The Study, Measurement, and Prevention of Tarnish on Immersion Silver Board Finishes

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Abstract

With increased environmental legislation against lead in the electronics industry[1], circuit board manufacturers are expecting chemical suppliers to formulate lead free alternatives with the same functionality as tin/lead. These alternatives are needed for board finishes, in the solder, and on the components adhered to the circuit board. It is a benefit for the chemical supplier to educate the assembler and Original Equipment Manufacturer (OEM) on the differences experienced with these new alternatives. The appearance and characteristics of these new finishes vary somewhat from the incumbent lead-containing standards. Functionality remains the same if not better in some cases. The main focus of this study was the immersion silver surface finish. As interest moves away from HASL final finishes there has been a greater attraction to immersion silver in particular. This paper will explore the effects of operating and storage environments on immersion silver surface finishes and help to explain the functional capabilities the finish has after accelerated aging conditions.

Introduction

With efforts to reduce the use of Hot Air Solder Level (HASL) as a solderability preservative in the electronics industry, there has been considerable growth in the use of alternate final finishes. Government and industry experts are concerned about technical and environmental limitations of tin/lead on circuit boards.[1] Alternate finishes include electroless nickel/immersion gold, organic coatings, immersion tin, and immersion silver. According to industry estimates, the newest of the alternative circuit board finishes, immersion silver, is now used in 8% of the market.[2] Chemical suppliers have offered immersion silver since the early 1990's, however some board fabricators and OEM's have been hesitant to convert to this final finish. Concerns principally fall into two categories: fear of dendritic growth with applied current and fear of surface corrosion. These concerns have resulted in a demand to quantify the occurrence of the phenomena and to measure their affect on performance.

Advances in technology translate into a greater demand on the performance of a board's surface finish. Flatness, wettability, shelf-life, physical durability, contact functionality, and cosmetic criteria all contribute to the production success of a board finish. Each of these criteria may be affected by a perceived weakness of immersion silver, the tendency to tarnish. Present day finishes such as immersion silver must maintain reliability for long-term storage and operation in the final product without functional loss from tarnish.

This paper will explore the effects of tarnish on solderability, electrochemical migration and surface conductivity. By understanding the changes occurring on the deposited metal, appropriate experimental data will quantify the functional changes of the surface finish. Experimentation will include electrochemical migration, contact reliability and solderability after various environmental conditioning. Most importantly, data will quantify the depth of corrosion as silver is exposed to various environments. This will allow users to predict the functionality of the resulting product.

Immersion Silver Deposition

Chemically, immersion deposits are advantageous to the board fabricator because there is no use of chemical reducers to drive the reactions. In systems such as electroless nickel, chemical reducers and their supporting chemicals can breakdown, requiring a great deal of chemical maintenance.[3] Immersion silver deposition occurs as a result of the oxidation of the base metal, in this case copper. The entire reaction is driven by the electromotive series. The presence of the underlying metal drives the reaction; once the silver has deposited over the copper surface, the reaction slows down.[4] This type of reaction also eliminates the use of activation steps and therefore reduces other problems such as extraneous plating. The simplicity of the immersion (galvanic displacement) mechanism is a significant benefit to PCB manufacturers.

$$\text{Equation (1)}\ 2\,Ag^{+} + Cu^{0} \rightarrow 2\,Ag^{0} + Cu^{++}$$

Physically, immersion deposits are more planar than traditional HASL surfaces. While variation in thickness of HASL may be forty or more microns, typical variation in an immersion silver deposit is measured in nanometers.

The kinetics of the reaction result in a silver deposit that mimics the copper surface. The nature of the reaction produces a thin layer of silver. For perspective, the thickness of immersion silver is less than one thousandth of the thickness of copper circuitry. The flat surface makes placement of small devices much easier at component assembly.

When exposed to contaminating environments, silver metal will react with anions from the atmosphere and convert them to silver tarnish on the surface. The tarnish is actually a reduction/oxidation corrosion product. Tarnish species include silver chloride, silver sulfide and silver sulfate. These principal corrosion products of silver have three different electromotive potentials.[5] This makes it possible to determine the type and amount of contamination on the surface of the silver using instrumentation, including Sequential Electrochemical Reduction Analysis (SERA), Auger, Secondary Ion Mass Spectroscopy (SIMS), and Electron Spectroscopy for Chemical Analysis (ESCA).

One disadvantage to using the SERA method is that silver sulfate and copper sulfate exhibit the same reduction potential. Therefore, SERA cannot distinguish between these two important surface species. Low silver thicknesses normally result in copper sulfate contamination due to incomplete copper coverage. In failure mode analysis, silver thickness should be determined prior to running the SERA to determine if the silver thickness is too low. Below 0.15 microns, extremely heavy oxidation is usually due to the formation of copper sulfate as a result of under-protected copper.

Preliminary testing was conducted to help determine if visible tarnish resulted from the formation of copper sulfate or silver sulfate with respect to deposited silver thickness. Figure 1 is a Scanning Electron Microscope (SEM) image of a thin silver deposit over copper. The thickness of the deposit was 0.1 microns. The image shows dark areas scattered throughout the deposit. Electron Dispersive Spectroscopy (EDS) of the dark areas indicates that these areas are rich in copper (Figure 2). Plating for an increased amount of time results in a thicker silver deposit. The increased plating time enables to silver to cover more area. In turn there is a decrease in copper pore sites as seen in Figure 3. An EDS of this area shows a deposit rich in silver (Figure 4). A small copper peak can be detected as a result of "shoot through" due to the accelerating energy of 20kv of the microscope.

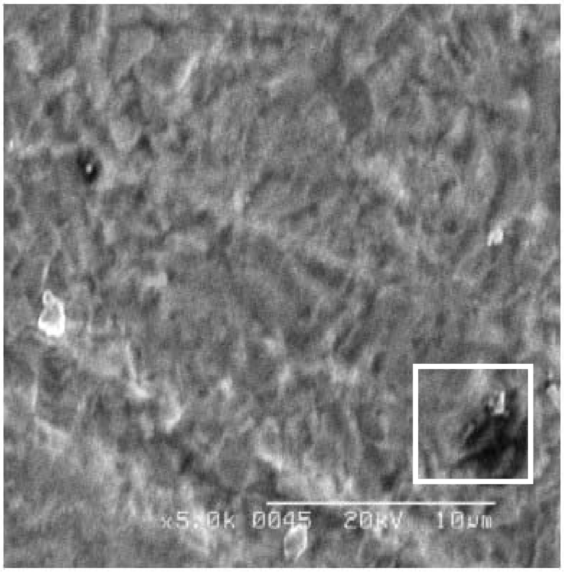

Figure 1 - Low Silver Thickness (0.1 microns)
EDS Area Highlighted

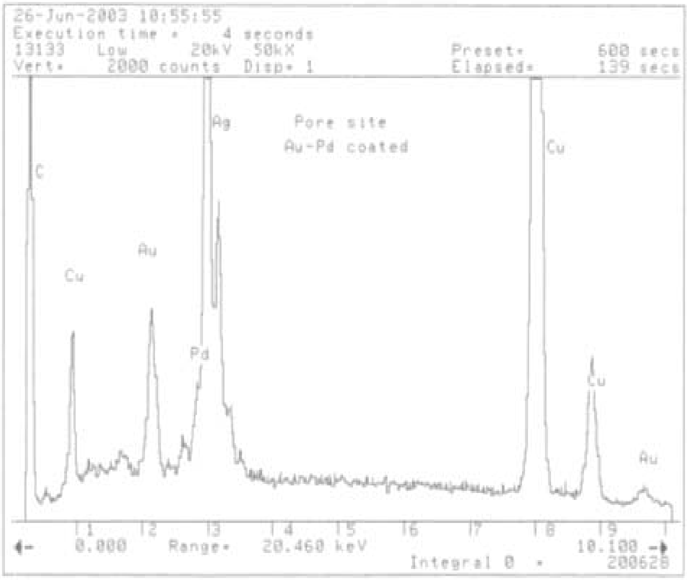

Figure 2 - EDS of Pore in Low Silver Thickness Sample

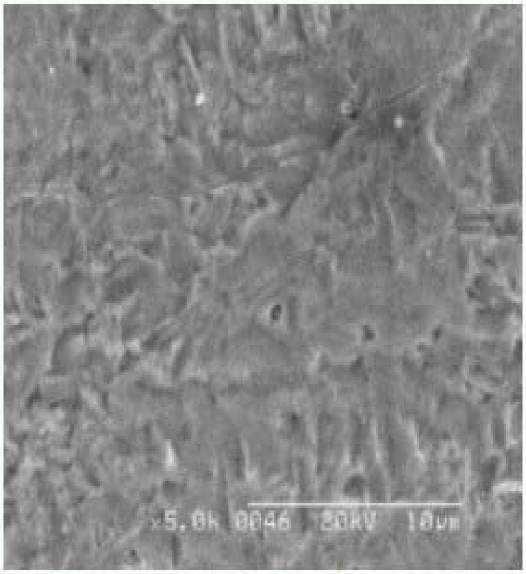

Figure 3 - High Silver Thickness (0.3 microns)
EDS Area Highlighted

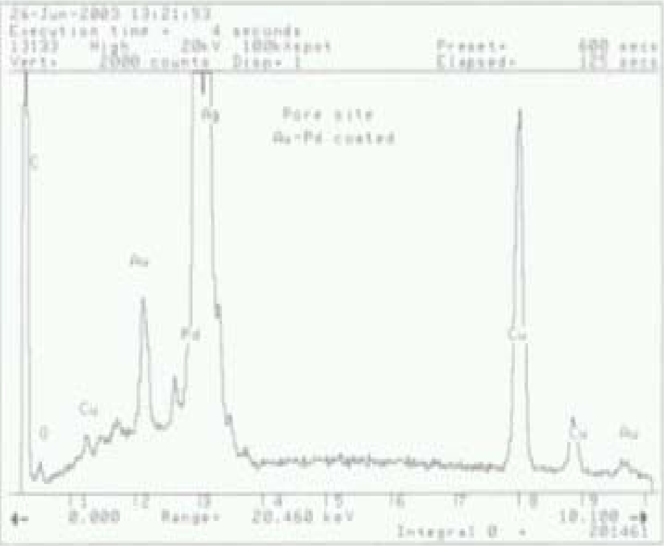

Figure 4 - EDS of High Silver Thickness Sample

Early in the development of immersion silver processing, such thickness studies confirmed the preference for higher silver thicknesses. Results from the fundamental testing indicated that circuit boards should be plated to a silver thickness target centered at 0.25 – 0.3 microns. This thickness guideline was followed for the subsequent experimentation. The proper silver thickness would insure that the data are a result of silver corrosion and not copper corrosion.

Experimental

In several experiments dealing with the effect of tarnish on solderability, electromigration and contact resistance, a standard set of test vehicles was employed. Electroplated copper test coupons were processed through immersion silver cycles. The cycle included an acid cleaner, a modified persulfate microetch, a pre-dip for bath replenishment and finally an immersion silver bath with various proprietary organic additives.[6] Silver plating time was run at two different durations to achieve a deposit of 0.1and 0.3 microns.

Through Hole Solderability

Test coupons (Figure 5) containing surface mount pads and eighty plated through holes (PTH) were processed through a standard immersion silver process to achieve an average silver thickness of 0.3 micrometers. Thickness was measured by X-ray Fluorescence (XRF) and produced a range of 0.22 – 0.33 microns. The panels were then enclosed in a chamber containing a sulfur solution and a fan for circulating the air (Figure 6). The sulfur solution used was a mixture of 0.1g/L sodium bisulfide in de-ionized water with 1mL/100mL concentrated HCl. The solution was divided into three containers set on one side of the chamber. The fan directed airflow across the containers parallel to the hanging samples. A test coupon was removed every thirty minutes. Total tarnish was measured by Sequential Electrochemical Reduction Analysis (SERA) on surface pads. Finally, the through holes were floated on molten solder at 245ºC for three seconds and evaluated according to industry standard ANSI/IPC J-STD 003a.[7]

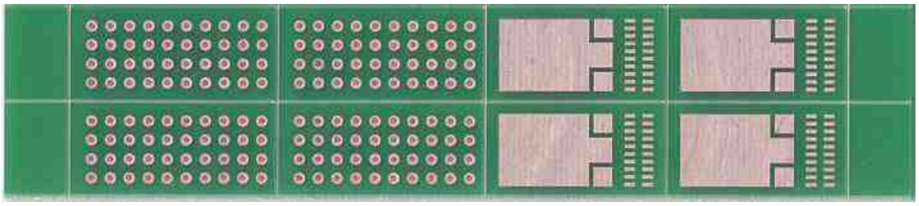

Figure 5 - PTH Test Coupon

Figure 6 - Sulfur Chamber

Electromigration

A set of IPC B-25 test coupons (Figure 7) were processed through a standard immersion silver process. The boards were exposed to Class II Mixed Flowing Gas.[8] (Method G) for nine days at Aspen Labs in a Batelle Chamber. Within the chamber, panels are subjected to chloride, sulfide and sulfate. The test panels included both immersion silver panels and a copper control. Mixed Flowing Gas exposure was measured on a scale calibrated by its effect on copper.

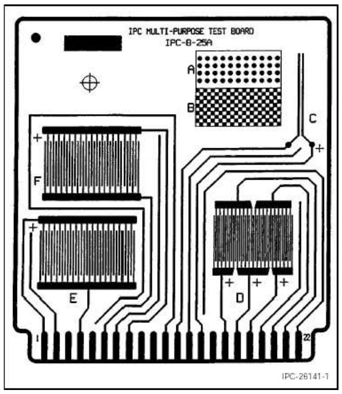

Figure 7 - B-25 Test Vehicle

Surface Conductivity/Contact Resistance

The last functional test performed was a simulation of a cabinet insertion test. Electroplated copper laminate was processed through immersion silver and electroless nickel/ immersion gold, separately. The samples were exposed to the same Mixed Flowing Gas as described in the Electromigration section for 0, 5, and 9 days. The level of tarnish on the samples was measured after 24 hours, 5 and 9 days. A second set of these boards was placed in a Humidity Chamber at 85°C and 85% relative humidity (85C/85%RH) for up to five weeks. After the MFG and humidity exposures the boards were inserted to a cabinet (Figure 8) which causes friction to occur on the edges of the boards. Three pieces of copper laminate were placed on top of each bare board prior to insertion to simulate the weight of components on the board. The samples were inserted for 0, 1, 15, and 50 times and measured for surface contact resistance. Cabinet rails were cleaned with IPA and DI water between each insertion set.

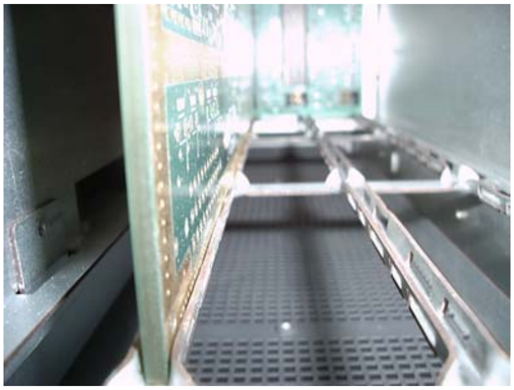

Figure 8 - Circuit Board in Cabinet Rail

Contact testing was conducted using a 50-microinch gold plated copper alloy burr free spherical radius probe. The probe had a diameter of 0.0625 inches. Resistance was measured by EIA 364 Test Procedure with a 100ma-test current and a 20mV open circuit voltage. A probe force of 25, 50, and 75 grams was used.[9] For an OEM involved in the study, maintenance of low-resistance electrical conductivity in a potentially contaminating environment is a key concern.

Results and Discussions

Overall results indicate the longer the exposure to the sulfur the greater the amount of total tarnish detected on the surface of the through hole test boards. Results from the fifth hour do not show an increased level of tarnish. This could be due to a less porous deposit. The chart does indicate that higher levels of total tarnish result in lower through hole solderability (Figure 9). Once 200 angstroms (Å) of tarnish form on the surface, visual appearance is affected. Silver samples begin to appear yellow or golden at this point. As the level of tarnish increases, the color changes to brown and may ultimately become an iridescent blue (Figure 10).

Figure 10 shows images of varying tarnish. The first sample is a new silver sample that was not exposed to any environment. Typically, a shiny silver deposit has a range of 0 – 100Å of total tarnish. The second sample shows a slight yellowing this is characteristic of 200 – 500Å of tarnish. The final sample shows a heavy amount of tarnish which indicates a level of 1500 – 2500Å of total tarnish.

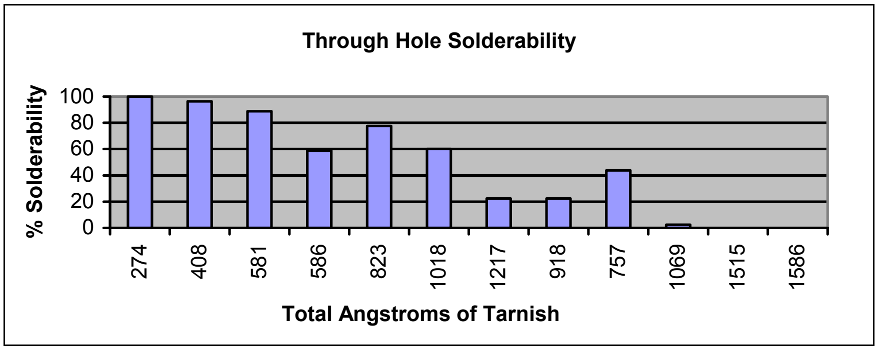

Figure 9 - Through Hole Solderability versus Total Tarnish

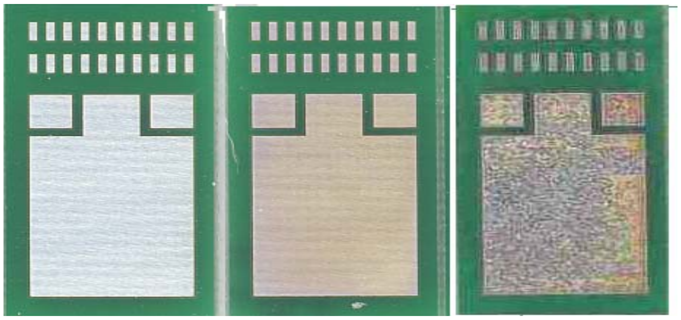

Figure 10 - Varying Silver Tarnish Levels

Electromigration

The nine-day exposure to Mixed Flowing Gas resulted in a total corrosion film thickness of approximately 3500Å as measured by coulometric reduction of copper. The 3500Å equaled 59-micrograms/cm^2 weight gain on copper. The industry accepted age correlation is 12–16 micrograms/cm^2 equals one year in the field. The levels of corrosion indicate that this test may represent 4-5 years of accelerated age. All silver samples including the copper control displayed relatively uniform levels of 'heavy' tarnish. The boards were then subjected to Electromigration testing at Trace Laboratories, according to Bellcore GR-78-CORE, Issue 1, Section 13.2.7.[10] All boards passed the test for electrical and visual requirements for electromigration (Table 1). This test requires the maintenance of electrical resistance between adjacent conductors of within at least one decade of the original (96 hour) value.

Table 1 - Electrical Characteristics of Silver After Mixed Flowing Gas

Board ID	#test Points	96 hr	168 hr	332 hr	500 hr
Ag Control	8	1.41E10	1.99E10	2.13E10	2.31 E10
Cu MFG	8	2.69E10	2.37E10	2.48E10	2.30 E10
Ag MFG	16	1.57E10	2.06E10	2.34E10	2.01 E10
Trace Copper Control	8	1.78E10	1.58E10	1.25E10	1.20E10

The samples exposed to MFG were also measured for total corrosion after 24 hours, 5, and 9 days. The levels averaged 850, 4000, and 9500Å, respectively as copper corrosion. After the accelerated environmental exposure, the coupons were then sent to Contech Research for contact resistance testing. The samples were measured using 25, 50, and 75 gram force loads, as per the earlier discussion.

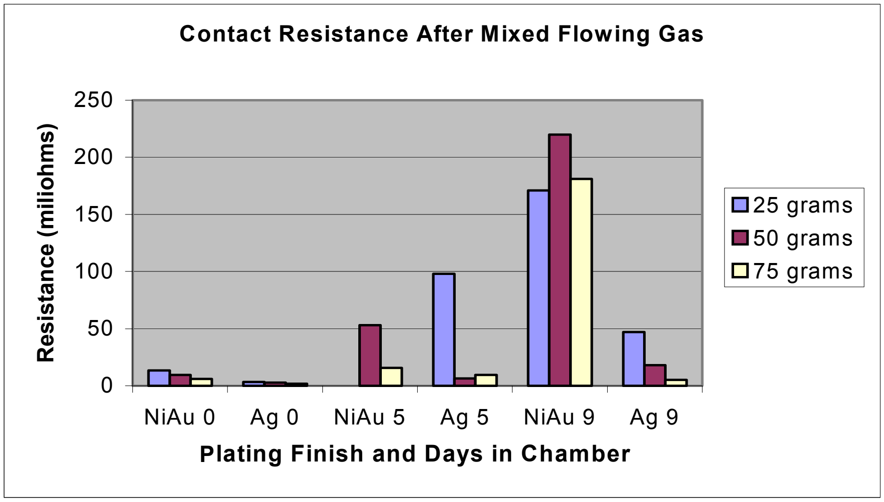

Figure 11 - Contact Resistance after Mixed Flowing Gas for 0, 5, and 9 days

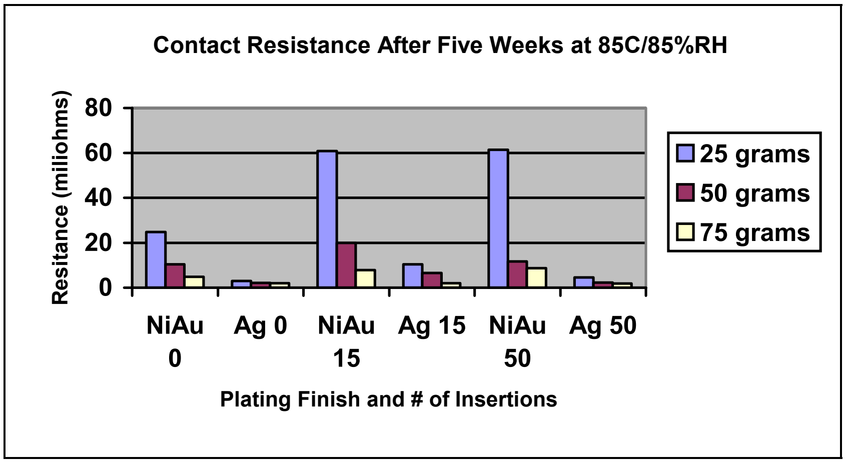

Figure 12 - Contact Resistance After Five Weeks Humidity

Consistently, the contact resistance data shows that an increase in force load will result in a decrease of resistance as the test probe overcomes any surface corrosion. For the immersion silver deposits, resistance stayed below 50 miliohms up to 9 days in the Batelle chamber for each force load. The electroless nickel/immersion gold samples began to show large increases in resistance after 5 days. The humidity and cabinet insertions also appeared to have little effect on the contact resistance of immersion silver. Again the silver results maintained a small deviation through the testing even with increased insertion and extended humidity exposure. Similar trends were observed with surfaces that had been aged with 85ºC/85%RH.

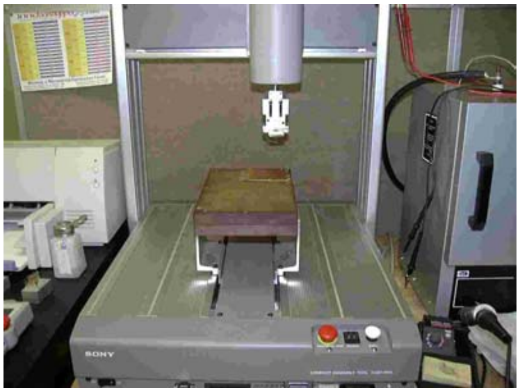

Figure 13 - Contact Resistance Testing

Conclusion

There are many advantages to using immersion silver as an alternative to lead-containing final finishes. The simplicity of the chemistry and the kinetics of the reactions enable easy processing during board fabrication and at the assembly house. Though appearance of the deposited metal may change with aggressive environments, functionality remains reliable.

The above testing indicates that environment does have cosmetic effects on immersion silver finishes. Visual defects should not be linearly associated with functional deficiencies. The above experiments indicate that moderate visual tarnish does not effect the performance of the surface finish. Through hole solderability remained acceptable up to 800angstroms of tarnish. Dendritic growth was not observed on any of the boards tested for electromigration and electrical resistance did not degrade a decade throughout testing. Contact resistance testing showed silver maintained high conductivity with a small deviation even at high levels of tarnish.

References

1. Lead Free Homepage: http://www.leadfree.org.
2. D. Cullen; “HASL Alternatives.” <u>PC Fabrication</u>, July 1999.
3. G. Mallory. Electroless Plating; 1990 AESF Publications.
4. D. Cullen, L. Toscano, “Immersion Metal PWB Surface Finishes: A direct Comparison of Selected Fabrication, Assembly, and Reliability Characteristics,” IPC Works September, 2000.
5. Bratin, P., Pavlov, M. *PC Fab,* **1999,** May p.30-37**.**
6. Redline, R., Sawoska, D. U.S. Patent 6 544 397, 2003.
7. IPC/EIA J-STD-003A, April 1992.
8. M. Kelsey, “Report 33142 Class IIa MFG” Aspen Research Corporation, November 2002.
9. M. Peel, “Report 201274 Probe Test” Contech Research, March 2003.
10. R. Michalkiewicz, “Report 48991 Bellcore GR-78 Core 13.2.7,” Trace Laboratories East, March 2001.