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The Use of Insoluble, Mixed Metal Oxide Coated Titanium Anodes to Improve Quality and Decrease Plating Times for Circuit Boards

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Abstract
Copper plating in the printed circuit board industry has traditionally used soluble copper anodes in a vertical configuration. Newer, high speed, horizontal plating lines utilize insoluble anodes which provide better current distribution and throwing power, higher operating current density, fixed and closer anode/cathode spacing, and lower copper cost. This paper presents results of a direct comparison between soluble and insoluble anodes on the plating performance on various types of printed circuit boards. This includes ductility, copper finish, and operating current density versus throwing power. Addition agent consumption at insoluble anodes and copper ion replenishment, as required for insoluble anodes, are discussed.

Introduction

Soluble Anodes

Currently, copper is plated onto printed wiring board surfaces, through-holes and vias in an acid metal sulfate bath. Organic agents are added to provide a bright copper surface and enhance throwing power. Metal concentration in the bath is maintained by dissolution of copper anodes by the following reaction:

$$Cu^0 \rightarrow Cu^{++} + 2\,e^-$$

These anodes must be phosphorized and oxygen free to avoid undue polarization, or even eventual passivation, and allow operation at reasonable current densities. In addition, a small chloride content must be maintained in the electrolyte to further reduce polarization.

Soluble anodes are usually in the form of balls or rounds contained in a titanium basket or as bars cast around a current conductor. Porous cloth bags encase the soluble anode to reduce the amount of particulates introduced into the bath, since these can have an adverse effect on plating quality. The bags must be replaced routinely, resulting in down time and maintenance costs.

The best current distribution (and therefore plating distribution) between anode and cathode occurs when the surfaces are evenly matched; a planar circuit board is best matched with a planar anode. Best performance is obtained when the soluble anode approximates a flat surface, equidistant from, and substantially the same size as, the cathode. Therefore, anode baskets must be continually charged with copper to maintain uniform current flux between the board and the anode. Large anode/cathode gaps, as seen in vertical plating machines, also assist in evening out the current distribution.

Significant variations in current distribution are also caused by contact resistance between individual copper rounds (or other form factors) as well as polarization/ passivation. Galvanic dissolution of copper is best done below about 30 amps per square foot. Above this the copper becomes coated with a poorly conductive layer of copper oxide and the anodes will first polarize and ultimately passivate. When this occurs current shifts away from the affected area of copper to another, less passive region. Therefore, current is continually shifting within the bed of copper in a basket or even across the face of a plate anode.

Other sources for resistance are uneven contact between the “hook” and the copper bars from which the anodes are suspended and poor physical contact between the copper bars and the intercell bus. Figure 1 graphically shows how differing current densities can cause thickness variations on the circuit board.

Increasing current density causes these lines of flux to become more uneven under the same operating conditions, limiting the maximum allowable current. A significant improvement in plating performance could, therefore, be expected by improvement in anode design.

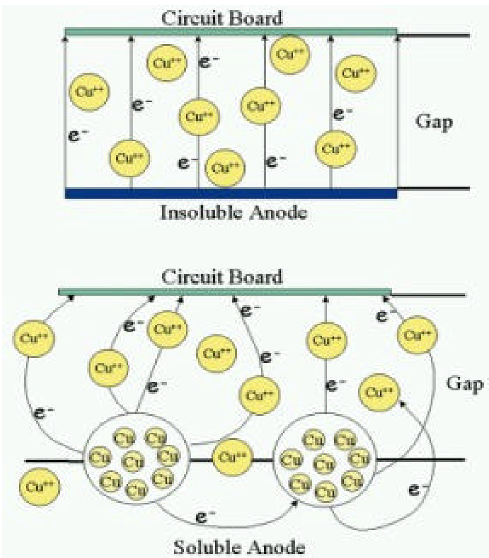


Figure 1 – Current Distribution: Continuous Planar Anodes vs. Typical Soluble Anodes

Insoluble, Mixed Metal Oxide Anodes

"Insoluble" anodes discussed in this paper refer to titanium anode structures coated with mixed metal oxide (MMO) coatings. These coatings are used in a variety of applications, most notably for production of chlorine gas and sodium hypochlorite, in electrophoretic painting and general metal finishing to name a few. Insoluble anodes are increasingly being utilized to replace soluble anodes in many commercial plating operations. For example, zinc electro-galvanizing (high speed plating of zinc onto steel strip) has almost completely converted to DSA® anodes, for which ELTECH Systems Corporation is the supplier in North America.

In the electronics industry, the new high speed, horizontal copper plating machines use insoluble anodes to eliminate the constant replacement of copper and to provide better current distribution at higher current densities. Such anodes are also compatible with pulse plating which is increasingly utilized to plate into smaller vias and higher aspect ratio holes. Much copper foil is also made using mixed metal oxide/titanium structures.

The mixed metal oxide coatings are generally a mixture of precious metal oxides (such as ruthenium oxide or iridium oxide) and valve metal oxides (such as titanium oxide or tantalum oxide), with formulations specific for different applications. Copper plating uses an iridium oxide/tantalum oxide mixture that is thermally formed on a titanium structure. After extended use the anode must be refurbished by removing the residual MMO coating and applying a new coating. The titanium substrate can be recoated many times, barring mechanical damage or severe corrosion.

The mixed metal oxide matrix is a high surface area, "mud-cracked" surface that allows the anode to operate at a low polarization, even at high current densities. Indeed, operation at current densities in excess of 7,00A/Ft^2 is routine for both electrogalvanizing and copper foil manufacture.

In the SEM photomicrograph of a typical MMO anode coating (Figure 2) shown below, the characteristic high surface area, and mud-cracked surface is apparent. The low polarization is illustrated by the potential versus current density curve of a typical MMO anode as shown in Figure 3. MMO anodes have low polarization even at high current densities.

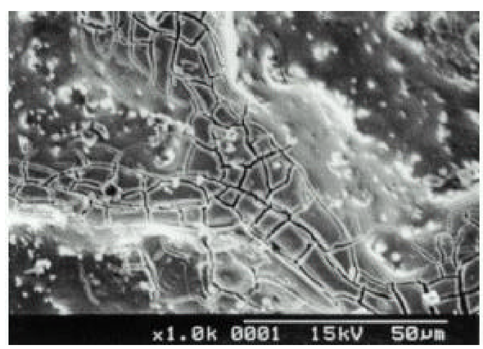


Figure 2 – SEM Photomicrograph

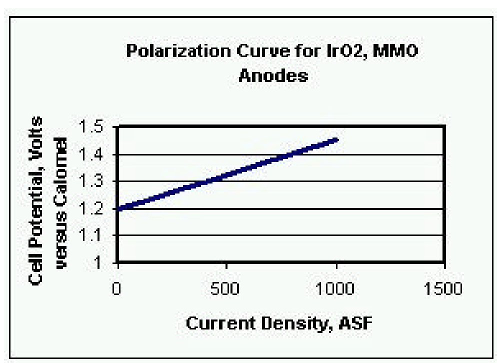


Figure 3 – Anode Potential vs. Current Density

Retrofitting from soluble to insoluble anodes can be easily accomplished since the titanium/MMO anodes can be readily manufactured into a wide range of configurations. Unlike soluble anodes, the titanium substrate is lightweight, significantly reducing installation issues. Since the titanium is relatively impervious to acid attack, the anodes and conductor bars will suffer minimal corrosion.

A typical configuration used for plating baths consists of a single panel of mesh, coated with the appropriate MMO and continuously welded onto a solid titanium conductor bar. The mesh panel is typically the width of the tank, or at least the same size as the plated parts. The edges of the mesh are formed to stiffen it and eliminate potential deflection caused by high electrolyte circulation. The conductor bar size, mesh thickness and mesh expansion pattern are sized on the basis of the overall operating current density to provide a uniform current distribution. To ensure a long-term low electrical resistance, the titanium bar may be plated with platinum where it connects to the common anode current distributor bar. This type of structure optimizes anode/cathode current distribution and minimizes electrical resistances while presenting a planar surface to the cathode. Figure 4 is a schematic of a typical MMO anode used for metal plating applications.

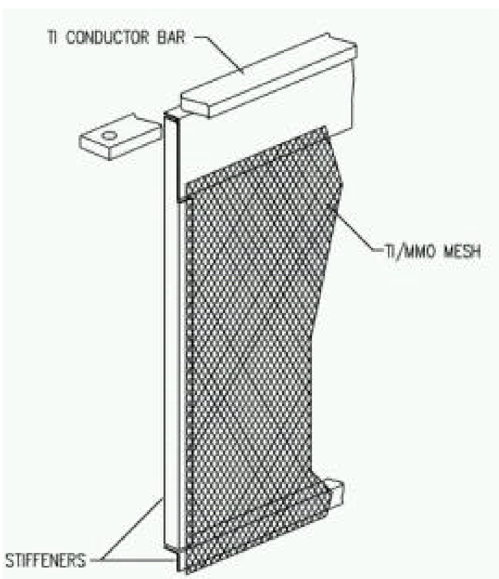


Figure 4 – Typical Titanium/MMO Structure Used For Plating Operations

The electrochemical reaction occurring at the insoluble anode is the decomposition of water to form oxygen and hydrogen ions (acid). Note that no gas is evolved at the cathode.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The acid balance in the bath, however, is identical to that of soluble anodes so no added attention to acidity control is required.

Since copper is not introduced into the bath electrochemically, the copper must be dissolved externally to the plating tank with a “digester”. The design and implementation of this are discussed later.

Discussion

The proven advantages of insoluble anodes in horizontal plating equipment as well as other related commercial systems has led to the evaluation of their use in PWB plating baths using vertical anodes and circuit boards. Insoluble anodes should provide better current distribution, constant and closer anode-cathode spacing, and better throwing power. Since higher current densities can be obtained without significant anode polarization, more throughput and shorter turn around times can be achieved if desired. In addition, there are no anode bags needing periodic replacement, no particulates to affect plating quality, no need for periodic addition of anode balls or replacement of anode bars. Overall, considerably less maintenance time will be required with the use of insoluble anodes. Finally, insoluble anodes can easily replace existing soluble anode systems making it possible to upgrade existing plating tanks.

Copper Digester

One of the primary differences between the use of insoluble anodes and soluble anodes is the need to continually add copper to the plating bath. Several methods are available for addition of the copper ions. The simplest method is the addition of concentrated copper sulfate. This method is especially effective for plating small amounts of copper; as a test or for limited runs of pattern-plated parts. This is relatively expensive method of copper replenishment and results in electrolyte growth.

Addition of copper oxide powder is an alternative that maintains electrolyte, acid, and water balance more effectively than copper sulfate addition. This method requires a side tank loop for addition and a filter system to ensure that particulates are not introduced to the plating tank. This method is currently practiced in the horizontal copper plating systems. This method is also somewhat less expensive than copper sulfate addition. The basic reaction is:

$$CuO + 2H^+ \rightarrow Cu^{++} + H_2O$$

The most cost effective method for introducing copper ions is the use of a “digester”. This is essentially a tank containing a bed of high purity copper (such as chopped wire or chopped rod) into which air is bubbled and the electrolyte is circulated. Cost savings are recognized through the purchase of the chopped copper rather than phosphorized copper or copper oxide. The copper is dissolved into the acid electrolyte via the following reaction:

$$2Cu^0 + O_2 + 4H^+ \rightarrow 2Cu^{++} + 2H_2O$$

The dissolution rate is directly related to the amount of air (actually oxygen) introduced into the copper bed, the surface area of the copper bed and the temperature. Copper dissolution is typically controlled by the airflow rate. Digesters of this design are routinely used in the manufacture of copper foil. Such digesters are also quite compact. A system running at the author's laboratory, capable of digesting 250 pounds per month of copper, requires only about 7 square feet.

The system is closed loop, wherein a small portion of the electrolyte is circulated through the digester where the electrolyte is replenished with copper ions. The oxygen airflow rate is monitored and controlled with an airflow control valve. The digester tank is sized based on the dissolution rate needed and the frequency of copper addition. A schematic diagram of the dissolving system is shown below in Figure 5.

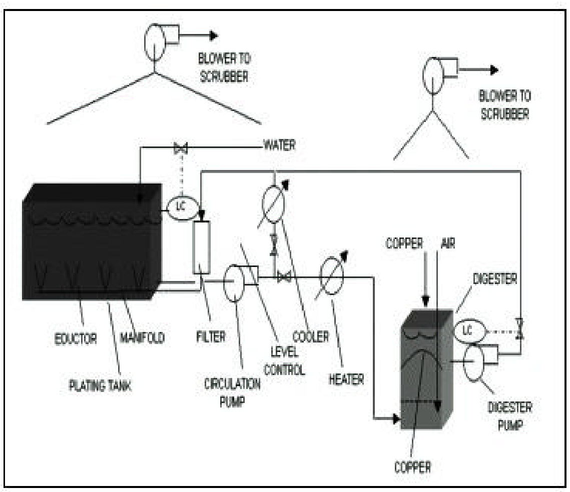


Figure 5 – Flow Diagram of a Copper Digester for Use with Insoluble Anodes

Copper Feedstock

Phosphorized copper is typically purchased as balls or rods with a diameter of about 1.25". The copper is galvanically dissolved in the plating tank as the counter reaction to the copper plating. Copper dissolved in a digester is not galvanically dissolved and therefore does not have the same compositional or form factor constraints as soluble anodes. Copper oxide is typically purchased as a powder that can be easily metered into an addition tank. Bulk chopped copper is added in excess to the digester tank and the dissolution controlled by rate of airflow. Bulk chopped copper has the lowest cost of these alternatives and is equivalent in purity when properly specified.

Destruction of Organic Additives

One difficulty in the utilization of insoluble anodes to replace soluble anodes for copper plating is the undue oxidation of organics like brighteners and leveling agents. The electrode potential of insoluble anodes is 0.5 – 0.8 volts higher than soluble anodes, allowing some direct organic oxidation to occur. Indeed, typical MMO anodes destroy these expensive additives up to about 45 times faster than soluble anodes, making chemistry costs extremely high. In response, the author's *Synergy™* anode coating system was developed to minimize direct organic oxidation. This proprietary anode coating system is highly stable in the plating solution. Water is easily transported to the electrocatalytic layer to support the electrochemical reaction. However, the larger organic molecules are excluded and are therefore not subjected to direct electrochemical oxidation (Figure 6). As seen, using this coating system there is little difference between soluble and insoluble anodes in their interaction with the chemistry system (Figure 7). Indeed, this technology is enabling for the use of MMO anodes in PWB copper plating.

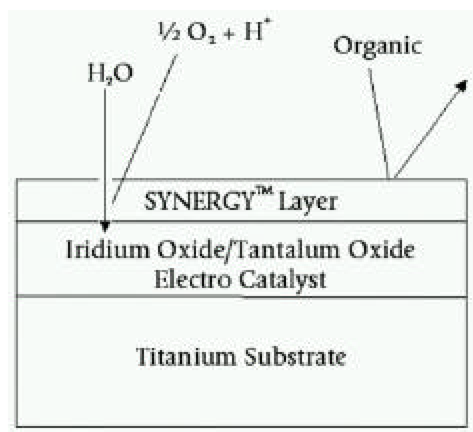


Figure 6 – Addition Agent Protection Using Proprietary Coating System

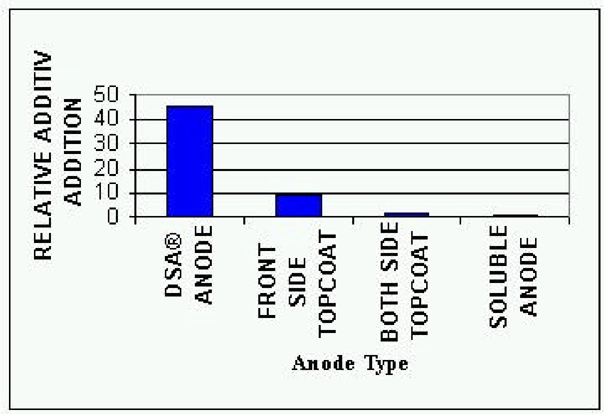


Figure 7 – Oxidation of Commercial Brightening and Leveling Agents Anode and Typical Insoluble Anodes Compared with Soluble Anodes

Experimental

Because of the many potential advantages offered by insoluble anodes to improve PWB plating characteristics, an experimental program was undertaken to compare these directly with soluble anodes. The insoluble anodes were titanium mesh coated with mixed metal oxides (MMO). This mesh was then further treated with the author's proprietary system intended to protect the addition agents from oxidation at the anode. Results were compared with soluble anode bars placed in the same plating tank and using the same spacing as was used in normal production. Samples for comparison were made in the same tank in consecutive runs. All experimental work was done at the DDI facility in Anaheim, CA.

The plating bath used proprietary chemistry systems available from major manufacturers with the temperature controlled to 30°C. The anodes discussed on this page, were of one-piece construction, extending the entire width and depth of the plating tank (see Figure 3). The soluble anodes were copper bars, approximately 6 inches wide and 24 inches long, cast around a central conductor core. Two to three soluble anodes were placed opposite the circuit board per the typical DDI protocol. The soluble anodes were shrouded by anode bags to better simulate typical performance characteristics. Both the anodes and the bags had been previously used in order to more accurately reflect standard plating practice. The PWB was positioned between two anodes. The anode/cathode spacing was approximately 6 inches. The current density was varied from 10 asf to 30 asf. The circuit boards were mechanically agitated by forward/ backward oscillation. The electrolyte was internally circulated in the tank via educators with no air agitation. The soluble and insoluble anode tests were done sequentially, not concurrently.

Experimental Results

Mechanical and Metallurgical Testing

Tensile Strength and Elongation

A study was undertaken to determine if the copper mechanical properties are affected by the anode. Several sets of samples were prepared on stainless steel so that freestanding copper sheets could be stripped from the cathodes. The samples were about 3 mils thick. Samples from soluble and insoluble anodes were plated under otherwise identical operating conditions and compared. All specimens met the IPC specifications. The tensile strength ranged from 44,000 to 46,000 PSI and was essentially identical for both soluble and insoluble anodes. Elongation was 18% for the soluble anodes, and 25% for the insoluble anodes. The improved elongation is most likely due to better current distribution. The result is more uniform copper thickness and smaller, more equiaxial grains with few internal defects. The combination of these microstructural and macrostructural improvements increases ductility.

The improvement in elongation found for copper plated with insoluble anodes is substantial. This improved ductility can be expected to provide a benefit during thermal excursions of finished boards in both assembly and operation.

Inter-Laminar Bond Enhancement

During testing, it was noticed that boards prepared using insoluble anodes developed a distinctly matte appearance compared with the shiny surface of boards prepared using soluble anodes. Tests were then undertaken to determine if this matte, or slightly rougher surface finish, should improve the inter-laminar bonds. A set of boards was prepared at a current density of 10 asf, per the operating conditions presented above, in order to run a T260 test. These were treated with a normal non-black oxide finish to enhance the inter-laminar bond and then laminated to epoxy prepreg in the usual way. The finished boards were then compared in the T260 test. This test measures the time to delamination of the board at a constant temperature of 260°C. The boards prepared with insoluble anodes gave T260 results more than two times greater versus the T260 results observed for boards prepared with soluble anodes.

The matte finish produced using insoluble anodes should also provide improved adhesion to dry film photoresists with or without micro etching. The combined T260 improvement and higher elongation of the copper are expected to provide improved results in thermal shock during both assembly and application.

Plating Performance Tests

A group of circuit boards were prepared at a variety of current densities using soluble and insoluble anodes. The boards were then sectioned, mounted and the metal thickness was measured by traditional microscopic means.

Copper Thickness Vs. Current Density

Panel samples were prepared in the production tank at current densities considered normal and at twice this value. The cathode/anode spacing was the same for both sets of samples. At twice the normal current density panels plated with insoluble anodes exhibited no burning or other visible problems with the deposit. Discoloration is often noticed when using soluble anodes under these conditions. At twice the normal current densities soluble anodes produced copper about 20% less thick than insoluble anodes, indicating a drop in plating efficiency. The effect of current density on copper plating efficiency is shown below in Figure 8.

Because of excellent current distribution, insoluble anodes offer the unique ability to increase current density. This will result in both faster cycle times and increased throughput. The anode/cathode spacing can also be reduced to lower voltage and allow more efficient usage of the plating tank space.

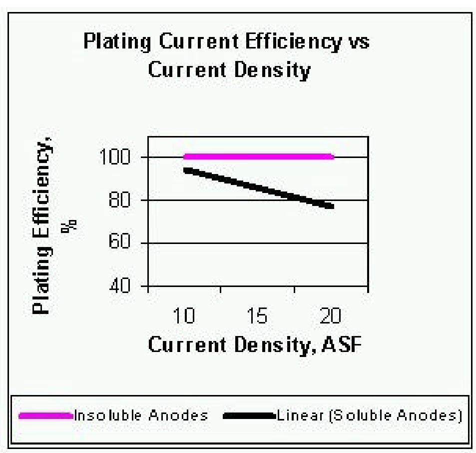


Figure 8 – Current Density Versus Plating Efficiency

Throwing Power

A comparison of throwing power was done by plating small through holes in a thick board. The board chosen was 0.075 inch thick. The through holes were 0.015 mils in diameter. The thickness at the surface and at a point in the center of the hole were measured. The ratio of the thickness between the center and the outside edge was taken as a direct measure of throwing power. In all cases the edge of the hole had a thicker copper plate than did the center. At the normal current density for production, the ratio for soluble anodes was 91% while the ratio for insoluble anodes was 95%. At twice the normal current density, the soluble anodes gave a ratio of only 79%, indicating a lack of ability to throw into the hole at the higher current density. In contrast, insoluble anodes continued to provide an acceptable ratio of 93%. Higher current densities were not tested so the limit for insoluble anodes isn't known. A comparison of the ratios of copper in the through holes is shown in Figure 9.

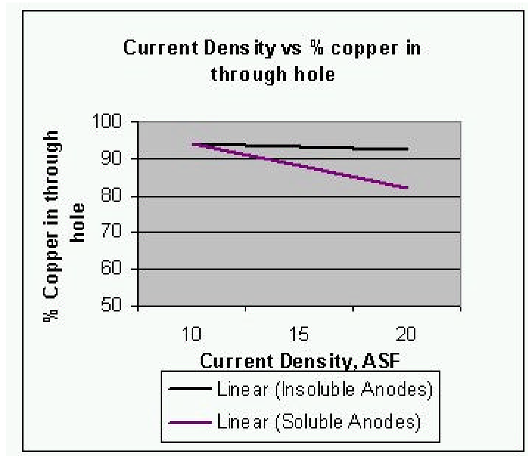
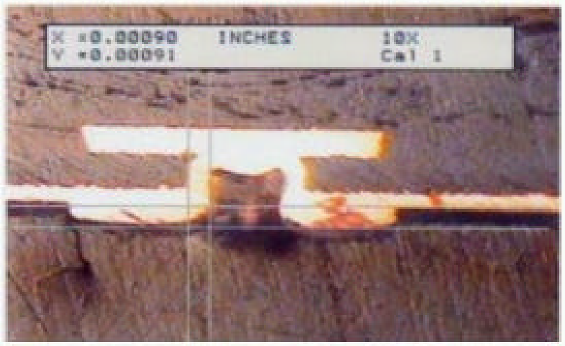


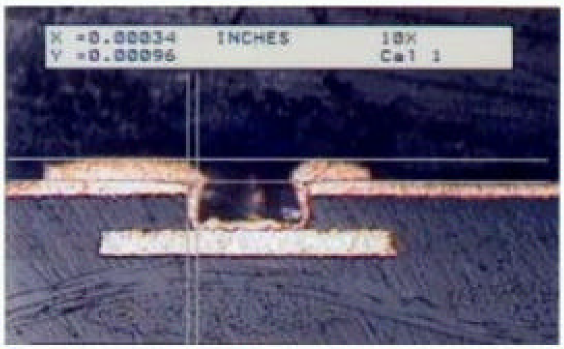
Figure 9 – Current Density Versus Ratio Of Copper In The Through Hole

Blind Vias

Due to the superior throwing power of insoluble anodes, it was anticipated that they would give better results in the plating of small, blind vias. The boards chosen had surface vias of 6 mils in diameter and 1.6 mils deep. At the commercially normal current density both soluble and insoluble anodes gave similar results. The plating thickness in each case was about 70% of the copper thickness in a through hole. At twice the normal current density, the soluble anodes gave the same thickness as they produced at the normal current density. The insoluble anodes at twice the normal current density gave 2.5 times the thickness obtained at the normal current density. In fact, the copper thickness was 90% of the thickness of copper in the through hole. The improvement in plating can be seen in Figures 10a and 10b, which compare blind vias, plated using both soluble and insoluble anodes at twice the normal current density. The copper thickness, measured by cross-section, shows 0.9 mils of copper in the hole with insoluble anodes, compared to .34 mils in the hole for soluble anodes. Table 1 summarizes this data.



(a)



(b)

Figure 10a and 10b –Cross Sections of Micro Vias Plated at Different Current Densities

Table 1 – Throwing Power and Efficiency Advantages of Insoluble Anodes Compared to Soluble Anodes

	Mils Copper in Via	
Current Density, ASF	***Soluble Anodes***	***Insoluble Anodes***
10	0.36	0.40
15	0.30	0.50
20	0.34	0.90

Summary and Conclusions

Insoluble anodes provide better throwing power and higher plating efficiencies than soluble anodes. This results in more copper in through holes and remarkable performance improvement in throwing power into blind vias. Plated blind vias saw essentially no drop in current efficiency as current density was increased, allowing for reduced cycle times. By comparison, soluble anode systems saw enormous drops in current efficiency in the blind vias as current density was increased.

Tests using soluble and insoluble anodes indicated that the latter has similar tensile strength and 50% greater elongation. This improved ductility can be expected to provide a benefit during thermal excursions of finished boards in both assembly and operation. T260 tests for interlaminar bonding indicated that the matte finish provided by the insoluble anodes gives more than twice the bond strength. This should improve adhesion to dry film photoresists prior to or after microetching. The combined T260 improvement and higher elongation of the copper should provide improved results in thermal shock during both assembly and application.

The major reason for this improved performance is the vastly improved current distribution of insoluble anodes as compared with soluble anodes.

Insoluble anodes should also result in improved quality through the elimination of anode sludge and other particulate matter in the plating tanks.

In addition to the clear performance advantages, insoluble anodes can also provide an economic incentive resulting from decreased maintenance costs and lower copper feedstock costs, and improved throughput. It is also possible to decrease the anode/cathode gap, leaving room for more boards in the same tank. This would also decrease cell voltage and

Acknowledgements

1. ***Synergy™*** DSA anodes have BOTH economic and performance characteristics to justify converting from soluble anodes.
2. DSA® is a North American registered Trademark of ELTECH Systems Corporation.
3. ***Synergy™*** is a Trademark of ELTECH Systems Corporation.