Alkaline Replenisher Evaluation for Printed Wiring Board Fabrication

Federal Manufacturing & Technologies

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ALKALINE REPLENISHER EVALUATION FOR PRINTED WIRING BOARD FABRICATION

D. R. Tucker and S. E. Goldammer

Published April 1997

Topical Report

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Abstract

An alkaline chemistry and modifications of the chemistry were evaluated for use in a flood rinse module during alkaline etching of printed wiring boards.

Summary

MacDermid's Metex® Ultra Etch FL and modifications to the Ultra Etch FL chemistry were evaluated as replacements of a discontinued replenisher, Ultra Etch Aqueous. Ultra Etch FL with additions of water to lower the total alkalinity and ammonium chloride to maintain the chloride level was found to produce acceptable results and, in fact, had a similar chemical composition to Ultra Etch Aqueous.

Discussion

Scope and Purpose

Ultra Etch FL, a proprietary alkaline etch replenisher and modifications of Ultra Etch FL were evaluated for the alkaline etch process in the Printed Circuit Boards Fabrication Department. The flood rinse module replenisher was used to

1. rinse off etch residues as printed circuit boards exited the main etch sump and
2. overflow into the main etch sump to help maintain the chemical balance of the etch solution.

This evaluation was needed to find a suitable replacement flood rinse module chemistry for the etch process because the production replenisher, MacDermid's Ultra Etch Aqueous, was no longer going to be manufactured.

Activity

Background

Photoresists used in the printed wiring board fabrication processes to protect copper circuits during the etch process were sensitive to alkaline chemistries. In fact, following the etch process, an alkaline chemistry (pH between 10.5 and 14.0) was used to remove (strip) the photoresist.

Ammoniacal copper chloride, an alkaline chemistry (pH between 7.6 and 7.8), was used to etch the copper areas adjacent to the photoresist-covered circuit patterns. The chemistry pH in the etching process had to be high enough for efficient copper etching, but not so high that the chemistry would damage the photoresist. As the etch bath was used, the copper content, chloride content, and pH changed. The pH lowered during the etch process but was maintained with additive chemistries such as ammonium hydroxide and proprietary replenishers (which were also used to maintain copper and chloride content). As circuit boards exited the etch module, they entered the flood rinse module, where a replenisher chemistry was "flooded" onto the printed circuit boards to remove any active etch residues.

A diagram of the alkaline process flow is shown in Figure 1.

Two alkaline replenishers were used during the etch process, MacDermid's Ultra Etch 50 and MacDermid's Ultra Etch Aqueous. MacDermid's Ultra Etch 50 had a slightly higher pH (pH between 9.0 and 10.0) than the Ultra Etch Aqueous (pH between 8.0 and 9.0). Ultra Etch 50 was pumped directly into the etch sump to help maintain the etch chemistry. Although the pH of Ultra Etch 50 was high enough to damage the photoresist, this replenisher was mixed with the large volume of low pH etch chemistry before being directly sprayed onto the printed circuit boards.

Figure 1. Process Flow Diagram of the Alkaline Etch Process

Used or "spent" etch solution was pumped from the etch sump to the spent barrel. As the product left the etch module, it entered the flood rinse modules where the flood rinse chemistry was "flooded" directly onto the product.

Two etch systems were used during this evaluation. One was a Chemcut Model 547, and the other was an Atotech Sigma Series etcher. The Chemcut system had two flood rinse modules and the Atotech system had three. In both systems, dragout from the etch module was introduced into the first flood rinse module as panels traveled through the system. Likewise, dragout from the first flood rinse module was introduced into the second flood rinse module, and dragout from the second was introduced into the third flood rinse module (Atotech system). Because of the dragout phenomenon, the fresh flood rinse chemistry was pumped directly into the last flood rinse module, which overflowed into the preceding flood rinse module(s), which overflowed into the etch sump.

The incoming fresh flood rinse replenisher came in direct contact with the product. In order to prevent damage to the photoresist, the Ultra Etch Aqueous with its low pH and total alkalinity was used for flood rinsing. A diagram of the etch line which shows the addition and removal of etch chemistries is shown in Figure 2.

In the summer of 1995, AlliedSignal Federal Manufacturing and Technologies (FM&T) plant in Kansas City, Missouri, was informed that MacDermid, the supplier of Ultra Etch Aqueous replenisher, would no longer be making Ultra Etch Aqueous. Printed wiring board (PWB) engineers contacted MacDermid regarding a recommended replacement. MacDermid recommended Ultra Etch FL with a pH between 8.5 and 9.5. MacDermid also suggested using the Ultra Etch 50 in the flood rinse module as well as in the main etch sump but lowering the Ultra Etch 50's pH prior to entering the flood rinse module.

Figure 2. Diagram of the Alkaline Etch Process (Chemcut Model 547)

Ultra Etch FL (FL stands for fine lines) was previously evaluated along with Ultra Etch Aqueous during the solvent-to-aqueous processing studies in the late 1980s at FM&T. The Ultra Etch FL was advertised as producing better sidewalls in etched copper features and, as a result, was the preferred replenisher for etching patterns with fine lines and spaces (<0.005" in width). Ultra Etch FL, however, had a slightly higher pH (7.6 - 8.4) than the Ultra Etch Aqueous (advertised pH at that time was between 7.6 - 8.0) and was more expensive. For the FM&T circuit line and space width requirements during the time of the initial study, the etch quality between the Ultra Etch FL and Ultra Etch aqueous was insignificant. The Ultra Etch Aqueous was chosen as the replenisher because it produced acceptable results, was less expensive, and was not as likely to degrade the photoresist due to its lower pH, thereby increasing the processing latitude.

Evaluation

The replenisher in the flood rinse module needed to contain ammonium hydroxide and water in order to remove the etch residues. The Ultra Etch Aqueous replenisher that was being used contained water, ammonium hydroxide, and ammonium chloride. The ammonium chloride was added to help sustain the chloride level in the main etch sump. (The spent flood rinse chemistry emptied into the etch sump as new flood rinse chemistry entered the flood rinse modules.) While a higher concentration of ammonium hydroxide and ammonium chloride might be considered added insurance in removing etch residues, excessive alkalinity levels resulting from these chemistries degrade the aqueous processable dry film photoresists used in defining copper circuit patterns during the etch process.

Ultra Etch FL was considered to be the best candidate based on its similarities (except for pH and total alkalinity) to Ultra Etch Aqueous and the supplier's recommendation. A comparison from the Material Safety Data Sheets (MSDS) is shown in Table 1.

Table 1. Comparison of Ultra Etch Aqueous, Ultra Etch FL, and Ultra Etch 50

Properties	Ultra Etch Aqueous	Ultra Etch 50	Ultra Etch FL
<i>Ammonium chloride (NH₄CL)</i>	20 - 30%	10 - 25%	20 - 30%
<i>Ammonium hydroxide (NH₄OH)</i>	<2%	20 - 40%	12 - 18%
<i>pH</i>	8.0 - 9.0	8.2 - 8.8	9.35
<i>Specific gravity</i>	1.07	1.021	1.05
<i>Total Alkalinity (Normality)</i>	0.1N	6.5N	3.5N

The effect of Ultra Etch FL on the copper etching process was previously known from earlier studies; however, its effect on the photoresists being used for production, DuPont's 4615 and DuPont's 9015, was not known. MacDermid suggested that although excessive pH was detrimental to the aqueous processable photoresists in the etch module, the total alkalinity, more so than excessive pH, of the flood rinse chemistry would be detrimental to the photoresist. MacDermid suggested modifications to the Ultra Etch chemistry and to the etch system that may provide acceptable results. These suggestions included

- adding deionized water to the flood rinse chemistry to lower the total alkalinity (and pH),
- increasing the exhaust at the flood rinse module to reduce the pH, and
- lowering the flow or completely shutting off the flood rinse in the last set of flood rinse tubes since that was the location where the incoming (high pH and alkalinity) replenisher was added.

Experiment #1 - Evaluating Worst Case Conditions of Ultra Etch FL

To determine if Ultra Etch FL used under "worst-case" conditions would degrade the photoresists, fresh or "as-received" Ultra Etch FL was used in the flood rinse module, and the exhaust at the flood rinse module was shut off. Because thick copper requires a longer etch time—longer exposure of the photoresist to the etch and flood rinse modules—3-ounce copper clad laminate (laminate covered on each side with 3 ounces of copper per square foot) was used instead of the 0.5-ounce or 1-ounce copper normally processed.

Standard 12" X 12" panels were used. DuPont's 4615 photoresist was laminated to 24 of the copper clad panels, and DuPont's 9015 photoresist was laminated to the remaining 24 copper clad panels. The panels were imaged with a special test pattern with a series of 0.005", 0.004", and 0.003" path widths. (See Appendix A.)

Initially, 12 panels with each photoresist type were etched using fresh Ultra Etch Aqueous for a baseline comparison, and 12 with each photoresist type were to be etched using fresh Ultra Etch FL. An Atotech Sigma series etch system, made by The Chemcut Equipment Group, was used to etch panels during this experiment.

Ultra Etch Aqueous was used in the flood rinse module first. At an estimated normal etch time for 3-ounce copper, 8 inches per minute conveyor speed (6.25 minutes), the 9015 photoresist was completely stripped during the etch process and about 50% of the 4615 photoresist was stripped. The etch time was excessive even for 3-ounce copper; therefore, the conveyor speed was increased to 15 inches per minute (3.33 minutes). Again, all of the 9015 photoresist was stripped. The 4615 photoresist patterns wider than 0.010" (border areas, phototool identification, etc.) remained. The etch time was reduced once more to 2.5 minutes (conveyor speed set at 20 inches per minute). Most of the 9015 photoresist was removed, but most of the 4615 photoresist patterns wider than 0.010" remained and 75% of the 4615 photoresist remained on the patterns less than 0.010" in width.

The remaining panels were etched at decreasing etch times to determine how much time each photoresist could take in the etch chamber before breaking down. At a conveyor speed of 25 inches per minute (2 minutes), all of the 4615 was acceptable and even some of the 9015 remained on the narrow patterns. Since the predominate copper thickness for FM&T product was 1 ounce or less, one panel with 4615 and one panel with 9015 were etched at 35 inches per minute (1.43 minutes), the speed commonly used for etching 1-ounce copper. All of the 4615 photoresist was acceptable and about 85% of the 9015 photoresist was acceptable.

Based on the results of the Ultra Etch Aqueous and since the higher pH of the Ultra Etch FL was assumed to be more aggressive at degrading the photoresists, etching panels at the long etch time required for 3-ounce copper was not done. Instead, the first panels, etched using Ultra Etch FL in the flood rinse module, were etched at 35 inches per minute to determine if the fresh Ultra Etch FL could be considered as a replacement—even for etching 1-ounce copper. Most of the 4615 photoresist appeared to be acceptable; however, only 50% of the 9015 photoresist remained on the panels. There was no need to subject the photoresists to longer etch times.

From this evaluation it appeared that the baseline photoresists and Ultra Etch Aqueous in the flood rinse module were not acceptable for fine line etching of thick copper clad product. Fresh Ultra Etch FL was only slightly more aggressive in attacking photoresist than was the Ultra Etch Aqueous. Also, the 4615 photoresist was found to be more resistant to chemical attack than the 9015.

Experiment #2 - Evaluating Best Case Conditions of Ultra Etch FL

Modifications were made to the etch process as MacDermid recommended to determine if the Ultra Etch FL under ideal conditions would be acceptable. The exhaust near the flood rinse module was fully opened, the replenisher flow to the last set of spray tubes in the flood rinse module was shut off, and the replenisher was allowed to age for three days in the flood rinse module sump prior to the experiment, to allow the pH to drop.

Also, two etch systems were used to determine if the difference in etch equipment designs was significant. The older system, a Chemcut model 547, was compared to the newer system, an Atotech Sigma Series etch system, made by Chemcut Equipment Group.

Five 12" X 12" panels with 2-ounce copper on each side were coated with 4615 photoresist and five more were coated with 9015 photoresist. A pattern with a broad range of path widths was used to image the photoresist. (See Appendix B.) Four of each were etched in the new etcher and one of each in the old etcher (which was using the baseline Ultra Etch Aqueous in the FRM).

The tank analyses of the Chemcut and Atotech etchers prior to etching the panels are shown in Table 2.

Table 2. Chemical Analysis Prior to Etching Panels

	Copper (grams/liter)	Chloride (grams/liter)	pH
OPERATING LIMITS	145 - 165	177 - 212	7.6 - 7.8
ATOTECH Sigma	160.6	190.0	7.7
Chemcut 547	156.0	205.0	7.6

The system operating parameters are shown in Table 3.

Table 3. Comparison of Chemcut and Atotech System Operating Parameters

Parameter	Chemcut 547	Atotech Sigma
Conveyor speed (inches/minute)	25	20
Etch time (minutes)	1.8	2.5
Spray pressure (psi)	10 lower 10 upper	18 lower 20 upper
Oscillation rate (cycles/minute)	N/A	30

The panels etched on the Atotech etcher had photoresist paths lifted from all lines below 0.010" in width; however, the panels etched on the Chemcut etcher had better results.

A sample of the Ultra Etch Aqueous from the old etcher's flood rinse module sump was found to have a pH of 8.4--higher than the pH of the replenisher in the new etcher's flood rinse module sump. These results indicated that a difference in etch system designs, such as the etchant spray mechanics or design of the flood rinse module or exhaust location, may be significant.

Table 4 lists the comparisons between the old and new etch system's nozzle configuration. The nozzle flow rate, spray shape, and distance to the workpiece were the same for both systems. The nozzle density (quantity per square feet of chamber space) was known to be different, but the difference was thought to be insignificant. The lower spray pressure and higher nozzle density of the old system may have been the contributor.

Table 4. Comparison of Chemcut and Atotech System Nozzle Configuration

	Chemcut 547	Atotech Sigma
Spray area	9.375 ft ² (45" long X 30" wide)	12.5 ft ² (50" long X 30" wide)
Spray tubes, upper	7	6
Spray tubes, lower	7	6
Nozzle type	Solid cone	Solid cone
Nozzles per tube	8	7
Nozzles/ft²	6.0	3.4
Nozzle flow rating @ 40 psi	1.5	1.5

When undiluted Ultra Etch FL was evaluated as a replacement replenisher for Ultra Etch Aqueous, the aqueous processable photoresist was attacked. However, the attack was not as severe in one etch system (Chemcut 547) as it was in the other etch system (Atotech Sigma Series).

Because the photoresists were attacked in both systems, a third experiment was designed which included adjustments to the Ultra Etch FL chemistry.

Experiment #3 - Modification to the Ultra Etch FL Chemistry

Standard 12" X 12" panels were used. Panels were processed as shown in Appendix C. Some panels had 1-ounce copper on each side and some had 2-ounce copper on each side. DuPont's 4615 and 9015 dry film photoresists were used. Some of the panels were imaged with a special test pattern with a variety of line and space widths as well as other features (see Appendix B, Tool-Made Sample Artwork), and some were imaged with a special test pattern used for conductor analysis testing (see Appendix D, Conductor Analysis Test Pattern). Panel numbering sequence is shown in Appendix E. Panels were etched using the Chemcut Model 547 spray etching system.

The etch bath or "Chem 3" bath requirements for production etching were

Copper content	145 - 165 grams/liter
Chloride content	177 - 212 grams/liter
pH	7.6 - 7.8

The chemical analysis of the Ultra Etch FL and the three adjustments that were used are shown in Table 5.

Table 5. Chemical Analysis of the Ultra Etch FL and Ultra Etch Variations

Chemistry	Ncl	Chloride	pH	Total Alkalinity
<i>FL As Received</i>	4.36M	154.8 grams/liter	9.7	3.4N
<i>FL, Dilute 50%</i>	1.96M	69.7 grams/liter	9.6	1.4N
<i>FL, Dilute 25%</i>	0.83M	29.6 grams/liter	9.4	0.5N
<i>FL, Dilute 5%</i>	0.17M	5.9 grams/liter	9.4	0.05N

The "as-received" Ultra Etch FL was used in the flood rinse module first. The known analysis of the etch bath and flood rinse module chemistry at the close of the previous day are shown in Table 6. The pH was found to be low so ammonium hydroxide was added to the etch sump in order to bring the pH up. A second pH measurement of Chem 3 verified that the pH was within production operating limits.

On the day of the experiment, a sample of the etch bath was removed prior to etching but the analysis was done several hours later and was not known prior to etching. The results that came from the laboratory from this sample are also shown in Table 6.

Table 6. 100% Ultra Etch FL and Chem 3 Analysis

Chemistry	Copper (grams/liter)	Chloride (grams/liter)	pH	Total Alkalinity
Chem 3 (previous day)	150.5	210.4	7.3	-
Chem 3 pH after adjusting			7.7	
FL from barrel		154.8	9.7	3.4N
Chem 3 (beginning of evaluation)	127.6	200.9	*8.2	

*pH was over the upper limits.

Two panels with 2-ounce/2-ounce copper, one with the 9015 photoresist and one with the 4615 photoresist patterned with the tool-made sample pattern, were etched. When the panels came out of the dryer, both photoresists were completely stripped off. Even though the photoresists were stripped, the copper patterns (except for those with conductor widths less than 0.010" and space widths less than 0.005", Coupon C, Area 8) were in tact and the surface of the conductors was flat and shiny in appearance, indicating that the photoresist had been damaged late in the etch module or in the flood rinse module. Had the photoresist been damaged early in the etch module, the copper surface of the 0.010" wide lines would have been slightly etched, having a matte appearance.

This was repeated once again and the same results were observed.

During normal production etching with the Ultra Etch Aqueous replenisher in the flood rinse modules, it is not uncommon to have photoresist failure on narrow features (below 0.005" in width). The etch process at FM&T/KC was never required to perform and therefore never characterized for features smaller than these.

Suspecting the alkalinity of the full strength Ultra Etch FL to be a major contributor to the photoresist degradation, the full strength Ultra Etch FL was removed from the flood rinse modules and replaced with a mixture of 50% Ultra Etch FL and 50% deionized (DI) water. The analysis of this chemistry and Chem 3 prior to further etching is shown in Table 7.

Table 7. 50% Ultra Etch FL and Chem 3 Analysis

Chemistry	Copper (grams/liter)	Chloride (grams/liter)	pH	Total Alkalinity
Chem 3	126.4	203.3	8.2	
50% Ultra Etch FL		69.7	9.6	1.4
FRM 1	2.5	153.7	9.4	
FRM 2	6.4	152.5	9.4	

Two of the 2-ounce/2-ounce copper clad panels with 4615 photoresist and two with the 9015 photoresist, patterned with the tool-made sample pattern, were etched.

There was some attack on the 4615 photoresist. The photoresist was stripped from areas with feature widths less than 0.005", loosened in some areas, and adhered in other areas. Copper features 0.010" and wider were acceptable.

All of the 9015 photoresist was stripped off during the etch operation, but again copper features 0.010" and wider were acceptable.

In order to determine if the flood rinse chemistry was contributing to the degradation of the photoresist, the flood rinse was shut off and two more panels (one with 9015 photoresist and one with 4615 photoresist) were etched.

The 4615 photoresist was loose in some places but only in those areas with feature widths less than 0.005" wide. The 9015 photoresist was loose but not completely removed.

At this time, the laboratory analysis was received from the sample removed at the beginning of the day. (See Table 6.) Because the pH in the etch bath was excessive (8.2) and the copper content low, the etch bath was adjusted by etching 90 ounces of copper in the etch bath. A sample of Chem 3 after the copper addition was analyzed and found to be 7.9.

With the flood rinse still shut off, one of the 2-ounce/2-ounce copper clad panels with 4615 photoresist and one with the 9015 photoresist, patterned with the tool-made sample pattern, were etched with the 7.9 pH etch chemistry. No difference was noticed on the panels with 4615 photoresist that were etched with the 8.2 pH chemistry.

The 9015 photoresist, however, looked much better after lowering the pH of the etch bath. Photoresist was still attached to the 0.010" wide lines.

With the etch bath now in operating limits, the flood rinse module was turned on to evaluate the effects of the flood rinse. Again, one of the 2-ounce/2-ounce copper clad panels with 4615 photoresist and one with the 9015 photoresist, patterned with the tool-made sample pattern, were etched. The 9015 photoresist was completely stripped and most of the 4615 photoresist was attacked and loosened. This was an indication that the 50% Ultra Etch FL was still too aggressive on the photoresist. The flood rinse was shut off and two more panels were etched to verify that the flood rinse chemistry was indeed the contributor to photoresist failure. Both the 4615 and 9015 photoresists were acceptable after etching.

The 50% Ultra Etch was removed from the flood rinse modules and replaced with a solution of 25% Ultra Etch FL. The analysis of the various chemistries is shown in Table 8.

Table 8. 25% Ultra Etch FL and Chem 3 Analysis

Chemistry	Copper (grams/liter)	Chloride (grams/liter)	pH	Total Alkalinity
Chem 3	127.0	195.0	7.8	
25% Ultra Etch FL		29.6	9.41	0.5

One 2-ounce/2-ounce copper panel with 4615 photoresist and one with 9015 photoresist, patterned with the tool-made sample pattern, were etched. Both photoresists appeared to be more degraded than with the normal production etch process. The total alkalinity (0.5 normal) of the flood rinse module was still higher than the production replenisher, Ultra Etch Aqueous, with a total alkalinity of 0.1.

Two 1-ounce/1-ounce copper clad panels with 9015 photoresist, patterned with the conductor analysis test pattern (Appendix D), were etched.

The photoresist on the top of the panels was completely stripped off. The photoresist on the bottom of the panels was loose but still in place. The effects of etchant puddling on the top side of the panels was most likely the contributor to the premature photoresist failure.

The 25% solution of Ultra Etch FL was removed from the flood rinse modules, and the Ultra Etch was diluted down to 5%. The analysis of the barrel and the analysis of the other chemistries are shown in Table 9.

Table 9. 5% Ultra Etch FL, Chem 3, and FRM Analysis

Chemistry	Copper (grams/liter)	Chloride (grams/liter)	pH	Total Alkalinity
Chem 3	125.1	191.5	7.6	
5% Ultra Etch FL		5.9	9.4	0.05
FRM #1 (5% FL)	2.5	35.5	8.6	
FRM #2 (5% FL)	24.1	67.4	8.5	

During this run, both replenisher pumps were continually running. One pumped fresh Ultra Etch 50 directly into Chem 3 (to maintain pH, copper concentration, and chloride concentration), and the other pumped fresh 5% Ultra Etch FL into flood rinse modules 1 and 2.

One 2-ounce/2-ounce copper clad panel with 4615 photoresist and one with 9015 photoresist, patterned with the tool-made sample pattern, were etched. Both were acceptable, being typical of normal production.

Fourteen 1-ounce/1-ounce copper clad panels with 9015 photoresist and patterned with the CAT Pattern were etched. All of the panels looked similar. Four were run at a speed of 53 inches per minute, two were run at 55, seven were run at 60, and one panel was run at 65 inches per minute.

Panels 113, 114, and 115, which were etched at a speed of 53 inches per minute, and panels 104, 106, 109, 110, 111, and 112, which were etched at a speed of 60 inches per minute, were tested electrically using the conductor analysis tester. Panel marking is shown in Appendix E. The results summarized in Tables 10 and 11 and are detailed in Appendix F.

**Table 10. Electrical Test Data of Panels Etched at a Speed of 53 Inches Per Minute
(Panels #113, 114, 115) [Tested 300 modules (areas) for each feature]**

FEATURE AND SIZE	DEFECT COUNT	FEATURE YIELD	DEFECTS PER MILLION INCHES OF LINE/SPACE LENGTH
TOP SIDE OF PANEL			
0.005" line	32	89.33%	8051
0.005" space	0	100.00%	0
0.006" line	23	92.33%	5750
0.006" space	0	100.00%	0
0.007" line	13	95.67%	3222
0.007" space	0	100.00%	0
0.008" line	10	96.67%	2485
BOTTOM SIDE OF PANEL			
0.005" line	1	99.67%	238
0.005" space	0	100.00%	0
0.006" line	1	99.67%	241
0.006" space	1	99.67%	245
0.007" line	0	100.00%	0
0.007" space	0	100.00%	0
0.008" line	0	100.00%	0

**Table 11. Electrical Test Data of Panels Etched at a Speed of 60 Inches Per Minute
(Panels #104, 106, 109, 110, 111, 112) [Tested 300 modules (areas) for
each feature]**

FEATURE AND SIZE	DEFECT COUNT	FEATURE YIELD	DEFECTS PER MILLION INCHES OF LINE/SPACE LENGTH
TOP SIDE OF PANEL			
0.005" line	36	94%	4417
0.005" space	2	99.67%	243
0.006" line	17	97.17%	2072
0.006" space	2	99.67%	245
0.007" line	18	97.00%	2216
0.007" space	1	99.83%	124
0.008" line	13	97.83%	1607
BOTTOM SIDE OF PANEL			
0.005" line	6	99.00%	717
0.005" space	33	94.50%	4117
0.006" line	2	99.67%	241
0.006" space	19	96.83%	2364
0.007" line	1	99.83%	121
0.007" space	18	97.00%	2258
0.008" line	1	99.83%	122

The data listed represents line and space yields. A line defect is detected when there is a break or "open circuit" in a line. A space defect is detected when a short is detected between the lines on either side of the space. The line yields were slightly better at a conveyor speed of 60 inches per minute, but the space yields were better at a conveyor speed of 53 inches per minute. At the slower speed of 53, the conveyor is allowing additional copper to be removed from the spaces between the conductors. At a faster speed of 60, the panels are not etched as long and conductor widths are slightly wider. Any place along the conductor that is marginal enough to pass at 60 inches per minute would have been a defect at a longer etch time (slower conveyor speed).

At the end of the day, chemical analyses were taken. Those results are shown in Table 12.

Table 12. 5% Ultra Etch FL, Chem 3, and FRM Final Analysis

Chemistry	Copper (grams/liter)	Chloride (grams/liter)	pH	Total Alkalinity
Chem 3	118.7	177.3	7.6	
5% Ultra Etch FL		5.9	9.4	0.05
FRM #1 (5% FL)	1.9	11.8	9.3	
FRM #2 (5% FL)	11.4	23.6	9.4	

During this evaluation no ammonium chloride was added to the modified Ultra Etch FL. Although this chemistry, without the ammonium chloride, was adequate for rinsing off etch residues, with continued use, the chloride level in the etch bath would have dropped due to the addition of the low-chloride flood rinse chemistry.

The amount of ammonium chloride that would have been needed to raise the chloride level in solution to operating limits was calculated and added to the solution. The subsequent analysis showed that the chloride level did increase and that it increased to the desired value.

Some panels were etched with this chemistry and were found to be acceptable.

Accomplishments

Ultra Etch FL, by itself, attacked the two photoresists used during the evaluation (DuPont's 9015 and 4615 dry film). As the Ultra Etch FL was diluted with water to decrease the total alkalinity, the photoresist attack was decreased. Modified Ultra Etch FL was an effective flood rinse chemistry provided the total alkalinity was below 0.1 normal. Adding water and ammonium chloride to Ultra Etch FL provided acceptable results in the flood rinse function and prevented damage to the aqueous processable photoresists.

In December 1996, this information was presented to a Qualification Evaluation Team made up of FM&T and customer (Sandia National Laboratory) associates in Livermore, California. The Qualification Evaluation Team approved the modified Ultra Etch FL as a replacement for Ultra Etch Aqueous.

Appendix A
Conductor Analysis Test Artwork

Conductor Analysis Artwork

From CAT, Inc.¹, used by permission.

¹CAT, Inc., Conductor Analysis Technologies, Inc., Albuquerque, New Mexico

Appendix B
Tool-Made Sample Artwork

Tool Made Sample Artwork

Coupon C, Area	1	2	3	4	5	6	7	8	9	10
Line width (mil)	2	2	2	2	5	5	5	10	10	10
Space width (mil)	2	5	10	15	5	1-	15	5	10	15

Appendix C
Test Panel Processing Sequence

Test Panel Processing Sequence

CHEMICAL CLEAN

Metex P-507	Concentration	17.3
	Conveyor Speed	38 inches/minute
	Metex Temperature	142.6°F
	Pressure, upper	20 psi
	Pressure, lower	19 psi
Water rinse	Pressure, upper	19 psi
	Pressure, lower	13 psi
Sodium	Temperature	75.5°F
persulfate &	Conveyor Speed	80 inches/minute
sulfuric acid	Copper concentration	10.5 grams/liter
microetch	Sodium persulfate conc.	106 grams/liter
	Pressure, upper	29 psi
	Pressure, lower	27 psi
Water rinse	Pressure, upper	16 psi
	Pressure, lower	19 psi
Warm air dryer		

PHOTORESIST LAMINATION

DuPont's 4615	Roll temperature	100°C
	Board exit temp	125/127°F
	Speed	0.5 meters/min.
DuPont's 9015	Roll temperature	105°C
	Board exit temp	121 °F
	Speed	0.5 meters/min.

EXPOSURE

DuPont's 4615	Step, (Stouffer 21)	9
	Setting	90
	Time	16.8 seconds
DuPont's 9015	Step, (Stouffer 21)	9
	Setting	110
	Time	20 seconds

DEVELOP

	Solution temp	84 °F
	pH	11.1
	Sodium carbonate conc.	1%
DuPont's 4615	Conveyor speed	2.25 feet/minute
DuPont's 9015	Conveyor speed	2 feet/minute

ETCH

	Temperature	@ 126°F
	Upper spray pressure	*26 psi
	Lower spray pressure	12 psi
1 oz/1 oz Cu.	Conveyor speed	53 - 65 in/min.
	Etch time	51 - 41 seconds
2 oz/2 oz Cu	Conveyor speed	26 in/min.
	Etch time	104 seconds

*Upper spray pressure gauge was not working properly. The pressure was most likely around 15 psi based on the regular setting of the valve.

Appendix D
Conductor Analysis Test Artwork 5 to 8 Mil Lines

Conductor Analysis Test Artwork 5 to 8 Mil Lines

Appendix E
Panel Numbering and Description

Panel Numbering and Description

Panels 90-1 - 90-6	9015 photoresist, 2-ounce/2-ounce copper TMS Artwork
Panels 46-1 - 46-6	4615 photoresist, 2-ounce/2-ounce copper TMS Artwork
Panels 101 - 116	9015 photoresist, 1-ounce/1-ounce copper, CAT Artwork
Panels 201 - 208	4615 photoresist, 2-ounce/2-ounce copper TMS Artwork
Panels 209 - 216	9015 photoresist, 2-ounce/2-ounce copper TMS Artwork

Appendix F
Conductor Analysis Electrical Test Results

Feature Yield & Defect Density Results

(From CAT, Inc.², used by permission.)

Data Not Censored

All 100 Modules

Top Side of Panels

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	300	Open	32	268	89.33	8051
5.00	6.00	Space	300	Short	0	300	100.00	0
6.00	5.00	Line	300	Open	23	277	92.33	5750
6.00	7.00	Space	300	Short	0	300	100.00	0
7.00	6.00	Line	300	Open	13	287	95.67	3222
7.00	8.00	Space	300	Short	0	300	100.00	0
8.00	7.00	Line	300	Open	10	290	96.67	2486

Bottom Side of Panels

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	300	Open	1	299	99.67	238
5.00	6.00	Space	300	Short	0	300	100.00	0
6.00	5.00	Line	300	Open	1	299	99.67	241
6.00	7.00	Space	300	Short	1	299	99.67	245
7.00	6.00	Line	300	Open	0	300	100.00	0
7.00	8.00	Space	300	Short	0	300	100.00	0
8.00	7.00	Line	300	Open	0	300	100.00	0

Top & Bottom Sides Combined

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	600	Open	33	567	94.50	4038
5.00	6.00	Space	600	Short	0	600	100.00	0
6.00	5.00	Line	600	Open	24	576	96.00	2943
6.00	7.00	Space	600	Short	1	599	99.83	123
7.00	6.00	Line	600	Open	13	587	97.83	1593
7.00	8.00	Space	600	Short	0	600	100.00	0
8.00	7.00	Line	600	Open	10	590	98.33	1233

AlliedSignal FM&T
 FL Etchant - Run @ 53
 Pattern: Multi-pitch
 Design: [5] 5 [6] 6 [7] 7 [8]

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Conductor & Space Yield by Panel

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FL Etchant - Run @ 53
Pattern: Multi-pitch
Design: [5] 5 [6] 6 [7] 7 [8]

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Pattern: Multi-pitch
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Feature Yield & Defect Density Results

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All 100 Modules

Top Side of Panels

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	600	Open	36	564	94.00	4417
5.00	6.00	Space	600	Short	2	598	99.67	243
6.00	5.00	Line	600	Open	17	583	97.17	2072
6.00	7.00	Space	600	Short	2	598	99.67	245
7.00	6.00	Line	600	Open	18	582	97.00	2216
7.00	8.00	Space	600	Short	1	599	99.83	124
8.00	7.00	Line	600	Open	13	587	97.83	1607

Bottom Side of Panels

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	600	Open	6	594	99.00	717
5.00	6.00	Space	600	Short	33	567	94.50	4117
6.00	5.00	Line	600	Open	2	598	99.67	241
6.00	7.00	Space	600	Short	19	581	96.83	2364
7.00	6.00	Line	600	Open	1	599	99.83	121
7.00	8.00	Space	600	Short	18	582	97.00	2258
8.00	7.00	Line	600	Open	1	599	99.83	122

Top & Bottom Sides Combined

Artwork Feature Size (mils)	Target Feature Size (mils)	Feature Type	Feature Count	Defect Type	Defect Count	Number Good	Feature Yield (%)	Defects per Million Inches
5.00	4.00	Line	1200	Open	42	1158	96.50	2543
5.00	6.00	Space	1200	Short	35	1165	97.08	2154
6.00	5.00	Line	1200	Open	19	1181	98.42	1150
6.00	7.00	Space	1200	Short	21	1179	98.25	1297
7.00	6.00	Line	1200	Open	19	1181	98.42	1161
7.00	8.00	Space	1200	Short	19	1181	98.42	1183
8.00	7.00	Line	1200	Open	14	1186	98.83	861

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