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Alkalinity characterization of permanganate etching of polycyanate ester resins

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**ALKALINITY CHARACTERIZATION OF
PERMANGANATE ETCHING OF
POLYCYANATE ESTER RESINS**

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San José State University

In Partial Fulfillment of the Requirements for the Degree

Master of Science

By

Thomas Carson

May 2000

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ABSTRACT

Alkalinity Characterization of Permanganate Etching of Polycyanate Ester Resins

By Thomas Carson

The effects of permanganate etch alkalinity on the surface preparation quality for a carbon fiber – polycyanate ester resin weave is examined using copper plating and subsequent stud pull adhesion test. A sodium permanganate etchant with alkalinity varying from 0 to 80 grams per liter of sodium hydroxide (NaOH) is used during the surface preparation. Copper is plated 30 μ -inches thick. Based upon adhesion strength results, variations of the alkalinity of the permanganate etch used in preparation of the surface exhibits three distinct regions of response. Etch alkalinity below 15 grams per liter NaOH produces poor adhesion (600 PSI). A transitional region where adhesion improves with increased etch alkalinity is observed between 15 and 40 grams per liter NaOH. Above 40 grams per liter NaOH, adhesion strength averages 1500 PSI and is independent of the etch alkalinity. Included in this work is a surface preparation and plating procedure.

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Table of Contents

1	INTRODUCTION.....	1
1.1	PROJECT INTRODUCTION	1
1.2	PROJECT OVERVIEW	2
1.3	SURFACE PREPARATION	3
1.4	COMPOSITE SUBSTRATE.....	3
1.4.1	Carbon Fiber	4
1.4.2	Binding Resin.....	5
1.5	PROJECT GOALS	6
2	LITERATURE REVIEW	7
2.1	LITERATURE REVIEW INTRODUCTION	7
2.2	OVERVIEW AND PLATING PROCEDURE	7
2.3	ETCH PROCESS CONDITIONS	9
2.4	EFFECT OF ETCH PROCESS CONDITIONS ON ADHESION.....	10
2.4.1	Etch Time Effect on Adhesion.....	10
2.4.2	Etch Permanganate Concentration Effect on Adhesion	12
2.4.3	Etch Alkalinity Effect on Adhesion	13
2.5	LITERATURE REVIEW SUMMARY	17
3	RESEARCH HYPOTHESIS AND OBJECTIVE.....	18
3.1	HYPOTHESIS.....	18
3.2	JUSTIFICATION	18
3.3	OBJECTIVE	19
4	EXPERIMENTAL PROCEDURES.....	20
4.1	EXPERIMENTAL APPROACH	20
4.2	EXPERIMENTAL APPARATUS	22
4.3	MATERIALS AND CHEMICALS	23
4.4	EXPERIMENTAL PROCEDURE FOR SURFACE PREPARATION	27
4.5	EXPERIMENTAL PROCEDURE OF ELECTROLESS DEPOSITION OF COPPER METAL ..	28
4.6	EXPERIMENTAL PLAN.....	30
4.7	DATA COLLECTION AND ANALYSIS METHODS.....	33
4.7.1	Preparation of the Plated Samples for Testing.....	34
4.7.2	Stud pull testing.....	35
4.7.3	Data Analysis Methods.....	37
5	RESULTS AND DISCUSSIONS.....	38
5.1	INTRODUCTION.....	38
5.2	SURFACE ETCHING	38
5.3	EFFECTS OF EXCESSIVELY LOW ETCH ALKALINITY	41

5 4	STUD PULL ADHESION RESULTS	43
6	OVERALL CONCLUSIONS	49
7	RECOMMENDATIONS FOR FUTURE RESEARCH	50
8	REFERENCES.....	53

Table of Figures

FIGURE 1	CARBON FIBER WEAVE AFTER SPREADING.....	4
FIGURE 2	SEMI-CURED CYANATE ESTER RESIN.....	5
FIGURE 3	CYANATE ESTER POLYMER	6
FIGURE 4	SURFACE PREPARATION STEPS.....	9
FIGURE 5	ETCH TIME EFFECTS ON ADHESION STRENGTH.....	11
FIGURE 6	PERMANGANATE CONCENTRATION EFFECTS ON ADHESION STRENGTH	12
FIGURE 7	ALKALINITY DEPENDENCE OF EPOXY AND ABS PLASTICS	14
FIGURE 8	PERMANGANATE/MANGANATE COVERION IN THE PRESENCE OF NAOH.....	16
FIGURE 9	EXPERIMENTAL FLOW CHART FOR PHASE I AND PHASE II	21
FIGURE 10	SURFACE PREPARATION LINE	22
FIGURE 11	COPPER PLATING LINE	23
FIGURE 12	SUBSTRATE CURING METHOD.....	24
FIGURE 13	UNPROCESSED TARGET SUBSTRATE COUPON BAG FACE	25
FIGURE 14	UNPROCESSED TARGET SUBSTRATE COUPON TOOL FACE.....	25
FIGURE 15	SEBASTAIN-FIVE STUD PULL APPARATUS	33
FIGURE 16	ADHESION TEST STUD MOUNT	34
FIGURE 17	SEBASTAIN-FIVE STUD CHUCK.....	36
FIGURE 18	UNETCHED SAMPLE SURFACE.....	38
FIGURE 19	40 GRAMS/LITER NAOH PERMANGANATE ETCHED SAMPLE.....	38
FIGURE 20	EXPOSED FIBER BUNDLE TOPS FROM 40 GRAMS NAOH PER LITER PERMANGANATE ETCH.....	39
FIGURE 21	EROSE SURFACE NEEDED FOR PLATING FROM 40 GRAMS PER LITER NAOH PERMANGANATE ETCH.....	40
FIGURE 22	BLISTERED PLATED SAMPLE - 20 GRAMS PER LITER NAOH	41
FIGURE 23	UNPLATED SAMPLE ETCHED BY PERMANGANATE SOLUTION WITH OUT ANY NAOH.....	42
FIGURE 24	TAPE TEST OF A BLISTERED SAMPLE – 10 GRAMS/LITER NAOH	43
FIGURE 25	PLATED SAMPLE READY FOR ADHESION TESTING	44
FIGURE 26	STUD PULL SITE	44
FIGURE 27	BLISTERED PULL SITE FROM SAMPLE ETCHED WITH NO ADDITION OF NAOH TO PERMANGANATE ETCH.....	45
FIGURE 28	COPPER ADHIESION STRENGTH DEPENDENCE ON ETCH ALKALINITY	47

FIGURE 29 EXPERIMENTAL REPRODUCIBILITY.....	48
FIGURE 30 UNPROCESSED COUPON BAG-SIDE FACE.....	51

Table of Tables

TABLE 1 CHEMICAL BILL OF MATERIALS FOR SURFACE PREPARATION.....	26
TABLE 2 CHEMICAL BILL OF MATERIALS FOR PLATING.....	26
TABLE 3 EXPERIMENTAL PHASE I.....	31
TABLE 4 EXPERIMENTAL PHASE II.....	32
TABLE 5 ADHESION STRENGTHS FROM VARIOUS ALKALINITY ETCHES.....	46

1 Introduction

1.1 Project Introduction

Plastics and composite materials are replacing traditional metal construction for many applications. Increased strength to weight ratio, corrosion resistance, radio frequency (**RF**) transparency, and dimensional stability are some of the advantages of composites. Utilizing composites in electrical applications requires that a conductive metal film be deposited on the composite material. Literature indicates a micro-roughened surface created by etching is essential for plated metal adhesion. This study investigates the effect of etchant alkalinity on composite surface preparation for plating.

This section presents an overview of surface preparation and the target substrate. Chapter 2 presents the current technology in this field and a review of published work on the subject. The hypothesis, justifications for this investigation, and objectives are presented in Chapter 3. The experimental methods employed to verify the hypothesis are explained in Chapter 4. The experimental results and analysis of the acquired data are presented in Chapter 5 followed by a discussion of these results. Chapter 6 presents the conclusions of this research. Lastly, recommendations for further investigation in this field are presented in Chapter 7.

1.2 Project Overview

This investigation is sponsored by Space Systems Loral (SSL). SSL desires to produce lighter, stronger and more resistant aerospace structures. The cost per pound premium for each component of a satellite or aircraft motivates this search. SSL manufactures electronic wave guides from a carbon fiber - polycyanate ester resin composite. These electronic wave guides weigh considerably less than an equivalent aluminum wave guide. A thin metallic film is required on the inside of the wave guide to make the wave guide electronically conductive. Due to the geometry of these wave guides, a non-line-of-sight metal deposition process is required. Since the composite is nonconducting, an electroless plating process is used.

SSL has determined that 1000 pounds per square inch (**PSI**) is the minimum strength required for their satellite applications. This study investigates the effects of etch bath alkalinity on the adhesion strength of the copper plate film.

1.3 Surface Preparation

The metal must adhere to the composite substrate to be effective. Micro-roughening the composite surface before plating is critical for metal adhesion.

Chemically etching the composite surface provides the necessary erose topography. Wet chemical etching provides a geometry independent, cost effective, and versatile method to provide the mechanical anchoring sites necessary for good adhesion.

1.4 Composite Substrate

The composite substrate consists of two materials; a strong fiber and a resin system. One common composite is fiberglass bound with an epoxy resin. Recently, the need for improved composite properties has facilitated the development of stronger and lighter fibers such as kevlar, hyperlon, and carbon bound by resins with better moisture resistance and higher glass transition temperatures such as polycyanate ester resin.

Although epoxies and polyester resins dominate the composite market, cyanate ester resins are gaining acceptance since their first syntheses in 1963 (Grigat, Putter, and Angew 1967). The first commercial use for cyanate resins was for printed circuit boards. Cyanate ester circuit boards are more moisture resistant and able to withstand higher soldering temperatures than their fiberglass counterparts. Recently, the enhanced properties of cyanate resins have been appreciated in other fields. Designers of satellites and other spacecraft desire the thermal and dimensional stability, and low outgasing

properties of cyanate resins. Weight is paramount to spacecraft designers. Composite matrices involving cyanate resins give these designers the performance they require, yet weigh considerably less than an equivalent metal structure.

1.4.1 Carbon Fiber

Carbon fiber can be fashioned in a variety of textures; including matting, unidirectional tapes, and weaves. Woven carbon fibers bound interstitially by solidified polycyanate ester resin is examined here. An example of a carbon weave is seen in Figure 1.

Figure 1 Carbon Fiber Weave after Spreading
(Mohri, 1998)

The ductile carbon fiber bundles give strength to the composite. Because the fibers are cross-woven, the composite strength is independent of the stress direction and the matrix

is dimensionally stable. However, the carbon fibers themselves are not rigid and need a binding agent such as a resin.

1.4.2 Binding Resin

Cyanate resin stiffens the composite. The resin flows into and fills the carbon-fiber weave. Then the resin is partially cured to form the chemical structure depicted in Figure 2.

Figure 2 Semi-Cured Cyanate Ester Resin
(Lee, 1990)

The still tacky fiber-resin composite can then be worked into the desired shape. Once the final shape is formed, the part is cured at elevated temperature and pressure. This heat

polymerizes the cyanate ester resin and sets the matrix into its final form. The polymerized resin is depicted in Figure 3.

Figure 3 Cyanate Ester Polymer
(Lee, 1990)

The combination of fiber weave and polymer binding agent yields a strong yet lightweight composite.

1.5 Project Goals

This study characterizes the effects of permanganate etch alkalinity on the surface preparation of a carbon fiber – polycyanate ester resin composite. The surface preparation quality is measured by a stud pull of electroless plated copper from the composite surface.

2 Literature Review

2.1 Literature Review Introduction

A large volume of work is available discussing the general concept of electroless plating. These works concur that proper surface preparation before plating is a prime factor for good adhesion. Although published work agrees that the permanganate etchant must be alkaline, there has been little research that quantifies the effects of alkalinity on the surface roughness.

The existing published work is useful in clarifying three areas: a general overview of the plating procedure, effects of etching, and the qualitative effects of alkalinity on etching.

2.2 Overview and Plating Procedure

It is useful to understand the basic concepts of a process before diving into the minutia of details. A brief description of the plating industry, bath chemistry, process steps, metal deposit properties, and applications of electroless copper plating is discussed by Deckert (1995a and b). A concise description of the plating chemistry is given as;

The minimum necessary components of an electroless plating solution are a metal salt and an appropriate reducing agent. An additional requirement is that the solution, although thermodynamically unstable, is stable in practice until a suitable catalyzed surface is introduced.

(Deckert, 1995a) p.48

Prior to plating, the surface of the substrate must be properly cleaned and possess a certain topography that is favorable to plating (Thorn, Edwin, and Walsh, 1991). Many methods exist to provide a micro-roughened surface (Sohal, 1999) such as; mechanical abrasion (Xu, 1998), plasma etching (Villamizar, Rojas, and Frias, 1981), chemical spray etching (Kao, 1992), and chemical immersion etching. This research focus on a wet chemical permanganate etch method.

As shown in Figure 4, a typical permanganate surface preparation consists of four steps: cleaning, conditioning, etching, and neutralization (Xu, 1998). Cleaning removes surface contaminants. Any contaminants would inhibit proper adhesion if allowed to remain on the surface. During conditioning, a solvent diffuses into the matrix and swells the laminate. The etching process micro-roughens the surface providing the mechanical anchoring sites necessary for good adhesion. Neutralization removes residual manganate that forms on the part surface during the etching process.

Figure 4 Surface Preparation Steps

Xu (1998) was able to achieve copper plated weaves tape test adhesion strengths of classification 3 out of a possible 5 per ASTM Test Method D-3359 using the surface preparation method shown in Figure 4.

2.3 Etch Process Conditions

Permanganate etching techniques for micro-roughening composites were originally developed for fiberglass – epoxy composites (Thorn, Edwin, and Walsh, 1991). The three main process steps are conditioning (Schröer, Nichols, and Meyer, 1995), etch (Tomaiuolo, 1986), and neutralization (Van Ast, 1996).

The conditioning process involves diffusing a solvent into the matrix to expand the polymer network. The part is immersed in the solvent conditioner for 4 to 10 minutes at 150 °F. During this time, some polymer-to-polymer bonds are replaced by polymer-to-solvent bonds. These polymer-to-solvent bonds are more readily broken during the permanganate attack. The infusion of conditioner lowers the system activation energy

and increases the rate at which the permanganate ions can attack the surface (Thorn, Edwin, and Walsh 1991).

The part is then etched for 5 to 20 minutes in a 170 °F alkaline permanganate solution. Typical permanganate etching solutions contain approximately 5 to 10 wt% caustic soda. The permanganate solution etches the composite matrix by attacking the chemical bonds within the polymer structure. The resulting lower molecular weight fragments dissolve into the etching solution. Some molecular fragments are further cleaved to result in single carbon atoms that form CO₂.

During the etching, an insoluble film of manganese dioxide (MnO₂) forms on the oxidized surface. If this precipitate were not removed from the surface, the MnO₂ film would prevent the copper from bonding during the plating process. To remove this film, the part is immersed from 4 to 10 minutes in a 150 °F neutralizing bath consisting of a cyclic amine reducing agent in acidic solution.

2.4 Effect of etch Process Conditions on Adhesion

2.4.1 Etch Time Effect on Adhesion

Polycyanate ester (Sohal, 1999) provides higher copper plate adhesion strength until a point when the sample is over etched. Once this point is reached, further etching

will diminish the adhesion strength between the substrate and film. An increase of adhesion followed by a decrease is noted by Sohal (1999) and expressed the 300 g/L line in Figure 5.

Figure 5 Etch Time Effects on Adhesion Strength
(Sohal, 1999)

Xu (1998) noted similar results for test on neat polycyanate ester resins. Xu observed, as etch time increased from 4 minutes to 12 minutes, the surface roughness of neat polycyanate ester resins increased. Kirmann, Sohal, and Xu all observed that etching time effects the resin surface roughness.

2.4.2 Etch Permanganate Concentration Effect on Adhesion

Examining epoxy and polycyanate ester composites/neat resins Xu (1998) and Sohal (1999) observed changes in surface topography that were dependent on etch permanganate concentration. Xu worked exclusively with potassium permanganate. Sohal concluded the higher solubility of sodium permanganate provided the necessary permanganate concentration needed for etching polycyanate ester composites. The results of Sohal's work can be seen in Figure 6.

Figure 6 Permanganate Concentration Effects on Adhesion Strength
(Sohal, 1999)

Increased concentration yields increased adhesion until the substrate is weakened. Over etching the substrate surface happens at lower concentrations if the substrate is etched longer.

Xu (1998) observed similar results using potassium permanganate etching unidirectional carbon fiber- polycyanate ester resin composites. Xu achieved the highest adhesion, as measured by tape test, by etching samples for 12 minutes at permanganate concentrations ranging between 20 and 40 grams per liter permanganate. Etching at higher concentrations, around 60 grams per liter, completely exposed the fibers in the laminate, resulting in lower adhesion strengths as postulated by Xu.

2.4.3 Etch Alkalinity Effect on Adhesion

Process recipes for permanganate etching of composites found in the available literature use alkaline solution. Recipes use at least 40 grams per liter of sodium hydroxide. Adhesion peel strengths for plating metal on epoxy and acrylonitrile-butadiene-styrene (**ABS**) resins have been noted to be permanganate etch pH dependent (Polichette , Leech, and Branigan, 1975). Polichette , Leech, and Branigan peel strength observations are shown in Figure 7.

Figure 7 Alkalinity Dependence of Epoxy and ABS Plastics
(Polichette , Leech, and Branigan, 1975)

Polichette , Leech, and Branigan observed a correlation between etch alkalinity and resulting adhesion strength. That correlation differs dependent on the target material. Polichette , Leech, and Branigan recommend a range of pH 11 to pH 13 for a permanganate solution etching either epoxies or ABS plastics, with an optimum of approximately pH 12.5. Polichette , Leech, and Branigan reported the effects of

alkalinity of permanganate etch on metal plate adhesion only on ABS and epoxy. Karas and Chao (1993) claim the hydroxide concentration for YLA RS-3 Polycyanate ester resin should be from 0.5 Molar (pH 10) to 4.0 Molar (pH>14). Karas and Chao provide this pH range without giving enough information to characterize how the alkalinity of a permanganate etching solution effects the resulting adhesion.

The permanganate available to etch the composite can itself be effected by the alkalinity for the etching solution. Mandich and Krulik (1992) studied the stability of permanganate in alkaline solution, and found permanganate concentration does not change as a function of alkalinity for the range of 0 to 100 grams per liter of NaOH. Mandich and Krulik observed the concentrations seen in Figure 8.

Figure 8 Permanganate/Manganate Conversion in the Presence of NaOH
(Mandich and Krulik, 1992)

The rapid decline of permanganate concentration above 100 grams per liter shown in Figure 8 suggests that little permanganate is available for oxidation in excessively alkaline solutions. However, at moderate alkalinity, the available permanganate is independent of the etching solution alkalinity. The 40 grams per liter NaOH common in surface preparation recipes is well within the stable range shown in Figure 8.

2.5 Literature Review Summary

Considerable data exist defining the plating process. Reviewed literature agrees that surface preparation, and in particular etching, is a key factor in improving the adherence of copper to a composite substrate. Kirmann, Sohal, and Xu examined the effects of etching time and etchant concentration on resulting copper plate adhesion. They found that increasing etch strength, by either time or concentration, will increase the adhesion until a point where degradation of the substrate occurs. After this point, over etching reduces the resulting adhesion. Polichette, Leech, Branigan, Karas and Chao specifically looked at the effects of alkalinity on adhesion. Polichette, Leech, and Branigan observed poor adhesion at low and high alkalinity that differed dependent upon material (epoxy or ABS). Karas and Chao recommend an etch alkalinity of 0.5 to 4.0 Molar NaOH for polycyanate ester resin, but does not describe how changing this alkalinity effects adhesion.

3 Research Hypothesis and Objective

3.1 Hypothesis

The alkalinity of a permanganate etch effects the surface preparation quality of the composite, and correspondingly, the adhesion strength of an electroless copper film.

3.2 Justification

The number of applications and demand for composite materials is increasing. Many of these applications will require the electrical conductance provided by metal plating the composite. The need for refining surface preparation techniques is intensified by this increased demand for plated composites.

Literature has shown etching to be one of the crucial process steps for providing good copper adhesion to the composite substrate. Process recipes for permanganate etching of composites use alkaline solutions. These recipes have been developed for common substrates like epoxy on fiberglass or ABS resins. These recipes use approximately 40 grams of NaOH per liter of permanganate etching solution. Polichette, Leech, and Branigan (1975) states that adhesion strength of ABS and epoxy vary with differing etch alkalinity. Karas and Chao claim an etch alkalinity range of 0.5 to 4.0

Molar NaOH yields acceptable adhesion for copper on polycyanate ester resin, but does not describe how changing this alkalinity effects adhesion.

3.3 Objective

The objective of this study is to characterize how the alkalinity of a permanganate etching solution effects the surface preparation quality of a specific graphite fiber - polycyanate ester resin matrix. The quality of surface preparation is measured by plating copper on the composite then determining the adhesion strength of the plated film.

4 Experimental Procedures

4.1 Experimental Approach

The quality of a copper plated film is determined by both the actual plating process and the surface preparation of the substrate prior to plating. The purpose of this study is to determine the effect alkalinity has on the etch step of this surface preparation. The alkalinity of the etchant was varied while keeping all other parameters of the surface preparation process and plating process constant. In addition to keeping the wet chemical process constant, all target substrate test pieces were cut from the same manufacture lot, and care was taken to maintain constant testing technique. The general experimental flow can be seen in Figure 9.

Figure 9 Experimental Flow Chart for Phase I and Phase II

4.2 Experimental Apparatus

Two distinct procedures were used in this study; surface preparation and electroless copper plating. Surface preparation of the substrate cleans and micro-roughens the composite using the process shown in Figure 10.

Figure 10 Surface Preparation Line

This process replicates the work done by Sohal (1999) and Xu (1998).

The plating process plated 30 μ -inch copper film on the composite using the process line shown in Figure 11.

Figure 11 Copper Plating Line

4.3 Materials and Chemicals

Space Systems Loral provided the substrate for use in this study. The substrate consisted of woven carbon fiber and cured polycyanate ester binding resin. Test parts called coupons were cut from this piece in approximately 1 inch squares. Each coupon had a bag side face and a tool side face. The vacuum curing method used in the production of the laminate is shown in Figure 12 and results in different textures on the diametrically opposing faces.

Figure 12 Substrate Curing Method

The tool side face is formed on the composite surface which rests against the smooth forming die when the composite is cured. This smooth face is the critical surface where copper-plate adhesion strengths were measured. The bag side face maintains the rough texture of the vacuum bag used during the thermal cure of the resin. Typical unprocessed coupons can be seen in Figure 13 and Figure 14. The crosshatched marks seen in Figure 13 are individual fiber bundles.

**Figure 13 Unprocessed Target
Substrate Coupon Bag Face**

**Figure 14 Unprocessed Target
Substrate Coupon Tool Face**

A unique identification number was scribed on the bag side face. This identification number corresponds to those shown in Table 3 and Table 4. Two racking holes were drilled in each coupon. Coupons were racked using a 20 gauge copper wire looped through one of these holes. The opposite end of the wire was wrapped around a glass rod that served as a flight bar during processing. The copper wire was kept long enough to suspend the coupon in the middle of the preparation solutions.

Table 1 shows a list of chemicals and manufactures used for surface preparation of the substrate.

Table 1 Chemical Bill of Materials for Surface Preparation

Chemical	Description	Source
Sodium Hydroxide (for Alkaline Clean)	Solid Pellets	Alan Baker
Sulfuric Acid	Liquid	Stock
Sodium Permanganate	Proprietary liquid mixture (Eprep-201)	Electo-Chemicals
Sodium Hydroxide (for Etch Alkalinity)	Proprietary liquid mixture (Eprep-202)	Electo-Chemicals
N-Methyl Pyrrolidone	Proprietary liquid (Hole Cleaner 340)	Electo-Chemicals
Organic Cyclic Amine	Proprietary liquid (Eprep Neutralizer)	Electo-Chemicals

Concentrations listed in Table 1 are *as received* and were diluted as needed. Table 2 shows a list of chemicals and manufactures used for electroless copper plating.

Table 2 Chemical Bill of Materials for Plating

Chemical	Description	Source
Stannous Chloride	Proprietary liquid mixture (PD Pre-Catalyst)	Ato-Tech
Palladium – Tin	Proprietary liquid mixture (PTC Catalyst)	Ato-Tech
EDTA and NaOH	Proprietary liquid mixture (Accelerator)	Ato-Tech
Copper Sulfate	Proprietary liquid mixture (MR-A)	Ato-Tech
Sodium Hydroxide	Proprietary liquid (MR-B)	Ato-Tech
Sulfuric Acid	Liquid	Stock
Proprietary Organic Coating	Proprietary liquid (Oxyban)	Dynachem

Concentrations listed in Table 2 are *as received* and were diluted or mixed as needed.

4.4 Experimental Procedure for Surface Preparation

All process steps in the surface preparation procedure are followed by 2 minute immersion rinses to prevent cross contamination of process baths and samples. As shown in Figure 10, coupons were cleaned in the first step. The objective of this cleaning is to remove foreign matter from the substrate surface. Since the identities of the foreign materials were not known, the coupons were cleaned in an alkaline solution to remove alkaline soluble material and then in acidic solution to remove acidic soluble material. Coupons were immersed in a 65 °C 12 molar sodium hydroxide solutions for two minutes. Once rinsed, the coupons were immersed for 2 minutes in an ambient temperature 3 volume percent solution of sulfuric acid.

The clean parts were immersed in a conditioner to swell the matrix: making it more susceptible to the permanganate attack. This conditioning was achieved by immersion for five minutes in a 50 volume percent solution of n-methyl pyrrolidone (NMP) at 65 °C. The clean and swollen parts were then ready for etching.

Wet etching was employed to micro-roughen the substrate surface. All coupons were etched for 25 minutes in a 300 grams per liter solution of sodium permanganate at a temperature of 65 °C. The alkalinity of this etchant was varied. The NaOH concentration was varied from 0 to 80 grams per liter.

Particulate inclusions in the matrix are exposed when the binding resin is removed by etching. Precipitates such as manganese dioxide also form a film on the substrate surface. If allowed to remain, this film would inhibit copper adhesion. To remove this film, the coupon was immersed in a solution of 8 volume percent E-prep Neutralizer and 8 volume percent sulfuric acid. The coupon was immersed in the 45 °C neutralizer for 5 minutes.

4.5 Experimental Procedure of Electroless Deposition of Copper Metal

Plating the coupons consisted of re-cleaning the surface, increasing the hydrophilic nature of the surface, deposition of a palladium-tin colloid, removing tin from the surface colloid leaving the active palladium sites to catalyze the copper plate reaction, then plating.

After the coupons were cleaned, as per the two first steps of the surface preparation procedure, they were immersed for 5 minutes in an ambient temperature Pd Pre-Catalyst surfactant. The now hydrophilic surface absorbs the stannous chloride (SnCl_2) from solution. The coupons were taken from this tank, and were immediately immersed in an ambient temperature palladium-tin catalyst tank. Nucleation of metallic palladium on the substrate surface occurs when the palladium ion is reduced on the surface by the impregnated stannous ion. After rinsing in DI water for 2 minutes, the

coupons were immersed in an ambient temperature acceleration bath for 7 minutes to remove the oxidized stannic ion. The coupons were taken from the acceleration bath, rinsed in DI water for 2 minutes, then plated.

The palladium impregnated composite was plated using a mixture consisting of Ato-Tech Medium Rate Electroless Plating solutions; MR-A and MR-B. The mixture of copper sulfate and formaldehyde undergo the plating RedOx reaction, as expressed in equations 1 through 3, depositing metallic copper on the composite surface. Additional ingredients in the solution; EDTA and sodium hydroxide control this rate of reaction. The deposition rate and the plating time determine the plate thickness. Plating time was held constant at 30 minutes yielding a copper film thickness of approximately 30 μ -inches.

Equation 1 Anodic Reaction

Equation 2 Cathodic Reaction

Equation 3 Combined Reaction

Coupons were placed in the ambient temperature copper-plating tank. Load size for the one-liter tank was kept between 4 and 38 square inches of plating surface, and averaged approximately 12 square inches. After plating, the coupons were rinsed for 2 minutes with DI water.

The post plate treatment is designed to neutralize and remove any remaining plating solution and to protect the copper coating. After plating, the coupons were rinsed in DI water for 2 minutes. Then the parts were neutralized in an ambient temperature solution of 3 percent sulfuric acid for 2 minutes. The coupons were rinsed again with DI water. An anti-oxidant, Oxyban, was applied to protect the copper coating. Parts were immersed in the ambient temperature Oxyban solution for 2 minutes. Then they were rinsed in DI water for 2 minutes. Finally, the parts were dried using compressed air, and placed in an oven for 30 minutes at 75 °C to further dry the part.

4.6 Experimental Plan

Permanganate etch alkalinity was the only process parameter modified in this investigation. Experimentation was accomplished in two phases. Phase I located the dynamic region of etch alkalinity. Phase I included and bracketed the etch alkalinity used by both Sohal (1999) and Xu (1998). Adhesion response to etch alkalinity of 0, 40, and 80 grams NaOH per liter permanganate etching solution was observed. The Phase I test scheme can be seen in Table 3.

Table 3 Experimental Phase I

Run #	NaOH Concentration (grams/Liter)	Coupon ID
1	0	0300A
		0300B
		0300C
2	40	0340A
		0340B
		0340C
3	80	0380A
		0380B
		0380C
4	0	0200A
		0200B
		0200C
5	40	0240A
		0240B
		0240C
6	80	0280A
		0280B
		0280C

Denoted in Table 3 is a repeatability measure achieved by etching three coupons per alkalinity. Reproducibility was measured (runs 4 – 6 in Table 3) by repeating etch alkalinity range on another day using a different copper-plate bath.

Once the first section of Phase I (runs 1 – 3 in Table 3) was complete, experimental test Phase II (shown in Table 4) was develop to provide more information in the regions Phase I indicated to have dynamic alkalinity response. Phase I results indicated this dynamic region was between 0 and 40 grams per liter of NaOH. Coupons were also

etched at 60 grams per liter NaOH and plated to determine if a maximum existed between 40 and 80 grams per liter NaOH, or if adhesion strength is independent of etch alkalinity for highly alkaline etches. One coupon for each alkalinity run was etched but left unplated. Visual observations of this surface were used to relate surface topography to the resulting copper adhesion.

Table 4 Experimental Phase II

Run #	NaOH Concentration (grams/Liter)	Coupon ID
1	10	0110A
		0110B
		0110C
2	20	0120A
		0120B
		0120C
3	30	0130A
		0130B
		0130C
4	60	0160A
		0160B
		0160C
5	10	0210A
		0210B
		0210C
6	20	0220A
		0220B
		0220C
7	30	0230A
		0230B
		0230C
8	60	0260A
		0260B
		0260C

A stud was bonded to the tool side of the copper plated test coupon using an epoxy resin. The shank of the stud was gripped in the chuck as shown drawn on Figure 15. The stud was then pull vertically down by the Sebastian-five apparatus until the coating failed. The force at which the coating failed was divided by the surface area of the stud face to yield the adhesion strength of the copperplate.

4.7.1 Preparation of the Plated Samples for Testing

All studs used for adhesion test were 0.106 inch diameter epoxy coated aluminum studs (Quad Group part # 901106). The test sample was sandwiched between the thermal-set epoxy face of the stud and an thermal-set epoxy coated 0.866 inch square ceramic backing plate (Quad Group part # 901866) as shown in Figure 16.

Figure 16 Adhesion Test Stud Mount

The spring clip shown in Figure 16 provided the necessary clamping force to keep the stud perpendicular to the coupon face while the epoxy cured. A ceramic backing plate was used to add rigidity to the test sample ensuring the stud and the sample face remained

perpendicular during the stud pull. The test coupons were mounted in these clips and placed into a 150 °C oven for one hour. After an hour the backing plate, coupon, and stud, now adhered together, were allowed to cool to room temperature. The clamping clips were removed and the coupons tested using the Sebastian-five apparatus.

4.7.2 Stud pull testing

All coupons were tested at SSL using a Sebastain-Five stud pull apparatus. The test coupon was placed stud face down with the stud passing through a 0.106 stud sized vertical test die. The pull chuck seen in Figure 17 gripped and pulled the stud.

Figure 17 Sebastain-five Stud Chuck

The Sebastain-Five force limit knob was set to 100%, the scaling switch was set to force, and the rate knob was set to $\frac{3}{4}$ of maximum rate. All samples were tested with these same settings. The Sebastain-Five was started on its testing algorithm and the final pull force logged. A good adhesion test is made by a true perpendicular pull removing all copper, but not fiber, from an exact known circular area. If fiber is removed with the plated copper, the failure mode has changed to that of the composite and the pull test is no longer measuring the copper adhesion strength of the copper, but rather the binding resin strength.

4.7.3 Data Analysis Methods

Pull forces were measured. These forces were converted into their corresponding adhesion strengths by dividing the pull force by the pull area (0.008823 square inches). The adhesion pull strength was plotted against the alkalinity of the permanganate etch that produced the surface topography. Error bars on this plot were calculated based on a 95% confidence (2σ) calculated using both original and repeated runs.

5 Results and Discussions

5.1 Introduction

Results are shown for composite coupons prepared and plated by methods listed in Chapter 4. These results include adhesion strengths measured by stud pull, and high power microscope photographs depicting the results of etching the composite surface. Photographs of blistered copper plating show the results of an improperly prepared surface.

5.2 Surface Etching

The permanganate etch is strong enough to expose the fiber bundles. Figure 18 shows the surface of an unetched coupon. Figure 19 shows an example of an etched laminate.

Figure 18 Unetched Sample Surface

**Figure 19 40 grams/Liter NaOH
Permanganate Etched Sample**

The smooth and slick surface shown in Figure 18 would be difficult to plate. The copper has no “finger holds” to adhere. The surface shown in Figure 19 has etch pits of removed resin that provide mechanical anchoring sites for the copper to bond. Figure 20 shows a laminate where the etching has removed the resin material to expose fiber bundles indicated by the lighter shading.

Figure 20 Exposed Fiber Bundle Tops from 40 Grams NaOH per Liter Permanganate Etch

The lighter sections shown in Figure 20 are the tops of the fiber bundles where one bundle has crossed over another in the fiber weave.

In addition to bulk removal of the surface resin, anisotropic etching occurs. Locations on the composite that are stressed from chemical conditioning etch more. These locations are the pits that provide the mechanical anchoring sites needed for sufficient adhesion. Figure 21 shows a close up of the sample seen in Figure 20 and shows these pits.

Figure 21 Erode Surface Needed for Plating from 40 Grams per Liter NaOH Permanganate Etch

Slight exposure of the fiber and micro-pitting the resin surface as shown in Figure 21 is desired and this topography is indicative for samples with adhesion strengths greater than 1000 PSI.

5.3 Effects of Excessively Low Etch Alkalinity

Coupons that were etch in permanganate solution containing less than 30 grams per liter sodium hydroxide blistered. One of the samples that blistered can be seen in Figure 22.

Figure 22 Blistered Plated Sample - 20 Grams per Liter NaOH

Blisters are regions of no copper adhesion to the substrate. The raised sections of copper seen in Figure 22 are blisters. Samples that were etched in low alkaline solutions blistered. An example of an unplated surface that was etched by a permanganate solution without the addition of any sodium hydroxide can be seen in Figure 23.

Figure 23 Unplated Sample Etched by Permanganate Solution with out any NaOH

This surface is too smooth to plate well. The surface topography is similar to that of the unetched sample shown in Figure 18. None of the samples etched with bath alkalinity below 30 grams per liter plated without blistering. These blistered samples exhibited low and inconsistent copper adhesion. A tape-test as shown in Figure 24 provides a quick qualitative examination of the copper plate adhesion.

Figure 24 Tape Test of a Blistered Sample – 10 grams/Liter NaOH

These blistered samples demonstrate the requirement for permanganate etch bath alkalinity of at least 40 grams per liter of sodium hydroxide.

5.4 Stud Pull Adhesion Results

Tests using a Sebastain-Five stud pull apparatus are used to provide quantitative adhesion data. The stud is adhered with epoxy perpendicular to the test sample as shown in Figure 25.

Figure 25 Plated Sample Ready for Adhesion Testing

The epoxy on the stud pulls the copper off the sample leaving only the composite laminate as shown in Figure 26.

Figure 26 Stud Pull Site

A good adhesion test is made by a true perpendicular pull removing all copper, but not fiber, from an exact known circular area. Blistered samples often exhibited non-precise pull area as shown in Figure 27.

Figure 27 Blistered Pull Site from Sample Etched with No Addition of NaOH to Permanganate Etch

The inaccurate pull areas yielded inconsistent pull forces, and explains much of the data variation shown in Table 5.

The data from these pull tests are correlated with the etch bath alkalinity that prepared each test sample and are shown in Table 5.

Table 5 Adhesion Strengths from Various Alkalinity Etches

Etch Alkalinity (Grams NaOH/Liter)	Average Adhesion Strength (PSI)	Number of Data Points Used in Average	2 σ Confidence ($\pm$ PSI)
0	717	4	949
10	593	4	1287
20	799	3	629
30	1160	4	557
40	1410	2	507
60	1385	4	860
80	1655	4	125

Table 5 shows the adhesion strengths of samples where the copper separated from the substrate surface. Two adhesion measurements from samples etched at 40 grams per liter NaOH were excluded because the substrate yielded before the copper-plate. These pulls, though indicating good adhesion, produced a measurement of the matrix strength rather than the copper-plate adhesion strength. One measurement at 20 grams per liter NaOH was excluded because the stud pulled at an angle. The ripping action or an angular pull yields a lower than true adhesion strength.

The copper plate adhesion strength dependence on permanganate etch alkalinity can be seen in Figure 28.

Figure 28 Copper Adhesion Strength Dependence on Etch Alkalinity

Figure 28 shows three general regions. Below 15 grams per liter of NaOH etch concentration yields low adhesion without direct dependence on alkalinity. A transition area exist between 15 and 40 grams per liter NaOH where adhesion strength depends on etch alkalinity. In a region between 40 and 80 grams per liter NaOH etch strengths are the highest of those measured and are not dependent on the alkalinity of the etch bath. This alkalinity concentration region is the most stable to operate a permanganate etch bath.

The repeatability of these results was measured by repeating the surface preparation process and plating a different set of coupons on a different day. This second set of test coupons exhibited the same adhesion response to alkalinity as the first experimental regiment. The results of both experimental tests and the average of the two can be seen in Figure 29.

Figure 29 Experimental Reproducibility

6 Overall Conclusions

A permanganate etch bath for polycyanate ester resin should contain at least 40 grams of NaOH per liter of etching solution. Lower than 40 grams per liter NaOH will result in a blistered copper coating when plated. No discernable adhesion dependence on etch alkalinity is noted between 40 and 80 grams per liter NaOH. Copper plate adhesion strength of approximately 1400 PSI is achievable when operating in this alkalinity range.

This investigation was successful in that the effect of etch alkalinity on copper plate adhesion was characterized. Moreover, an alkalinity range of 40 to 80 grams per liter NaOH was found that produces SSL's requirement of at least 1000 PSI copper adhesion.

7 Recommendations for Future Research

As the demand of materials with improved properties grows so will the need to research fabrication methods. Recommendations for future research into plating composites can be classified into two areas; an examination of process variables effecting the chemical methods described in this thesis, and the utilization of different chemistries to prepare and plate composites.

One of the factors effecting the surface topography is the amount of resin on the surface. As shown in this thesis, exposing some carbon fibers improves the adhesion. Both Sohal (1999) and Xu (1998) noted increased adhesion by etching until the point of weakening the composite. One future study could examine the effects of resin starvation or excess resin on the composite surface. Though beyond the scope of this work, one observation during this work indicated that resin starvation effect adhesion. The diametrically opposing coupon faces plated very differently. Even at low alkalinity when the plated tool-side face blistered the bag-side face of the same coupon did not. As seen in Figure 30, the bag-side is resin starved.

Figure 30 Unprocessed Coupon Bag-side Face

Fabrication methods may be able to produce a pre-roughened surface. Ideally a surface that is produced innately micro-roughened would only need to be cleaned before plating.

Another promising area for further research involves an evaluation of other chemical methods to achieve the same plated composite end result. These new chemistries can achieve the same end result with less impact on the environment. One such examination is replacing formaldehyde in the copper plating solution. Formaldehyde is a toxin. It presents a danger to both the process technician and the environment. Other reducing

agents can be researched and presented to replace formaldehyde in the copper bath. Different conditioners can also be investigated.

As mentioned earlier in this thesis, electroless plating is necessary because the substrate does not conduct electricity. Once a thin film of copper is deposited onto the surface, electrolytic plating is possible. Different ratios of electroless and electrolytic plating should yield different plate properties, and are realms for further investigation.

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