Reliability Testing of Oxides and Oxide Alternatives for Inner Layer Bonding

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In order to bond pre-preg resin to inner layer copper circuitry, the copper must have some form of barrier coating on it, or the package will delaminate when exposed to soldering temperatures. The predominant technology since the beginning of multilayer fabrication has been copper oxide conversion coatings created by solutions containing sodium or potassium hydroxide, and chlorites as oxidizers. The original formulations were derived from brass and bronze finishing. Oxide technology has gone through a tremendous amount of refining in the last twenty years, and many variations have been developed, but in the end the coating itself always consisted of some mixture of cuprous and cupric oxides. In the late 1990's, a consensus emerged that oxide technology had been taken as far as it was going to go, and an intense effort was put into the development of replacement technologies.

Several different oxide replacement technologies are now available commercially. The most widely accepted technology uses hydrogen peroxide and sulfuric acid to etch the copper surface; while other additives in the system, typically azoles or amines, react with the copper to form an organometallic conversion coating. Roughly 20% of inner layers are now made with oxide alternatives.

In order to convert from oxide to the new coatings, some qualification testing needs to be done to convince both the board fabricator and his customers that the new process will produce reliable parts. From the supplier's point of view, understanding the market's criteria for acceptance is essential to designing and developing a new process. Unfortunately, there is no industry consensus at all on conversion coating requirements. When we researched this issue, we not only found that the tests required varied enormously from region to region and customer to customer, but also found that opinion was just as varied as to what the tests meant, and what the target values should be. We have been able to cope with the situation by running qualifications one fabricator at a time, but the whole experience clearly illustrated the need for the industry to re-examine the issue of requirements for bond-promotion conversion coatings. We will discuss what we have found across the industry, show how the number of tests can be dramatically reduced, and offer insight into how rational acceptability requirements can be determined.

Some of the more commonly referenced tests, with comments on their applicability to inner layer conversion coatings:

1. **Peel strength (IPC-TM-650 2.4.40):** Peel strength testing requires a special test vehicle, wherein bare copper foil is coated, then pressed coated-side down onto prepreg. The foil side is imaged etched after lamination, to create a strip, which can be pulled off by a pull tester apparatus such as the Instron. The best feature of this test is that it directly, quantitatively measures adhesion of coated surface to prepreg. The negative aspects are:

- The test vehicle is not necessarily representative of an actual board
- The foil does not see all of the processes that an actual core would see
- Peel strength is strongly influenced by a number of factors besides the conversion coating, such as resin variety, resin content of prepreg, humidity, press cycle, and the metallurgy of the copper foil
- High peels are no guarantee against subsequent delamination, nor are low peels necessarily a sign of problems

2. **Acid resistance:** Acid resistance tests are used to predict bonding quality by applying mineral acid, typically dilute hydrochloric or dilute sulfuric, directly to the conversion coating, and measuring the time required for the coating to disappear and expose bare copper. They can be performed on both test pieces and actual production cores, by line operators or lab technicians, and take only a few minutes. The problem is that these tests have predictive value only for DMAB-reduced oxide coatings. There is no benefit to doing them on other oxide variations, or on non-oxide conversion coatings.
3. **Thermo-mechanical analysis (TMA, T-260(IPC-TM-650 2.4.24.1), T-280 or T-300):** The thermo-mechanical analyzer can be programmed to run the T-260 test, or the newer T-280 or T-300 tests, as well as being used to determine the T_g .of the cured laminate. TMA measures the change in z-axis dimension of a small "plug" of sample board as a function of temperature. In the T-260 test, the sample includes a bonded inner layer. The sample is subjected to a controlled rate of temperature rise to 260 C, and then held at that temperature until a sudden, irreversible change occurs in size. The time it takes for this to occur after 260 C is reached is recorded as "time to delamination". For T-280 or T-300, everything is the same except for the hold temperature, 280 or 300 respectively. The test can be run on actual production parts, and the sudden dimensional change usually is inner layer delamination. The test process does bear some relation to what happens in fabrication and assembly. However:

- The strongest influence on the values obtained is the resin type
- Results are sensitive to the construction, including glass type and resin content of prepregs and cores
- The assumption about inner layer delamination is not always correct, nor can it easily be verified
- The presence of water or other volatile substances anywhere in the sample will strongly influence the results

- The board has to be close to completely fabricated before the test can be run

4. **Repetitive thermal stress followed by cross-sectioning (IPC-TM-650 2.4.13.1):** There are countless variations on this theme, involving solder pots and/or hot air solder leveling (HASL) machines, different temperatures, different dwell times, variable number of repetitions, floats vs. immersions, and various other parameters. The objective is always the same, however: Verify that a sample of finished circuit board will survive sufficient thermal stress beyond that expected at assembly and/or rework, so that the fabricator and assembler is assured of no delamination or other defects at assembly, that are observable visually or by micro-section. The strength of this test is that it directly simulates assembly soldering. The negatives:

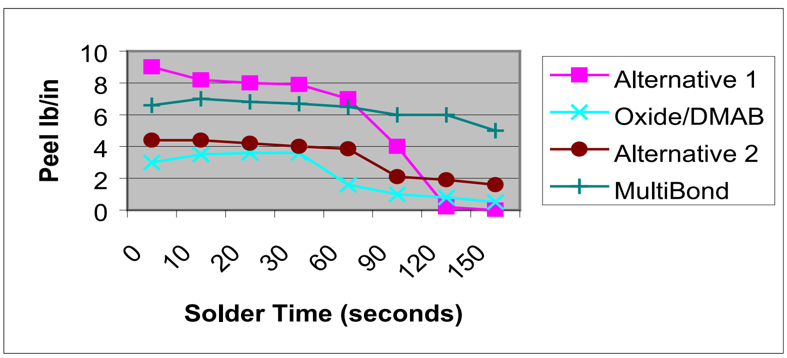
- It has to be run on a finished board
- It's time-consuming
- It is qualitative rather than quantitative
- It is sensitive to construction, resin types, and a host of process parameters unrelated to the conversion coating process

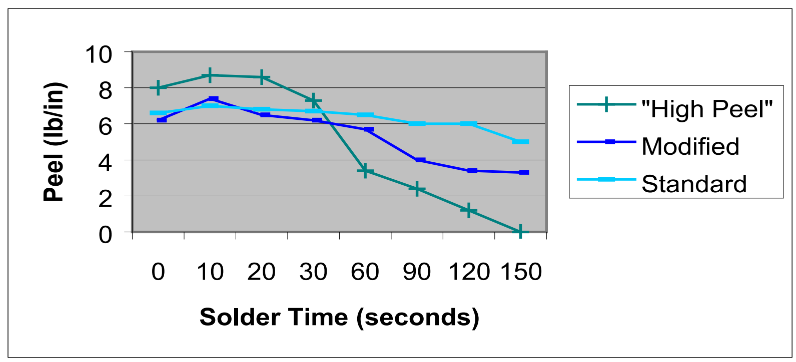
5. **Thermal shock, followed by cross-sectioning (IPC-TM-650 2.6.7):** This test involves subjecting a sample board to a specified number of temperature excursions between high and low extremes, such as ⁻65 C to 125 C, and then evaluating its condition. Observations relevant to inner layer bonding are observed by microsectioning. While these are rigorous tests of overall board reliability, particularly for the extreme environments of military and aerospace applications, they are extremely time consuming and expensive, and have not shed any new light on the quality of conversion coatings.
6. **Steam aging (UL Test 796; MIL-STD-202F), followed by cross-sectioning; Pressure cooker, followed by cross-sectioning(IPC-TM-650 2.6.16):** Both tests involve degrading a sample board with a combination of heat and humidity. Neither test has brought out bonding vulnerabilities not detectable with simple thermal stress, and therefore have not shown themselves to be worth the additional time and trouble when evaluating conversion coatings.
7. **Fluidized sand bed testing; hot oil testing(IPC-TM-650 2.4.6):** The sand bed and the hot oil are both alternate ways to apply thermal stress to a sample board without using solder, which eliminates copper dissolution into the solder. Various cycles can be used. Neither test has determined the bonding quality as well as the use of solder-based thermal stress.

To summarize, the best current test method for conversion coatings is to build a board, subject it to repetitive solder shocks, and try to decide how many shocks the board has to pass without delaminating. This is qualitative, fairly time-consuming, construction-specific, and cannot be used for timely evaluation of production; but it does assure that the board will not delaminate in assembly. A faster way of determining the bond-promotion quality of the coating is needed for in-process evaluation, and a quantitative test which would predict the outcome of thermal stress would greatly simplify the qualification and acceptance process.

Looking over the tests on our list, we find that the only test (other than the coating-specific acid resistance test) which doesn't require making a finished board is peel strength. As a quantitative, direct measure of adhesion, it should tell us everything we need to know if we control the fabrication of the test vehicle properly. Why doesn't it? More specifically, why doesn't peel strength correlate to delamination under thermal stress? And why is a 1.5 lb./in. peel more than adequate for polyimide resins, while 5-7 lb./in. is expected for multifunctional epoxies?

The answer to these questions is that peel strength changes during thermal stress. Usually, it drops, particularly with lower T_g resins that degrade rapidly at solder temperatures, but it often rises before falling again. Therefore, the value that matters is the peel strength at the last high-temperature thermal excursion, normally the final IR or wave solder assembly process. That value is *cannot* be extrapolated from the peel strength taken immediately after lamination. Below are graphs showing why. The graphs plot peel strength vs. immersion time in solder at 288 C. All samples were made from the same lot of 1-oz. foil, and pressed with identical cycles to 5 plies of Nelco 4000-2 resin on 1080 glass. The data shown on the left were generated from foils sent to various production shops worldwide for conversion coating, and then returned to MacDermid for lamination and testing. The data shown on the right are from an internal MacDermid study.

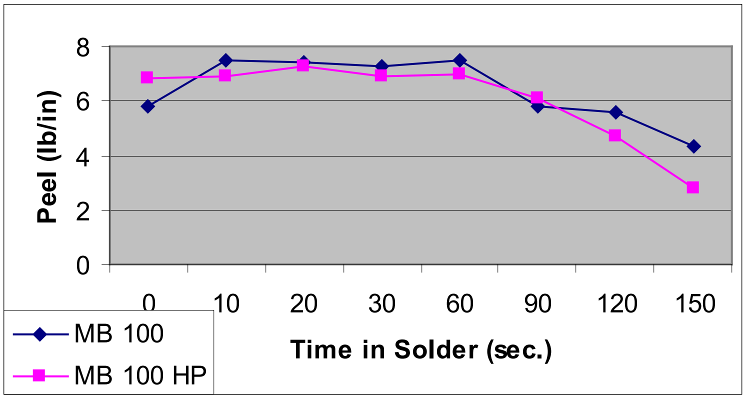




3 Variations of an Oxide Alternative | **Production Bath Samples**

The left-hand graph shows how dramatic the differences in peel strength degradation can be from one process to the next. The "Alternative 1" sample is very typical of oxide alternative processes which have been optimized for unsoldered peel strength alone. Attempts to raise the initial value very high (with this resin and test vehicle, over 7 lb./in.) invariably result in rapid degradation after 60 seconds solder immersion.

The right-hand graph shows the effects of modifying the bath make-up. The "Modified" formulation was acceptable when evaluated to 20 seconds solder immersion, but the peel strength of it degraded faster than the standard make-up when the solder time was extended. The "High Peel" variation was tested to validate early field claims of higher peel strength. The claims were valid, but the price to be paid in reduced solder resistance was shown to be unacceptable, and this particular variation was abandoned. The graph below shows a safer way to obtain somewhat higher initial peel strengths:



This test procedure has allowed us to correlate blistering and delamination with peel strength. The test pieces will typically start to delaminate when the peel strength drops below 0.5 lb./in. Problems can sometimes be seen with difficult, highly stressed constructions when the matching peel strength is 0.5-1.0 lb./in. In the course of these studies, we have not seen delamination occur with matching peel strength over 1.0 lb./in. Extending the solder time beyond 150 seconds is not reasonable for most resins, as substantial degradation and charring is evident with most of them at that point. More differentiation could be seen with polyimide and other high temperature resins past 150 seconds, but it does not appear currently that anyone needs their boards to survive more thermal stress anyway.

A final observation is that all Designs of Experiments for oxide alternatives that we have run since we developed this procedure point to the same formulation optima *regardless of resin system* if the extended thermal stress data are used as responses. Different resins will appear to require different formulations if initial peel strength is used. This finding has made it possible to minimize formulation variation, and allows the fabricator to run multiple resin systems with the assurance that all product will be reliable.

The real utility of peel strengths to evaluate inner layer conversion coatings and lamination processes is now apparent. Peels do predict bonding quality if they are measured after relevant thermal excursions. It is entirely reasonable that polyimide constructions hold together at 1.5 lb./in. peel, as those peels won't drop much (and may rise!) after thermal stress. We can also see how very high initial peels may fall so fast that the construction delaminates.

Specifications can be set in a rational way if they are based on:

1. The resin system and glass style to be used, which dictate the test vehicle construction.
2. The amount of thermal stress the circuit board is expected to survive. 60 seconds, roughly equivalent to 6 X 10 second solder floats, seems to be adequate for much of the industry.
3. The minimum peel strength (our suggestion is 1 lb./in.) required after the specified thermal stres

Conclusions:

The use of thermally stressed peel strength test vehicles can be the basis for valid specifications for inner layer conversion coatings, and lamination cycles as well. The values obtained will accurately predict the resistance of circuit boards made with those processes to thermally-induced delamination. Standardization of test vehicles is possible, and different specifications for specific resin types and industry application classifications should be made.