

# DIRECT METALLIZATION SYSTEM FOR FLEXIBLE PRINTED CIRCUIT BOARD

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## ABSTRACT

Flexible Printed Circuits (FPC) are the key enabling technology in the design and fabrication of advanced handheld electronic devices such as smartphones, tablets, camcorders – not to mention their importance to the automotive, defense and aviation industry throughout the last decades.

The rapid expansion of Smartphone and tablet markets coupled with consumer demand for thinner and lighter products is causing the growth of the FPC segment to be the fastest in the PCB market. FPC provides electronic equipment designers greater design freedom when faced with further miniaturized circuitry (thinner line/pitch and smaller via) while simultaneously needing to reduce overall cost and increase functionality.

The limitation to further FPC adoption is due to challenges in fabrication, primarily the metallization of the flexible dielectric materials. Metallization challenges are the greatest for adhesiveless polyimide materials due to the higher cross-linked material which is less receptive to standard electroless plating chemistries. Conventional electroless copper processes are also cost prohibitive when it comes to horizontal FPC processing. Other options such as carbon/graphite based direct metallization processes have had limited success for plating complex, multilayer boards with microvia designs. However, new conductive polymer based direct metallization technologies provide a breakthrough process for FPC fabrication.

This paper will discuss the recent development of a conductive polymer based direct metallization system that enables FPC fabrication of complex designs as a cost effective alternative to traditional electroless methods. Results from a series of statistically designed experiments to understand the interaction between conductive polymer based systems and various advanced polyimide materials will be presented here. Guidelines will be provided to FPC fabricators to assist in choosing the most cost effective solution to meet their customers need.

Key Words: Flexible Printed Circuits (FPC), Direct Metallization, Polyimide, Conductive Polymer, Microvia

## INTRODUCTION

Flexible Printed Circuits are defined by IPC [1] as: “A patterned arrangement of printed circuitry and components that utilizes flexible base material with or without a flexible cover lay.” Simply put, a flexible circuit is a conductive pattern laid on a flexible dielectric film. Whilst early 1900s (metal on wax paper) and 1950s (etched metal patterns on insulating polymers or coated paper) inventions strived for replacing complex discrete wiring harnesses, today’s state-of-the-art FPC manufacture utilizes e.g. unreinforced Polyesters (low cost), PEEK, Polyimides (high reliability) as substrates for any conductive pattern [2].

Figure 1 shows a typical multi-layer FPC stack up [3]. Within a flexible-circuit construction, the dielectric film forms the base layer, with adhesives used to bond the conductors to the dielectric. In multilayer flexible circuits, adhesives are used to bond the individual layers together. Adhesives can also be used in a protective capacity to cover the final circuit to prevent the ingress of moisture and dirt; hence they are termed ‘cover lays’ (also ‘cover layers’) or ‘cover coats’.

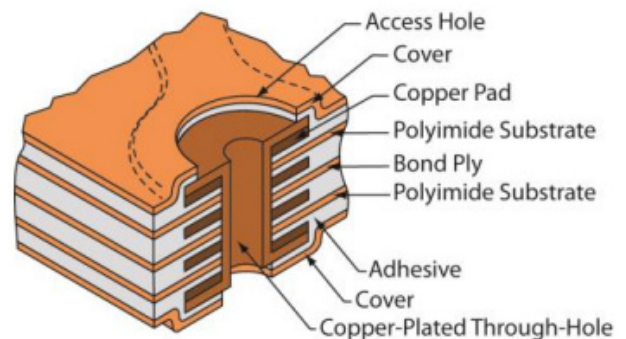


Figure 1. Typical multi-layer FPC stack up

Most flexible circuits are passive wiring structures that are used to interconnect electronic components such as integrated circuits, resistors, capacitors and the like, however some are used only for making interconnections between other electronic assemblies either directly or by means of connectors. In other words, FPC offers the same design options as Printed Circuit Boards (PCB) with the added benefit of vibration resistance (e.g. airborne/space applications) and three dimensional configurations.

## FPC TECHNOLOGY

A basic flexible circuit has three major components. They are conductor, adhesive and dielectric/insulator film.

Conductors are usually electrodeposited or rolled-annealed copper foils with various weights/thicknesses. These copper foils are bonded to the dielectric film using an adhesive film or by applying an adhesive-less construction technique. Adhesive-less construction has certain advantages over an adhesive base construction, such as thinner and more flexible circuits with better electrical properties. However, this advantage is reduced when an adhesive base cover coat is used.

When it comes to the choice of adhesive for FPC, acrylic and epoxy based adhesives are the most commonly used systems. Specific application requirements dictate which choice is the best.

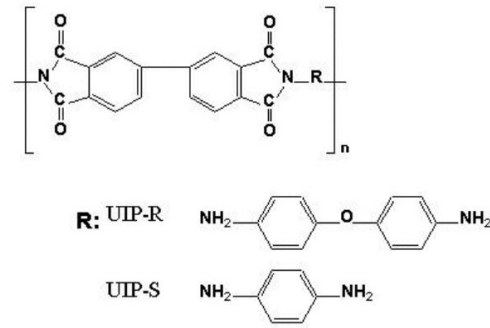
All three components, conductor, adhesive and dielectric have specific roles in making a robust FPC. However, the choice of dielectric film is considered to be the most critical in a flexible circuit. Most commonly used dielectric materials are unreinforced polyester based substrates for low end applications whereas for complex, high reliable FPCs polyimides are the materials of choice. The end application usually dictates the type of dielectric film used to build flexible circuits. Table 1 [4] shows key characteristics of the most commonly used dielectric films. Among the dielectric films listed in table 1, Polyimide is the most popular and the focus of this discussion.

CHARACTERISTIC	UNIT OF MEASURE	POLYIMIDE FILM	FEP FILM	POLYESTER FILM
Dielectric Strength	V/Mil-1 Mil	4500	5000	7000
Dielectric Constant	1 kHz	3.4	2.1	3.1
Dissipation Factor	1 kHz	.0016	.0003	.005
Tensile Strength	PSI	20000	4000	25000
Elongation	%	70	300	100
Water Absorption	% By Weight	3	< .01	.8
Operating Temperature	°C	150	204	149
Absolute Max Temperature	°C	300	274	149
Low Temp. Embrittlement	°C	-55	-85	-50
Melt Point	°C	816	280	248
Weather Resistance	MIL-STD-2026	Excellent	Excellent	Fair
Fungus Resistance	MIL-E-5272	Non-Nutrient	Non-Nutrient	Non-Nutrient
Chemical Resistance	N/A	Excellent	Excellent	Excellent

**Table 1.** Characteristics of Thin Film Dielectrics [4]

### Polyimide (PI) Substrate

Polyimides are a class of thermoset polymers with excellent flexing and electrical properties. It has superior resistance to high temperature hence is an excellent choice for lead free soldering conditions. The outstanding physical properties (e.g. dielectric strength, stability on thermal impacts, flexural strength) and excellent chemical resistance of Polyimides are a consequence of the highly crosslinked nature of the basic polymer as shown in figure 2 in its simplest form. The degree of crosslinking determines the thermal properties of the polyimide, such as glass transition temperature (Tg). Table 2 shows Tg for commonly used polyimides.

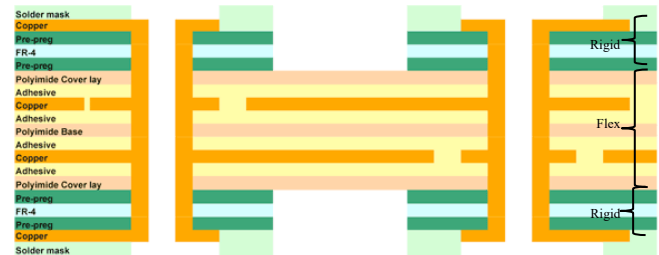


**Figure 2.** Simplified structure of Polyimides

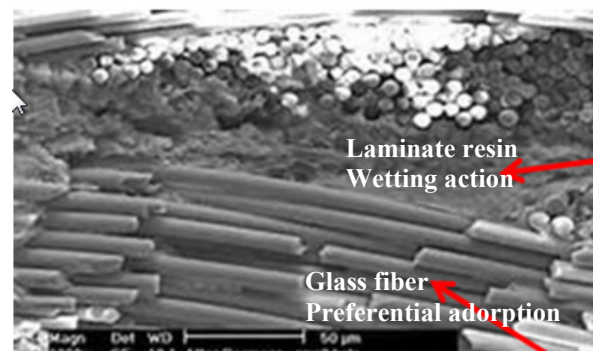
Flexible PI Brand/Vendor	Glass Transition Temperature T <sub>g</sub> (°C, TMA)
DuPont	220
Azotec	300 – 350
Thinflex	320
Panasonic	343
Doosan	245 – 320

**Table 2.** Glass transition temperature for PI substrate [5]

The specific attributes of Polyimides, which make it highly desirable for use in flexible circuit applications, also make it highly challenging for the metallization of drilled holes. Especially with resin/woven glass reinforced composite structures of a rigid flexible substrate. Figure 3 [6] shows a typical four-layer rigid-flex construction with two rigid and two flexible layers. Figure 4 shows an expanded view of the glass reinforced rigid layer. The conditioner needs to prepare the resin surface along with glass fibers to be receptive to deposition of MnO<sub>2</sub>, which is the key to the polymerization of the conductive polymer.



**Figure 3.** Typical four-layer rigid-flex construction



**Figure 4.** Typical rigid flex substrate detail

Special treatment is necessary to prepare the drilled hole surface, especially with glass reinforced rigid substrates for

metallization. There are different approaches to achieve this objective. Of which, Direct Metallization is one of the most desirable processes due to some of its unique advantages. These are lower energy consumption and greener technology. Figure 5 shows a typical direct metallization process known as DMS-E. Flexible as well as rigid-flexible PCBs do pose substantially enhanced challenges on manufacturing because of cost sensitivity and the need for high reliability making the use of direct metallization systems and optimized pretreatment procedures essential.

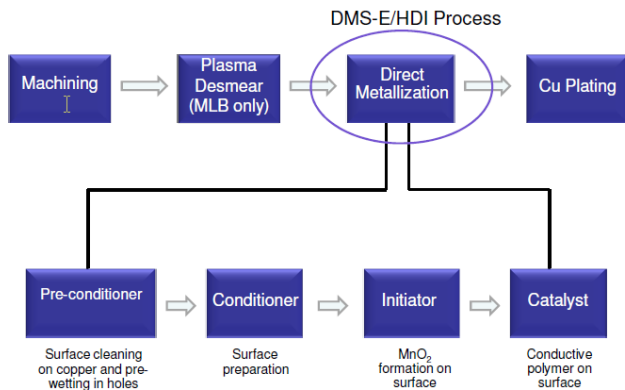


Figure 5. DMS-E process

### DMS-E PROCESS

DMS-E technology is based on intrinsic conductive polymers that allow metallization of dielectric and electrically non-conductive areas without electroless copper as a seed layer. The conductive polymer film is generated in situ by a 3-step process (Conditioner, Initiator and Catalyst) on the non-conductive areas of the PCB as shown in figure 6.

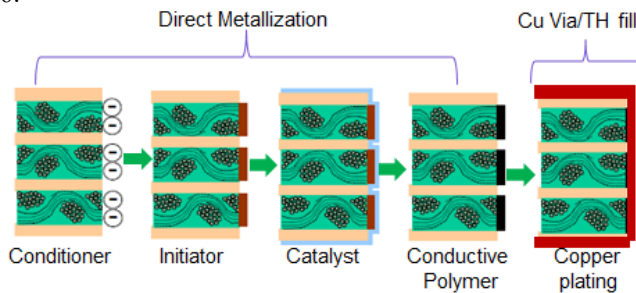


Figure 6. DMS-E process

### Conditioner

The primary function of the conditioner is to wet the non-conductive part of the drilled hole to prepare for the initiator step. One possibility for a conditioner is to use a sweller in combination with reducing agent to modify the PI surface for a better attack of the Initiator depositing  $MnO_2$ .

### Initiator

Initiator is usually an aqueous solution of Potassium or Sodium Permanganate that makes an oxidative reaction to selectively form Manganese Dioxide ( $MnO_2$ ) on the conditioned dielectric area of the hole wall.  $MnO_2$  is essential in the polymerization of the conductive polymer on the wall surface. The conductivity of the subsequently

deposited polymer-layer is highly dependent on the right amount of  $MnO_2$  presence on the surface.

### Catalyst

The catalyst in DMS-E process is an aqueous mixture of sulfonic acid and a micro emulsion of EDT that reacts with  $MnO_2$  as oxidizer. EDT radicals, created by the oxidation step, react spontaneously to form the polymer chain as shown in figure 7.

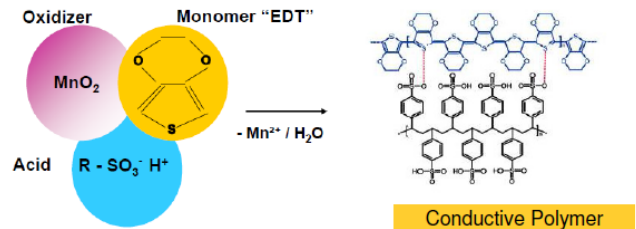


Figure 7. Conductive polymer formation

The high  $T_g$  ( $T_g$  220 – 350 °C) Polyimide flexible laminates require an extremely effective conditioning, i.e. an hydrophilicity step prior to chemical bonding of the conductive catalyst layer. The task of an effective conditioner system is the wetting of the resin and glass as well as preferential adsorption of the wetting agent to the fibers as shown in figure 8. The objective of this study has been to develop conditioning systems to provide required wetting and hydrophilicity of PI laminate as well as resin/glass with rigid inner layers of Polyimide based laminates. Results from the flexible substrate are discussed here. Rigid flex, which may need an additional glass conditioning compound is not discussed here.

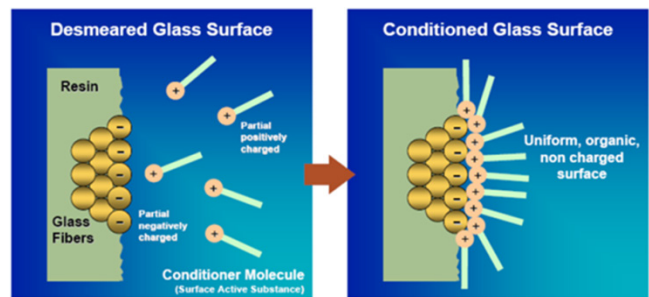


Figure 8. Conditioning of glass surfaces

### EXPERIMENTAL

The experimental strategy was to formulate a low temperature novel conditioning system for polyimide substrate that is compatible with the initiator and long life catalyst for DMS-E process. Three key focus areas of the formulation work were to identify optimum bath pH, sweller, and reducer compounds that perform well at low operating temperature. Each of these components plays a critical role in preparing the PI substrate for the subsequent step, which is to absorb  $MnO_2$ , which is a vital part of the DMS-E process.

The sweller compound “swells” the surface of the PI substrate resulting in a larger surface area and higher surface roughness. This makes the substrate more susceptible to the

other additives. An alkaline pH cleaves the polymer end groups and creates functional groups which are more receptive to the reducer compounds. The function groups of the PI substrate are modified by the reducer which allows an optimal reduction and therefore a better formation of MnO<sub>2</sub> by the permanganate in the Initiator.

A series of statistically designed experiments were conducted to develop a robust process that included formulation and process parameters optimization. The initial screening experiment focused on the formulation part and included two different types of sweller, two different types of reducer and two different types of caustic for pH adjustment. Table 3 shows the initial screening experimental matrix. Different types of flex substrates were included in the evaluation to gauge the effectiveness of the conditioner.

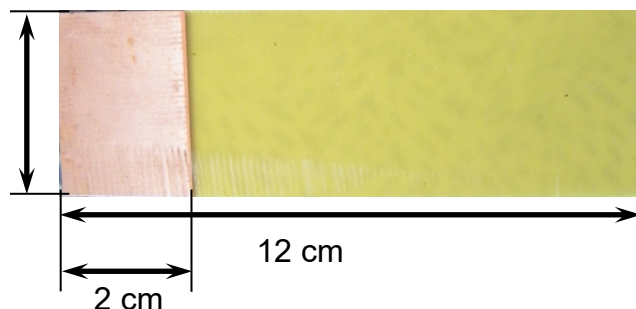
Factor	LEVELS	
	(-)	(+)
Reducer	R1	R2
Sweller	S1	S2
Caustic	C1	C2

**Table 3.** Screening experimental matrix

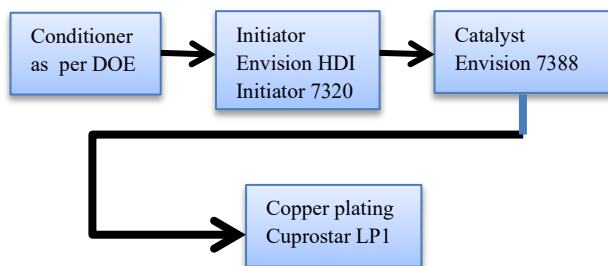
### Test Vehicle

The test vehicle used in this experiment was a simple, double sided flex substrate. Depending on supplier, the substrate also had drilled holes. Prior to the DMS-E process, each test coupon was stripped of copper to expose the PI surface. A typical test coupon is shown in figure 9.

Each test condition was monitored for two primary responses: Lateral Copper Growth (LCG) and Plated Through Hole (PTH) coverage. LCG was developed as an internal test parameter which can provide an indication of the copper growth properties without needing to evaluate PTH. While the PTH coverage indicates functional attributes. Figure 10 shows the experimental sequence for LCG and PTH coverage determination.



**Figure 9.** LCG Test coupon



**Figure 10.** Process flow

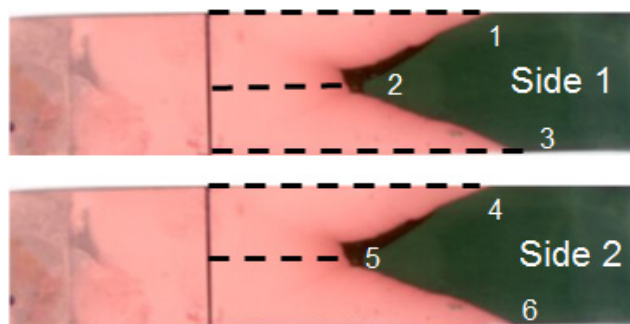
Results from the screening experiment guided us to a stable formulation where additional DOE's were performed to optimize the formulation, process parameters and establish a robust process window. An example of the Optimization DOE matrix is shown in table 4. Following the optimization DOE smaller experiments were carried out to refine the operating window of the significant parameters. As before, all DOEs were blocked over different types of PI substrate.

Factor	LEVELS	
	(-)	(+)
Reducer Conc	Low	High
Sweller type	S1	S2
Sweller Conc	Low	High
Caustic Conc	Low	High
Plating time	Low	High
Plating temp	Low	High

**Table 4.** Example of DOE matrix for process optimization

### LCG Evaluation

The test coupon as shown in figure 9 is used to measure lateral Copper growth. Following the DMS-E process the coupon was plated in an acid Copper bath (Enthone Cuprostar ST2000 or LP1) for 5 minutes at 2 ASD. The coupon is then rinsed and dried before evaluation. As the edge of the test coupon has usually a higher copper growth than the center, an average value is used for LCG analysis. The difference in Copper growth between the edge and center is due to the roughness of the substrate at the edges which allows more MnO<sub>2</sub> to be adsorbed. This results in a higher conductivity and hence higher lateral copper growth. Copper growth takes place not only from the top, but also from the edges to the center of the coupons. The average growth is determined by measuring 6 points on the surface as shown in figure 11 and getting an average of the 6 points.



**Figure 11.** Measurement location for LCG growth



### PTH coverage evaluation

For the through hole evaluation a test coupon with sufficient holes is required. These coupons are treated in the same way as the LCG test samples except that the plating time in the acid copper bath was increased to 30 minutes. The coverage is evaluated from a cross section as Through Hole Efficiency (THE). Equation 1, along with figure 12 describes the through hole efficiency calculation method.

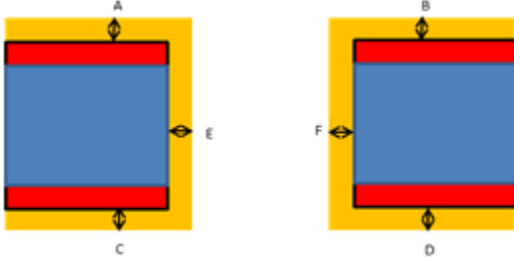


Figure 12. Measurement locations for TH Efficiency

$$THE (\%) = \frac{(E+F)}{(A+B+C+D)/2} \times 100 \quad (1)$$

For substrates where it was not possible to prepare separate coupons for through hole evaluation, samples were taken from the LCG test coupon with through hole and a different evaluation method was employed. Due to the shorter plating time for copper, a quantitative evaluation of Through Hole Efficiency was difficult. For these samples a qualitative method was used to estimate the Through Hole Coverage (THC). This is shown in equation 2 and figure 13.

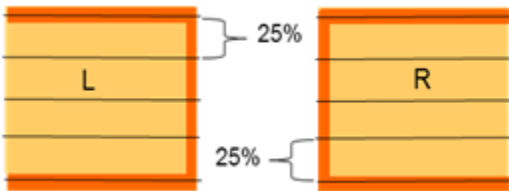


Figure 13. Measurement location for TH Coverage

$$THC (\%) = \frac{\%Coverage L + \%Coverage R}{2} \quad (2)$$

### RESULTS AND DISCUSSION

Common PI substrates, as provided by different customers have been used to develop an optimized conditioner system for DMS-E process. Presenting results from all substrates used in this experimental work is beyond the scope of this paper. Hence the discussion will be focused on a customer supplied, hard to plate adhesive base PI substrate labeled as “A”. During the experiment, only the conditioner was varied; all subsequent steps of the DMS-E and copper plating processes followed the standard process.

#### Screening Experiments

Results from the screening experiments are shown below through a series of graphs showing the effect of individual factors on the two key response variables. Figures 14-16 show the effect of pH, reducer and sweller on both LCG and

THC/THE for substrate “A”. It is evident from these figures that the through hole performance is not significantly affected by the three chosen factors. However the LCG is affected by all three factors. The graphical analysis shows alkaline (higher) pH, reducer 2 and sweller 1 provided higher LCG. As LCG is a good indicator for plating speed, this finding was considered to be significant. This was also true for most of the substrates tested in this study. Based on this analysis, the follow up DOE was conducted with high pH and reducer 2. Both the swellers were kept in the optimization DOE to further understand its effect on different standard flexible and rigid substrates.

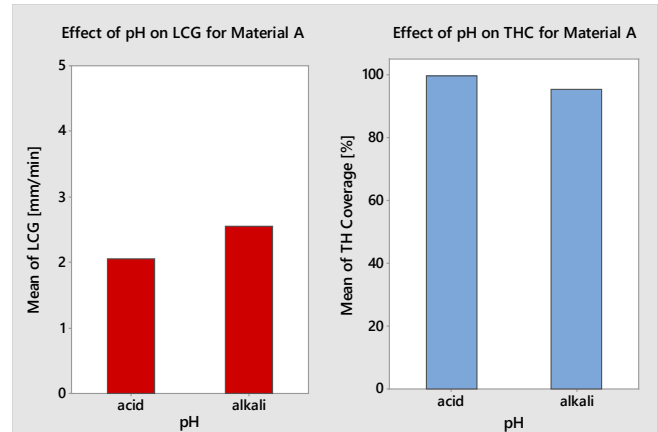


Figure 14. Effect of pH on LCG and THC

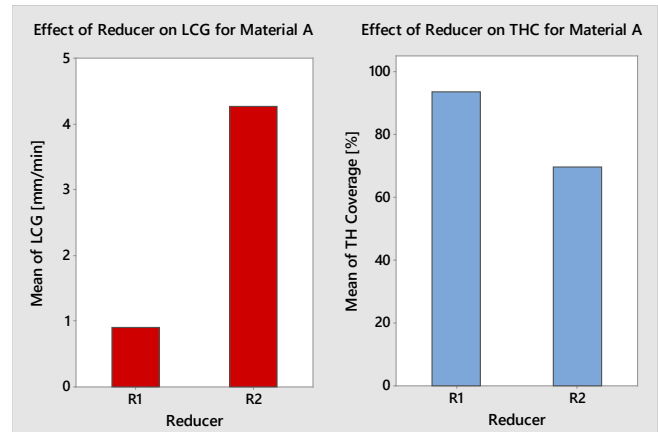


Figure 15. Effect of reducer on LCG and THC

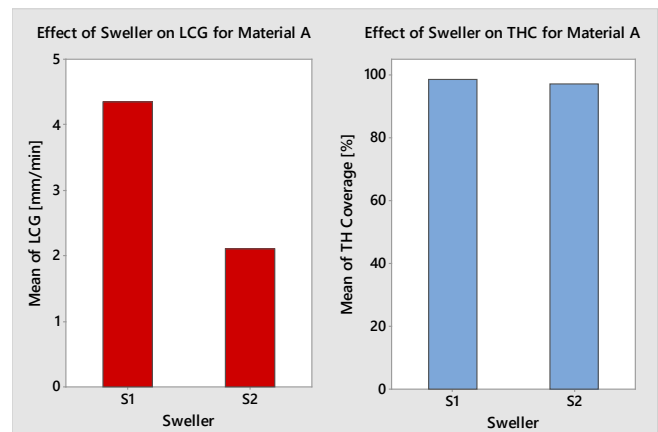


Figure 16. Effect of sweller on LCG and THC

## Optimization Experiments

The LCG result from the optimized DOE (table 4) was analyzed using MiniTab. The main effect plot and the ANOVA table are shown in figures 17 and 18 respectively. It is clear from the ANOVA analysis that both temperature and caustic (pH) concentration are statistically significant. However sweller type and concentration proved to be insignificant as was seen before. Furthermore, it shows LCG growth is higher with high temperature and pH.

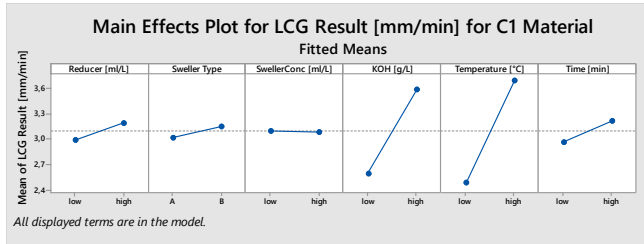


Figure 17. Main effect plots for LCG growth

Analysis of Variance for C1 Material					
Source	DF	Adj SS	Adj MS	F-Value	p-Value
Model	8	43,8181	5,4773	15,39	0,000
Linear	6	41,1833	6,8639	19,28	0,000
Reducer [ml/L]	1	0,7014	0,7014	1,97	0,165
Sweller Type	1	0,3112	0,3112	0,87	0,353
KOH [g/L]	1	15,8338	15,8338	44,48	0,000
Temperature [°C]	1	23,4014	23,4014	65,73	0,000
Time [min]	1	0,9264	0,9264	2,60	0,112
2-Way Interaction	2	2,6348	1,3174	3,70	0,030
Reducer [ml/L]*Sweller Type	1	1,4702	1,4702	4,13	0,046
SwellerType*Time [min]	1	0,1646	1,1646	3,27	0,075
Error	63	22,4278	0,3560		
Curvature	1	0,3102	0,3102	0,87	0,355
Lack-of-Fit	8	2,9031	0,3629	1,02	0,433
Pure Error	54	19,2144	0,3558		
Total	71	66,2459			

Figure 18. ANOVA Tables for LCG Growth

Following the process optimized DOE, several smaller DOEs were run to optimize the process window. A typical optimization condition is shown in table 5. Confirmation runs were made to determine the performance of the new conditioner with several different substrates. The LCG results for the PI materials with the optimum running conditions are shown in figure 19. The substrate list included PI materials from suppliers such as Thinflex, Doosan, DuPont, and Shenyi. Due to confidentiality, exact product name/number has been omitted here. It is clear from figure 19 that the LCG result varies depending on the PI substrate tested, but the new conditioner has excellent LCG values indicating fast plating times.

Reducer	45 ml/L
Sweller Type	A
Sweller Content	250 ml/L
Caustic Content	20 g/L
Plating Time	3 min
Plating Temperature	45 °C

Table 5. Typical Set Up for the Optimized Conditioner System

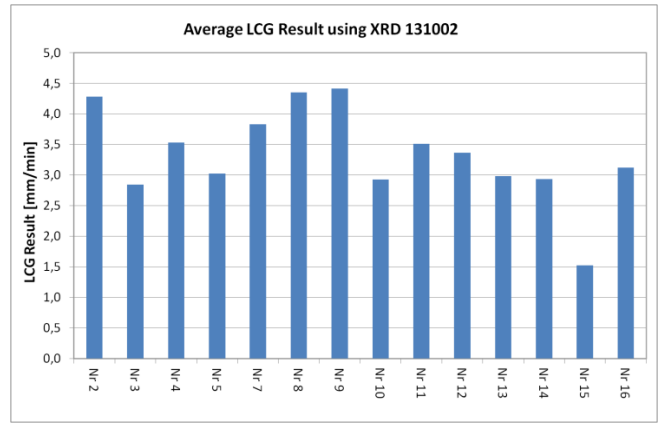


Figure 19. LCG result for various PI substrates with the optimum conditioner set up

Out of the 14 different types of substrate tested, seven were further tested for through hole coverage (10-16). These seven substrates included materials from ThinFlex, Doosan and Shenyi. The results are shown in figure 20. As it can be seen from this graph, the new conditioner provided excellent through hole coverage for all seven substrates.

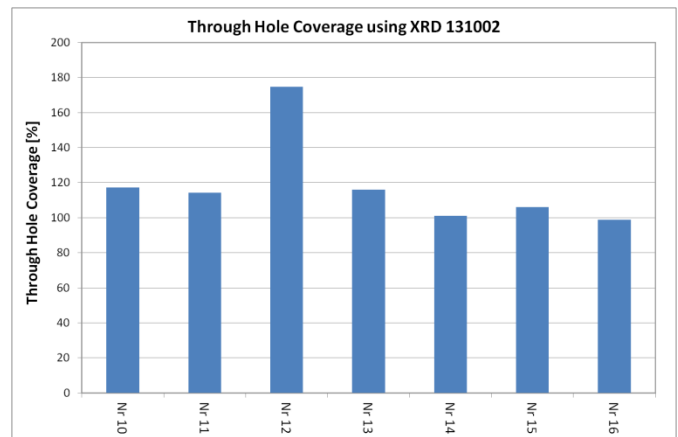


Figure 20. Through hole efficiency for selected substrates

## SUMMARY/CONCLUSION

A novel, one step conditioning system for the pretreatment of drilled Flexible Printed Circuits has been developed for direct metallization utilizing the DMS-E process. The new conditioning system uses an alkaline solution of wetter, reducing agent and sweller. The system operates effectively at a lower operating temperature for most of the PI substrates tested in this study. Based on the experimental results, we can conclude that the new conditioner is highly effective in treating “hard to plate” PI substrates.

## PATH FORWARD/RECOMENDATION

The current conditioner system has been tested with several PI substrates under controlled pilot scale environment. All results shows excellent LCG and TH coverage as described in this paper. However, further optimization will be necessary by the users to implement the system in a high volume manufacturing environment. Furthermore, as PI materials are highly sensitive to sweller and reducer, further

optimization may be necessary for the process to be effective for specific types of PI material.

#### **ACKNOWLEDGMENT**

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