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PTFE Wettability for Electroless Copper and Direct Metallization

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Abstract
PTFE material is very hydrophobic and among the most difficult to deposit electroless copper or direct metallization. These materials have very low friction, which makes a surface non-wettable. Plasma technology has the ability to create wettable through holes by removing fluorines from the surface, leaving the hole walls activated for metallizing. There are several process gases used to treat PTFE material. Each gas has a different effect on surface wettability. Chemical etching also changes the wettability of PTFE material by activating the surface.

Although both plasma technology and chemical etching render a wettable surface, there is a recovery time in which the PTFE material returns to its original state due to fluorine migration. This paper evaluates the results of a DOE comparing three plasma processes and chemical etching in relationship to wettability, recovery time and plating adhesion.

Background
Four processes, three plasma and one chemical etching, were applied to two types of material to evaluate surface activation (refer to Table 1). The two materials evaluated were Taconic RF35P and RF60 because their construction is commonly used in PCB manufacturing (hereinafter referred to as Material A and Material B). Sixteen panels of each type were used in the DOE.

- Material A is a ceramic-filled woven glass reinforced PTFE material. It has a Crystalline Melt greater than 315 °C and a Z CTE of 64 PPM/°C. The dielectric constant is 3.5.
- Material B is a ceramic-filled woven glass reinforced PTFE. It has a Crystalline Melt >315º and a Z CTE of 75 PPM/°C. The dielectric constant is 6.0.

Panel specifications were the same for both material types:

- Panel size: 254 x 457 mm (12 x 18 in.)
- Material thickness: 1.58 mm (0.062 in.)
- Through hole diameter: 0.508 mm (0.020 in.)
- Unclad (for surface plating)

Methodology
The activation in through holes is critical for electroless coverage; there are only a few methods to achieve good wettability. The methodology of this paper is to determine the change in surface energy and wettability over four different processes monitored for four days, to evaluate changes in recovery and their relationship to contact angle, plating coverage, adhesion, and peel strength. The purpose of testing four processes was to determine the degree of flexibility a PCB manufacturer has in processing PTFE material prior to metalizing.

Process Description
The first two processes selected were those most widely used for activating PTFE material: a chemical process using Sodium etch and a plasma process using a combination of H_2 (Hydrogen) and N_2 (Nitrogen). Since there has also been success with plasma using He (Helium) and N_2, these processes were also tested.

Since both Material A and B have ceramic and glass fillers, all plasma parameters required a two-segment process. A mix of CF_4 (Carbon Tetrafluoride), O_2 (Oxygen) and N_2 was used in the first segment to pre-treat the fillers, followed by a second segment to activate the PTFE material.

Table 1 - Summary of DOE Processes

PLASMA	GAS	FLOW	POWER	FREQUENCY	TIME
Process 1	H_2/N_2	2 SLM	4000W	40 KHz	25
Process 2	100% He	2 SLM	4000W	40 KHz	25
Process 3	100% N_2	2 SLM	4000W	40 KHz	25
Process 4	Sodium	2 min	Agitation in Sodium etch followed by an alcohol and hot water rinse		

Data Recording

All the panels of Material A and B were processed on the same day. On four consecutive days, four panels of Material A and four panels of Material B (representing the four processes) were released to plating. On each day, the panels were plated over the 4-day period, and the contact angle and surface energy data was recorded for cross-reference to plating results. The plating process used was Formaldehyde electroless copper followed by an acid-based electroplate copper with an average thickness of 18-µm (0.0007 in.).

Metrology

1. Contact Angle: the angle formed by a droplet in contact with a solid surface, measured by a goniometer prior to plating. Contact angle measurement can be used to quantify surface wetting. High contact angle (water beading) indicates that the material has a low surface energy and poor wetting characteristics. Values greater than 90° are common for untreated PTFE surfaces. Low contact angles indicate good wetting characteristics. Values below 60° can be achieved on properly treated PTFE surfaces.
2. Surface Energy: the ability of a surface to attract a liquid, measured in units of Dyne. Water has a surface energy of about 70 Dyne/cm. Untreated PTFE material has a surface energy below 20 Dyne/cm. Higher surface energies indicate better wettability. Each of the four processes has the capability of increasing the surface energy. Typically, surface energy values of 50 Dyne/cm are considered wettable.
3. Back Lighting: after all panels were plated, each was evaluated with black back lighting to determine if any of the processes had allowed voiding.
4. Plating Adhesion: the second evaluation after plating was pressure-sensitive tape testing to check for adhesion. Tape measuring 12.7 x 50.8 mm was placed on the plated surface, and then pulled in a rapid motion at a 90º angle.
5. Solder Float: following tape testing, two coupons from each panel were solder floated at 550 ºF for 10 seconds. After solder floating, the coupons were micro-sectioned and evaluated for hole wall pull-away.
6. Peel Strength: the final evaluation on each of the plated panels was peel strength. A Tinius Olsen Lo-Cap tensile tester was used to determine the peel strength with an applied range of 6 lbs. and a constant pull rate of 2 lbs/min. The peel strength data was used to compare the results of all four processes, not to establish acceptable or rejectable limits.

Results

Contact Angle Measurement

The untreated Material A and B had contact angle measurements of 100° and 105° respectively. These contact angles were in a non-wettable range. Plating coverage and adhesion were poor on the untreated materials and, as a result, the remainder of the test could not be performed on these untreated materials.

On Day 1, all contact angles for the treated Material A and B samples measured in the wettable range. Each of the contact angles values increased over the four days. On Day 4, all four plasma processes for both Material A and B had returned to the pre-treated angles. Sodium etch had the least fluctuation in contact angles in relationship to recovery. Of the three plasma processes, the H_2/N_2 segment had the lowest contact angle and took the longest to recover. (Refer to Table 2 for exact contact angles.)

Surface Energy

All Dyne measurements were less than 30 on the untreated materials, which indicates a poor surface for plating. All four processes yielded a surface energy greater than 60 Dynes on Day 1, indicating good wettability for plating. Over the 4-day period, the surface energy on the He and N_2 plasma processes changed to 30 and 40 Dynes, slightly above the pre-treated condition. The H_2/N_2 plasma and sodium process held readings of greater than 60 Dynes for all four days. (Refer to Table 2 for actual surface energy measurements.)

Back Lighting

The first evaluation after plating was performed using backlighting. All the plated through holes were examined for voiding. Even though the contact angle increased with the plasma processes over four days, there was no evidence of voids after plating. The contact angle after Sodium etch remained the same and also showed no voiding. (Refer to Table 3 for the results and to Figure 1 for the summary chart.)

Table 2 - Contact Angle Data

Gas Used: H_2 - N_2		Product	Contact Angle #1	Contact Angle #2	Contact Angle #3	Average	Standard Deviation	Dyne Test
	Day 1	Material A	20	18	30	22.67	6.43	>60
	Day 2	Material A	55	60	67	60.67	6.03	>60
	Day 3	Material A	67	67	70	68.00	1.73	>60
	Day 4	Material A	90	90	90	90.00	0.00	>60
	Day 1	Material B	50	50	55	51.67	2.89	>60
	Day 2	Material B	60	65	70	65.00	5.00	>60
	Day 3	Material B	45	50	65	53.33	10.41	>60
	Day 4	Material B	100	100	100	100.00	0.00	>60

Gas Used: He		Product	Contact Angle #1	Contact Angle #2	Contact Angle #3	Average	Standard Deviation	Dyne Test
	Day 1	Material A	78	85	90	84.33	6.03	>60
	Day 2	Material A	90	93	95	92.67	2.52	>60
	Day 3	Material A	95	95	100	96.67	2.89	>60
	Day 4	Material A	100	100	100	100.00	0.00	>40
	Day 1	Material B	96	90	96	94.00	3.46	>60
	Day 2	Material B	95	95	100	96.67	2.89	>60
	Day 3	Material B	95	95	100	96.67	2.89	>55
	Day 4	Material B	100	105	105	103.33	2.89	>40

Gas Used:N_2		Product	Contact Angle #1	Contact Angle #2	Contact Angle #3	Average	Standard Deviation	Dyne Test
	Day 1	Material A	70	70	80	73.33	5.77	>60
	Day 2	Material A	95	95	98	96.00	1.73	>50
	Day 3	Material A	90	95	100	95.00	5.00	>40
	Day 4	Material A	90	90	100	93.33	5.77	>30
	Day 1	Material B	96	98	100	98.00	2.00	>60
	Day 2	Material B	95	98	100	97.67	2.52	>60
	Day 3	Material B	95	98	100	97.67	2.52	>50
	Day 4	Material B	100	100	105	101.67	2.89	>40

Sodium (Na) Etch		Product	Contact Angle #1	Contact Angle #2	Contact Angle #3	Average	Standard Deviation	Dyne Test
	Day 1	Material A	57	60	60	59.00	1.73	>60
	Day 2	Material A	50	75	78	67.67	15.37	>60
	Day 3	Material A	60	65	60	61.67	2.89	>60
	Day 4	Material A	60	65	70	65.00	5.00	>60
	Day 1	Material B	40	40	60	46.67	11.55	>60
	Day 2	Material B	50	50	50	50.00	0.00	>60
	Day 3	Material B	62	62	62	62.00	0.00	>60
	Day 4	Material B	65	68	68	67.00	1.73	>60

Table 3 - Back Lighting Coverage Results

Gas Used: $H_2 - N_2$	Product	Coverage Results (%)	Gas Used: He	Product	Coverage Results (%)
Day 1	Material A	100	Day 1	Material A	100
Day 2	Material A	100	Day 2	Material A	100
Day 3	Material A	100	Day 3	Material A	100
Day 4	Material A	100	Day 4	Material A	100
Day 1	Material B	100	Day 1	Material B	100
Day 2	Material B	100	Day 2	Material B	100
Day 3	Material B	100	Day 3	Material B	100
Day 4	Material B	100	Day 4	Material B	100

Gas Used: N_2	Product	Coverage Results (%)	Sodium (Na) Etch	Product	Coverage Results (%)
Day 1	Material A	100	Day 1	Material A	100
Day 2	Material A	100	Day 2	Material A	100
Day 3	Material A	100	Day 3	Material A	100
Day 4	Material A	100	Day 4	Material A	100
Day 1	Material B	100	Day 1	Material B	100
Day 2	Material B	100	Day 2	Material B	100
Day 3	Material B	100	Day 3	Material B	100
Day 4	Material B	100	Day 4	Material B	100

Plating/Adhesion

In a normal manufacturing process, only the through holes require activating prior to plating. For this DOE, the material was unclad so plating adhesion tests could be done. However, this presented a bigger challenge for all four processes since the surface area required to activate was much greater. There was no copper left on the tape after the tape-pull test for all panels. Even the processes that had both recovered in contact angle and had low surface energy after four days showed good plating adhesion.

Solder Float

The most critical test for all four processes was solder floating. This is the method most commonly used by PCB manufacturers to determine the reliability of the plated through hole. Cross-sections of the through holes did not show any signs of hole wall pull away. Day 4 coupons looked as good as those from Day 1. This evaluation indicated that hole walls were sufficiently activated from all processes in order to plate a reliable hole even after recovery had occurred. (Refer to Figure 2 for cross-section photos.)

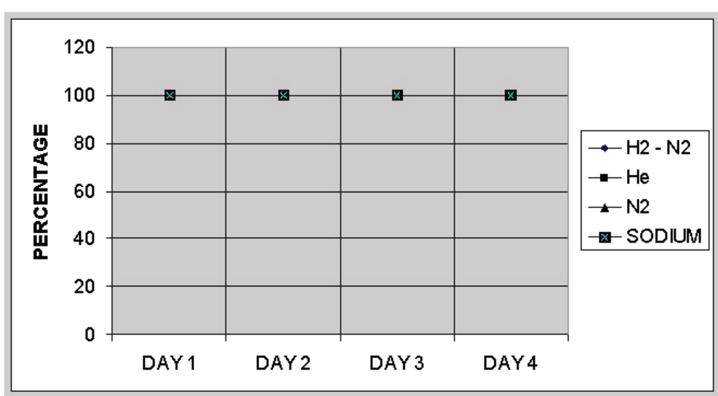
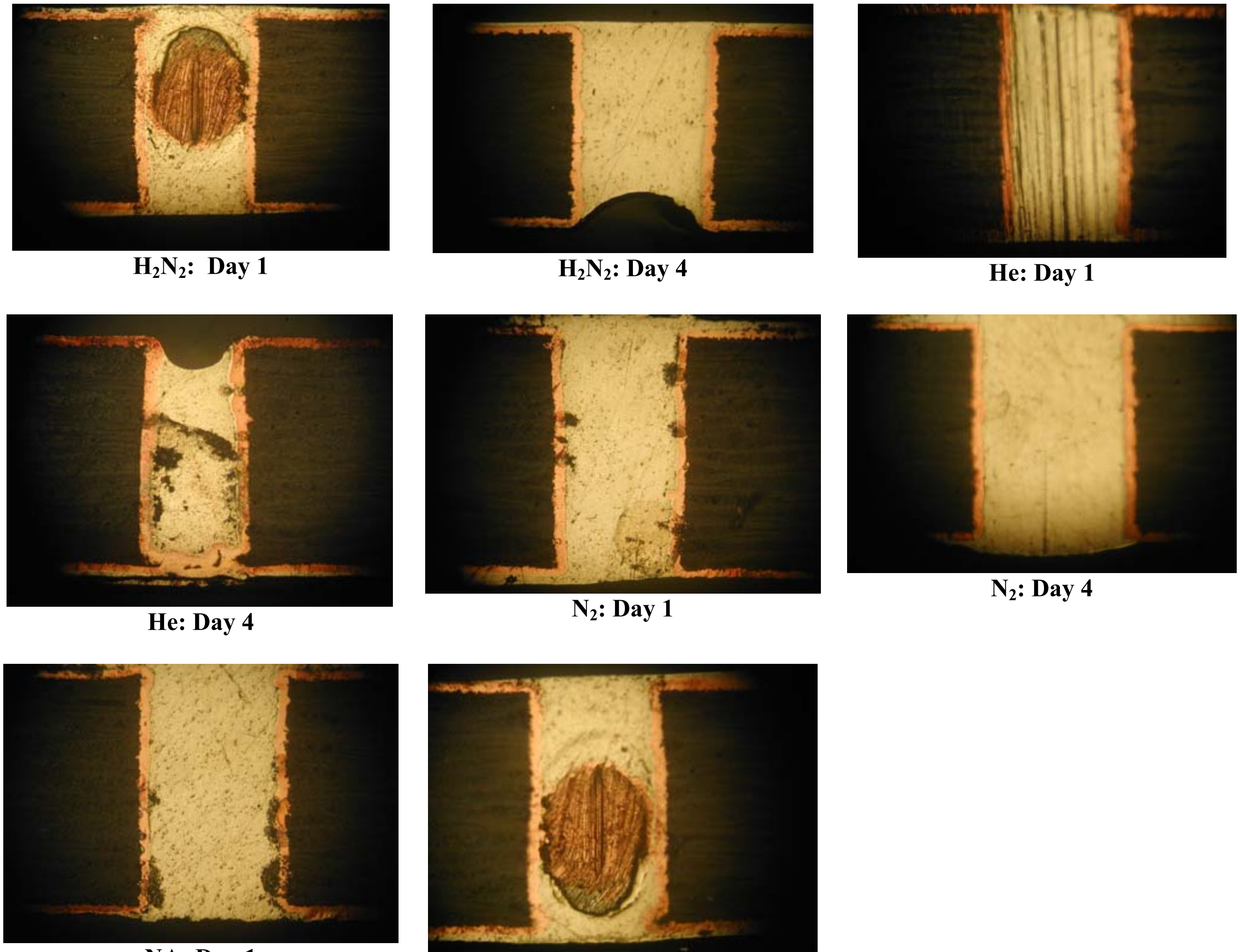


Figure 1 - Back Lighting Coverage Results



H_2N_2: Day 1 | H_2N_2: Day 4 | He: Day 1

He: Day 4 | N_2: Day 1 | N_2: Day 4

NA: Day 1 | NA: Day 4

Figure 2 - Cross Sections Following Solder Float

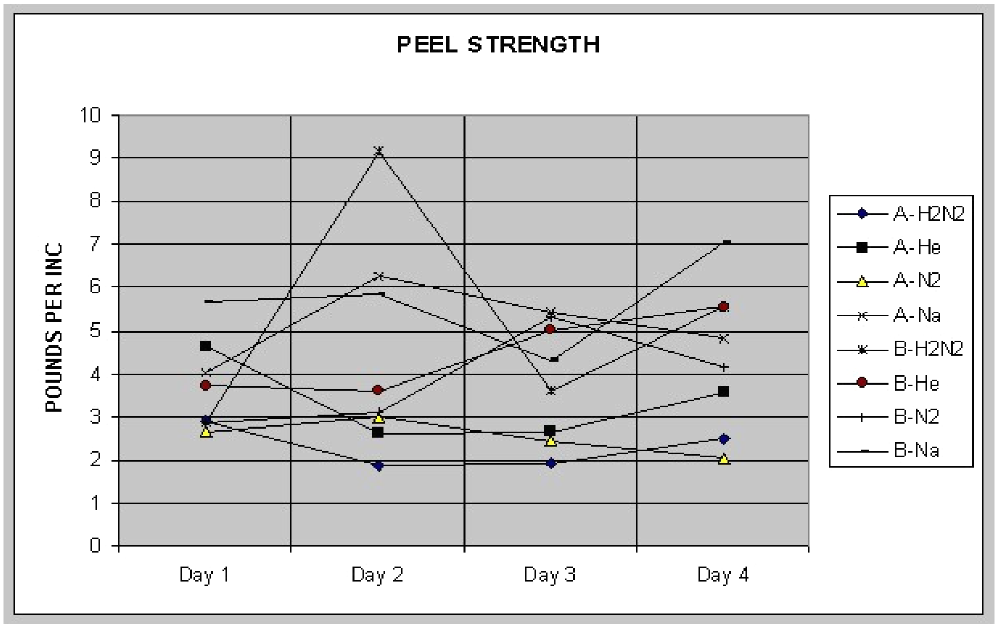
Peel Strength

Following the solder float, peel tests were done to establish any differences between the four processes. This data was also collected over four days. Overall, the Sodium etch had higher peel strength readings. Of the three plasma processes, He had a higher overall peel strength. The readings on Day 4 showed very little changes from Day 1, and in some cases the peel strengths were higher. This peel strength data also demonstrates that as the materials began to recover after four days, there was still sufficient wettability to allow good adhesion even on the large surface area of the unclad panels. (Refer to Table 4 and Figure 3 for Peel Strength data.)

Table 4 - Peel Strength Data

Reference: Test Report A030947 from Constellation Technology Corporation

Material	Day	Peel Load (lbs)	Peel Strength (lbs/in)
A-H_2N_2	1	0.73	2.92
A-He	1	1.16	4.64
A-N_2	1	0.66	2.64
A-Na	1	1.01	4.04
B-H_2N_2	1	0.72	2.88
B-He	1	0.93	3.72
B-N_2	1	0.72	2.88
B-Na	1	1.42	5.68
Material	**Day**	**Peel Load (lbs)**	**Peel Strength (lbs/in)**
A-H_2N_2	2	0.47	1.88
A-He	2	0.65	2.60
A-N_2	2	0.75	3.00
A-Na	2	1.57	6.28
B-H_2N_2	2	2.29	9.16
B-He	2	0.90	3.60
B-N_2	2	0.78	3.12
B-Na	2	1.46	5.84
Material	**Day**	**Peel Load (lbs)**	**Peel Strength (lbs/in)**
A-H_2N_2	3	0.48	1.92
A-He	3	0.66	2.64
A-N_2	3	0.61	2.44
A-Na	3	1.36	5.44
B-H_2N_2	3	0.90	3.60
B-He	3	1.26	5.04
B-N2	3	1.33	5.32
B-Na	3	1.08	4.32
Material	**Day**	**Peel Load (lbs)**	**Peel Strength (lbs/in)**
A-H_2N_2	4	0.62	2.48
A-He	4	0.89	3.56
A-N_2	4	0.51	2.04
A-Na	4	1.20	4.80
B-H_2N_2	4	1.39	5.56
B-He	4	1.39	5.56
B-N2	4	1.04	4.16
B-Na	4	1.76	7.04



Mat'l - Process	Day 1	Day 2	Day 3	Day 4
A-H_2N_2	2.92	1.88	1.92	2.48
A-He	4.64	2.60	2.64	3.56
A-N_2	2.64	3.00	2.44	2.04
A-Na	4.04	6.28	5.44	4.80
B- H_2N_2	2.88	9.16	3.60	5.56
B-He	3.72	3.60	5.04	5.56
B- N_2	2.88	3.12	5.32	4.16
B-Na	5.68	5.84	4.32	7.04

Figure 3 - Peel Strength

Summary

The purpose of this DOE was to review several processes used to activate PTFE material to determine which was best in manufacturing PTFE panels. Most manufacturers of PTFE panels are familiar with chemical processing for activating through holes. However, plasma technologies offer an environmentally benign process that is now preferred over a chemical process. As mentioned throughout this paper, since the material used was unclad, it presented a very difficult surface to activate based on the total area that was plated. Of all the processes, the plasma H_2/N_2 had the lowest contact angle on Day 1. However, all plasma processes continued to recover over the four days. Sodium etch did not have as low a contact angle, but also did not recover from the reading on Day 1. Based on the data collected, all the processes had sufficiently activated the surface to allow good wettability for plating regardless of the recovery. This indicates that the contact angle need only be slightly lowered to achieve sufficient wettability for plating. The data collected over four days also gives an indication of how long panels can be held prior to plating.

Please note: This study was based on two different types of reinforced PTFE material; other constructions may not have the same results. However, based on this DOE, a PCB manufacturer has the option to choose a chemical process or one of several plasma processes to activate PTFE materials.

Acknowledgments

Drill:	Kyocera/Tycom, Irvine, CA
Plating, solder floating:	Future Circuits, St. Petersburg, FL
Peel strength:	Constellation Technologies Corporation, Largo, FL
Sodium etch:	Tyco Electronics, Stafford Springs, CT

Biography

Lou Fierro manages applications and contract services at March Plasma Systems' Florida facility. He is responsible for process development, technical support, and plasma contract services. Lou has worked in the printed circuit industry for over 20 years.