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Latent Fingerprint Enhancement on a Brass Metal Surface using Paint Electrodeposition

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LATENT FINGERPRINT ENHANCEMENT ON A BRASS METAL SURFACE USING PAINT ELECTRODEPOSITION

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in partial fulfillment of the requirements
for the degree of
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DEDICATION

This thesis is dedicated to the three most important people in my life: my mom, brother, and sister. I thank each of you for your unconditional love, encouragement, and support as I fulfill my dream of becoming a Forensic Chemist.

ABSTRACT

Fingerprint evidence recovered at a crime scene plays a key role in apprehending a suspect. Cyanoacrylate fuming is one the most successful methods of enhancing fingerprints from metallic surfaces. Despite the success of cyanoacrylate fuming, fingerprint recovery on fired cartridge casings is rarely successful. Therefore, a new fingerprint development method is needed to enhance fingerprint evidence that may still be present on fired cartridge casings. The aim of this research project is to study the use of metal and paint electrodeposition to enhance fingerprints on a brass metal surface.

High throw power paint was used in the initial study; high throw power paint is formulated to coat the surface of the metal disks as well as any pits or crevices on the surface. These initial experiments showed that commercial high throw power paint had a tendency to cover not only the bare metal surface, but the fingerprint residue. In the next round of experiments, adjustments to the formulation were made to decrease the binder concentration by addition of carbon black and polyethylene glycol. The pH of the high throw power paint was adjusted with the addition of acetic acid and ammonium hydroxide. Dilution of paint showed a modest increase in fingerprint enhancement. Changes in paint morphology upon adjustment of the binder and non-aqueous components were observed.

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The process to completing my Master’s thesis began six years ago as I started my journey as an undergraduate at the University of New Haven. I would like to thank professors in both the Chemistry and Forensic Science departments for the foundation that was poured into me. Specifically, Dr. Adamowicz and Dr. Saliby, Thank You both for answering any and all questions that arose while I was a student and your willingness to constantly write letters of recommendation.

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TABLE OF CONTENTS

CHAPTER PAGE

1: INTRODUCTION 1

1.1: Purpose of the Project 1

1.2: Overview of the Project 1

1.3: Aim and Scope of the Project 1

2: LITERATURE REVIEW 3

2.1: Fingerprint Background 3

2.1.1: Fingerprint Ridge Characteristics and Patterns 3

2.1.2: Fingerprint Composition 4

2.2: Latent Fingerprint Enhancement Methods 4

2.2.1: Fingerprint Powder Technique 4

2.2.2: Ninhydrin 4

2.2.3: Cyanoacrylate Fuming 5

2.3: Development Techniques used on Cartridge Casings 5

2.4: Limitations of Fingerprint Development on Cartridge Casings 6

3: METHODS AND MATERIALS 7

3.1: Materials and equipment 7

3.2: Metal Deposition Solutions 7

3.2.1: Copper Metal Solutions 7

3.2.2: Nickel Metal Solutions 7

3.3: High Throw Power Paint Solutions 7

3.3.1: Powercron 6000CX Solutions Diluted with Deionized Water 7

3.3.2.: Powercron 6000 CX Solution Modified with Carbon Black 8

3.3.3: Powercron 6000 CX Solution Modified with Polyethylene Glycol 8

3.3.4: Powercron 6000 CX Diluted with Acids and Bases 8

3.3.4.1: Modified with Acetic Acid 8

3.3.4.2: Modified with Ammonium Hydroxide 8

3.4: Deposition Setup and Process 8
  3.4.1: Brass Disk Electrode Preparations 8
  3.4.2: Fingerprint Deposit 8
  3.4.3: Metal Deposition Experiments 9
    3.4.3.1: Potentiostat Settings 10
  3.4.4: High Throw Power Paint Deposition Experiments 10
    3.4.4.1: Power Supply Settings 11
    3.4.4.2: pH Measurements 11
4: METAL DEPOSITION RESULTS AND DISCUSSION 12
4.1: Introduction 12
4.2: Copper (II) Sulfate Deposition Results 13
  4.2.1: Copper (II) Sulfate without PEG 13
  4.2.2: Copper (II) Sulfate with PEG 15
4.3: Nickel (II) Sulfate Deposition Results 17
4.4: Discussion and Conclusions 18
5: PAINT DEPOSITION RESULTS AND DISCUSSION 20
5.1: Introduction 20
5.2: High Throw Power Paint Results 21
  5.2.1: Conclusion 24
5.3: Powercron 6000CX Solution Diluted with Deionized Water Results 25
  5.3.1: Conclusions 28
5.4: Powercron 6000CX Solution Modified with Carbon Black Results 28
5.5: Powercron 6000CX Solution Modified with Polyethylene Glycol 29
5.6: Powercron 6000CX Solution pH Measurements 30
5.7: Powercron 6000CX Solution Modified with Acids and Bases 31
  5.7.1: Modified with Acetic Acid 32
  5.7.2: Modified with Ammonium Hydroxide 32
5.8: Future Directions 33

5.9: Conclusions..34

6: CONCLUSION..36

6.1: Metal Deposition Conclusions..36

6.2: Paint Deposition Conclusions..36

6.3: General Conclusion..36

WORKS CITED..38

APPENDIX A: METAL DEPOSITION RESULTS SUMMARY TABLES AND CURVE PLOTS..40

APPENDIX B: PAINT DEPOSITION RESULTS SUMMARY TABLES..50

LIST OF FIGURES

FIGURE PAGE

2.1: Fingerprint Ridge Characteristics 3

2.2: Fingerprint Morphology Patterns 4

3.1: Image of the metal disk set-up 9

3.2: Image of the potentiostat and metal solution setup 9

3.3: Image of Power Supply, paint solution, and multimeter setup. 11

4.1: Images of Metal Disks after Copper (II) Sulfate Deposition using Amperometric i-t Curve for 300 seconds with the following conditions: (Disk 1) -0.6V, resulting in a an average current of 0.03A, total charge of 9C, and a calculated thickness of 1.15 µm; (Disk 2) -0.6V, resulting in an average current of 0.019A, total charge of 5.7C, and a calculated thickness of 0.73 µm. 14

4.2: Amperometric i-t Curves produced from copper metal deposition in Figure 4.1 (a) typical of Disk 1; (b) typical of Disk 2 14

4.3: Images of Metal Disks after Copper (II) Sulfate Deposition using Chronocoulometry for 300seconds at -5V followed by +5V for 300 seconds. 15

4.4: Charge-Time Curve produced from copper metal deposition in Figure 4.3 15

4.5: Image of Metal Disk 4 after Copper (II) Sulfate Deposition with PEG using Amperometric i-t Curve for 300 seconds at -0.6V, resulting in an average current of 0.025A, total charge of 7.5C, and a calculated thickness of 0.96 µm. 16

4.6: Images of Metal Disks after Copper (II) Sulfate Deposition with PEG using Chronopotentiometry: (Disk 5) -0.3V, resulting in an average current of 0.01A, a total charge of 3C and a calculated thickness of 0.38µm; (Disk 6) -0.5V, resulting in an average current of 0.03A, a total charge of 9C, and a calculated thickness of 1.15 µm. 16

4.7: Potential vs Time Curve produced from copper metal deposition in Figure 4.7: (a) Disk 5; (b) Disk 6 17

4.8: Images of Metal Disks after deposition from a Nickel (II) Sulfate solution using Amperometric i-t: (Disks 7a and 7b) -0.6V for 300sec., resulting in an average current of 0.0185A, a total charge of 5.55C,and calculated thickness of 0.66 µm; (Disk 8) -0.8V for 500 sec., resulting in an average current of 0.032A, a total charge of 16C, and calculated thickness of 1.91 µm; (Disk 9) -0.4V for 500 sec., resulting in an average current of 0.0004A, total charge of 0.2C, and calculated thickness of 0.02 µm. 18

4.9: Current vs Time Curves produced from nickel metal deposition in Figure 4.8: (a) Disks 7a and 7b; (b) Disk 8, (c) Disk 9 18
5.1: Positively charged resin encapsulating pigment particle 20
5.2: Image of Metal Disk after Powercron 6000CX Paint Deposition using Amperometric i-t Curve (pictured) for 300 seconds at -10V, resulting in an average current of 0.0018A and total charge of 0.54C. 21
5.3: Images of Metal Disks after Powercron 6000CX Paint Deposition: (Disk 2) 500V for 9s; (Disk 3) 401V for 150s; (Disk 4) 350V, 7.4s; (Disk 5) 200V for 240.7s; (Disk 6) 100V for 30.5s; (Disk 7) 50V for 360s. 22
5.4: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 150V for 300 seconds for each disk. 22
5.5: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 150V for 300 seconds for each disk. 23
5.6: Current vs Time Curve produced from Powercron 6000CX Paint Deposition in Figure 5.5; represents normal current vs time curve for paint deposition experiments. 24
5.7: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 149V resulting in an average current of 1A: (Disk 14) with a total charge of 10C after 10 sec; (Disk 15) with a total charge of 5C after 5sec. 24
5.8: Image of Metal Disks after Powercron 6000CX Paint Deposition (50% Diluted) with an applied voltage of 150.7V, a final current of 2 mA after 8 seconds. 25
5.9: Image of Metal Disks after Powercron 6000CX Paint Deposition (25% Diluted); (Disk 17) applied voltage of 151.8V, resulting in a final current of 2 mA after 7 seconds; (Disk 18) applied voltage of 76.5V, resulting in a final current of 1mA after 10 seconds; (Disk 19) applied voltage of 40.85V, resulting in a final current 1mA after 11 seconds; (Disk 20) applied voltage of 10.61V, resulting in a final current of 3mA after 10 seconds; (Disk 21) applied voltage of 5.94V, resulting in a final current of 8mA after 6 seconds. 26
5.10: Image of Metal Disks after Serial Diluted Powercron 6000CX Paint Deposition after 180 seconds for each disk: (Disk 22) 10% concentration, applied voltage of 151.2V; (Disk 23) 8% concentration, applied voltage of 151.3V; (Disk 24) 4% concentration, applied voltage of 148.4V; (Disk 25) 2% concentration, applied voltage of 150; (Disk 26) 1% concentration, applied voltage of 151.3V 27
5.11: Schematic Representation of the diffusion layer of the hydroxyl ions 27

5.12: Reaction Scheme of Reduction of Paint Throw Power after the addition of Carbon Black Powder 28

5.13: Image of Metal Disks after Powercron 6000CX Paint Modified with Carbon Black Deposition: (Disk 27) 2% paint concentration and 25 mg/mL carbon black with an applied voltage of 151.3V for 20 seconds; (Disk 28) 15% paint concentration and 15 mg/mL carbon black with an applied voltage of 151.2V for 41 seconds. 29

5.14: Current vs Time Curve produced from Powercron 6000CX Paint Deposition modified with Carbon Black Fingerprint Powder. 29

5.15: Image of Metal Disks after Powercron 6000CX Paint Modified with Polyethylene Glycol: (Disk 29) 25 mg/mL 3350 PEG, an applied voltage of 151.2V for 180 seconds; (Disk 30) 25 mg/mL 8000 PEG, an applied voltage of 151.7V for 75 seconds; (Disk 31) 25 mg/mL 400 PEG, an applied voltage of 151.2V for 180 seconds. 30

5.16: Current vs Time curve plot for 2% and 1% diluted paint solutions deposition experiments; (top) 2%; (bottom) 1%. 31

5.17: Image of Metal Disks after Powercron 6000CX Paint Modified with Acetic Acid with an applied voltage of 150.8V for 180 seconds: (Disk 32) 25mg/mL Glacial Acetic Acid; (Disk 33) 25 mg/mL 6M Acetic Acid; (Disk 34) 25 mg/mL 1:10 Diluted Acetic Acid 32

5.18: Image of Metal Disk after Powercron 6000CX Paint Modified with Dilute Ammonium Hydroxide with an applied voltage of 151.4 for 180 seconds. 33

5.19: Electrografting Reaction of Benzenediazonium salt: (Scheme 1): Reduction of Benenediazonium on carbon, metal, or silicon surface; (Scheme 2): Polymerization of Benenzediazonium to produce film on carbon surface 33

5.20: Chronoamperometric curve of benezenendiazonium electrografting reaction with different R-substituents (a): R is a Nitro group; (b) R is a hydrogen 34

LIST OF TABLES

TABLE PAGE

2.1: Fingerprint Development Techniques used in a recent Research Experiment 5
4.1: Literature Values for Equations 4.1-4.5 13
4.2: Summary of Nickel Electrodeposition Conditions 17
5.1: Summary of 25% Diluted Paint Electrodeposition Conditions 25
5.2: Summary of Serial Diluted Paint Electrodeposition Conditions 26
5.3: Average pH Measurement of each Powercron 6000CX Paint Solution 30
5.4: Average pH Measurement of each Powercron 6000CX Paint Solution after Modification with Acetic Acid 32

LIST OF EQUATIONS & REACTION SCHEMES

EQUATIONS & REACTION SCHEMES PAGE

2.1: Chemical Reaction between Ninhydrin and Amino Acids to produce Ruhemannn's purple 5
3.1: Constant Current Equation; Variables are as follows: Q—Charge in Coulombs; I—Current in amperes; t—Time in seconds. 10
4.1-4.5: Metal Deposit Thickness Equations 12
5.1: Production of Hydroxide ions and Pigment Particles without a surface charge 20

ABBREVIATIONS

Amperes	A
Aqueous State	Aq
Centimeter	cm
Coulombs	C
Current versus Time	i-t
Micrometer	µm
Milliamperes	mA
Molecular Weight	MW
Polyethylene Glycol	PEG
Unit of Concentration (grams per liter)	g/L
Unit of Concentration (milligrams per milliliter)	mg/mL
Unit of Concentration (Molar)	M
Unit of Density (grams per cubed centimeter)	g/cm^3
Unit of Molecular Weight (grams per mole)	g/mol
Unit of Volume (milliliter)	mL
Voltage	V

CHAPTER 1

INTRODUCTION

1.1: Purpose of the Project

Fingerprint evidence recovered at a crime scene play a key role in apprehending a suspect. Both patent and latent prints can be recovered from the crime scene. A patent print is visible to the naked eye [1]. A latent print is a hidden print that requires some form of development [1]. Most commonly used development techniques are fingerprint powder with a gel lifter, ninhydrin, and cyanoacrylate (super glue) fuming [1]. Cyanoacrylate fuming is one of the most successful methods to obtain fingerprints from metallic surfaces [2]. Despite the success of cyanoacrylate fuming, a research experiment at the Bureau of Alcohol, Tobacco, Firearms, and Explosives concluded only 0.12% of fingerprint developments produce identifiable fingerprints [3]. The high temperature reached when a gun is fired damages fingerprint residues that were present from the suspect who fired the gun. Therefore, a new fingerprint development method is needed to enhance fingerprint evidence that may still be present on fired cartridge casings. The aim of this project is to experiment the use of paint electrodeposition to enhance a latent fingerprint on a brass metal surface.

1.2: Overview of the Project

The goal of the project is to investigate methods of depositing material on a bare metal surface of a fingerprint pattern while leaving fingerprint residue coated areas uncovered, resulting in enhancement of latent fingerprints. Ideally, a coating of the bare metal areas would lead to a highly contrasting surface compared with the lipid residue coated areas of the pattern. Electroreduction rather than electrooxidative processes were chosen for investigation since copper in shell casings can be oxidized, but not reduced. Two chemical systems were chosen for study; electrodeposition of metals and electrodeposition of paint.

1.3: Aim and Scope of the Project

Preliminary electrodeposition experiments were completed using copper and nickel metal solutions on brass metal disks. Metal deposition was studied because the formulations are well characterized and the electrodeposition occurs at nearly 100% coulombic efficiency [4]. This high efficiency means that the thickness of the electrodeposited metal can be controlled by controlling the amount of current. Previous work suggests that about 50% of the fingermark area is insulated and that growth of films on the order of 0.3-2 μm high does not overfill the trenches [5]. However, the thickness of fingerprint residue may be as thick as 0.1 μm with considerable variability due to factors including the moisture on the fingertip, applied pressure and condition of the substrate [6]. Preliminary experiments were completed to determine the optimal coating thickness for deposited fingerprints on a brass metal surface. Constant current and constant voltage conditions were studied and the average total charge was determined. Two different compositions of copper (II) sulfate solutions and one nickel (II) sulfate solution were studied. Both copper (II) sulfate solutions were prepared using copper (II) sulfate, concentrated sulfuric acid, sodium chloride and deionized water. Only one copper (II) sulfate solution had the addition of polyethylene glycol. Copper metal deposits with the addition of polyethylene glycol were compared to the metal deposits without the addition of the brightener. A nickel (II) sulfate solution was prepared using nickel (II) sulfate, nickel (II) chloride, boric acid, and deionized water. Metal solutions studied included chloride ions to provide high throwing power and polyethylene glycol as a brightener.

Paint electrodeposition was completed on brass metal disks as completed in the automotive industry [7]. Two brass metal disks approximately 1cm apart was submerged into a high throw power paint solution. A fingerprint was deposited onto one of the brass metal disks. A voltage was applied to the system and a current passed through the disks. As the current passes through, water molecules are reduced to hydrogen gas and hydroxide ions. The hydroxide ion forms on the surface of the metallic disk and diffuses away from the electrode where it encounters paint particles [8]. The hydroxide ion deprotonates the paint particles which causes the paint particles in solution to precipitate on the metal surface in the reaction: $\text{Paint}^{+}_{(aq)} + \text{OH}^{-} \rightarrow \text{Paint}_{(solid)}$. Modifications to the paint formulation were completed using deionized water, carbon black fingerprint powder, three molecular weights of polyethylene glycol (MW 400, 3350, 8000 g/mol), acetic acid, and ammonium hydroxide. Both constant current and constant voltage conditions were evaluated with various solution formulations.

CHAPTER 2

LITERATURE REVIEW

2.1: Fingerprint Background

A fingerprint is friction ridge skin that leaves an impression of its shape when it comes into contact with an object [1]. There are three types of fingerprints: patent, latent, and plastic. Patent fingerprints are visible to the naked eye left in blood, paint or ink [1]. Latent prints are fingerprints invisible to the naked eye and need physical or chemical enhancements to be seen [1]. Plastic fingerprints are 3D imprints made in clay, putty, or melted plastic [1].

2.1.1: Fingerprint Ridge Characteristics and Patterns

Ridge characteristics and morphology patterns make each fingerprint unique and individual [9]. Figure 2.1 shows examples of different ridge characteristics. The main ridge characteristics are ridge endings, bifurcations, ridge dots, and enclosures. A ridge ending terminates within the friction ridge structure [1]. Bifurcations are new ridges splitting from existing primary ridges [1]. A ridge dot is an isolated ridge detail. An enclosure is ridge detail that bifurcates and rejoins after a short course and continues [1]. Fingerprints also have unique morphological structures.

Whorls, loops, and arches are the three main types of morphology patterns present in a fingerprint. Figure 2.2 provides an example of each type of pattern. Loops are ridge lines that enter from one side of the print and curve around to exit the same side [9]. A whorl is a rounded or circular shaped ridge pattern [9]. An arch is a ridge line that enters from one side of the print and flows out the other side [9]. An average fingerprint has approximately 150 ridge characteristics making fingerprints individual, unique characteristics used for identification.

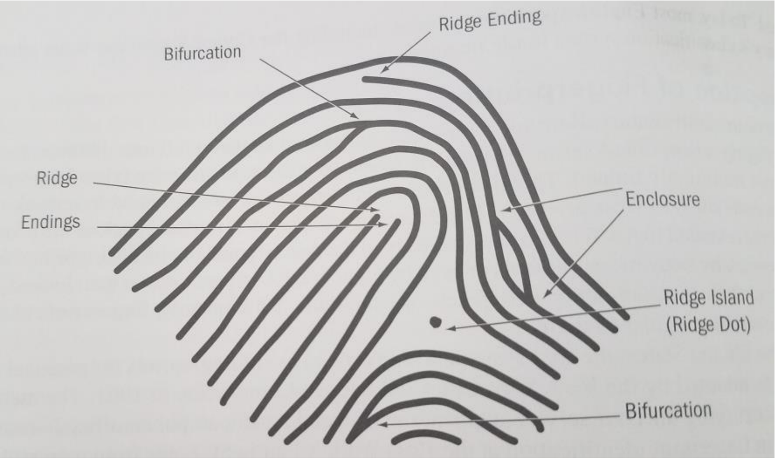


Figure 2.1: Fingerprint Ridge Characteristics

Source: Saferstein, R. *Criminalistics: An Introduction to Forensic Science,* 10th ed.; Pearson: New Jersey, 2011; pp. 391-392, 394, 423

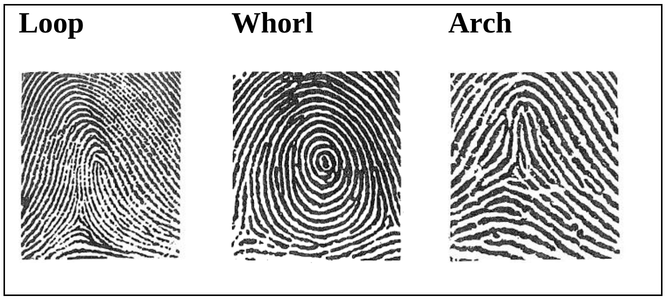


Figure 2.2: Fingerprint Morphology Patterns

2.1.2: Fingerprint Composition

Deposited fingerprints are composed of natural secretions from the eccrine and sebaceous glands in the skin. [10]. Eccrine sweat consists of mostly water, a complex mixture of organic (amino acids and proteins) and inorganic material (sodium, potassium, chloride, and trace metal ions) [10]. Eccrine sweat glands are most commonly found on the palms of the hands and soles of the feet [1]. Sebaceous secretions are predominantly composed of fatty acids, glycerides, cholesterol and squalene [10]. Sebaceous sweat glands are abundant on the scalp, face, nose, mouth, and external portions of the ear [10].

2.2: Latent Fingerprint Enhancement Methods

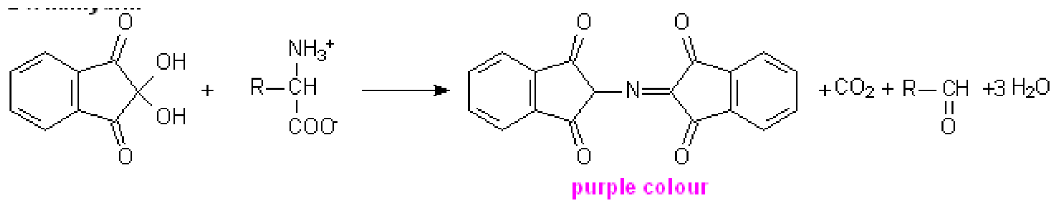
Latent fingerprints are commonly found at crime scenes and require an enhancement technique to be visible to the naked eye [10]. The most commonly used latent fingerprint enhancement techniques are fingerprint powder, ninhydrin, and cyanoacrylate fuming.

2.2.1: Fingerprint Powder Technique

Fingerprint powder involves the application of fine particles that adhere to the aqueous and oil components in latent print residue on non-porous surfaces [1]. Non-porous surfaces are surfaces that do not absorb moisture such as glass, metal, and plastics [1]. Carbon based fingerprint powders are composed of a pigment and a binder [1]. The pigment provides contrast against the background surface and the binder provides maximum adhesion to the latent fingerprint residue [1]. Magnetic fingerprint powder is another type of fingerprint powder that utilizes the ferromagnetic properties of iron powder mixed with pigment powders [1]. Magnetic fingerprint powder utilizes a bristle-free, magnetized rod that reduces the chance of destroying or damaging the latent print [9]. A fingerprint powder is selected based on the best color to contrast the surface being dusted for latent fingerprints [9]. After enhancement, an adhesive, known as gel lifters or tape, removes the fingerprint and is placed on a background that provides contrast to the fingerprint powder [9].

2.2.2: Ninhydrin

Latent fingerprints deposited on paper or other porous surfaces are developed using ninhydrin [1]. Ninhydrin is a chemical reagent, that forms Ruhemann’s purple after a reaction with amino acids present in fingerprint residues; the reaction is presented in Reaction Scheme 2.1 [9].The evidence is dipped into a ninhydrin solution and air-dried at room temperature to allow the solvent to evaporate [1]. A fuming chamber may also be used to develop latent fingerprints using ninhydrin [1].



Reaction Scheme 2.1: Chemical Reaction between Ninhydrin and Amino Acids to produce Ruhemannn's purple

2.2.3: Cyanoacrylate Fuming

The most effective and commonly used method for developing latent fingerprints containing eccrine and sebaceous residues is cyanoacrylate fuming [1]. Cyanoacrylate fuming develops latent fingerprints on non-porous surfaces through a polymerization reaction [1]. Initially, cyanoacrylate ester monomer interacts with the fingerprint residue and is bonded with initiators on the residue [1].The monomer reacts with another cyanoacrylate monomer forming a dimer [1]. This dimer reacts with another cyanoacrylate monomer and the interaction of monomers continues eventually forming a polymer which is terminated [1]. Cyanoacrylate fuming leads to a developed white fingerprint visible to the naked eye [1]. To introduce contrast on surfaces, fluorescent dye staining can be applied to the developed fingerprint [1]. A forensic light source can be used to examine the latent fingerprint, as well.

2.3: Development Techniques used on Cartridge Casings

Research experiments have been completed to test the ability of latent fingerprint development methods on unfired and fired cartridge casings. Girelli and associates completed a research study using fingerprint powder, cyanoacrylate fuming, fluorescent dye, gun bluing, and acidified hydrogen peroxide [11]. Latent fingerprints were developed on brass disks, unfired cartridge casings, and fired cartridge casings [11]. Table 2.1 provides the six different development techniques that were completed in experiments reported in this article. Gun bluing refinishes gun barrels using selenious acid, and cupric salt [1]. Basic yellow 40 is a fluorescent dye used after cyanoacrylate fuming [1]. Acidified hydrogen peroxide is an etching method similar to gun bluing [1]. The research experiment concluded that the sequential application of cyanoacrylate fuming, gun bluing, and basic yellow 40 dye produced the best latent fingerprint development on both fired and unfired cartridge casings. Another experiment was completed using fired cartridge casings from a 0.38 Webley revolver [12]. Results indicated that cyanoacrylate fuming in a vacuum chamber followed by basic yellow 40 dye provided sharper ridge definition of the latent fingerprint. In addition, Pratt studied fingerprint development using cyanoacrylate fuming and rhodamine 6G dye stain on 6,686 cartridges [3]. Only 8 identifiable fingerprints were obtained for a success rate of only 0.12% [3].

Table 2.1: Fingerprint Development Techniques used in a recent Research Experiment

1. Cyanoacrylate Fuming + Regular Powder Dusting
2. Cyanoacrylate Fuming + Magnetic Powder
3. Cyanoacrylate + Gun Blue Solution

Table 2.1 (continued)

4.	Cyanoacrylate + Basic Yellow 40 Dying
5.	Gun Blue Solution
6.	Acidified Hydrogen Peroxide with Glacial Acetic Acid

Source: Di Bari, G.A. *Modern Electroplating Chapter 3: Electrodeposition of Nickel*, 5TH ed.; Schlesinger, M., Paunovic, M.; John Wiley & Sons, Inc., 2010, pp. 114

2.4: Limitations of Fingerprint Development on Cartridge Casings

A cartridge contains primer, gunpowder, a bullet and the cartridge casing. When a trigger is pulled the weapon's firing pin is released [9]. The firing pin strikes the primer igniting the gun powder [9]. The burning gunpowder causes an expansion in gases propelling the bullet forward through the barrel pushing the cartridge casing back with equal force [9]. The blowback of the hot gases produced wipes part of the outside surface of the cartridge [11]. Fingerprint ridge residue may be lost or transformed during the blowback process [12]. Expansion of the cartridge due to the high temperatures maximizes friction between the outside surface and the chamber [11]. Lastly, development of latent fingerprints is affected by the generation of blowback gas byproducts [11]. In general, the high temperature and pressure reached once the trigger is pulled hinders the ability to recover and enhance latent fingerprints that were deposited on the cartridge casing.

CHAPTER 3

METHODS AND MATERIALS

3.1: Materials and equipment

Electrodes were prepared using brass sheet metal (Online Metals, C260 brass 0.016” thick), insulated lead wire (Remington Industries 300V), conductive glue (RadioShack) and 5-minute epoxy (Devcon Home) as described below.

Powercron 6000CX Cationic Epoxy Electrocoat High Throw Power paint (PPG Industrial Coatings, Springdale PA), atomic brand fingerprint powder (Criminal Research Products, LLC) and all reagent grade chemicals (Fisher) were used as received.

Metal deposition experiments were completed using a CH Instruments Model 400B Series Electrochemical Quartz Crystal Microbalance Potentiostat. Paint deposition experiments were initially completed with a HBI Haake Buchler Instruments 500V Power Supply. Thereafter, a LKG Bromma 2197 Power Supply was used for the remaining paint deposition experiments. A Neiko Stainless Hardened Electronic Digital Caliper was used to measure the approximate distance between the metal disks used in each trial. pH measurements of the solutions used for the paint electrodeposition were taken using an ORION Model 610 pH probe. A Leica L2, Leica EC3 Microscope was used to take microscopic images after each deposition. A Micronta Auto Range Digital Multimeter was used and placed in parallel during the paint deposition to measure the voltage that was being applied. Lastly, a Lab-Line Instruments LabChron 1400 Timer was used.

3.2: Metal Deposition Solutions

The compositions of high throw power copper (II) and nickel (II) sulfate solutions were based on formulations in the literature [4, 13].

3.2.1: Copper Metal Solutions

The first copper (II) sulfate solution was prepared with 80 g/L copper (II) sulfate, 230 g/L concentrated sulfuric acid, 75 g/L sodium chloride and 1 liter of deionized water. The second copper (II) sulfate solution was prepared in the same manner with the addition of 2 g/L polyethylene glycol (MW 3350 g/mol). Polyethylene glycol was added in the solution as a brightener [4].

3.2.2: Nickel Metal Solutions

A high throw power nickel (II) sulfate solution was prepared with approximately 300 g/L nickel (II) sulfate, 35 g/L nickel (II) chloride, 45 g/L boric acid, and 1 liter of deionized water.

3.3: High Throw Power Paint Solutions

3.3.1: Powercron 6000CX Solutions Diluted with Deionized Water

Deionized water was added to Powercron 6000CX paint to produce solutions which were 50%, 25%, 15%, 10%, 8%, 4%, 2%, and 1% of the original.

3.3.2.: Powercron 6000 CX Solution Modified with Carbon Black

Powercron 6000CX paint was diluted with deionized water to 25% of the original concentration and 25 mg/mL of carbon black powder was added. A more dilute solution was also made by dilution to 15% of the original paint concentration and addition of 15 mg/mL of carbon black powder. End over end mixing produced uniform solutions.

3.3.3: Powercron 6000 CX Solution Modified with Polyethylene Glycol

Polyethylene glycol (MW 400, 3350, and 8000 g/mol) was dissolved in deionized water and used to dilute Powercron 6000 CX to final concentrations of 25% paint: 25 mg/mL PEG and 15% paint: 15 mg/mL PEG.

3.3.4: Powercron 6000 CX Diluted with Acids and Bases

Aqueous solutions were used to dilute the high throw power paint solution. The solutions were glacial acetic acid, 6M acetic acid, dilute glacial acetic acid, and dilute ammonium hydroxide.

3.3.4.1: Modified with Acetic Acid

Concentrated glacial, 1:10 diluted and 6M acetic acid were used. For each solvent, a solution was prepared using 25% concentrated paint and 25 mg/mL of acetic acid.

3.3.4.2: Modified with Ammonium Hydroxide

Concentrated ammonium hydroxide was diluted to a concentration of 7.25×10^{-4} M. Once diluted, a solution of 25% concentrated paint and 25 mg/mL of the diluted ammonium hydroxide was prepared.

3.4: Deposition Setup and Process

3.4.1: Brass Disk Electrode Preparations

The purchased brass sheet metal was cut into ¾” size disks using a disk cutter. The 22 gauge wire was cut into pieces and both ends were stripped to expose the stranded wiring. One end was placed onto the back of the metal disk and covered using the RadioShack conductive glue. Enough glue was added to ensure that the end of the wiring was fully covered. The disks were placed into the ThermoScientific Heratherm oven at 110˚C for 1 hour to ensure that the glue was fully dried. Once completely dried, 5 minute epoxy was added to the back of the metal disk ensuring the wiring and the backing was fully covered. Each disk was freshly prepared for each trial and only used once.

3.4.2: Fingerprint Deposit

Each trial used two metal disks. One disk was the reference with no fingerprint deposit; it was just a bare surface. The other was the working disk with a fingerprint deposited. The fingerprint was deposited onto the opposite side of the wiring and the epoxy. Prior to depositing the fingerprint, a swipe of both the forehead and chin occurred. The fingerprint was then pressed onto the surface of the metal disk.

3.4.3: Metal Deposition Experiments

For the metal deposition experiments, a CH Instruments Model 400B Series Electrochemical Quartz Crystal Microbalance Potentiostat was used to provide the current and voltage. The reference and working disks were placed on top of each other with both front sides facing down. The disks were placed approximately 1 centimeter apart using a cardboard strip that had two slits to measure the necessary distance. Once the disks were correctly positioned, this spacing was maintained by pinching together both lead wires using a pinch clamp. Figure 3.1 shows the set-up of the two metal disks. Once clamped, the two disks were placed into a 20 mL beaker containing 10-15 mL of either the nickel (II) sulfate solution or the copper (II) sulfate solution. Enough solution was used to fully cover both disks when submerged into the metal (II) sulfate solution.

The potentiostat had a red reference lead, a white counter lead, and a green working lead. The red and white leads were connected together and then connected to the reference disks that did not have a fingerprint using alligator clips. The green working lead was connected to the working disk that had a fingerprint using alligator clips. Figure 3.2 shows the set-up using the potentiostat.

Once the deposition was completed, the disks were rinsed using fresh distilled water in a 100 mL beaker. The disks were air dried for approximately 5 minutes and then using a Leica L2, Leica EC3 Microscope microscopic images were taken of the working disk.

Figure 3.1: Image of the metal disk set-up

Figure 3.2: Image of the potentiostat and metal solution setup

3.4.3.1: Potentiostat Settings

The techniques used for the metal deposition experiments were the amperometric i-t curve, chronopotentiometry and chronocoulometry. The voltage, current, and time were altered for each trial. In addition, the charge was calculated using the current and time as shown in equation 3.1. The voltage settings ranged from -0.4 to -0.8 volts. The current ranged from 0.4 to 32 milliamperes. Time ranged from 300 to 500 seconds.

$$Q = I \; x \; t$$

Equation 3.1: Constant Current Equation; Variables are as follows: Q—Charge in Coulombs; I—Current in amperes; t—Time in seconds.

3.4.4: High Throw Power Paint Deposition Experiments

For the paint deposition experiments, a HBI Haake Buckler Instruments 500V Power Supply was used to supply the voltage. After a fuse was blown, a LKG Bromma 2197 Power Supply was used to supply the voltage and current. With the LKG Bromma power supply, a Micronta Auto Range Digital Multimeter was used in parallel to measure the current that was being supplied to the paint solution.

Similar to the metal deposition setup, the disks were placed approximately 1 centimeter apart using a cardboard strip that had two slits to measure the distance. The working disk was still above the reference disk. However, different from the previous setup, the disks were facing each other to allow the current to flow through the disks. The disks were held together using a pinch clamp. Once clamped, the two disks were placed into a 20 mL beaker containing 10-15 mL of the paint solution. Enough solution was used to fully cover both disks when submerged into the paint solution.

Both power supplies had a red lead and a black lead. The red lead was connected to the reference disk that did not have a fingerprint and then connected to the positive outlet on the power supply. The black lead was connected to the working disk that had a fingerprint and then connected to the negative outlet on the power supply.

When using the LKG Bromma power supply, the voltage was set by the power supply and read accurately on the multimeter. The multimeter was placed in parallel with the power supply and the metal disks. The power supply adjusted the current based on the voltage that was set and the current was measured. All connections were made using alligator clips. The setup using the LKG Bromma Power Supply is shown in Figure 3.3.

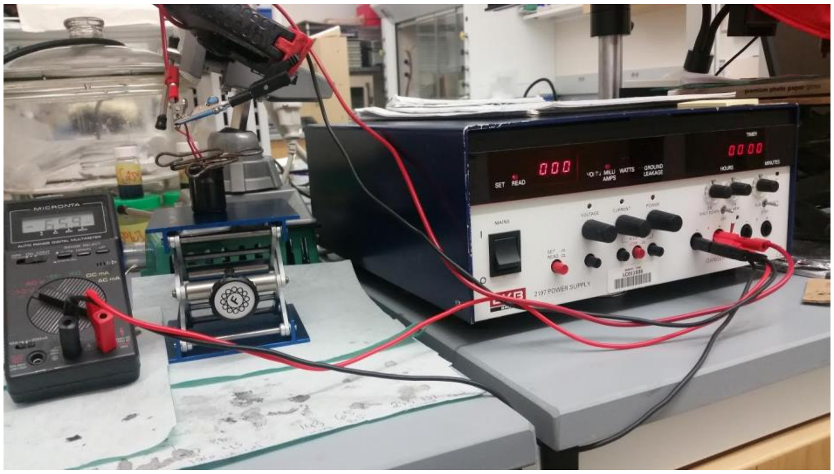


Figure 3.3: Image of Power Supply, paint solution, and multimeter setup.

Once the deposition was completed, the disks were rinsed using fresh distilled water in a 100 mL beaker. The disks were air dried for approximately 5 minutes and then using a Leica L2, Leica EC3 Microscope microscopic images were taken of the working disk.

3.4.4.1: Power Supply Settings

For the HBI Haake Buckler Instruments power supply, only the voltage could be altered. The voltages studied ranged from 50 to 500V. The time studied ranged from 9 to 360 seconds. For the LKG Bromma power supply, voltage ranged from 5 to 301 volts. The current ranged from 1 to 250 milliamperes and time ranged from 5 to 300 seconds.

3.4.4.2: pH Measurements

Triplicate pH measurements were taken of each paint solution. Measurements were taken with an ORION Model 610 pH probe. Measurements of each solution were taken before and after being used in the deposition experiments. The pH probe was rinsed thoroughly before and in between each reading to ensure no carryover into the next reading.

CHAPTER 4

METAL DEPOSITION RESULTS AND DISCUSSION

4.1: Introduction

Copper and nickel metal deposition were the first experiments completed to study the enhancement of a latent fingerprint. Copper electrodeposition is efficient at plating the surface and is commonly used in automotive bumpers and printed wiring boards [13]. Nickel electrodeposition is used as a surface-finisher and other decoration purposes [4]. Copper (II) sulfate solutions with and without the addition of polyethylene glycol (3350 g/mol) were studied. Polyethylene glycol (MW 3350 g/mol) was added as a brightener to the copper (II) sulfate solution [4]. PEG provides good leveling characteristics when the metal is deposited [4]. Levelers reduce the surface roughness during deposition resulting in a smooth deposit [14]. A nickel (II) sulfate solution was also studied.

A CH Instruments Model 400B Series Electrochemical Quartz Crystal Microbalance Potentiostat was used to complete each deposition study. Three different types of settings were used: amperometric i-t curve, chronopoentiometry, and chronocoulometry. Amperometric current-time curve has a constant current applied; the current is recorded as a function of time. Chronopotentiometry records potential as a function of time. Chronocoulometry passes a charge through the working electrode; the charge is recorded as a function of time. For each setting, the voltage, current, and time was varied to observe the amount of metal that deposited onto the metal disk electrode. All metal disk images and corresponding curve plots are provided in Appendix A. The charge was calculated using Equation 3.1. The amount of charge produced for each experiment is proportional to the amount of metal that will be deposited. As more charge is produced, more metal is expected to deposit onto the disk surface. The thickness of the metal deposit on the surface is dependent on the current density [4]. With the calculated total charge, the thickness of the metal coating (in micrometers) was calculated using Equations 4.1 through 4.5. The literature values used in each equation are provided in Table 4.1.

1. $Moles\ of\ Metal = \dfrac{\frac{Charge\ (C)}{Faraday's\,Constant\ C}}{Number\ of\ electrons}$
2. $Mass\ of\ Metal\ (g) = Moles\ of\ Metal\ x\ Molar\ Mass\ of\ Metal$
3. $Volume\ of\ Metal\ (mL) = \dfrac{Mass\ of\ Metal\ (g)}{Density\ of\ Metal\frac{g}{mL}}$
4. $Thickness\ of\ Coating\ (cm) = \dfrac{Volume\ of\ Metal\ cm^3}{Disk\ Area\ cm^2}$
    a. Disk Area (cm^2)= π(radius of disk)^2
5. Thickness of Coating (µm)= (Thickness in cm) * 10000

Equations 4.1-4.5: Metal Deposit Thickness Equations

Table 4.1: Literature Values for Equations 4.1-4.5

*Faraday's Constant	96,500C
Molar Mass of Copper[15]	63.55 $\frac{g}{mol}$
Molar Mass of Nickel	58.69 $\frac{g}{mol}$
Density of Copper [15]	8.94 $\frac{g}{cm^3}$
Density of Nickel	8.907 $\frac{g}{cm^3}$
*Radius	0.9525 cm
*Electrons required for reduction of metal ion [4]	2

**For both Nickel and Copper Metal Thickness Calculations*

Source: Di Bari, G.A. *Modern Electroplating Chapter 3: Electrodeposition of Nickel*, 5TH ed.; Schlesinger, M., Paunovic, M.; John Wiley & Sons, Inc., 2010, pp. 114
Source: Sigma-Aldrich A Part of Millipore Sigma, Copper Beads. http://www.sigmaaldrich.com/catalog/product/aldrich/254177?lang=en&region=US (accessed Mar. 8. 2017)

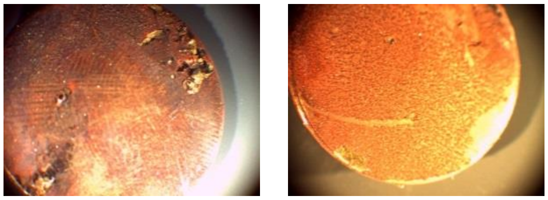
Seven copper (II) sulfate depositions were studied; three of which had the addition of PEG. Rough copper deposits were visually observed on metal disks without PEG. Copper deposits from formulations with PEG were smooth, flat, and brighter. Four nickel (II) sulfate depositions were performed. Many of the experiments produced approximately 5-7 coulombs of charge. For one experiment, 3-fold the normal amount of charge was applied and the deposited nickel metal fully covered the metal disk. Also, one experiment produced fingerprint ridge detail after the nickel metal deposited. Despite only one deposition producing ridge detail, the metal deposition study helped in refining the electrochemical cell setup configuration and electrochemical conditions studied in the later paint electrodeposition work.

4.2: Copper (II) Sulfate Deposition Results

4.2.1: Copper (II) Sulfate without PEG

Figure 4.1 shows images of brass disks with an applied latent fingermark after copper (II) sulfate deposition using the amperometric i-t curve setting for 300 seconds with -0.6V applied. Figure 4.2 provides representative current-time curve plots for Disk 1 and Disk 2. New disks were given a different number. In the current-time curve plots for both Disks 1 and 2, there is a parabolic shape to the curve. The initial decrease in the curve indicates that a capacitance current is occurring. During this period, electrons are flowing to the surface of the metal disk and water molecules are attracted to those electrons and will flip their dipoles to produce a small charging current. After this initial period, the current remained relatively steady as metal deposited. For

Disk 1, the average current was about 0.03A which corresponds to a total charge of 9C over the 300 second deposition period. For Disk 2, the average current was modestly lower at 0.019A, corresponding to a total charge of 5.7C. While the currents for each disk were expected to be similar, physical differences in the coating were observed which correspond with the differences in total charge. Disk 1 was calculated to have a thicker coating of 1.15 µm copper metal deposited compared to Disk 2 (0.73 µm). Visually comparing, chunks of copper metal are present on the edges in Disk 1 whereas there is a smaller film of copper in deposition 2 on the edges. Disk 1 had a large charge and current so it is not surprising that more copper metal was observed in deposits as compared to Disk 2.



1 2

Figure 4.1: Images of Metal Disks after Copper (II) Sulfate Deposition using Amperometric i-t Curve for 300 seconds with the following conditions: (Disk 1) -0.6V, resulting in a an average current of 0.03A, total charge of 9C, and a calculated thickness of 1.15 µm; (Disk 2) -0.6V, resulting in an average current of 0.019A, total charge of 5.7C, and a calculated thickness of 0.73 µm.

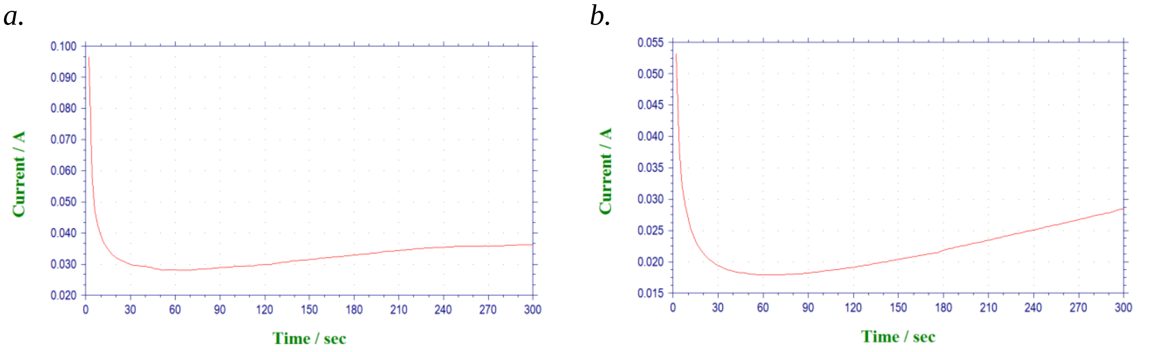
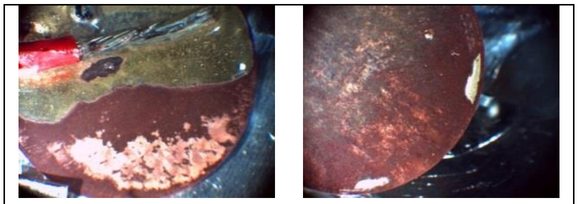


Figure 4.2: Amperometric i-t Curves produced from copper metal deposition in Figure 4.1 (a) typical of Disk 1; (b) typical of Disk 2

Figure 4.3 shows images after using the chronocoulometry setting for 300 seconds with -5V applied followed by 300 seconds at +5V. Figure 4.4 provides the charge-time plot for this study. Both the deposition and plot look different than those using the amperometric setting. In this deposition, the copper metal was initially plated onto the surface in the first 300 seconds. The steep increase that occurs shortly after 300 seconds is the capacitance current that was previously observed. After which, the metal disk and copper metal were reduced and then oxidized thus dissolving the copper metal that deposited. Comparing the images in Figure 4.3 to those in Figure 4.1, there is a smaller amount of copper metal deposited onto the metal disk edges. Reduction of metal followed by oxidation might potentially allow fine control of the metal film thickness, but these initial results were not encouraging enough to pursue.



3a 3b

Figure 4.3: Images of Metal Disks after Copper (II) Sulfate Deposition using Chronocoulometry for 300seconds at -5V followed by +5V for 300 seconds.

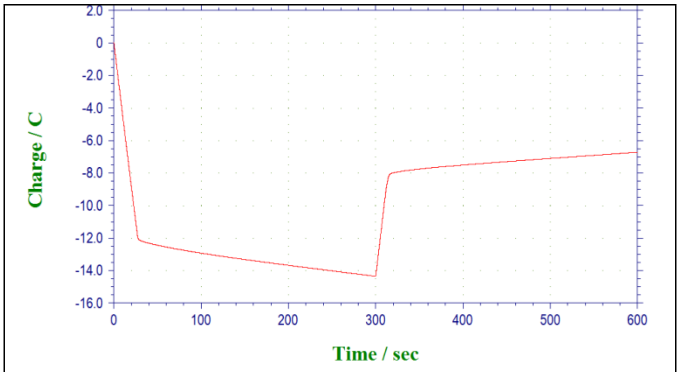


Figure 4.4: Charge-Time Curve produced from copper metal deposition in Figure 4.3

4.2.2: Copper (II) Sulfate with PEG

An initial experiment was completed using the same conditions used for Disk 2 (-0.6V for 300s). Figure 4.5 provides the image of the disk. Comparing metal Disk 2 with Disk 4, visually the same amount of copper deposited on both disks. A thickness of 0.96 μm was calculated for both disks. The copper that deposited in Disk 4 is visually different due to its brightness. The deposited copper is shiner than the copper that was deposited without the PEG. The deposited copper is smoother and more flat compared to the previous copper deposits without PEG.

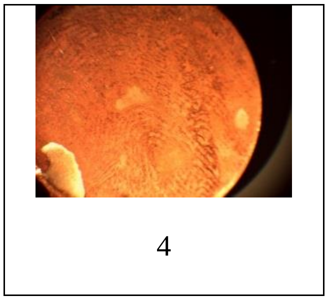


Figure 4.5: Image of Metal Disk 4 after Copper (II) Sulfate Deposition with PEG using Amperometric i-t Curve for 300 seconds at -0.6V, resulting in an average current of 0.025A, total charge of 7.5C, and a calculated thickness of 0.96 µm.

Coatings on Disks 5 and 6, as seen in Figure 4.6, were deposited using chronopotentiometry at 0.01A and 0.03A, respectfully. The respective potential versus time plot for each disk is shown in Figure 4.7. The higher current produced a lower voltage of -0.5V. Three times the amount of charge was produced with Disk 6 compared to Disk 5. Three times the amount of coating thickness deposited was calculated on Disk 6 (1.15 µm) compared to Disk 5 (0.38 µm). Visually, more copper metal deposited on Disk 6. Disk 1 and Disk 6 were prepared with 9C of charge and visually appear to have similar amounts of deposited copper after coating; however Disk 6 is visibly brighter than Disk 1 because of the addition of PEG in the solution used with Disk 6. Copper deposits with PEG produced visible ridge detail compared to copper deposits without PEG. Fingerprint ridge detail can be seen in Disk 4 and Disk 6.

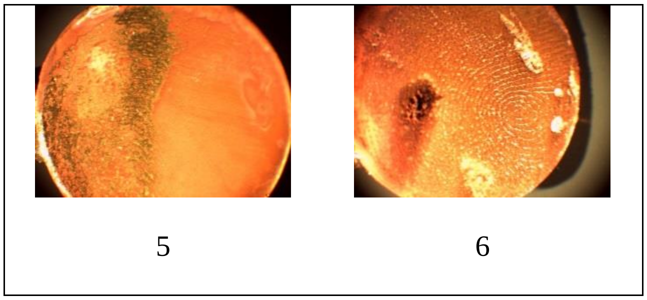


Figure 4.6: Images of Metal Disks after Copper (II) Sulfate Deposition with PEG using Chronopotentiometry: (Disk 5) -0.3V, resulting in an average current of 0.01A, a total charge of 3C and a calculated thickness of 0.38µm; (Disk 6) -0.5V, resulting in an average current of 0.03A, a total charge of 9C, and a calculated thickness of 1.15 µm.

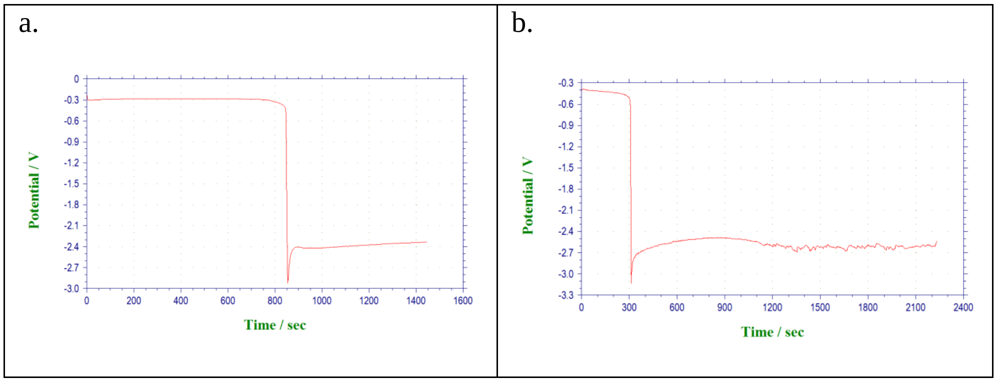


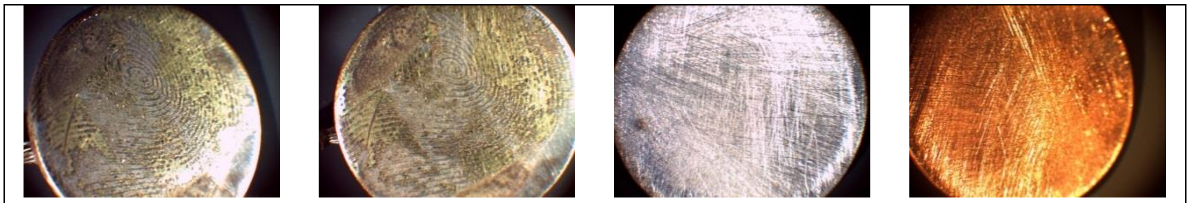
Figure 4.7: Potential vs Time Curve produced from copper metal deposition in Figure 4.7: (a) Disk 5; (b) Disk 6

4.3: Nickel (II) Sulfate Deposition Results

A latent fingerprint was applied to brass disks and then coated using a nickel (II) sulfate solution. The conditions are summarized in Table 4.2 with images of the coatings shown in Figure 4.8 and the respective current versus time plots provided in Figure 4.9. . The thickness of the nickel coating roughly corresponded to the amount of charge passed during deposition, as expected. Some fingerprint ridge detail was evident on Disk 7a and 7b. No fingerprint ridge detail was evident on Disks 8 and 9 prepared with much higher and lower amounts of charge.

Table 4.2 Summary of Nickel Electrodeposition Conditions

Disk	Technique	Set Voltage or Current	Time (sec)	Produced Voltage or Current	Coulombs	Thickness (µm)
7a and 7b	Chronoamperometry	-0.6V	300	0.0185A	5.55	0.66
8	Chronoamperometry	-0.8V	500	0.032A	16	1.91
9	Chronoamperometry	-0.4V	500	0.0004A	0.2	0.02



7a 7b 8 9

Figure 4.8: Images of Metal Disks after deposition from a Nickel (II) Sulfate solution using Amperometric i-t: (Disks 7a and 7b) -0.6V for 300sec., resulting in an average current of 0.0185A, a total charge of 5.55C,and calculated thickness of 0.66 µm; (Disk 8) -0.8V for 500 sec., resulting in an average current of 0.032A, a total charge of 16C, and calculated thickness of 1.91 µm; (Disk 9) -0.4V for 500 sec., resulting in an average current of 0.0004A, total charge of 0.2C, and calculated thickness of 0.02 µm.

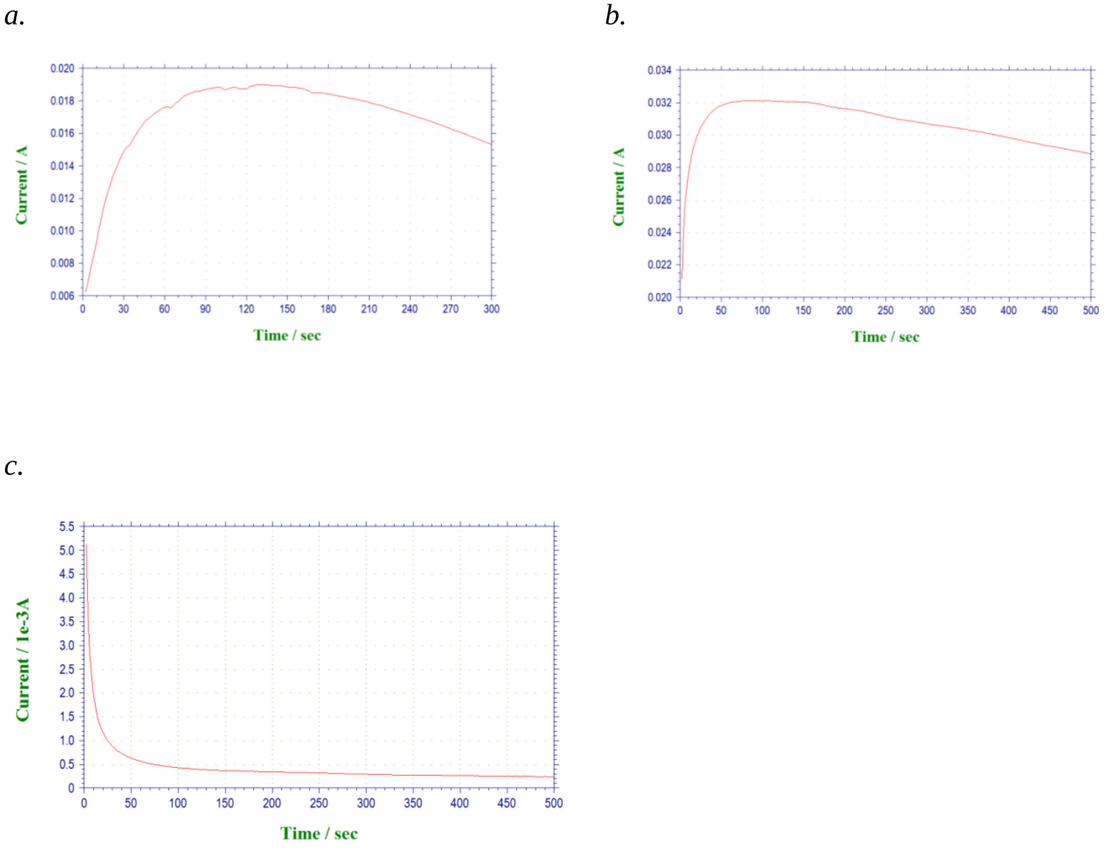


Figure 4.9: Current vs Time Curves produced from nickel metal deposition in Figure 4.8: (a) Disks 7a and 7b; (b) Disk 8, (c) Disk 9

4.4: Discussion and Conclusions

Both copper and nickel metal were deposited on brass metal electrode surfaces using copper (II) sulfate and nickel (II) sulfate solutions. A CH Instruments Model 400B Series

Electrochemical Quartz Crystal Microbalance Potentiostat was used to complete each deposition experiment. The voltage, current, and time were varied to observe the efficiency of both copper and nickel metal depositing. The charge was calculated for each experiment using Equation 3.1. The amount of charge produced for each experiment is indicative to the amount of metal that will deposit; disks with more metal deposited were observed when larger charges flowed during their preparation. The thickness of the deposited metal was calculated using Equations 4.1-4.5

Seven coatings were deposited from the copper (II) sulfate solution and three coatings were deposited from the copper (II) sulfate solution with added polyethylene glycol (MW 3350 g/mol) which is known as a brightener and a leveler. Without PEG chunky copper metal was observed to deposit on the edges of the metal disk. In chronoamperometric experiments at -0.6V for 300 seconds, modestly higher average currents (0.03A) were observed on Disk 1 than on Disk 2 (0.019A). The modestly thicker coatings visually observed and calculated on Disk 1 compared with Disk 2 were consistent with the higher total charge in producing the coatings. Addition of PEG resulted in deposited copper that was brighter and smoother.

Four coatings were deposited from the nickel (II) sulfate solution. In chronoamperometric experiments at -0.6V and -0.8V, modestly higher average currents were observed on Disks 7a and 7b compared with Disk 8. The modestly thicker coatings visually observed and calculated on Disk 8 compared with Disks 7a and 7b were consistent with the 3-fold higher total charge in producing the coatings.

Metal deposition studied the enhancement of a fingerprint by using two different metal solutions and by varying current, voltage, and time. Nickel metal deposition on Disks 7a and 7b produced some fingerprint ridge detail. The metal deposition work was an introduction to the setup that was used for paint electrodeposition experiments.

CHAPTER 5

PAINT DEPOSITION RESULTS AND DISCUSSION

5.1: Introduction

Paint electrodeposition experiments were completed to study the enhancement of a latent fingerprint. Paint electrodeposition is used in the automotive industry for car-body priming under direct current [16]. As direct current is passed through the paint solution, water molecules are reduced to produce hydroxide ions and hydrogen gas. As shown in Figure 5.1 there are pigment particles present in the paint solution that are surrounded by a hydrophobic, positively charged resin chain. The hydroxide ions will interact with the resin chain on the surface of the pigment particle to produce the free base form of the resin chain. The free base form does not have a charge and makes the pigment particle less soluble than the initial acidic form with the ionized ammonium group; thus formation of the free base form leads to precipitation of the pigment particle. Reaction Scheme 5.1 summarizes the precipitation of the pigment particle. At high pH, the particles will aggregate together. The aggregated paint particles will deposit onto the metal surface as the metal surface is less polar than that of water. As more paint is deposited, less water molecules can move through the solution to reach the electrode surface and be reduced to the hydroxide ion. Ideally, coating of the bare metal surface would lead to a highly insulating surface, a decrease in direct current and deposition of the paint to only cover the bare metal surface of the electrode and not the lipid coated areas where fingerprint residue was deposited.

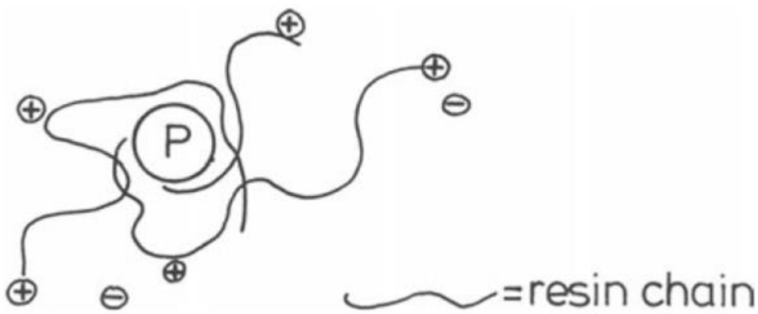
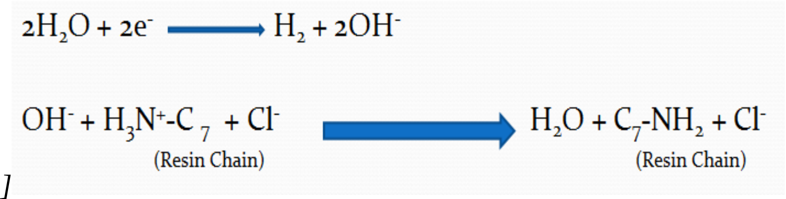


Figure 5.1: Positively charged resin encapsulating pigment particle

Source: Streitberger, H.J.; and Osterloh, R.P. *Surface Coatings: Chapter 2 Electrodeposition of Paints*, 1998, pp. 39-66



]

Reaction Scheme 5.1: Production of Hydroxide ions and Pigment Particles without a surface charge

High throw power Powercron 6000CX black paint is used in initial experiments. High throw power paint is formulated to coat the surface of the metal disk as well as any pits or crevices on the surface. A total of seventy-five paint deposition experiments were completed; the corresponding metal disk images are provided in Appendix B. Initial experiments showed that commercial high throw paint had a tendency to cover not only the bare metal surface, but also the fingerprint residue. Thus, the paint solution was modified by dilution with deionized water and addition of several substances in an effort to find a paint formulation that formed an insulating coating over the bare metal surface while leaving the lipid fingerprint residue pattern uncoated. Substances added to the paint formulation were carbon black fingerprint powder and three different molecular weights of polyethylene glycol. The pH of the paint was also adjusted with acetic acid and ammonium hydroxide in exploratory experiments.

5.2: High Throw Power Paint Results

Figure 5.2 shows the image of the first brass disk with an applied latent fingerprint after paint electrodeposition using amperometric i-t curve setting for 300 seconds with -10V applied. Figure 5.2 includes the representative current-time curve plot for this experiment as well. An average current of 0.0018A was produced corresponding to a total charge of 0.54C. Minimal amounts of paint deposited onto the surface of the disk. With the small current and charge it is not surprising that a small amount of paint deposit was observed in this experiment.

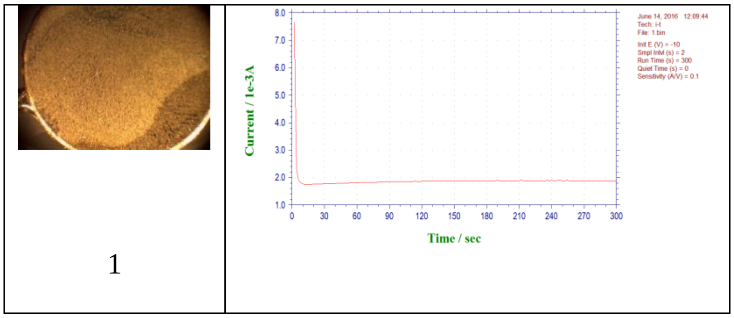


Figure 5.2: Image of Metal Disk after Powercron 6000CX Paint Deposition using Amperometric i-t Curve (pictured) for 300 seconds at -10V, resulting in an average current of 0.0018A and total charge of 0.54C.

Due to the small amount of current and total charge produced during the paint deposition in Figure 5.2, a HBI Haake Buchler Instruments 500V Power Supply was used to allow higher applied voltages during paint deposits. Figure 5.3 provides the images of metal disks after paint deposition experiments with applied voltages ranging from 50V to 500V. Disk 2 and Disk 3 has applied voltages of 500V and 401V, respectfully. With this large amount of voltage applied, copious amounts of hydroxide ions and hydrogen gas were produced. Within 9 and 30 seconds, the paint overflowed out of the beaker due to hydrogen gas production. Both metal disks were fully covered with a thick paint coating with pits present. The large amount of gas production contributed to the pits present. As the applied voltage was decreased in Disks 4 through 7, the thickness of the deposited paint, as assessed by visual observation, appeared to decrease. In each deposition experiment, the paint deposit fully coated the brass metal disk without evidence of the latent fingerprint pattern.

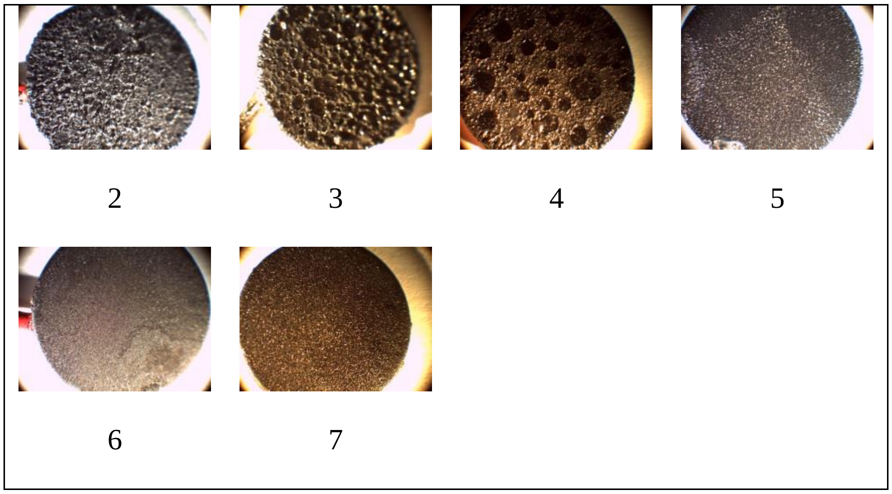


Figure 5.3: Images of Metal Disks after Powercron 6000CX Paint Deposition: (Disk 2) 500V for 9s; (Disk 3) 401V for 150s; (Disk 4) 350V, 7.4s; (Disk 5) 200V for 240.7s; (Disk 6) 100V for 30.5s; (Disk 7) 50V for 360s.

A blown fuse in the HBI Power Supply resulted in the use of a LKG Bromma 2197 Power Supply for the remaining Powercron 6000 CX paint deposition experiments. Disk 8, Disk 9, and Disk 10 were completed to determine the reproducibility of the previous deposits obtained with the HBI Power Supply. For each disk present in Figure 5.4, paint was deposited with an applied voltage of 150V for 300 seconds. The closest previous experiment was with Disk 5 (200V for 240s). When comparing Disk8 through Disk 10 with Disk 5, Disk 5 had a much darker paint coating. Disks 8-10 have similar paint coatings to Disk 7, which had a much lower applied voltage of 50V compared to 150V. The initial paint deposit results with the LKG Power Supply visibly did not produce similar results to the HBI Power Supply. A salt water solution with copper metal was used to study the set applied voltage and current that was produced.

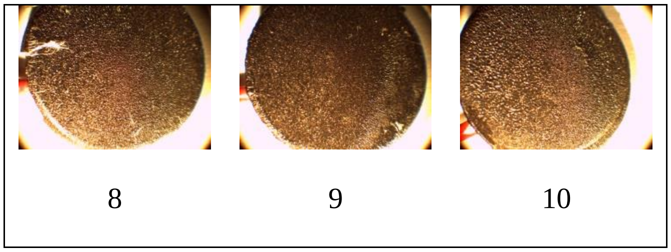


Figure 5.4: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 150V for 300 seconds for each disk.

A Micronta Multimeter was placed in parallel with the LKG Power Supply, copper wire, and a salt water solution. As a voltage was applied, a large amount of current was passed through the circuit. In addition, the solution turned green and gas bubbles were present on the surface of the salt-water solution. Different from the HBI Power Supply, both the voltage and current can be set and read on the LKG Power Supply. Through this exploratory study, it was determined that the voltage that was set to complete paint depositions from Disk 8, Disk 9, and Disk 10 were not reaching the full 150V because it was being capped by a 21.5 mA current maximum that was set on the power supply during these experiments. Therefore, it is unknown how much voltage was applied during the paint depositions in Disk 8, Disk 9, and Disk 10; the power supply simply increased the voltage until 21.5 mA passed through the circuit. Visually based on the deposited paint, it appears as though only 50V was applied when compared to Disk 5. For the remainder of the paint deposition experiments, the multimeter remained in parallel to read the accurate voltage that was applied, and the current was read on the power supply. The current was changed to the maximum that the power supply is capable of supplying, 250 mA, for the remaining experiments.

The next three paint deposition experiments for Disk 11, Disk 12, and Disk 13 were each completed using the previous settings of 150V for 300 seconds. The image for each disk is shown in Figure 5.5. The paint deposit fully coated the metal disk. Comparing the disks in Figure 5.4 to the disks in Figure 5.5, visibly the deposited paint is much darker in Disk 11, Disk 12, and Disk 13.

11 12 13

Figure 5.5: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 150V for 300 seconds for each disk.

During the deposition experiments, an electronic multimeter set to measure the applied voltage was placed in parallel in the circuit allowing an independent measurement of the applied voltage. The current at various times after application of the voltage was manually recorded Figure 5.6 provides a current-time plot that shows the current decreases fairly quickly over time as the metal surface is coated with insulating paint. Initially, the current is increased to 250mA. Within 5-10 seconds, the current rapidly decreases and stabilizes, while the applied voltage is constant. The current stabilization is an indication that there is limited bare metal surface remaining. Thus, a thick coating of paint deposit is present on the metal disk hindering the ability to enhance the latent fingerprint. By stopping the power supply immediately after the main current decrease, it is hoped that the paint will not overcoat the metal surface allowing for the enhancement of the latent fingerprint.

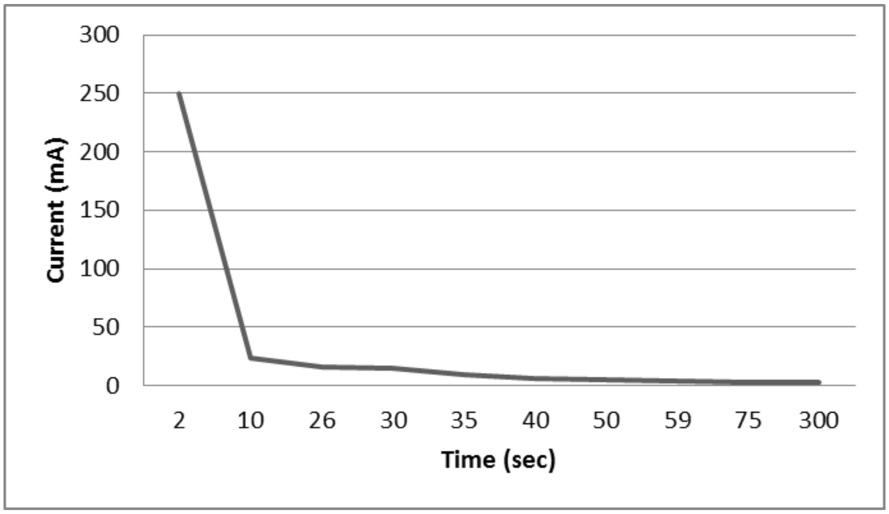


Figure 5.6: Current vs Time Curve produced from Powercron 6000CX Paint Deposition in Figure 5.5; represents normal current vs time curve for paint deposition experiments.

For Disk 14 and Disk 15, the power supply was immediately stopped after the main current decrease within 5 to 10 seconds. Images for the paint deposit for each disk are shown in Figure 5.7. Both Disk 14 and Disk 15 were fully coated. The results from each experiment confirmed that the major current decrease is an indication that the paint has coated the metal surface to a full or nearly full extent.

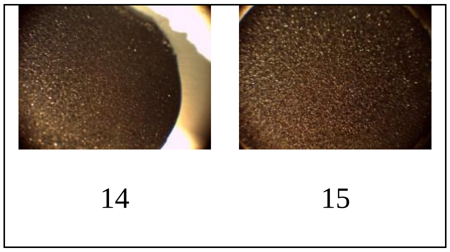


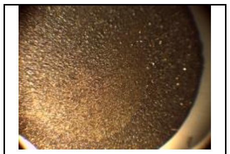
Figure 5.7: Images of Metal Disks after Powercron 6000CX Paint Deposition with an applied voltage of 149V resulting in an average current of 1A: (Disk 14) with a total charge of 10C after 10 sec; (Disk 15) with a total charge of 5C after 5sec.

5.2.1: Conclusion

Thick paint deposits, as judged by visual observation, were produced with application of increasing voltages over the range of 50 to 500 volts The paint deposits fully coated the metal surface with pits present from the production of hydrogen gas. Reproducible paint depositions were studied using the normal conditions of an applied voltage of 150V for 300 seconds. Under those normal conditions, a uniform coating of the paint deposited. A multimeter was placed in parallel with the power supply, the paint solution, and the metal disks to measure the applied voltage during each deposition study. It was observed that the current is rapidly increased to the maximum 250 mA. After this initial increase, the current decreased and stabilized. This increase, decrease, and stabilization of the average current occur within 5-10 seconds of the voltage being applied. The power supply was stopped after the current stabilized to observe the differences in the paint deposits. The paint deposits were visually different than the deposition experiments ran for 300 seconds. In each study, no fingerprint ridge detail was present. The next phase of the research experiment focused on the dilution of the paint solution to reduce its throw power to increase the probability of enhancing the deposited latent fingerprint.

5.3: Powercron 6000CX Solution Diluted with Deionized Water Results

Deionized water was added to Powercron 6000CX paint to produce solutions which were 50%, 25%, 15%, 10%, 8%, 4%, 2%, and 1% of the original. Paint deposited on Disk 16 in Figure 5.8 with an applied voltage of 150.7V for eight seconds. The paint used was 50% of the original. The paint deposited on Disk 16 is visually lighter than the concentrated paint deposits on Disk 14 and Disk 15. Also, there is a clear outline of the deposited latent fingerprint.



16

Figure 5.8: Image of Metal Disks after Powercron 6000CX Paint Deposition (50% Diluted) with an applied voltage of 150.7V, a final current of 2 mA after 8 seconds.

A paint solution that was 25% of the original was used to produce the paint deposits present in Disk 17, Disk 18, Disk 19, Disk 20, and Disk 21. The conditions are summarized in Table 5.1 and images of the coatings are shown in Figure 5.9. The deposited paint on each disk is visibly lighter than the deposited paint on Disk 16. There is an outline of the deposited latent fingerprint in each deposition study. In addition to the outline, ridge detail is present on both Disk 17 and Disk 19.

Table 5.1: Summary of 25% Diluted Paint Electrodeposition Conditions

Disk	Set Voltage	Time (sec)	Final Current (milliamps)
17	151.8V	7	2
18	76.5V	10	1
19	40.85V	11	1
20	10.61	10	3
21	5.94	6	8

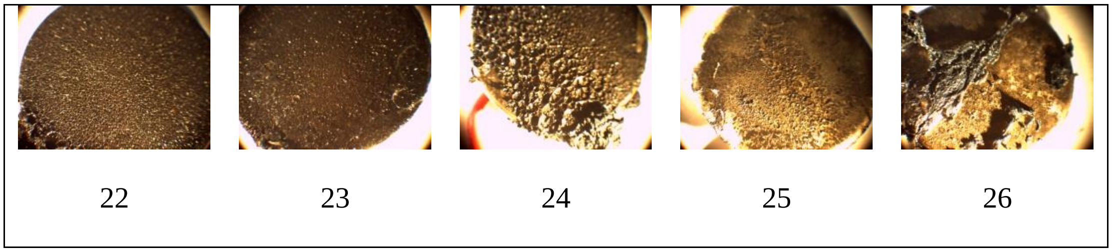
17 18 19 20 21

Figure 5.9: Image of Metal Disks after Powercron 6000CX Paint Deposition (25% Diluted); (Disk 17) applied voltage of 151.8V, resulting in a final current of 2 mA after 7 seconds; (Disk 18) applied voltage of 76.5V, resulting in a final current of 1mA after 10 seconds; (Disk 19) applied voltage of 40.85V, resulting in a final current 1mA after 11 seconds; (Disk 20) applied voltage of 10.61V, resulting in a final current of 3mA after 10 seconds; (Disk 21) applied voltage of 5.94V, resulting in a final current of 8mA after 6 seconds.

Table 5.2 provides a summary of the conditions studied to produce coatings for Disks 22-26 in Figure 5.10 from serial diluted Powercron 6000CX paint solutions to concentrations of 1% to 10%. Each experiment was completed using the normal conditions of a set applied voltage of 150V with a time of 180 sec. As the concentration decreased, the paint deposited in a more concentrated area of the metal disks. In the experiments corresponding to Disk 22 and Disk 23 the paint deposit fully covered the metal disk surface. In Disk 26, chunky paint deposits are present on some parts of the metal disk; on other portions of the metal disk minimal amounts of paint deposits are present.

Table 5.2: Summary of Serial Diluted Paint Electrodeposition Conditions

Disk	Paint Concentration	Set Voltage	Time (sec)
22	10%	151.2	180
23	8%	151.3	180
24	4%	148.4	180
25	2%	150	180
26	1%	151.3	180



22 23 24 25 26

Figure 5.10: Image of Metal Disks after Serial Diluted Powercron 6000CX Paint Deposition after 180 seconds for each disk: (Disk 22) 10% concentration, applied voltage of 151.2V; (Disk 23) 8% concentration, applied voltage of 151.3V; (Disk 24) 4% concentration, applied voltage of 148.4V; (Disk 25) 2% concentration, applied voltage of 150; (Disk 26) 1% concentration, applied voltage of 151.3V

Figure 5.11 provides a scheme that represents the diffusion of hydroxide ions into the paint solution. As current passes through the two metal disks, hydroxide ions are produced from the reduction of water. There is a high concentration of hydroxide ions present near the metal disk surface; indicated by the larger spheres in Figure 5.11. The hydroxide ions diffuse away in solution to a lower concentrated area of hydroxide ions further away from the electrode; indicated by the smaller spheres in Figure 5.11. The hydroxide ions will neutralize the paint particles in solution producing the free base form. The neutralized particles will aggregate together. The metal disk surface is less polar than water, so the aggregated paint particles will deposit onto the metal disk surface. As the concentration of paint is decreased, there are less paint particles in solution because the paint is less concentrated. The hydroxide ions will diffuse much further away to those particles in solution. The neutralized particles are much further apart because there are much less in the solution and are further away from the metal disk surface. As the neutralized particles are diffusing back to the metal disk surface, the particles will aggregate together and deposit onto the surface in a chunky manner as seen in Disk 26.

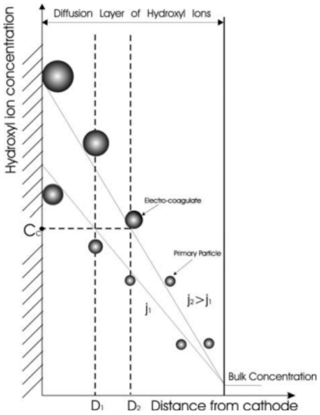


Figure 5.11: Schematic Representation of the diffusion layer of the hydroxyl ions

Source: Ranjbar, Z; Moradian, S.; and Rastegar, S. Formation of a percolating cluster in films prepared by cathodic electrodeposition of a mixture of lower and higher molecular weight epoxy-amine adducts. *Journal of Colloid and Interface Science,* **2003**, 264, pp. 429

5.3.1: Conclusions

Deionized water was added to Powercron 6000CX paint to produce solutions which were 50%, 25%, 15%, 10%, 8%, 4%, 2%, and 1% of the original. Diluting the Powercron 6000CX paint solution to 50% and 25% of the original produced an outline of the applied latent fingerprint after paint deposition. The best fingerprint enhancement is visibly present with the 25% concentration paint solution deposition experiments. Therefore for the remaining dilution experiments, 25% concentrated paint will be standard.

5.4: Powercron 6000CX Solution Modified with Carbon Black Results

Carbon black fingerprint powder was added to the paint solution with the thought that some of the adsorbed resin on the pigment particles would transfer to the carbon particles. The reduced amount of resin on the pigment particles would then require less hydroxide ion to be neutralized. Thus, the coating of the paint would be modified and perhaps produce coating over the bare metal surface while not coating the lipid fingerprint residue. Figure 5.12 provides a general scheme demonstrating how the addition of the carbon black fingerprint powder reduces the amount of charged resin on the pigment particle. The resin present around the pigment particle will adhere to the carbon black powder. This will remove resin from the pigment particle therefore decreasing the throw power of the paint. While it is difficult to predict the behavior of the formulation with added carbon black, it may be that less paint is precipitated on the surface prior to forming a fully insulating coating. This may be due to the decrease in formation of free base from the interaction of less resin particle with electrically generated hydroxide ions.

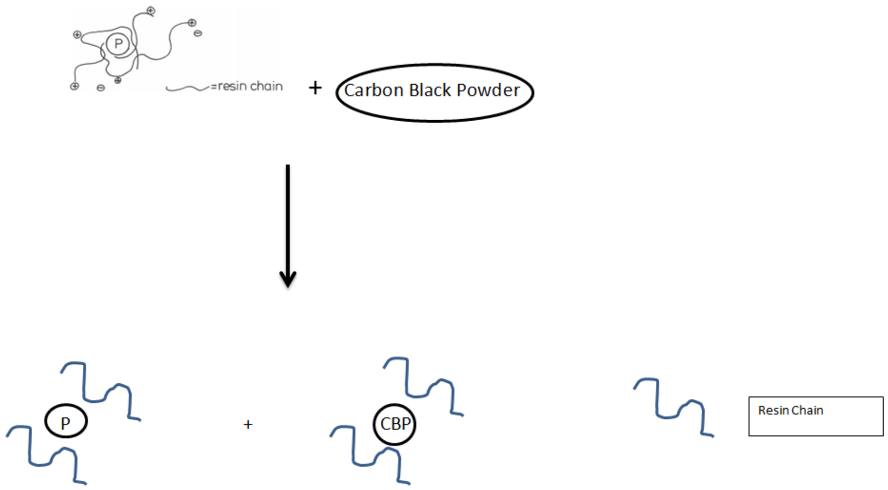


Figure 5.12: Reaction Scheme of Reduction of Paint Throw Power after the addition of Carbon Black Powder

Figure 5.13 provides the images of paint deposits after the addition of 25 mg/mL and 15 mg/mL of carbon black fingerprint powder to 25% and 15% concentrated paint solution. Both disks were completed at approximately 151 V for 20 seconds (Disk 27) and 41 seconds (Disk 28). The paint deposited on Disk 27 is darker than the deposited paint on Disk 28. The paint deposited on Disk 27 has a higher concentration of paint solution and powder, therefore it is expected that the deposited paint would be darker. Figure 5.14 provides the current versus time plot for the deposition study. A rapid decrease in current followed by stabilization at approximately 2 mA is present. The addition of carbon black fingerprint powder resulted in paint deposits that fully covered the surface of the metal disks without an outline of the fingerprint or any ridge detail present.

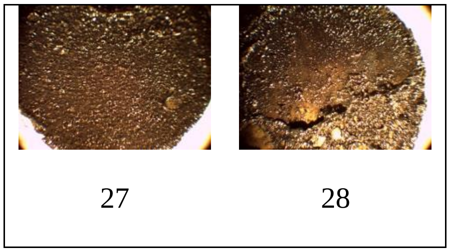


Figure 5.13: Image of Metal Disks after Powercron 6000CX Paint Modified with Carbon Black Deposition: (Disk 27) 2% paint concentration and 25 mg/mL carbon black with an applied voltage of 151.3V for 20 seconds; (Disk 28) 15% paint concentration and 15 mg/mL carbon black with an applied voltage of 151.2V for 41 seconds.

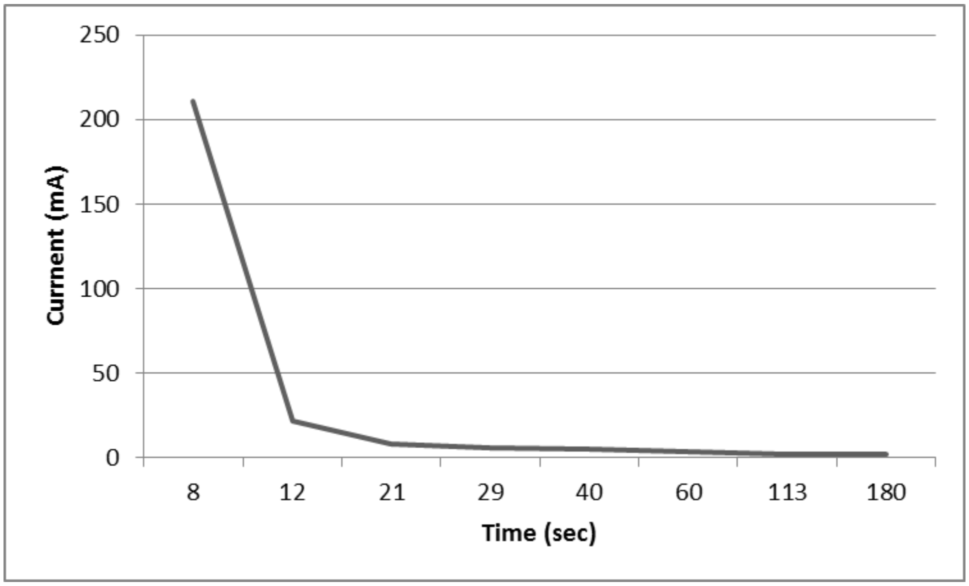


Figure 5.14: Current vs Time Curve produced from Powercron 6000CX Paint Deposition modified with Carbon Black Fingerprint Powder.

5.5: Powercron 6000CX Solution Modified with Polyethylene Glycol

Three different molecular weights of polyethylene glycol were used: 3350 g/mol (Disk 29), 8000 g/mol (Disk 30), and 400 g/mol (Disk 31). A concentration of 25 mg/mL of each molecular weight PEG was added to a 25% concentrated paint solution. For each study, the paint deposited with an applied voltage of approximately 151V during 180 seconds. Deposited paint fully covered the metal disk surface with pits present in each deposit as seen in Figure 5.15. The same rapid decrease in current was observed with each paint deposit experiment in Disk 29, Disk 30, and Disk 31 (similar to Figure 5.14, data not shown). The addition of polyethylene glycol did not result in an outline of the fingerprint or any ridge detail present.

29 30 31

Figure 5.15: Image of Metal Disks after Powercron 6000CX Paint Modified with Polyethylene Glycol: (Disk 29) 25 mg/mL 3350 PEG, an applied voltage of 151.2V for 180 seconds; (Disk 30) 25 mg/mL 8000 PEG, an applied voltage of 151.7V for 75 seconds; (Disk 31) 25 mg/mL 400 PEG, an applied voltage of 151.2V for 180 seconds.

5.6: Powercron 6000CX Solution pH Measurements

High throw power paint is generally formulated with an acidic pH ranging from 5.5 to 6.0 [18]. pH measurements in triplicate were taken of each paint solution that was used. Table 5.3 provides the average pH measurement of each Powercron 6000CX paint solution. The pH of the fully concentrated high throw power paint solution was slightly more acidic than the literature pH range. The pH of most of the paint formulations remained in a fairly narrow range (pH 4.92-5.39). The most dilute paint solutions (1% and 2% solutions) had significantly higher pH's, likely due to the low buffer capacity of these dilute solutions combined with the larger amount of hydroxide ions produced during paint deposition with these solutions. Since a completely insulating coating was not formed with the 1% and 2% solutions, the current remained at the maximum power supply value of 250mA (2%) and approximately 30mA (1%) for 180 seconds resulting in generation of much more hydroxide ion than when the maximum current was present for less than 5-10 seconds in cases where the disk was completely coated. Figure 5.16 shows the current versus time plot resulting from a non-insulating coating. The higher constant current observed for the 2% concentration solution resulted in a higher pH observed because a larger amount of hydroxide ions were produced compared to the 1% concentration solution. The pH of the carbon black formulations was also higher; additional work would be required to understand what factors lead to these results. After observing the pH ranges for the previously tested solutions, experiments were completed using solutions that were modified with acetic acid and ammonium hydroxide.

Table 5.3: Average pH Measurement of each Powercron 6000CX Paint Solution

Powercron 6000CX Paint Solution Concentration	Average pH Measurement
100%	5.11 ± 0.02
50%	5.23 ± 0.00
25%	5.08 ± 0.03
10%	4.92 ± 0.06
8%	4.93 ± 0.01

Table 5.3 (continued)

Powercron 6000CX Paint Solution Concentration	Average pH Measurements
4%	5.39 ± 0.01
2%	9.39 ± 0.03
1%	7.28 ± 0.22
25 mg/mL Carbon Black + 25% Paint	5.59 ± 0.00
15 mg/mL Carbon Black + 15% Paint	8.87 ± 0.03
25 mg/mL 3350 PEG + 25% Paint	5.39 ± 0.1
15 mg/mL 3350 PEG + 15% Paint	5.30 ± 0.05
25 mg/mL 8000 PEG + 25% Paint	5.38 ± 0.01
25 mg/mL 400 PEG + 25% Paint	5.06 ± 0.09

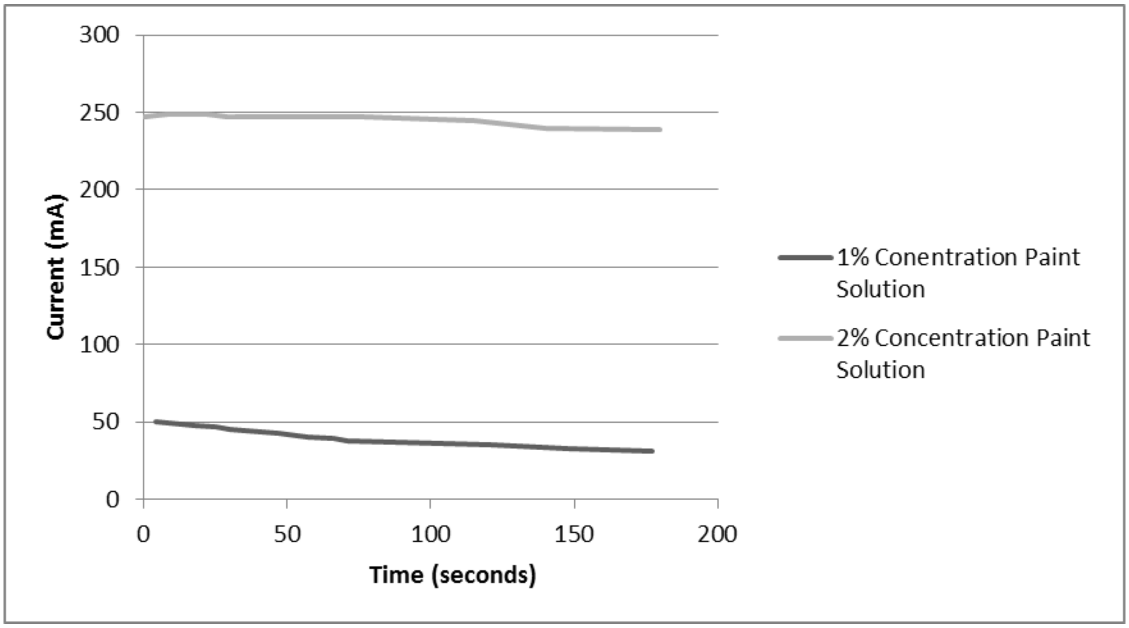


Figure 5.16: Current vs Time curve plot for 2% and 1% diluted paint solutions deposition experiments; (top) 2%; (bottom) 1%.

5.7: Powercron 6000CX Solution Modified with Acids and Bases

By adjusting the pH, the throw power of the paint may change. Paint deposition experiments using different concentrations of acetic acid and dilute ammonium hydroxide were completed to study the influence of pH on the deposition of paint.

5.7.1: Modified with Acetic Acid

Three different concentrations of acetic acid were studied; glacial acetic acid, 6M acetic acid, and 1:10 diluted acetic acid. Each paint deposition experiment was completed at approximately 150.8V for 180 seconds. Addition of glacial acetic acid to the paint solution used for Disk 32 resulted in a final pH of 2.84. Addition of 6M acetic acid to the paint solution used for Disk 33 resulted in a final pH of 3.29. Addition of diluted acetic acid to the paint solution used for Disk 34 resulted in a final pH of 3.70. The addition of acetic acid changed the buffering capacity of the paint solution producing acidic pH measurements presented in Table 5.4. For each experiment, the metal disk surface was fully coated with paint deposits. Paint still successfully deposited on the metal disk as seen in Figure 5.17 despite the significant decrease in pH and increase in the buffering capacity. A current change over time, similar to that shown in Figure 5.14 was present in each deposition experiment (data not shown). However, deposited paint from paint solutions adjusted with acetic acid did not reveal latent fingerprint patterns.

Table 5.4: Average pH Measurement of each Powercron 6000CX Paint Solution after Modification with Acetic Acid

Powercron 6000CX Paint Solution Concentration	Average pH Measurement
25 mg/mL Glacial Acetic Acid + 25% Paint	2.84 ± 0.05
25mg/mL 6M Acetic Acid + 25% Paint	3.29 ± 0.01
25 mg/mL 1:10 Diluted Acetic Acid + 25% Paint	3.70 ± 0.01

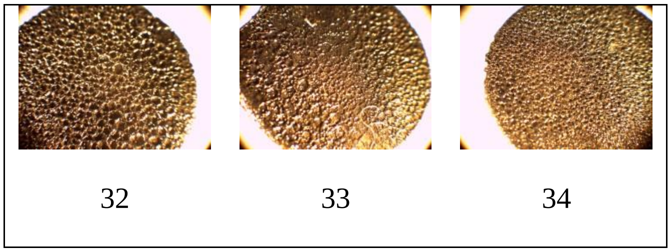


Figure 5.17: Image of Metal Disks after Powercron 6000CX Paint Modified with Acetic Acid with an applied voltage of 150.8V for 180 seconds: (Disk 32) 25mg/mL Glacial Acetic Acid; (Disk 33) 25 mg/mL 6M Acetic Acid; (Disk 34) 25 mg/mL 1:10 Diluted Acetic Acid

5.7.2: Modified with Ammonium Hydroxide

Dilute ammonium hydroxide solution was added to the paint solution. The concentration of ammonium hydroxide needed to be diluted enough ensuring that the paint particles did not precipitate prior to the deposition experiment. With concentrated ammonium hydroxide solutions, a large amount of hydroxide ions are present in solution that will deprotonate the resin chain producing the free base form of the amine, resulting in paint precipitation. After the addition of the ammonium hydroxide a pH of 9.43 resulted. Paint deposited on Disk 35, in Figure 5.18, using an applied voltage of 151.4V for 180 seconds. The deposited paint was initially watery compared to the other paint deposits in the previous experiments. The same trend with the current over time as seen in Figure 5.14 was present in this deposition study. No fingerprint enhancement of the deposited fingerprint was present after paint deposition.

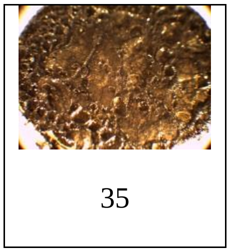


Figure 5.18: Image of Metal Disk after Powercron 6000CX Paint Modified with Dilute Ammonium Hydroxide with an applied voltage of 151.4 for 180 seconds.

5.8: Future Directions

With minimal enhancement of the latent fingerprint, future experiments with electrografting of diazonium salts should be conducted. Electrografting is an electrochemical reaction that permits binding of an organic layer to a solid conducting substrate [19]. The next phase of this research project will study the electrochemical reduction of a diazonium salt, benzenediazonium, on metals leading to covalent bonding of aryl groups on conductive metal surfaces as shown in Figure 5.19 [20].

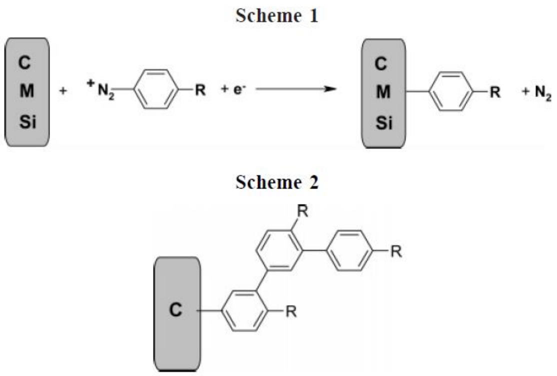


Figure 5.19: Electrografting Reaction of Benzenediazonium salt: (Scheme 1): Reduction of Benenediazonium on carbon, metal, or silicon surface; (Scheme 2): Polymerization of Benenzediazonium to produce film on carbon surface

Source: Adenier, A.; Combellas, C.; Kanoufi, F.; Pinson, J.; and Podvorica, F.I. Formation of Polyphenylene Films on Metal Electrodes by Electrochemical Reduction of Benzenediazonium Salts. *Chem. Mater.* **2006,** 18, 2021-2022

A radical is produced from the reduction of benzenediazonium that binds to the metal surface [20]. A hydrophobic, organic layer is formed on the surface which repels that charged diazonium cation [19]. A corresponding current vs. time curve is shown in Figure 5.20 with different R groups present on the salt. The bottom curve corresponds to when the R group is hydrogen and the top curve is when R is a nitro group. The peak in the bottom curve indicates the reduction of the diazonium salt. The decrease is showing that the product from Scheme 1 is now easier to reduce followed by the formation of the film as shown by the stabilization in the current. The current stabilization present in the top curve indicates an insulating film is formed over time. Based on the properties of the benzendiazonium salt, it is hypothesized that it has a self-limiting property as observed with the paint deposition experiments. An insulating film would form and the current would “shut-off”. In addition, it is hypothesized that the film thickness would correspond to the amount of current produced and charge present as seen in the metal deposition studies.

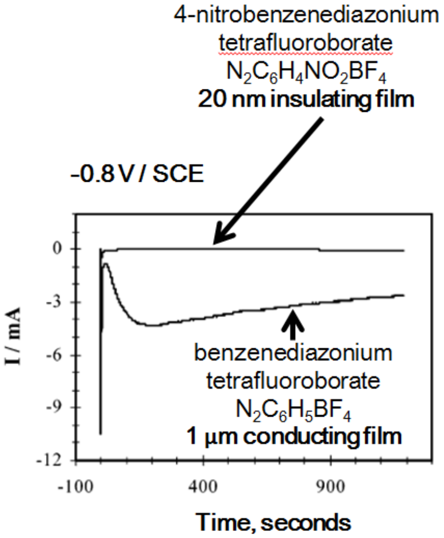


Figure 5.20: Chronoamperometric curve of benezenendiazonium electrografting reaction with different R-substituents (a): R is a Nitro group; (b) R is a hydrogen

Source: Adenier, A.; Combellas, C.; Kanoufi, F.; Pinson, J.; and Podvorica, F.I. Formation of Polyphenylene Films on Metal Electrodes by Electrochemical Reduction of Benzenediazonium Salts. *Chem. Mater.* **2006,** 18, 2021-2022

5.9: Conclusions

The purpose of the research experiment was to find a cathodic paint formulation which deposits paint on a bare metal surface while leaving fingerprint residue coated areas uncovered, resulting in enhancement of latent fingerprints. Ideally, coating of the bare metal areas would lead to a highly insulating surface, a decrease in direct current and essentially stopping paint deposition with latent fingerprint enhancement. Initial experiments used a high throw power Powercron 6000CX paint solution. Initial experiments showed that commercial high throw paint coated the bare metal surface and fingerprint residue.

Modifications of the paint solution were studied using deionized water, carbon black fingerprint powder, three molecular weights of polyethylene glycol, acetic acid, and ammonium hydroxide. Dilution experiments of the commercial paint using deionized water produced an outline of the latent fingerprint when the paint solution was 50%, 25% and 15% of the original paint concentration. Ridge detail was present in paint deposits with 25% of the original paint solution. Addition of carbon black fingerprint powder produced paint deposits that fully covered the metal disk. Each polyethylene glycol addition produced paint deposits that fully covered the metal disk. Adjustment of the pH using acetic acid and ammonium hydroxide was studied.

CHAPTER 6

CONCLUSION

6.1: Metal Deposition Conclusions

Preliminary experiments were completed using copper and nickel metal solutions on brass metal disks. Metal deposition was studied because the thickness of the electrodeposited metal can be controlled by controlling the amount of current. Copper (II) sulfate solutions with and without the addition of polyethylene glycol (MW 3350 g/mol) were studied. A nickel (II) sulfate solution was also studied. Using a CH Instruments Model 400B Series Electrochemical Quartz Crystal Microbalance Potentiostat, the voltage, current, and time were varied to observe the efficiency of both metal depositing onto the brass metal surface. The calculated total charge for each experiment was indicative to the amount and thickness of metal that was deposited.

Seven copper (II) sulfate deposition experiments were completed and three deposition experiments were completed using the copper (II) sulfate solution with the addition of polyethylene glycol. Chunky copper metal deposits were observed on the metal disks. With the addition of polyethylene glycol, brighter and smoother copper metal deposits were observed. Copper metal deposited without the enhancement of the latent fingerprint. Four nickel (II) sulfate deposition experiments were completed. Modestly thicker coatings were observed. Fingerprint ridge detail was present in the nickel metal coatings.

6.2: Paint Deposition Conclusions

Paint electrodeposition experiments were completed using high throw power Powercron 6000CX paint solution. A deposited fingerprint on a brass metal surface was submerged into the paint solution. A voltage was applied to the system and a current passed through the disks. During the coating process, water is reduced to hydroxide ions that diffuse away from the electrode and interact with paint particles present in solution. The paint particles are deprotonated by the hydroxide ion, causing the paint particles to precipitate onto the metal disk surface. Initial paint depositions coated the bare metal surface and the latent fingerprint residue.

Modifications to the paint formulation were completed using deionized water produced an outline of the latent fingerprint when the paint solution was 50% and 25% of the original paint concentration. Latent fingerprint ridge detail was present in paint deposits with 25% of the original paint solution. Additions of carbon black and three molecular weights of polyethylene glycol produced deposits that fully covered the metal disk and the latent fingerprint. Modifications of the paint solution using acetic acid and ammonium hydroxide changed the pH and the buffering capacity of the paint solution to produce paint deposits without the enhancement of the latent fingerprint. .

6.3: General Conclusion

The specific objective of this project, per 1.2: Overview of the Project, was to investigate methods of depositing material on a bare metal surface while leaving fingerprint residue coated areas uncovered. Both electrodeposition of metals and electrodeposition of paint were explored.

The formation of thin metal films and the formation of dark paint coatings with fingerprint outlines demonstrate the potential of the electrodeposition approach taken and an additional electroreductive polymerization system for future studies identified. A new latent fingerprint enhancement method is needed to enhance latent fingerprints on retrieved fired cartridge casings from crime scenes. Current commonly used fingerprint enhancement techniques are not successful at recovering latent fingerprints and the high temperature and pressure reached once a gun if fired is an important contributing factor.

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APPENDIX A

METAL DEPOSITION RESULTS SUMMARY TABLES AND CURVE PLOTS

APPENDIX A

METAL DEPOSITION RESULTS SUMMARY TABLES AND CURVE PLOTS

Table A1: Copper (II) Sulfate Metal Deposition Results

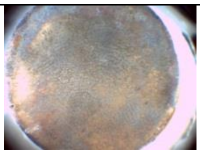
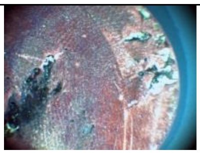
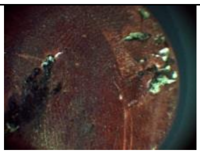
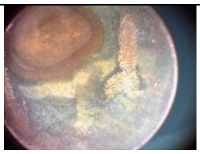
Disk #	Image	Potentiostat Setting	Voltage (V)	Current (A)	Time (sec)	Charge (C)
1						
2						
3		Amperometric i-t Curve	-0.6V	0.03A	300 sec.	9C
4		Amperometric i-t Curve	-0.6V	0.03A	300 sec	9C
5		Amperometric i-t Curve	-0.6V	0.03A	300sec.	9C

Table A1 (continued)

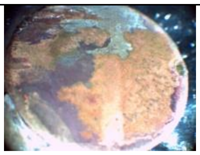
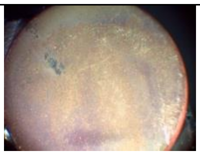
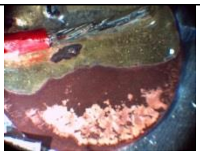
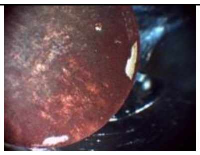
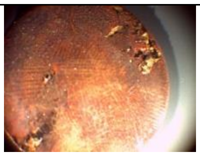
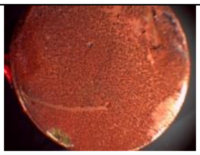
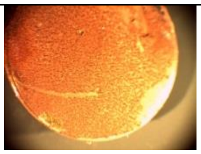
Disk #	Image	Potentiostat Setting	Voltage (V)	Current (A)	Time (sec)	Charge (C)
6		Chronopotentiometry	-0.4V	0.02A	300sec	6C
7		Chronopotentiometry	-0.4V	0.02A	300sec	6C
8		Chronocoulometry	-5V; +5		300sec each	-
9		Chronocoulometry	-5V; +5V		300sec. each	-
10		Amperometric i-t Curve	-0.6V	0.03A	300sec.	9C
11		Amperometric i-t Curve	-0.6V	0.019A	300sec.	5.7C

Table A1 (continued)

Disk #	Image	Potentiostat Setting	Voltage (V)	Current (A)	Time (sec)	Charge (C)
12		Amperometric i-t Curve	-0.6V	0.019A	300sec.	5.7C

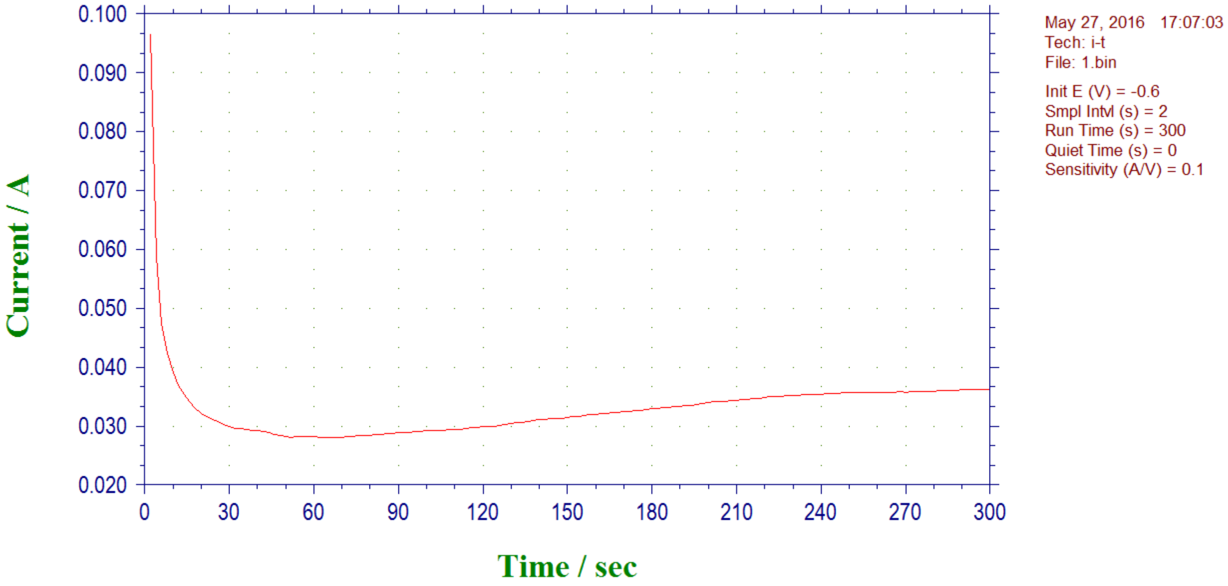


Figure A1: Amperometric i-t Curve corresponding to Disks 3, 4, 5, and 10

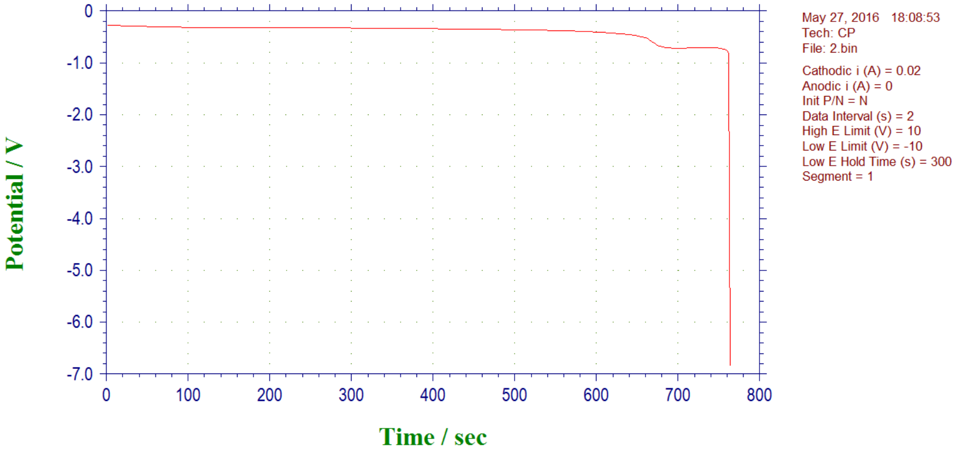
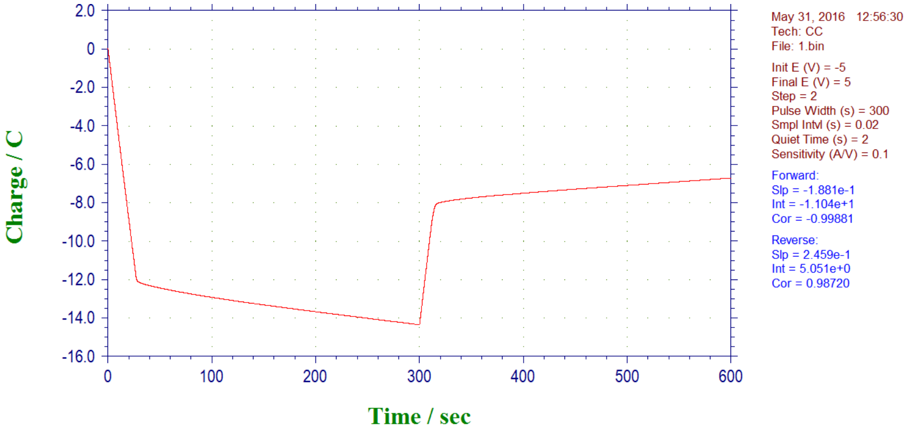


Figure A2: Potential versus Time Curve corresponding to Disks 6 and 7



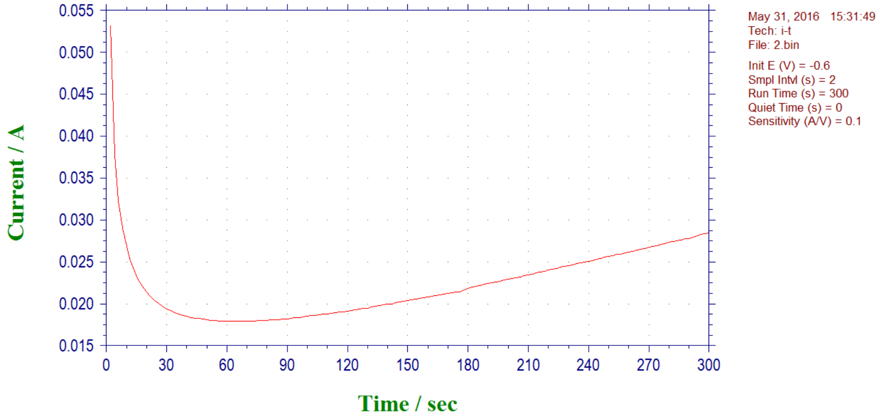
May 31, 2016 12:56:30
Tech: CC
File: 1.bin

Init E (V) = -5
Final E (V) = 5
Step = 2
Pulse Width (s) = 300
Smpl Intvl (s) = 0.02
Quiet Time (s) = 2
Sensitivity (A/V) = 0.1

Forward:
Slp = -1.881e-1
Int = -1.104e+1
Cor = -0.99881

Reverse:
Slp = 2.459e-1
Int = 5.051e+0
Cor = 0.98720

Figure A3: Charge versus Time Plot corresponding to Disks 8 and 9



May 31, 2016 15:31:49
Tech: i-t
File: 2.bin

Init E (V) = -0.6
Smpl Intvl (s) = 2
Run Time (s) = 300
Quiet Time (s) = 0
Sensitivity (A/V) = 0.1

Figure A4: Amperometric i-t Curve corresponding to Disks 11 and 12

Table A2: Copper (II) Sulfate with Polyethylene Glycol (MW3350 g/mol) Metal Deposition Results

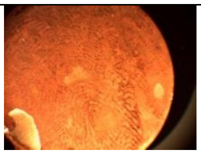
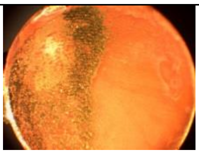
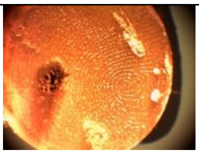
Disk #	Image	**Potentiostat Setting**	**Voltage (V)**	**Current (A)**	**Time (sec)**	**Charge (C)**
13		Amperometric i-t Curve	-0.6V	0.005A	300sec.	1.5C

Table A2 (continued)

14		Chronopotentiometry	-0.3V	0.01A	300sec.	3C
15		Chronopotentiometry	-0.5V	0.03A	300sec.	9C

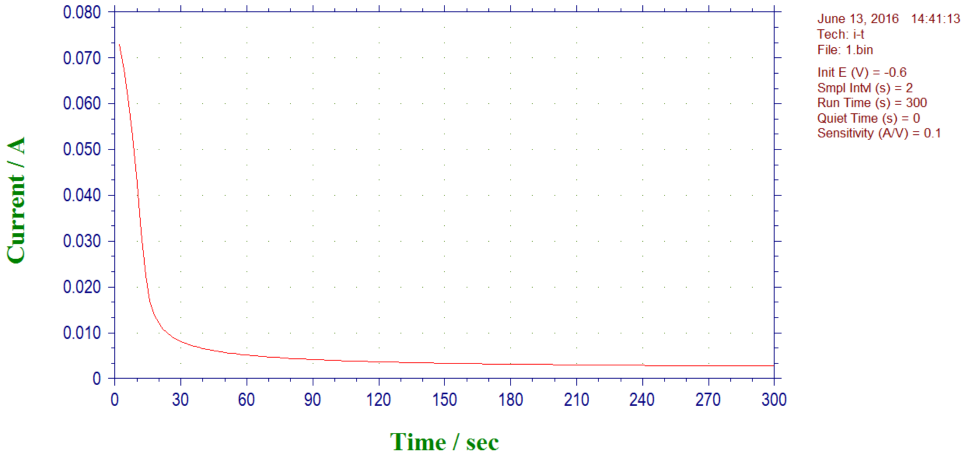


Figure A5: Amperometric i-t Curve corresponding to Disk 13

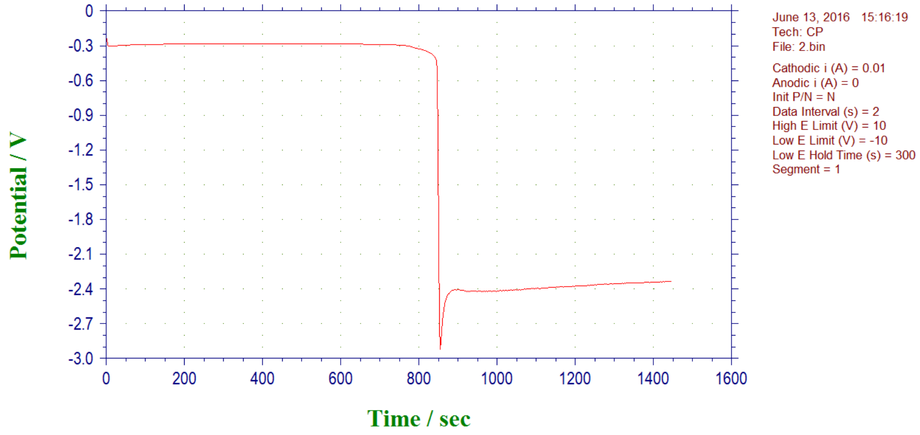


Figure A6: Amperometric i-t Curve corresponding to Disk 14

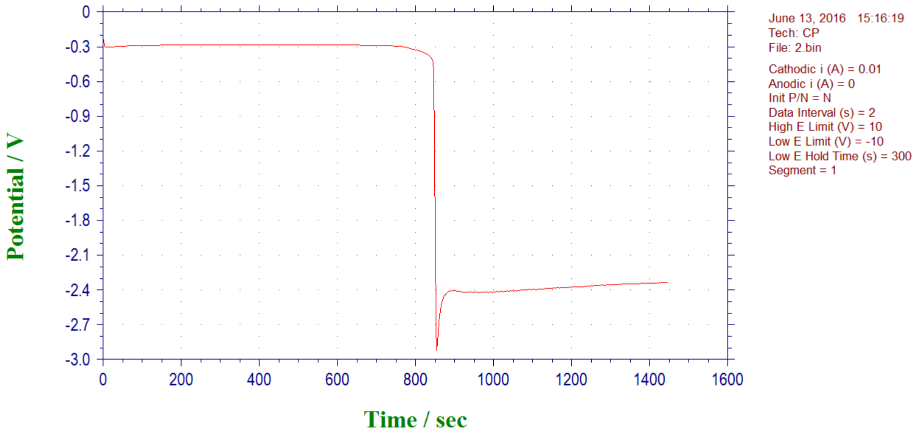


Figure A7: Amperometric i-t Curve corresponding to Disk 15

Table A3: Nickel (II) Sulfate Metal Deposition Results

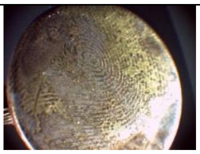
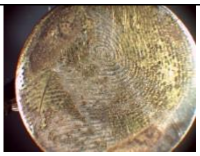
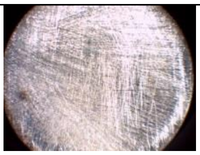
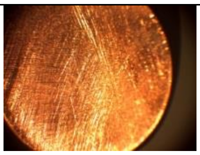
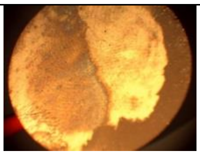
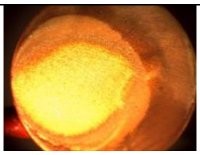
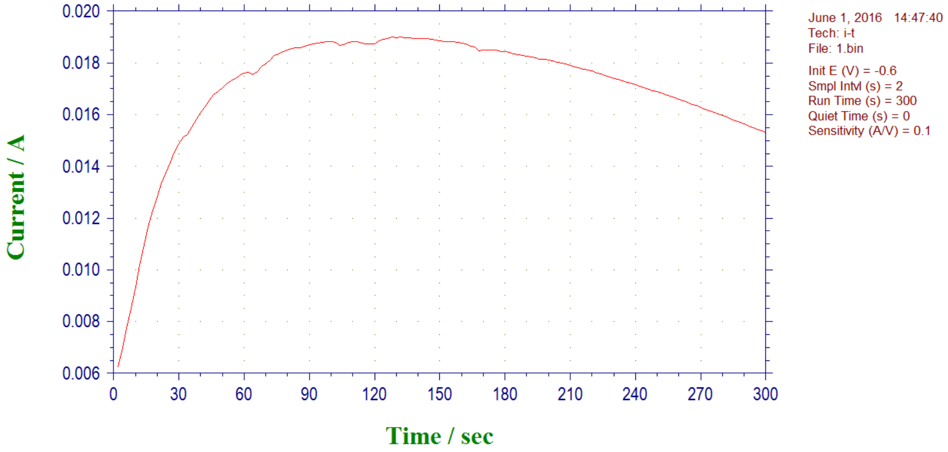
Disk #	Image	Potentiostat Setting	Voltage (V)	Current (A)	Time (sec)	Charge (C)
16		Amperometric i-t Curve	-0.6V	0.0185A	300sec.	5.55C
17		Amperometric i-t Curve	-0.6V	0.0185A	300sec.	5.55C
18		Amperometric i-t Curve	-0.8V	0.032A	500sec.	16C

Table A3 (continued)

Disk #	Image	Potentiostat Setting	Voltage (V)	Current (A)	Time (sec)	Charge (C)
19		Amperometric i-t Curve	-0.4V	0.0004A	500sec.	0.2C
20		Chronopotentiometry	-1.3V	0.05A	300sec.	15C
21		Chronopotentiometry	-1.3V	0.05A	300sec.	15C



June 1, 2016 14:47:40
Tech: i-t
File: 1.bin

Init E (V) = -0.6
Smpl Intvl (s) = 2
Run Time (s) = 300
Quiet Time (s) = 0
Sensitivity (A/V) = 0.1

Figure A8: Amperometric i-t Curve corresponding to Disks 16 and 17

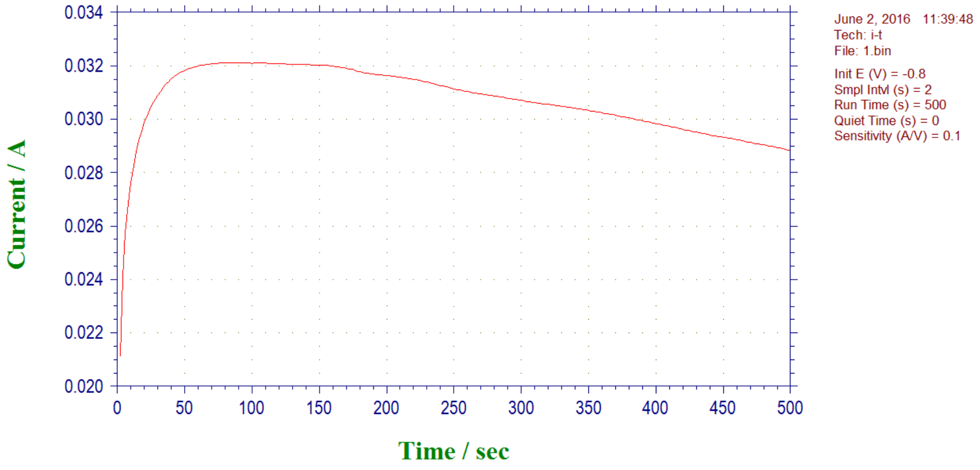


Figure A9: Amperometric i-t Curve corresponding to Disk 18

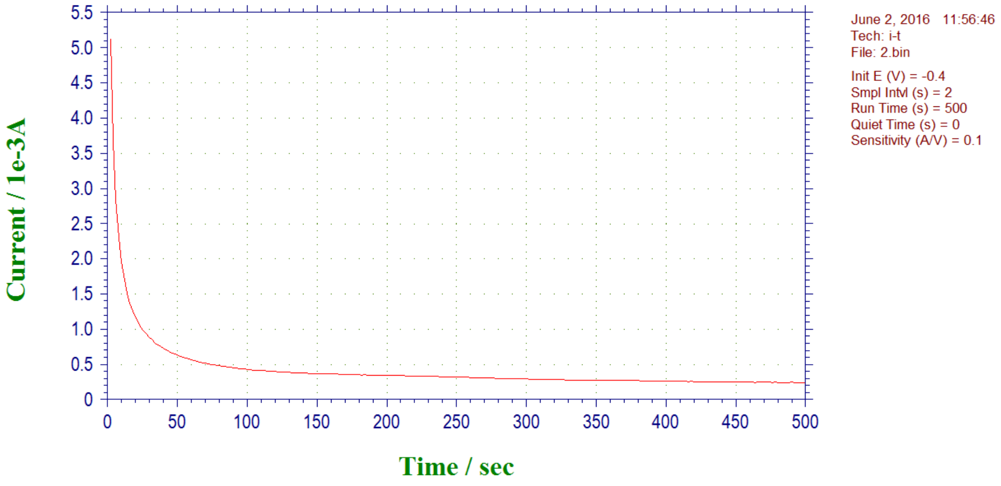
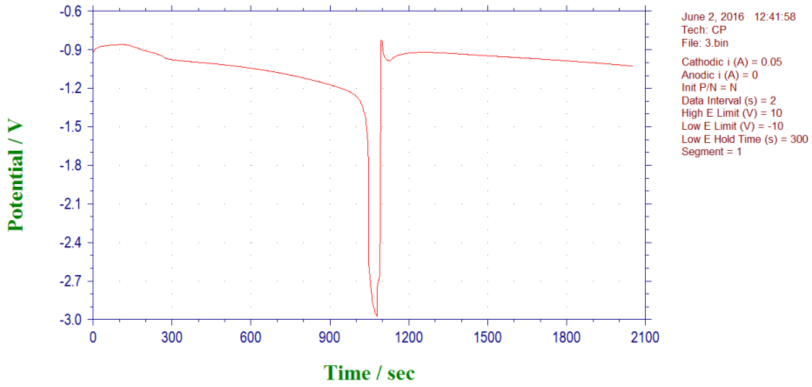


Figure A10: Amperometric i-t Curve corresponding to Disk 19



June 2, 2016 12:41:58
Tech: CP
File: 3.bin

Cathodic i (A) = 0.05
Anodic i (A) = 0
Init P/N = N
Data Interval (s) = 2
High E Limit (V) = 10
Low E Limit (V) = -10
Low E Hold Time (s) = 300
Segment = 1

Figure A11: Potential versus Time Curve plot corresponding to Disks 20 and 21

APPENDIX B

PAINT DEPOSITION RESULTS SUMMARY TABLES

APPENDIX B

PAINT DEPOSITION RESULTS SUMMARY TABLES

Table B1: Initial High Throw Power Paint Deposition Results using Potentiostat

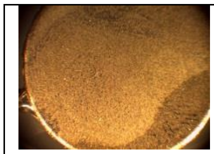
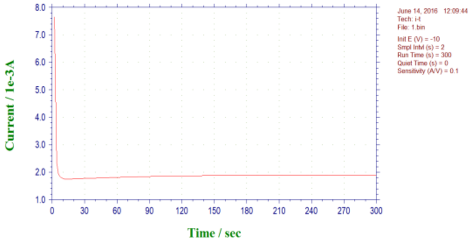
	

Table B2: High Throw Power Paint Deposition Results with HBI Haake Buchler Instruments 500V Power Supply

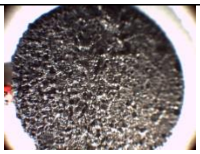
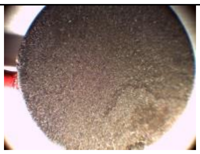
Disk #	Image	Voltage (V)	Time (sec)
2		500	9
3		100	30.5
4		200	240.7

Table B2 (continued)

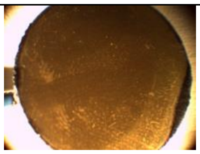
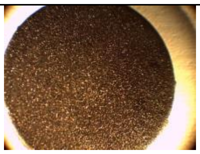
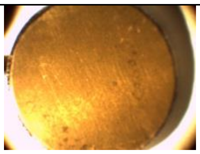
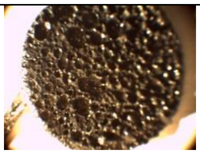
Disk #	Image	Voltage (V)	Time (sec)
5		125	180
6		50	360
7		50	360
8		301	360
9		301	360
10		401	30

Table B2 (continued)

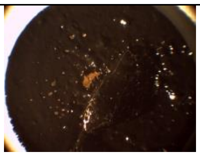
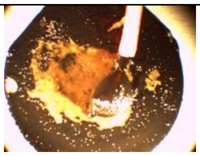
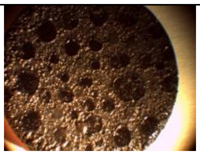
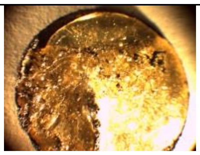
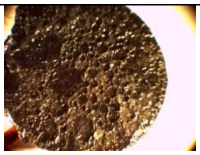
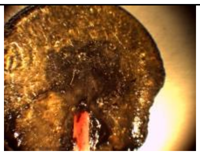
Disk #	Image	Voltage (V)	Time (sec)
11		400	150
12		350	500
13		350	7.4
14		350	7.4
15		350	18.4
16		350	18.4

Table B2 (continued)

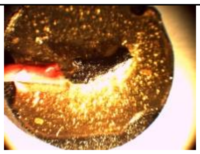
Disk #	Image	Voltage (V)	Time (sec)
17		150	300.5
18		150	308

Table B3: High Throw Power Paint Deposition Results with LKG Bromma 2197 Power Supply

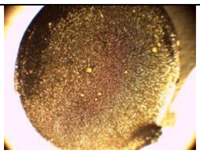
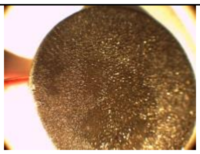
Disk #	Image	Voltage (V)	Time (sec)
19		31	60
20		157	60
21		150	500
22		150	300

Table B3 (continued)

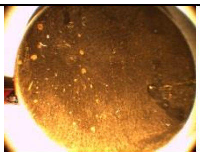
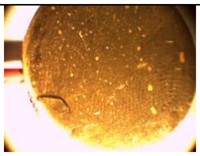
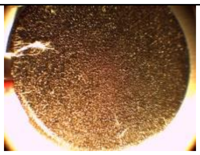
Disk #	Image	Voltage (V)	Time (sec)
23		150	20
24		150	300
25		150	300
26		150	300
27		150	300
28		150	300

Table B3 (continued)

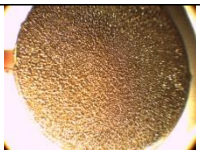
Disk #	Image	Voltage (V)	Time (sec)
29		150	300

Table B4: High Throw Power Paint Deposition Results with LKG Bromma 2197 Power Supply with Voltmeter

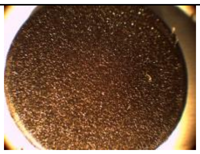
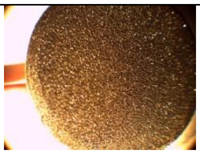
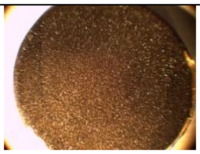
Disk #	Image	Voltage (V)	Time (sec)	Total Time (sec).
30		150	10	300
31		150	9	300
32		150	8	300
33		150	17.5	

Table B4 (continued)

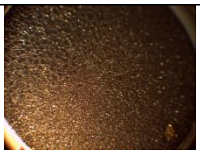
Disk #	Image	Voltage (V)	Time (sec)	Total Time (sec).
34		150	16.5	
35		150	17.3	
36		150	45.8	
37		151.9		300
38		151.8	5	300
39		151.7	6	300

Table B4 (continued)

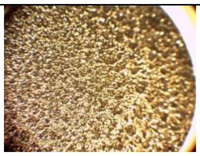
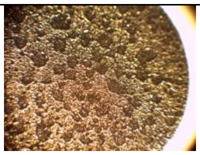
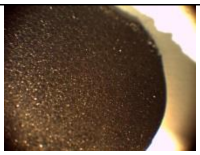
Disk #	Image	Voltage (V)	Time (sec)	Total Time (sec).
40		151.9	5	300
41		251	4	300
42		301	10	300
43		149	10	
44		149	5	

Table B5: High Throw Power Paint Diluted with Deionized Water Deposition Results and Settings

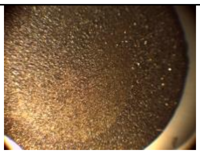
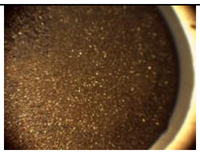
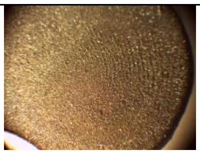
Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
45		50%	150.7	8	
46		50%	150.2	7	
47		50%	101.1	7	
48		25%	151.8	10	300
49		25%	151.8	7	

Table B5 (continued)

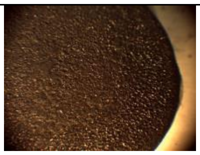
Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
50		25%	76.5	10	
51		25%	40.85	11	
52		25%	10.61	10	
53		25%	5.94	6	
54		15%	151.4	6.3	
55		15%	50.9	9.7	

Table B5 (continued)

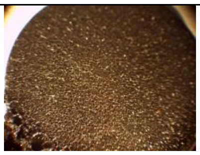
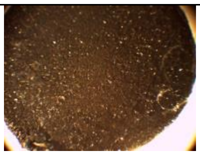
Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
56		15%	20.9	3.6	
57		10%	17.8	38	
58		10%	151.2	6	180
59		8%	151.3	4	180
60		4%	148.4	160	180
61		2%	150		180

Table B5 (continued)

Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
62		1%	151.3		180

Table B6: High Throw Power Paint Diluted with Carbon Black Powder Deposition Results and Settings

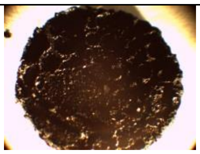
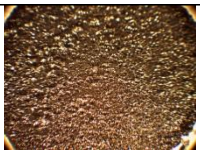
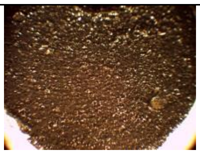
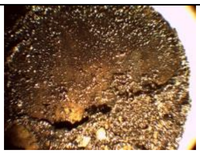
Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
63		25% Paint + 25 mg/mL CB	151.9	21	180
64		25% Paint + 25 mg/mL CB	151.6	4	180
65		25% Paint + 25 mg/mL CB	151.3	6	20
66		15% Paint + 15 mg/mL CB	151.2	41	

Table B7: High Throw Power Paint Diluted with Polyethylene Glycol Deposition Results and Settings

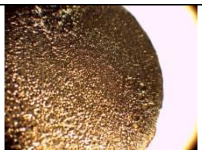
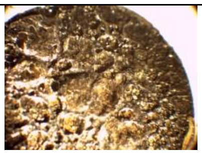
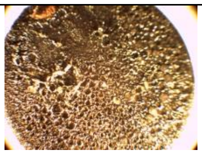
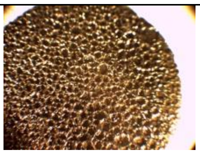
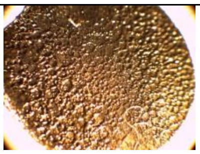
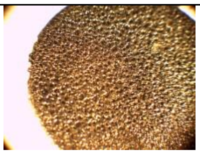
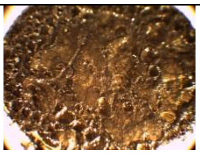
Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
67		25% Paint + 25 mg/Ml PEG (3350)	151.2	5	100
68		15% Paint + 15 mg/mL PEG (3350)	151.7	13	180
69		25% Paint + 25 mg/mL PEG (8000)	151.3	63	75
70		25% Paint + 25 mg/Ml PEG (400)	151.2	9	180
71		25% Paint + 25 mg/mL PEG (400)	151	12	180

Table B8: High Throw Power Paint Diluted with Acids and Bases Deposition Results and Settings

Disk #	Image	Concentration	Voltage (V)	Time (sec)	Total Time (sec).
72		25% Paint + 25 mg/mL Glacial Acetic Acid	150.7		180
73		25% Paint + 25 mg/mL 6M Acetic Acid	150.8		180
74		25% Paint + 25 mg/mL (1:10) Diluted Glacial Acetic Acid	150.8		180
75		25% Paint + Dilute Ammonium Hydroxide	151.4		180

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