### Peroxy-Sulfuric Oxide Replacements – A Pathway to Improved Technology for Fine Line Processes

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#### Abstract

Traditional reduced black oxide processes for inner layer bonding have been superseded by a newer generation of peroxidesulfuric texturing processes. These lower cost processes, based on an organically controlled microetch, have proven to be simpler, faster, and more energy efficient. They have eliminated traditional problems such as: re-oxidation caused by baking and storage, high resistance shorts and pink ring defects.

However, the relentless trend of miniaturization and the inexorable pressures for cost reduction continue to push the envelope. Lower etch factors are necessary for controlled impedance and fine line applications, and higher copper loadings are a prerequisite for increased capacity / reduced cost of ownership. The paper describes the major challenges faced, and the resulting technical progression which has been achieved, to evolve the next generation of high performance processes capable of meeting this target.

#### Introduction

From the early 1990s to present day, both the volume and complexity of multilayer boards have increased dramatically. This is very evident in terms of the increases in average layer counts, coupled with the steady influx of more advanced / higher  $T_g$  dielectric materials, both of which have paved the way for the necessary increases in interconnect densities. PWB Fabricators have found that their traditional inner layer production systems are being continually challenged to deliver higher quality products with finer lines and spaces, and with improved yields, all at essentially a lower cost.

Through the last decade, the traditional 'black oxide' (or 'brown oxide') bonding processes became constrained by a range of technical issues. These included a rising propensity of: drill related micro-delamination and/or pink ring (impacted by smaller holes and the increased surface visibility afforded by smaller pads); low and high resistance shorts (caused by the ingress of conductive contamination between fine traces); and bond failures with advanced materials such as polyimide, cyanate ester, BT and GETEK® \*.

The introduction of the Dimethylamine-borane (DMAB) 'reduced' oxide process helped to address pink ring by improving the copper to dielectric bond integrity and simultaneously increasing the acid resistance of the oxide plane. Despite the widespread adoption of reduced oxide within the industry, in hindsight, this was no more than a band-aid to the oxide finish for two distinct reasons:

- 1. The reduced copper oxide conversion coating was chemically active and would quickly re-oxidize, limiting the ability to apply pre-lamination bake cycles to moisture sensitive dielectric materials.
- 2. The powerful DMAB reduction step would convert any copper oxide agglomerates and/or scale (products of the oxide bath) into a highly conductive medium. Hence any such deposits entrapped within the circuitry would become almost perfect conductive 'shorts'.

Not withstanding these technical issues, the 'total' oxide process cost, heavily skewed by the expensive DMAB material (coupled with the inherent waste treatment, energy and water cost elements), also became an increasing burden. As layer counts increased, and multilayer board prices became radically more competitive, process costs became increasingly sensitive. It was not surprising that the peroxy-sulfuric ('oxide-replacement') processes, which required only two (or three) lower temperature process steps, quickly began to find favor in this environment. Such peroxy-sulfuric technology, which typically uses a primary organic additive to enhance the surface texturing, was shown to deliver excellent bond integrity. Not only were process costs lower but also peel strengths, thermal shock resistance,  $T_{260}$  results (time to delamination), pink ring resistance and ionic contamination levels were all shown to be as good or better than conventional oxide. These benefits were discovered to be of increased value when used with advanced and/or high Tg dielectrics. The ease of automating the short,

fast, low temperature processes and the lack of copper oxide precipitates also factored in the rapid acceptance of the peroxysulfuric systems.

About 1997 the technology shift began in earnest, and the use of the peroxy-sulfuric replacement process gathered momentum to a point where it is now the most dominant innerlayer bonding system. As it stands today, the features and the user benefits are broadly understood, well documented, and the process is now a standard for the industry. However, within the framework of the electronics revolution, the inexorable patterns of change have continued unabated. PWB Fabrication processes and manufacturing materials continue to be challenged to deliver 'more for less'.

#### The Challenges

The current peroxy-sulfuric 'oxide replacement' process works on a "controlled etch" mechanism that removes typically 50 - 75 microinches  $(1.2 - 1.9 \mu)$  of copper. The innerlayers are first cleaned and then conditioned in an alkaline medium, rinsed and then finally processed directly in the peroxy-sulfuric micro-etching bath. The copper capacity of this bath is finite and, historically speaking, would be of the order of 18-22 g/L. Over the past three years, some leading processes have shown a consistent capability in high-level production environments, with a copper capacity approaching 30 g/L. This capacity increase has largely been a result of improved copper solubility coupled with an increase in the stability of the process. This has been necessary to reduce by-product generation and to retard the decay of the (etch rate-determining) primary organic within the highly oxidizing, low pH conditions. The oxidizing effect of the strongly acidified, hydrogen peroxide-based medium is significant, and is further catalyzed by incremental levels of copper ions (Cu<sup>2+</sup>). To achieve target levels of 50 g/L copper loading, major improvements in stability are mandatory to provide a robust process.

For any leading edge process, the requirements for the high yield production of controlled impedance and fine line inner layers are also mandating further reductions in copper etch factors. The need to achieve improved bonding performance, with the removal of only 30 - 45 microinches (0.75-1.1µ) of copper, has become the target capability for a 'best in class' process. Within this challenge, higher values for peel strength and increased  $T_{260}$ s (time to delamination) are continuously sought and the current process is being further challenged to deliver even more advanced performance. This impacts process development in two ways:

- 1. Additional bonding enhancers are necessary to boost the micro texturing of the surface and to improve the dielectric adhesion to the peroxy-sulfuric conversion coating. This is essential at lower etch factors, where traditional thinking has supported higher etch levels as being the key to higher bond strengths.
- 2. The lower copper ingress into the peroxy-sulfuric bath reduces the bath turnover rate (which is driven by replenishment) and increases the residence time of the chemistry, placing even greater demands on bath stability and performance consistency. As a result, a bath operating at 50 g/L Cu and 40 microinches etch sees only 40% of the turnover in solution volume compared to a system working at 30 g/L and 60 microinches. The bath residence time is, therefore, 2.5 times longer and the stability needs to be proportionately higher.

As can be imagined, the changing dynamic equilibrium of the bath, combined with increased residence time of the reaction products, create a complex model. A complete understanding of the impact of these variables on the bonding performance of the resulting copper conversion coating is necessary to develop a robust process. Different dielectrics will respond in different ways and ensuring that the bath performance will be optimized for a basket of materials is an essential requirement. This is important throughout the process operating range, from very low copper levels (new make-up) right up to the design maximum of, say, 50 g/L copper for a process operating under high load, feed and bleed conditions with a controller.

#### Bond Strength relative to Primary Organic Levels and Etch Rates

To better understand the overall performance of the system, it is necessary to study the interactive performance with a range of copper and dielectric materials. As indicated previously, the copper etch rate and associated surface texturing, is clearly driven by the active concentration of the primary organic. However, the etch rate is also a direct function of temperature, hydrogen peroxide level and the type of copper material being processed. This gives rise to a series of fundamental questions: What is the relative impact on dielectric bonding performance of all these factors which change etch rate and total etch depth? Are they equally important? Are there any synergistic effects, positive or negative? These are critical considerations when considering a low-etch / high copper capacity process and working to assess its true capability.

To address many of these issues, a series of comprehensive DOEs have been applied to study the performance of a range of inner layer materials, with low and high  $T_g$  FR4 epoxy materials at one end of the spectrum, and materials like GETEK®\* and Polyimide at the other. The testing and resulting product development, as reviewed in this paper, has looked primarily at peel strength, but also factored in thermo-mechanical analysis ( $T_{260}$  tests - to assess time to delamination) and other measures of performance.

In the initial screening tests, a comparison was made of a range of etch factors from 25-75 microinches  $(0.6 - 1.9\mu)$ , which were achieved in two ways: Firstly through a matrix of temperature, time and peroxide levels (holding other factors constant), and secondly by holding time, temperature and peroxide levels constant and varying the primary organic additive levels. The results showed that large variations of the former had little impact on peels, but changes in the primary organic level showed a direct and far-reaching effect on peel strength and bonding performance.

In fact, maintaining a minimum concentration of the organic package became a critical requirement for consistent performance of a high load /low etch system. These results are shown in Figures 1 and 2.

Having established the ground rules, comparative development studies then focused on the effect of copper level in the system (as  $Cu^{2+}$ ), and the secondary effect of bath aging as a function of bath turnover time. The standard process parameters (time, temperature, total acid and peroxide levels) were held constant. Response curves were generated for various dielectrics. The bath turnover time (based on the displacement from feed/bleed replenishment), which is typically once every 1-2 days in days in a medium to high volume process, was stretched to 7 or more days to assess the impact of stagnation on bath performance. The data for  $170 T_g$  FR4 and GETEK® is shown in the following Figures 3 and 4.



Figure 1 – Peel Strength v Etch Factor (Peroxide/Temperature adjustment)



Figure 2 – Peel Strength v Etch Factor (Primary Organic Adjustment)



Figure 3 – FR4 170 Tg Peel Strength v Copper v Bath Age



Figure 4 – GETEK Peel v Copper v Bath Age

Based on these earlier process studies, both the bath age and copper level have a significant impact on bonding performance. FR4 materials typically show high peel strengths 'right off the bat' with a new chemical make-up, and these peel strengths eventually fall as the primary organic is depleted (if no replenishment). However, some advanced materials like polyimide and GETEK® can show a significant improvement in peel strength with increasing copper loading, which also reaches a peak with bath aging. As a consequence, the development of an improved process requires a smoothing of these factors and the system must be capable of providing improved peels at low copper levels in relatively new baths to ensure that the process window, from initial start up (at zero Cu<sup>2+</sup>) to full load, is as broad as possible. Studies have shown that secondary organic additives can be used to further enhance the texture of the conversion coating and increase its bondability. This is a prerequisite within any advanced high capacity chemical process, which must provide consistent peel strength over a wide range of copper levels, bath loadings and bath turnover frequencies. The stability of the primary organic is the key factor to facilitate this, described as follows.

#### **Peroxy-Sulfuric Bath Stability**

The primary organic additive performs a key function in the bath. It not only determines the rate and primary etching characteristic on the copper substrate, but also controls the texturing pattern. It simultaneously impacts the formation of the predominantly cuprous oxide/organic conversion coating on the textured surface. Its function is, therefore, critical to the performance of the system and its concentration needs to be maintained within a well-defined working range. Primary organics used in such a system are essentially aromatic nitrogen compounds, which are clearly susceptible to oxidation in the presence of hydrogen peroxide and extremely low pH. Studies have shown that the rate of organic breakdown is accelerated with increases both in operating temperature and copper concentration, as shown in Figure 5. The general impact on relative values of peel strength and etch rate are also shown in the Figure 6.



Figure 5 - Decay Rate Primary Organic v Bath Temperature and Copper Concentration



Figure 6 - Influence of Primary Organic on Etch Rate and Peel Strength

#### Impact of Bath Stability and Organic Level on Performance

In practical terms, the functional stability of the primary organic will directly impact etch-rates, peel strengths and T260 values. The effect of the organic level on FR4 peel strengths using different coppers, when processed in a typical operating system, is shown in Figure 7.



Figure 7 – Impact of Primary Organic on Peel Strength THE and Standard Foils (170 Tg FR4)

Better bath stability not only improves the ability to maintain the primary organic at required levels under dynamic feed and bleed conditions, but also facilitates better control of the chloride level, which is also critical to process performance.

In a poorly stabilized system, the hydrogen peroxide itself will also break down under normal operating conditions, which has a further negative impact on the etch rate and necessitates corrective additions. The impact can be quite dramatic at higher copper levels. It is important to regulate the working bath by appropriate adjustment of the bath turnover rates (feed/bleed volumes). To prevent these factors from destabilizing the bath, proprietary formulations include additional stabilizers. Major strides have been made to reduce organic and peroxide breakdown, resulting in much improved performance of the latest generation systems, as shown in Figures 8 and 9.



Figure 8 – Primary Organic Decay Rates v g/L copper (1<sup>st</sup> Generation System)



Figure 9 – Primary Organic Decay Rates v g/L Copper (2<sup>nd</sup> Generation System)

Additional formulation improvements have eliminated any tendency for precipitation, or sludge formation, at higher copper levels within the bath. These advances, collectively, have enabled the practical implementation of systems which now achieve 50 g/L copper and which operate at lower etch factors of 36-45 microinches (0.9-1.1  $\mu$ ). Such systems have only approximately 40-50 % of the bath turnover rate and are clearly reliant on the additional stability. These new systems, for both horizontal and vertical operation, have shown a dramatic improvement in clarity of chemistry, when utilized in volume production applications. As a result, the process equipment is kept much cleaner and is easier to maintain.

#### Bond Strength Improvements from Novel Secondary Organic Additive

Having gained the additional copper capacity and the inherent bath stability to maintain the primary organic operating concentration at high copper levels, a critical requirement is to sustain consistent bond strength values over the full operating range of the system. This has been achieved through the use of secondary organic additives, together with the optimization of

the operating chloride level as shown below in Figure 10. The secondary organic additives also clearly benefit from the improved stabilization systems employed in the new generation of processes.

Chloride level is also an important contributor to bonding performance and will reduce peel and  $T_{260}$  values if the level falls. By contrast, too high a chloride level will suppress etch rates and influence the cosmetics of the surface coating. Historically, chloride levels have been impacted by bath stability and the precipitation of organo-copper breakdown products, which in turn have been affected by the copper loading of the system (g/L Cu<sup>2+</sup>). However, because of improved bath stability and the elimination of unwanted precipitation, the latest generation technologies are able to better regulate chloride levels through normal replenishment. These new technologies operate much more consistently at different copper loading levels without the need for additional analysis or adjustment as shown in the Figure 11.



Figure 10 – Impact of Formulation Optimization on Peel Strengths (170 Tg FR4 and GETEK)



Figure 11 – Percent Loss of Chlorides v Bath Aging

#### **Overall Benefits of the New System**

As a result of the improved stability and bond strength enhancers, it is possible to operate the new processes over a wide range of copper loading. This ranges from 0 to 50 g/L in conveyorized (flood immersion) mode and typically up to40g/L in vertical immersion mode. In conveyorized systems, a production loading performance curve using DSTF (drum side treated foil) is shown in Figure 12.

This illustrates the higher initial etch factors which fall indirectly with initial copper loading and then settle in the 40-45 micro inch range (as measured at 45 seconds dwell time at 95°F) at 45-50 g/L copper. The peel strength values for 170 T<sub>g</sub> FR4 remain fairly constant throughout the range from 0 to 50+ g/L copper. Peel values for GETEK® are also shown in chart 12, and although these typically reach peak levels at the normal "feed and bleed" operating range of 45-50 g/L, performance is still good at low copper levels.

An additional benefit is seen with the consistency of peel strength values when the improved process is operated at lower bath utilization lower levels of feed and bleed. This is illustrated in Figure 13, which shows the consistent performance gained by the improved bath stability, which maintains the primary organic at optimal levels for much longer than earlier technologies.



Figure 12 – Peel Strength and Etch Rate vs. Copper Load (170 Tg FR4 and GETEK)



Figure 13 - Peel Strength 170 Tg FR4 v Bath Age (45 g/L Copper - No Replenishment)

#### T<sub>260</sub> Time to Delamination Testing

Although test results with 140 T<sub>g</sub> FR4, GETEK® and Polyimide tend to be much higher, the use of 170 T<sub>g</sub> FR4 is arguably a more critical test. Comparative evaluation with the higher 170 T<sub>g</sub> FR4 material gives a meaningful barometer of performance across the copper loading range. The relative benefits of the new technology are again demonstrated for both Peel Strength and T260 time to de-lamination, as shown in Figures 14 and 15. Both test parameters show the consistency of performance across the copper loading range. This is particularly important at the higher operating levels of 45-50 g/L, which are typical in high performance production systems.



Figure 14 - Peel Strength vs. Copper Level 170 Tg FR4 with Std, THE and DSTF Foils



Figure 15 – Time to Delamination (T260) 170 Tg FR4 with THE and DSTF Foils

#### **Surface Profile**

An examination by scanning electron microscope (SEM) of the surface provides some explanation of the enhanced performance at lower etch factors. The surface texture created by a 40 micro inch  $(1\mu)$  etch with the 2<sup>nd</sup> generation process shows a comparable surface area enhancement to that produced by the older process using a 65 micro inch etch factor. This comparison is shown in Figures 16 and 17.



Figure 17 – SEM 2<sup>nd</sup> Generation System 40 Microinch Etch

#### **Etch Rates**

Although the etch rates of different coppers will vary, the improved process has the ability to delivery consistent bond strength over a range of lower etch factors. This is important as the level of solution agitation may vary depending on equipment type. When etching at averages of 35-40 microinches  $(0.9 - 1.0\mu)$ , it is important that the process will continue to perform both above and below the average etch levels. The data shown in Figure 18 shows the relative etch factors seen with Standard, HTE and Drum Side Treated Foil at different copper loadings. Figure 19 shows the very consistent peel strength capability over the range of 26-48 microinches  $(0.65 - 1.22\mu)$  using 140 Tg FR4 and DSTF foil.



Figure 18 - Comparative Etch Factors different Foils v Bath Loading



Figure 19 - Peel Strength (Lb/in) vs. Etch Factor 140 Tg FR4 - Flood Immersion Conveyor

Minimizing copper removal from the traces (for improved compatibility for controlled impedance) has been a key driver for the introduction of the low etch systems. It is therefore important to understand the level of copper removal relative to the pattern dimensions (trace height and trace width).

Etch factors are typically derived from weight loss measurements taken from test coupons with 100% copper area. For this reason they represent the reduction in copper height (etch depth) and not the lateral etch (line width reduction). Figure 20 presents data from a production system operating at 3 M/min with an etch factor set at 40 microinches (1 $\mu$ ), with a dwell time of 45 seconds. The typical line width reduction of 0.16 mils (4.1 $\mu$ ) per pass includes the material removed from the foot of the trace, and is about 30% less than a first generation process operating at a 65 – 70  $\mu$ -inch (1.6 – 1.8 $\mu$ ) etch factor. This is clearly important for minimizing loss to tightly controlled conductor widths.



Figure 20 – Line Width Loss after Multiple Passes (40 Micro-Inch Etch – Flood Conveyor)

#### **Vertical Applications**

The improved bath stability and enhanced bonding capability at lower etch factors also enables a much broader operating capability for vertical mode applications. Although bath volumes can be higher, relative to the production loading in ft2/gal/hr, the vertical systems show good process consistency at intermediate copper loading levels of 30 - 40 g/L. The improved system is also able accommodate the lower etch rates resulting from the lower solution flow-rates / flow rate variance within dip tanks. Figures 21 and 22 show typical performance on  $170^{\circ}$ C T<sub>g</sub> FR4 relative to copper loading and bath aging at 30 g/L.



Figure 21 – Peel Strengths (lb/in) v Bath Load 170 Tg FR4 with THE – Vertical Process



Figure 22 – Peel Strengths (lb/in) v Bath Age 170 Tg FR4 and THE – Vertical Process (30 g/L Cu)

Very competent dip performance has been demonstrated using polyimide materials, which show substantial improvements in peel strengths over conventional oxide, particularly at higher copper loadings. If required, bond strengths can be further enhanced by the implementation of a simple post treatment system. This reduces the small residual level of cupric oxide in the actual conversion coating produced by the peroxy sulfuric system. The predominantly cuprous oxide surface which results shows higher peel strength and further improved acid resistance (Figure 23). The "Time to Delamination" ( $T_{260}$ ) data, in vertical dip mode, also confirms excellent bonding performance over a range of loading conditions. See Figure 24, where the  $T_{260}$  numbers at higher copper loadings all exceeded the 30-minute test cut-off time.



Figure 23 – Peel Strengths (Polyimide) Vertical Process with and without Post Dip



Figure 24 - Time to Delamination T260 Polyimide/THE Foil - Vertical Process

#### Conclusions

Since their inception into volume production in the market (circa 1997), peroxy-sulfuric oxide replacements have made significant strides to meet the challenges of advanced multi-layer manufacture.

The benefits of a streamlined sequence, coupled with greater energy-efficiency and improved water (and waste-water) conservation have been clearly demonstrated. The clear advantages when applied to high Tg and advanced dielectrics have also been effectively proven. As a result, such lower-cost peroxy-sulfuric replacements have developed a commanding position, and have replaced conventional "reduced black oxide" processes in large areas of the market.

Despite the inexorable trend towards fine line, high density interconnects and the associated need for minimum copper removal, the next generation of oxide replacement technology continues to meet the PWB fabrication challenges. The evolving low etch / high capacity processes are now capable of delivering improved bond strengths and greater resistance to thermal delamination, at lower etch factors of 30-45 micro-inches (0.8-1.1  $\mu$ ) and higher copper loading of 45-50 g/L. This is largely due to considerable improvements in bath stability, and enhanced surface texturing at low levels of copper removal, enabled by secondary organic additives. In combination, these attributes provide the additional benefits of greater process consistency; improved cleanliness of operation and reduced PM requirements. More importantly they provide a pathway forward for fine line interconnect fabrication while satisfying the insatiable need for the reduced cost of ownership coupled with enhanced performance. By definition these are criteria by which any successful process is measured, and is perhaps the hallmark of the electronic business – 'the challenge to deliver more for less'.

#### **References and Acknowledgements**

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\* GETEK is a registered trademark of General Electric

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# Picture 1. SEM 1st Generation System 65 microinch etch





# Picture 2. SEM 2nd. Generation System 40 microinch etch































