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Electroless copper plating on graphite/epoxy and graphite/cyanate ester laminates

Hong Xu
San Jose State University

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**ELECTROLESS COPPER PLATING ON GRAPHITE/EPOXY AND
GRAPHITE/CYANATE ESTER LAMINATES**

A Thesis

Presented to

**The Faculty of the Department of Chemical Engineering
San Jose State University**

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Hong Xu

December 1998

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ABSTRACT

ELECTROLESS COPPER PLATING ON GRAPHITE/EPOXY AND GRAPHITE/CYANATE ESTER LAMINATES

by Hong Xu

This thesis addresses the effects of surface preparation conditions on electroless copper plating of graphite/epoxy and graphite/cyanate ester laminates. An alkaline permanganate etchant was applied to the substrates by three methods: immersion, ultrasonic immersion and spray etching. Three etching parameters were investigated: permanganate concentration, etching temperature and etching time. A High Power Microscope was used to characterize the surface topography of the etched and plated laminates.

Results showed that permanganate concentration and etching time were two major factors in etching. Immersion, ultrasonic immersion and spray etching methods resulted in different surface topography. Some of the laminates plated in the electroless copper deposition bath for 1 minute could pass tape test. While at copper deposition time of 15 minutes, the adhesion of tape test classification 3 was achieved on untoughened graphite/cyanate ester laminates. Poor plating could be explained by insufficient surface roughness.

ACKNOWLEDGMENTS

The author would like to thank her thesis advisor, Dr. Melanie A. McNeil, for her guidance in developing experimental plans, her valuable assistance in obtaining necessary chemicals from the Chemistry Department, and her great patience in revising this thesis. Another person who comes to the author's mind is the committee chairperson, Dr. Gregory L. Young. The author appreciates his guidance in the direction of every stage of experiments, his efforts to take High Power Microscope photographs, his patience in revising this thesis and his encouragement during the whole progress of this study. The author would like to thank the consultant, Mr. Dave Kinghorn, for his great efforts to set up the electroless copper plating baths and his training for plating. The author also would like to thank another committee member, Dr. Peter S. Gwozdz, for his advice on spray etching.

Special thanks also go to Dr. Brenda S. Kesler at the Chemistry Department for her help in understanding the chemistry of cyanate ester resins, Mr. Paul Woods also of the Chemistry Department for supplying necessary chemicals, Dr. Patrick P. Pizzo of the Materials Engineering Department for supplying necessary High Power Microscope films and his training for conducting stud pull test, and Dr. Pizzo's student, Steve Papanicoliaou at the Materials Engineering Department, for his kindness and great patience in helping take some High Power Microscope photographs so that this thesis could be finished on time.

The author would like to thank Space Systems/Loral for the financial support and Solution Technology Systems for donating electroless plating chemicals.

Finally, the author would like to thank her parents in helping take care of her little daughter so that she could concentrate on this thesis study. Special thanks go to her husband. Without his great encouragement and financial support, this thesis study is impossible.

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1.0 INTRODUCTION TO ELECTROLESS COPPER PLATING ON GRAPHITE/ EPOXY AND GRAPHITE/CYANATE ESTER LAMINATES

1.1 History of Epoxy Resins and Cyanate Ester Resins

Epoxy resins form a well-developed group of high-temperature thermosetting polymers (Hamerton, 1994). They were commercially introduced into the United States in the late 1940's where they have established themselves as unique building blocks for high performance coatings, adhesives and reinforced plastics (Bauer, 1979). Their wide usage is due to their ease of handling and processability. For example, they can be cured at low temperature (121-177 °C) and pressure (70-100 lb/in²) (Hamerton, 1994). In 1987, epoxy resins comprised over 90% of matrix composites and the forecast for 2000 is about 80% (Hamerton, 1994). The major disadvantage with the use of epoxies is their hot/wet performance. Their upper temperature limit for structural performance is around 177°C, which drops to 149°C when exposed to a moist environment (Hamerton, 1994).

Developed after epoxy resins, cyanate ester resins form another group of high-temperature thermosetting polymers. In the 1960s, Bayer AG developed a practical synthetic route to manufacture stable aryl cyanate esters (Hamerton, 1994). Subsequent developments in molecular architecture have produced second generation cyanate esters with glass transition temperature (T_g) between 190 °C and 290 °C, superior toughness,

lower moisture absorption, lower dielectric-loss properties (the common denominator for circuitry design) and higher peel strength than epoxies (Hamerton, 1994). The major disadvantage of cyanate ester resins is their relatively high price. In the early 1990s, the cost of cyanate ester resins was \$20-45/lb, while the cost of epoxy resins was \$10-30/lb (Hamerton, 1994).

Since the late 1970s, cyanate ester resins have been primarily used to form a structural matrix for printed wiring board laminates and this remains their primary application (Hamerton, 1994). It is estimated that cyanate ester resins together with polyimides will comprise 12-15% of matrix composites in 2000 (Hamerton, 1994).

1.2 Introduction to Epoxy Resins

By definition, any molecule containing the tri-cyclic group is called an epoxy. Epoxy resins are formed from low molecular weight prepolymers containing epoxy end-groups. The most important are diglycidyl ether prepolymers prepared from bisphenol-A (Young and Lovell, 1991). Usually prepolymers are cured by the use of multi-functional amines which undergo a polyaddition reaction with the terminal epoxy groups (Young and Lovell, 1991). Epoxy resins exhibit properties such as: resistance to chemicals, good electrical insulation, high dimensional stability and good mechanical properties (Lubin, 1982).

1.3 Introduction to Cyanate Ester Resins

Cyanate ester resins are used to describe both prepolymers and cured resins. The prepolymer contains reactive ring-forming cyanate ($\text{-O-C}\equiv\text{N}$) functional groups. Curing the prepolymers occurs via cyclotrimerization process. This process is a typical step growth network building process. The final polymer is called polycyanurate which consists of oxygen linked triazine (or cyanurate) (Hamerton, 1994). Figure 1 shows the process of polycyanurate formation.

The resulting thermoset network has a high degree toughness. The polycyanurate cross linked with a triazine ring is very stable and particularly resistant to oxidation. High T_g temperatures are attributed to the presence of ether-oxygen linkages. A symmetrical arrangement of electromagnetic oxygen and nitrogen atoms around electropositive carbons contributes to the properties such as low dielectric loss and low moisture absorption (Hamerton, 1994).

1.4 Significance of Plating on Graphite/Resin Matrix Laminates

Metals offer a high degree of ductility, strength and electrical conductivity but are generally much heavier than graphite/resin matrix laminates. Graphite/resin matrix laminates are nonconductive but have similar ductility and strength as metals (Granger

Figure 1. Formation of polycyanurate process.

and Miller, 1996). Deposition of a metal coating via electrolytic or electroless plating onto a graphite/resin matrix laminate is a novel way to realize the benefits of both metals and graphite/resin matrix laminates. Since increased product weight is a concern in the aerospace industry, the use of plated graphite/resin matrix laminates has become increasingly important (Granger and Miller, 1996).

1.5 Current Problems

Even though plating of plastics was introduced in the 1960s (Parkinson, 1994), plating on undoped graphite/epoxy and graphite/cyanate ester laminates is still a current issue in space applications where the resin is resistant to swelling, corrosion or absorption of water. Previous experience shows that plating of metal onto these types of materials is particularly difficult because the metal does not adhere well to the laminate substrates (Granger and Miller, 1996).

2.0 LITERATURE SURVEY AND REVIEW

2.1 Literature Review Scope

Plastic surfaces are usually smooth and metal does not adhere to them well. A surface roughening step called etching is essential to obtain good adhesion between metal deposit and the plastic substrate. A micro-roughened surface provides more anchoring sites for the metal deposit than a smooth surface. Currently, chemical etching, plasma etching and mechanical abrasion are the major processes used to micro-roughen a plastic substrate. Chemical etching can be subdivided into acid and alkaline etching. For acid etching, chromic acid etching was the predominant etching method used in the past. However, hexavalent chromium is an environmentally regulated heavy metal and ultimate disposal is problematic. Concentrated sulfuric acid is not regenerable and is not favorable for a production process. Alkaline permanganate etching overcomes most of these problems. For example, alkaline permanganate etching is shown to achieve both an uniform and controlled etching rate (Simpkins, 1989). Additionally, alkaline permanganate systems are regenerable and are more environmentally friendly (Simpkins, 1989). Plasma etching is an alternative etching method which utilizes a plasma cloud to roughen the surface. This method has the drawback of high equipment costs and extra process time. Surface roughening can also be achieved by mechanical abrasion using grit blasting or physically scrubbing the surface with an abrasive pad. This method is not

favorable when a substrate has a complex configuration. This literature review only focuses on alkaline chemical etching systems.

Electroless copper plating is typically used in industry to deposit copper onto composites. After electroless copper plating, the composite substrate becomes conductive and electrolytic copper plating is used to obtain the required thickness of the copper film (Viswanathan, 1993 and Poon and Law, 1995). Adequate etching is necessary to achieve good metal to substrate adhesion and is considered the key for good plating (Thorn and Walsh, 1991).

2.2 Alkaline Permanganate Etching of Glass Fiber/Epoxy Composites

Alkaline permanganate etching of glass fiber/epoxy composites has been well established in the literature. The etching methods proposed can be divided into two kinds: immersion and spray etching. Researchers such as Carano (1994), Mandich and Krulik (1992) and Thorn and Walsh (1991) studied the immersion etching formula, possible etching mechanisms and surface topography associated with alkaline permanganate etching of glass fiber/epoxy composites. Preparing the substrate by immersion etching, Carano (1994) pointed out that it was important to properly control the etching by-products such as manganate and manganese dioxide. Kao, Stenger, Georgakis, Covert *et al.* (1992) introduced a new spray etching system to replace the

traditional immersion etching method, and they proposed that spray etching was more effective than conventional immersion etching.

Carano (1994) systematically studied the alkaline permanganate immersion etching formula. He determined that an etching formula consisted of 70-90g/l KMnO_4 and 40-45g/l NaOH produced sufficient surface roughness for glass fiber/epoxy composites used in Printed Circuit Board (PCB) industry. The optimum temperature was reported to be in the range of 165°F to 175°F, and the etching rate was about 20 microinches per minute.

Thorn and Walsh (1991) studied the etching mechanism for alkaline permanganate etching of glass fiber/epoxy composites. They proposed that the permanganate solution etched the epoxy by oxidizing the covalent bonds within the polymer network by first cleaving the crosslink sites, then breaking down the monomers into soluble components which were further degraded to CO_2 .

Thorn and Walsh (1991) and Tomaiuolo and Montangero (1986) studied the topography of glass fiber/ epoxy composites etched by alkaline permanganate. They found that surface topography of the etched composites was the major factor affecting the adhesion strength of copper. Changes in the topography of glass fiber/epoxy composite surfaces produced by alkaline permanganate treatment could greatly increase the adhesion strength of metal deposits. Figure 2 shows the topography of a glass

Figure 2. Permanganate etch showing good micro-roughened surface for optimum adhesion.

fiber/epoxy composite which resulted in an optimum adhesion.

When potassium permanganate (KMnO_4) was used as the etchant, Carano (1994) pointed out that permanganate oxidation reaction was limited not only by permanganate concentration, operating temperature and pH, but also by the reaction by-products such as manganate and manganese dioxide. It was determined that reduction of permanganate would produce manganate and manganese dioxide. Only permanganate was proven to be effective as an oxidant for glass fiber/epoxy substrates. The relationships among manganate build up, alkalinity and temperature are shown in Figure 3 and Figure 4, respectively. Figure 3 and 4 indicate that manganate formation was slowed by reducing alkalinity, permanganate concentration and operation temperature. But a decrease in KMnO_4 concentration or etching temperature will result in a decrease in etching rate. Another problem associated with alkaline permanganate etching is manganese dioxide formation. Manganese dioxide (MnO_2) is reported to form a film on the substrate surface which blocks the surface etching process. Manganese dioxide also acts as a catalyst to promote the decomposition of permanganate to manganate. A neutralizer, which consists of an acidic solution (typically HCl) and reducing agents such as hydrazine or hydroxylamine sulfate, can remove the MnO_2 film from hole walls by converting MnO_2 to soluble Mn^{2+} .

As an alternative to immersion etching, Kao *et al.* (1992) proposed a spray etching method. Figure 5 illustrates a simplified spray etching system. A spray etcher

Figure 3. Decomposition of potassium permanganate versus sodium hydroxide level at different permanganate level at 170°F.

Figure 4. Decomposition of potassium permanganate versus sodium hydroxide level at different temperatures at 80g/l permanganate.

Figure 5. A spray wet etch system.

consists of an etch chamber and a sump tank. This wet etching process is based on a powerful spray of a chemical etchant onto the substrate with the help of a nitrogen gas flow. The sump tank continuously collects the overflow from the etching chamber and the etching solution is pumped back to the etching chamber. In this way, the etching solution can be reused. Four controlling factors for the spray etching process reported were: etchant concentration, etching time, pressure and temperature. In KMnO_4 immersion etching of glass fiber/epoxy composites, a thin film of MnO_2 is formed on the composite surface. This film inhibits the transport of etchant to the composite surface, thus decreases the amount of etching activity. Spray etching, on the other hand, increases mass-transfer of etchant because a fresh supply of etchant is sprayed onto the substrate continuously. Therefore, spray etching process offers shorter etching times and higher throughput.

2.3 Etching of Graphite/Cyanate Ester Composites

Graphite/cyanate ester composites were proposed to replace glass fiber/epoxy composites used in PCB industry because of their superior toughness, low moisture absorption and low dielectric loss (Hamerton, 1994). However, plating metal films onto graphite/cyanate ester composite surfaces was reported to be very difficult (Granger and Miller, 1996). Surface preparation is the key to solve this problem. Chemical etching and mechanical abrasion methods for graphite/cyanate ester composites were proposed in

the literature. Karas and Chao (1994) introduced an alkaline permanganate immersion etching method, while Granger and Miller (1996) presented an alkoxide immersion etching method. Instead of relying solely on chemical etching, Converse and Lary (1996) proposed a combination of grit blasting and chemical etching method.

Karas and Chao (1994) introduced a series of surface preparation steps using alkaline permanganate followed by a concentrated nitric acid treatment as shown in Table 1. This procedure was reported to be suitable for the surface preparation of graphite/cyanate ester composites. The cyanate ester used was a Fiberite 954-3 resin. Experimental results showed that surface preparation by alkaline permanganate and concentrated nitric acid might be combined to provide a good surface preparation.

Granger and Miller (1996) proposed another etching method for graphite/cyanate ester composites. This procedure was also reported to be suitable for the surface preparation of graphite/cyanate ester 954-3 composites. The substrate surface was treated with a preheated solution containing an alkali metal salt of an alkoxide. However, the reported ranges of controlling factors were very broad. The concentration of alkoxide salt ranged from 1-50 wt%, the controlling temperature was between 70°C and 120°C, and the etching time was from 10 seconds to 20 minutes.

Although the exact alkoxide etching mechanism was unclear, Granger and Miller

Table 1. A surface preparation procedure for graphite/cyanate ester composites using alkaline permanganate and concentrated nitric acid treatment.

Procedure	Parameter	Operating Range
Alkaline Permanganate Etching	NaMnO ₄ conc.	0.75-1.25 M
	NaOH conc.	1-2 M
	Temperature	50°-90°C
	Etching time	2-15 min.
HNO ₃ treatment following etching	HNO ₃ conc.	50%-70% (weight percent)
	Time	1-5 min.
	Temperature	20°-30°C

(1996) hypothesized that an alkoxide ion might nucleophilically attack the cured cyanate ester surfaces. Granger's hypothesis agreed with the explanation proposed by Mercier, Abed and McGrath (1997). Mercier *et al.* proposed that the C≡N groups in a triazine ring were analogous to nitriles. Figure 1 shows that ester groups (RO) are connected to the triazine rings in the structure of cured cyanate ester resin. Since the RO groups reduced the electron densities on both the carbons and nitrogens, it was expected that the triazine would be more reactive toward nucleophilic addition reactions than ordinary nitriles. An alkali metal salt of an alkoxide is a typical nucleophilic agent. It may randomly attack electron-deficient atoms in the triazine ring and remove them as short chains which are further dissolved in solution. The order of reactivity of several nucleophilic agents (Garbassi, Marco and Ernesto, 1994) is as follows:

hydroxide<tert-butoxide<sec-propoxide<methoxide<ethoxide

Although both alkaline permanganate treatment proposed by Karas and Chao (1994) and alkoxide etching proposed by Granger and Miller (1996) claimed to improve the adhesion between metal deposits and the etched surface, the plated substrates prepared by these two different methods could only pass tape tests. Tape test classification 5 means that the adhesion of the metal film is high enough to pass the tape test.

Converse and Lary (1996) studied graphite/cyanate ester composites plated with

copper and silver. By combining grit blasting and chemical etching, the adhesion strength of metal films can reach between 1200 and 2000 psi. Unfortunately, no detailed information of the surface preparation was reported in this paper. Figure 6 shows an etched surface reported in this paper.

Figure 6. SEM (1000x) of an etched surface (fiber T300/cyanate ester RS-3 composite).

2.4 Electroless Copper Plating

After a substrate has been well etched, copper can be deposited onto this substrate by electroless or electrolytic copper plating. Nonconductive graphite/resin matrix laminates require electroless deposition prior to any electrolytic process.

Figure 7 shows a typical electroless copper deposition procedure. Viswanathan (1993) and Anis (1994) studied the four major steps involved in the electroless copper plating: sensitization, activation, acceleration and electroless copper deposition. In the sensitization step, a substrate is immersed in acid stannous chloride solution (SnCl_2). The purpose of this step is to yield superior wetting of SnCl_2 on hydrophobic substrates. The activation step involves immersion of the sensitized substrate in acid palladium chloride solution. Nucleation of palladium occurs through the reaction between Pd^{2+} and Sn^{2+} as shown in Equation (1). This reaction produces a metallic alloy colloid of Pd and Sn surrounded by stabilizing layer of SnCl_2 and $\text{Sn}(\text{OH})_2$. Dispersion of finely divided Pd requires good adsorption of the sensitizers (SnCl_2) achieved in the sensitization step. Palladium has been proven to provide a catalytic surface required for electroless copper deposition. The catalytic effect increases once a film of Cu is deposited and the copper deposition rate increases. Accelerators such as NaOH and EDTA are effective in removing the tin from the palladium/tin colloid to increase the initial rate of copper deposition. Electroless copper deposition is achieved in an

Figure 7. An electroless copper deposition procedure.

electroless copper plating bath. Copper sulfate (CuSO_4) is used as a copper source and formaldehyde (HCHO) is used as a reducing agent. Two major reactions taking place in this bath are shown in Equations (2) and (3), respectively. The overall reaction is shown in Equation (4). By following the above procedure, copper can be deposited onto the substrate.

Anodic reaction:

Cathodic reaction:

The overall reaction can be written as:

2.5 Summary of Literature Review

Metallized fiber/epoxy and fiber/cyanate ester composites are mainly used in the PCB industry and aerospace applications because these materials can significantly reduce product weight. However, plating copper films onto these composite substrates is reported to be very difficult. Etching is a key step to achieve good adhesion between

metal deposits and the composite substrate. This literature review shows that glass fiber/epoxy composites can be immersion or spray etched by alkaline permanganate. Graphite/cyanate ester composites can be etched by three different methods: alkaline permanganate immersion etching, alkaline metal salt of an alkoxide immersion etching and a combination of grit blasting and chemical etching.

3.0 RESEARCH HYPOTHESIS AND OBJECTIVE

3.1 Hypotheses

Surface preparation is a key step in achieving good adhesion between copper deposits and graphite/resin laminates. Chemically etching the surface with alkaline permanganate solution should produce a surface topography that is favorable to electroless copper deposition. Three different etching methods: immersion, ultrasonic immersion and spray can be used to improve adhesion of copper films onto graphite laminated structures.

3.2 Justification

Five articles presented in the literature support the above hypotheses. Mandich and Krulik (1992) reported that alkaline permanganate immersion etching could micro-roughen glass fiber/epoxy composites. Karas and Chao (1994) proposed the use of alkaline permanganate for immersion etching of graphite/cyanate ester composites. The adhesion strength of the deposited films was reported to be about 200 psi.

Ultrasonic and spray etching are two methods used to enhance chemical etching

effects of permanganate. Although ultrasonic etching was not reported to be applied for either glass fiber/epoxy or graphite/cyanate ester composites, it has played an important role in the anisotropic etching of silicon (Ohwada, Negoro, Konaka and Oguchi, 1995). When ultrasonic vibration was applied during immersion etching, cavities were generated on the etched surfaces (Ohwada *et al.*, 1995). Kao *et al.* (1992) reported using a spray method to etch glass fiber/epoxy composites. Compared with immersion etching, spray etching could shorten etching time and result in a constant etching rate.

The substrates used in this thesis study have a very thin layer of resin, about 80 μ -inches, on top of the laminates. The resin systems used in the fabrication of the laminates are designed to be resistant to swelling and corrosion. The etching parameters such as: etching concentration, etching time and temperature need to be optimized for the substrates used in this study.

3.3 Objectives

The objective of this study is to find optimum surface preparation conditions so that copper can be plated onto graphite/epoxy and graphite/cyanate ester laminates. The thickness of the copper film after electroless plating should be between 100 and 200 μ -inches, and the desired adhesion strength of the film should be between 1000 and 2000 psi.

4.0 EXPERIMENTAL PROCEDURES

4.1 Experimental Apparatus

A small-scale surface preparation line for immersion etching consisted of five 250 ml beakers is shown schematically in Figure 8. There was a DI water rinse between each step which is not shown in Figure 8. Four heated beakers used for alkaline cleaning, resin conditioning, immersion etching and neutralizing were required for this process. Heater plates were used to control the temperature. A magnetic stir bar was used to maintain a uniform temperature within each of the four heated beakers. The temperature was controlled within $\pm 3^{\circ}\text{C}$ of a given setpoint.

Ultrasonic immersion or spray etching was achieved by replacing the immersion etching of step 4 (Figure 8) with the appropriate apparatus as shown in Figure 9 and 10, respectively.

The ultrasonic immersion etching apparatus is shown in Figure 9. Etching was conducted by putting the immersion etching apparatus in a temperature controlled ultrasonic tank (Type: Branson 5210). The tank could generate ultrasonic waves continuously for required periods of time. 0.5% (volume) surfactant (Type: Ultra DAWN Concentrated Dishwashing Detergent) was added into the ultrasonic tank to decrease the

Figure 8. A schematic of a surface preparation line for alkaline permanganate immersion etching.

Figure 9. An ultrasonic immersion etching apparatus.

Figure 10. A schematic of a spray etching system.

surface tension of water.

The spray etching chamber was mounted on top of a three-gallon polypropylene tank as shown in Figure 10. The etching solution was stored inside the tank and could be sprayed onto the substrate with the help of a pump (PP-LBS3) supplied by Custom Masters. The tank was also acted as a sump tank to collect etching solution from the etching chamber. In this way, the etching solution could be gathered and reused. The temperature inside the tank was controlled by a heater controller (DME 302-LC) supplied by Harrington Plastics.

The electroless copper plating line as shown in Figure 11 consisted of eight nine-gallon polypropylene tanks. Electroless copper plating was performed at room temperature (25°C).

4.2 Materials and Chemicals

Three different Fiberite resin systems were used for this study: epoxy 934, cyanate esters 954-3 and 954-2A (thermal toughened). The thickness of the resin on top of laminates averaged approximately 80 μ -inches. The fiber system used for the laminates was a M60J fiber manufactured by Toray. The dimension of the laminates is about 4.5 cm x 4.5 cm x 0.1 cm. Space Systems/Loral is the supplier of all substrates

Figure 11. A schematic of an electroless copper plating line.

used in this study.

Five major chemicals were used in the surface preparation process. Analytical grade potassium permanganate, sodium hydroxide and sulfuric acid were supplied by the Chemistry Department at San Jose State University. The Electro-Brite E-Prep Solvent II used for resin conditioning and E-Prep neutralizer used for the removal of manganese dioxide films formed during alkaline permanganate etching were supplied by Space Systems/Loral.

Plating chemicals including pre-dip, activator, accelerator, electroless copper concentrate (MR-A and MR-B) and anti-oxidant were supplied by Alanbaker Company.

4.3 Experimental Procedures

Experimental procedures were divided into two sections: surface preparation and electroless copper plating. Figure 12 shows a flow chart for experimental procedures used in this study.

Surface preparation was subdivided into immersion etching of neat resins and etching of laminates. Three different etching methods used to etch the laminates were: immersion, ultrasonic immersion and spray. Immersion etching was performed in the

Figure 12. A flow chart for experimental procedures.

system shown in Figure 8. Ultrasonic immersion and spray etching were performed in the systems shown in Figure 9 and 10, respectively. Table 2 shows a complete surface preparation procedure. The surface preparation procedure included: alkaline cleaning, acid cleaning, alkaline permanganate etching and neutralization. Three etching parameters investigated were: KMnO_4 concentration, etching temperature and time. NaOH concentration was kept at 40g/l for all etching experiments.

Immersion etching of neat resins was used as a preliminary screening test. The purposes of this test were two folds: (1) to study the effects of etching parameters on the surface topography of the neat resins, and (2) to provide data for the etching of laminates.

Surface topography after etching was characterized by High Power Microscope. Topography characterization was conducted both at Space Systems/Loral and San Jose State University. The criteria of a well-etched laminate were: (1) the laminate surface was micro-roughened, and (2) graphite fibers were only partially exposed after the etching.

Based on the results of the surface preparation, selected laminates were plated with copper. Etched samples were plated by following a standard electroless copper plating procedure shown in Table 3. A standard graphite/934 laminate, which had been successfully plated at Space Systems/Loral, was used to test the reliability of the plating fabrication line. This standard sample was plated at San Jose State University and sent to

Table 2. A complete surface preparation procedure.

No.	Procedure	Function	Temperature (°C)	Time (minute)
1	Alkaline clean (12M NaOH)	Get rid of organic contaminants	75	3
2	DI water rinse	Rinse between major steps	Room	2
3	Acid rinse (3% (volume) H ₂ SO ₄)	Get rid of salts	Room	1
4	DI water rinse	Rinse between major steps	Room	2
5 ^(a)	Resin conditioning using E-Prep Solvent II	Swell the resin and make it more venerable to etching	60	10
6	DI water rinse	Rinse between major steps	Room	2
7 ^(b)	KMnO ₄ +NaOH etching	Micro-roughen the surface of laminates	Follow testing matrix	Follow testing matrix
8	DI water rinse	Rinse between major steps	Room	2
9	Neutralize using 5% (volume) E-Prep neutralizer	Remove maganese dioxide films formed on the etched surface	43	5
10	DI water rinse	Rinse between major steps	Room	2

(a) This step is recommended but not required.

(b) This step can be replaced by ultrasonic immersion or spray etching.

Table 3. Electroless copper plating procedures

Step	Procedure	Function	Temperature (°C)	Time (min.)
1	Neutralization by 5% (volume) E-Prep neutralizer	Remove MnO ₂ residues generated during the etching step	43	5
2	DI water rinse	Rinse between major steps	Room	2
3	Alkaline cleaning (2M NaOH)	Get rid of organic contaminants	75	2
4	DI water rinse	Rinse between major steps	Room	2
5	Acid cleaning (10% sulfuric acid)	Get rid of salts	Room	1
6	DI water rinse	Rinse between major steps	Room	2
7	Pre-dip	Yield superior wetting of SnCl ₂ on hydrophobic substrates	Room	5
8	Activation	Produce metallic alloy colloid of Pd/Sn	Room	5
9	DI water rinse	Rinse between major steps	Room	2
10	Acceleration	Remove Sn from the Pd/Sn colloid to increase the initial rate of copper deposition	Room	7
11	DI water rinse	Rinse between major steps	Room	2
12	Electroless copper deposition	Deposit copper onto the substrate	Room	1 or 15
13	10% sulfuric acid neutralization	Neutralize the sample	Room	2
14	Anti-oxidation (Oxyban)	Prevent copper oxidation	Room	2
15	DI water rinse	Rinse between major steps	Room	2
16	Air dry	Dry the sample	Room	3

Space Systems/Loral to measure the thickness and adhesion strength of the copper film. The thickness of the copper film for this standard sample was used to estimate the copper deposition rate in the electroless deposition bath.

Adhesion strength of the plated copper film was measured by tape test according to ASTM Test Method D-3359. The detailed information about the tape test is described in Appendix A. Tape test classification of 5 indicates the highest adhesion strength and classification of 0 indicates the lowest adhesion strength. Since the tape test is a qualitative measurement of the adhesion, tape test classification of 5 indicates that the adhesion of metal films is strong enough not to be removed by the tape during the tape test. Duplicate samples of each condition were tested.

5.0 RESULTS AND DISCUSSIONS

5.1 Introduction

This section presents results of experiments outlined in section 4.0. This section is divided into three parts: (1) immersion etching of neat resins; (2) etching of laminates using immersion, ultrasonic immersion and spray methods; and (3) electroless copper plating of all laminates. Surface topography was characterized by use of a High Power Microscope.

5.2 Immersion Etching of Neat Resins-Preliminary Screening

Photographs 1 and 2 show the surface topography of unetched epoxy 934 and cyanate ester 954-2A neat resins, called “blanks”. Photographs 1 and 2 indicate that there was an initial surface roughness for both epoxy 934 and cyanate ester 954-2A neat resins. The surface of the unetched epoxy 934 neat resin is relatively smooth compared with the surface of the unetched cyanate ester 954-2A neat resin. This phenomenon can be explained by the rheological properties of the different resins. The resin samples were placed on a tool in liquid formed and cured at 350°F. The flow properties of the resin, while curing, determine the surface of the sample. The testing matrix for immersion etching of neat resins is shown in Table 4. Three etching parameters investigated were:

Photograph 1. Unetched epoxy 934 neat resin topography
(500x).

Photograph 2. Unetched cyanate ester 954-2A (toughened)
neat resin topography (500x).

Table 4. Immersion etching of neat resins.

Run	Temperature (°C)	KMnO ₄ (g/l) NaOH: 40 g/l	Etching Time (minute)
1	65	60	4
2	65	60	12
3	65	90	4
4	65	90	12
5	85	60	4
6	85	60	12
7	85	90	4
8	85	90	12

etching temperature at 65°C and 85°C, permanganate concentration at 60g/l and 90g/l and etching time at 4 minutes and 12 minutes. Since no topography change was observed on cyanate ester 954-3 neat resins after the etching, only topography results for epoxy 934 and cyanate ester 954-2A are presented.

5.2.1 Effect of Temperature on Immersion Etching of Neat Resins

Photographs 3 to 6 present temperature effects on immersion etching of neat resins. Photographs 3 and 4 are topography results of epoxy 934 neat resins immersion etched at two different temperature: 65°C and 85°C, respectively. The topography results shown in photographs 3 and 4 indicate that there is very little topography change when etching was performed at 65°C and 85°C, respectively. Similar results can be obtained by comparing photographs 5 and 6 for cyanate ester 954-2A neat resins. Photographs 3 to 6 indicate that temperature was not a major factor in etching in the temperature range between 65°C and 85°C when KMnO_4 concentration and etching time were kept as constants.

5.2.2 Effect of Permanganate Concentration on Immersion Etching of Neat Resins

Photographs 7 to 10 present KMnO_4 concentration effects on immersion etching of neat resins when etching temperature and etching time were kept at 85°C and 12 minutes, respectively. When KMnO_4 concentration was increased from 60g/l to 90g/l, photographs 7 and 8 show that the surface of epoxy 934 neat resins had a tendency to become smooth, while photographs 9 and 10 show that the surface roughness of cyanate

Photograph 3. Epoxy 934 neat resin immersion etched
@ temperature 65°C, KMnO_4 60 g/l for
4 minutes (500x).

Photograph 4. Epoxy 934 neat resin immersion etched
@ temperature 85°C, KMnO_4 60 g/l for
4 minutes (500x).

Photograph 5. Cyanate ester 954-2A (toughened) neat resin immersion etched @ temperature 65°C, KMnO_4 60 g/l for 4 minutes (500x).

Photograph 6. Cyanate ester 954-2A (toughened) neat resin immersion etched @ temperature 85°C, KMnO_4 60 g/l for 4 minutes (500x).

Photograph 7. Epoxy 934 neat resin immersion etched @
KMnO₄ 60 g/l, temperature 85°C for 12
minutes (500x).

Photograph 8. Epoxy 934 neat resin immersion etched @
KMnO₄ 90 g/l, temperature 85°C for 12
minutes (500x).

Photograph 9. Cyanate ester 954-2A (toughened) neat resin immersion etched @ KMnO_4 60 g/l, temperature 85°C for 12 minutes (500x).

Photograph 10. Cyanate ester 954-2A (toughened) neat resin immersion etched @ KMnO_4 90 g/l, temperature 85°C for 12 minutes (500x).

ester 954-2A neat resins increased. Photographs 7 to 10 indicate that KMnO_4 concentration had different effects on the surface topography of epoxy 934 and cyanate ester 954-2A neat resins.

5.2.3 Effect of Etching Time on Immersion Etching of Neat Resins

The effect of etching time is shown in photographs 8, 10, 11 and 12. Photographs 11 and 12 show the topography results of epoxy 934 and cyanate ester 954-2A neat resins immersion etched at KMnO_4 concentration of 90 g/l, temperature at 85°C and etching time for 4 minutes. When etching time was increased from 4 minutes to 12 minutes, photographs 8 and 11 show that the surface roughness of epoxy 934 neat resins decreased, while the surface roughness of cyanate ester 954-2A neat resins increased as shown in photographs 10 and 12. Photographs 8, 10, 11 and 12 indicate that etching time had different effects on epoxy 934 and cyanate ester 954-2A neat resins.

5.2.4 Conclusions of Immersion Etching of Neat Resins

Immersion etching of neat resins indicated that temperature is not a major factor in the temperature range investigated between 65°C and 85°C , because the temperature range investigated was too narrow to show the temperature effects on etching. This result can be obtained by comparing photographs 3 and 4 for epoxy 934 neat resins, and photographs 5 and 6 for cyanate ester 954-2A neat resins. A larger range was not selected because it was hard to control the etching temperature above 85°C under the present experimental conditions.

Photograph 11. Epoxy 934 neat resin immersion etched @ KMnO_4 90 g/l, temperature 85°C for 4 minutes (500x).

Photograph 12. Cyanate ester 954-2A (toughened) neat resin immersion etched @ KMnO_4 90 g/l, temperature 85°C for 4 minutes (500x).

Permanganate concentration and etching time are two major factors in etching. When KMnO_4 concentration or etching time was increased, the surface of epoxy 934 neat resins had a tendency to become smooth. This indicates that immersion etching of epoxy 934 neat resins is preferable in the horizontal direction which is parallel to the resin surface, thus results in a smoothly etched surface.

With the increase of KMnO_4 concentration or etching time, no topography changes were detected on cyanate ester 954-3 neat resins, while the surface roughness for cyanate ester 954-2A increased. The topography results for cyanate ester 954-2A and 954-3 neat resins indicate that incorporation of thermal tougheners into cyanate ester neat resin systems contributes to the surface roughening during the etching process. It is very likely that the thermal toughener was etched away by alkaline permanganate at a different rate than the cyanate ester. If the etching rates for thermal toughener and cyanate ester neat resins are different, a rougher surface would result on the thermal toughened cyanate ester 954-2A neat resins than on cyanate ester 954-3 neat resins.

There are two possible reasons why no topography change was observed on cyanate ester 954-3 neat resins. One possible reason is that no etching occurred. Another possible reason is that the etching was so uniform that no topography change could be detected. Since no attempt was made to measure the thickness before and after the etching, whether etching occurred or not could not be determined by this run of experiments. This phenomenon will be discussed in section 5.3.2.3.

5.3 Etching of Laminates

Immersion, ultrasonic immersion and spray etching were used in laminate etching experiments. Because immersion etching of neat resins indicated that temperature was not a major factor in etching in the temperature range between 65°C and 85°C, only the effects of permanganate concentration and etching time were investigated for the etching of laminates. Etching temperature was kept at 65°C for all laminate etching experiments.

5.3.1 Immersion Etching of Graphite/Epoxy 934 Laminates

Photograph 13 presents the surface of an unetched graphite/epoxy 934 laminate. Photograph 13 shows that the surface of the unetched graphite/epoxy 934 laminates is smooth and few pores could be observed on top of this blank laminate. Fibers underneath the resin could also be observed according to photograph 13. The topography of unetched graphite/cyanate ester 954-2A and graphite/cyanate ester 954-3 laminates was similar to that of the blank graphite/epoxy 934 laminate. Immersion etching of laminates was first performed on graphite/epoxy 934 laminates. The testing matrix for immersion etching of graphite/epoxy 934 laminates is shown in Table 5. Three different KMnO_4 concentrations investigated were 20g/l, 40g/l and 60g/l. Etching time was at 2 minutes and 4 minutes, respectively.

Photograph 13. Unetched graphite/epoxy 934 laminate topography (500x).

Table 5. Immersion etching of graphite/epoxy 934 laminates.

Temperature: 65°C NaOH: 40 g/l

KMnO ₄ (g/l)	Time (min.)	
20	2	4
40	2	4
60	2	4

5.3.1.1 Effect of Permanganate Concentration on Immersion Etching of Graphite/Epoxy 934 Laminates

Photographs 14 to 16 present the topography results of graphite/epoxy 934 laminates immersion etched at KMnO₄ concentration of 20g/l, 40g/l and 60g/l at 65°C for 2 minutes. These photographs indicate that the exposure of fibers increased when KMnO₄ concentration was increased. Photographs 14 and 15 show that fibers are partially exposed at KMnO₄ concentration of 20g/l and 40g/l, while photograph 16 shows that fibers were completely exposed when immersion etching was performed at KMnO₄ concentration of 60 g/l. Over exposure of fibers is not favorable because fibers have poor flatwise tensile strength. As a result, plating directly to the fibers will result in poor adhesion strength. The common phenomenon that can be observed in photographs 14 to 16 is that the etched resin located between fibers was smooth no matter which KMnO₄ concentration was chosen. Since few pits which means few pores could be observed on the resin surface, this indicated that the resins between fibers were uniformly etched.

Photograph 14. Graphite/epoxy 934 laminate immersion etched @ KMnO_4 20 g/l, temperature 65°C for 2 minutes (500x).

Photograph 15. Graphite/epoxy 934 laminate immersion etched @ KMnO_4 40 g/l, temperature 65°C for 2 minutes (500x).

Photograph 16. Over etched graphite/epoxy 934 laminate immersion
etched @ KMnO_4 60 g/l, temperature 65°C for 2
minutes (500x).

5.3.1.2 Effect of Etching Time on Immersion Etching of Graphite/Epoxy 934

Laminates

Photographs 14, 15, 17 and 18 show the effect of etching time on the surface topography of graphite/epoxy 934 laminates. Photographs 14 and 17 show the topography results when immersion etching was performed at KMnO_4 concentration of 20g/l for 2 and 4 minutes, respectively. Photographs 15 and 18 show the surface topography of graphite/expoy 934 laminates immersion etched at a KMnO_4 concentration of 40g/l for 2 and 4 minutes, respectively. Photographs 14 and 17 indicate that the exposure of fibers was slightly increased with the increase of etching time at KMnO_4 concentration of 20g/l. At KMnO_4 concentration of 40 g/l, photographs 15 and 18 show that the exposure of fibers was also increased when etching time was increased. Since partial fibers were exposed as shown in photographs 14, 15, 17 and 18, KMnO_4 concentration of 20g/l and 40g/l. etching time of 2 minutes and 4 minutes were considered appropriate for the etching of graphite/epoxy 934 laminates. Also few pits could be observed on the resin surface as shown in photographs 14, 15, 17 and 18, this indicates that increase of KMnO_4 concentration or etching time did not result in the increase of surface roughness on the graphite/epoxy 934 laminates.

5.3.1.3 Conclusions of Immersion Etching of Graphite/Epoxy 934 Laminates

Photographs 14, 15, 17 and 18 show that KMnO_4 concentration of 20 and 40g/l, and etching time of 2 minutes and 4 minutes are appropriate for immersion etching of graphite/epoxy 934 laminates because fibers were partially exposed under the etching

Photograph 17. Graphite/epoxy 934 laminate immersion etched @ KMnO_4 20 g/l, temperature 65°C for 4 minutes (500x).

Photograph 18. Graphite/epoxy 934 laminate immersion etched @ KMnO_4 40 g/l, temperature 65°C for 4 minutes (500x).

conditions. Etching at KMnO_4 concentration of 60g/l for a short time such as several seconds was not successful. Since few pits can be observed on the etched resin systems as shown in photographs 14, 15, 17 and 18, this phenomenon indicates that immersion etching of neat resin systems in laminates resulted in uniform etching. Increase of KMnO_4 concentration or etching time did not improve the surface roughness of the resin systems. Uniform etching of neat resin systems in laminates was not favorable for copper plating since copper has few pores to anchor onto the smooth surface. Experimental results for immersion etching of laminates show that immersion etching does not roughen the resin systems in laminates. Because of the uniform etching of epoxy neat resin systems in graphite/epoxy laminates, no immersion etching was conducted on graphite/cyanate ester laminates.

5.3.2 Ultrasonic Immersion Etching of All Laminates

Because of the uniform etching encountered in the immersion etching of graphite/epoxy 934 laminates, two other etching methods used to improve the surface roughness of the resin systems were: ultrasonic immersion and spray etching. Ultrasonic etching and spray etching were two etching methods reported in the literature to result in anisotropic etching effects. The results of ultrasonic immersion etching are presented in this section and the results of spray etching will be presented in section 5.3.3. The testing matrix for ultrasonic immersion etching experiments is shown in Table 6. For graphite/epoxy 934 laminates, etching was performed at KMnO_4 concentration of 20g/l and 40g/l, and etching time at 2 minutes and 4 minutes, respectively. Etching of

graphite/cyanate ester laminates was performed at KMnO_4 concentration of 40g/l. The etching time for graphite/cyanate ester 954-2A laminates was 2, 6 and 9 minutes and the etching time for graphite/cyanate ester 954-3 laminates was 2, 4 and 6 minutes. The reason why KMnO_4 concentration of 40g/l was chosen for the etching of graphite/cyanate ester laminates will be discussed in section 5.3.2.1. The reason why different etching time was chosen for graphite/cyanate ester 954-2A and graphite/cyanate 954-3 laminates will be discussed in section 5.3.2.2.

Table 6. Ultrasonic immersion etching of graphite/epoxy 934, graphite/cyanate ester 954-2A (toughened) and graphite/cyanate ester 954-3 laminates.

Temperature: 65°C NaOH: 40g/l

Laminate	KMnO_4 (g/l)	Time (min.)		
934	20	2	4	N/A
	40	2	4	
954-2A	40	2	6	9*
954-3		2	4*	6

* Will be discussed in section 5.3.2.2.

5.3.2.1 Effect of Permanganate Concentration on Ultrasonic Immersion Etching of All Laminates

Photographs 19 and 20 present the surface topography of graphite/epoxy laminates immersion etched for 4 minutes at two different KMnO_4 concentrations: 20g/l

Photograph 19. Graphite/epoxy 934 laminate ultrasonic immersion etched @ KMnO₄ 20 g/l, temperature 65°C for 4 minutes (500x).

Photograph 20. Graphite/epoxy 934 laminate ultrasonic immersion etched @ KMnO₄ 40 g/l, temperature 65°C for 4 minutes (500x).

and 40g/l. Photograph 19 shows that small pits were generated on the resin surface and these pits were formed along fibers. Also only partial fibers were exposed under the etching condition. Photograph 20 shows that bigger pores were generated on the resin surface when etching was performed at KMnO_4 concentration of 40g/l. The surface topography shown on photograph 20 is considered to be more favorable to copper deposition than that shown on photograph 19 because copper has more anchoring sites on the rougher surface. Based on this result, KMnO_4 concentration was kept at 40g/l for the ultrasonic immersion etching of graphite/cyanate ester laminates. KMnO_4 concentration over 40g/l was not used because of the immersion etching trials results.

5.3.2.2 Effect of Etching Time on Ultrasonic Immersion Etching of All Laminates

The effect of etching time on ultrasonic immersion etching of graphite/epoxy 934 laminates can be obtained by comparing photographs 19, 21 and 20, 22. Photographs 19 and 21 show that the exposure of fibers was slightly increased and the number of pores on the laminate surface increased when etching time was increase from 2 minutes to 4 minutes at KMnO_4 concentration of 20g/l. At KMnO_4 concentration of 40g/l, the effect of etching time can be clearly observed by comparing photographs 20 and 22. At etching time of 2 minutes, small pores were formed on the resin system as shown in photograph 22, while at etching time of 4 minutes, larger pores were generated on the laminate surface as shown in photograph 20. When etching time was increased from 2 minutes to 4 minutes, photographs 19 and 21 show that there were few topographical changes when etching was performed at KMnO_4 concentration of 20g/l. This is because at low KMnO_4

Photograph 21. Graphite/epoxy 934 laminate ultrasonic immersion etched @ KMnO_4 20 g/l, temperature 65°C for 2 minutes (500x).

Photograph 22. Graphite/epoxy 934 laminate ultrasonic immersion etched @ KMnO_4 40 g/l, temperature 65°C for 2 minutes (500x).

concentration, the etching rate is too slow to show the etching time effects at 2 and 4 minutes. Photographs 20 and 22 show a great increase in surface roughness on the epoxy 934 neat resin systems in laminates. This is because when KMnO_4 concentration was increased from 20g/l to 40g/l, more etchant was available to attack the resin systems and the etching rate was high enough to show the time effects on etching.

Photographs 23 to 26 present the topography of graphite/cyanate ester 954-2A and graphite/cyanate ester 954-3 laminates ultrasonic immersion etched for 2 and 6 minutes. At KMnO_4 concentration of 40g/l, the topography change of graphite/cyanate ester 954-2A laminates was minor when etching time was increased from 2 to 6 minutes. Although pores were generated on the cyanate ester 954-2A resin system, the exposure of fibers looks similar based on photographs 23 and 24.

Different surface topography results can be observed in photographs 25 and 26 for graphite/cyanate ester 954-3 laminates. Photograph 25 show that pores were generated on the cyanate ester 954-3 resin system and these pores were close to fibers. Also fibers were only slightly exposed at etching time of 2 minutes. Photograph 26 indicates that fibers were completely exposed when etching was performed for 6 minutes. Photograph 26 also indicates that the resin surface was micro-roughened although fibers were completely exposed. By comparing photographs 23, 25 and 24, 26, the following result is observed. More fibers were exposed on the surface of graphite/cyanate ester 954-3 laminates than on graphite/cyanate ester 954-2A laminates for identical operating

Photograph 23. Graphite/cyanate ester 954-2A (toughened) laminate ultrasonic immersion etched @ KMnO_4 40g/l, temperature 65°C for 2 minutes (500x).

Photograph 24. Graphite/cyanate ester 954-2A (toughened) laminate ultrasonic immersion etched @ KMnO_4 40 g/l, temperature 65°C for 6 minutes (500x).

Photograph 25. Graphite/cyanate ester 954-3 laminate
ultrasonic immersion etched @ KMnO_4
40 g/l, temperature 65°C for 2 minutes
(500x).

Photograph 26. Graphite/cyanate ester 954-3 laminate
ultrasonic immersion etched @ KMnO_4
40 g/l, temperature 65°C for 6 minutes
(500x).

parameters. This indicates that etching of graphite/cyanate ester 954-3 laminates was faster than that of graphite/cyanate ester 954-2A laminates. Based on this result, etching time of 9 minutes for graphite/cyanate ester 954-2A laminate and etching time of 4 minutes for graphite/cyanate ester 954-3 laminate were added to the testing matrix as shown in Table 6. Photograph 27 shows the topography of graphite/cyanate ester 954-2A laminate ultrasonic immersion etched for 9 minutes. This photograph indicates that a group of small pores were generated on graphite/cyanate ester 954-2A laminates at etching time of 9 minutes. Photograph 28 presents the topography of graphite/cyanate ester 954-3 laminate ultrasonic immersion etched for 4 minutes. Photograph 28 indicates that large pores were formed on graphite/cyanate ester 954-3 laminates at etching time of 4 minutes. Photographs 27 and 28 indicate that it takes a shorter time to generate pores on graphite/cyanate ester 954-3 laminates than on graphite/cyanate ester 954-2A laminates. These two photographs further proved that etching of graphite/cyanate ester 954-3 laminates was faster than that of graphite/cyanate ester 954-2A laminates. The possible reason is that etching of cyanate ester is faster than etching of thermal toughener. The effect of etching time on graphite/cyanate ester 954-2A laminates can be obtained by comparing photographs 23, 24, 27, and the effect of etching time on graphite/cyanate ester 954-3 laminates can be obtained by comparing photographs 25, 26 and 28. Photographs 23 to 28 indicate that bigger pits were formed and more fibers were exposed on the surface of graphite/cyanate ester laminates when etching time was increased.

Photograph 27. Graphite/cyanate ester 954-2A (toughened) laminate ultrasonic immersion etched @ KMnO_4 40 g/l, temperature 65°C for 9 minutes (500x).

Photograph 28. Graphite/cyanate ester 954-3 laminate ultrasonic immersion etched @ KMnO_4 40 g/l, temperature 65°C for 4 minutes (500x).

5.3.2.3 Conclusions of Ultrasonic Immersion Etching of All Laminates

The topography presented on photographs 19 to 28 showed that KMnO_4 concentration and etching time are two factors in ultrasonic immersion etching of laminates. Also, pits were formed on the surface of laminates when ultrasonic immersion method was used. This effect can be clearly observed on photograph 25. Since etching of resins was observed on graphite/cyanate ester 954-3 laminates, this indicates that the reason no etching was detected on cyanate ester 954-3 neat resins was an indication that the immersion etching was uniform. Ultrasonic immersion etching experiments shows that ultrasonic immersion etching can roughen the resin systems in laminates.

5.3.3 Spray Etching of All Laminates

Since spray etching is an alternative way to result in anisotropic etching, it was also used to etch all laminates. Because ultrasonic immersion etching of graphite/epoxy laminates showed that there were few topographical changes when etching was performed at KMnO_4 concentration of 20g/l when etching time was between 2 and 4 minutes, KMnO_4 concentration was kept at 40 g/l for all spray etching experiments. Etching time was varied so that the effect of etching time on surface topography could be obtained. The testing matrix for spray etching experiments is shown in Table 7. The etching times investigated were: 2 minutes and 4 minutes for graphite/epoxy 934 laminates, 4 minutes and 6 minutes for graphite/cyanate ester laminates. The ranges for the etching time were determined based on topography results of ultrasonic immersion etching as shown in photographs 19 to 28.

Table 7. Spray etching of graphite/epoxy 934, graphite/cyanate ester 954-2A (toughened) and graphite/cyanate ester 954-3 laminates.

Temperature: 65°C NaOH: 40g/l KMnO₄: 40 g/l

Laminate	Time (min.)	
934	2	4
954-2A	4	6
954-3	4	6

5.3.3.1 Effect of Etching Time on Spray Etching of All Laminates

Photographs 29 to 34 present the effect of etching time on surface topography of laminates etched by spray method. Photographs 29 and 30 show that small pores were scattered on the graphite/epoxy 934 laminates when etching time was increased from 2 to 4 minutes. Fibers were partially exposed under the etching condition. Photographs 31 and 32 present the topography results of graphite/cyanate ester 954-2A laminates spray etched at 2 and 4 minutes, respectively. The effect of etching time was difficult to investigate because a smooth surface was observed in both photographs 31 and 32. This phenomenon will be discussed in section 5.3.4. Photograph 33 shows that when etching was performed at 4 minutes, the surface of graphite/cyanate ester 954-3 laminates was micro-roughened. When etching time was increased from 4 minutes to 6 minutes, large pores were generated on the laminate surface as shown in photograph 34. Photographs 29, 30, 33 and 34 indicate that pits were formed when etching time was increased.

Photograph 29. Graphite/epoxy 934 laminate spray etched
@ KMnO_4 40 g/l, temperature 65°C for
2 minutes (500x).

Photograph 30. Graphite/epoxy 934 laminate spray etched
@ KMnO_4 40 g/l, temperature 65°C
for 4 minutes (500x).

Photograph 31. Graphite/cyanate ester 954-2A (toughened) laminate spray etched @ KMnO_4 40 g/l, temperature 65°C for 4 minutes (500x).

Photograph 32. Graphite/cyanate ester 954-2A (toughened) laminate spray etched @ KMnO_4 40 g/l, temperature 65°C for 6 minutes (500x).

Photograph 33. Graphite/cyanate ester 954-3 laminate spray etched @ KMnO_4 40 g/l, temperature 65°C for 4 minutes (500x).

Photograph 34. Graphite/cyanate ester 954-3 laminate spray etched @ KMnO_4 40 g/l, temperature 65°C for 6 minutes (500x).

5.3.3.2 Conclusions of Spray Etching of All Laminates

Spray etching showed that a KMnO_4 concentration of 40g/l was appropriate since only partial fibers were exposed under the etching condition. The etching time had different effects on the surface topography of graphite/epoxy 934 and graphite/cyanate ester laminates. Under the same etching conditions, the pores were scattered on the surface of graphite/epoxy 934 laminates as shown in photograph 30, while the pores were crowded along fibers on the surface of graphite/cyanate ester 954-3 laminates as shown in photograph 33. Spray etching experiments show that spray etching can roughen the resin systems in laminates.

5.3.4 Conclusions and Discussions of Laminate Etching Experiments

Etching of laminates showed that etching depends not only on permanganate concentration and etching time, but also on the kind of laminates used. For example, photographs 22, 23 and 26 present the topography of three different laminates etched by ultrasonic immersion method. Under the same etching conditions, a few pores were formed on graphite/epoxy 934 laminates as shown in photograph 22, many pores were generated along fibers on graphite/cyanate ester 954-2A laminates as shown in photograph 23, and fibers were completely exposed on graphite/cyanate ester 954-3 laminates as shown in photograph 26. This indicates that the order of etching rate for ultrasonic immersion etching is: graphite/cyanate ester 954-3 laminates > graphite/cyanate ester 954-2A laminates > graphite/epoxy 934 laminates.

Photographs 18, 20 & 30 are topography results for graphite/epoxy 934 laminates etched by three different etching methods: immersion, ultrasonic immersion and spray under the same etching conditions. Photograph 18 shows that few pores were generated on the resin system in laminates by the immersion etching method. Photograph 20 shows that relatively large pores were generated on the resin systems when the ultrasonic immersion etching method was used. Photograph 30 indicates that small pores were scattered on the resin surface when spray etching was applied. Photographs 18, 20 & 30 indicate that immersion etching resulted in relatively uniform surfaces compared with ultrasonic immersion and spray etching. Few pits could be observed on the etched surfaces by this method. Ultrasonic immersion and spray etching were two methods to improve surface roughness of laminates. Photographs 19 to 28 show that pits were formed on laminates etched by the ultrasonic immersion method. Ultrasonic wave is high-energy sound, which weakens the chemical bonds of the substrate to enhance the effects of chemical etching (Ohwada *et al.*, 1995). Photographs 29 and 34 show that some pits were formed on the surface of laminates when the spray etching method was used. Spray etching is used in the PCB industry to generate anisotropic etching effects (Kao *et al.*, 1992) because the etchant is sprayed onto the substrate in the direction perpendicular to the laminate surface with high speed to increase the etching rate in the vertical direction. Anisotropic etching means that the etching rate is not the same in all directions. Compared with immersion etching, spray etching generates etching in both horizontal and vertical directions and the etching rates for these two directions are comparable. This is the reason why pits were formed on the laminate surface when spray

etching was used, while uniform etching was observed when immersion etching was applied. However, some smooth surfaces were observed on graphite/cyanate ester 954-2A laminates when the spray etching method was performed in this study as shown in photographs 31 and 32. It was difficult to investigate this phenomenon because the nozzle used for spray etching produced a stream of etchant rather than a fine mist. A stream only attacked part of the laminate surface and left the rest of the surface unetched, while mist can cover the entire sample surface to provide a relatively uniform pore distribution on the laminate surface. The smooth surface observed on graphite/cyanate ester 954-2A laminates is very likely the surface which was not attacked by the stream during the spray etching.

5.4 Plating

A standard graphite/epoxy 934 laminate which had been successfully etched and plated with electroless copper at Space Systems/Loral was used to verify the plating line at San Jose State University. This standard was stripped and replated at San Jose State University successfully. The successful plating of this sample verified that the plating line at SJSU is operating properly.

Based on the surface topography of the etched laminates presented in section 5.3, electroless copper plating was performed on laminates etched under selected etching conditions as shown in Table 8, 9 and 10.

Table 8. Plating results for graphite/epoxy 934 laminates.

Etching Method & Laminate	Etching Conditions T=65°C NaOH=40g/l		Adhesion			
			Electroless Copper Deposition Time (min.)			
			1		15	
			Tape Test		Tape Test	
	KMnO ₄ (g/l)	Time (min.)	No. 1	No. 2	No. 1	No. 2
934 (B*)	N/A		4	5	no adhesion	
934 (I*)	20	2	3	1	0	0
	20	4	2	5	0	0
	40	2	1	3	0	0
	40	4	2	3	0	0
934 (U*)	20	2	3	5	0	0
	20	4	5	5	0	0
	40	1	3	1	0	0
	40	2	5	4	0	0
934 (S*)	40	2	4	4	0	0
	40	4	5	5	0	1

*Notes:

B: unetched ("Blank")

I: immersion etching

U: ultrasonic immersion etching

S: spray etching

Table 9. Plating results for graphite/cyanate ester 954-2A laminates.

Etching Method & Laminate	Etching Conditions T=65°C NaOH=40g/l		Adhesion			
			Electroless Copper Deposition Time (min.)			
			1		15	
			Tape Test		Tape Test	
	KMnO ₄ (g/l)	Time (min.)	No.1	No.2	No.1	No.2
954-2A (B*)	N/A		3	2	no adhesion	
954-2A (I*)	40	2	5	5	0	0
	40	4	5	5	0	0
	40	6	5	5	0	0
954-2A (U*)	40	4	5	5	0	0
	40	6	5	5	1	0
	40	9	5	5	0	0
954-2A (S*)	40	4	5	5	0	0
	40	6	5	5	0	0

*Notes:

B: unetched ("Blank")

I: immersion etching

U: ultrasonic immersion etching

S: spray etching

Table 10. Plating results for graphite/cyanate ester 954-3 laminates.

Etching Method & Laminate	Etching Conditions T=65°C NaOH=40g/l		Adhesion			
			Electroless Copper Deposition Time (min.)			
			1		15	
			Tape Test		Tape Test	
	KMnO ₄ (g/l)	Time (min.)	No.1	No.2	No.1	No.2
954-3 (B*)	N/A		5	5	no adhesion	
954-3 (I*)	40	2	5	5	1	2
	40	4	5	5	1	0
	40	6	5	5	1	1
954-3 (U*)	40	2	5	5	3	2
	40	4	5	5	0	0
	40	6	5	5	0	0
954-3 (S*)	40	4	5	5	3	3
	40	6	5	5	1	3

*Notes:

B: unetched ("Blank")

I: immersion etching

U: ultrasonic immersion etching

S: spray etching

5.4.1 Effect of Plating Time on Adhesion Strength of Copper

Blank samples were plated in the electroless copper deposition bath for 15 minutes and 1 minute, respectively. Photograph 35 shows the topography of the plated blank graphite/cyanate ester 954-3 laminate when the deposition time was kept at 15 minutes. Photograph 35 shows that numerous blisters were formed on the plated graphite/cyanate ester 954-3 laminate surface and there was no adhesion between the copper deposits and the blank graphite/cyanate ester 954-3 laminate. Similar topography results were obtained for the plated blank graphite/epoxy 934 and graphite/cyanate ester 954-2A laminates when the deposition time was kept at 15 minutes. The adhesion data for plated blank laminates illustrated in Table 8, 9 and 10 showed that there was no adhesion between copper deposits and all unetched laminates.

At electroless copper deposition time of 15 minutes, tape test results shown in Table 8 and 9 indicate that the adhesion strength of copper was zero for graphite/epoxy and graphite/cynante ester 954-2A laminates. Among all the adhesion results for electroless copper deposition time at 15 minutes, the highest adhesion strength of copper was achieved on graphite/cyanate ester 954-3 laminates. The adhesion strength of copper for this plated sample was tape test classification 3 as shown in Table 10 and the corresponding topography of the etched surface was shown in photograph 25. All the etched laminates plated in the electroless copper deposition bath for 15 minutes could not achieve the highest (strongest adhesion) tape test result. This indicates that the adhesion strength of copper was very weak. Also, numerous small blisters could be seen on the

Photograph 35. Unetched graphite/cyanate ester 954-3 laminate (500x).

plated surfaces. Photograph 36 shows that blisters were formed on the plated graphite/cyanate ester 954-3 laminates when the deposition time was 15 minutes.

Photographs 37 and 38 show that no blisters were observed on the plated graphite/cyanate ester 954-3 laminates when the deposition time was 1 minute. Similar topography was observed on the plated laminates including blank samples. When the electroless deposition time was reduced from 15 minutes to 1 minute, no blisters were observed on the surface of laminates and the adhesion strength of copper was improved. Some of the laminates plated for 1 minute passed the tape test as shown in Table 8, 9 and 10.

Based on the adhesion data for electroless copper deposition time of 1 and 15 minutes as shown in Table 8, 9 and 10, a common trend could be obtained. The adhesion strength of copper increased when plating time was decreased. The differences between the adhesion strength of copper plated for 1 minute and 15 minutes could be explained by insufficient surface roughness and thickness of film. Photograph 25 presents the surface of the graphite/cyanate ester 954-3 laminate etched by ultrasonic immersion method. This surface topography corresponds to the highest adhesion strength of copper (tape test classification of 3) in this thesis study. Photograph 25 shows that pits generated by ultrasonic immersion etching are crowded along fibers, and these pits are isolated from fiber to fiber. This kind of surface topography may not be optimum for copper deposition because pores are not uniformly distributed on the resin surface. The copper film on top

Photograph 36. Graphite/cyanate ester 954-3 laminate ultrasonic immersion etched @ KMnO_4 40 g/l, temperature 65°C for 2 minutes; plated for 15 minutes (400x).

Photograph 37. Graphite/cyanate ester 954-3 laminate
ultrasonic immersion etched @ KMnO_4
40g/l, temperature 65°C for 2 minutes;
plated for 1 minute (400x).

Photograph 38. Graphite/cyanate ester 954-3 laminate
ultrasonic immersion etched @ KMnO_4
40 g/l, temperature 65°C , for 2 minutes;
plated for 1 minute (50x).

of the pore rich area is strong while the copper film on top of the smooth resin surface is weak. The theory of pore size and pore size distribution (Poa, Wan and Wu, 1977) could help explain why poor plating was happened on the topography shown in photograph 25. Abuelazaim (1994) found out that pore size and pore distribution affected the adhesion strength between copper deposits and ABS plastics. When the surface shown in photograph 25 was plated for 1 minute, blisters were not formed because the plating time was too short to form blisters. When the electroless deposition time was increased, the deposited film became thicker. As a result, the internal stress within the copper layer increased. Since the surface was not well micro-roughened, the plated copper film could not withstand the internal stress and blisters were formed as a result of this stress.

5.4.2 Conclusions of Plating

Photograph 35 shows that copper could not be deposited on unetched laminates when these laminates were plated in the electroless copper deposition bath for 15 minutes. After etching, copper films could be deposited on the laminates although some blisters were formed on the plated surfaces as shown in photograph 36. Photographs 35 and 36 show that etching is an effective way to enhance the adhesion of copper to the laminates. Surface roughness (Villamizar, Rojas and Frias, 1981) and formation of chemical bonds (Ho, 1989) were considered two main factors affecting plating. For the same substrate, chemical bonding of the substrate to copper could be considered the same. Increase the surface roughness of graphite/cyanate ester 954-3 laminates etched by either ultrasonic immersion or spray method could improve adhesion strength of copper.

This is evidence to prove that mechanical interlocking plays an important role in plating.

The best adhesion strength of copper achieved in this study was on graphite/cyanate ester 954-3 laminates etched by either ultrasonic immersion or the spray method. Although the adhesion of copper to graphite/cyanate ester 954-3 laminates was stronger than that to graphite/epoxy 934 and graphite/cyanate ester 954-2A laminates as shown in Table 8, 9 and 10, the adhesion strength of copper on graphite/cyanate ester 954-3 laminates was still very weak. The tape test classification 3 was achieved on graphite/cyanate ester 954-3 laminates when copper deposition time was 15 minutes. Ultrasonic immersion and spray etching could slightly improve the adhesion strength of copper on graphite/cyanate ester 954-3 laminates from tape test classification 1 for immersion etching to tape test classification 3 for ultrasonic immersion and spray etching when the electroless copper deposition time was kept at 15 minutes.

The thickness of copper film plated in the electroless copper deposition bath for 1 and 15 minutes was about 10 μ -inches and 20 μ -inches, respectively. The desired thickness of copper was between 100 and 200 μ -inches. This desired value could not be achieved because blisters were already formed on the laminated surfaces plated in the electroless deposition bath for 15 minutes as shown in photograph 36.

6.0 OVERALL CONCLUSIONS

Immersion etching showed that temperature was not a major factor to affect surface topography of neat resins in the temperature range between 65°C and 85°C. Potassium permanganate concentration and etching time were the two main factors in etching. Since the thickness of the resin layer on the top of laminates used in this study is only about 80 micro-inches, the optimum permanganate concentration for etching was between 20 and 40 g/l, and the optimum etching time was between 1 to 9 minutes. Etching performed at KMnO_4 concentration of 60g/l had dramatic destruction on the laminate surface because fibers were completely exposed. Over exposure of fibers are not favorable because fibers have poor flatwise tensile strength.

Immersion, ultrasonic immersion and spray etching methods resulted in different surface topography. Immersion etching generated relatively uniform surfaces and few pits were formed on the surface of laminates. Ultrasonic and spray etching were two methods to result in anisotropic etching. Pits were formed on laminated surfaces etched by these two methods. The effects of spray etching were difficult to be investigated because the nozzle of the spray etching system was not the optimum choice.

Graphite/epoxy 934, graphite/cyanate ester 954-2A and 954-3 laminates could not be plated with electroless copper to the desired thickness of 100 to 200 μm . All laminates plated for 15 minutes could not pass the tape test. Laminates plated in

electroless copper deposition bath for 1 minute had better adhesion strength of copper than laminates plated for 15 minutes. Poor plating could be explained by insufficient surface roughness.

The highest adhesion strength of copper was achieved on graphite/cyanate ester 954-3 laminate. This substrate was etched by either ultrasonic immersion or the spray method. Ultrasonic immersion and spray etching had similar effects on plating.

7.0 FUTURE WORK

This study shows that surface preparation is the key factor for good plating. Two directions are recommended for future surface preparation: one related to surface preparation and the other related to plating. In the surface preparation part, three areas of study may be conducted to improve the surface topography of laminates. First, investigate NaOH concentration effects on etching since sodium hydroxide concentration was kept as a constant for this study. Carano (1994) showed that manganate build-up was increased with the increase of NaOH concentration. Build-up of manganate will directly affect the etching capability of KMnO_4 . Second, investigate spray etching by using a correct nozzle for the spray etching system so that the etchant can be sprayed onto the substrate instead of poured onto the substrate. Third, try other etching agents such as sodium methoxide and study their effects on surface topography of laminates. Granger and Miller (1996) proposed to use alkali metal salts of an alkoxide to etch graphite/cyanate ester 954-3 laminates.

Plating could be improved in the following two aspects. First, investigate the effects of dipping time in catalyst and acceleration baths on plating. McNeil and Gurly (1992) found that the dipping time in catalyst and acceleration baths effected the adhesion between copper and ABS plastics. No attempt was made to optimize the plating process in this study. Second, using an alternative plating chemistry may result in improved plating. Catalyst from other companies may have better wettability for the

laminates used in this study. Uniform catalyst film could also initiate uniform copper deposition.

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Appendix A: Tape Test

Tape test is a qualitative method to test the adhesion strength of metal films. The test kit used for this thesis study is GARDCO Paint Adhesion Test Kit. It consists of a cross cut tester used to prepare standard grids on the tested surface, a roll tape to test the adhesion and other accessories such as a scrub brush. Figure 1 (Appendix A) shows this test kit.

Figure 1 (Appendix A). GARDCO Paint Adhesion Test Kit.

The testing procedure includes three steps. First, cut grids on the tested surface as shown in Figure 2 (Appendix A) by using a cross cut tester. Second, put a piece of tape onto the grids and then pull away the tape. Third, classify the substrate according to Figure 2 (Appendix A). Tape test classification 5 indicates that the adhesion is at least 200 psi. Tape test classification 0 indicates that there is no adhesion strength for the deposited film.

Surface of cross-cut area from which flaking has occurred. (Example for six parallel cuts)	NONE					GREATER THAN 65%
CLASSIFICATION	5	4	3	2	1	0

Figure 2 (Appendix A). Tape test classification.

IMAGE EVALUATION TEST TARGET (QA-3)

APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989

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