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# Effect of surface preparation on adhesion of copper to carbon fiber laminates

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# EFFECT OF SURFACE PREPARATION ON

# ADHESION OF COPPER TO CARBON FIBER

# LAMINATES

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment of the Requirements for the Degree

Master of Science

By

Jaspal S. Sohal

December 1999

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# ABSTRACT

## EFFECT OF SURFACE PREPARATION ON ADHESION OF COPPER TO CARBON FIBER LAMINATES
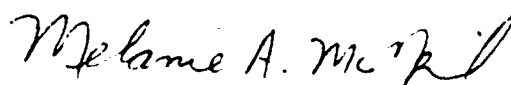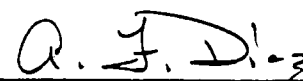
By Jaspal S. Sohal

This thesis addresses the effect of etchant concentration and etching time on the surface topography and subsequent adhesion of copper to the carbon fiber laminate. Two permanganate salt solutions were used in this study: sodium permanganate and potassium permanganate. After etching with one of the salt solutions, all samples were electrolessly plated with copper metal. Surface topography was characterized by electron microscope. The plated samples were then subjected to stud pull testing that resulted in adhesion strength recorded in Psi.

Results showed that potassium permanganate was an insufficient etchant due to its low solubility. Etching, using sodium permanganate, at lower concentrations and higher etching times resulted in the highest adhesion strength. Variation of etchant concentration had a more rapid effect on the surface topography than variation of etching time. Etching at 300 g/L for 10 minutes resulted in the best adhesion strength (1251 Psi) and standard deviation (143 Psi).

# Acknowledgments

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# 1 INTRODUCTION

## 1.1 Project Introduction

Over the past decade, the aerospace and electronic industries have shown a high interest in metal plated non-conductive laminates. Significant work has been done in developing a process that improves the adhesion strength between a copper film and a non-conductive laminate surface. Literature reports that one of the keys to improving the adhesion strength is the surface preparation. This study focuses on investigating the effect of etchant concentration and sample immersion time on the adhesion of an electrolessly deposited copper layer onto a carbon fiber laminate. An overview of various surface preparation techniques will be discussed in this section. Chapter 2 reviews the past work and literature that supports this study. In Chapter 3, the research hypothesis, justification for the investigation, and the major objectives of the study is stated. The experimental procedures detailing the surface preparation and electroless plating processes and all materials used in this investigation will be discussed in Chapter 4. Results and data analysis will be presented in Chapter 5 followed by a discussion of the results in Chapter 6. The conclusion and recommendations for new research will be discussed in Chapter 7 and 8 respectively.

## 1.2 Project Overview

Due to advances in composite materials manufacturing electronic and aerospace applications are utilizing carbon fiber laminates. For example, in the aerospace industry metal waveguides are being replaced by composite metal-plated waveguides. These metal plated waveguides can perform and carry electrical signals similarly to their metal counterparts. One advantage of using metal plated composites over conventional metal parts is the reduction in mass. The cost of launching and manufacturing a satellite is directly proportional to the product's mass.

This investigation was sponsored by Space Systems Loral. The ultimate goal would be to use this study in the design of a full-scale metal deposition process. Keeping in mind the end goal of this study and the application, Space Systems Loral required a process that is independent of geometry. After undergoing the proper surface treatment, the composites were electrolessly plated with a copper metal film.

The key step in this investigation was to achieve the proper surface to successfully deposit an electroless copper film onto the composite surface. Space Systems Loral set a defined guideline for sufficient adhesion strength at approximately 900- 1000 Psi (pounds per square inch). The material being studied in this investigation was a cyanate ester resin carbon fiber laminate system. Due to product sizes ranging from 3 inches to over 6 feet the electroless plating process was used instead of the more conventional electrolytic process. This study was performed on sample coupons of the carbon laminate.

## 1.3   Surface Preparation

The surface preparation of non-conductive material is extremely critical to successful

adhesion between a copper film and the substrate surface (Xu, 1998). Many carbon fiber

laminates similar to the one used in this study have surfaces that are prohibitive to metal

deposition. These laminate surfaces lack the binding or anchoring sites necessary to

achieve the proper bond strength to attach the metal film to the non-conductive surface

(Xu, 1998). Achieving sufficient adhesion between the laminate surface and the metal

film requires a treatment that produces these surface-binding sites. The surface treatment

is commonly referred to as "micro roughening". Several techniques have been utilized

for effective micro roughening of the smooth laminates. These processes produce the

necessary binding sites for sufficient metal to surface adhesion. The binding sites can be

either chemical bonds or mechanical interlocking bonds. Figure 1 shows an illustration

of mechanical interlocking bonds. Surface preparation or micro roughening can be

achieved by several etching techniques: plasma etching, acid etching and permanganate

etching.
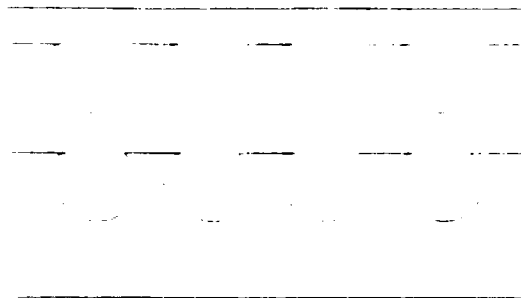
**Figure 1 Mechanical Interlocking after Micro Roughening.**

## 1.3.1 Dry Etching

Plasma etching, a dry etch process, utilizes a plasma cloud made up of dissociated positively and negatively charged particles as well as neutral particles to react with the smooth surfaces of the material (Campbell, 1996). The process occurs under vacuum and uses a RF-field to create the plasma cloud. It is pointed out by Campbell (1996) that plasma etch processes have to undergo six critical steps as seen in Figure 2. The versatility of the plasma process means it can be used for a full range of cleaning and etch tasks. For example, plasma etching is used in removing small amounts of contaminants in the final clean process and in more demanding areas such as desmear and etchback in the printed circuit boards industry (Campbell, 1996).

In their research on commercially available copolymers known as Teflon FEP, Inagaki et al. (1998) reported that plasma treatment causes both defluorination and oxidation of the FEP surface. The modification of the FEP surface by remote hydrogen plasma is effective in improving the adhesion to the copper layer (Inagaki et al., 1998). Prior to the metallization of the FEP surface, the surface of the FEP must be made hydrophilic in order to wet it with an electroless plating solution and for the palladium catalyst to attach to its surface (Inagaki et al., 1998)
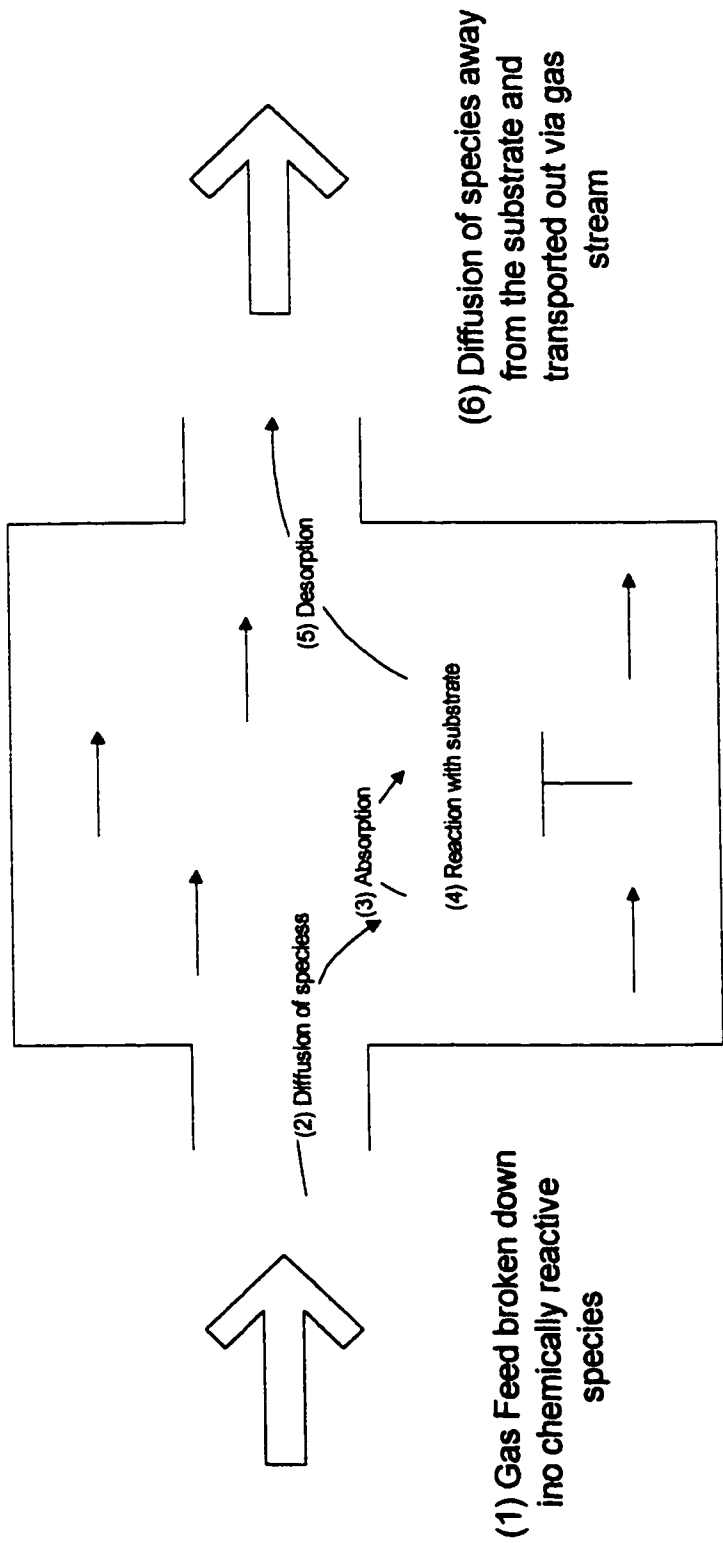
**Figure 2 Six Critical Steps in Plasma Etch Process**

(1) Gas Feed broken down ino chemically reactive species

(2) Diffusion of speciess

(3) Absorption

(4) Reaction with substrate

(5) Desorption

(6) Diffusion of species away from the substrate and transported out via gas stream

### 1.3.2 Wet Etch Processes

Wet etch processes, also known as chemical etching, use acidic or alkaline-based solution to vigorously attack the resin portion of the laminate substrate (Xu, 1998). A typical acid etch process utilizes sulfuric or chromic acid. A typical oxidizing etchant utilizes an alkaline permanganate solution (Deckert, 1995).

Murphy and Gurly (1971) used a chromic acid etch for the surface treatment of various plastics prior to plating. The surface of ABS plastics was micro-roughened using a chromic-sulfuric acid etchant. The results showed that acid etched away small microscopic butadiene spheres from the surface of the ABS surface leaving small holes that served as mechanical interlocking points to where the copper film can attach itself (Murphy and Gurly, 1971).

### 1.3.3 Alkaline Permanganate Etching Process Steps

Mandich and Krulik, Thorn and Walsh, and Deckert all agree that the immersion etching process using a permanganate etchant cannot be conducted in a single step process. Several pre-etch and post etch steps are necessary. Thorn and Walsh (1991) discussed a three-step surface preparation process detailing the mechanism of each step and the optimum parameters it involved. Thorn and Walsh proposed a desmear process utilizing three critical steps and discussed the chemistry involved at the surface of the

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laminates. The process shown in Table 1 involved the following major steps: conditioning, etching, and neutralizing. The conditioner diffused into the epoxy expanding the polymer network to increase the surface area. Mandich and Krulik (1992) pointed out that the choice of conditioner was important for optimum etching performance. This allowed the permanganate solution to penetrate the laminate structure and create the necessary topography for depositing the metal. The conditioner also worked to replace the polymer-polymer bonds with solvent –polymer bonds that lowered the laminate activation energy and increased the rate at which the permanganate etched the surface (Thorn and Walsh, 1991). In the etching step, the permanganate solution etched and cleaved the crossed linked sites and then broke down the monomer into soluble components that further degraded to $CO_2$ (Thorn and Walsh, 1991). Finally, the neutralizing step was used to reduce and remove the manganese oxide film that formed on the oxidizing epoxy surface in the etching step. This step was critical to the preparation process because the manganese film can cause void spots leading to unsuccessful plating and poor adhesion (Thorn and Walsh, 1991). The process used in this study also utilized these three major steps: conditioning, etching and neutralizing. However, a cleaning step prior to the conditioning step was added to remove any contaminants that had accrued on the sample. Heating plates were used to control the temperatures of each solution.

**Table 1 Process steps for an alkaline permanganate immersion etch process
proposed by Thorn and Walsh, (1991).**

| Step No. | Procedure | Temperature ( °F) | Time (minutes) |
|---|---|---|---|
| 1 | Epoxy Conditioning | 150 | 4-10 |
| 2 | DI Water Rinse | Room | 2 |
| 3 | Epoxy etching (alkaline permanganate solution) | 170 | 5-20 |
| 4 | DI Water Rinse | Room | 2 |
| 5 | Epoxy neutralizing | 150 | 4-10 |
| 6 | DI Water Rinse | Room | 2 |

## 1.4   Target Substrate

The target substrate is a carbon fiber polycyanate ester resin laminate as shown in

Figure 3. This new resin material is being employed in three major divisions of the space

technology industry, Satellite Structures, Airframe/Missile Structures and Electronic

Applications. The laminate has many features that make it highly attractive to these

various divisions. In satellite structures it provides low microcracking during

thermocycling, low moisture absorption, and low modulus loss after radiation exposure.

In the airframe/missile structures the carbon fiber laminate is best utilized for its superior

toughness and good hot/wet performance. Finally, for electrical applications, the laminate has a low volume change during cure. (YLA Report, 1990).

## 1.5   Project Goals

This project investigates the effect of sample immersion time and etchant concentration on the adhesion strength of electrolessly-plated copper film. The adhesion strength is obtained by a standard stud pull test and is used to quantify the surface preparation conditions for this process.
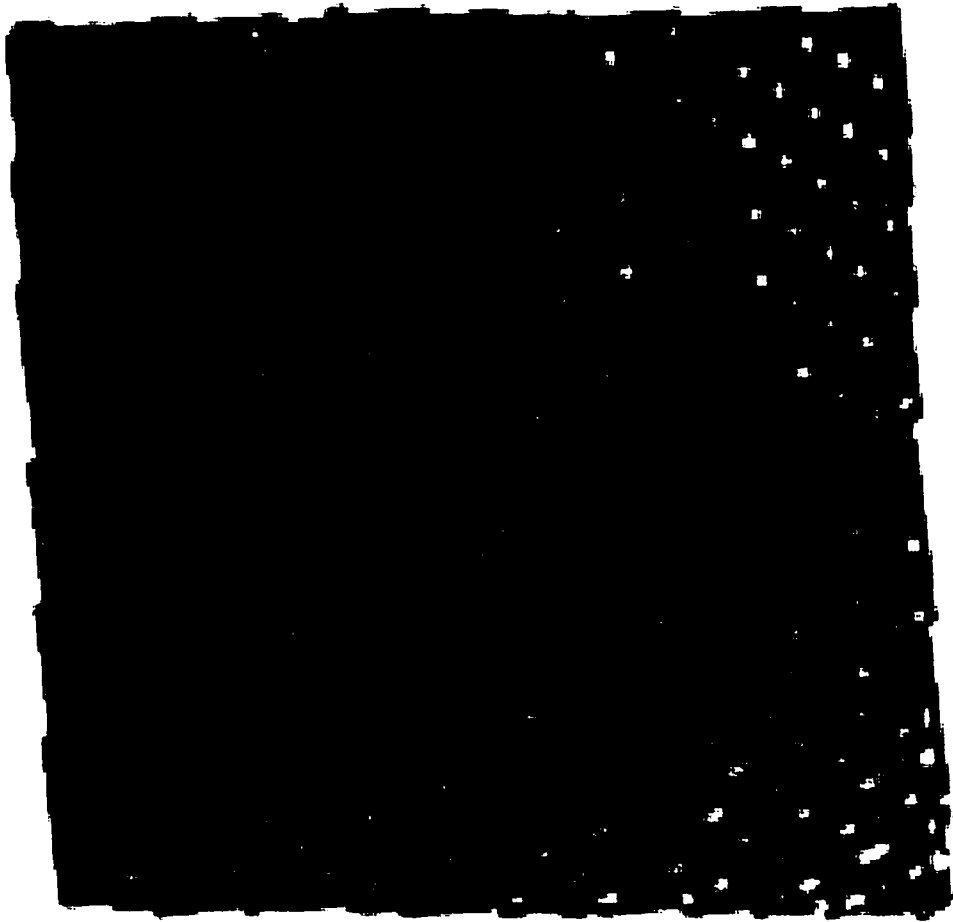
**Figure 3 Target Substrate**

# 2   LITERATURE REVIEW

## 2.1   Literature Review Introduction

A review of the literature showed that an increase in the demand for lightweight,

metal plated laminates has sparked much interest in many investigators (Kirmann et al.,

1998). This increase for materials, such as a carbon fiber laminate, has researchers

investigating new processes for surface preparation that will provide sufficient adhesion

strength between metal and a substrate surface. One of the key factors involved in

achieving sufficient adhesion during plating is the surface preparation (Thorn and Walsh,

1991). This literature review focuses on the effect of varying two process parameters in

an alkaline permanganate etching system: etching time and etchant concentration.

## 2.2   The Effect of Alkaline Permanganate Etching Time on Various Substrates.

Through their research with glass and carbon fiber-reinforced epoxy composites,

Kirmann et al. (1998) concluded that the adhesion of the copper film and the mean peak-

to-valley height increased as the etching time was increased. It can be seen from Figure 4

that for greater etching times higher peel strength was obtained for both substrates.

However, for a given time the metal adhesion was always higher for carbon-reinforced

epoxy composites than for glass epoxy composites due their differences in surface texture

after etching (Kirmann et al. 1998). Kirmann et al. (1998) explain that the distribution of

peaks and valleys was linked to the adhesion strength with valleys being more preferential to etching. Carbon-reinforced epoxy composites had more valleys than peaks after etching than did glass epoxy composites (Kirmann et al., 1998). Figure 5 shows the mean peak to valley in 3D form to emphasize that a certain roughness is required for plating. Xu (1998) showed for epoxy neat resins and cyanate ester neat resins that the etching time effected the topography. Xu concluded that as the etching time was increased from 4 minutes to 12 minutes the surface roughness of epoxy neat resins decreased while the surface roughness for cyanate ester neat resins increased. Figures 6 and 7 show two epoxy neat resins and two cyanate ester resins respectively etched at the same concentration but different etching times. Closely examining Figure 6, it is evident that the surface roughness decreased as the etching time was increased. There was more pitting seen in photo A of Figure 6 than in photo B. The exact opposite is seen in Figure 7 where more pitting is seen at the higher etching time than the lower one. Photo B of Figure 7 shows large areas where resin has been etched away completely. This is not the case in photo A of the same Figure. Xu explained that etching of epoxy neat resins was preferable in the horizontal direction, which was parallel to the resin surface, thus results showed a smoother surface. However, the cyanate ester resin system became more rough as the etching time was increased due to differences in etch rates of the thermal toughener and the cyanate ester resin. Both Xu and Kirmann et al. showed that etching time does effect the surface topography.
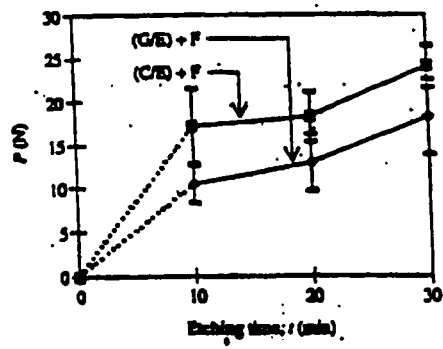
**Figure 4 Peel strength versus etching time (Kirmann et al., 1998).**
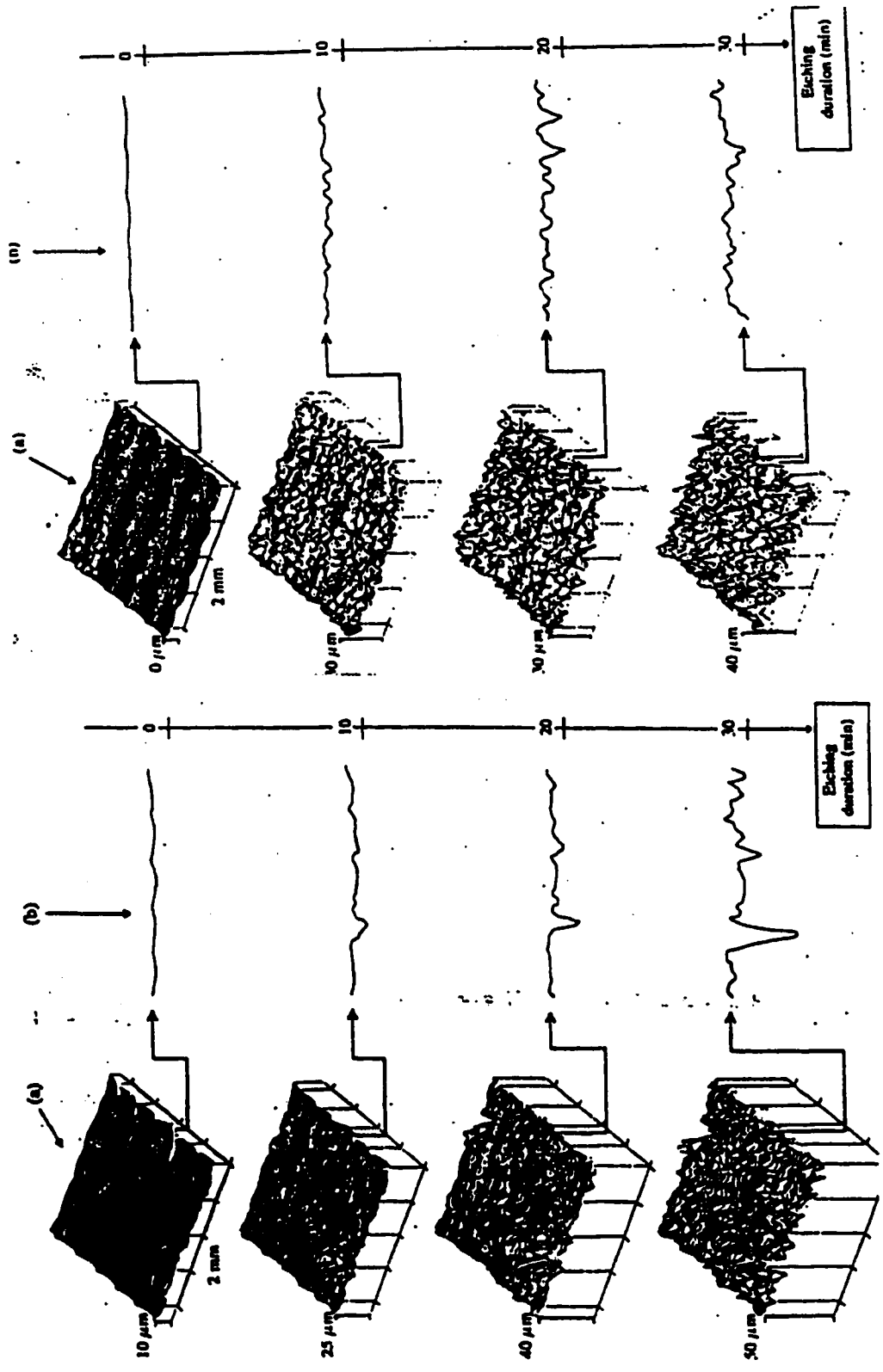
Figure 5 3D projection of surface roughness at various etching times (Kirmann et al., 1998).

Photo A

The surface seems to be rough at lower etching time. More visible pits.

Photo B
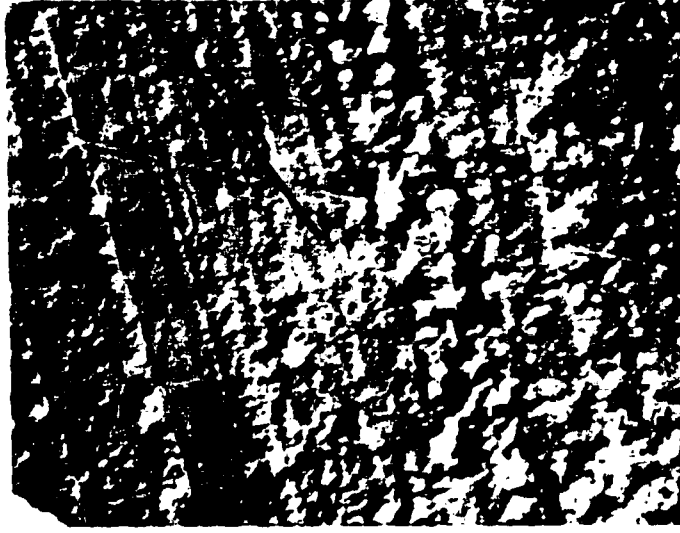
As the etching time was increased the surface roughness decreased.

**Figure 6 Epoxy neat resin system. Concentration was 90 g/L etching time of photo A was 4 minutes and photo B was 12 minutes (Xu, 1998).**

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Photo A

Photo B

The surface is more smooth at a lower etch time

The increased etching time has increased surface roughness resulting in bulk removal of resin.

Figure 7 Cyanate ester resin system concentration was 90 g/L etching time of photo A was 4 minutes and photo B was 12 minutes (Xu, 1998).

## 2.3 Effect of Alkaline Permanganate Concentration on Various Substrates.

Xu (1998) studied the effects of permanganate concentration on two types of substrates: neat resins and laminates. The etching temperature and etching time were kept constant at 85 °C and 12 minutes, respectively. For neat resins, epoxy and cyanate ester, two concentrations were studied: 60 g/L and 90 g/L. Xu concluded that for epoxy neat resins the surface became smoother with the increase in permanganate concentration. However, for cyanate ester neat resins the surface roughness increased. Figures 8 and 9 clearly show how increasing the etching concentration effects both resin systems differently. Again, this phenomena leads back to the etching orientation in epoxy neat resins and variation in etch rates between the thermal toughener and cyanate ester resin system. Figures 10 and 11 show the effect of permanganate concentration on graphite/epoxy laminates studied by Xu (1998). The samples studied by Xu possessed fibers that were bundled uni-directionally. Xu pointed out that as the concentration was increased from 20 g/L to 40 g/L the fibers were gradually beginning to become exposed. However, at a higher concentration of 60 g/L the fibers are completely exposed, meaning the substrate was over etched. Over exposure of fibers is not favorable because fibers have poor flatwise-tensile strength (Xu, 1998).

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Photo A

Photo B

For cyanate ester resin lower etching concentration results in smoother surface

At higher concentrations resin was completely etched at certain areas of the sample.

**Figure 8 Cyanate ester resin system. Etching time was 12 minutes and concentration of photo A was 60 g/L and concentration of photo B was 90 g/L (Xu, 1998).**

Photo A

Photo B

Resin system appears smooth as the etching concentration was increased

More surface roughness at a lower concentration

Figure 9 Epoxy neat resin system. Etching time was 12 minutes and concentration of photo A was 60 g/L and concentration of photo B was 90 g/L (Xu, 1998).

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Photo B

Slightly higher
etching
concentration
Uni-directional
fibers good
etching results.

Photo A
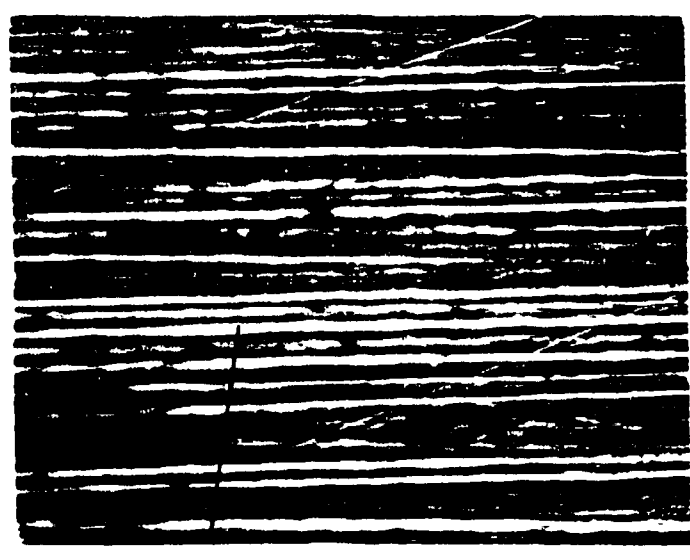
Uni-directional
fibers good
etching results.
Resin still
intact.

Figure 10 Graphite/epoxy laminate. Etching time was 2 minutes and concentration of photo A was 20 g/L and
concentration of photo B was 40 g/L (Xu, 1998).

20
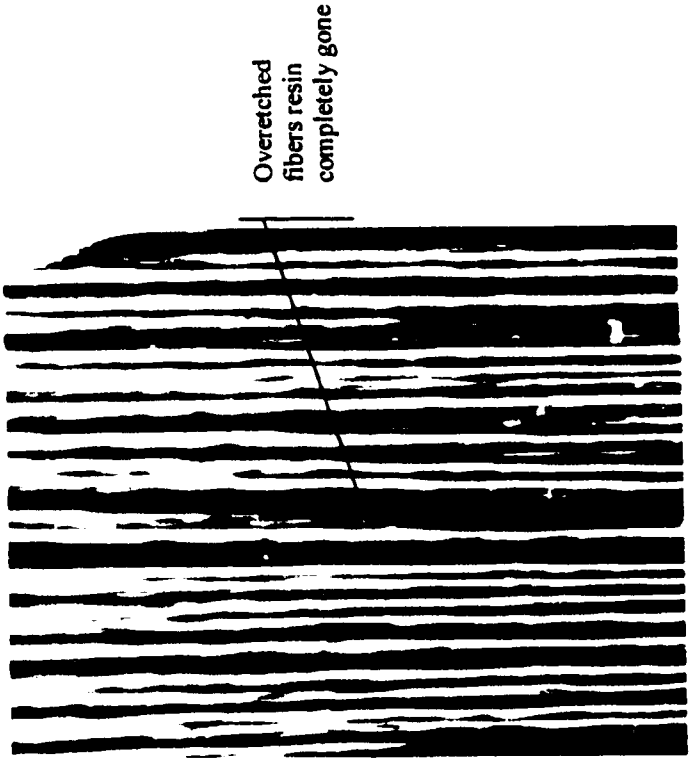
Overetched
fibers resin
completely gone

Figure 11 Graphite/epoxy laminate. Concentration was 60 g/L and etched for 2 minutes. This sample was over etched (Xu, 1998).

## 2.4 The Comparison of the Effect of Alkaline Permanganate on Various Substrates.

Many investigators have found similar results on how etching time and etchant concentration effect the surface topography and adhesion of copper film. For example, Mandich and Krulik, Kirmann et al., and Xu all have qualitatively studied various substrates under similar conditions. Their results showed that the effect was varied across substrates of different families as well as substrates from the same family. Mandich and Krulik, (1992) studied four different resin types: standard epoxy, Tetrafunctional epoxy, polyimide, and BT (Reaction of polymide and B-triazol). Mandich and Krulik showed how each resin type compared to an increase in etching time. Figure 12 shows a graph of Etchback (mil) plotted against the process time (minutes). Mandich and Krulik, (1992) concluded that different resins will etch variably in different permanganate etchback systems depending on their particular chemistries, which must be determined experimentally. Kirmann et al.'s, (1998) results for glass and carbon fiber-reinforced epoxy composites also show a variance in surface topography and metal film peel strength as shown previously in Figures 4 and 5. Xu's (1998) work on both neat resins and laminate clearly showed that from substrate to substrate permanganate etching had a diverse effect.
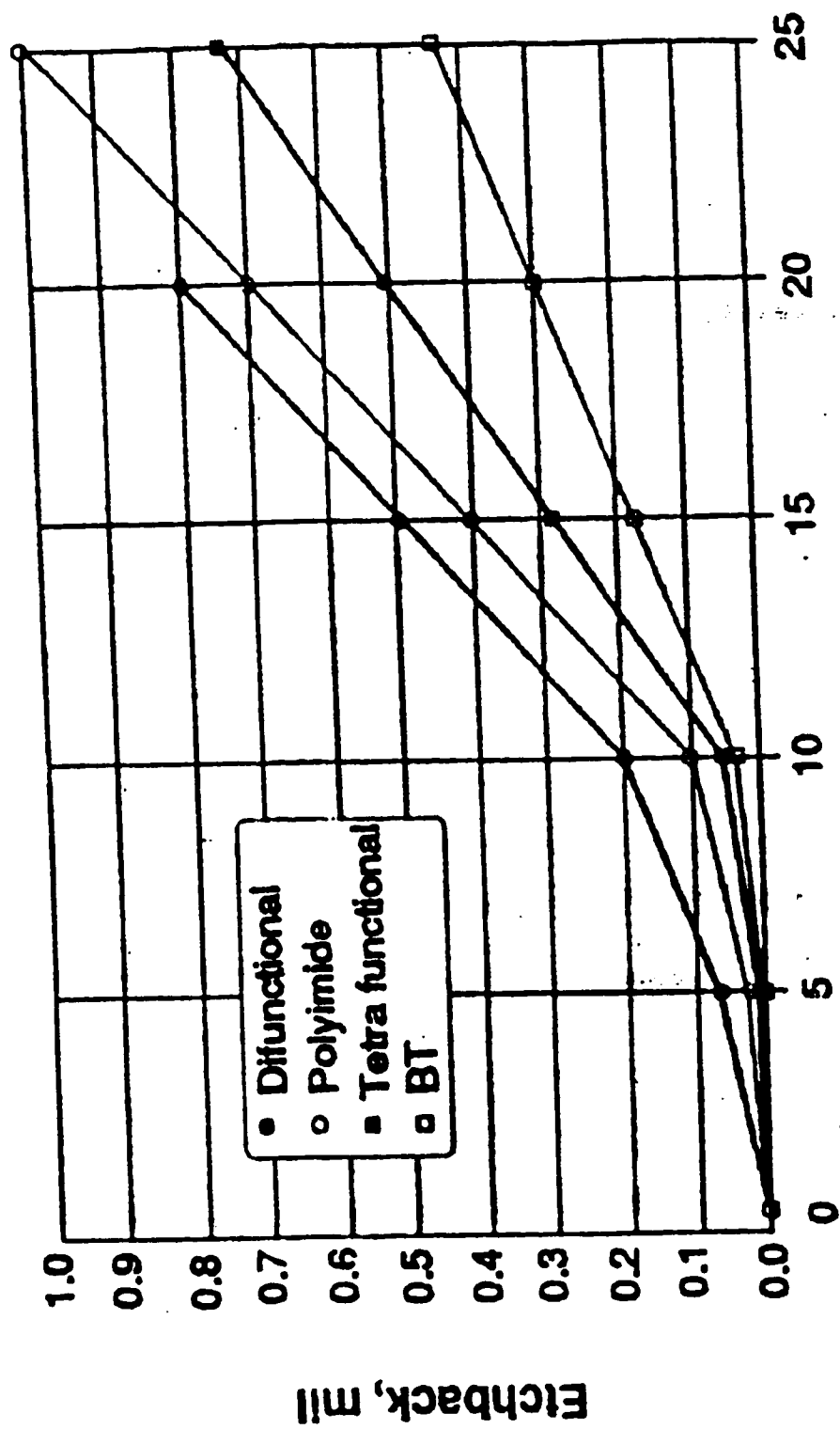
Figure 12 Etchback versus Process Time (Mandich and Krulik 1992).

## 2.5    Electroless Copper Plating

Xu (1998) looked at the plating line in more detail explaining some of the chemistry involved in plating. Step one, sensitization, the substrate was immersed in acid stannous chloride solution ($SnCl_2$). The step caused the hydrophobic substrate to become highly wettable. The activation step involved immersion of the sensitized substrate in an acid palladium chloride solution. This caused nucleation of palladium through a reaction between $Pd^{2+}$ and $Sn^{2+}$ as shown in Equation 1. The reaction produced a metallic alloy colloid of Pd and Sn surrounded by a stabilizing layer of $SnCl_2$ and $Sn(OH)_2$. Dispersion of finely divided Pd required 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 increased once a film of Cu was deposited and the copper deposition rate increased. 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 was achieved in an electroless copper plating bath. Copper sulfate ($CuSO_4$) was used as a copper source and formaldehyde (HCHO) was used as the reducing agent. Two major reactions that took 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 was deposited onto the substrate (Xu, 1998).

$$Pd^{2+} + Sn^{2+} \rightarrow Pd + Sn^{4+} \tag{1}$$

Anodic reaction:

$$HCHO + 2OH^- \xrightarrow{\text{catalytic surface}} HCOO^- + \frac{1}{2}H_2 + H_2 + H_2O + e \tag{2}$$

Cathodic reaction:

$$Cu^{2+} + 2e \xrightarrow{\text{Catalytic surface}} Cu \tag{3}$$
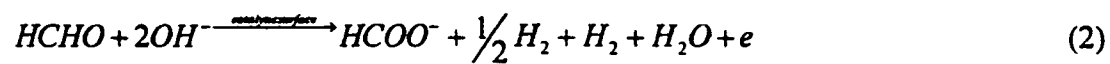
The overall reaction is written as:

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2 \tag{4}$$
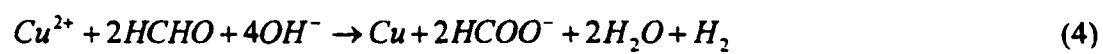
## 2.6 Summary of Literature Review

The literature review showed that the etchant concentration and etching time had an effect on the substrate topography. Xu and Kirmann et al. qualitatively illustrated these effects on various substrates indicating that each substrate reacts differently to any changes to the process. Xu's work with epoxy neat resins and cyanate ester resins provided the insight that etching time and etchant concentration are critical parameters in a process that modifies the substrate surface. Any variation of these parameters proved to effect the surface topography.

Xu also showed, through her work with uni-directional laminates, that at longer etching times the substrate becomes overetched making it unfavorable for any further process steps such as metal deposition.

Most literature found showed qualitative results on the effects of etching time and etchant concentration of the surface topography. Some investigators such as Xu, Mandich and Krulik and Kirmann et al. used a tape test to quantify their results. This test does not validate the actual adhesion strength of the metal film but rather gives an approximated value (0-5) related to the fraction of material lost when the tape is removed, where a 5 indicates an adhesion strength greater than 200 Psi and 0 indicating no adhesion.

# 3  RESEARCH HYPOTHESIS AND OBJECTIVES

## 3.1  Hypothesis

Alkaline permanganate concentration and sample immersion time are key factors that affect the surface etching of a cyanate ester laminate. Varying the permanganate concentration and immersion time will affect the amount of micro roughening of the substrate surface. The amount of micro roughening will affect the resultant adhesion strength between electrolessly-plated copper and carbon fiber laminate.

## 3.2  Justification

The aerospace industry requires lightweight material to reduce the cost of a satellite. The cost to launch a satellite is directly proportional to its mass. Currently, RF signals are transmitted and received by constructs made of copper and aluminum. Substituting a lightweight composite material plated with an electrically conductive metal film is a novel approach to reducing the mass of a satellite. In order to achieve the necessary electrical conductivity, a metal film is electrolessly deposited onto the laminate part.

Literature has shown that one of the keys to good adhesion between a metal film and a smooth laminate is the surface preparation. Investigators such as Xu (1998), Mandich and Krulik, (1992), Thorn and Walsh (1991) and Deckert, (1995) have all investigated

how surface preparation using an alkaline permanganate solution is favorable both economically and environmentally. Xu showed that etchant concentration and etching time varied the surface roughening, thus effecting the adhesion strength. Deckert states that immersion etching is an aggressive process used to remove debris and foreign matter from the substrate and etch the surface. All of the above investigators claim that surface preparation provides the proper anchoring sites allowing the metal to adhere to the composite surface. Most nonconductive material, similar to the one used in this study, possess smooth surfaces preventing the metal to adhere onto it. A surface roughening or "micro-roughening" technique is required to create the necessary bonding sites that ultimately lead to good metal to surface adhesion.

## 3.3  Objectives

The objective of this study is to investigate the effect of the etchant concentration and immersion time on the surface topography and adhesion strength between the copper film and the substrate. The adhesion strength of the copper film will be evaluated via a standard stud pull test. Additionally, scanned electronic micrographs (SEM) will be used to qualitatively characterize the substrate surface topography.

# 4  EXPERIMENTAL PROCEDURES

## 4.1  Experimental Apparatus

The experiments involved in this study were divided into two phases: the actual etching or micro-roughening of the samples and the electroless deposition of the copper film. The etching process shown in Figure 13 consisted of five 250-ml beakers that contained the appropriate solutions followed by a DI water rinse. This process was set up based on previous work done by Thorn and Walsh, Mandich and Krulik, Xu and Deckert.

The plating process shown in Figure 14 consisted of seven nine-gallon tanks containing the standard plating solutions. The plating was performed in a batch mode using one-liter trays.

## 4.2  Materials and Chemicals

The target substrate was a carbon fiber polycyanate ester resin laminate. All samples were approximately one square inch in size, and supplied by Space Systems Loral. Table 2 shows a list of chemicals, quantities and manufactures used in this study.
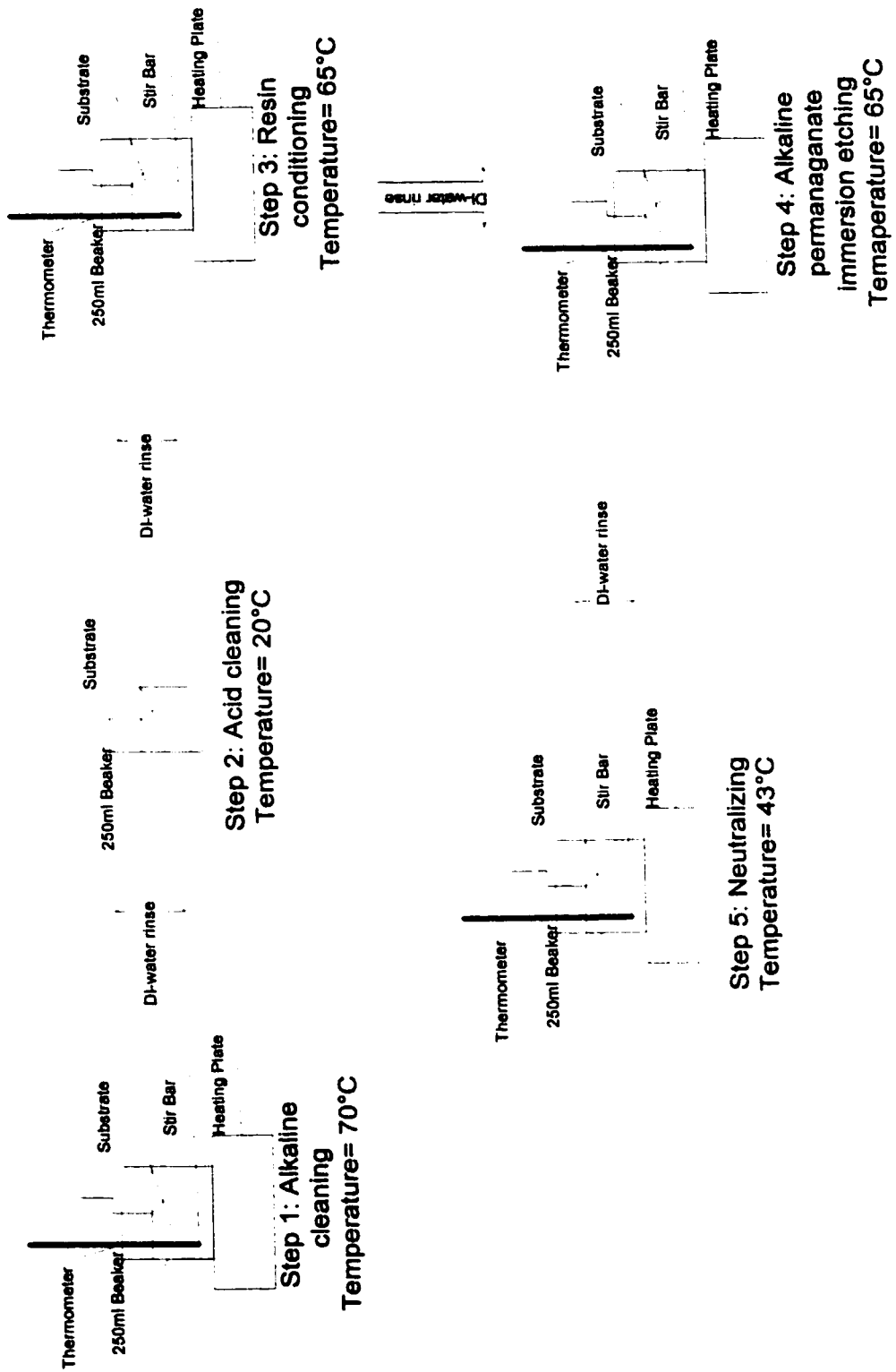
**Figure 13 Surface Preparation process for immersion etching in alkaline permanganate.**

Step 1: PD pre catalyst

Step 2: PD catalyst

Step 3: DI-Rinse

Step 4: Accelerator

Step 5: DI-Rinse

Step 6: Plating Sol.

Step 7: 3% $H_2SO_4$

Step 8: Oxyban Anti-oxident

Sample

9 Gallon Tank

1 Liter Tray
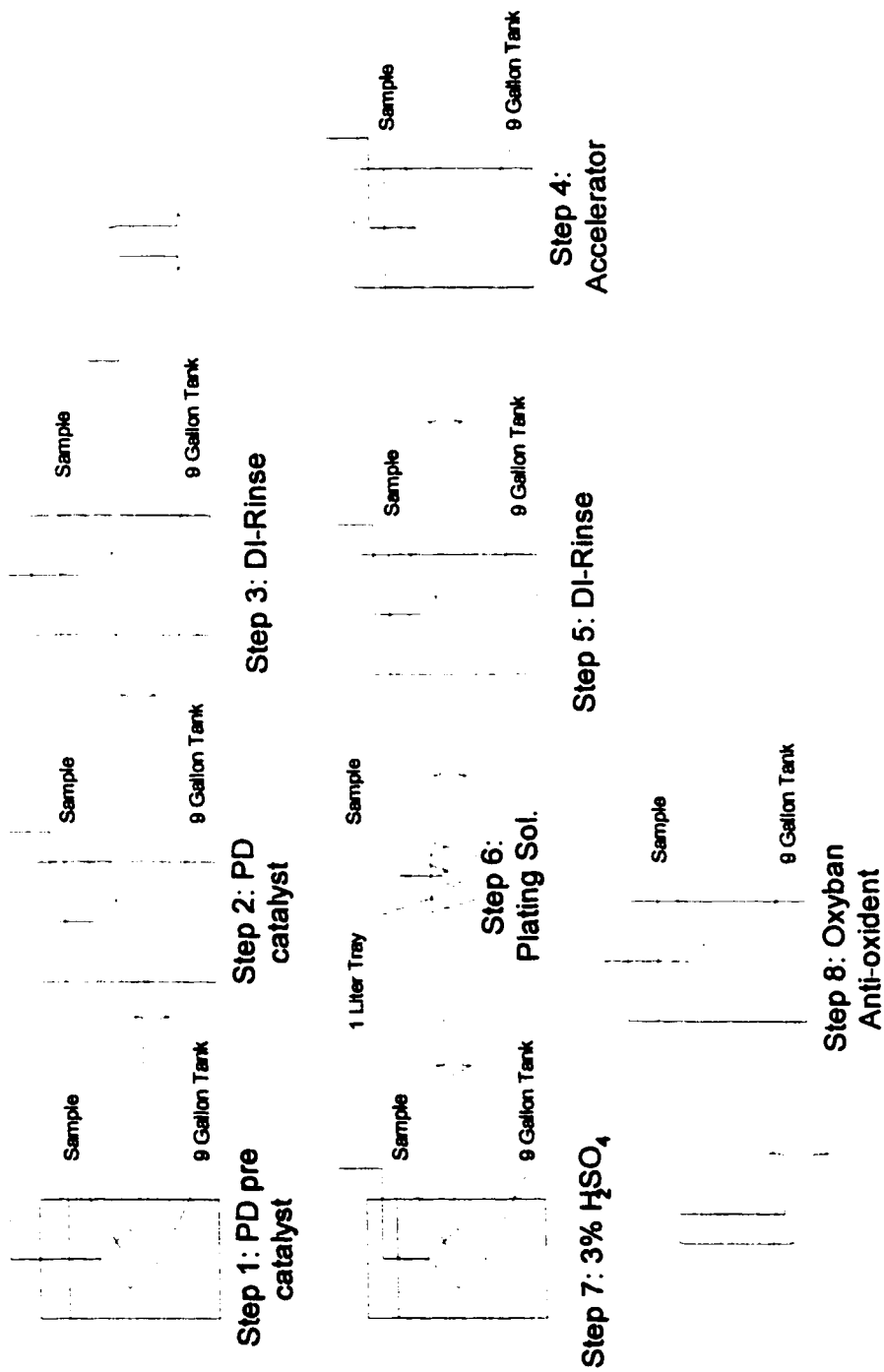
Figure 14 Electroless plating line.

**Table 2 List of chemicals used in this study.**

| Chemical Used | Concentration | Supplier |
| --- | --- | --- |
| Sodium hydroxide | 12 M | Generic |
| Sulfuric acid | Variable (3-10 % by vol.) | Generic |
| Alkaline permanganate | Variable (3-10 % by vol.) | Generic |
| n-methylprylidone | Concentrated | Electro-Chemicals |
| Neutralizer | Concentrated | Electro-Chemicals |
| Accelerator | Concentrated | AtoTek |
| Pre-dip | Concentrated | AtoTek |
| Activator | Concentrated | AtoTek |
| Anti-oxidant | Concentrated | AtoTek |
| Electroless plating solutions (MR-A and MR-B) | Concentrated | AtoTek |

## 4.3   Experimental Procedure for the surface preparation.

Since the electroless plating process was used solely as an indicator of the surface

preparation process, it was not varied in this study. The procedure for the surface

preparation is outlined in detail in Table 3. To account for repeatability and

reproducibility, samples were prepared in sets of three for each specific experimental run.

Samples were inscribed with a specific run number and corresponding letter (a, b, or c) to

distinguish each run. The pre-cleaning procedure as seen in Figure 13, involved dipping

the substrate into an acid and base wash to remove any residues or organic contaminants

left on the samples. First the samples were dipped into 12-M sodium hydroxide for two

minutes at 70 °C followed by a DI-water rinse. The samples were next immersed into an

acid wash consisting of 3 percent sulfuric acid at room temperature. After pre-cleaning

the samples were immersed in a conditioner, n-methylprylidone also known

commercially as E-prep 340 hole cleaner. The samples were immersed into the

conditioner with a concentration of 50 percent by volume for five minutes at a

temperature of 65 °C. This step was used to swell the resin making it more vulnerable to

attack by the alkaline permanganate solution. The samples were then introduced to the

alkaline permanganate solution where the micro-roughening and actual surface

preparation takes place. The final step of the surface preparation process was the

neutralization, which removed the manganese oxide formed during the etching step. This

involved using the E-prep Neutralizer at 43 °C for five minutes.

## 4.4 Experimental procedure for electroless deposition of copper metal.

The plating procedure is outlined in Table 4. Samples (a and b) of each run were

immersed in the neutralizer again for five minutes to further remove any manganese

oxide formed after etching. Afterwards, the two coupons were put through another

cleaning step to remove any contamination left after etching and over night storage.

After neutralizing and cleaning, the substrate was sent through the plating line detailed in

Figure 20 for metal deposition. The electroless plating process involved the following

steps: pre-cleaning of the substrate, wetting of substrate surface by $SnCl_2$, production of

metal colloid Pd/Sn, removal of Sn from Pd/Sn colloid, metal deposition, neutralization

in sulfuric acid, and finally immersion in anti-oxidant solution.

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**Table 3 Surface preparation process for alkaline permanganate immersion etching.**

| Step No. | Procedure | Function | Temperature ( C) | Time (minute) |
|---|---|---|---|---|
| 1 | Alkaline Clean (12M NaOH) | Get rid of organic contaminates | 70 | 3 |
| 2 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 3 | Acid Rinse (3% (volume) H$_2$SO$_4$ | Get rid of salts | 20 | 1 |
| 4 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 5 | Resin Conditioning using Eprep 340 Hole Cleaner | Swell the resin and make it more vulnerable for etchant attack | 65 | 5 |
| 6 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 7 | **Eprep Commercial solutions of NaMnO$_4$ + 40 g/L NaOH solution** | **Micro-roughen the surface of the carbon fiber laminate** | 65 | **Variable according to test matrix** |
| 8 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 9 | Neutralize (8% (volume) Eprep Neutralizer) + (8% (volume) H$_2$SO$_4$) | Remove manganese dioxide films formed on the etched surface | 43 | 5 |
| 10 | DI Water Rinse | Rinse between major steps | 20 | 2 |

**Table 4 Electroless plating process with initial cleaning steps.**

| Step No. | Procedure | Function | Temperature ( C) | Time (minute) |
|---|---|---|---|---|
| 1 | Neutralize (8% (volume) Eprep Neutralizer) + (8% (volume) H₂SO₄) | Remove manganese dioxide films formed on the etched surface | 43 | 5 |
| 2 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 3 | Alkaline Clean (12M NaOH) | Get rid of organic contaminates | 70 | 3 |
| 4 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 5 | Acid Rinse (3% (volume) H₂SO₄ | Get rid of salts | 20 | 1 |
| 6 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 7 | Pre-dip | Yield superior wetting of SnCl₂ on Hydrophobic substrates | 20 | 5 |
| 8 | Activation | Produce metallic colloid of Pd/Sn | 20 | 5 |
| 9 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 10 | Acceleration | Remove Sn from the Pd/Sn colloid to increase the initial rate of the copper deposition | 20 | 7 |
| 11 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 12 | Electroless copper deposition | Deposit copper onto substrate | 20 | 30 |
| 13 | 10% sulfuric acid neutralization | Neutralize the sample | 20 | 2 |
| 14 | Anti-oxidation (Oxyban) | Prevent copper oxidation | 20 | 2 |
| 15 | DI Water Rinse | Rinse between major steps | 20 | 2 |
| 16 | Air Dry | Dry Sample | 20 | 3 |

## 4.5 Experimental Plan and Test Matrix.

Two parameters were looked at in this investigation: the etchant immersion time and the permanganate concentration of the etchant. The experimental plan for this study was broken down into two phases. Phase I consisted of using two etchant immersion times and two permanganate concentrations. The values chosen for phase I experiment were based on work done by Xu (1998). Phase II was a refinement of phase I to show repeatability and reproducibility. Once the bounds were set by phase I, phase II was used to obtain detailed information about the surface preparation within the bounds. The test matrix for phase I of this study is seen Table 5. Figure 15 shows a process flow chart that explains the major steps involved in this study.

### Table 5 Phase 1 Test Matrix.

| 80 g/L | Run 1 | Run 3 |
|---|---|---|
| 40 g/L | Run 2 | Run 4 |
| | 4 minutes | 20 minutes |

## 4.6 Method for Data Analysis

The objective of this study was to investigate the surface preparation parameters: time and concentration that provided adhesion strength of 900 to 1000 Psi between the copper metal and the cyanate ester laminate. Standard stud pull tests were used analyze the

adhesion strength of the plated copper film. The studs used in this study were attached onto the sample surface with an epoxy adhesive and cured in an oven at 150°C. The sample was allowed to cool back down to room temperature and then placed in the Sebastion-5 stud pull apparatus. A set amount of force was applied until the stud was physically detached from the surface of the laminate. Figure 16 shows a simple schematic of the Sebastion-5 stud pull system. All stud pull tests were performed at Space System Loral within a week after metallization. A Scanning Electron Microscope (SEM) was used to qualitatively characterize the effect of the alkaline permanganate etch process. Each sample was scanned to illustrate the difference in topography under the specific run conditions. The surface preparation parameters were plotted against the stud pull results to show the effect of change of each etching parameter.
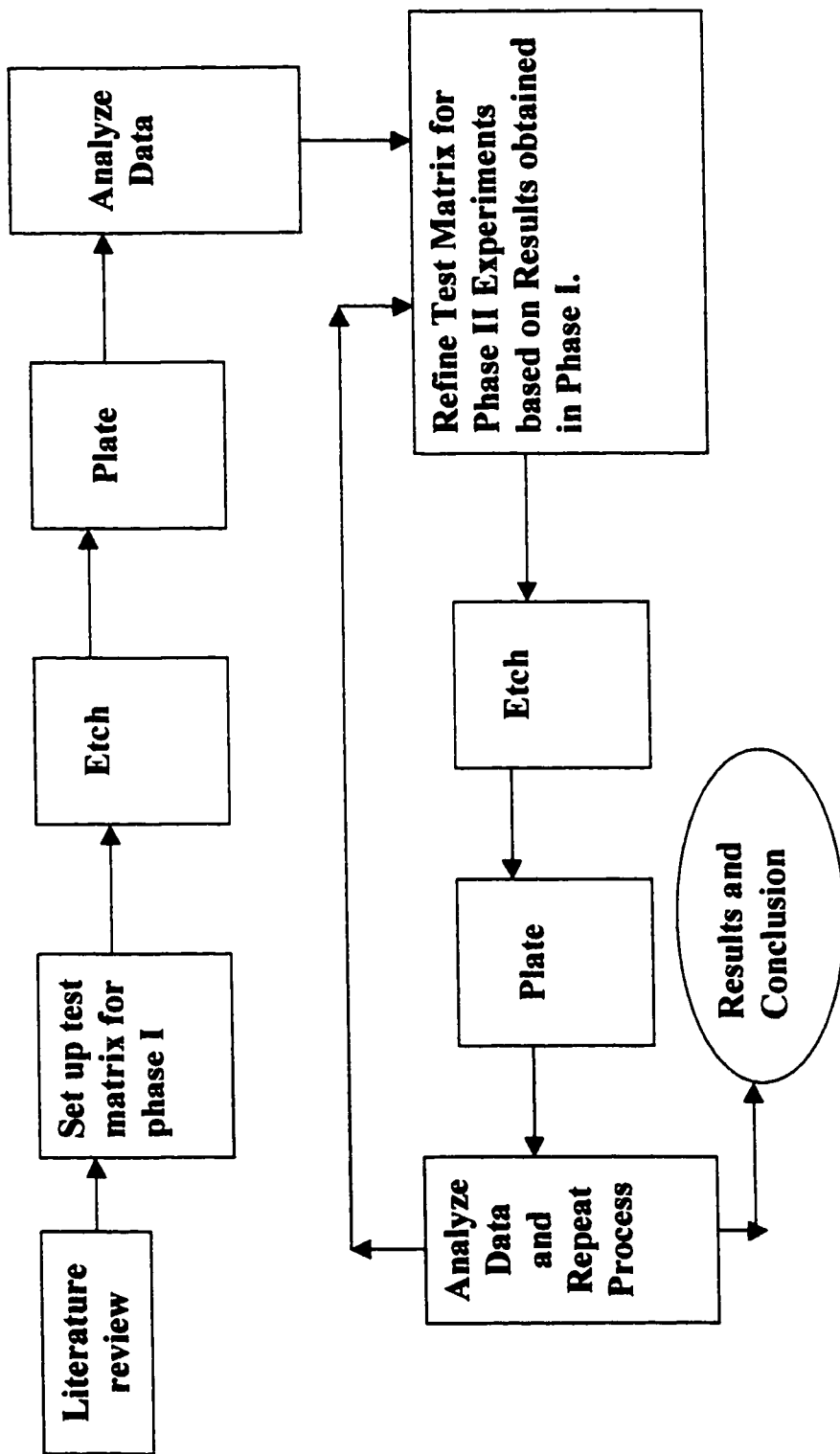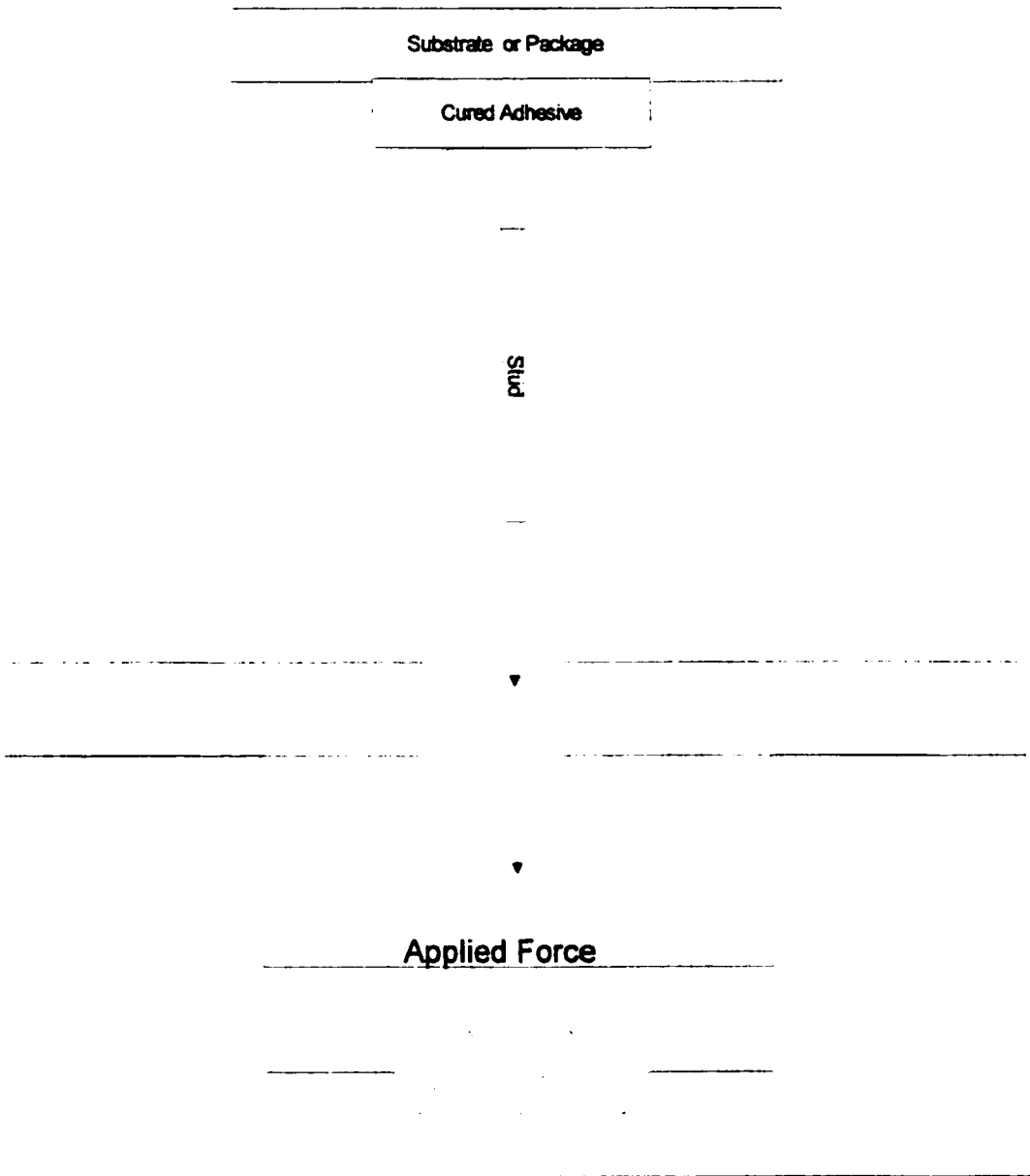
Figure 15 Process Flow Chart for Phase I and Phase II.

Substrate or Package

Cured Adhesive

Stud

▼

▼

Applied Force

Sebastion-5 Stud Pull System

**Figure 16 Sebastion-5 Stud Pull System.**

# 5    RESULTS AND DISCUSSION

## 5.1    Introduction

This section contains the results and discussion of the experiments outlined in chapter 4 of this study. The section is subdivided into two parts corresponding to each phase discussed earlier in the experimental plan: (1) Effect of etching time and concentration using a potassium permanganate etchant; (2) Effect of etching time and concentration using a sodium permanganate etchant.

## 5.2    Phase I Results Using A Potassium Permanganate Etchant.

Based on Xu's (1998) work, Phase I of this investigation utilized a potassium permanganate etchant at a concentration range of 40 g/L to 80 g/L and etching times ranging from 4 minutes to 20 minutes. A more detailed test matrix for experiments conducted using a potassium permanganate etchant is seen in Table 6.

The plated sample, seen in Figure 17, showed blisters across the surface. Therefore no adhesion results could be measured. One cause for blistering of the copper film was the effect of a poorly prepared surface. There were no anchoring or binding sites for the metal to adhere to causing it to lift off. The poor surface conditions were caused by the low concentration of permanganate in the potassium permanganate solution. This

indicated that the original test matrix was insufficient for this particular system. A higher concentration of permanganate was needed to create the adequate surface conditions in achieving good adhesion results. However, the permanganate concentration could not be increased using the potassium permanganate salt due its solubility limit of 60 g/L. To obtain higher concentration of permanganate in the solution, the permanganate salt was changed to sodium permanganate. Sodium permanganate has a solubility of 600 g/L.

**Table 6 Test Matrix Utilizing a Potassium Permanagante Etchant.**

| 80 g/L | Run 1 | Run 3 |
|--------|-------|-------|
| 40 g/L | Run 2 | Run 4 |
|        | 4 minutes | 20 minutes |

Figure 17 Blistered sample.

## 5.3 Phase II Results Using a Sodium Permanganate Etchant.

Results from phase I indicated that the permanganate concentration was too low using a potassium permanganate solution. Since sodium permanganate has a higher solubility than potassium permanganate, the switch was made from using a potassium permanganate etchant to a sodium permanganate etchant in phase II experiments. Sodium permanganate was commercially bought from Electro- Chemicals at a concentration of 600 g/L. Table 7 represents the new test matrix formulated based on the results obtained in phase I of this study. Again four etching times and three etchant concentrations were used ranging from 4 minutes to 20 minutes and 150 g/L to 450 g/L respectively.

**Table 7 Test Matrix Utilizing a Sodium Permanganate Etchant.**

| 450 g/L 75% solution | Run 1 | Run 4 | Run 7 | Run 10 |
|---|---|---|---|---|
| 300 g/L 50% solution | Run 2 | Run 5 | Run 8 | Run 11 |
| 150 g/L 25% solution | Run 3 | Run 6 | Run 9 | Run 12 |
| | 4 minutes | 10 minutes | 15 minutes | 20 minutes |

### 5.3.1 Qualitative Results Showing the Effect of Etching Time and Etchant Concentration.

Figures 20 through 31 qualitatively show the effect of etching time and etchant concentration on the surface of the substrate. It is apparent from these photographs that changing the etchant concentration or etching time produces an effect on the surface topography. Looking at Figures 20-23, where the etchant concentration was fixed at 150 g/L and etching time was increased from 4 minutes to 20 minutes, it can be concluded that the surface roughness increased. As the etching time is increased the pitting increased in size and count. It is evident by the exposed fibers seen in Figure 23 that at a high etch time and a low etchant concentration the substrate becomes overetched. Therefore etching for longer periods results in an overetched surface and may lead to poor adhesion during metal deposition.

Modification of the etchant concentration showed similar results as for the etching time. Based on Figures 20, 24,and 28, where the etching time was constant at 4 minutes and the concentration was increased from 150 g/L to 450 g/L, it can be concluded that surface roughness increased. Increasing the concentration increased the pitting. The effect of increasing the concentration from 150 g/L to 300 g/L had a greater effect than increasing the etching time. Pitting is seen to intensify more rapidly in Figures 20, 24, and 28 where the concentration is being varied than in Figures 21 and 22 where the time is being varied.

## 5.3.2 Quantitative Results Showing the Effect of Etching Time and Etchant Concentration.

After being etched the samples were electrolessly plated with a copper film. The film strength was characterized by the adhesion strength provided by the standard stud pull test. Table 8 shows the adhesion strength, the average stud pull, and standard deviation measured for each condition of experiments conducted in phase II. The results were then plotted to quantitatively show the effect of the etching time and etchant concentration on the adhesion strength between the copper film and substrate surface.

Figure 18 shows plots of the adhesion strengths (Psi) versus etching times (minutes) at a constant etchant concentrations (g/L). The plot indicates that for any etchant concentration the adhesion strength increases with etching time, reaches a maximum, and then decreases. At an etchant concentration of 150 g/L the plot shows the adhesion strength increasing linearly and approaching its maximum (1337 Psi) after 20 minutes of etching. However, at an etchant concentration of 300 g/L the maximum (1251 Psi) is reached much earlier at 10 minutes then decreases. A similar trend is present throughout the plot for all concentrations. One can interpolate from the graph that at higher etchant concentrations the maximum adhesion strength is reached much quicker than at lower etchant concentrations. However, as seen in Figure 19, the overall adhesion strength decreases as the etchant concentration is increased over 300-g/L. This is the result of the substrate being over etched.

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Following the trends in Figure 19 it can be concluded that the adhesion strength of the copper film decreases if the etching time is greater than 10 minutes and the etchant concentration is above 300 g/L. At the lowest concentration of 150 g/L the adhesion strength increased and ranged from 600 Psi to 1300 Psi as the etching time was increased. However, at the highest concentration of 450 g/L the results only ranged from 600 Psi to 900 Psi. This indicates that the etching time effects the adhesion strength more at lower concentrations than at higher concentrations.

These results coincide with the qualitative results discussed in the previous section. Figures 20-23 illustrate the increase in surface roughness as etching time is increased and similarly, Figure 18 shows the increase in adhesion strength as etching time increased. However, the adhesion strength starts to decrease after reaching a maximum. This indicates that after a certain amount of etching the substrate starts to become overetched causing the adhesion strength to drop. At the highest concentration of 450 g/L the profile seems to deviate from the common trend as the etching time is increased form 15 minutes to 20 minutes. This indicates that at higher etching times in conjunction with higher etchant concentrations the adhesion strength becomes sporadic and unpredictable. Based on the 1000-Psi criteria pre-set by Space Systems Loral the desired adhesion strength was achieved.

**Table 8 Stud Pull Results with Average Pull and Standard Deviation.**

|  | Conc. = 150 g/L | Conc. = 300 g/L | Conc. = 450 g/L |
|---|---|---|---|
| **Time = 4 min** | # of Pulls: 4<br>Average: 566<br>Std Dev.: 206 | # of Pulls: 2<br>Average: 851<br>Std Dev.: 173 | # of Pulls: 3<br>Average: 654<br>Std Dev.: 429 |
| **Time = 10 min** | # of Pulls: 7<br>Average: 983<br>Std Dev.: 323 | # of Pulls: 5<br>Average: 1251<br>Std Dev.: 143 | # of Pulls: 3<br>Average: 903<br>Std Dev.: 461 |
| **Time = 15 min** | # of Pulls: 3<br>Average: 1303<br>Std Dev.: 266 | # of Pulls: 4<br>Average: 1217<br>Std Dev.: 261 | # of Pulls: 3<br>Average: 793<br>Std Dev.: 265 |
| **Time = 20 min** | # of Pulls: 6<br>Average: 1337<br>Std Dev.: 226 | # of Pulls: 7<br>Average: 946<br>Std Dev.: 223 | # of Pulls: 3<br>Average: 828<br>Std Dev.: 420 |
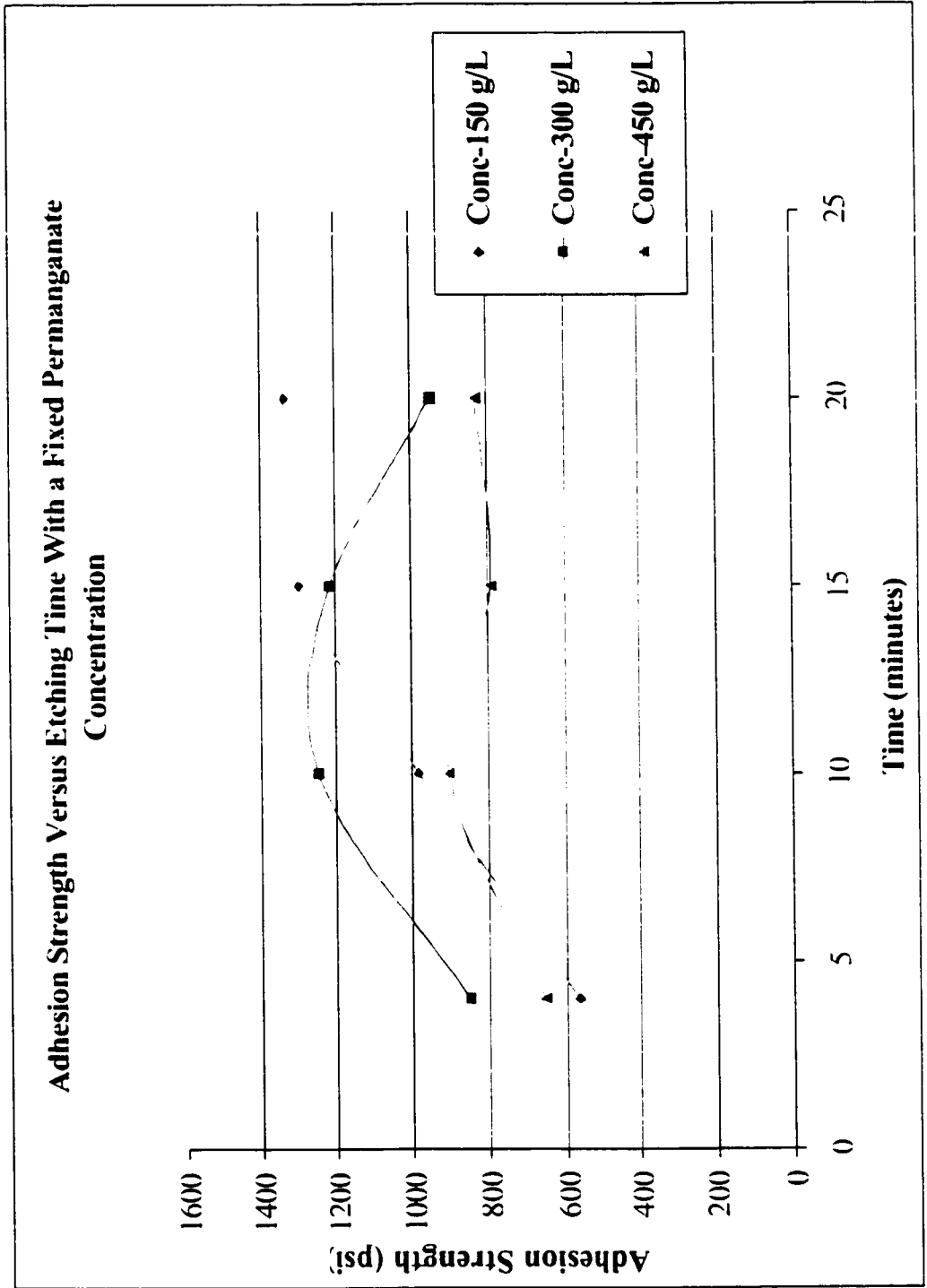
Figure 18 Plot of Adhesion Strength versus Etching Time.
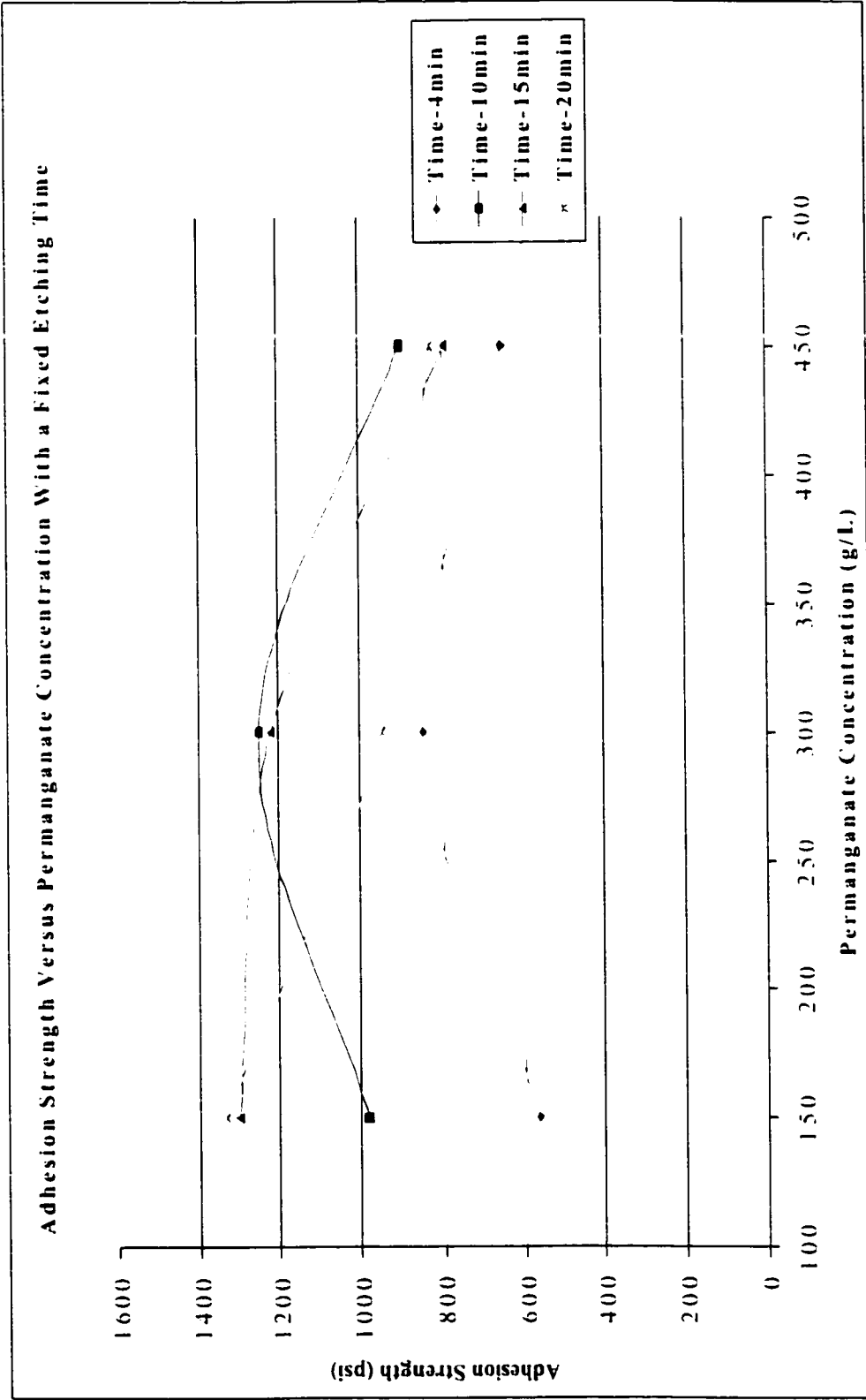
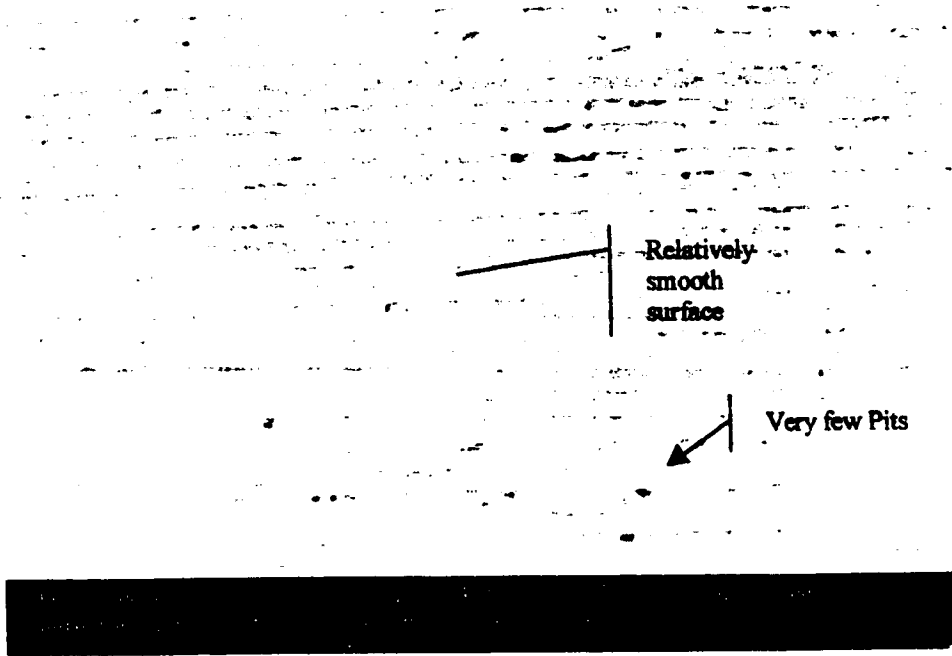Figure 19 Plot for Adhesion Strength versus Etchant Concentration.

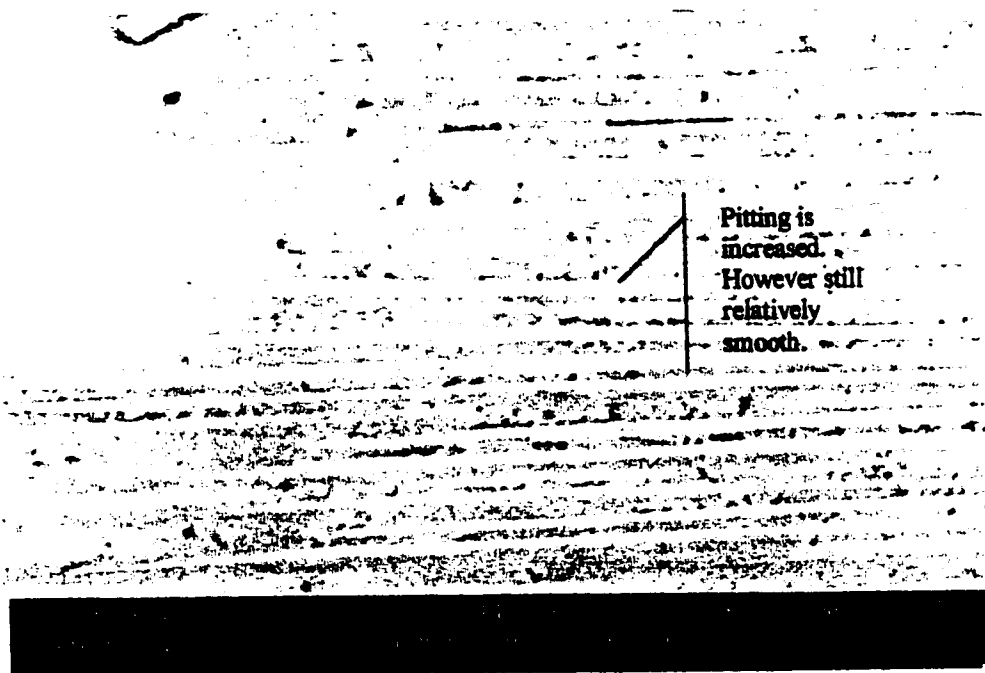**Figure 20 Concentration 150 g/L Etched for 4 minutes.**



**Figure 21 Concentration 150 g/L Etched for 10 minutes.**
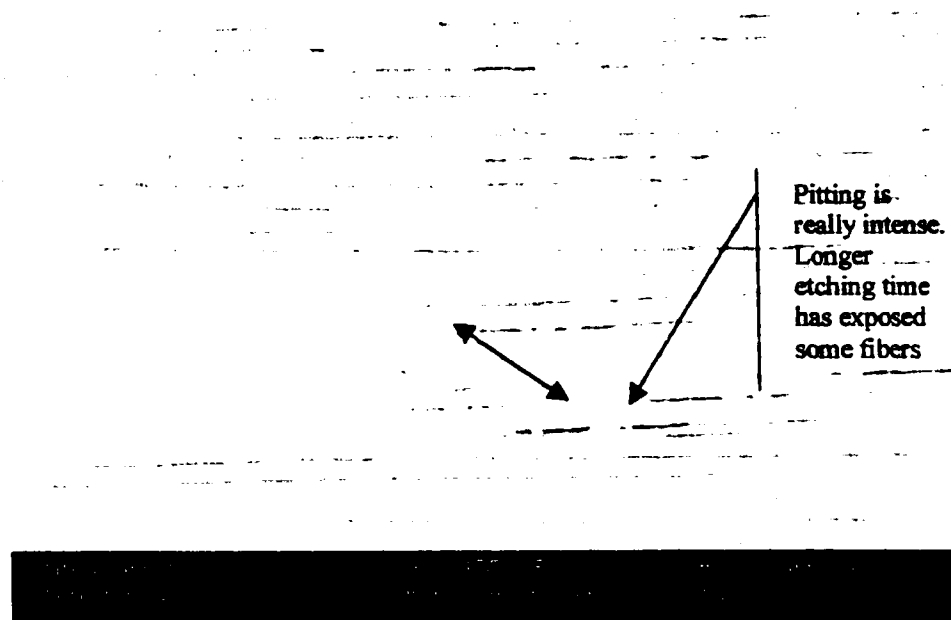
Pitting is really intense. Longer etching time has exposed some fibers

**Figure 22 Concentration 150 g/L Etched for 15 minutes.**



Sample are overetched. Lots of fibers exposed.
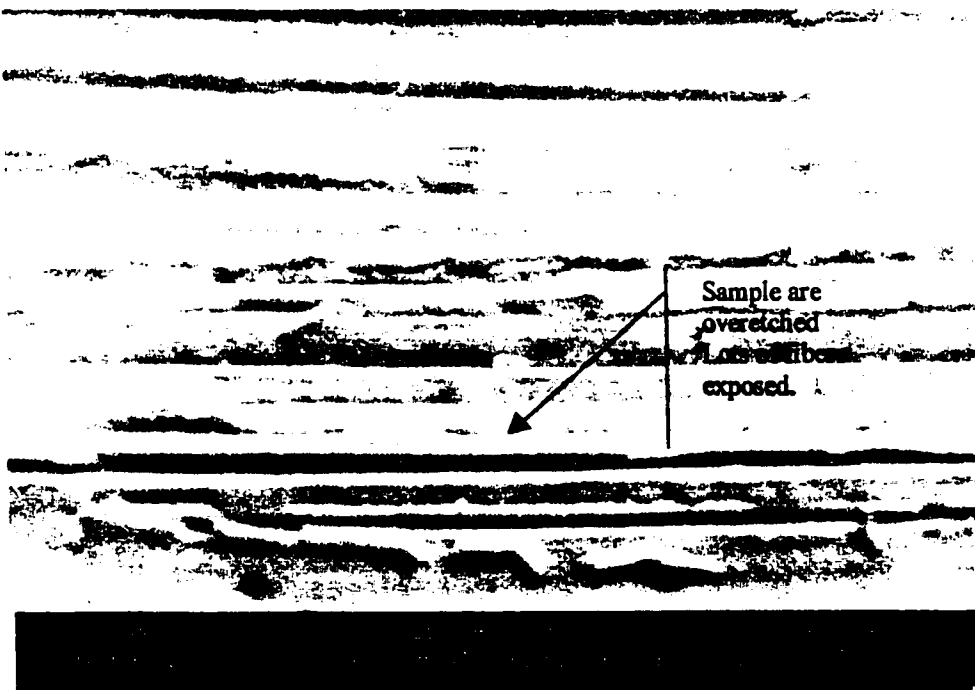
**Figure 23 Concentration 150 g/L Etched for 20 minutes.**

At higher concentration
pitting becomes intense
and increase in shorter etch time.
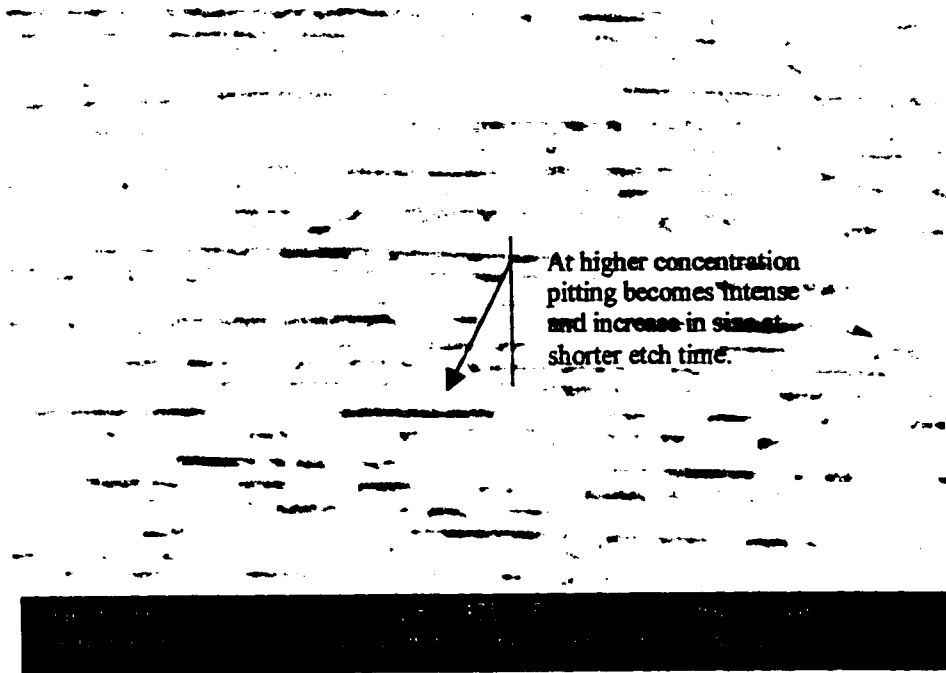
**Figure 24 Concentration 300 g/L Etched for 4 minutes.**

Pitting seems uniform
across sample surface. The
adhesion strength was the
greatest at these conditions.
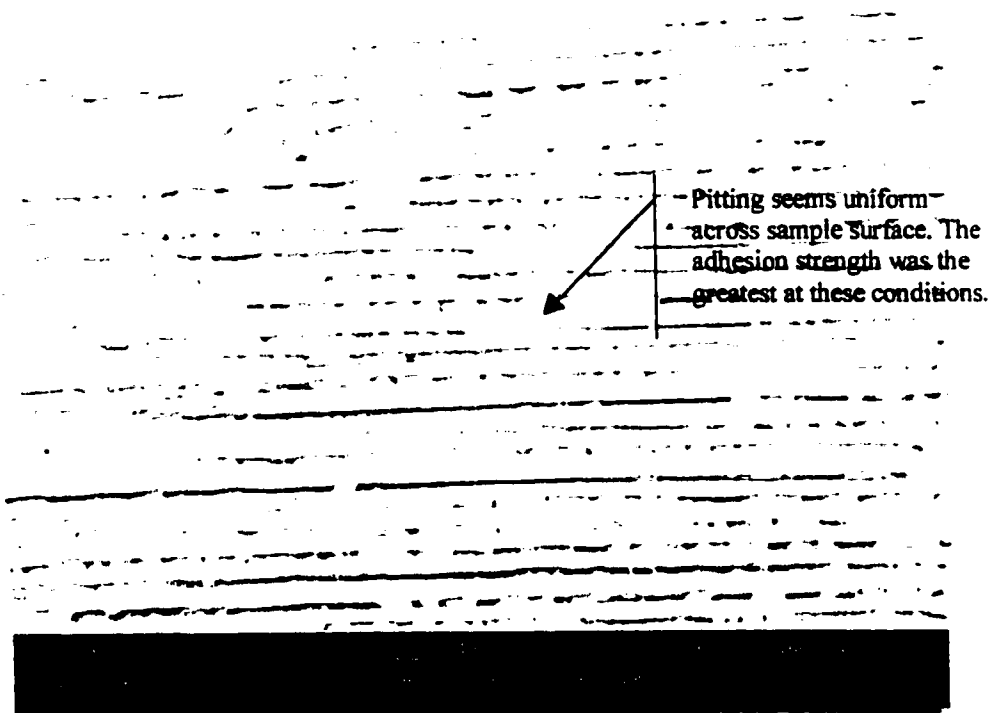
**Figure 25 Concentration 300 g/L Etched for 10 minutes.**

Pitting less uniform. More fibers are starting to be exposed.
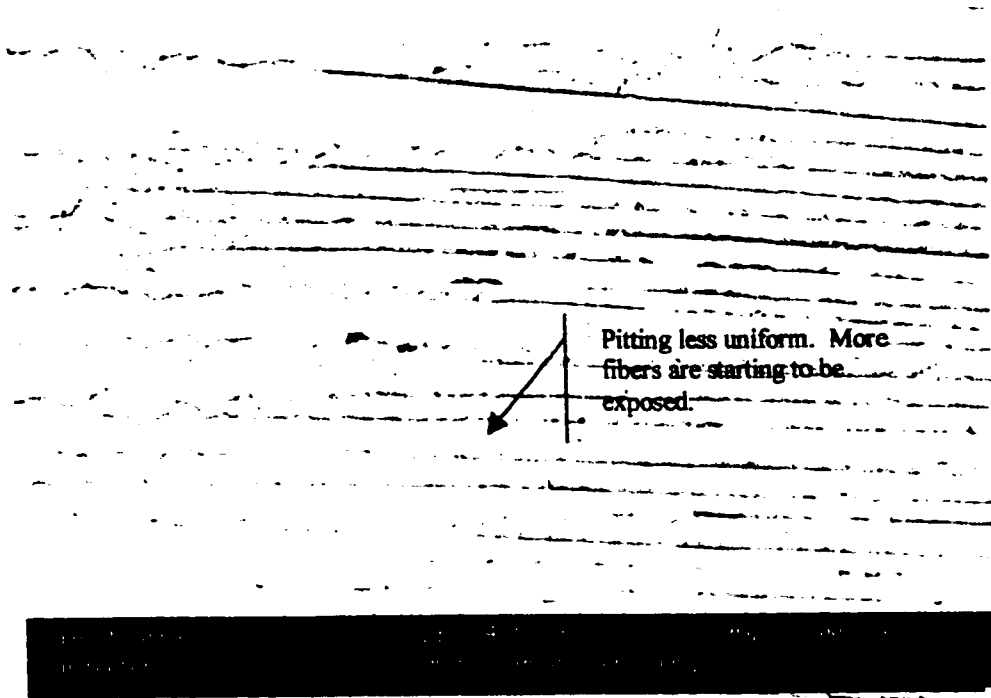
**Figure 26 Concentration 300 g/L Etched for 15 minutes.**



More Fibers exposed. Sample starting to become overetched.
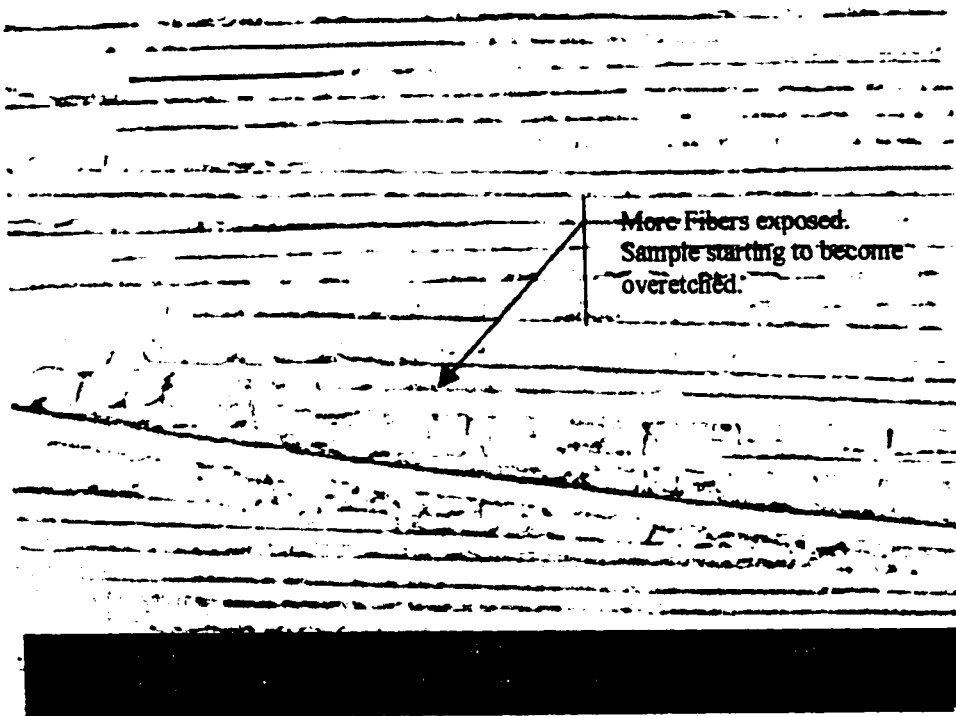
**Figure 27 Concentration 300 g/L Etched for 20 minutes.**

At lowest etching time and
greatest etchant
concentration a lot of pitting
some fibers exposed.
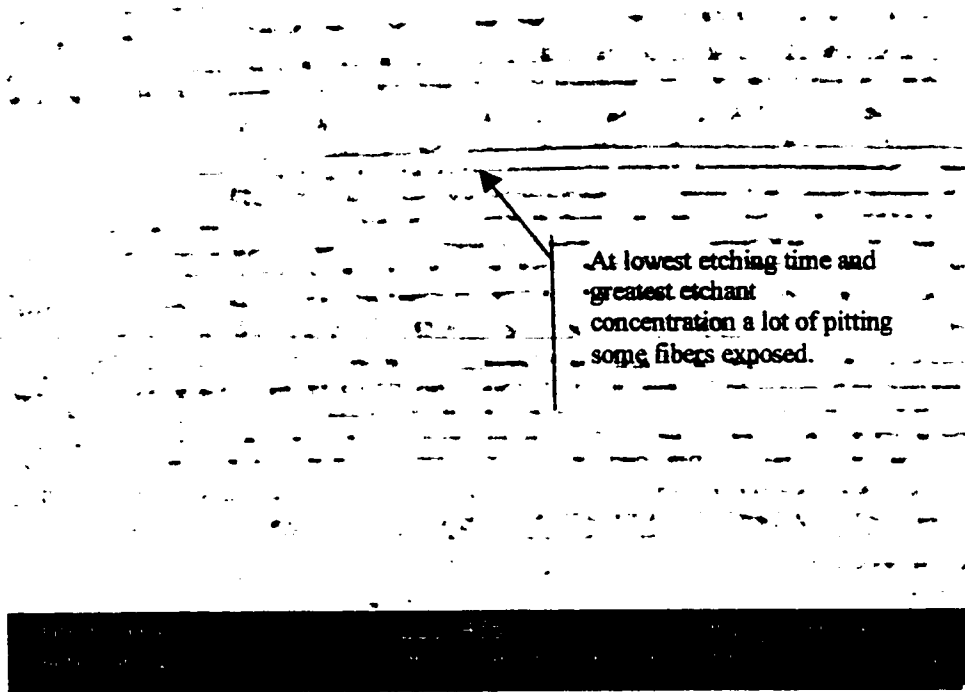
**Figure 28 Concentration 450 g/L Etched for 4 minutes.**

Lots of fibers sample
becoming overetched.
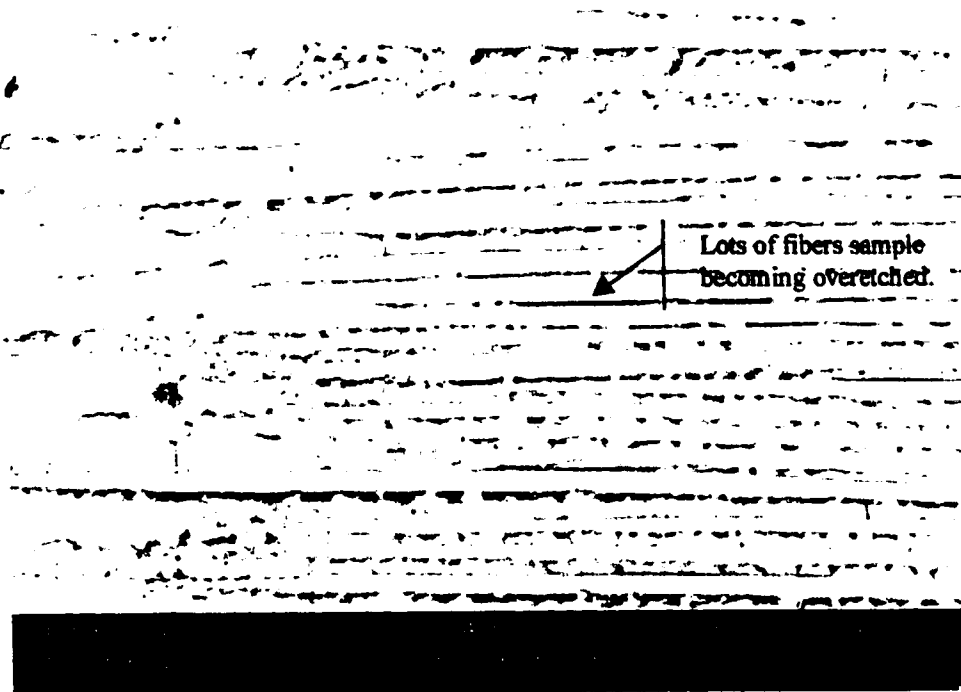
**Figure 29 Concentration 450 g/L Etched for 10 minutes.**

More Fibers leading to overetched sample.
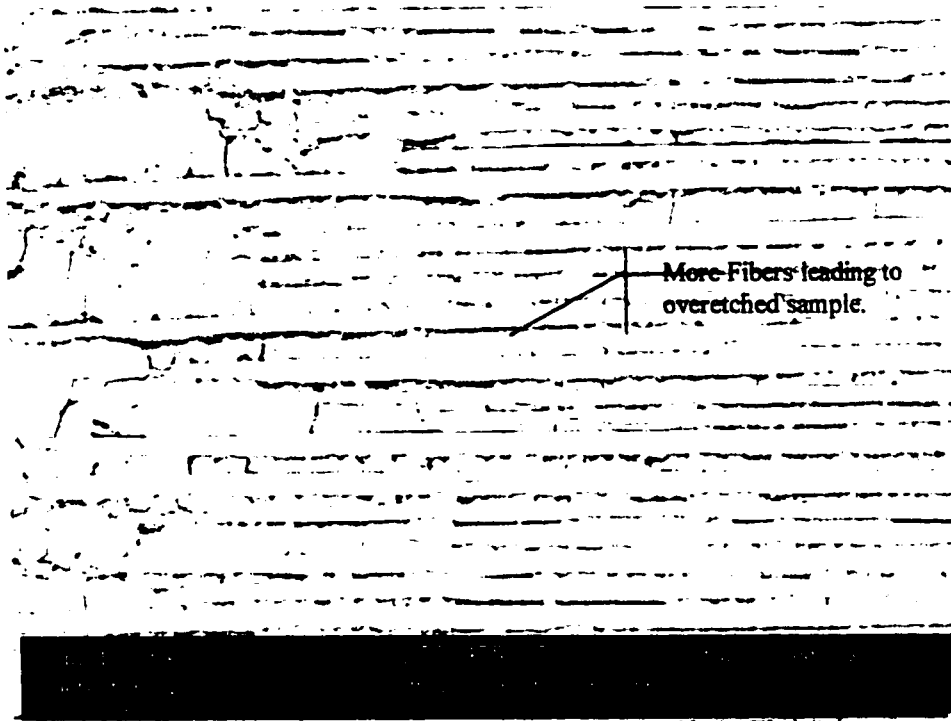
**Figure 30 Concentration 450 g/L Etched for 15 minutes.**



fibers and pit

**Figure 31 Concentration 450 g/L Etched for 20 minutes.**

## 5.4 Cross Sectional View of the Plated Film

Cross-sections were taken of some samples to show the effect of the plated film on the surface of the substrate. Figure 32 perfectly illustrates how the binding sites play an important role in this process. The copper film is seen wrapped around the fibers locking itself in place. Starting from the top of the sample and moving down, all of the various layers can be characterized from this Figure.

Copper film
wrapped
around fibers

Bundled
Fibers

Uniform
copper
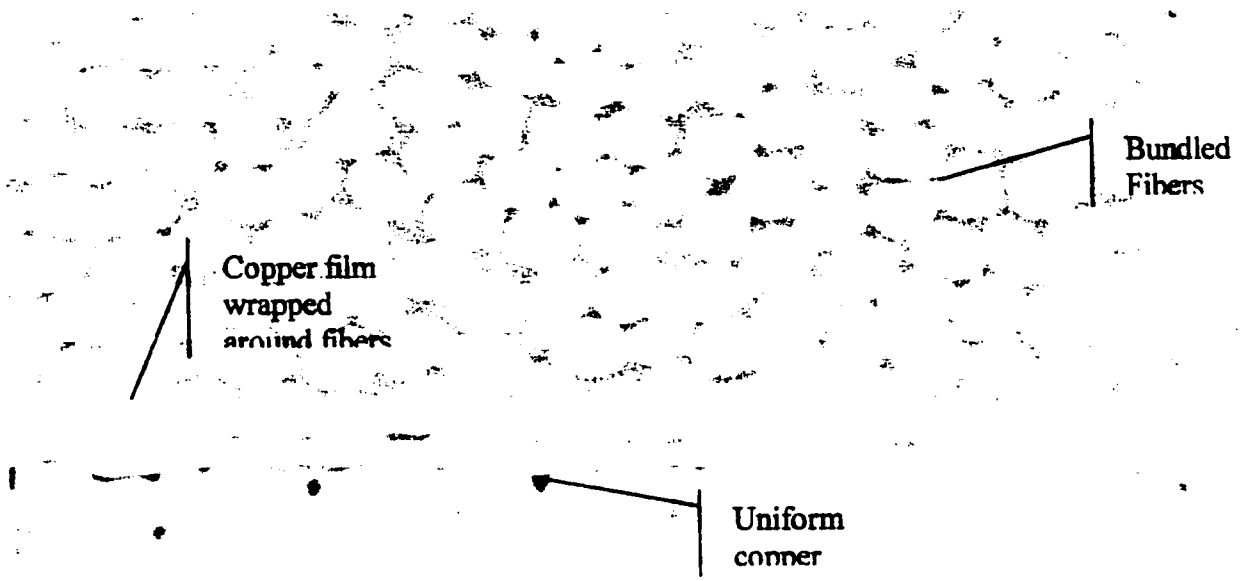
**Figure 32 Cross- Sectional View of a Plated Substrate.**

# 6 CONCLUSION

## 6.1 Overall Conclusion

For this particular process, potassium permanganate was an insufficient etchant because of its low solubility. The concentration of permanganate was not adequate to effectively etch the surface of the substrate. After being etched with the potassium permanganate, the copper film blistered off indicating poor adhesion. Based on these visual results the etchant was changed to sodium permanganate.

Changing etchants and operating at a higher concentration immediately improved the adhesion results. Samples etched at higher concentrations reached maximum adhesion strength faster than lower samples etched at lower concentrations. At higher concentrations, of 300 g/L and 450 g/L, the adhesion strength decreased for etching times greater than 10 minutes. The decrease of adhesion strength was due to degradation in substrate. As etching time was increased and the sample became over etched adhesion strength was lost.

Operating at the lowest concentration in conjunction with a longer etching time resulted in adhesion strength of over 1300 Psi. However, when operating at the highest concentration and shorter etching times the adhesion strength dropped dramatically to 650 Psi. These results indicate that variation of the etchant concentration has a greater effect on the surface topography than variation of the etching time. As the etchant

concentration was increased the variation between adhesion strengths for a specific etching time decreased. It can be seen from Figure 21 that the overall average of the adhesion strength decreased as the concentration was increased from 150 g/L to 450 g/L.

Overall the investigation was successful in proving that etching time and etchant concentration are critical parameters that affect the amount of micro roughening to the surface of the carbon fiber laminate. Adhesion strength ranging from 1000 Psi to 1300 Psi was sufficient in meeting the requirements set out by Space Systems Loral.

# 7 FUTURE WORK

## 7.1 Future Work and Recommendations.

Research and development of new materials such as the carbon fiber laminate used in this study will continue to grow in the future. There are many other variables that can be investigated other than the etching time and etchant concentration. For example, the alkalinity of the etchant can be studied by varying the sodium hydroxide concentration and keeping the permanganate concentration constant. Another parameter that can be investigated is the conditioner. As Mandich and Krulik(1992) pointed out the choice of the conditioner is critical to getting the correct surface roughness. Therefore experimenting with various conditioners could be beneficial. Looking at different metal deposition rates. Another focus could be spent on studying plating methods. For example to speed up process times using electroplating rather than electroless plating. Using a different metal film like nickel could also be investigated.

# 8 BIBLIOGRAPHY

"RS-3 A Toughened Polycyanate" YLA Incorporated: Advanced Composite Materials, YLA Incorporated, Benicia, CA 1990.

Campbell, Stephen A., The Science and Engineering of Microelectronic Fabrication pp. 258-259 Oxford University Press, New York 1996.

Converse, William E; Larry Frank P, "Metallization of Polycyanates", 28th International SAMPE Technical Conference, 28, pp. 1122-1135 1996.

Deckert, Cheryl A., "Electroless Copper Plating A Review: Part I and II", Plating And Surface Finishing, 71, pp. 48-64 1995.

Granger Diana D.; Miller Leroy J., United States Patent, NO 5,569,493, October 1994.

Inagaki, N; Park, Y.W.; and Tasaka S., "Effects of Surface Modifications by Remote Hydrogen Plasma on Adhesion in the Electroless Copper/Tetrafluoroethelyene-Hexafluoropropylene copolymer (FEP) system", Journal of Adhesion Science and Technology, 12, pp.1105-1119 1998.

Kao, Alan S.; Stenger H.G.; Covert K.L.; and others, "Etch Profile Development in Spray Etching Process", Journal of Electrochemical Society, 139, pp. 2202-2211 1992.

Karas Bradley R.; Chao Herbert S., United States Patent, NO 5,286,530, February 1994.

Kirmann, J.; Roziard, X.; Pagetti J.; Halut, J., "Effects of Alkaline Permanganate Etching of Epoxy on the Peel Adhesion of Electrolessly Plated Copper on a Fiber-reinforced Epoxy Composite", Journal of Adhesion Science and Technology, 12, pp. 383-397 1998.

Mandich, N.V.; Krulik G.A., "Chemistry of Modern Permanganate Etch-back Systems for Printed Circuit Board Production", Plating And Surface Finishing, 72, pp. 56-61 1992.

Mann, George E., United States Patent, NO 5,575,868, November 1996.

Murphy, N.F. ; Gurly E.S., "Role of Chromic-Sulfuric Acid Etches in the Plating of Epoxies", Plating, 58, pp. 583-587 1971.

Ohwada, K.; Negoro Y.; KonakaY.; and Oguchi T., "Uniform Groove-depths in (110) Si Anisotropic Etching by Ultrasonic Waves and Application to Accelerometer Fabrication", Journal of Sensors and Actuators, 50, pp. 93-98 1995.

Poon, K.; Wan C.C.; Wu C.J., "Optimization of Copper Pattern Plating Process with Planned Experimentation and Response Surface", Journal of Electronics Manufacturing, 5, pp. 39-47 1995.

Simpkins, Norm, "Electroregeneration of Permanganate Desmear/etchback Solutions For PCB's ", Electronic Manufacturing 35, pp. 32-33 1989.

Thorn, C. Edwin; Walsh Michael K., "The Mechanism of Permanganate Desmear", Printed Circuit Fabrication, 10, pp. 30-32 1991.

Tomaiuolo, Francesco; Montangero Paolo, "Alkaline Permanganate Treatment on Etchback Processes", Metal Finishing, 84, pp. 45-48 1986.

Villamizer, C.A.; Rojas J.; and Frias P., "Chemical Etching Versus Plasma Etching in Electroplating ABS Resin Surfaces", Metal Finishing, 79, pp. 27-33 1981.

Xu, Hong, "Electroless Copper Plating on Graphite/Epoxy and Graphite/Cyanate Ester", Thesis San Jose State University 1998.