Process Development and Process Control Methodology of a Carbon-Black Dispersion Technology for Direct Metallization

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Abstract

Direct plating technologies have acquired a rapidly expanding share of the plated through hole market over the past three years. Although considered by many to still be in its infancy, many direct plate technologies are in their third or forth product life cycle. Since direct plate technologies are fundamentally different than conventional electroless copper processes, efforts focused on continuous improvement of these technologies is warranted. The further refinement of these technologies centers not only on improvement of the chemistry, but improvements to the process control tools and techniques necessary to successfully implement these technologies in a production environment.

This paper discusses the product development methodology of a unique carbon black dispersion technology, from conception of the idea to the development of a production proven process control methodology. A five stage product development protocol is described, beginning with statistical experimental design work focusing on the identification and optimization of critical variables not only within the direct plate technology, but within interdependent processes such as electrolytic copper as well. The culmination of this work, an extended Capability Study performed at a production installation, is also described.

By utilizing a systematic approach to product development, successful process control strategies were developed in conjunction with new chemistry formulation, providing critical process control methodologies prior to production application of this technology. These process control tools, which are universally applicable to many commercially available direct plating technologies, are designed to be manufactured by the customer utilizing actual production parameters for variables such as drilling and laminate. The reliability of this process control tool has been verified by extensive production and statistical experimental design testing.

Introduction

Electroless Copper based plated-through-hole (PTH) technology, a standard in our industry, is still the predominant PTH technology in use today. Environmental, Safety, Process Control and Cost Reduction are the main factors driving the search for PWB manufacturers to find reliable alternatives to PTH processing. The direct plating process, Blackhole®, focuses on meeting these industrial challenges.

The Blackhole® direct plate process is a carbon black dispersion technology which eliminates the need for electroless copper in the PWB manufacturing process. The Blackhole® process contains no heavy metals, no formaldehyde, and minimizes the use of chelating agents. As it is now formulated, Blackhole® is commercially available as an automated, horizontally conveyorized system known as Blackhole® Process II. A manufacturing process utilizing Blackhole® proceeds normally from innerlayer fabrication through desmear and then continues through the Blackhole® Process II conveyorized system as illustrated in Figure 1. Panels are processed twice through the conditioning and carbon black process steps in order to assure complete plated-through-hole coverage following acid copper electroplating.

Figure 1
Blackhole® Process II Cycle

Position	Process
1	Blackhole® Clean 110-C
2	Rinse
3	Blackhole® Bath #1
4	Air Knife Dry
5	Rinse
6	Blackhole® Condition 115-C
7	Rinse
8	Blackhole® Bath #2
9	Heated Dry
10	Blackhole® Microclean
11	Rinse
12	Blackhole® Antitarnish
13	Rinse
14	Dry

Following this conveyorized process, panels are processed through additional fabrication steps. These may include either pattern or panel plate operations and continue through to final board fabrication.

PWB's manufactured with the Blackhole® Process II technology undergo a wide variety of production and end-user reliability testing. Figure 2 shows some examples of current reliability testing and pass/fail criteria.

Figure 2
Blackhole® Process II Reliability

Reliability Test	Test Method	# of Cycles	Results
Thermal Stress Test	IPC TM-2.6.8	6	Pass
Fluidized Sand Thermal Cycle Test	IPC TM-2.6.8.2 (AT&T FSB)	40	Pass
Air to Air Thermal Cycle Test	MIL-T-Cycle	400	Pass
Component Rework Simulation	IPC TM-2.4.36	5	Pass
Military Approval	MIL-P-55110D	-	Pass

The success of this current process is shown by its continued acceptance into the marketplace with upwards of 140 PWB manufacturing facilities running the Blackhole® process representing a total of 150 MM square feet of PWB's produced.

In the spirit of continuous improvement at MacDermid and to meet competitive challenges our efforts have focused on the development of a new single pass carbon black dispersion technology for direct metallization. The goal for the single pass process is enhanced performance and reliability to the current Blackhole® Process II system. Single-pass processing would reduce the number of process steps and reduce the costs associated with equipment requirements and process control. Additionally, cycle time reduction would be achieved.

New Process Development

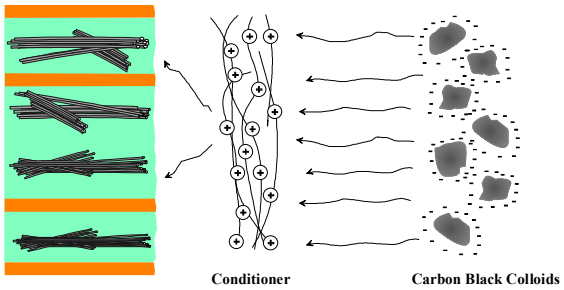
Past experience with Blackhole® proved that single-pass reliability could not be achieved with the existing Blackhole® formulation. In fact, it was due to this lack of reliability with single-pass processing that led to the development of the double-pass (Process II) system.

In order to determine if we could improve the performance of Blackhole® in a single-pass mode we needed to look at the entire process cycle and determine which process steps were the most influential for through-hole plateability and reliability. Focused efforts were directed at the conditioning and carbon black dispersion chemistries including the individual raw materials in the formulation to determine which component or components had the greatest influence on performance. Specific processing parameters were also evaluated as to their effect on performance.

Conditioner

The role of the conditioner in the Blackhole® process is similar to most other through-hole plating technologies. In the Blackhole® process the conditioner imparts a uniform positive charge throughout the substrate making it suitable for the attraction of the negatively charged carbon black particles.

Figure 3
Conditioning Mechanism



The present formulation for Blackhole® conditioning includes a cationic conditioning agent and a surface tension reducing (wetting) agent in an alkaline buffering matrix.

Generation of degradation products from one of the components in the Conditioner formulation was proposed as the source of performance deterioration over time. In order to confirm this mechanism and to isolate the responsible component a study was run using an acid copper propagation performance evaluation. Performance was judged by backlight evaluation of through-hole propagation in a specific time frame. In an example of this testing, three Conditioner solutions were made-up according to the normal formulation except that each was missing one of the basic components of the formula. A standard Conditioner solution was included for comparison. The baths were then allowed to age until the conditioning performance could be monitored for diminished capability. The missing component was then added back to each of the three test solutions and the plating performance was measured. Figure 4 illustrates the experiment conducted and the performance results.

Figure 4
Conditioner Degradation Evaluation

Solution	Additions After 4 weeks	Performance After 4 weeks Propagation @ 10' flash
Alkaline Matrix Cationic Cond. Wetting Agent	-	70%
Alkaline Matrix Wetting Agent	Cationic Cond.	72%
Alkaline Matrix Cationic Cond.	Wetting Agent	70%
Cationic Cond. Wetting Agent	Alkaline Matrix	95%
-	Alkaline Matrix Cationic Cond. Wetting Agent	>95%

This data indicated that performance deterioration was associated with the alkaline matrix used in the present formulation. The aged solution to which the fresh alkaline matrix materials were added showed performance equivalent to a fresh Conditioner make-up.

Further development focused on a replacement for this alkaline matrix. It has been found that performance life and consistency could be improved when the alkalinity is provided by an alternative alkaline matrix media.

Working Conditioner baths were made-up using alternative alkaline matrices. All baths were maintained at an operating temperature of 130 F for a 4 week evaluation period in order to determine performance based on product consistency. Panels were processed through a Blackhole® Process comparing each of the made-up Conditioners. The panels were then flash plated for 1' in acid copper and evaluated for percent through-hole propagation. Results from the performance tests over this 4 week period are shown in Figure 5.

Figure 5
Conditioner Performance Consistency

Run	Control	Alk. Matrix 1	Alk. Matrix 2	Alk. Matrix 3
1	84%	70%	99%	98%
2	52%	61%	89%	92%
3	69%	74%	92%	84%
4	57%	50%	91%	89%
5	69%	72%	92%	91%
6	67%	71%	98%	98%
7	61%	70%	92%	94%
8	66%	64%	90%	93%
Avg.	65.6%	66.5%	92.9%	92.4%
Range	32%	24%	10%	14%

The table illustrates an improvement in performance consistency observed with 2 of the 3 alkaline matrices tested. Alk. Matrix 2 proved to be most consistent in acid copper propagation.

To evaluate the performance based on product life, a working bath made with Alk. Matrix 2 was compared to the present formulation as a control. Both solutions were placed in standard Blackhole® process equipment for conditioners and operated at 130 F for 10 hours /day. Backlight evaluation, based on a 1' acid copper flash, was performed on a weekly basis. After 3 weeks of operation, well beyond the typical bath life, the performance for Alk. Matrix 2 was at 65% whereas the control was at <20%.

A patent application has been submitted encompassing the types of alkaline matrices which showed improvement in the conditioning mechanism for through-hole plating. The improvements to the Conditioner are applicable to current Blackhole® processes and are being incorporated into continued product development of the Blackhole® SP process.

Carbon Black

Our development efforts started with the properties of the carbon black used in the Blackhole® formulation. The carbon black performance is defined by several physical and chemical properties, including particle size, surface area, structure, surface chemistry and physical form. Some of these properties are naturally occurring while others are imparted or enhanced by chemical and/or physical treatments. Several treatment methods for carbon black were developed and studied in our research efforts. Initial process screening began by looking at a variety of these treated and untreated carbon blacks and determining which of the imparted modifications, if any, gave improved through-hole propagation of acid copper over a standard carbon. A patent has been granted based on these modifications and the resultant surface properties which enhance through-hole plating.

Once the desirable properties were determined, experimentation continued with actual through-hole copper propagation evaluated by backlight observations. The data in Figure 6 shows performance test results obtained from potential candidates.

Figure 6
Carbon Black Modification v. 1' Flash Plate Performance

Carbon Black Modification	Run #1	Run #2	Run #3	Run Avg.
CB1 (control)	13%	23%	7%	14%
CB2	18%	28%	9%	18%
CB3	8%	12%	5%	8%
CB4	38%	60%	28%	42%
CB5	26%	42%	32%	33%
CB6	82%	99%	70%	84%
CB7	43%	72%	51%	55%

Dispersing Agent

The role of the dispersant is to surround the carbon particles preventing them from agglomerating and settling out. The anionic dispersant imparts an anionic charge to the particles. The anionic charge sets up a repulsion between particles and thus leads to a dispersion.

When developing carbon-based dispersions for direct plating it is important to choose dispersing agents that can readily form stable dispersions with the carbon of choice. Ideally the dispersing agent should exhibit the ability to form dispersions where the distribution of particle sizes is uniform and the mean value of the particle size falls within a specified range. For carbon black based dispersions that mean value is typically in the range of 80 - 120 nanometers.

The key to making a commercially viable carbon black dispersion for PWB manufacturing lies in being able to find a formulation that maximizes the stabilizing effects while minimizing the loss of acid copper propagation. Figure 7 reflects the results obtained from a study of the effect of different blends of carbon black and dispersant. It compares the change in particle size over a 2 week period, the acid copper propagation rate, and the interconnect reliability after 6 solder shocks.

Figure 7
Carbon/ Dispersant v. Performance

Carbon/ Dispersant Blend	P.S. t=0h (nm)	P.S. t=336h (nm)	Δ P.S. @ t=336h	1' Flash Through Hole Propagation	ICD @6X SS
C:D1 (control)	115	126	9.6%	24%	0/400
C:D2	95	132	38.9%	89%	0/400
C:D3	100	98	2.0%	93%	0/400
C:D4	100	95	5.0%	81%	0/400
C:D5	90	87	3.3%	76%	0/400

pH

With a specific carbon black modification and dispersing agent, the effect of pH on performance in this formulation was tested. The rationale for this evaluation came from information received from European installations. From work done with previous versions of a single pass process it appeared that the through-hole propagation could be improved by lowering the pH to 10.0 from the prescribed 10.5. However, the action of the dispersing agent is strongly influenced by pH. In fact, analytical methods employ the use of pH adjustment to break the dispersion in order to measure the amount of carbon black in the solution. In order to avoid adverse effects on the carbon dispersion while maximizing any improvement on performance rate at lower pH, a pH study was run on the new Blackhole® dispersion by varying the pH between 9.0 and 10.5 in 0.5 pH unit increments. Figure 8 shows the performance data obtained.

Figure 8
pH v. Performance

pH	Δ P.S. @ t=336h	1' Flash Through Hole Propagation	ICD @6X SS
Control	9.6%	54%	0/400
9.0	26.8%	100%	1/400
9.5	17.4%	96%	1/400
10.0	11.0%	98%	0/400
10.5	8.4%	91%	0/400

Generally, the lower the pH the greater the propagation rate. There were some minor adverse influences at pH levels below 10.0, the most important of which was the decreased stability of the carbon dispersion. Incidences of ICD's were negligible. This evaluation indicated that operating the Blackhole® working bath at a pH of 10.0 would improve the through-hole propagation of the acid copper without causing significant deterioration in the dispersion stability.

Contact Time

Further development efforts focused away from the chemical formulation and instead on the processing parameters including contact time. The contact time is critical because it establishes specific requirements for equipment including chamber lengths and/or conveyor speed, both of which ultimately affect productivity. The influence of contact time was evaluated by determining through-hole propagation given a fixed acid copper plating time and current density. Experiments were run in which the Blackhole® contact time was varied while Conditioner contact time remained constant. Additionally, both Conditioner and Blackhole® contact times were varied at a constant Conditioner to Blackhole® contact time ratio of 1 : 2, typical of Blackhole® processing. The data for contact time performance, run against a control, are shown in Figure 9.

Figure 9
Contact Time v. Performance

Conditioner Contact Time (sec.)	Blackhole® Starter Contact Time (sec.)	% Coverage New	% Coverage Control
30	30	91.0%	-
30	60	88.0%	38%
30	90	90.0%	-
15	30	95.0%	-
30	60	92.0%	22.0%
45	90	90.0%	-

The results show that contact time does not strongly influence process performance. Maintaining a contact time of 30" in the Conditioner and 60" in the Blackhole® should provide through-hole plating coverage. It should be understood that actual production performance may be influenced by the processing equipment, where mechanical constraints/limitations may dictate actual processing times.

Performance Comparison

Once the new formulation was established and optimized we compared it to other through-hole plating systems for process performance. A comparison study was run using M-Systems/M-85 electroless copper, the New Blackhole® Dispersion, a Blackhole® Control, and a competitive Graphite process. Desmeared double-sided and multi-layer panels were full plated and cross sectioned. The results are shown in Figure 10.

Figure 10
Performance Comparison

	1' flash plate	Hole Wall Pullaway		Voids		Post Separation	
		DS	M/L	DS	M/L	DS	M/L
Blackhole® SP	95.0 %	20%	15%	No	No	N/A	0/40
M-Systems	100 %	20%	15%	No	No	N/A	0/40
Graphite	76.0 %	75%	30%	No	No	N/A	3/40
BH Control	40.0 %	25%	15%	No	No	N/A	0/40

This performance evaluation shows that the Blackhole® SP process closely matches the performance standards set by conventional PTH processing (M-Systems) as well as the performance of the BH control. The performance of the Graphite process was inferior in both through-hole propagation as well as the degree of HWPA observed.

Armed with this data we secured, through our PDP team, a field trial site to evaluate the performance of the Blackhole® SP in a production environment utilizing the process cycle illustrated in Figure 11.

Figure 11
Blackhole® SP Process Cycle

Position	Process
1	Blackhole® SP Conditioner
2	Rinse
3	Blackhole® SP
4	Heated Dry
5	Blackhole® Microclean
6	Rinse
7	Blackhole® Antitarnish
8	Rinse
9	Dry

Production Evaluation and Process Control

Once the Blackhole® SP had been optimized for performance in a laboratory setting, it then went to Beta site testing at a customer site in Germany. The system was evaluated in four major areas:

A. Propagation and Plating Coverage
B. Functional Test Performance
C. Process Reliability
D. Process Capability

Additionally, a number of process control/process characterization tools and techniques were unitized in the Beta site testing. Generally, test methods that are capable of characterizing process performance are candidates for use in process control. One of the drawbacks of all Direct Metallization systems is determining process reliability. It is not possible to visually inspect Direct Metallization deposits after application as is possible with traditional electroless copper systems. Developing consistently reliable predictive methods for measuring process performance has been a critical part of the overall development effort. A number of different process control methods and vehicles were evaluated at the Beta site.

A. Propagation and Plating Coverage

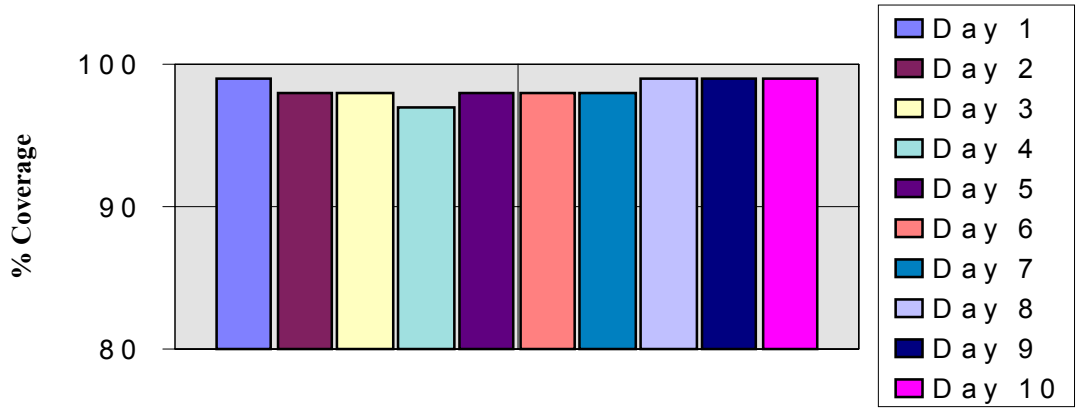
Backlight Testing

This process control technique has been used very effectively with electroless copper systems for a number of years. Adapting this type of test to Direct Metallization presents some difficulties since the backlights must be evaluated after some period of electroplating. One method used is to evaluate samples that have been acid copper flash plated. The use of an acid copper flash is necessary for the inspection of all direct plating processes since this is the only quick method to allow for visual inspection of the samples.

The initial Beta site customer already had a backlight testing procedure in use with its current system and that same method was used for this evaluation. The test panel is 0.078" in thickness and has holes ranging in diameter from 0.148" to 0.016". For the test a panel is processed through the standard conveyorized Blackhole® line. After Blackhole® processing the panel is next processed through the dry film developer (1% w/w sodium carbonate). After the developer the panel is processed through the standard acid copper pre-treatment (acid cleaner, microetch, and sulfuric dip) and then flash plated at 2.5 ASD for 10 minutes.

Fifteen holes for each of the hole diameters are bisected and examined by backlight technique. The coverage values are recorded as the actual percentage of the hole wall that is covered. If any single hole has less than 90% coverage then that fact is recorded as well. The average of all the backlight values is then taken and this number is recorded.
The data for the first two weeks is shown in the graph below. The customer had an internal specification that the backlight value must exceed 90% to be considered acceptable. The Blackhole® SP process easily met this standard with an average backlight value of 99%.The data can be seen in Figure 12.

Figure 12
Backlight Testing



Although the backlight method of inspecting acid copper flashed Blackhole® deposits has proven to be a reliable indicator of process performance, customers had requested that some new test method be made available. The request stemmed from a desire to develop a test method that did not require the use of a short electroplating acid copper flash on the actual production line. For some customers that have large automatic electroplating lines it is inconvenient for them to try to process the backlight panels while also processing actual production work.

Propagation

To address these concerns an innovative test method was developed by MacDermid that uses through hole propagation rates to assess the performance of the Blackhole® deposit. The through hole propagation rate is a key performance characteristic of Direct Metallization systems. Through hole propagation is impacted by a number of critical variables in both the Blackhole process as well as inter-related processes (such as electroplating). We utilize test methods to determine the through hole propagation rate as outlined previously in IPC Technical Paper "Developing Reliable Process Control Tools for Blackhole Direct Metallization" published in May of 1995. Propagation rates were analyzed both directly at the beta site in the automatic plating line using the DTV-Chain panel, as well as in the laboratory using a hull cell with the DTV-Chain Hull panels. The DTV-Chain panel evaluates propagation rate as a function of hole diameter and aspect ratio and is electroplated utilizing the standard production plating cycle. For simplicity, propagation rates are expressed in the number of holes propagated with higher numbers giving better propagation. Propagation rates can also be expressed as an actual rate, such as mm/min, by calculating the distance the propagation has traveled (# of holes X panel thickness) and dividing it by the plating time.

Chain Hull Cell Testing

In the Chain Hull cell test method, Hull cell sized test panels are processed through the Blackhole® line. These panels are next processed through any process steps whose effects are to be investigated and then electroplated in a Hull cell at 1 Amp for 10 minutes. These panels have two daisy chain areas where a total of 16 holes are connected together in series. Since the acid copper will propagate sequentially from one hole to the next in each of these areas it is possible to measure the relative propagation of the test sample.

Additionally, there are two other areas having through-holes on the panel. One area has holes of progressively smaller diameters while the

other has holes aligned in the low current density area of the panel. These test areas also give the opportunity for additional comparison between samples

After each panel is processed the number of holes that have propagated is recorded. For the 17 ASF and the <5 ASF holes, simply record the number of holes that plated through to the back side of the panel.

For the chains at 25 ASF and 10 ASF, the number of holes that have propagated from the bottom of the panel upwards is recorded. The panel is graded according to Figure 13.

Figure 13
Chain Hull Cell Rating

Result	25 ASF	10 ASF
Excellent	> 6	> 5
Good	5 - 5.5	4 - 4.5
Average	4 - 4.5	3 - 3.5
Below Average	3 - 3.5	2 - 2.5
Poor	< 3	< 2

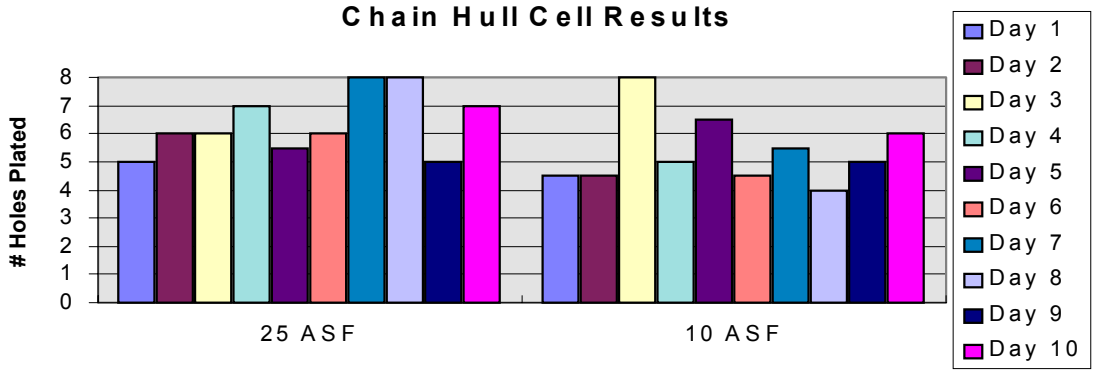
Representative data for the first two weeks is shown in the graph below. These results are for panels that have been processed through Blackhole® SP, dry film developer, and acid cleaner before being electroplated. It can be seen from the data in Figure 14 that the Chain Hull cell results are quite good.

It should also be noted that a single test according to this method is not considered an absolute indicator of the condition of Blackhole® and the related processes. However, this method works well to "red flag" any abnormal conditions that are affecting the system. This test gives the process engineers an indication when closer inspection of the system is warranted. The results of this inspection determine whether more comprehensive testing and diagnosis of the state of the system is necessary.

Additionally, the general trend of these analyses as well as the running average of the Chain Hull test results are a very useful tool in maintaining process control. Furthermore the flexibility of this method allows for much easier differentiation of the effects of things like acid cleaner type and acid copper additive since these items can easily be manipulated during laboratory testing.

The Blackhole® SP process has been shown to provide a 25-50 % increase in acid copper propagation when compared to Blackhole® Process II.

Figure 14
Chain Hull Propagation



Resistance

One other process control/process characterization method evaluated in the test program was resistance. Direct measurement of the conductivity of the Direct Metallization deposit in the holes has been used by many differing systems. The simplest technique is measuring the ohmic resistance between the outer layers of an entire test panel. This yields an average of all the through holes (and edges) of the panel. Double sided panels generally measure from 10 to 200 ohms with Blackhole. This is dependent on panel thickness, hole diameters, and number of holes. Our 10 layer DTV-M multilayer test vehicle averages from 200 to 2000 ohms depending on processing conditions.

B. Functional Test Performance

To assess the capability of the Blackhole® SP process, both double-sided and multi-layer test panels were processed alongside the production work at the Beta site. Every other day over a two week period test panels were processed through the Blackhole® line and packaged for shipment. They were then returned to MacDermid Research for copper plating, solder float cycling, and microsection evaluation.

Figure 15
Test panel specifications

	DTV-CAP 062	DTV-M
Construction	Double-sided	Multi-layer
Layer Count	-	10
Panel Thickness	.062”	.093”
Hole Diameter	.016” .023” .060”	.013” .020” .040”
Aspect Ratio	3.9 : 1 2.7 : 1 1.0 : 1	7.2 : 1 4.7 : 1 2.3 : 1
Current Design	daisy chain (hole barrel connection)	daisy chain (internal layer connections)

Once the panels were received at MacDermid they were coated with dry film resist and pattern plated with acid copper and acid tin etch resist. The panels were then dry film stripped and etched to define the circuits. At this point the individual daisy chain blocks were tested for continuity using a multimeter. No open circuits were found.

Test coupons were then punched from each of the samples. The coupons were prepared and subjected to 6 solder float cycles according to the IPC testing procedure. The coupons were then mounted and examined by microsection.

The double-sided DTV-CAP 062 panels were inspected for voids, evaluated for hole wall pullaway (HWPA), and evaluated for any residual carbon on the copper surface which would typically manifest itself as corner contamination/defect (CD). No voids or evidence of residual carbon was found. The amount of hole wall pullaway seen was comparable to an electroless copper test standard that was included as a reference. The results are shown in Figure 16 on the following page.

Figure 16
Double-Sided Performance Evaluation
@ 1X Thermal Shock

	Hole Dia. = .016”	Hole Dia. = .023”	Hole Dia. = .060”

Date	Void	HWPA	CD	Void	HWPA	CD	Void	HWPA	CD
9/18	No	< 10%	0	No	< 10%	0	No	< 20%	0
9/20	No	< 10%	0	No	< 10%	0	No	< 20%	0
9/22	No	< 10%	0	No	< 10%	0	No	< 20%	0
9/25	No	< 10%	0	No	< 10%	0	No	< 15%	0
9/27	No	< 10%	0	No	< 10%	0	No	< 20%	0
9/29	No	< 10%	0	No	< 10%	0	No	< 15%	0

The multi-layer DTV-M panels were inspected for voids, interconnect defects (ICD), and were evaluated for hole wall pullaway (HWPA). No voids or interconnect defects were seen. Again, the amount of hole wall pullaway was comparable to an electroless copper test sample that was included as a reference.

Figure 17
Multi-layer Performance Evaluation @ 6X Thermal Shock

	Hole Dia. = .013"			**Hole Dia. = .020"**			**Hole Dia. = .040"**		
Date	Void	HWPA	ICD	Void	HWPA	ICD	Void	HWPA	ICD
9/18	No	< 10%	0	No	< 10%	0	No	< 10%	0
9/20	No	< 10%	0	No	< 10%	0	No	< 10%	0
9/22	No	< 10%	0	No	< 10%	0	No	< 10%	0
9/25	No	< 10%	0	No	< 10%	0	No	< 10%	0
9/27	No	< 10%	0	No	< 10%	0	No	< 10%	0
9/29	No	< 10%	0	No	< 10%	0	No	< 10%	0

The results of this testing showed that the reliability of this process is comparable to the industry standard of electroless copper.

C. Process Reliability

During the Beta site evaluation an experimental design test program was carried out to measure performance variation as a function of five Blackhole SP process variables and one inter-related process variable (electroplating). A modified D'Optimal design was utilized consisting of 22 individual test runs.
The DOE testing achieves two purposes. First, it confirms (or rejects) laboratory findings with the benefit that the testing is done in a typical production environment. Secondly, it allows for statistical testing of potential process control methods and vehicles.. Results from these tests were analyzed as a function of response to changes in process (and inter-related process) variables and compared to functional performance on production test vehicles.

Factors Evaluated in the DOE

Age of Conditioner

Previous testing had identified a negative impact on performance with older Cleaner\conditioner solutions with Blackhole Process II. In this DOE, tests compared a new Cleaner to a solution that had processed 2.8 M^2/L (≈200 ssf/gal) of production. In the DOE testing the original formulation for the cleaner was used (without the previously discussed enhancements to the alkaline matrix). This was done to isolate the performance effects from the improved dispersion technology. Additional field testing was performed later to isolate the impact of the new alkaline matrix on Cleaner formulations.

Contact time in the Conditioner

To help optimize future equipment designs for the single pass process, varying contact times in the Conditioner were tested for efficacy. Contact times tested included 30, 45, and 60 seconds.

pH of the Blackhole SP dispersion

Previous testing has lead to maintaining the pH of the Blackhole in the lower end of the control range. In this DOE, we tested the range of 9.95 to 10.46 for effect.

Contact time in the Blackhole SP dispersion

To help optimize future equipment designs for the single pass process, contact times of 60, 75, and 90 seconds were evaluated.

Etch rate in the micro clean

Testing to evaluate any impact on the new dispersion from changes in etch rate. Two etch rates were evaluated, 0.75 micron and 1.45 micron. Temperature and peroxide concentration (G-5) were used to change the etch rate; contact time was held constant.

Type of acid copper plating solution

Previous testing identified a significant impact on through hole metallization with Blackhole Process II from acid copper plating, either type and/or additive levels. In this DOE two different suppliers acid copper solutions were used to determine if the new dispersion was also impacted by acid copper plating.

Test Results

The experimental design testing confirmed many of the laboratory findings. Propagation and backlights results were equivalent or better than results obtained with Blackhole Process II in previous evaluations. The following two response surfaces demonstrate the effects of aging on the Clean 110C. The average number of holes propagated using the DTV-Chain panel are reduced ≈15% with the older Clean 110C. This is consistent with previous findings. Note also the significant impact from the acid copper electroplating solution type. Supplier #2 electroplating solution averages ≈20% higher propagation rates under identical conditions.

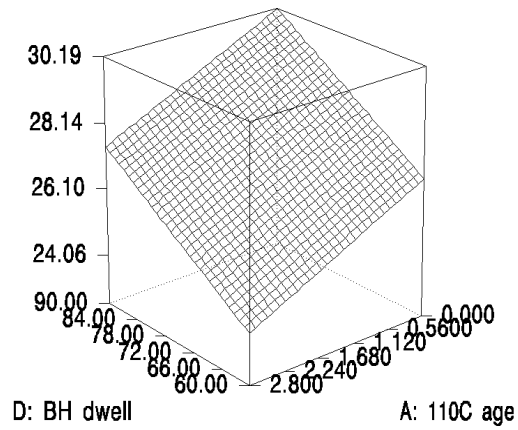


Figure 18. DTV-Chain propagation Supplier #1 acid copper

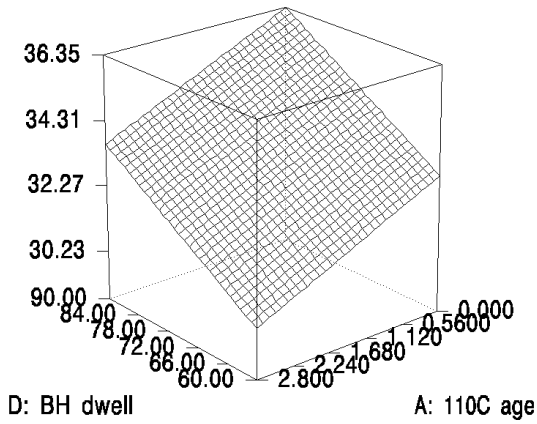


Figure 19. DTV-Chain propagation Supplier #2 acid copper

Plating coverage as measured by backlight testing varied consistently with the propagation rate testing for Cleaner\conditioner 110C solution age, Blackhole SP contact time, and acid copper supplier. Backlights also were impacted by the etch rate in the Micro-clean. The next two response surfaces show Cleaner\conditioner 110C age and Micro-clean etch rate with Blackhole SP contact time.

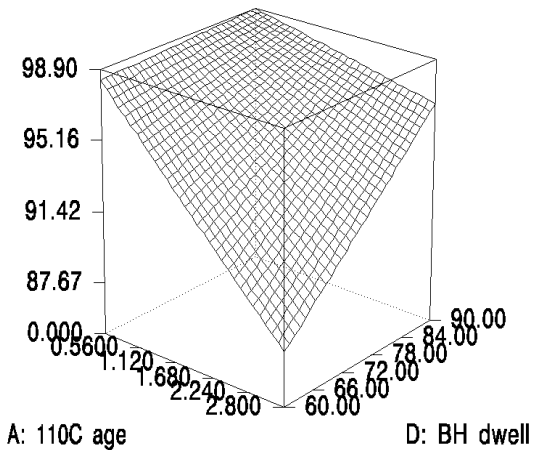


Figure 20. Backlight values

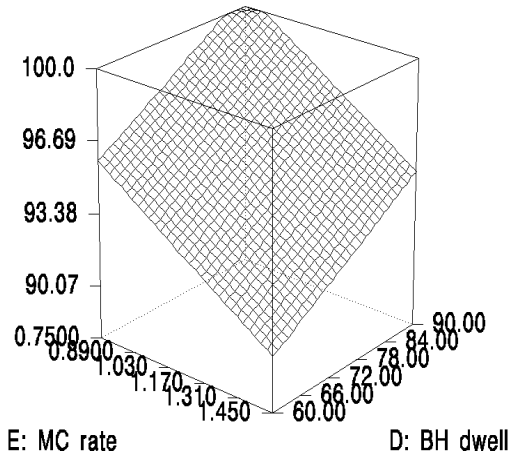


Figure 21. Backlight values

The next two response surfaces compare age of 110C and contact time in the Blackhole at the extremes of etch rate and acid copper type.

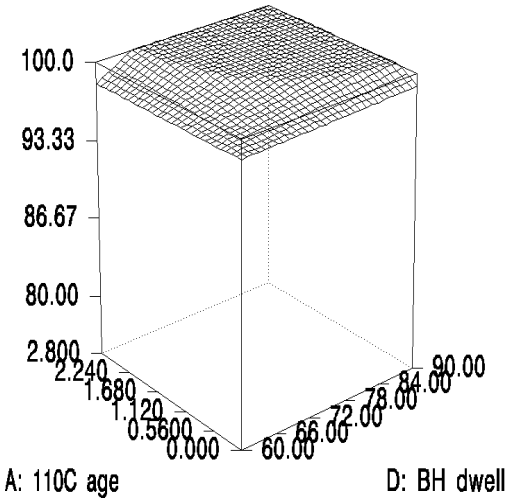


Figure 22. Backlight values
Etch rate = 0.75 micron
Supplier #2 acid copper

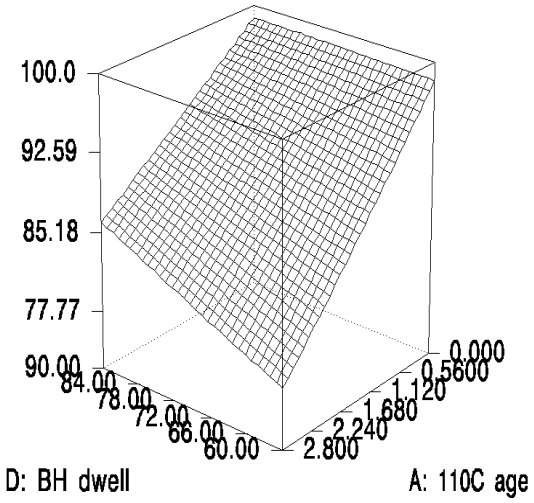


Figure 23. Backlight values
Etch rate = 1.455 micron
Supplier #1 acid copper

The preceding response surfaces indicate that with increasing Blackhole SP contact time (BH dwell) both propagation rates and backlight coverage were improved. This was not seen in the laboratory testing using the 1' flash plate coverage test. However, the laboratory testing used the Cleaner formulation with the new alkaline matrix, which likely had an impact on the results.

The analysis of resistance on both the double sided and multilayer test vehicles did not show any statistically significant findings except for the Micro-clean etch rate variable. For the high level of the etch rate (1.45 micron) the resistance measured, on average, double that found at the low level. This has been seen with previous testing, and is the result of the increased etch rate opening up a wider gap at the interface between the foil copper and the Direct Metallization deposit in the hole. This effect is also the reason that multilayer test panels with increasing numbers of innerlayers always exhibit much higher inherent resistance. When using resistance as a process control tool it is critical to consider the effect of etch rate on the data.

The testing also showed that some variables have little measurable effect on performance. In the case of the Blackhole SP solution pH, no functional effect was seen within the pH range tested.. Also, no statistically significant impact was seen from the Conditioner contact time within the 30 to 60 second range. Both of these findings confirmed the previous laboratory testing.

Two process control methods, through hole propagation rate testing and backlights, exhibited good response to process variation. This testing confirmed that these two process control techniques can be utilized successfully with Direct Metallization.

D. Process Capability

After the conclusion of the Blackhole SP beta site evaluation, the Blackhole SP process was commercialized. The next step in the development program was to perform a direct side by side comparison to the original Blackhole Process II chemistry. The capability study was designed to achieve two objectives:

- Direct comparison of Blackhole Process II and Blackhole SP
- Extended reliability testing of both processes

The capability study was designed to test the process robustness of both Blackhole processes over an extended period of time. Instead of running tests under carefully controlled conditions as in the experimental designs, the aim of a capability study is to test the Blackhole process(es) reliability within the normal variation of typical production conditions.

A further goal of the capability study was to test a number of critical board requirements. These include aspect ratio's up to 7:1, board thickness up to 0.125" (3.1 mm), interconnect reliability on high layer count - high aspect ratio multilayer boards, and through hole propagation rates.

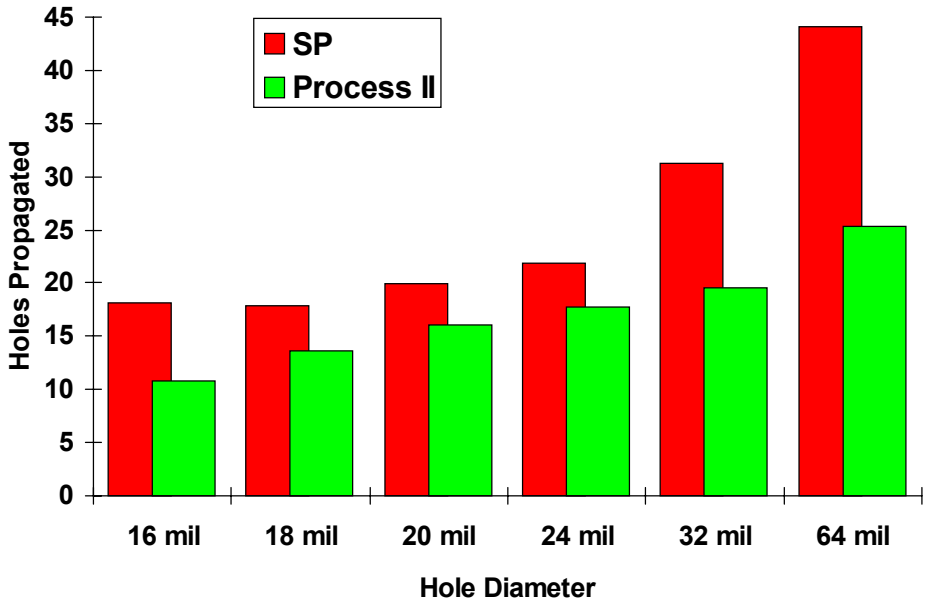
A final goal of the capability study was a comparison of the two different Blackhole processes. Both the Process II and Blackhole SP tests were run simultaneously, with all other process steps performed together. This resulted in a direct comparison of the Blackhole SP to the Process II.

Capability Study Test Results

In comparing the two processes only resistance measurements and propagation rates were significantly different. In the case of resistance, it would appear that higher average resistance with the SP does not correspond to any process deficiencies. Instead, the consistently higher resistance with the SP process is likely a function of the different dispersion technology only, and has no effect on performance. Previous testing had indicated that different dispersions could have widely varying resistance measurements with no correlation to propagation or other functional attributes. This demonstrates why coating resistance is not a reliable indicator of propagation speed.

The propagation rates indicated that the Blackhole SP averaged ≈50% faster than the Process II. The consistently higher propagation rates with the SP are most likely the result of the new dispersion technology and the use of the improved Cleaner formulation that provides a more uniform conditioning effect over the life of the solution. Figure 24 shows the propagation rate comparisons using the DTV-Chain test vehicle.

Figure 24
DTV-Chain propagation rate comparison



The capability study demonstrated the reliability of both the current Process II and new SP Blackhole chemistries. This reliability extended to panels up to 0.125" (3.1 mm) thick with aspect ratio's of 7:1. The DTV-M 10 layer multilayer panels with 6:1 aspect ratio's and nearly 7% Z axis expansion were all processed successfully. The new Blackhole SP exhibited equivalent reliability to Process II in a simpler process using shorter and less expensive equipment.

Conclusion

The objective of the Blackhole® SP research effort was to develop a single-pass carbon based direct plating process that would meet or exceed the results achievable with Blackhole® Process II. When compared to the current system it was found that the Blackhole® SP process:

- Provided improved conditioning performance
- Was able to maintain the same highly-stable carbon black dispersion characteristics
- Showed increased acid copper propagation rates
- Demonstrated the same high levels of functional performance

in a single-pass conveyorized process. Patents related to these technological advances in this unique through-hole metallization process have been granted.

Furthermore, through extensive testing programs process control techniques have been developed and evaluated. The use of these methods will ensure the reliable operation of Blackhole Direct Metallization systems. While these techniques have primarily been tested on Blackhole only, other Direct Metallization systems can benefit from the application of these techniques.

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3. MacDermid Technical Report No. 109, *Blackhole® SP Process Characterization Using Statistical Experimental Design Methodology*, January 1996

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