Blister Free PTH Processes for High Tg and Exotic Base Materials

Introduction

PCB manufacturers must permanently contend with difficulties associated with production of PCBs with ever more complex designs, technology requirements and increased lifetime / reliability requirements. Issues pertaining to the laminate material used, via sizes, copper layer thickness and electrical requirements, which significantly affect the manufacturing process are often the prerogative of PCB designers with extremely limited if at all any consultation of manufacturers.
Most importantly introduction of the Restriction of the use of Hazardous Substances (RoHS) directive in Europe from July 2006, has obliged PCB fabricators to use RoHS compliant materials. RoHS affects the metals Lead, Mercury, Chrome (VI), and the bromine containing resins PBB and PBDE. The main concern for PCB fabricators are the bans on Pb and Cd as these affect the choice of laminate materials and consequently the performance and requirements for the desmearing and metallization processes.
Other countries most notably China from the 1st of March 2007 are set to follow with similar directives.

Consequences of Lead Free Soldering

New lead free soldering processes mainly those based on Sn/Ag/Cu (SAC) alloys have emerged. These have melting points that are about 30 °C above that of the conventionally used Tin Lead Alloy (Sn63Pb37). Lead free soldering, not only results in higher temperature but also results in longer exposure at the higher temperature. This combined effect results in significantly higher thermal stress of the base material and suitable laminate materials must be used.
The logical reaction of many laminate manufacturers has been to develop new epoxy based halogen free materials with higher T_g and higher T_d. Another typical trend for these materials is the inclusion of filler materials mainly to reduce CTEs. The result is laminates with lower CTEs and the ability to withstand higher temperatures, thus reducing the risk of delamination. This leads to less stress on copper in through holes and significantly reduces the probability of barrel cracks and inner layer connection defects occurring.
Experiments have shown that high T_g laminates exhibit a higher resistance to chemical attack expressed through reduced weight loss and less roughening tendency during permanganate attack. As a consequence high T_g materials require more aggressive permanganate etching for the same cleaning effect as with conventional laminates
The filler materials often have a different response to permanganate attack, compared with the laminates in which they are imbedded. Desmear parameters must therefore be finely adjusted for optimum attack of both the resin and filler materials to prevent unacceptable geometrical deformations of features such as BMVs.

Consequences of Halogen Free Laminates

The removal of bromine from the basic formulation of laminate materials means that alternative flame retardant systems have to be implemented. Typical alternative flame-retardants are based on phosphor compounds included in the resin system or added separately. Also a significant number of modern halogen free materials tend to include fillers. It appears that there is again a significant change in the formulation of materials entering the laminate market so that they are able to fulfill the halogen free directive. This means that the PCB manufacturer has to assess the impact on the production process and make suitable adjustments.

Implications for Process Qualification

The proliferation of new laminates means that many PCB manufacturers and their suppliers must modify and re-qualify their production processes. Thermal cycle testing, interconnect stress testing and thermal shocking are the predominant test methods for thermal robustness. More complex test vehicles which are designed to ensure more stressful conditions through the inter-

connect and the barrel of a via are being developed for more stringent reliability requirements. ICD evaluation is used to evaluate reliability of the electroless copper process whereas barrel cracks give information on the galvanic copper process.

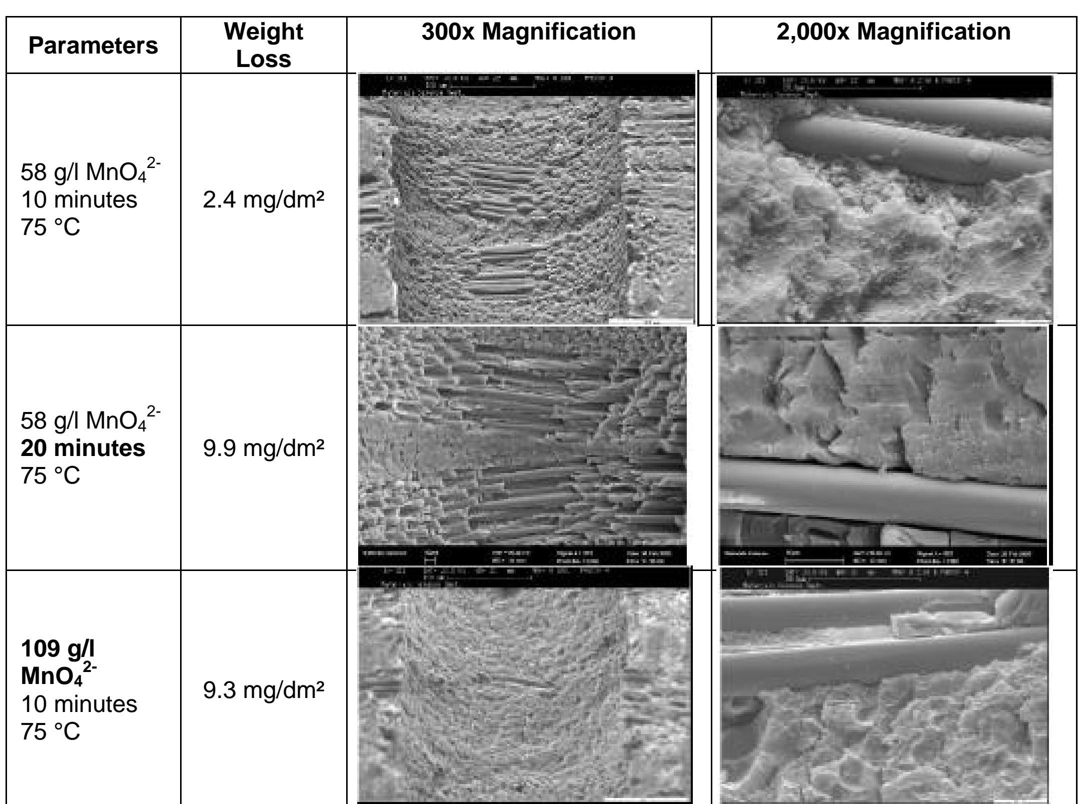
Modifications to thermal shock testing include 6x or 9x at 316 °C or 326 °C as opposed to the standard 288 °C. Increasing the space between through holes and structuring inner and outer layers has been shown to increase the stress on the interconnect.

Desmear Process

Lead and halogen free materials have a higher polymer cross-linking density, which increases their resistance to chemical attack. This reduces weight loss and roughening tendency during permanganate attack. Less functional groups in the resin matrix are believed to reduce copper adhesion leading to reduced peel strength on bare resin and increased possibility of blistering. Consequently high Tg materials generally require more aggressive permanganate etching for the same cleaning effect as with conventional laminates.

Experiments were undertaken to find out the influence of a more aggressive permanganate etching solution or a longer dwell time. The standard sweller called "Sweller P" was used on Matsushita material R1766T. As illustrated below, it appears that either doubling the concentration of permanganate solution or doubling the immersion time has the similar effect of increasing the weight loss by almost four times.

Weight loss with aggressive permanganate parameters



Parameters	Weight Loss	300x Magnification	2,000x Magnification
58 g/l MnO_4^{2-} 10 minutes 75 °C	2.4 mg/dm²		
58 g/l MnO_4^{2-} **20 minutes** 75 °C	9.9 mg/dm²		
109 g/l MnO_4^{2-} 10 minutes 75 °C	9.3 mg/dm²		

The use of ultrasonic in the permanganate module has also shown to be especially effective for enhanced cleaning of high Tg laminates.

Due to the use of more aggressive parameters during permanganate etching, more waste products are generated, requiring a more efficient MnO_4^- regeneration system to maintain bath lives. An example of such a regeneration system would be the Oxamat IV system, which has

double the efficiency of the previous Oxamat III system. It also has a modular design allowing the installation of additional units to improve efficiency and capacity if and when necessary.

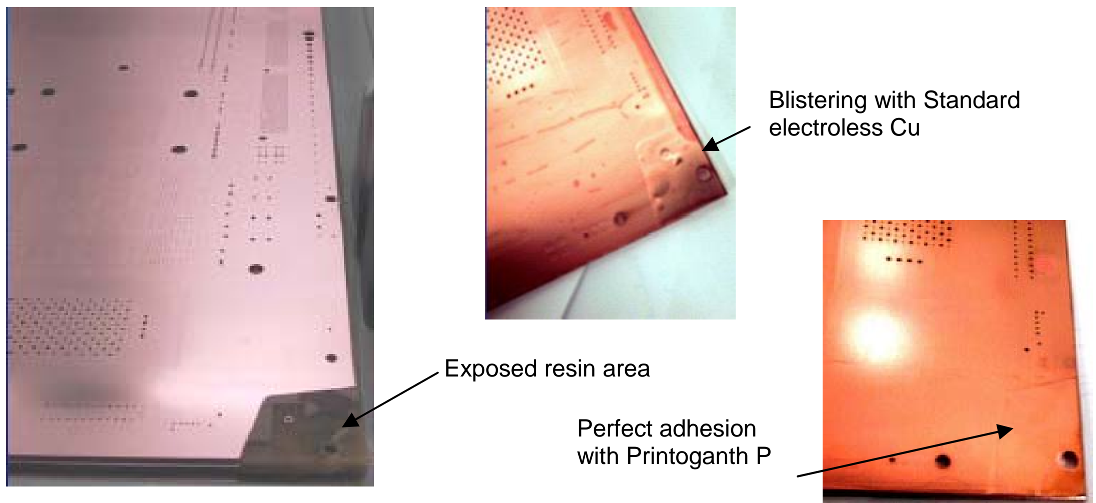
Metallization Process

As mentioned before less roughening is observed with high Tg, halogen free materials; in general a lead free material based on a “novolac” recipe (phenolic curing agent with multifunctional epoxy) will have a peel strength of laminate copper foil in the range of 55% that of a standard dicy cured 140 °C FR4 laminate. The result with standard processing parameters would be increased possibility of blistering and other defects such as hole-wall pull away. To aid adhesion, new electroless copper baths have to be developed. These must have a deposit with the following characteristics:

- low stress deposit
- good uniformity
- strong, dense crystal structure

The picture below shows the excellent deposition quality on exposed polyimide coverlay for a flex-rigid board, which was not plasma treated, with a new specially adapted electroless copper bath.

Blister Free Deposition on Polyimide with Printoganth P Process



For some new laminates modifications to components of the cleaner and etch cleaner steps might also be necessary to improve adhesion.

Summary

The increased awareness for the importance of environmental issues across the globe will speed up the implementation of green legislation such as RoHS in most countries. Europe is taking the lead but in China and even USA environmental issues have also been gaining a lot of steam in recent months. For PCB manufacturers, the load of new laminate materials shall continue to increase at a faster rate in the near future. This means a lot of qualification work and sometimes process modifications or even new process installations will be necessary in order to produce PCBs, which satisfy increasing lifetime/reliability demands of OEMs. At the same time developments in communications and other PCB related technologies indicate complexity of PCBs will continue to increase. With more and more electronics components finding use in automobiles including engine parts, requirements for reliability shall continue to increase probably with increased price pressures for this segment.
For PCB manufacturers this means new and exotic base materials will proliferate in the near future while highest reliability or quality issues will increasingly gain in importance as prerequisites in order to compete successfully.