Improvements in Inner Layer Bonding for Lead-Free construction

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Abstract
The age of Lead-free assembly has challenged many areas of PWB design and fabrication. While huge issues in their own right, the challenge is certainly not limited to just the selection of soldering alloys and final finishes. The sweeping technology changes have also ushered in a rapid influx of new and improved dielectric materials which, despite the increased thermal stress, must remain effectively bonded to the copper innerlayers. The advent of multiple sequential build-ups and growing HDI applications, in concert with the conversion to lead-free soldering, have all driven the need for improved oxide replacement technology. The inner layer dielectric bond must resist challenging multiple peak temperatures, some 30°C higher than eutectic applications. Based on statistically designed experiments, an optimized oxide alternative process has been developed, which delivers a more resilient copper conversion coating. This has shown improved bonding performance and greater stability at higher temperatures thus improving its capability to meet more thermal excursions, e.g. assembly-reflow cycles at >260°C, without failure. The article to follow focuses on the development criteria and performance evaluation including data on peel strength, solder float and IR-reflow testing. Benchmarking is described against two standard oxide replacement products.

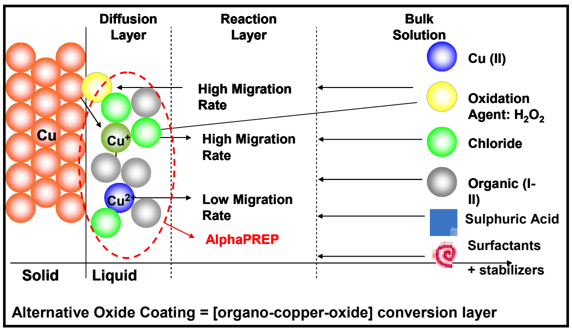
Introduction
The more recent global shift to lead-free assembly has driven sweeping changes to PWB fabrication processes, methods and material requirements. Lead-free assembly has not only driven changes in Final Finishes but also has directly impacted the dielectric material choices and the resulting inner layer bonding performance. Additional processes such as HDI construction with multiple sequential build up (SBU) steps, coupled with the use of new HF and High Tg dielectric materials, all add complexity. These factors, in addition to the much higher assembly soldering temperatures (some 25-30 C higher than Eutectic) required for lead free assembly, further challenge the bonding capability of existing oxide processes.

Inner Layer Bonding Chemistry
The majority of PWB fabricators are now using the typical peroxide-sulfuric 'oxide replacement' process. This works on a "controlled etch" mechanism that removes typically 45–75 microinches (1.1 – 1.9 μ) of copper in a process controlled by a primary organic which then becomes part of the 'alternative oxide conversion coating". 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, the leading processes have shown a consistent capability to achieve a copper capacity of 50 g/L in high-level production environments. The capacity increase has been largely a result of improved copper solubility coupled with significant improvements in chemical stability. This trend has been accompanied with a strong drive to reduce the etch factors down to 1 micron to meet the requirements for fine line and controlled impedance. It has also been necessary, in order to reduce the impact of the skin effect as operating frequencies continue to be pushed upwards. Sub 1 micron etch factors (<40 microinches) are indeed challenging, as better bonding

results have been seen traditionally at much higher etch factors (of >1.5µ). The issue has been to deliver as good or higher values for both peel strength and T_{260} / T_{288} (time to delamination), despite the lower etch.

As described earlier, the primary organic accelerates the etch, modifying the copper surface and also chemically combining with the copper to produce the characteristic oxide conversion coating. This organic coating is based mainly on cuprous ($Cu\ 1^+$) oxide (red colour) but also contains some cupric ($Cu\ 2^+$) oxide (dark/black). Together, these give the conversion coating its characteristic reddish-brown colour. The schematic formation of the alternative oxide coating is shown in figure 1.

Figure 1. Schematic of the Alternative Oxide Reaction



It is well understood that a cuprous-rich oxide coating typically delivers higher bond strength to the dielectric prep-preg. Cuprous oxide is more thermally stable than cupric oxide. In addition, a cuprous rich oxide has a higher chemical resistance to PTH chemistries, which can give rise to "pink ring" through the attack and separation of the oxide planes around the periphery of the holes. This chemical resistance is critical not only for the metallization of high aspect ratio through-holes, but especially for the capture pads in the blind micro-vias. It is possible to post treat the oxide conversion coating using an alkaline process, to remove the less resistant cupric oxide. Such a post treatment has the benefit of increasing the peel strength of the coating by 10-15%. However, this does not improve the resistance to thermal delamination as it can reduce both the coating thickness and resistance to oxidative breakdown.

Figure 2a. XPS Spectra of the Alternative Oxide and surface composition

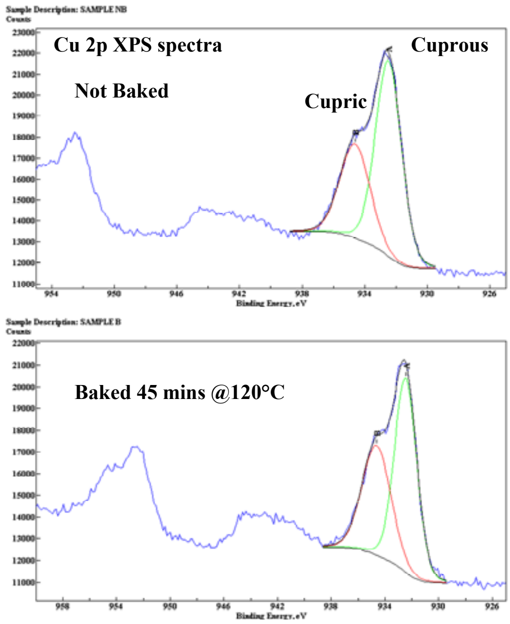


Table 2b. Elemental Coating Composition

XPS Surface Composition (Atomic %)	Elements Detected			
	C	O	Cu	N
As treated	62	13	8.6	17
After Baking	60	15	9.6	15

	Cuprous Cu 1+	Cupric Cu 2+	Cu 1+ / 2+ Ratio
As treated	64	36	1.8
After Baking	58	42	1.4

The elemental analysis is shown for both a standard and a baked coating (45 minutes @120°C). Figure 2a shows the actual XPS spectra of an "as-produced coating" and a baked coating (air oven). As would be expected, the baked layers have a slightly darker appearance, which is indicative of the increased cupric oxide content. From this it is easy to see the reduced concentration of the cuprous species. The relative coating composition is outlined in table 2b.

Impact of Lead-Free Assembly on the Alternative Oxide Bond
Firstly, the infra-red reflow soldering cycles used in assembly, apply a large amount of stress to both the core and the sequential build layers. Although the peak temperatures are targeted to be 245 – 250°C, they can clearly overshoot these values, potentially rising to 260°C or higher. At this point, or during the subsequent solder-wave application, the dielectric bonding can fail due to delamination. Large copper areas, especially those carrying very high densities of small holes, can be especially vulnerable. Delamination can be triggered by a combination of many factors, which are briefly listed as follows:-

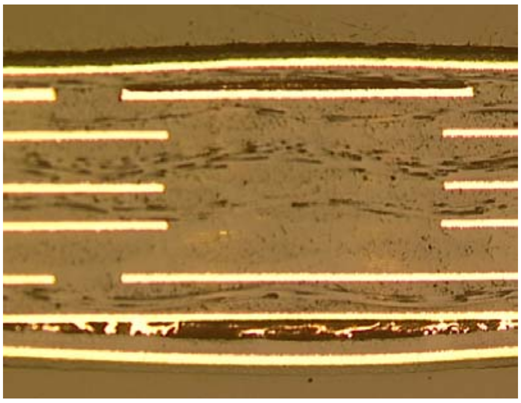
Some Factors influencing Delamination

- **Reflow**
  - Excessive Peak temperatures
  - Incorrect profiles / Rework ?
- **Material**
  - Incorrect material choice, Tg or compatibility
  - Breakdown of the dielectric material / quality ?
- **Lamination factors**
  - Incomplete lamination
  - Excessive lamination temperatures
  - Excessive moisture
  - Incorrect Tg achieved
- **Board construction / Design factors**
  - Inner layer build / copper distribution
  - Pre-preg build up / coarse glass interface / resin starvation
  - Hole cluster density
- **Copper: Dielectric Bond**
  - Inadequate or incomplete oxide coverage
  - Contamination of oxide or core dielectric
  - Breakdown of oxide coating?

In troubleshooting delamination problems, the first step in determining the failure mode is to answer the key question: Where is the delamination occurring (analysis by cross-section)? Is there a breakdown directly between the copper: dielectric (adhesive failure)?; or is this occurring within the dielectric itself (cohesive failure)? Examples of both are shown in pictures 3 and 4

Bearing in mind the larger potential contribution from the material, design and lamination factors, the objective of this study was to focus on the arguably smaller contribution from alternative oxide factors and how these can be improved from the chemical standpoint.

Picture 3. Failure of copper:dielectric interface.

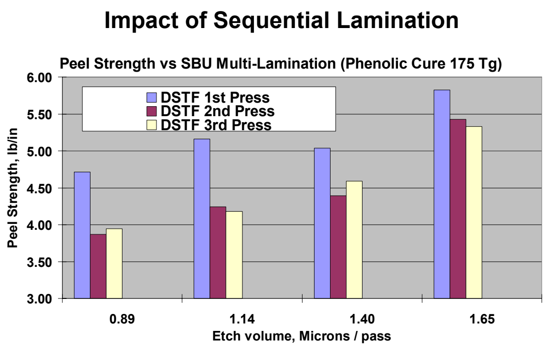


Picture 4. Failure within the dielectric itself

The Effect of Multiple Thermal Cycles
More and more printed wiring board designs, especially for thin card mobile or PDA-type product, call for multiple sequential lamination techniques. Here, each lamination cycle adds an additional thermal excursion to the inner layer bond within the

core construction. Dependent on the required lamination temperature, (typically 190-200ºC), these cumulative thermal stress cycles can reduce the bond strength prior to final soldering, further pushing the need for improved thermal integrity. The impact on peel strength caused by sequential bonding cycles is shown in figure 5.

Figure 5. Peel strength change with 1-3 sequential lamination cycles



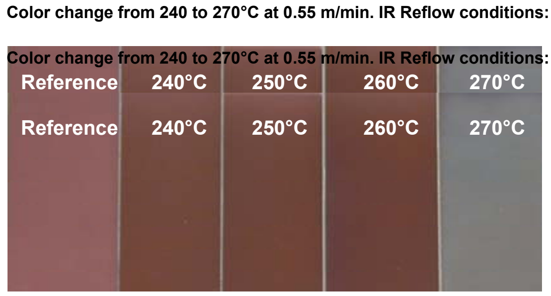
These repeated thermal cycles from SBU fabrication, together with the effects of the higher temperature more aggressive lead-free soldering cycles, further challenge the bonding performance of the PWBs

Contributing factors related to the Alternative Oxide

The alternative oxide coating is based on an organo-copper conversion layer. So it is not surprising that the surface can ultimately breakdown at an escalated temperature. Extensive studies, carried out on the first generation alternative oxide using auger analysis, have shown a significant transition in the elemental structure, which starts at around 260°C. This is clearly seen in the colour change associated with the oxide coating as seen in picture 6.

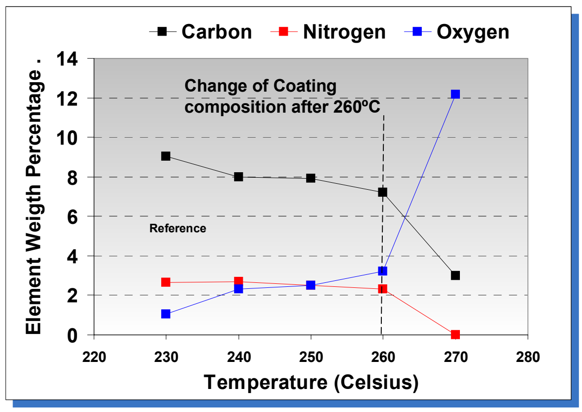
At this point, the nitrogen and carbon atomic levels, which are a signature of the organo-coating, both start to fall-off dramatically. At the same time, some significant oxidation takes place. The Auger analysis results are shown in figure 7. Although this work was

Picture 6. The visual effect of heating on the Alternative oxide coating



based on heating using IR Reflow under atmospheric air conditions, it was argued that the same trend would be expected on layers encapsulated within the PWB, but with a slower transition rate.

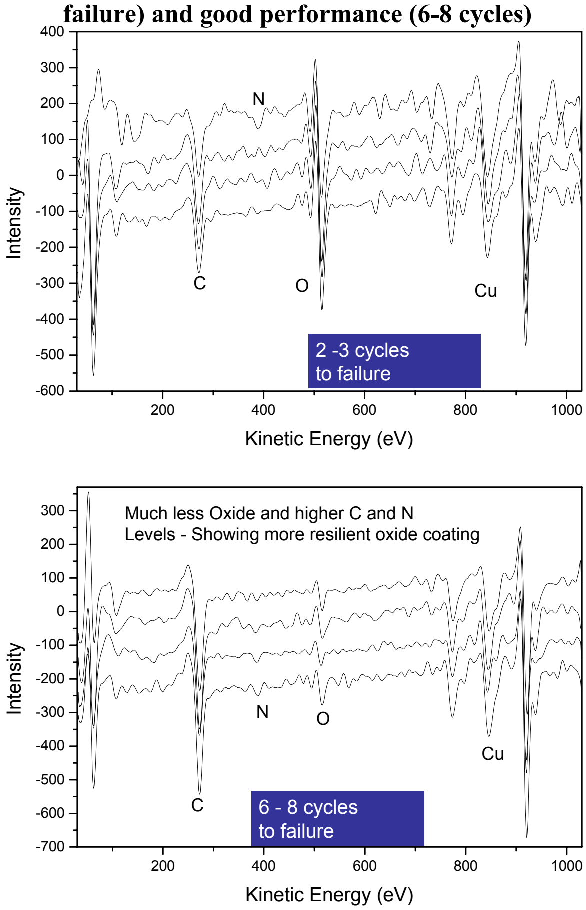
Figure 7. Impact of Heating on Atomic composition of Alternative Oxide (Auger)



This work clearly demonstrated that the tolerance of the first generation alternative oxide technology to lead-free soldering temperatures was, at best, only marginal.

In order to correlate the surface performance with the delamination results under actual lead-free assembly conditions, a further Auger examination was made on groups of circuits which showed different levels of delamination failure. The circuits were drawn from lots which had performance ranging from failure on the initial 2-3 IR reflow passes, up to acceptable performance on 6-8 multiple soldering cycles . Test samples, which had not been reflowed, were selected from each group and subjected to multiple solder dips at 270°C for 10 seconds until failure. This failure was defined as blistering or delamination. Immediately at this point, the blistered areas were peeled back and the alternative oxide surface was subjected to surface analysis using Auger spectroscopy.

Figures 8a and 8b Auger Spectra of Surface showing poor performance (2-3 cycles to failure) and good performance (6-8 cycles)



The bonded samples with the best thermal resistance (6-8 cycles before delamination) showed higher levels of carbon and nitrogen and much lower levels of oxidation than samples which failed after 2 cycles. These results were in agreement with the Auger results of the atmospheric IR-reflow testing of the unbonded surfaces described earlier. The Auger spectra of the delaminated surfaces are shown in figures 8a and 8b.

Conclusions from the Preliminary Work

Several conclusions were drawn from the initial investigative work and from the ensuing bond improvement approach. Some key points are as follows:

1. Many different dielectric material and bonding process factors can trigger delamination failure but clearly the Copper: Dielectric bond can experience breakdown. One contributing factor is the potential for breakdown of the [copper-oxide-organic] complex under excess reflow or lamination temperature(s).

2. Although proprietary alkaline post treatments, used to increase the Cu1+: Cu2+ (cuprous:cupric) ratio, can increase both peel strength and chemical resistance they can significantly reduce the overall delamination resistance especially if aggressive concentrations are used.

3. Unfortunately, Peel strength testing, made directly after the initial lamination, does not give a good indication of potential for assembly soldering failure. Multiple sequential lamination cycles can reduce the peels strength and the highest initial peels results do not necessarily reflect the best resistance to delamination.

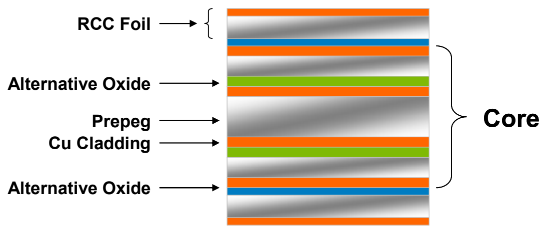
4. However, time-to-delamination testing (T260), peel strength after thermal shock and lap shear tests (not included in this study) seemingly provide more meaningful measures of bonding integrity and resistance to delamination. A combination of tests gives the best approach.

5. Finally, the much older first generation alternative oxide technology is operating at, or close to, its performance limit in demanding applications. Without any doubt, improved thermal resilience and improved bond integrity is now a requirement from

the current alternative oxide processes.

Product Improvement Approach
Following the lead-free transition, a large amount of work had already been completed by the development group, to provide alternative oxide products with improved high temperature performance. A prototype 25 g/L low copper capacity product (LCC), with improved thermal stabilization, had been developed from the first generation technology. This LCC prototype product was also used as the benchmark and had demonstrated good capability to withstand extended IR Pb-Free Reflow cycles. In addition, a 50 g/L high copper capacity / low etch product (HCC) had also been commercially introduced to meet the growing requirements of higher signal integrity, improved environmental capability (reduced waste); and lower cost of ownership.
The HCC technology used similar organic stabilization to the LCC product and had already demonstrated better preliminary performance for peel strength and thermal shock resistance in high volume production.

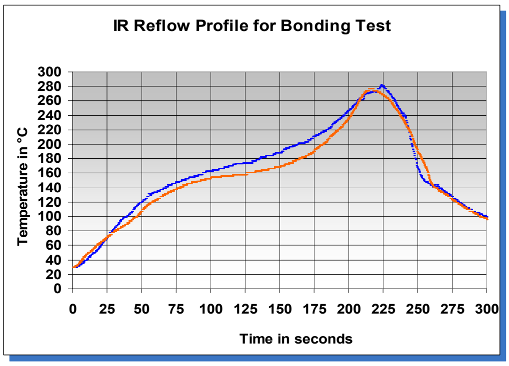
Figure 9. Simple Delamination Test Vehicle



The defined pathway forward was to further optimize the HCC technology through more exhaustive thermal stability testing, by using extensive L9 and L18 Taguchi methodology. To effectively test any improvement against the benchmarks, a more rigorous testing protocol was required. This included a test vehicle (figure 9.) which was based on a 4 layer rigid FR4 150 Tg core with layers 5 and 6, built from a resin coated copper foil construction, to simulate sequential build-up (SBU). Layers 2 and 4 of the core were electroplated with acid copper to simulate a buried via type construction, and also to examine the effects of plated copper construction. When subjected to repeated highly stressed IR-Reflow cycles, this test vehicle was capable of failing, either in the central core or within the surface layers. The IR-Reflow test condition incorporated a soak profile with a very high 270°C or 280°C peak temperature. This reflow profile is shown in figure 10.

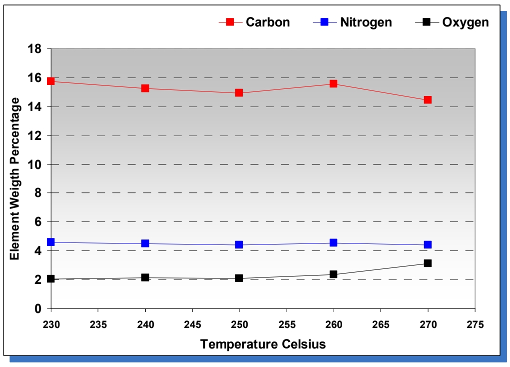
Standard HCC Benchmarking results
Using the IR profile described, some copper inner layers, treated with the standard HCC process, were subjected to repeated reflow cycles. Whereas the older generation technology had shown a significant colour change and pronounced thermal breakdown effect at temperatures over 260C, the HCC process was able to withstand the peak of 270C without any pronounced change of colour.

Figure 10. Stressed IR reflow profile



The Auger studies showed no significant loss (elements C, N) or oxidation of the organo coating. In addition, significant improvements in stability were seen over the lower soldering temperature range. No perceptible change, or evidence of slow but gradual oxidation as seen with the older technology, was experienced The Auger results are shown in figure 11.

Figure 11. Auger results v Temperature for the HCC technology



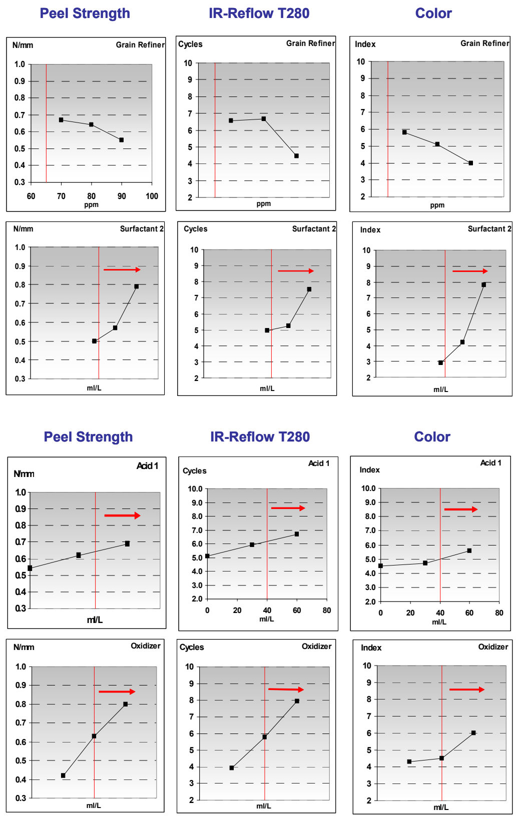
The HCC technology also demonstrated a 6-15% improvement in peel strength of the coated layers. Clearly, in combination, these results already represented a major step forward in improving the thermal resistance of the coating. Furthermore, at 270ºC the HCC technology was able to withstand an additional average number of 1.5 cycles before failure due to delamination, compared to the first generation technology. With a peak of 280°C, the improvement was close to an average of 2 additional cycles.

Having achieved a very satisfactory improvement with the high copper capacity formulation, the next steps were to look at the optimization of the HCC formula for thermal performance using the Taguchi approaches previously described.

DOE Optimization of the HCC Product

The applied series of test arrays included the following design of experiment factors :
a) The primary and secondary inorganic acids (influencing the etching characteristic and solubilizing the copper);
b) The organic components (for controlling the modified etch reaction rate, producing the organo conversion coating, and stabilizing the process and the coating);
c) The grain refiner (essentially a chloride based species);
d) The oxidizing agent - hydrogen peroxide (also driving the reaction-rate and texture depth).

Figures 12a/b. Taguchi responses on Development Optimization



The studied responses were coating colour, etch-rate, pull-peel strength after coating, and most importantly, the resistance to delamination using the aggressive multiple IR Reflow cycles with peaks temperatures of 270 and 280°C respectively.

Details of some of the individual component plots, drawn from one of the later L18 arrays employed, are illustrated in figures 12a/b. As expected, varying levels of response, and some interactions, were seen with many of the parameters employed.

The findings were interesting for several reasons. Firstly, although only one organic additive significantly affected the colour of the coating, several of the additives had a significant influence on the delamination resistance. By contrast, the peel strength was mainly impacted by two significant factors.

Secondly, and with an unexpected benefit from a developmental perspective*, more or less all the factors that positively influenced the thermal performance also improved the primary peel strength results and contributed to good coating colour and appearance. This can be seen within the similarity of the displayed Taguchi responses, which largely moved in unison. This was very helpful in facilitating an "optimized" HCC product formulation on which to base the confirmation runs. A summary of the Taguchi optimization is shown in table 13.

Note*: As the higher peel factors and darkest color do not always correlate to improved delamination resistance

Table 13. Summary of Taguchi Optimization for the HCC Alternative Oxide

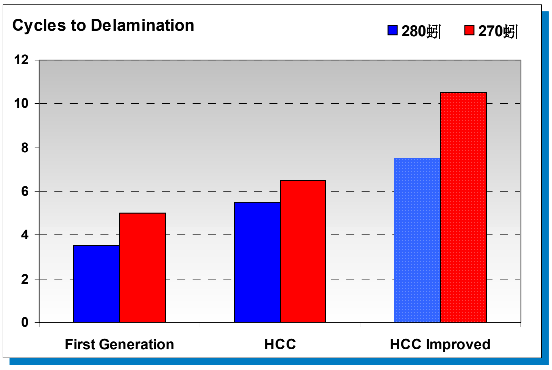
Summary of Taguchi Performance evaluation of 50 g/L HCC High Capacity Improved Alternative Oxide

Parameter		Reference	Theoretical Optimum		HCC
		AlphaPrep Std	Highest Peel Strength	Highest IR-Reflow	Optimized
Surfactant A	mg/L	100%	125%	104%	100%
Surfactant B	ml/L	100%	156%	156%	150%
Organic 1	ml/L	100%	111%	100%	100%
Grain Refiner	ppm	100%	108%	115%	108%
Organic 2	ml/l	100%	300%	200%	200%
Oxidizer	ml/l	100%	117%	117%	117%
Acid I	ml/l	100%	150%	150%	113%
Peel Strength	N/mm	0.7	1.2	1.1	>1.1
IR-Reflow (T280)	Cycles	3	11	13	>10
Color	Index	7.5	10	10	10

The confirmation testing which followed showed an expected and very positive gain with the achievement of >10 IR Reflow cycles without failure (based on the aggressive test vehicle and profiles involved). These resulting confirmation runs for delamination, as compared to the first generation technology and HCC standard benchmarks are shown in figure 14.

Having successfully completed this initial development work, and confirmed the improvement, work is now continuing to establish performance characterization in the appropriate scale-up mode.

Figure 14. Confirmation Run – IR Reflow Delamination Tests



Conclusions

The work described has encompassed a long period of design, development and testing, carried out over a three year period. Along the way, a lot of input has been received from the market in terms of both defining the challenge and applying best practices to meet the growing industry requirement for improved PWB thermal resilience.
Several leading edge fabricators have made significant progress in selecting improved materials and applying better lamination and process procedures, all of which open up the operating window for more demanding products. From this work, it is very clear that many of these other major factors can significantly and adversely outweigh the alternative oxide contribution in achieving the balance required for bullet proof performance.

This study has been focused solely on finding ways to improve the performance and contribution of the alternative oxide bonding technology. The goal has been to provide a more robust process with a wider operating window offering better thermal resilience.

The Final Conclusions are summarized as follows:-

1. Delamination failures due "Lead-Free" thermal stress can be caused by many factors, most significantly those involving the dielectric materials and lamination.

2. Although much industry opinion attests that dielectric selection and press parameters are major factors, the alternative oxide makes an important contribution, especially for large copper to dielectric areas.
3. Limitations can be seen with the older generation alternative oxide bonding technology which cannot consistently meet the emerging minimum industry requirement for delamination resistance. This is especially true in applications with highly advanced and performance sensitive designs. The stability of the respective organo-metallic conversion coating diminishes at 260ºC. a point where the bonding performance can fall-off with increasing thermal excursions, leading to potential delamination issues.
4. One conclusion which can be repeatedly drawn from this kind of work is that the industry standard 'peel-strength' measure cannot adequately predict bond strength and its resistance to delamination under thermal stress.
5. The work described in this paper has shown that improved LCC (low copper capacity) and HCC (high copper capacity) products have already demonstrated higher thermal stability than their earlier counterparts. These products have demonstrated better thermal resilience and greater capability to withstand multiple Pb-Free reflows at inflated peak IR Reflow temperatures of 270 and 280ºC.
6. The exhaustive laboratory work involved in this study has further established that the optimized HCC version, can even more effectively meet a >10 IR Reflow requirement.

In Summary

The product design specification, to deliver a low-etch attribute (1-1.2 microns) for controlled impedance, fine line integrity and improved High Frequency signal integrity has been a key factor in this approach. This has been embodied within the HCC improvement plan to meet the bonding integrity and IR reflow delamination resistance requirements of the developing HDI technology. Maintaining the required high copper capacity of 50 g/L delivers the best environmental capability and lowest cost of ownership. A patent has been awarded for this improved technology.