Converting Printed Wiring Product Processing to Aqueous Processable Dry Film Photoresist

Federal Manufacturing & Technologies

S. E. Goldammer

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CONVERTING PRINTED WIRING PRODUCT PROCESSING TO AQUEOUS PROCESSABLE DRY FILM PHOTORESIST

S. E. Goldammer

Published July 1996

Final Report
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ABSTRACT

Fully aqueous processable dry film photoresists were evaluated to determine which dry film in the Federal Manufacturing & Technologies printed wiring board facility performed the best. The photoresists were chosen for their compatibility in alkaline etching, copper electroplating, and tin-lead electroplating. The processing evaluation included both single layer and double layer dry film photoresist for pattern plating.

SUMMARY

In July 1988, the U.S. Department of Energy, AlliedSignal Inc. Federal Manufacturing & Technologies (FM&T), and Sandia National Laboratories mutually agreed to work toward a five-year goal to eliminate CHCs and CFCs to the greatest extent possible consistent with nuclear safety and stockpile reliability requirements. To comply with this goal, this project was initiated to eliminate the use of chlorinated hydrocarbons (CHCs) in favor of aqueous processable chemicals in the imaging processes used to manufacture printed wiring boards.

Fully aqueous processable dry film photoresists were evaluated and chosen as replacements for the solvent processable dry film photoresists. Du Pont's 1010, 1020, and 1230 solvent processable photoresists were replaced with Du Pont's 4615 for print and etch applications and Dynachem's HG for copper pattern plating and tin-lead electroplating. Each material was evaluated for compatibility with processing chemistries and repeatable line width resolution. The data produced from characterizing the materials were presented to the FM&T and Sandia qualification evaluation team for the printed wiring product facility, which approved the processes.

DISCUSSION

SCOPE AND PURPOSE

In July 1988, the U.S. Department of Energy, AlliedSignal Inc. Federal Manufacturing & Technologies (FM&T), and Sandia National Laboratories mutually agreed to work toward a five-year goal to eliminate chlorinated hydrocarbon (CHC) and chlorinated fluorocarbon (CFC) usage at the Kansas City Plant.

The goal was "by July 1993, to eliminate CHCs and CFCs to the greatest technical extent possible consistent with nuclear safety and stockpile reliability requirements." (Ref: letter from Louis Smith and EPA advance notice in the Appendix.)

To comply with this goal, the photoimaging process for the printed wiring boards had to be changed from chlorinated hydrocarbons (1,1,1-trichloroethane and methylene chloride) to aqueous processable materials.

The scope and purpose of this project was to eliminate the use of chlorinated hydrocarbons (CHCs) in the imaging processes used to manufacture printed wiring boards.

ACTIVITY

Background

The process of creating patterns with photosensitive dry films is known as photolithography, or photoimaging, in the printed wiring board industry. Prior to this project, solvents containing chlorinated hydrocarbons were used to pattern photoresists. FM&T began an effort in the late 1980s to eliminate solvents containing chlorinated hydrocarbons (CHCs) from the photoimaging processes when manufacturers began to supply photoresists that could be processed in aqueous-based chemistries. This report details the work that was done to convert from solvent-based to aqueous-based photoresist processes. These aqueous processable photoresists were used in pattern plating and in the print and etch processing of inner layers and panel plating, as shown in Table 1.

Photoimaging

In photoimaging, the dry film photoresist is laminated to a copper panel. This copper panel is typically a composite of two copper layers with a core dielectric material sandwiched between them. The method of lamination is either a hot roll laminator or a vacuum laminator. Each process involved a method of applying the dry film to the surface using heat and pressure. A phototool (artwork) is then used to expose the desired design to the photoresist. The phototool is a polyester film with the required pattern designed as opaque and transparent on the film. This film, or phototool, is then placed in intimate contact with the photoresist-covered panel and

exposed to the ultraviolet (UV) light source. This process is called the exposing operation. During UV exposure, the photoresist areas exposed to UV light are polymerized (negative acting dry film). The panels are then processed through a conveyORIZED spraying system referred to as a developer, which washes away the photoresist not directly exposed to the UV light (this would be the opaque areas of the phototool). The photoresist mask is thereby used to define the copper circuit patterns in the next operations.

Table 1. Photoresist Used by Product Type

PROCESS TYPE	PRODUCT TYPE	SOLVENT PHOTORESIST	AQUEOUS PHOTORESIST
PRINT AND ETCH OF INNER LAYERS	Inner Layer	Du Pont 1010	Du Pont 4615
	Flexible	Du Pont 1020	Du Pont 4615
PRINT AND ETCH OF PANEL ELECTROPLATE	Rigid	Du Pont 1020	Du Pont 4615
	Flex	Du Pont 1020	Du Pont 4615
PATTERN ELECTROPLATE	Rigid	Du Pont 1020	Dynachem HG
	Rigid/Flex	Double layer Du Pont 1020	Double layer Dynachem HG
CHANNEL/PATTERN ELECTROPLATE	Rigid	Du Pont 1230	Dynachem HG

The overall process flow is shown in Figure 1, which is the flow diagram for the PWB processes described in this report.

In the print and etch process, the photoresist is used to protect the copper from an etching solution. For pattern or channel plating processes, the areas not covered with photoresist will be plated with electroplated copper and tin-lead.

Figure 1. Process Flow for Manufacture of PWBs

Print and Etch Process

In the print and etch process, the photoresist pattern is used to protect the copper surface beneath the photoresist from the subsequent copper etching operation. Ideally, the copper circuit pattern resembles the polymerized photoresist pattern, which also resembles the pattern in the phototool.

The etching chemistry used was an alkaline, ammoniacal copper chloride. The solvent processable photoresists were resistant to this chemistry. Unfortunately, the new aqueous processable photoresists were not as resistant as those based on solvent. In fact, strong alkaline chemistry with a pH above 11 is used to strip aqueous processable photoresist films. An alkaline solution of pH 8.4 and higher will attack aqueous photoresists. The etch process had to be modified to accommodate the alkaline-sensitive films. This modification consisted of evaluating a replenisher that could be placed in the flood rinse module of the etching equipment which would not strip the photoresist. The problem was solved by using two replenishers, one feeding into the etchant sump with the higher pH (9-10) and one feeding into the flood rinse module having a lower pH (7-8) which would not attack the photoresist.

The print and etch process was used on single-sided, double-sided, and inner layer product that had through hole interconnects or on products that were previously drilled and panel plated.

Pattern Plating Process

In the pattern plating process, the desired copper pattern is not covered by polymerized photoresist after the developing operation and is plated with electroplated copper followed by electroplated tin-lead. The electroplated copper patterns become the circuit. That is, the copper

circuits in a pattern plating process resemble the opaque pattern in the phototool which creates the trace for copper and tin-lead.

Following tin-lead plating, the photoresist is then stripped and the original copper substrate beneath the stripped photoresist is etched. As the copper substrate is etched, some of the electroplated copper beneath the protective tin/lead is etched. Shorter etch times are desirable. For this reason, thin (0.0007 in.) copper is used as the base substrate for pattern plated product.

The pattern plating process is used on product with drilled holes that have not been previously plated. The electroplating process not only plates circuit patterns, but also plates inside the drilled holes for layer-to-layer interconnects. This is also the process of choice for extremely dense and precise patterns (4 mil lines and 4 mil spaces).

The solvent processable photoresists used for pattern plating were Du Pont 1020 (2 mils thick) and 1230 (3 mils thick).

Change From CHC Usage

The PWB industry began to minimize the use of solvents which contain chlorinated hydrocarbons when health hazards associated with using these solvents were confirmed. The Federal Manufacturing & Technologies set goals to drastically reduce and possibly eliminate the use of these solvents.

Photosensitive films that were predominantly processed with solvents containing chlorinated hydrocarbons are now being manufactured for processing in aqueous chemistries.

In the fabrication of printed wiring boards, solvents containing chlorinated hydrocarbons are used to develop and strip photoresists and solder masks, clean flux residues, and final clean product after inspection. Manufacturers of dry film photoresist and solder masks began supplying dry films that could be processed in aqueous chemistries instead of chlorinated hydrocarbon solvents.

This project dealt with the solvent-to-aqueous conversion for dry film photoresists. By March 13, 1990, Du Pont Riston 4615, an aqueous processable dry film photoresist, was being used for print and etch processing in the FM&T printed wiring board facility.

The intent of this evaluation was to assess the adequacy of the aqueous processable dry film photoresist and the associated processes to fabricate a print and etch product with no additional plating (copper-clad only).

A test pattern was specifically designed to represent the range of features required by current war reserve (WR) product. This pattern is shown in Figure 2 (front) and Figure 3 (back).

Characterization of Print and Etch

Inner Layer Evaluation

This portion of the study was focused on specifically qualifying an aqueous photoresist acceptable for the print and etch production. The inner layer evaluation used epoxy/glass PWB material with 1.0 oz/ft² copper, 0.010 inch thick. Panels were processed using Du Pont Riston 1010 solvent processable dry film photoresist and Du Pont Riston 4615 aqueous processable dry film photoresist.

The results were judged by the overall photoresist performance using 4615 in comparison to 1010 and 1020 for print and etch product. The photoresist had to be chemically resistant in the alkaline etch chemistry and be able to perform equal to or better than the 1010 and 1020 photoresists.

The panels were processed and then evaluated using cross sections, SEM photomicrographs, and path width measurement. Table 2 shows the sequence of the processing steps and the differences between aqueous and solvent processing. The following describes the results of the inner layer evaluation.

Photoresist sidewall results shown by SEM:

- Figures 2 and 3 show the phototool and the placement of the coupons in relationship to the panel. Coupons were taken after development as shown in Figure 4. Figure 4a is 4615 and Figure 4c is 1010 at the same magnification of 200X. Figure 4b is 4615 and Figure 4d is 1010 showing a side-by-side comparison of the photoresist. Figure 5a is 4615 and Figure 5c is 1010 at the same magnification of 200X. Figure 5b is 4615 and Figure 5d is 1010 showing a side-by-side comparison of the photoresist. These SEM photomicrographs show that the 4615 does have a straighter photoresist sidewall.

Conductor width:

- These measurements were taken by inspectors using a microscope. The path widths measured were 5 and 10 mil lines as shown in Figures 6 and 7. Figure 6 is the results of the photoresist measurements before etch, and Figure 7 shows the results of the copper conductor after etch. Each figure shows the phototool measurement as a straight line compared to the 4615 and 1010 measurements. Table 3 tabulates the data of 4615 and 1010 with the calculation of the standard deviation. In comparing after-develop and final conductor measurements, both photoresists have performed very similarly.

Table 2. Process Steps for PWB Photoimaging

STEPS	SOLVENT OPERATIONS (Old - Du Pont 1010)	AQUEOUS OPERATIONS (New - Du Pont 4615)
Clean	Chemical Equipment CE# 55762	Chemical Equipment CE# 55762
Lamination	Hot Roll Laminator CE# 54013/59225 Exit Temperature 120°F	Hot Roll Laminator CE# 54013/59225 Exit Temperature 120°F
Exposure	ORC - Optibeam 6000 Equipment CE# 66483 Scanex II Equipment CE# 55114 Stouffer Step Photoresist Step 6	ORC - Optibeam 6000 Equipment CE# 66483 Scanex II Equipment CE# 55114 Stouffer Step Photoresist Step 9
Develop	Equipment CE# 40905 Solvent - 1,1,1- Trichloroethane (MS 4702903-00-511)	Equipment CE# 64707 Chemistry - 1% by wt. Sodium Carbonate Monohydrate (MS 4553052-00-800) Temperature 80°F
Etch	Alkaline Etch Equipment CE# 54699 Chemistry - MacDermid Ultra Etch Make-up (MS 4702733) Replenisher Ultra Etch 50 (MS 4702981)	Alkaline Etch Equipment CE# 54699 Chemistry - MacDermid Ultra Etch Make-up (MS 4702733) Replenisher Ultra Etch 50 (MS 4702981) Replenisher Ultra Etch Aqueous (MS 4702980)
Strip	Equipment CE# 50542 Solvent - Methylene Chloride (MS 4702908-00-511)	Equipment CE# 64706 Chemistry - 3% by wt. Potassium Hydroxide (MS 4547151-01-521) Temperature 130°F

Figure 6. Inner Layer TMS, Photoresist Conductor Width Before Etch, 4615 Versus 1010

Figure 7. Inner Layer TMS, Final Copper Conductor Width After Etch, 4615 Versus 1010

Table 3. 4615 Versus 1010 ($\bar{x} \pm$ Standard Deviation, mils)

CONDUCTOR WIDTH (mils)	PHOTO- TOOL	AFTER DEVELOP		FINAL CONDUCTOR	
		4615	1010	4615	1020
5	5.5 $\pm$ 0.2	5.9 $\pm$ 0.3	6.0 $\pm$ 0.2	4.3 $\pm$ 0.5	5.8 $\pm$ 0.7
10	10.6 $\pm$ 0.2	10.9 $\pm$ 0.3	11.0 $\pm$ 0.3	9.4 $\pm$ 0.6	10.6 $\pm$ 0.7
15	15.6 $\pm$ 0.1	15.6 $\pm$ 0.3	15.8 $\pm$ 0.2	14.3 $\pm$ 0.8	15.6 $\pm$ 0.5

Double-Sided Evaluation

This portion of the evaluation consisted of specifically looking at epoxy/glass double-sided PWB material with 1.0 oz/ft² copper-clad, then panel plated with copper before the print and etch process.

Aqueous processable dry film photoresists were evaluated as potential replacements for existing solvent processable dry films. Du Pont's Riston 4615 dry film photoresist was chosen as the replacement for Du Pont's Riston 1020 solvent processable dry film photoresist.

This evaluation involved the same materials compatibility testing characterization as was done on the prior inner layer results. Du Pont's Riston 4615 was exposed to a variety of present and potential processing chemicals for extended periods of time. The 4615 dry film photoresist and both the developer and the stripper solutions were analyzed for significant changes as a result of chemical exposure. The imaging and developing processes were characterized to ensure an acceptable capability level and to achieve repeatable results. The double-sided evaluation results are described below.

Photoresist sidewall results shown by SEM:

- Figures 1 and 2 show the phototool and the placement of the coupons in relation to the panel. Coupons were taken after develop as shown in the 15-mil conductor in Figure 8. Figure 8a is 4615 and Figure 8c is 1020 at the same magnification of 100X. Figure 8b is 4615 and Figure 8d is 1020 as a side-by-side comparison of the photoresist. Figure 9a is 4615 and Figure 9c is 1020 at the same magnification of 100X. Figure 9b is 4615 and Figure 9d is 1020 as a side-by-side comparison of the photoresist. These SEM photomicrographs show that the 4615 does have a photoresist sidewall similar to the 1020. Figures 10 and 11 are 10-mil conductors.

a. 4615 Photoresist Sidewall, 100X

b. 4615 Photoresist Sidewall, 1000X

c. 1020 Photoresist Sidewall, 100X

d. 1020 Photoresist Sidewall, 1000X

Figure 8. Photoresist Sidewalls--Coupons Taken After Develop, 15 mil Conductor (Sample 1)

a. 4615 Photoresist Sidewall, 100X

b. 4615 Photoresist Sidewall, 1000X

c. 1020 Photoresist Sidewall, 100X

d. 1020 Photoresist Sidewall, 1000X

Figure 9. Photoresist Sidewalls--Coupons Taken After Develop, 15 mil Conductor (Sample 2)

Conductor width:

- These measurements were taken by inspectors using a microscope. The path widths were 5, 10, and 15 mil lines as shown in Figures 12, 13, 14, and 15. Figure 12 is the results of the 10 and 15 mil measurements before etch, and Figure 13 is the 5 and 10 mil measurements before etch. Figure 14 is the results of the 10 and 15 mil measurements after etch, and Figure 15 is the 5 and 10 mil measurements after etch. Each figure shows the phototool measurement as a straight line compared to the 4615 and 1020 measurements. Table 4 shows the data for 4615 and 1020 with the calculation of the standard deviation. In comparing after-develop and final conductor, both photoresists have performed very similarly.

Cross section:

- Figure 16 is a cross section of the 4615 after develop displaying the 5, 10, and 15 mil photoresist conductors. Figure 17 is the cross section of the 5, 10, and 15 mil copper conductors after etch and photoresist strip. Both sets of cross section photographs do not display any unusual features as typically seen using dry film photoresist and alkaline etching.

Print and Etch Conclusions

The final conductor shape or final conductor measurement has been shown not to be significantly different, whether processed with aqueous processable or solvent processable dry film photoresist.

The Du Pont 4615 dry film photoresist was shown to be a usable fully aqueous product to manufacture print and etch printed wiring boards. These photoresists were chemically resistant to the PWB plating chemistries and were able to produce 0.005 inch lines and spaces on final copper-etched and photoresist-stripped product.

Characterization of Pattern Plating Process

Solvent to Aqueous Photoresist Comparison

In the plating portion of this effort, copper and tin-lead were plated on the panels using the aqueous processable Dynachem HG photoresist. The panels were processed using a phototool pattern and the FM&T pattern/channel plating operations. Table 5 is a side-by-side comparison of the Dynachem HG aqueous dry film photoresist to Du Pont 1020 solvent dry film photoresist.

The panels were processed using Du Pont 1020 solvent photoresist and Dynachem HG aqueous photoresist. The material was epoxy/glass with 0.5 oz/ft² double-sided copper. The phototool is shown in Figures 1 and 2. Figure 18 gives a graphical display of the pattern plating process.

Figure 12. 4615 TMS: Photoresist Conductor Width Before Etch, Double-Sided Panel Plate, 10 and 15 mil

Figure 13. 4615 TMS: Photoresist Conductor Width Before Etch, Double-Sided Panel Plate, 5 and 10 mil

Figure 14. 4615 TMS: Copper Conductor Width After Etch, Double-Sided Panel Plate, 10 and 15 mil

Figure 15. 4615 TMS: Copper Conductor Width After Etch, Double-Sided Panel Plate, 5 and 10 mil

Table 4. Double-Sided, 4615 Versus 1020 ($\bar{x} \pm$ Standard Deviation, mils)

CONDUCTOR WIDTH (mils)	PHOTO-TOOL	AFTER DEVELOP		FINAL CONDUCTOR	
		4615	1020	4615	1020
5	5.1 $\pm$ 0.05	5.49 $\pm$ 0.2	5.6 $\pm$ 0.2	3.1 $\pm$ 0.5	3.4 $\pm$ 0.4
10	10.1 $\pm$ 0.09	10.4 $\pm$ 0.2	10.8 $\pm$ 0.3	7.7 $\pm$ 0.4	7.9 $\pm$ 0.7
15	15.1 $\pm$ 0.06	15.4 $\pm$ 0.2	15.6 $\pm$ 0.2	12.6 $\pm$ 0.6	12.8 $\pm$ 0.6

Results: Aqueous Pattern Processing Evaluation

Path width measurements were made by printed wiring board inspectors after photoresist developing, after the plated copper paths were etched and the tin-lead was stripped. Figure 19 is a chart of the 10-mil conductors with the one-layer photoresist. Figure 19 shows the phototool measurements, the solvent measurements, and the aqueous measurements. Figure 20 is similar to Figure 19 but shows the 5-mil conductor path measurements. These measurements were then compared to the actual phototool path width measurements and to the solvent and aqueous conductor paths. Five measurements were taken from each side of the panel in the C₂-9 and C₃- C₄-9 areas. These areas contain 5, 10, and 25 mil lines and spaces.

Figure 21 shows SEM photographs of Du Pont's solvent 1020 photoresist both before and after alkaline etch. Figure 21b does give some indication that there was a positive foot to the photoresist sidewall, which caused a slight negative foot in the plated copper.

After etching, Figure 21d shows that the 1020 sample is slightly rougher than the HG (Figure 22d).

Figure 22 shows SEM photographs of Dynachem's HG photoresist, both before and after alkaline etch. In comparing 1020 (Figure 21b) to HG (Figure 22b), the HG photoresist has a comparable copper sidewall.

Figures 23 and 24 are overall views of the circuit conductor edge. The two photographs in Figure 23 are Dynachem HG and are taken at 10X (Figure 23a) and 40X (Figure 23b) to show the straightness of the circuit path. A ragged edge ("mouse bites") in the plated copper and tin-lead would be a sign of poor photoresist processing. These two photographs reveal no significant difference in overall appearance when compared to solvent 1020 in Figure 24. When compared, these four pictures show no significant difference and are considered to show favorable results.

a. 5 mil, 250X

b. 10 mil, 250X

c. 15 mil, 250X

Figure 16. After Develop: 5, 10, and 15 mil Photoresist Conductors, 4615, Double-Sided, Panel Plate

a. 5 mil, 250X

b. 10 mil, 250X

c. 15 mil, 250X

Figure 17. After Etch: 5, 10, and 15 mil Copper Conductors, 4615, Double-Sided, Panel Plate

Table 5. Comparison of Solvent Operations to Aqueous Operations (Single Layer)

SOLVENT OPERATIONS (Old -- Du Pont 1020)	AQUEOUS OPERATIONS (New -- Dynachem HG)
(2) Prelamination Clean:	(2) Prelamination Clean:
(a) Wet Blast	(a) Wet Blast
(b) Clean	(b) Clean
(3) Lamination:	(3) Lamination:
Roll Temperature (104°C)	Roll Temperature (116°C)
Exit Temperature (125°F)	Exit Temperature (125°F)
(4) Exposure:	(4) Exposure:
Du Pont 1020 (Stouffer Step 6)	Dynachem HG (Stouffer Step 9)
(5) Develop:	(5) Develop:
Equipment #40905	Equipment CE# 64707
Solvent - 1,1,1-trichloroethane	Solution - 1% by Weight
(MS 4702903-00-511)	Sodium Carbonate Monohydrate
	(MS 4553052-00-800)
	Temperature - 80°F
(6, 7) Plate:	(6, 7) Plate:
Copper	Copper
Tin-Lead	Tin-Lead
(8) Strip:	(8) Strip:
Equipment - CE# 50542	Equipment - CE# 64706
Solvent - Methylene Chloride	Solution - 3% by Weight
(MS 4702908-00-511)	Potassium Hydroxide
	(MS 4547151-01-521)
	Temperature - 130°F
(9) Etching:	(9) Etching:
(a) Hand Scrub - Pumice	(a) Hand Scrub - Pumice
(b) Conveyorized Etch	(b) Conveyorized Etch

- a. Raw material,
no processing.

- b. Panel is drilled, deburred,
and holes are metallized with
electroless copper and
electroplated copper flash.

- c. Positive phototool used to
image dry film photoresist.

- d. Panel is deoxidized, laminated with
dry film photoresist, imaged with
phototool, developed, and is
ready for electroplated copper.

- e. Panel has been electroplated with copper
and tin-lead. The tin-lead will be the etch
maskant to protect the copper path and
plated-through holes during chemical
removal of unwanted copper.

- f. Photoresist has been chemically
removed; ready for chemical etch.

- g. Unwanted copper has been
chemically etched away.

- h. Finished copper/tin lead circuit.

Figure 18. Steps in Pattern Plating Process Evaluation

MEAN/RANGE CHART
 PATH WIDTH CONTROL AFTER ETCH
 (10 MIL CONDUCTORS)
 PATTERN PLATING USING ONE LAYER 2 MIL PHOTORESIST

Figure 19. Measurements of Phototool and Solvent and Aqueous Photoresists (10 mil)

MEAN/RANGE CHART
PATH WIDTH CONTROL AFTER ETCH
(5 MIL CONDUCTORS)
PATTERN PLATING USING ONE LAYER 2 MIL PHOTORESIST

Figure 20. Measurements of Phototool and Solvent and Aqueous Photoresists (5 mil)

a. After Photoresist Strip, Before Copper Etch, 100X

b. After Photoresist Strip, Before Copper Etch, 1000X

c. After Copper Etch, 100X

d. After Copper Etch, 1000X

Figure 21. SEM Photomicrographs of 1020 Photoresist Before and After Alkaline Etch

a. After Photoresist Strip, Before Copper Etch, 100X

b. After Photoresist Strip, Before Copper Etch, 1000X

c. After Copper Etch, 100X

d. After Copper Etch, 1000X

Figure 22. SEM Photomicrographs of HG Photoresist Before and After Alkaline Etch

a. Top, 10X, After Tin-Lead Plate

b. Bottom, 40X, After Tin-Lead Plate

Figure 23. Overall View of Circuit Conductor Edge Processed With Dynachem HG Aqueous Photoresist

a. Top, 10X, After Tin-Lead Plate

b. Bottom, 40X, After Tin-Lead Plate

Figure 24. Overall View of Circuit Conductor Edge Processed With Du Pont 1020 Solvent Photoresist

Figures 25 and 26 are cross section photographs of panels in a characterization study with HG photoresist. These photographs show how the HG sidewall is affected by exposure and developing variations. The variables that were changed are exposure, developer temperature, and developer pH.

The parameters for Figure 25 were as follows:

- a. Over exposed, low develop temperature
Expose 250, step 12
Develop temperature 70°F
pH 10.8
Concentration 1.02%
- b. Over exposed, high develop temperature, low pH
Expose 250, step 12
Develop temperature 90°F
pH 9.8
Concentration 0.66 %
- c. BEST PARAMETERS
Expose 155, step 10
Develop temperature 80°F
pH 10.6
Concentration 0.98 %
- d. Over exposed, low develop temperature, low pH
Expose 250, step 12
Develop temperature 70°F
pH 9.9
Concentration 0.64 %

The parameters for Figure 26 were as follows:

- a. Under exposed, low develop temperature, high pH
Expose 75, step 7
Develop temperature 70°F
pH 10.8
Concentration 1.02 %
- b. Under exposed, low develop temperature, low pH
Expose 75, step 8
Develop temperature 70°F
pH 9.9
Concentration 0.64%
- c. Under exposed, low develop temperature, low pH
Expose 75, step 8
Develop temperature 70°F
pH 9.9
Concentration 0.64%
- d. Under exposed, high develop temperature, low pH
Expose 75, step 7
Develop temperature 90°F
pH 9.8
Concentration 0.64%

a. 500X

b. 500X

c. 500X

d. 500X

Figure 25. Cross Sections of Panels Showing Sidewall Effects of Three Variables, Processed With HG Aqueous Photoresist, Sample 1

a. 500X

b. 500X

c. 500X

d. 500X

Figure 26. Cross Sections of Panels Showing Sidewall Effects of Three Variables, Processed With HG Aqueous Photoresist, Sample 2

The panel cross section in Figure 27a shows a 10 mil path after copper and tin-lead plating but before etch. The cross section in Figure 27b is shown after etch, with tin-lead overhanging the final etched copper conductor. These two cross sections are typical of those from the pattern plating process; they show that the aqueous photoresist process would manufacture circuits similar to the solvent process.

Results and Recommendations

- The study for prove-in of the aqueous dry film photoresist process at FM&T showed that it would perform within current acceptance requirements of the solvent dry film photoresist process.
- The results shown are that the aqueous photoresist does produce an acceptable PWB product. It is the author's recommendation that the pattern/channel plating process using the aqueous "HG" process as shown be accepted for WR production.

Double Layer Photoresist: Du Pont 1020 Versus Dynachem HG

Double Layer Evaluation Description

An evaluation was conducted to use double layer photoresist for plating applications that need more than 1 mil minimum of copper plating in the hole. Channel plating (Sandia Livermore originated term) used two layers of photoresist and exposed the phototool using a quarter wave retarder. The quarter wave retarder would only allow certain wavelengths of light through it, resulting in very collimated exposure. The present exposure equipment uses advanced collimated light sources which produce a higher resolution of the circuits, thereby eliminating the requirement for the quarter wave retarder. This evaluation used the same chemical processes as the single layer photoresist, with the exception of hot roll laminating two layers rather than the typical one layer (see Figure 28).

Test Panel Processing

The differences between aqueous and solvent processing for double layer photoresist photolithography operations are shown in Table 6.

The evaluation lot consisted of 12 panels, epoxy/glass double-sided with 0.5 oz. copper-clad. Eight panels were processed using two layers of 2.0 mil aqueous processable Dynachem HG photoresist and four panels were processed using two layers of 2.0 mil solvent processable Riston 1020 photoresist.

Table 6. Double Layer Evaluation: Solvent Versus Aqueous Processing

SOLVENT OPERATION (Old -- Du Pont 1020)	AQUEOUS OPERATION (New -- Dynachem HG)
Wet Blast:	Wet Blast:
Clean: Chemical Equipment CE# 55762	Clean: Chemical Equipment CE# 55762
Lamination: Vacuum Laminator CE# 60503 Exit Temperature 120°F	Lamination: Vacuum Laminator CE# 55762 Exit Temperature 120°F
Exposure: ORC -- Optibeam 6000 Equipment CE# 66483 Stouffer Step 9	Exposure: ORC -- Optibeam 6000 Equipment CE# 66483 Stouffer Step 10
Develop: Equipment CE# 40905 Solvent -- 1,1,1-Trichloroethane (MS 4702903-00-511)	Develop: Equipment CE# 64707 Solution -- 1% by Weight Sodium Carbonate Monohydrate (MS 4553052-00-800) Temperature 80°F
Plate: Copper Tin-Lead	Plate: Copper Tin-Lead
Strip: Equipment CE# 50542 Solvent -- Methylene Chloride (MS 4702908-00-511)	Strip: Equipment CE# 64706 Solution -- 3% by Weight (MS 4547151-01-521) Temperature 130°F

Figure 29. Conductor Width Before Plating (Double Layer, Processed With 1020 Solvent Photoresist and HG Aqueous Photoresist)

Figure 30. Conductor Width After Etch (Double Layer, Processed With 1020 Solvent Photoresist and HG Aqueous Photoresist)

Figure 30 is similar to Figure 29 in that the six left measurements are 1020 and the six right are HG. In looking at the data, it can be shown that both the panels processed with 1020 and those processed with HG result in very repeatable measurements. The data was reduced to obtain the mean and standard deviation for both conductor widths. The phototool conductor width measured 10.1 ± 0.3 and 26.1 ± 3.0 and produced the final conductor widths of 8.0 ± 2.1 and 24.1 ± 5.1 using Du Pont 1020; the readings were 8.0 ± 1.6 and 23.2 ± 3.9 using Dynachem HG. Table 7 shows the average width comparison before plating and the final conductor. The final conductor width is defined as the conductor after etching and tin-lead stripping.

Table 7. HG Versus 1020, Double Layer (Average Measurement, mils)

CONDUCTOR WIDTH (mils)	PHOTOTOOL		AFTER DEVELOP				FINAL CONDUCTOR			
			HG		1020		HG		1020	
	Front	Back	Front	Back	Front	Back	Front	Back	Front	Back
10	10.1	10.2	10.8	10.9	10.2	10.1	7.9	8.0	7.6	8.3
25	26.0	26.2	26.8	27.8	25.6	26.5	22.8	23.6	23.2	25.0

The next series of pictures shows cross sections of the double layer photoresist as processed through plating and the final etched circuit with the tin-lead stripped.

Conductor Sidewall After Alkaline Etching

Cross section photographs of the conductor after copper etch were taken as shown in Figure 31. These photographs show no significant difference in sidewall configuration of the conductors produced with Du Pont 1020 or Dynachem HG. Both conductors show tin-lead overhang which is a condition of tin-lead plating more than desired or etching more than desired. The photographs clearly show that solvent or aqueous photoresist does not make a difference in the final conductor.

Final Conductor Sidewall Cross Section

The final conductor after etch and tin-lead strip is shown in Figure 32. The final conductor cross section shows that there is no difference in appearance in the copper area. The sidewall squareness shows that similar plating and etching conditions would result with both the solvent and aqueous photoresists.

a. Processed Using 1020, 250X

b. Processed Using 1020, 250X

c. Processed Using HG, 250X

d. Processed Using HG, 250X

Figure 31. Cross Sections of Conductors After Alkaline Etching of Copper

a. Processed Using 1020, 250X

b. Processed Using HG, 250X

**Figure 32. Cross Sections of Final Conductors
After Etching and Tin-Lead Stripping**

Scanning Electron Microscope

Figures 33 and 34 are SEM photomicrographs of both solvent 1020 and aqueous HG. The overall top view of the photoresist after developing is shown in Figure 33. These photographs were taken with magnifications of 100X and 1000X. These photographs indicate no significant difference between resolution when processed using either Du Pont 1020 photoresist or Dynachem HG photoresist.

Figure 34 is the photomicrographs of the process directly after the copper and tin-lead plating but before photoresist stripping. These photographs show the expected results of the tin-lead plating.

Figure 35 is the final circuit before etch (Figure 35a) and after the alkaline etching operation (Figure 35b). The pictures show some over-plating of the tin-lead, but that is not uncommon to the pattern plating process. The overhang of the tin-lead is caused by the removal of the copper during the etch operation. Although this condition is not optimum, it does manufacture acceptable product. Further characterization of the pattern plating process would be needed to correct this condition, but that work was not within the scope of this project.

Pattern Plating Results

The final conductor shape and final conductor measurement were shown not to be significantly different, whether processed with aqueous-processable or solvent-processable dry film photoresist. The Dynachem HG dry film photoresist was shown to be a usable, fully aqueous product to manufacture pattern-plated printed wiring boards. This photoresist was chemically resistant to the PWB plating chemistries and was able to produce 0.005 inch lines and spaces on final product. This film was successfully laminated with double and single layer hot rolled photoresist, proving to be an acceptable material for printed circuit board production.

ACCOMPLISHMENTS

Fully aqueous processable dry film photoresists were evaluated and chosen as replacements for the solvent processable dry film photoresists that were used in printed wiring board production at FM&T.

The Du Pont 4615 dry film photoresist was shown to be a usable fully aqueous product to manufacture print and etch printed wiring boards. These photoresists were chemically resistant to the PWB plating chemistries and were able to produce 0.005 inch lines and spaces on final copper-etched and photoresist-stripped product. This film was successfully laminated with double and single layer hot rolled photoresist and was proven to be an acceptable material for printed circuit board production.

Du Pont's 1010, 1020, and 1230 solvent processable photoresists were replaced with Du Pont's 4615 aqueous processable photoresist for print and etch applications and with Dynachem's HG

aqueous processable photoresist for pattern plating of copper and tin-lead. The final conductor shape and measurement were shown to not be significantly different, whether processed with aqueous processable or solvent processable dry film photoresist.

The print and etch process was modified to accommodate alkaline-sensitive films. This modification consisted of evaluating a replenisher that could be placed in the flood rinse module of the etching equipment which would not strip the photoresist. The problem was solved by using two replenishers, one feeding into the etchant sump with the higher pH and one feeding into the flood rinse module having a lower pH which would not attack the photoresist.

a. HG, After Strip, Before Etch, 500X

b. HG, After Etch, 500X

Figure 35. Final Circuit Before and After the Alkaline Etching Operation

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Appendix

Elimination of CHCs and CFCs From Production Use

**THREE-PARTY AGREEMENT FOR THE ELIMINATION OF
CHLORINATED AND FLUORINATED HYDROCARBONS (CHCS & CFCS)
AT THE KANSAS CITY PLANT**

The Department of Energy, Allied-Signal, Inc., Kansas City Division, and Sandia National Laboratories mutually agree to work toward a three-year goal to eliminate CHC and CFC usage at the Kansas City Plant.

**THREE-YEAR GOAL: BY JULY 1993, ELIMINATION OF CHCs AND CFCs TO
THE GREATEST TECHNICAL EXTENT POSSIBLE
CONSISTENT WITH NUCLEAR SAFETY AND
STOCKPILE RELIABILITY REQUIREMENTS**

In order to reach the above targets, DOE, Sandia and Allied-Signal agree to cooperatively work toward changing design and processing requirements to preclude the usage of CFCs and CHCs. Each agency agrees to apply available technical resources to evaluate and qualify alternative approaches.

It is further stipulated that Sandia will continue to work with Allied-Signal and other Production Agencies to prepare a formalized coordinated Program/Strategy for reducing all types of manufacturing hazards for Sandia designed components. It is also agreed that Sandia and Allied-Signal will join with other Nuclear Weapons Complex Contractors to identify and implement relevant technical research projects within the DOE Office of Defense Programs and Office of Environmental Restoration & Waste Management programs managed by AL. These technical research projects will have as their goal significant reductions in environmental hazards, especially in the area of undesirable cleaning solvents such as CHCs and CFCs.

Louis W. Smith, Allied-Signal, KCD

Orval E. Jones, Sandia National Laboratories

July 10, 1990

Earl W. Bean, Department of Energy

chemicals may have. In addition, EPA is in the process of writing a National Emission Standard for Hazardous Air Pollutants (NESHAP) which will control ambient air emissions for perchloroethylene, trichloroethylene and methylene chloride. Moreover, since these chemicals are classified as probable human carcinogens, they are targets for EPA regulations concerning wastewater discharge. More importantly, many companies worried about the stigma of a probable human carcinogen classification may use TCA instead of the other solvent because of concerns over public image, liability and insurance expenses. For these reasons, additional layers of federal regulation may increase user preference for methyl chloroform.

Third, the reduction in CFC production and import required by the EPA rule implementing the Montreal Protocol may lead some CFC users to substitute methyl chloroform for CFCs. However, the Agency has made clear that it does not view shifting from CFC-113 to other chlorinated solvents which are currently under regulatory scrutiny as an acceptable solution to protecting the ozone layer.

D. CFC Substitutes

EPA has sponsored and co-chaired with industry a variety of technological and economic workgroups to discuss alternatives to CFCs in industrial and commercial uses. For example, EPA and industry are engaged in cooperative projects to determine whether electronic components and circuit boards can be cleaned with aqueous and terpene cleaners instead of CFC-113 or methyl chloroform. In addition, the Agency has been working with chemical manufacturers and industry representatives to find out the extent to which CFC-113 and methyl chloroform can be replaced in metal cleaning or degreasing.

EPA is coordinating the review of these substitutes among various Agency offices and with other federal agencies, to ensure that current federal regulations or policies do not unnecessarily hinder the switch away

from CFCs to other chemicals or processes. For example, the EPA is working with the U.S. Department of Defense (DOD) to revise and eliminate military procurement specifications that require manufacturers to specifically use CFC-113, methyl chloroform or other chlorinated solvents in electronic, precision and metal cleaning. Eliminating restrictive specifications would allow CFC-113 and methyl chloroform to be replaced with other chemicals, non-chemicals solutions, or processes that perform equally as well or better and do not contribute to ozone depletion.

D. Carbon Tetrachloride

Carbon tetrachloride is a relatively strong ozone depletor, and in fact has a greater ozone depleting potential than any of the CFCs currently listed in the Protocol. In the U.S. it is used primarily as a feedstock to produce other CFCs. Emissions from this use were believed to be small, and therefore it was reasonable to exclude carbon tetrachloride from the original Protocol. However, atmospheric levels have been found to be greater than would be expected from past emissions estimates. Preliminary evidence suggests that in Japan, the Eastern Block countries and less developed countries, carbon tetrachloride is used in the production of pesticides, as a solvent and in the production of synthetic rubber and dyes, among other things. Emissions estimates for these uses are still uncertain. Nevertheless, EPA believes that they may be significant and that it may be necessary to control them under the Protocol.

E. Public Comments Sought

As stated previously, EPA is issuing this ANPRM to solicit general comments on the role of methyl chloroform and carbon tetrachloride in stratospheric ozone protection efforts, and specific comments on the possible effect of adding methyl chloroform and carbon tetrachloride to the list of chemicals regulated by the Montreal Protocol. The Agency is specifically seeking comments on the following points.

(1) What substitutes exist for methyl chloroform in the following use categories: metal, precision and electronic cleaning, aerosols, and adhesives?

(2) What can EPA do to expedite and assist in finding substitutes for methyl chloroform in these use categories? What are the barriers to such substitution?

(3) Will the demand for methyl chloroform increase when the initial reduction in CFC use is effective, in July 1989?

(4) Should the international response be to freeze, reduce or eliminate methyl chloroform and carbon tetrachloride? How, and why or why not? Over what time period?

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