

Assessment and Solutions for Hole Wall Pull Away in High Tg and High Technology Laminate Materials

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ABSTRACT

Today the use of high Tg laminate materials (>150°C) is common place. The main reasons for their use is of course to have higher Tg points than the standard thermal cycle tests and for better physical properties like Coefficient of Thermal Expansion and electrical properties like Dielectric Constant etc.. As with all things there is a price to pay for relatively cheap laminate materials that have these special properties. The materials are more highly cross-linked, therefore more chemically resistant and so difficult to desmear and condition and they contain less functional groups in the final matrix so making the adhesion of copper an issue. Due to these two factors there is a high chance of hole wall pull-away, and blistering on bare resin areas.

This paper is split into two main parts; desmear characterisation and assessment of commonly used high technology laminate materials, and improvements that can be made with the electroless copper process to improve hole wall adhesion and reduce blistering. The desmear part will show the effect of swelling and etching these laminates with different commonly used solvents as well as weight loss results and an assessment of roughness. The electroless part will show the influence of the electroless copper properties and the adhesion

benefits that can be achieved by optimising formulations.

Main Factors Effecting Hole Wall Pull Away

- ◆ Hole wall Cleanliness / Conditioning
- ◆ Laminate resin Type
- ◆ Hole Wall Roughness
- ◆ Thermal Cycle Test Parameters / Pre-treatment
- ◆ Electroless Copper Character

If we consider that holes are effectively cleaned of drilling debris etc., correctly conditioned from the pre-treatment step and that the solder shock treatment is performed according to IPC directives then the main issues to consider are; Laminate Resin Type, Hole Wall Roughness and Electroless Copper Character.

Due to more demanding technical demands the resin systems being used for PCB manufacture are becoming more complex. There is of course always a trade-off, the processing of the materials becomes increasingly more difficult. Of most importance to hole wall pull away are the desmearing and metallisation of the holes. The newer, high technology resins have more cross-linking and are usually low in functional groups. The effects of this increased cross-linking and choice of resins, catalysts and hardeners are:

- ◆ Higher Tg Values
- ◆ Lower Copper Adhesion
- ◆ Higher Chemical Resistance
- ◆ Lower Roughening Tendency

Due to these factors the chances of hole wall pull away generally increase with the increase in technical capability of the material (this usually also includes an increase in Tg). To show the effect of this increase **TABLE 1** shows the influence of Tg and functionality of the material with copper peel strength of the laminate copper foil. As can be seen the adhesion of standard 1oz. copper foil to CAF resistant material is 45% less than that of the standard FR4 material.

This difference significantly increases the chances of hole wall pull away especially when combined with other processing issues as discussed later.

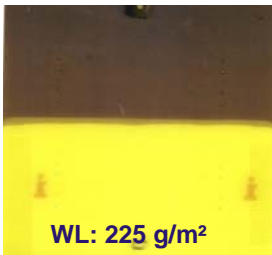
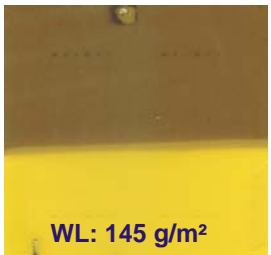
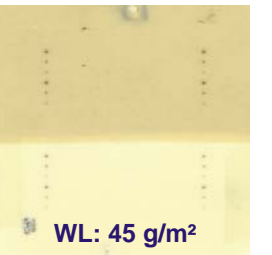
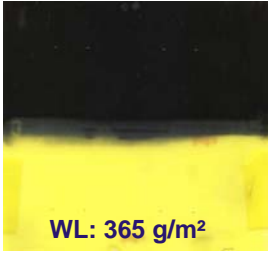
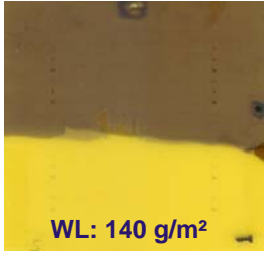
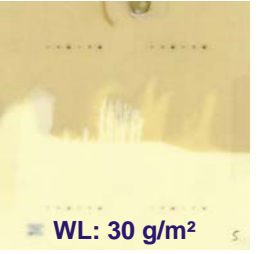
The increased matrix density has the influence of making the material more chemically resistant so desmearing becomes an issue. **TABLE 2** shows a set of coupons made from laminate material with all of the copper etched off. The coupons are then treated with one of 2 different solvent swelling systems and permanganate desmear. As can be seen the higher Tg material has less MnO₂ residues indicating less attack. This correlates nicely with the corresponding weight loss values.

Table 1

Material	IPC 4101A Dash Code	Tg (°C TMA)	Peel Strength (N/mm)	Material Type
1	/21	135	1.95	Standard FR4
2	/21	150	1.95	Higher Tg FR4
3	/24	170	1.40	High Tg FR4
4	/24	180	1.25	Low CTE / D _k
5	/24	170-180	1.07	CAF Resistant

Data Obtained from Laminate Supplier Technical Data Sheets

Table 2

Sweller	Material		
	1	3	4
1	 WL: 225 g/m ²	 WL: 145 g/m ²	 WL: 45 g/m ²
2	 WL: 365 g/m ²	 WL: 140 g/m ²	 WL: 30 g/m ²

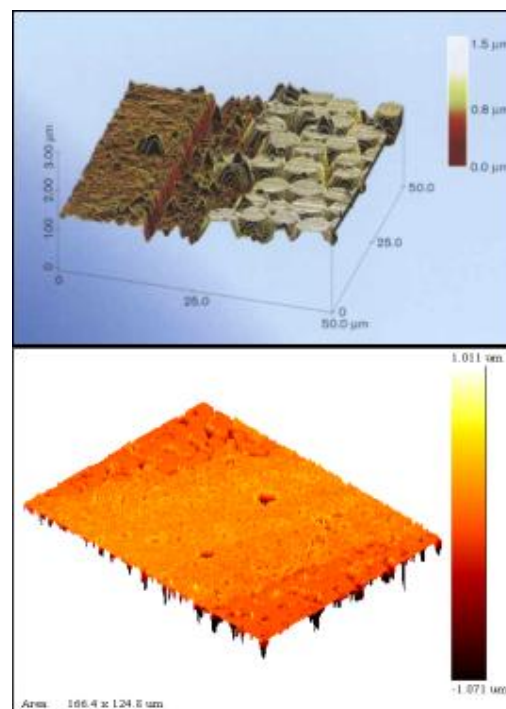
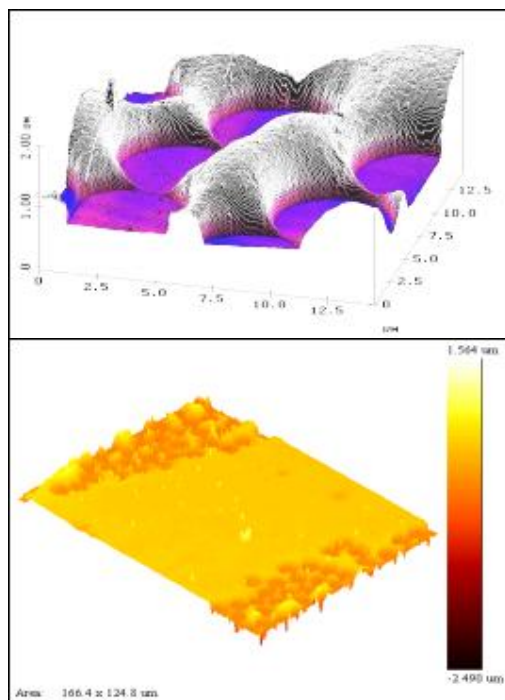
Due to the innate nature of the high technology materials for chemical resistance we required a way to predict their behaviour during pre-treatment. We devised a series of tests to characterise the performance of each material under standard desmear processing conditions. The first set of tests was made to determine the response of the resin system to swelling and also to subsequent permanganate etching. This was performed by sectioning the relevant material, embedding them in micro-sectioning resin and then polishing the surface flat before treating each in the relevant process bath. The effect of each process step was determined using an interference microscope to scan the structure of the surface and the change in height of the resin in comparison to that of glass fibre bundles. **PICTURE SET 1** shows the technique in action.

With this technique we were able to calculate a value for the response of

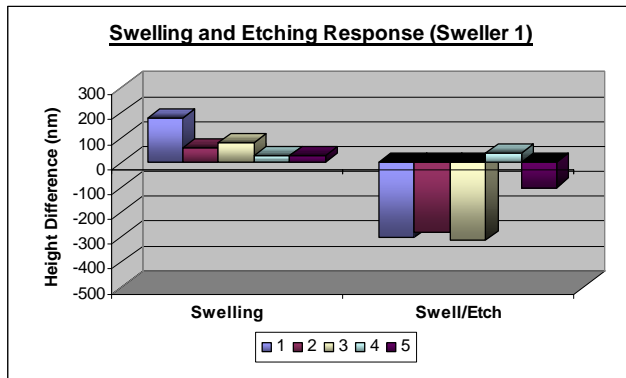
the resin to the solvent swelling chemistry and the subsequent permanganate etching process. Results are shown in **GRAPH 1 and 2**.

The graphs clearly show a step difference in the response of the resin systems for the two highest technology materials. These are designated as IPC 4101A/24 systems as compared to /21 for the other three materials. The response for these high technology materials to both solvent swell processing and permanganate etch is minimal. In general it can be seen that for the /21 materials the second solvent swelling system is more aggressive leading to a little more swelling and subsequent etching. The high Tg material 3 however, shows almost no difference between the two systems in terms of final etch depth. *(There is a slight issue with what may be remaining solvent in the resin matrix for the last solvent system causing positive height responses even after etching.)*

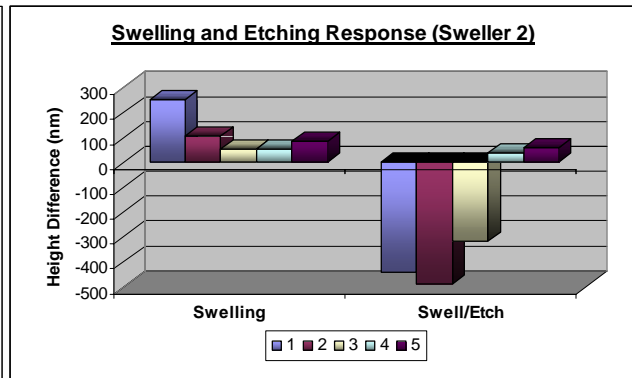
Picture Set 1



Graph 1



Graph 2

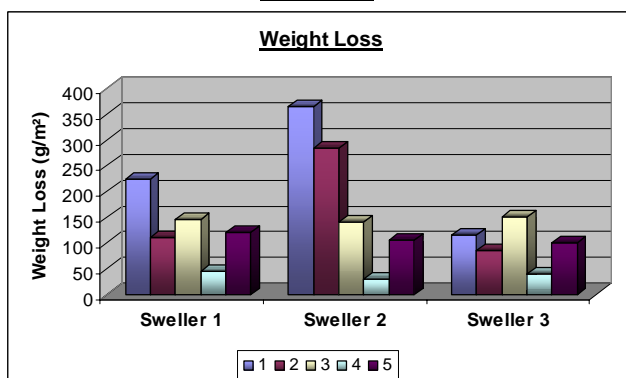


The weight loss of the resin system from the desmearing process is also an indicator of the chemical resistance. Coupons of laminate material were prepared by etching off the foil copper and then cutting them into suitably sized pieces for weight measurements. Drying was performed by baking in an oven and then cooling down to room temperature in a dessicator. The results are in **GRAPH 3**. From the graph it can be seen again that the higher technology resin systems are attacked less and so have a lower weight loss. The 4th material has the least response of them all to attack, even compared to the 5th material. This is in part in line with the slight differences in the Tg points of the materials. Again for critical materials like the 4th the response even to different solvent systems is low and about equal. This material is known to cause issues of hole wall pull away when processing, even when aggressively desmeared. Another study undertaken was to try to determine if there was any discernable

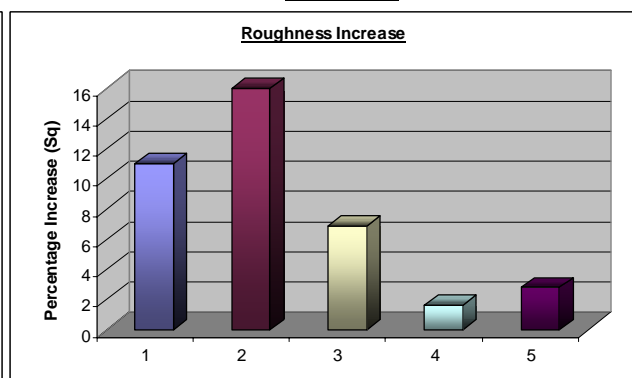
difference between the materials with respect to roughness when processed through a permanganate desmear.

To do this the copper was again etched from laminate surfaces and then the surface extensively scanned using an interference microscope to determine differences in the surface roughness before and after desmearing. This was extremely difficult to perform and the results are an average of multiple studies of different sample surfaces. The results in **GRAPH 4** show again that the materials associated with high technical capability, the 4th and 5th, show the least response for roughening. Again the 4th material shows the least response. It is known that for high Tg materials that multiple desmearing operations do not always improve the hole wall pull away issue and sometimes make it worse. This has been seen as a 'polishing' of the surface as no conventional permanganate desmearing roughness can be achieved on these high Tg materials and so excessive

Graph 3



Graph 4



desmearing only removes the drill marks left in the hole and so reduces the overall roughness.

TABLE 3 contains light microscope pictures of holes after desmear treatment. The pictures clearly show the lack of noticeable roughening for the higher Tg and technical materials.

TABLE 4 shows the effect of normal and excessive desmearing on a normal Tg material and a typical high Tg material. The normal FR4 becomes extremely rough when excessively desmeared but the effect on the high Tg material is actually the opposite. The high Tg material has become smoother as the roughness from the drilling process has been 'polished' away.

Table 3

		Material				
		1	2	3	4	5
Solvent Sweller 1						
Solvent Sweller 2						

Table 4

		Normal Desmear		Strong Desmear	
#1					
#3					

Characterisation Conclusions

The increase in cross-linking density and resin matrix chemistry increase the Tg but more importantly the chemical resistance of the material. This increase means that copper adhesion is reduced, especially for the high technology materials. The resistance to chemical attack from permanganate desmearing systems also reduces the roughness that can be achieved in hole walls as well as resin etch back. Even using excessively strong desmearing conditions and products does not improve matters much. In some cases excessive desmearing reduces surface smoothness even further. Due to this the chances of getting hole wall pull away issues in general increases the higher the Tg of the material and the higher the technical capability of the material. To improve hole wall pull away means that we have to look for other alternatives to improve the situation rather than just desmearing. One important operation in the processing of a PCB is the electroless copper step. The behaviour of the electroless copper deposit has a direct influence on hole wall pull away. Atotech has now developed and studied a new electroless copper system that is capable of reducing hole wall pull away by its inherent deposit characteristics.

Electroless Copper Improvement

Although the electroless copper process is a mature technique development is still continuing in order to meet the new challenges that appear in our industry. The hole wall pull away phenomenon for high Tg and technical laminate materials is one such challenge. To find a solution for this challenge we looked into formulations of our electroless copper process and assessed the best for

giving us favourable deposit characteristics.

- ◆ No or low stress in the deposit
- ◆ Good uniformity in the deposit
- ◆ Strong, dense crystal structure

To achieve this we found methods to reduce the internal stresses within the deposit as well as increasing the uniformity of the deposit. These changes to the electroless bath also generated a strong and dense crystal structure so giving us all the benefits we required.

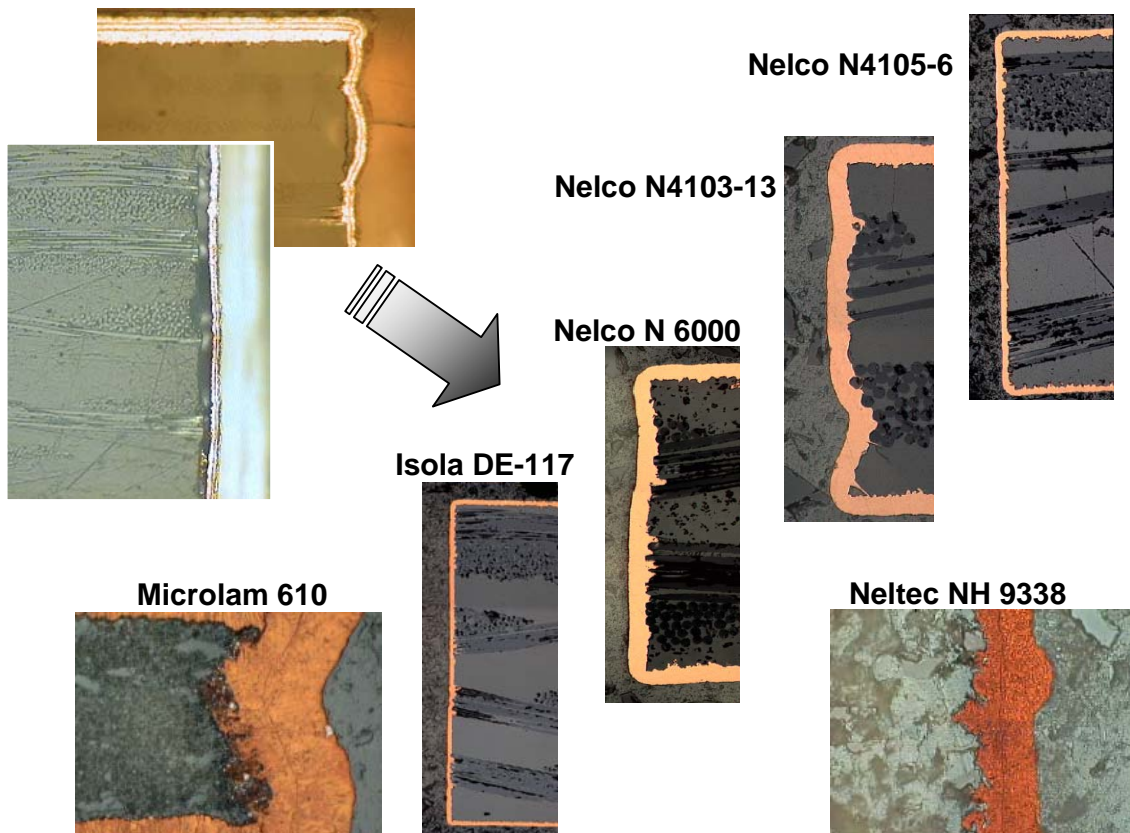
To test the ability of the electroless copper bath we installed it in a machine running at a customer manufacturing PCB's with critical laminate materials. All tests proved the capability of the system over existing processes. The results of the various tests are included in this report. The name that we have given to this process is **PRINTOGANTH P** for our horizontal system and **PRINTOGANTH PV** for our vertical system. We currently have several installations of the horizontal system and with the vertical system now being tested with customers' panels.

The system was tested with a variety of different, commonly used laminate materials and found to have no issues with hole wall pull away. The most demanding test was to see if blisters would appear on bare laminate regions of panels. To test this we processed panels of each material type through the standard desmear and electroless process after etching off all the foil copper. The panel was checked for blistering after the electroless bath and also after acid copper plating. In both instances no blisters were found for the new Printoganth P bath, unlike for the other electroless systems tested. These blister results are in **TABLE 5**. The group of pictures under table 5 show typical good hole wall adhesion of various high technology laminate materials.

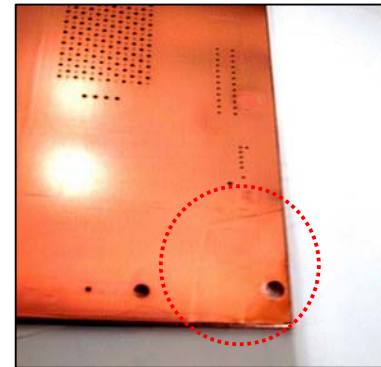
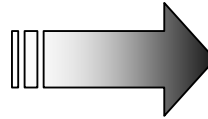
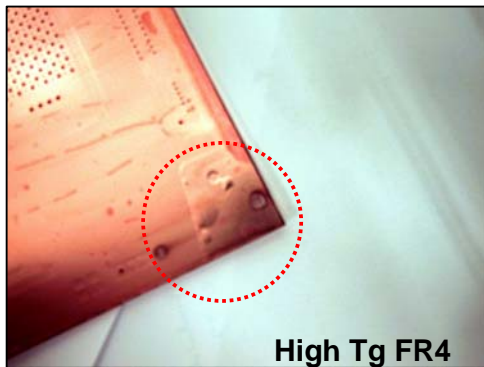
Table 5

Material	Description	Tg	Blistering	Coverage
Isola Duraver 104	FR4 Epoxy	135	No	✓
Isola Duraver 114	Higher Tg FR4 Epoxy	150	No	✓
Isola Duraver 117	High Tg FR4 Epoxy	> 160	No	✓
Isola Duramid 115	Aramid / Epoxy	150	No	✓
Isola Duramid 156	FR4 Halogen Free	>150	No	✓
Isola FR408	Low CTE/D _k	180	No	✓
Isola IS410	CAF Resistant	170-180	No	✓
Isola P97	Polyimide	>260	No	✓
Isola Gigaver 210	APPE	>175	No	✓
Nelco N4105-6FC	High Tg FR4 Epoxy	175	No	✓
Nelco N4000-13	Low CTE/D _k	210	No	✓
Nelco N4103-13	Low CTE/D _k	210	No	✓
Nelco N6000	APPE	210	No	✓
Hitachi LX-67	Cyanate Ester	185	No	✓

Improvements in hole wall pull away just by changing to the new **Printoganth P** electroless copper



Improvements for blistering on exposed bare resin on panel surfaces just by changing to the new **Printoganth P** electroless copper



CONCLUSIONS

The use of high Tg and high technology materials will continue to rise due to the increased demands of the electronics industry. This trend leads to increased difficulties in processing and the possibility of hole wall pull away. The preparation of hole walls for the subsequent metallisation process has some effect on reducing hole wall pull away but for the most demanding laminate materials the benefits of permanganate desmearing are limited. To reduce the amount of hole wall pull away the metallisation process has to be carefully chosen. The most commonly used metallisation process is electroless copper and it

has been proven that this step has a direct influence on hole wall pull away. To reduce the occurrence of hole wall pull away the choice of electroless copper should be a major consideration. When choosing an electroless copper process we must consider; the internal stress of the deposit, the uniformity of the deposit, the crystal structure and from these the ability to reduce blistering and hole wall pull away. A specifically engineered process **PRINTOGANTH P** or **PRINTOGANTH PV** from Atotech is one such electroless copper process that has proven results on the highest technology materials available today.