Quantifying Performance of Mechanical and Chemical Processes for Pre-Treatment Prior to Solder Mask Application

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Introduction

The electronics industry is continuously evolving, primarily due to advancements in technology and miniaturization. However, such progress poses ever-increasing challenges to the manufacturer of printed wiring boards (PWB), especially with regard to products fabricated for ultra-high-density assembly. For such multilayer boards, solder mask adhesion has become a key consideration. Traditionally, such surface preparation has been accomplished by mechanical means, such as pumice/aluminum oxide treatment or brushing. However, several factors are causing PWB manufacturers to consider alternatives, using chemical treatment as opposed to mechanical methods. The driving force behind these changes is the assembler, who requires compatibility between various solder masks and selective finishes. Current mechanical and chemical pretreatment methods exhibit compatibility issues with various selective finishes, often resulting in defects by blistering and localized lifting of the solder mask. As such, a new and advanced solder mask pretreatment process is required – one that offers the PWB manufacturer the capability and flexibility to meet the stringent requirements of their customers.

This paper examines and quantifies both mechanical and chemical solder mask pre-treatment processes. The comparison clearly identifies the notable performance improvements achieved with this new, advanced chemical pre-treatment process.

Background

The underlying reasons for loss of solder mask adhesion are well known within the PWB fabrication and assembly sectors:

- An obvious failure mechanism is the presence of surface contaminants that prevent proper adhesion between the solder mask and copper surface. Generally, it is necessary to have a proper pre-cleaned surface prior to solder mask application.
- Extended immersion times and high temperatures of selective finish processes, such as electroless nickel/immersion gold (ENIG) and immersion tin, may contribute to solder mask peeling. Furthermore, certain ingredients, such as methane sulfonic acid and thiourea used in the immersion tin chemistry, can be aggressive to the solder mask.
- During the immersion tin process, a replacement reaction occurs between copper and tin, thereby reducing the thickness of the copper circuitry. This condition provides an access path for the chemistry to creep between solder mask and copper surface. Therefore, higher surface adhesion may be required for immersion tin-treated boards in comparison to that required for hot air solder leveling (HASL) or ENIG. For immersion tin, in addition to a compatible solder mask resin, the surface roughness is often a key factor to prevent solder mask peeling.
- Another failure mechanism lies in the formation of copper oxide on the surface during the solder mask process steps. During subsequent selective finish processing, these copper oxide layers are easily removed and thereby cause loss of adhesion.
- The solder mask itself can be a source of adhesion loss. During the immersion nickel step of the ENIG process, atomic hydrogen is released which can react with residual carboxylic groups found in the solder mask, thereby deteriorating the solder mask. The atomic hydrogen can also react with residual contaminants on the copper surface, leading to spot peeling. The presence of residual carboxylic groups can be minimized by optimizing the photopolymerization and thermal curing procedures.

A new and advanced chemical pre-treatment process has been demonstrated to be suitable for use with all commonly used surface finishing methods. Commercially known as Adhere™, the process is fully compatible with HASL, ENIG, immersion tin, and immersion silver final finishes. This compatibility is achieved by providing both mechanical and chemical bonding between the treated copper surface and the solder mask. Mechanical adhesion is provided through the surface structure, since a properly roughened surface provides anchoring points for the solder mask. However, an overly rough structure can lead to reduced solder mask adhesion. By nature, solder mask is relatively viscous and therefore can not flow into very deep and narrow crevices, creating air gaps. This entrapped air may cause solder mask lifting, which can result in failure of the product. Therefore, a suitable pretreatment process will provide sufficient surface and sidewall roughness without causing air entrapment. Ideally, it should also remove all surface contaminants and provide an organic coating which acts as an adhesion promoter and an anti-tarnish. The Scanning Electron Microscopy (SEM) and Atomic force microscopy (AFM) images in Figures 1 through 6 illustrate the surface topographies created by the more traditional pretreatment processes.

The most commonly used solder mask pretreatment processes are mechanical in nature, including pumice-scrubbing, pumice jet, and brushing. These methods improve solder mask adhesion by removing surface contaminants and providing a roughened surface for adhesion.

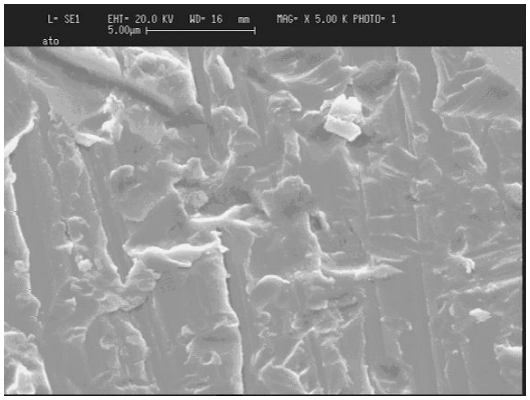


Fig 1 – SEM Image of Sample Treated with Pumice (5000X)

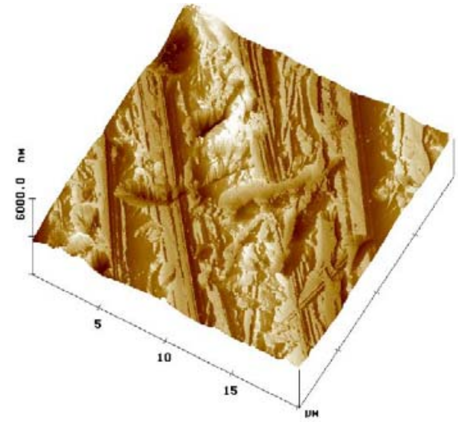


Fig. 2 - AFM Image of Sample Treated with Pumice (Size 20 µm x 20 µm)

Disadvantages with such mechanical treatment methods are the possibilities of trapping particles in via-holes, damaging the fine structures and/or substrate, and insufficient roughening of the sidewalls.

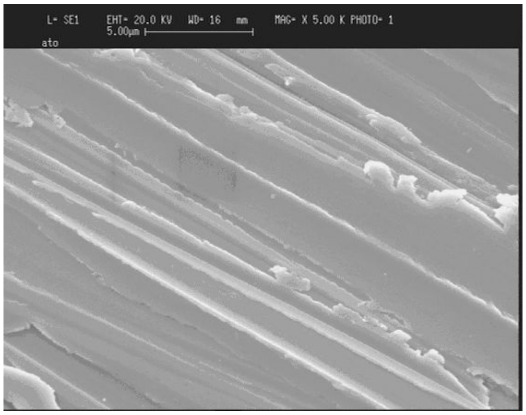


Fig 3 – SEM Image of Sample Treated by Brushing (5000X)

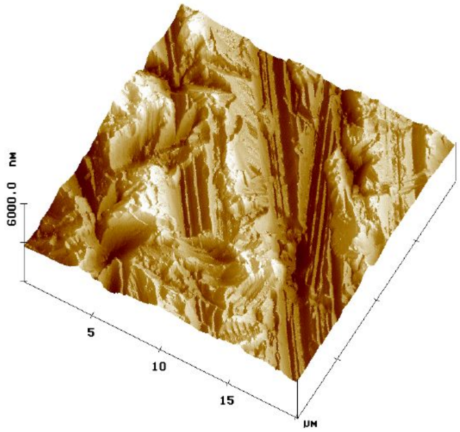


Fig. 4 - AFM Image of Sample Treated by Brushing (Size 20 µm x 20 µm)

For HASL final finishing these mechanical methods may be sufficient to obtain suitable solder mask adhesion. However, for more advanced selective finishes (i.e. ENIG, immersion tin, or immersion silver), they often encounter limitations.

Chemical pre-treatment processes are typically micro-etchants which remove surface contaminants and provide surface roughening. Advantages of chemical pre-treatment processes are:

- Cleaning and roughening of surface and side-walls
- Surface structure can be optimized by additives
- Possibility of addition of anti-tarnish and chemical adhesion promoters

- No damage of fine structures
- No damage of the substrate

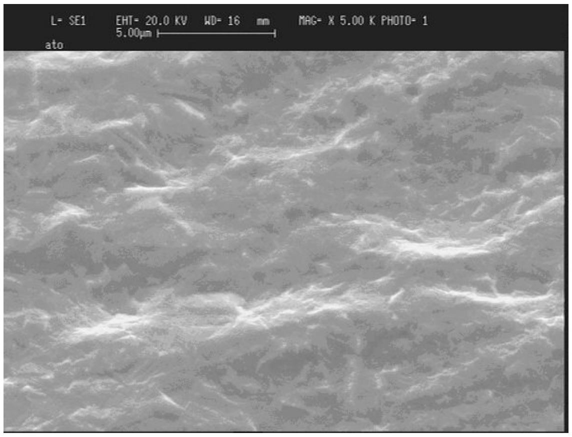


Fig 5 – SEM Image of Sample Treated with Persulfate (5000X)

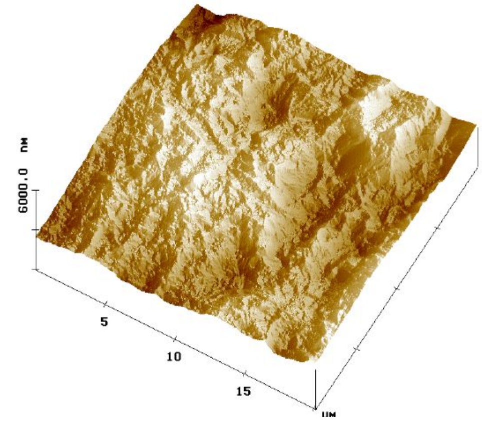


Fig 6 – AFM Image of Sample Treated with Persulfate (Size 20 µm x 20 µm)

The most commonly used chemical pre-treatment processes are sodium persulfate and sulfuric acid/hydrogen peroxide micro-etchants. These processes have very low operating costs, but provide only a “macro” roughened surface that is easily oxidized (Fig 5 and 6).

As an alternative, the new and innovative process is a modified sulfuric acid/hydrogen peroxide micro-etching process that achieves a high surface roughness by providing both “macro and micro” structures.

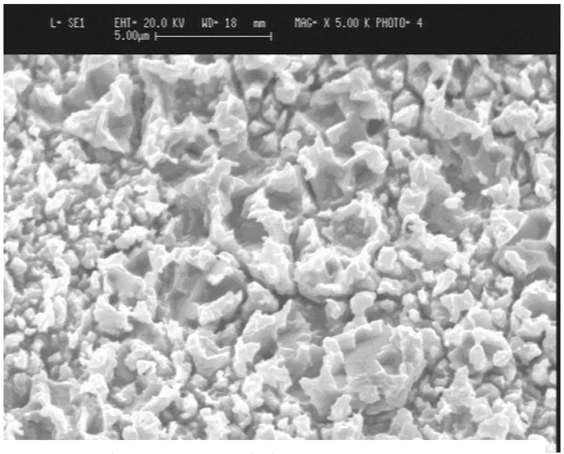


Fig. 7 – SEM Image of Sample Treated with Adhere™ (5000X)

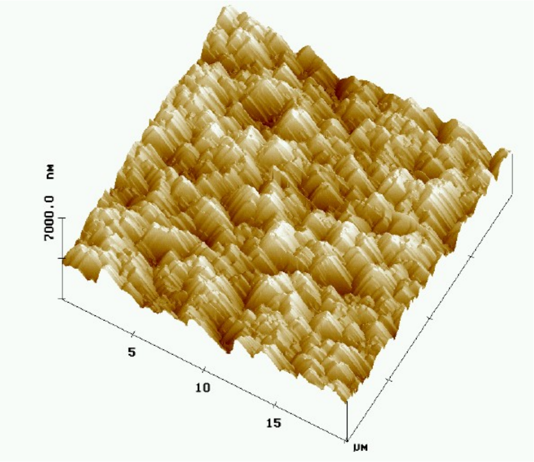


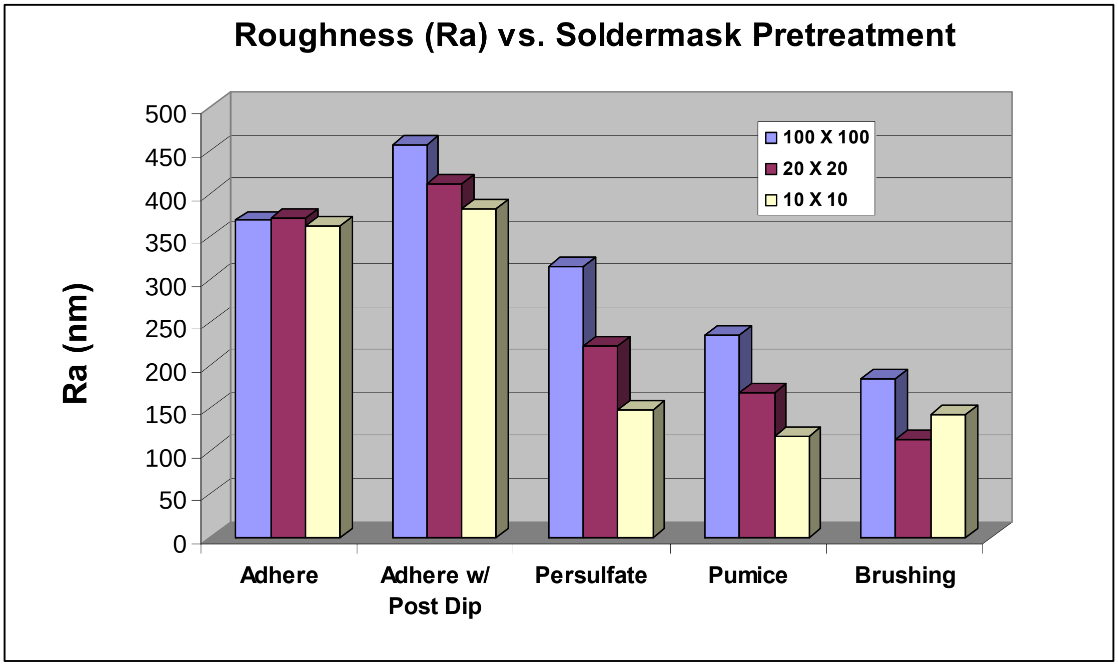
Fig. 8- AFM Image of Sample Treated with Adhere™ (Size 20 µm x 20 µm)

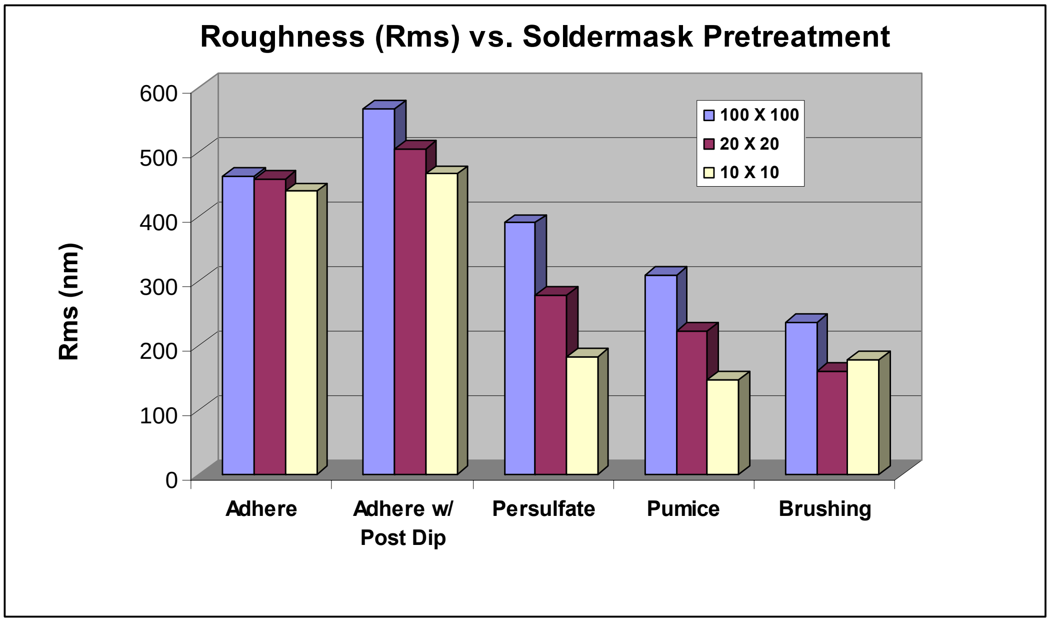
A corrosion inhibiting coating is also deposited on the copper surface, which greatly reduces the chance for oxidation. The surface structure created by this process provides excellent adhesion of solder mask upon subsequent exposure to aggressive chemical processes, such as immersion tin or ENIG. Each process step plays an important role in creating the desired copper surface. The process consists of three basic steps: (1) Clean, (2) Adhere™ (etch) and (3) Post Dip. The etch solution creates a very even (but extremely thin) organo-metallic coating on the copper surface. As a result of this coating, the copper is selectively etched along its grain boundaries to produce the desired topography. In the Post Dip step, this coating is then removed, creating the light color desired prior to solder mask application. However, the anti-tarnish function still remains on the copper surface. The SEM and AFM images in Figures 7 and 8 illustrate the surface topography created by the Adhere™ process, emphasizing both “macro-” and “micro-” roughness that is achieved.

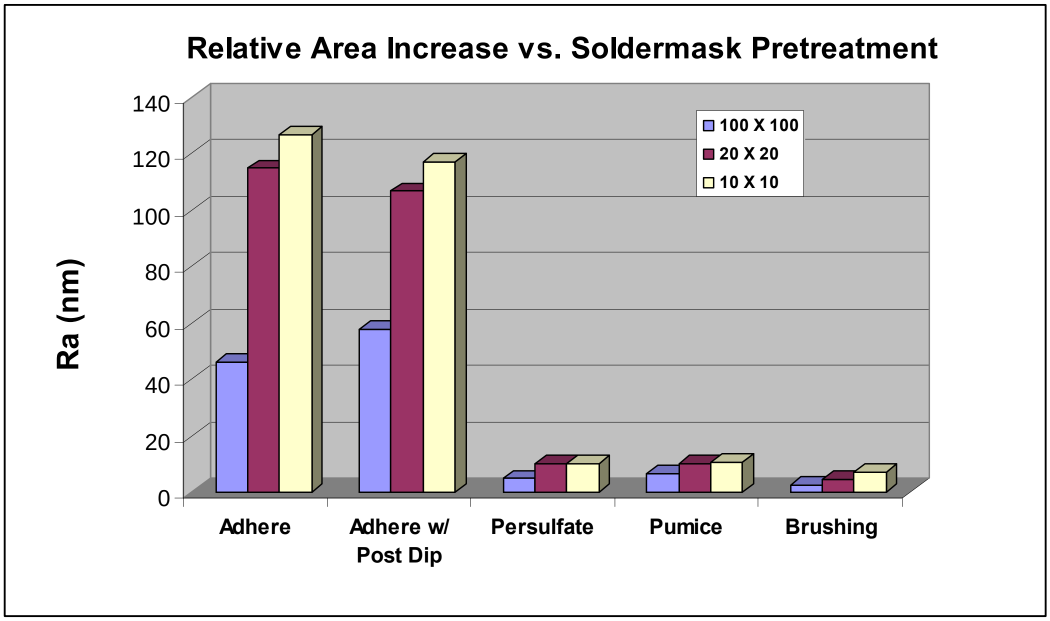
The AFM is a valuable tool for obtaining detailed information about surface topography and roughness. Because of the two-dimensional information obtained, SEM images can only provide an indication of the surface topography. However, AFM is able to provide precise three-dimensional images and highly accurate values for the surface roughness and surface area.

The AFM imaging is limited by the probe size. The typical opening angel is approximately 40 °C. If the surface is composed of structures with very steep side walls, not only the tip of the tip of the probe but also the side faces of the probe will be in contact with the sample. The Adhere™ samples are characterized by a significant micro-roughness with side walls of the individual structures being steeper than 70 °C.

The results of the AFM investigations are summarized in the following charts for several different solder mask pretreatment processes. The first two charts show two different roughness measurements (Ra and Rms) for the three different sample sizes (100 µm X 100 µm, 20 µm X 20 µm and 10 µm X 10 µm). The third chart shows the relative increase in surface area for the different pretreatment processes, again an indication of the presence of both “micro“- and “macro”-roughness.







Testing

The most common test method for evaluating solder mask adhesion is the so-called tape test (IPC-TM-650 2.4.28.1). The tape test is conducted after the final finish treatment by applying an adhesive tape to the solder mask surface and then abrubtly removing it. The tape and the board are then inspected for solder mask lifting along the copper traces. Examples of tape test results after immersion tin processing are shown in Figures 9 and 10. Figure 9 shows a typical tape test result for failed solder mask adhesion, with solder mask peel-off along the complete circuitry pattern. By comparison, Figure 10 shows perfect solder mask adhesion without a single spot of solder mask lifted.

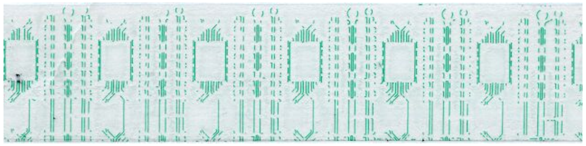


Fig 8 - Tape test result for failed solder mask adhesion

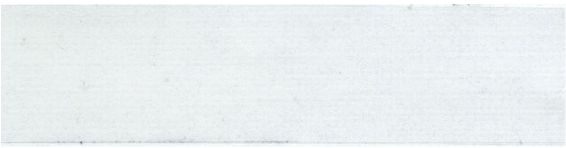


Fig 9 - Tape test result for perfect solder mask adhesion

This test provides a qualitative, but not quantitative analysis of the solder mask adhesion.
Stud pull tests are used in the coating industry for adhesion testing and provide quantitative results. The same technique was used in an attempt to obtain a quantitative measurement of the solder mask adhesion dependent on the pretreatment process. The equipment used was a Quad Group Romulus Multitester. The 0.66-mm studs are coated with an epoxy that must be cured at 150 °C for 60 minutes after attachment to the sample. For these tests, several DC plated inner layers were used. The test consisted of the following:

- Untreated sample
- Persulfate microetch panel
- Adhere-treated panel (w/Post Dip)

After treatment, the panels were screen-coated with Vantico 77S solder mask. The panels were then treated through the complete solder mask process, except no artwork was used for the printing and, therefore, the entire surface area was exposed. The studs, together with a ceramic support backing to prevent bending during the test, were mounted onto the samples using a spring-supported mount before the final curing step (to prevent over-curing of the solder mask). After the curing and cool-down, each sample was tested with the Romulus tester. The failure was always checked to ensure that adhesive failure between the solder mask and the copper surface occurred. In all cases, the failure was adhesive-related (i.e. the solder mask was completely lifted off the panel). As shown in Figure 11, the stud pull data shows on average a slightly higher pull strength for the Adhere™ treated samples, compared to persulfate and untreated plated copper samples.

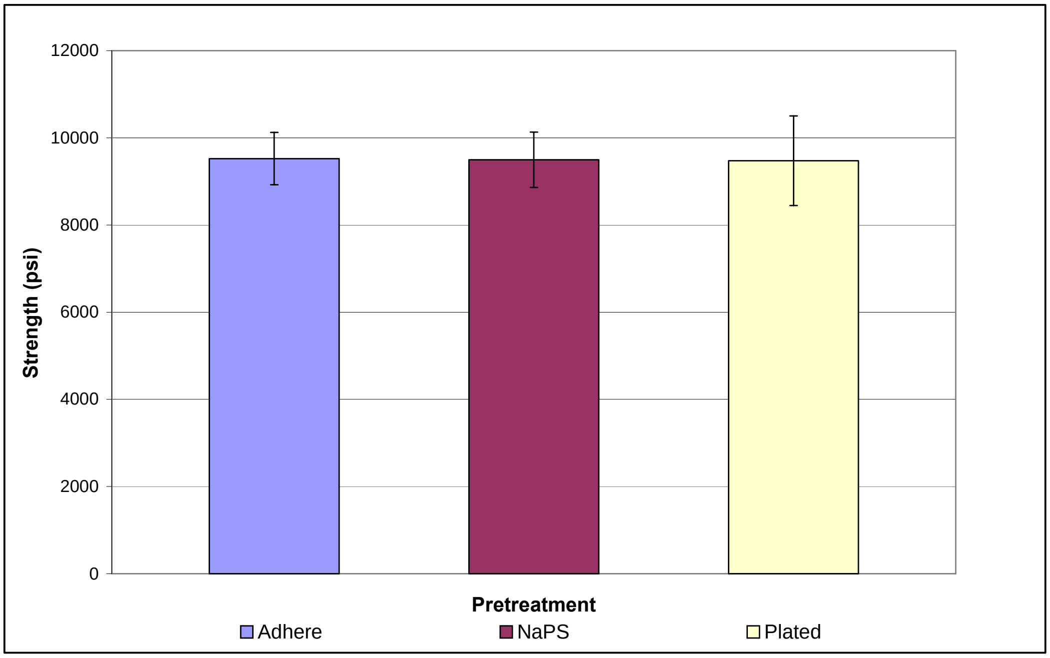


Fig 11 – Stud Pull Test Results

This slight increase is negligible, especially considering the standard deviation shown as error bars for the three tested sample types. Changing the parameters on the Romulus did not provide further insight. Furthermore, aging the samples at 100 °C for 140 hours did not change the pull strength results. In contrast to this pull strength data, conducting simple tape tests (after ENIG and immersion tin) on panels treated in the same way shows very significant differences in the various treatment processes. For both processes, immersion time and temperature were maximized according to the technical data sheet parameters. After immersion tin, the solder mask on untreated and persulfate-treated panels literally fell off, while the Adhere™ treated panels showed no peeling. This indicates that the measurable pull strength is not necessarily the factor in evaluating the solder mask adhesion to ensure compatibility of a pretreatment process with the various surface finishing processes.

To compare the different mechanical and chemical pre-treatment processes, it was necessary to re-evaluate the standard tape test. The test was conducted in two ways: (1) with a conventional circuit pattern for subjective evaluation, shown in Figure 12a and (2) with an artwork pattern that would permit a quantitative evaluation, shown in Figure 12b. The rating scale for the tape testing of the circuit pattern ranged from zero (representing no peeling) to five (representing complete or near-complete peeling). The pattern chosen for quantitative evaluation consisted of columns of different diameter (i.e. 50-, 75-, 100- and 125-µm). The artwork chosen was a pattern including four 20x20 column grids of both 50- and 75-µm columns (see patterns below). The tape test results for the column patterns were obtained by simply counting the number of columns lifted with the aid of a microscope.

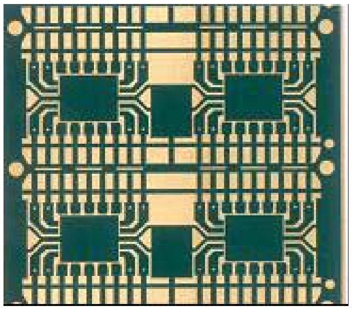


Fig 12a – Image of Circuit Pattern Used for Tape Test

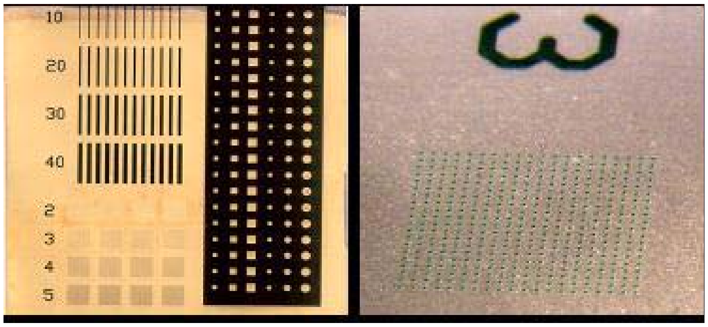


Fig 12b – Image of Column Pattern Used for Tape Test

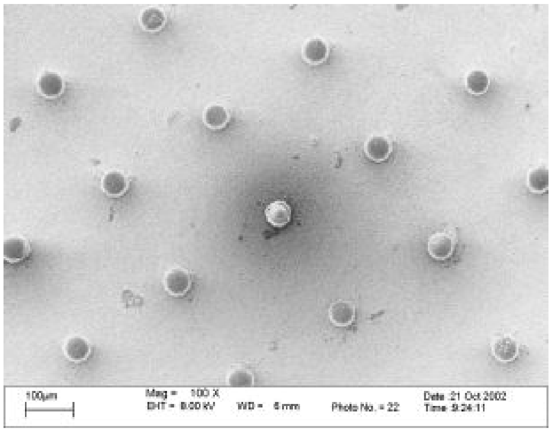


Fig 13 – SEM Image of 75-µm Column Pattern

Fig 14 – SEM Image of Single 75-µm Column

Panels were treated via the various mechanical and chemical pretreatment processes and the complete solder mask process. The samples were then processed through different selective finishing processes and subjected to the tape test (IPC-TM-650 2.4.28.1). The panels treated with Adhere™ showed no peeling, thus verifying the effectiveness of the new process as a solder mask pre-treatment. As shown in Table 2, testing of the Adhere™ treated samples was performed for solder masks supplied by several manufacturers.

Table 2 - Tape Test Results for Adhere™ (75-µm column)		
		Tape test

Solder Mask	Selective finish	Pattern Rating[1]	Columns Lost[2]
Taiyo PSR 4000 G23K	Immersion Tin	0	0
Taiyo PSR 4000 BN	ENIG, Immersion Tin	0	0
Taiyo PSR 4000 Z-26	ENIG, Immersion Tin	0	0
Vantico Probimer PR 77S	ENIG	0	0
Peters Elpemer SD 2467 SG-DG	ENIG, Immersion Tin	0	0
Eternal EC7800	HASL	0	0

1 Range of 0 to 5 **2** Total number of columns = 1,600

For purposes of comparison, Table 3 presents similar results of testing adhesion of one solder mask with different pretreatment processes. Testing was performed for both ENIG and immersion tin as the selective finish.

Table 3 - Tape Test Results for Alternative Pretreatment (75-µm column)
Solder mask tested: Peters Elpemer SD 2467 SG-DG

Solder Mask	Selective finish	Tape test	
		Pattern Rating[1]	Columns Lost[2]
Adhere™	ENIG	0	0
Adhere™	Immersion Tin	0	0
Persulfate	ENIG	1	< 23
Persulfate	Immersion Tin	5	1,600
Pumice	ENIG	0	0
Pumice	Immersion Tin	1	1120
Brushing	ENIG	0	18
Brushing	Immersion Tin	2	1300

1 Range of 0 to 5 **2** Total number of columns = 1,600

During the investigation, it was determined that the 50-µm columns are too fine for such solder mask adhesion testing. Even following treatment with Adhere™, many of the 50-µm columns failed the test; although panels treated by the other techniques did not have one single 50-µm column remaining.

Performance Reliability Testing

Adhere™ has been thoroughly tested with respect to its performance reliability. As shown in Table 3, Adhere™ passes the required thermal reliability testing in accordance with criteria established by the IPC test methods. Additional reliability testing was performed by an independent laboratory and is summarized in Table 4.

Table 3 – Thermal Reliability Testing Results

Test	Method	Criteria	Results
Solder Shock	IPC TM 650 2.4.13.1	>6 cycles No Delamination	>6 Cycles No Delamination
Thermal Shock	IPC TM 650 2.6.7.2	>100 Cycles no Delamination	>250 Cycles
Pressure Vessel with Solder Shock	IPC TM 650 2.6.16	No Delamination	No Delamination

Source: Atotech Customer Results

Table 4 - Reliability Testing Results

Test	Method	Criteria	Results
Surface Insulation Resistance (SIR)	IPC-B-25 “A” comb patterns 85°C/85% RH 500 hours 50VDC Bias and Measurement Voltage	> $5.0x10^{8}$ Ohms	All >$1.5x10^{9}$ Ohms
Resistivity of Solvent Extract	IPC-TM-650 2.3.25C	< 1.56 µgNaCl/cm^{2}	<0.2 µgNaCl/cm^{2}
Electromigration Resistance	IPC-TM-650 2.6.14.1	< one degrade reduction in resistance	Passed

Source: Trace Laboratories

Conclusion

A new pretreatment process for improved solder mask adhesion has been developed and introduced in response to limitations exhibited by traditional methods. SEM and AFM investigations have shown a significant difference in the structure of the surface achieved with the new process (Adhere™) in comparison to conventional mechanically and chemically pretreated samples.

To further support these findings, tape testing was performed using the conventional tape test in a somewhat modified fashion to further measure the effectiveness of the new process. To quantitative comparisons the 75 µm column matrix was used, to compare it's performance against conventional pretreatment techniques. This method has been shown to be effective and additional investigations using the modified tape test are now planned with other solder masks.

As part of this research the stud pull testing method was also used in an attempt to quantify solder mask adhesion. Although this testing method is widely used in other industries, its use within the PWB fabrication and assembly sectors is apparently not common. Unfortunately the results of the stud pull test do not provide any distinct differentiation between the adhesion properties of the Adhere™ and the other pretreatment methods examined. Testing will continue to optimize test parameters. Nevertheless, all tests conducted so far prove the effectiveness and reliability of this new advanced chemical pre-treatment process, Adhere™.

References

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