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The Perfect Copper Surface

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Abstract
In order to provide the functionality in today's electronics, printed circuit boards are approaching the complexity of semiconductors. For flexible circuits with 1 mil lines and spaces, this means no nodules, no pits, and excellent ductility with thinner deposits. One of the areas that has to change to get to this plateau of technology is acid copper plating. Acid copper systems have changed in minor increments since their introduction decades ago. However, the basic cell design using soluble anodes in slabs or baskets has for the most part remained the same. Soluble, phosphorized, copper anodes introduce particulate and limits the ability to control plating distribution.

The companies worked together to evaluate a new approach using insoluble anodes that are isolated from the main plating bath. Insoluble anodes are known to eliminate the particulate, provide consistent anode area and shape the anode to match the plated part. But isolating the insoluble anode dramatically reduces high consumption of organic additives typical with insoluble anodes. This new approach limits additive breakdown and & consumption normally seen at the soluble anode surface. The end result is a surface free of nodules, pits, and precise control of copper thickness distribution minimizing the impact of breakdown products.

This paper is to document the results from prototype testing through implementation into production. The system was first tested in pilot tanks at the companies to determine the impact on nodules and surface distribution. Data was generated looking at impact of anode design on plating distribution and surface for any defects. This data was utilized to design a full scale production line that is being used to quantify process improvement over existing production equipment. The goal for the work being done is a perfect copper surface.

Introduction
Technology is the main driver to change in the electronics industry. Systems that have produced acceptable high volume production for years typically do not undergo dramatic change. They may require some updating to improve yields or reduce costs, especially as a particular product reaches market maturity. However, processes will all have a certain point that requires a paradigm shift in order to reliably produce the next generation product.

Each new generation of electronics further erodes the line between wafer and PCB fabrication. Differences in these industries are becoming less distinct due to increased functionality and the reduction in size to improve mobility. To the PCB fabricator, this translates to finer features and thinner product, creating problems for acid copper plating. The overall requirement for a plated copper deposit is a thinner deposit, but with consistent higher ductility, improved thickness distribution and elimination of surface defects.

Current practices in acid copper plating have changed very little over the last few decades. There have been modifications in equipment and chemistry, but for all intents and purposes, the plating cell remains the same with an anode, the parts are the cathode, and typically some form of solution and work agitation. With a few exceptions, almost all PCB production utilizes the same phosporized copper in either baskets or slabs as an anode. While cost effective, soluble anodes are the weak link in the plating process.

Soluble anodes:

- Create debris in the plating solution.
- Create current flow that is difficult to control.
- Always change in shape and size.
- Cause a chemical reaction at the anode surface, destroying the additive and creating breakdown products that impact the deposit

Previously, the only alternative was use of insoluble anodes. Unlike phosphorized copper anodes, insoluble anodes never create debris, they can be easily machined for optimum distribution, and there is no change in anode area. However, insoluble anodes are less efficient, which in turn generates oxygen gas in the plating cell that oxidizes the additives and cause pitting on the surface. This makes the process difficult to control and while eliminating a major cause for nodules, insoluble anodes make it more difficult to control the deposit and introduce pitting as a major defect. The issues raised in the use of insoluble anodes can be completely eliminated by isolating the anodes from the plating solution.

Theory

By using membrane technology, the anode reaction can be isolated from the cathode reaction during acid copper plating. In theory, this separates the half-cell reactions specifically to the anode and cathode locations and organics like brighteners and carriers are only consumed during the deposition process at the cathode as the part is plated. With the proper membrane, the reaction at the anode is reduced to just electron donation, which completes the current flow and plates copper on the PCB surface. If the flow of electrons can be controlled, the distribution of the copper deposit can also be controlled.

For PCB production, this translates to:

- No gassing to cause pitting or breakdown of additive systems.
- Elimination of the major cause for nodules in acid copper plating.
- A consistent anode area that can be easily altered to control plating distribution.

The choice of membrane becomes critical to making this theory a reality.

In order to test the properties of different membranes, a specialized plating cell (Figure 1) was designed. It was a simple cell where different membranes could be inserted between the anode and cathode, allowing analysis of the chemical variation between the anode and cathode cells. The criteria for the membrane were: no penetration of additives, create a chemical equilibrium of all other inorganic materials, be robust enough for production and low cost.

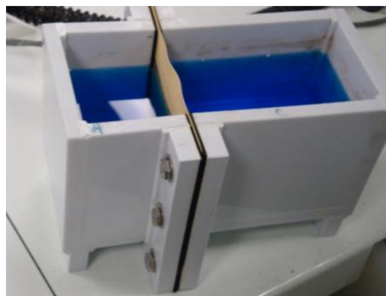

Figure 1 Membrane Test Cell

The testing of several membranes from a variety of vendors resulted in a specific choice to meet the technical, mechanical & cost requirements.

The observations made as different membranes were evaluated:

1. The voltage of the plating cell can be controlled by use of different membrane systems.
2. Chloride and organic additives can be kept exclusively in the cathodic plating cell.
3. Cu and acid will equilibrate between the anode and cathode cell.
4. Replenishment of CuO consumes the exact amount of acid during electrolysis.

These 4 points are critical in controlling the plating distribution, the deposit integrity, and the chemical balance in the plating solution.

There are a few potential choices for insoluble anodes. The insoluble anode selected was IrO on titanium mesh to reduce cost. The anode assembly (Figure 2) is the IrO anode enclosed in a polypropylene box with the membrane on the side facing the work. This provides a sealed cell for all chemical reactions that occur at the anode and insures gas that is generated during

plating is separated from the work. The organic additives for suppression and acceleration are separated from the anode eliminating breakdown of the additives. There is an increase in cell voltage with the use of insoluble anode boxes versus soluble phosphorized copper anodes. In this installation the voltage with the same part number and same current voltage would increase from 1 – 1.5 V with soluble anodes to 2-3V with the insoluble anode assembly.

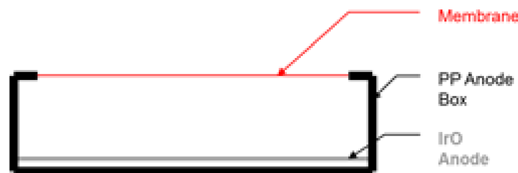

Figure 2 Insoluble Anode Box Design

This increased resistance and shielding from the polypropylene anode box provides the opportunity to direct current flow. Laboratory testing has shown that distribution with the anode box is almost a perfect shadow effect of the anode shape. As depicted in (Figure 3), the testing indicates an almost perfect straight line current flow versus the electromagnetic like flow typical with round baskets. If current flow can be directed, plating thickness will be more uniform over a surface.

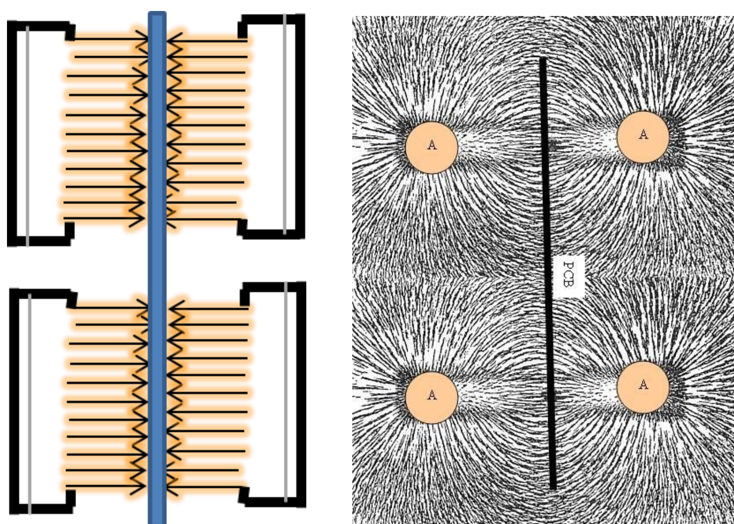

Figure 3 Current Flow Diagram Insoluble Anode Box Vs. Round Baskets With Soluble Anodes

To make insoluble anode viable for production, changes were also necessary to the equipment and in copper replenishment. There are a few different options that can be used to replenish the copper in insoluble systems. Copper oxide was chosen due to its availability, relative cost and ease of use. However, the source of copper oxide was critical to insure purity, low chloride content, and ability to dissolve quickly. It was found that the CuO manufacturing process was the key to the CuO grain structure (Figure 4) and that determined how easy it is to dissolve. Special automatic replenishment systems had to be developed to add and dissolve the copper oxide in order to maintain Cu levels in the plating solution.

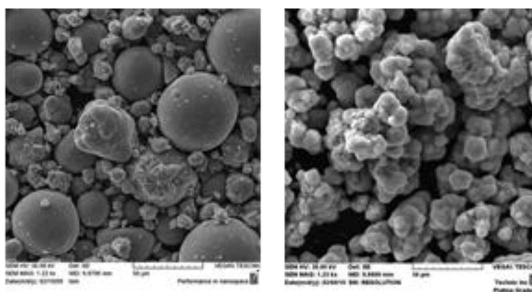

Figure 4 Grain Structure Of Different CuO Sources

In any acid copper installation, throwing power is always a major consideration. Where insoluble anodes will improve surface distribution and eliminate defects, throwing power is a function of several other variables including chemistry and solution flow. The solution resistance shown in the equation in Figure 5 is a result of the chemistry used. Where suppressing agents and accelerators have a major impact, the benefits of these systems cannot be realized unless the chemistry,

specifically the copper, is continually replenished in the through hole. Based on Coulombs law, calculations show that at 30 ASF, copper levels even in a 0.045mm hole in a 5:1 aspect ratio are completely exhausted in 2 seconds of plating. So to maintain good throwing power, solution replenishment in vias is critical.

- Difficulty Factor (potential drop down the hole)

$$E_{ir} = \frac{JL^2}{2kd}$$

Where E_{ir} = Voltage Drop Down Hole (energy lost)
J = Current density
K = Solution resistance
d = Hole diameter
L = Length of hole

- For thick boards, there will be a limiting achievable ASF in the hole
- Not all aspect ratios are equal due to L^2 impact

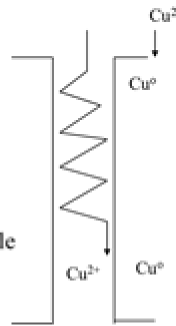

Figure 5 Factors Impacting Throwing Power

Equipment set up is a major factor in solution replenishment in vias and in surface distribution. Previous work done on VCP (vertical copper plater) equipment, demonstrate the benefits of surface distribution due to knife edge agitation. In VCP equipment, by passing the work across all of the anode surfaces, side distribution problems from cell set up are virtually eliminated. However, this in turn creates problems with solution movement/replenishment in vias. Typically to get good throwing power, panel agitation is preferred. But when both types of agitation are combined into a "Race Track System" it's possible to get the benefits of both. Race Track agitation improves surface distribution due to knife edge agitation and provides good through via flow to maintain throwing power with panel agitation.

Scaling Up the Theory

The companies decided to work together to test the impact of membrane technology on advanced flexible circuit boards. The product was to have 1mil traces and 2 and 3 mil diameter through holes. The end customer was tightening the allowable thickness distribution between lots of product, not just within the same part. The problem with existing equipment was that nodules and pits acceptable for standard product could not be tolerated. In addition, while extensive work had been done to the equipment to optimize plating distribution, the distribution could not meet the new requirements. So the decision was made to evaluate new options in prototype tanks and then design new equipment to meet these new requirements.

The size and amount of these nodules would be acceptable for most PCB applications, however, since nodules can be caused by several factors, step one was to evaluate the nodules that the companies were trying to eliminate. An extensive study was done looking at nodule formation on the product on incoming and after subsequent process steps. The nodules were evaluated visually, using SEM/EDS and by doing cross-sections. Both vertical and horizontal sections were done to see if foreign material was at the core of the nodule. This study did find some areas outside of copper plating like incoming material, laser drill and electroless as potential sources for nodules, however, the majority of these small nodules were pure Cu with a slight difference in grain structure at the center (Figure 6). This structure is typical of nodules developed during plating from either particulate coming off the anodes or additive imbalance. The existing plating cell utilized properly adjusted anode area, anode placement and rack thieving to optimized plating distribution. The anode film was excellent, solution filtration was good, and the maintenance done on the plating tanks was better than that utilized by most operations. But to get to the next level and further reduce nodules, the soluble anodes had to be replaced.

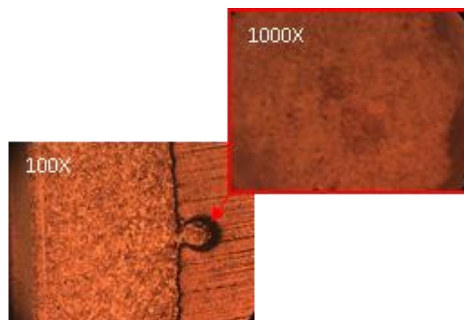

Figure 6 Horizontal Cross-section Of Nodule

Evaluating first for just nodules, full size parts (12 x 18") were plating in test tanks at both companies using 2, 6x18" insoluble anodes per side. The parts were Cu clad polyimide flex, with 2 and 6 microns of copper, 12 x 18 and held in a SS frame which added an additional 1" border. Tanks at both facilities had solution agitation with bottom eductors. Several runs were made with current densities of 10, 15, 20 and 25 ASF. Parts plated in both facilities with the insoluble anodes had zero nodules, where the same material plated with soluble anodes currently used in production had some minor nodules scattered across each sheet.

Typical plating parameters are 18ASF for 60 minutes. To better see distribution trends and identify nodules, a 90 minute plating cycle was used looking for 1.2 mil plating average. Initial testing was done with no work agitation and bottom eductors. A hand held copper thickness gage was used to map plating distribution over a 20 point grid pattern with 1" distance from the panel perimeter with a row going down the panel center. Initially, one anode assembly was used per side. This produced a range of 0.6 mils over an average thickness of 1.2 mils (Figure 7). After mapping the plating thickness, it was easy to identify high thickness on the top and edges of the plated part. At the same, time the cell voltage was above 4, indicating low anode area.

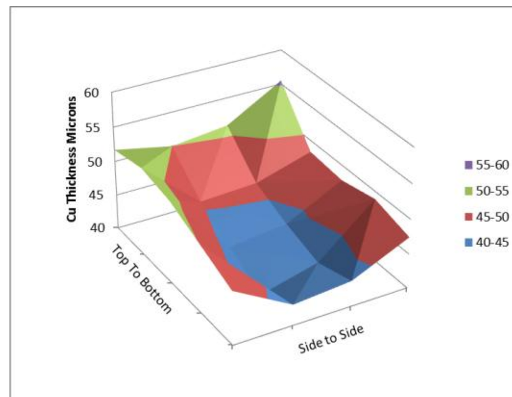

Figure 7 Cu Thickness Distribution 1 Anode Assembly No Work Agitation

A second anode assembly per side was placed in the plating cell. This reduced the thickness range to 0.3 mils, but there was still a top to bottom distribution and thicker deposits on one edge (Figure 8).

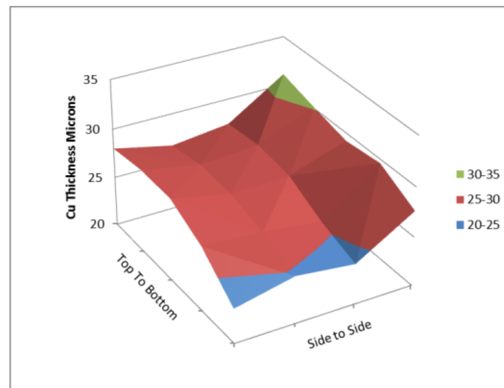

Figure 8 Cu Thickness Distribution 1 Anode Assembly No Work Agitation

Testing was moved to a second plating cell that was equipped with Race Track agitation. Anode height was adjusted so the bottom of the anode was 3" above the bottom of the plated part. This would be a typical arrangement for soluble anodes in Ti baskets. With agitation, the overall range did get worse with a range of 0.4 mils over an average thickness of 1.2 mils, but the plot in Figure 9 shows very uniform side to side distribution and a high range from the top of the panel to the bottom. This shows the introduction of race track agitation virtually eliminates the side to side distribution issues without the need for painstaking placement of anodes.

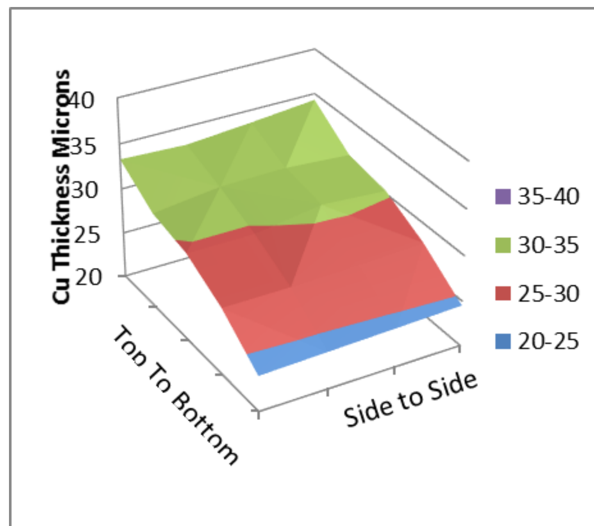

Figure 9 Cu Thickness Two Anode Assemblies Race Track Agitation

Since Figure 9 shows a top to bottom distribution issue, the insoluble anode was dropped by 2”. This provided a shadow area of the anode to be ~1” from the top and bottom edge of the plated part. This reduced the range to less than 0.1mils over 1.2 mil average or ~8% variation (Figure 10). This also demonstrates the ease of adjustment in distribution that insoluble anodes provide without the introduction and trial and error associated with anode shields. The overall results from this testing is summarized below in Figure 11. The chart clearly shows the progress that can be achieved in plating distribution by looking at all aspects of cell design in order to optimize results. This test data was then utilized as the design criteria for the production equipment.

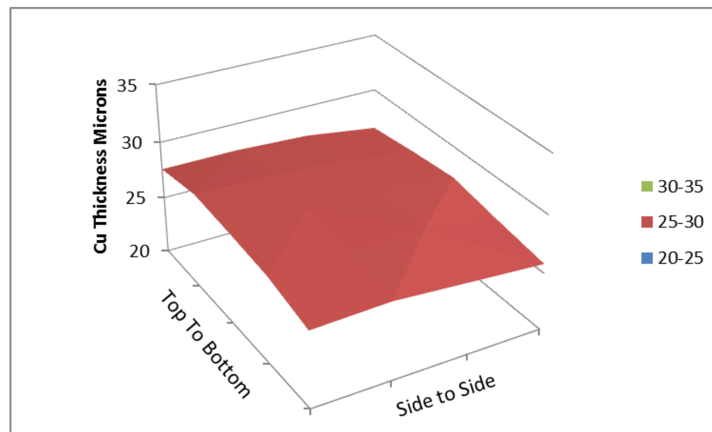

Figure 10 Cu Thickness Two Anode Assemblies, Proper Anode Height, Race Track Agitation

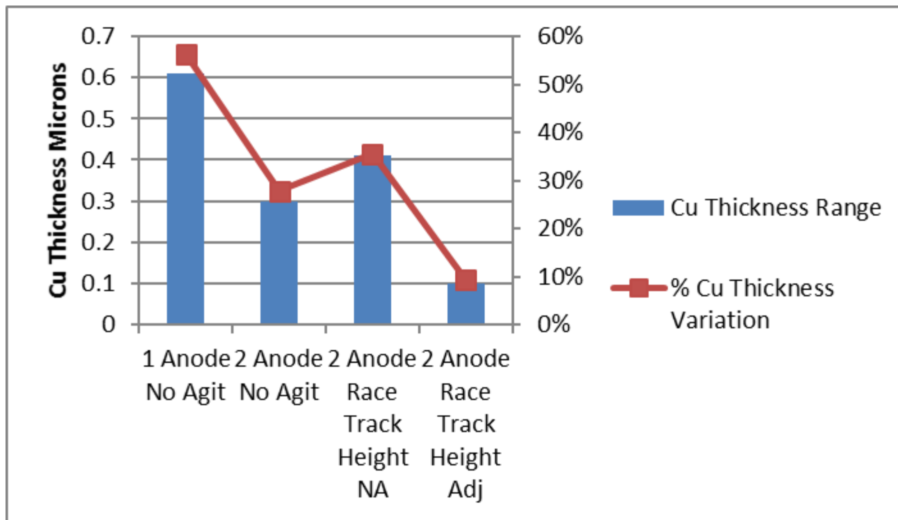

Figure 11 Cu Thickness Range And % Variation With Different Anode Set Up And Agitation

Implementation Into A Production Environment
The equipment was to be manual transfer of parts with automatic dossing of CuO based on amp hours plated. It was sized as two plating tanks capabible of plating 6 panels per tank per load. One MAG drive pump was used for each tank, with bottom eductors with a flow valve for each set of panels. Anode to cathode distance was 12” and race track agitation was utilized with a total of 2” knife edge and 2” through hole agitation. Being thin substrates, the aspect ratio is typically lower and solution flow is less critical, except this application had 2 and 3 mil laser drilled holes. Ideally, the end customer prefered to have the 2 and 3 mil through holes filled, which requires good solution exchange.

Surface distribution studies showed for this panel, the best anode area was two 5” wide strips with minimal separation. The use of insoluble anodes made it possible to easily shape the anode for the part being plated. The anode box design for this application (Figure 12) required centering the anode area on the part being plated. This resulted in forcing current flow from the outside edges to the center of the panel. The top to bottom distribution is controlled by adjusting the anode length and depth in the plating solution. Design criteria was simplified in this installation since part size remained constant. Adjustment to current flow for other applications with variable part geometries can be accomplished through either mechanical or electrical means.

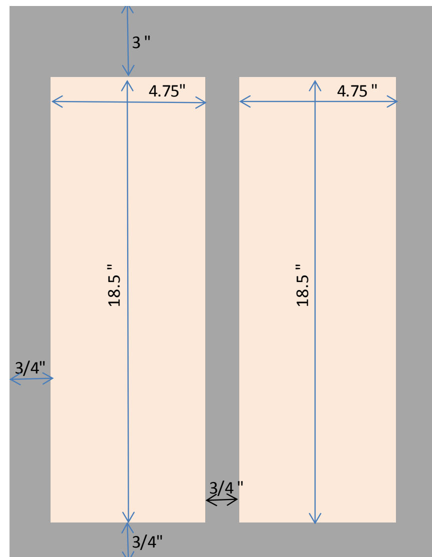

Figure 12 Anode Box Design For Tech Etch Installation

Initial surface distribution numbers shown in Figure 13 indicated that with 18ASF for 90 minutes a 0.9-1.2 a standard deviation occurred within each board. A slightly higher standard deviation of 1.7 occurred in tank two. This is slightly less than a 6% variation across 6 panels, however, the standard deviation in tank one was consiterably higher at 2.3 microns.

Looking at the data, it became obvious that there was a connection problem somewhere in tank 1. It was found that anode connections to the anode bar were marginal and special clamping devices were installed to improve consistency. This demonstrates the need to insure basic cell design rules must be followed or any improvement in equipment changes could be lost.

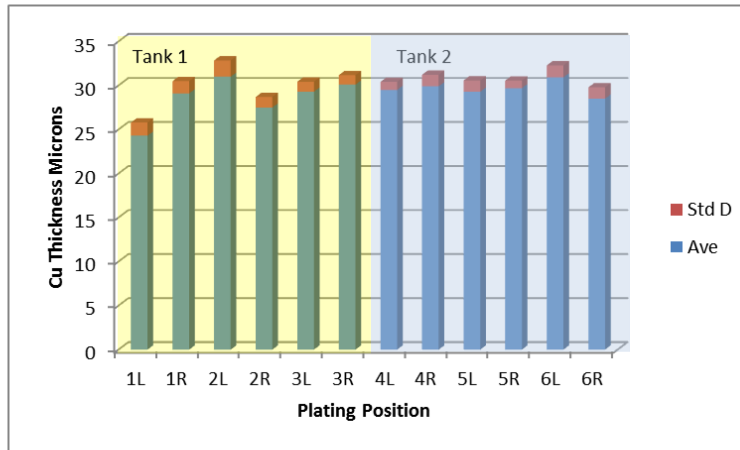

Figure 13 Average Plating Thickness and Standard Deviation By Plating Position

With improved contact across all anodes, the data from 12 plated panels was plotted in a bell curve (Figure14). It showed a normal bell curve with an average of 29.6 microns and a standard deviation of 1.3 microns. Statistically, this means that in a production environment, 99.7% of the thickness readings are between 25.7 and 33.5 microns. In the previous plating cell with no work agitation and soluble anodes, this distribution could not be met over one panel, never mind over 12. Typical distribution within a single panel was between 7 and14 microns in the old plating set up.

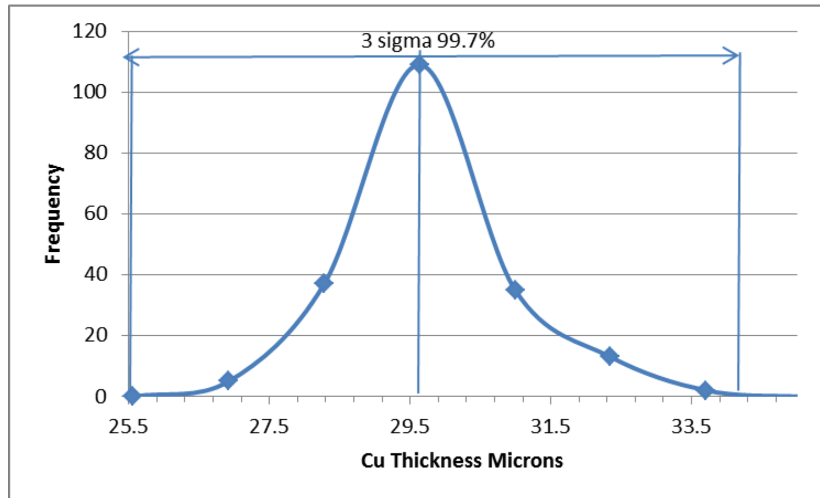

Figure 14 Bell Curve Cu Distribution Over 12 Panels

While throwing power was not a major objective of this study and is typically not a significant concern with flexible substrates, there are some customer requests for uniform Cu deposit in through vias. Plating at 5ASF is an option, but poor surface distribution and low solution movement make consistent Cu thickness in a production environment difficult. The new equipment with insoluble anode assembles and race track agitation has dramatically improved both plating distribution and solution flow. Initial testing with the new equipment has been positive for through vias (Figure 15) at as high as 18ASF.

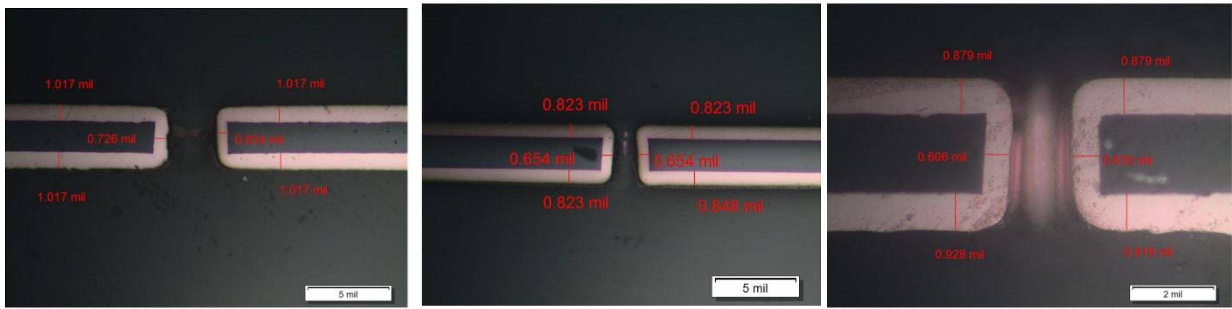

Figure 15 4, 3, and 2 mil Through Vias With 0.3-0.2 mil Foil

In other testing, the use of insoluble anode assemblies and good through hole solution flow has made it possible to successfully plate 30:1 aspect ratios with DC acid copper. (Figure 16). In both high aspect ratio plating and filling of small through vias, throwing power is improved by controlling the current flow and by insuring adequate solution flow in the small and or high aspect ratio through vias.

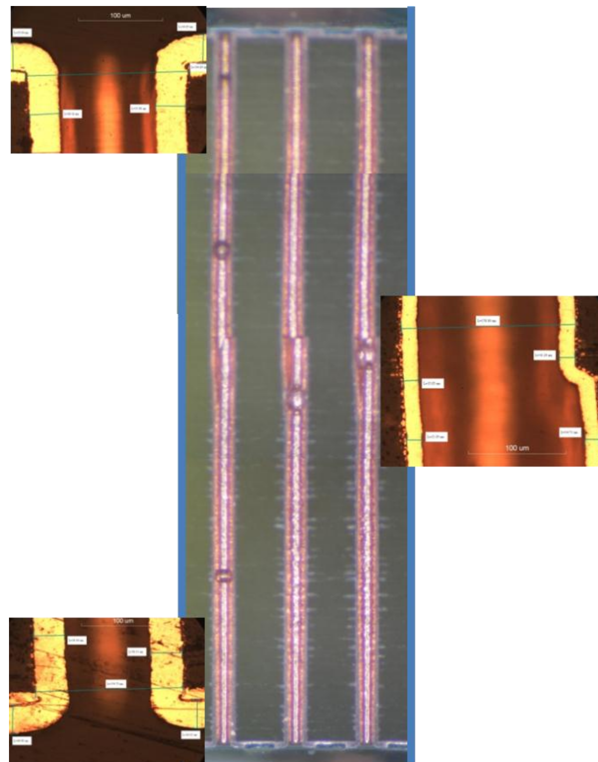

Figure 16 30:1 Aspect Ratio Through Hole

Summary and Conclusions

The use of insoluble anode assemblies with race track agitation has made it possible to meet the copper plating requirements for advanced PCB fabrication. Eliminating phosphorized copper anodes gets rid of the number one source for nodules in acid copper plating and the biggest variable in plating distribution. By using an anode assembly with proprietary membrane technology, insoluble anodes become a workable system by separating the IrO anode from the plating solution. The insoluble anode assembly also provides better control of current flow, which when properly applied, will give a plater control over copper distribution.

This work confirmed that all the benefits of the insoluble anode assembly may not be realized without proper equipment design. Work agitation is critical and the introduction of "Race Track" agitation provided improved surface distribution while insuring good throwing power. Basic cell design criteria like anodes properly placed with good connections, or solution agitation with controllable and uniform flow are all as essential to success as the insoluble anode assembly.

As a result of this testing, the product is now being produced easily, in a production environment, exceeding distribution requirements and providing a defect free surface. Getting to a perfect copper surface required more than just replacing soluble anodes with IrO anodes.

It required:

- New membrane technology to isolate the insoluble anode.
- Testing and implementing advanced equipment designs.
- Understanding the root causes for defects.
- Understanding the impact of basic cell design.

The conclusion is it takes more than just new equipment. It takes an understanding of the whole process and a holistic approach to move acid copper plating from current practices to an advanced level where it is possible to plate in production, The Perfect Copper Surface.