metal area can be left exposed after assembly where the solder has not fully spread. With increased expectations and performance criteria many end users are specifically leaving pads unsoldered. As the majority of electronics are mobile now and our global environments are getting more polluted, the concern for corrosion is eminent. MacDermid has worked with a high sulfur exposure to test to simulate an accelerated corrosion environment. The details of the MacDermid tarnish test has been published several times over the past decade [2], and so is well established. The test was developed to evaluate immersion silver and related coatings, when exposed to a sulfur bearing environment. This test is essentially a research tool that accelerates tarnish. In the test, a sealed chamber is used. A controlled quantity of water (to induce high humidity) and hydrogen sulfide gas is introduced which creates visible tarnish on the coating under test. Specifically, the tarnish chamber used is 10 cubic feet in volume and is heated to an internal air temperature of 45°C. The chamber contains 500mL of a sodium hydrosulfide solution, which when acidified releases hydrogen sulfide gas. The humidity level in the chamber is typically around 80%.

The test is conducted on parts after plating and after one lead free reflow exposure. This helps to demonstrate the tarnish resistance of the silver surface between fabrication and assembly as well as resistance of the surface post-assembly when the metal will remain unprotected in its end use. Figure 6 displays the reflow profile for multiple pads sizes across the test vehicle. The peak temperature for the profile is 245°C.

![Figure 7: Lead Free Reflow Profile](image)

Corrosion rates in the tarnish chamber and in all environments are highly affected by humidity and temperature. Small increases in either can affect the corrosion rate. On average, the corrosion rate on copper for this test is 25 µm/hour. Due to fluctuations in temperature and in turn humidity, an uncoated immersion silver deposit on a copper substrate control is always used for comparison against any coating under evaluation. The control panel is also used as a gauge for test duration.

Below is a comparison of a traditional Imm. Ag deposit versus the proposed new coating. Visual observations of the samples show a dramatic difference in appearance between immersion silver on copper versus silver deposited on electroless nickel after exposure in the tarnish chamber.
Both control sets of silver on copper display tarnish which ranges from brown on the as plated samples to light yellow on the parts that had been reflowed. The NiAg samples do not display discoloration of the silver surface.

It is known that immersion silver has slightly better tarnish resistance after a reflow, this is due to a light a silver oxide acting as a protection. The silver on copper still shows some yellowing after chamber exposure even with the reflow excursion. The silver plated on nickel maintains a uniform silver appearance.

When silver is exposed to a high sulfur bearing environment it is expected to tarnish but what is not always understood is that the majority of the heavy tarnish is a result of the underlying copper. During sulfur chamber exposure, the combination of the humidity and the sulfur draw the copper through the pores of the silver deposit. Once the sulfur "sees" the copper, the oxide is formed and can progress to a blue of purple corrosion product very quickly. When a nickel barrier layer is used, the tarnish is the silver appears to be dramatically slower. This is because the visual observation is only a light silver sulfide and not a heavy copper sulfide product. This can be proven and further understood by EDS analysis.

To understand the corrosion resistance on a microscopic level, samples were analyzed using Electron Dispersive X-ray Spectroscopy (EDS) before and after chamber exposure. For simplicity, the results discussed below are for samples that were not conditioned prior to the tarnish chamber exposure. EDS maps of immersion silver on copper show a uniform layer of silver. Copper can be seen in the EDS map, this is attributed to penetration of the beam through the thin silver deposit. Without areas of intense silver or copper it can be deduced that the silver layer is uniform and consistent. EDS maps of the NiAg reveal no copper on the board surface. The nickel barrier layer is too thick to allow beam penetration. Analysis of the surface finishes taken after the chamber exposure show an increase in copper observed through the silver deposit, when the silver is plated directly on copper. The EDS shows an increased concentration of copper in the deposit as a whole (figure 8). This reaction seems similar to the mechanism frequently described for creep corrosion. No copper is present in the NiAg EDS maps as coated or after the tarnish chamber conditioning. In both instances, a rich silver deposit remains (figure 9). The nickel barrier layer is preventing humidity and contamination from reacting with the underlying copper and allowing it to become mobile.
Solderability Ball Shear

To demonstrate the surface finish soldering quality, ball shear testing was conducted. One test vehicle used at MacDermid contains a BGA with both soldermask defined and metal defined pads. Overall, the BGA design contains 200 of each pad design. Lead free solder is manually printed on the BGA design with an 8-mil stencil with Kester SAC 305 lead free solder. Lead free spheres are then hand placed using a second stencil for guidance. The parts are reflowed using the profile in figure 6. During the reflow process the solder sphere collapses over the metal defined pad rendering a very strong solder joint. When ball shear testing is conducted on a metal defined pad the results normally display the strength of the copper pad to the laminate. The solder mask defined pads are not as strong due to the restrictions of solder flow caused by the soldermask height. Comparative images of these joints are displayed in figure 10. To test strictly the surface finish ball shear was conducted on the solder mask defined pads.

Figure 8: (A) CuAg Before Tarnish (B) CuAg After Tarnish

Figure 9: (A) NiAg Before Tarnish (B) NiAg After Tarnish

Figure 10: Solder Spheres Collapse Comparison

(A) Metal Defined

(B) Soldermask Defined Pad
Twenty-five spheres per surface finish were sheared.

The NiAg process performs very similar to the ENIG process. This is expected as both surface finishes result in a solder joint made with the electroless nickel. Immersion silver on copper shows higher ball shear forces due to the strong solder joint made with copper.

**Reflectance**

More recently there has been interest in using silver as a reflective surface. There are a number of applications where this can be applied and one must understand the overall performance requirements of the application. For example, we understand that gold is a very good surface for wire bonding but it is not known to have high reflectivity. Figure 13 give a comparison of pure aluminum, silver and gold.

![Figure 13: Reflectance Values for Metals](image)

Silver of course is a very reflective material and the new NiAg process is deemed a good performer for wire bonding as well.

To get a stronger understand of how plated silver and the potential effects of surface pretreatment, MacDermid uses a Konica Minolta CM 2600d Spectrophotometer. This unit is capable of reading both specular and diffused reflectance. For comparison and the use of this paper, the follow chart in figure 14 shows the specclar reflectance of different metals and surface finishes in comparison to the new NiAg at a wavelength of 460nm. The majority of the reflectance comes from the nature of the metal but some changes in the percentage can be achieved by altering the surface roughness under the plated metal.

![Figure 14: Specular Reflectance Chart](image)
Conclusions
A combination of electroless nickel/immersion silver offers a surface finish with the beneficial characteristics of both immersion silver and ENIG but at a greatly reduced cost when compared to ENIG. This process also delivers superior functional performance for the new generation of packaging which requires both wire bonding and solderability capability.

References


[5] Frenhoffer paper


[8] Improving Air Quality in Asian Developing Countries, Chinese NRI Activities, Phase 1 Final Report, Asian Regional Research Programme On Environmental Technology (ARRPET), May 2004


