Co-deposition of Pigment Particles with Nickel through Electrodeposition

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Department of Materials Science and Engineering
University of Toronto

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Abstract

This research focuses on the synthesis of a nickel-pigment composite coating in an effort to produce coloured nickel electrodeposits via the codeposition approach. A blue pigment, Copper Phthalocyanine (CuPc) Blue was codeposited to create Ni-CuPc composite coatings. Top surface and cross-sectional Scanning Electron Microscopy (SEM) images confirmed the codeposition of pigment particles within the nickel matrix throughout the entire coating thickness. The top surface of the Ni-CuPc composite coating showed an unexpected metallic copper colour. X-Ray Photoelectron Spectroscopy (XPS) analysis indicates the presence of metallic copper confined to the top surface. It was speculated that this phenomenon is due to the galvanic displacement reaction between copper from the pigment and nickel from the matrix. Upon removing the copper surface layer the colour of the composite remained metallic silver despite the presence of the pigment particles.
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Chapter 1: Introduction

1 Introduction

1.1 Motivation for this Research

Nickel electrodeposits are widely used for many engineering application due to their outstanding physical and mechanical properties such as hardness, wear resistance, coating uniformity, and corrosion resistance. The ability to plate nickel onto both conductive and non-conductive substrate materials makes nickel coatings a versatile and cost effective alternative to more expensive metal alloys with equivalent performance [Schlesinger et al. 2010]. It also allows the recovery of locally worn out or damaged components by applying a nickel coating at the fraction of the cost required to replace entire components [Watson 1989]. Therefore electrodeposited nickel is extensively used in many different industries including the aerospace, automotive, food equipment and nuclear power industry, providing a protective layer against corrosive environment while providing strength and hardness to the structure.

However, in addition to the functional properties that electrodeposited nickel possess, another major aspect that is often overseen is the aesthetics of the coating. From a consumer’s point of view, the aesthetic aspect of a metal surface finish can be just as crucial as its basic functionality. A good example of this can be found in the dyed anodized aluminum layer used as surface finish on electronic devices.
Figure 1.1 shows a popular portable media player by Apple in which the surface finish exhibits a variety of visually appealing colours. The colours come from the dyes and pigments that are filled and sealed within the porous structure of the anodized aluminum layer. This results in a finish that provides a functional protective layer and also serves a decorative purpose. Such surface finish is possible in the case of aluminum oxide due to its porous oxide structure [Takahashi 2003]. However, this imposes a challenge to the electrodeposited nickel as it exhibits a surface finish that is limited to the colour of the nickel itself, various shades of metallic silver. Nickel oxide does not possess a porous structure that can entrap pigment particles. However, by utilizing the electrodeposition process, there is the potential to co-deposit the pigment particles with nickel to create a nickel-pigment composite coating. By incorporating pigment or dye during the electroplating process, decorative functionality could potentially be added into nickel electrodeposits so that they exhibit various desired colours and replace the ordinary metallic silver finish. Thus, the motivation for this thesis is to create coloured nickel electrodeposits that not only provide the benefits of Ni coatings but also serve decorative purposes.
1.2 Existing Decorative Coating Processes

In addition to simple paints, there are a number of existing processes that are commonly used in the industry to apply decorative coatings on a desired metallic substrate: PVD, Powder Coating, and electrophoretic painting.

![Diagram of PVD, electrostatic powder coating, and electro-painting processes](image)

**Figure 1.2 – Schematic diagrams for decorative coating processes (starting from the left): PVD, electrostatic powder coating, and electro-painting [Ashby 2009].**

PVD is a well-established industrial process that can be used to create metallic decorative coatings by depositing simple metals or metal alloys [Schulz 2001]. It is a film deposition process where a target material in the solid state is vapourized to the gaseous state in a vacuum or low-pressure environment, which subsequently condenses into a solid film on a desired substrate [Mattox 1998]. Various PVD methods including thermal vacuum deposition, sputter deposition, arc deposition, or ion-assisted deposition can be used to deposit decorative coatings. Colours obtained from PVD coatings are often limited to metallic tones. For instance, the metallic tone can range from bright yellow/gold achieved by using gold or more commonly TiN alloys to yellow brown, grey violet and bluish grey with TiAl alloys. The PVD process has its shortcomings in corrosion resistance and leveling. Thin PVD coatings can fail to completely cover the defects on the substrate surface, leaving small areas of the substrate exposed to...
corrosive attack. Local corrosion is further accelerated as the inert hard coating material often has high positive electrochemical potential [Schulz 2001]. The PVD process imposes constraints on the geometry of the substrate to be coated due to its line of sight transfer. Deposition of the targeted material cannot be achieved for complex geometry such as the inside of tubular components. The limited variety of colour to only metallic tones and the geometrical constraint on the substrate pose significant challenges in applying decorative coatings with the PVD process.

Electrostatic powder coating involves a powder mixture of pigment and resin that is sprayed onto the substrate through a charged nozzle. The charged powder particles are electrostatically attracted to the surface of the electrically grounded substrate, and form a thin layer of powder mixture. The substrate and the adhered powder are subsequently heated and cured in an oven to fuse the layer into a continuous film. This results in a uniform decorative coating which exhibit different colours that correspond to the pigment colour. However, the high curing temperature and the line of sight deposition during spraying limits this process for substrates that are sensitive to the processing temperature or have complex geometry [Ashby 2009].

Electrophoretic painting is another well-established process used in the industry to apply a decorative finish on products. The process involves immersing a part in a bath that consists of resin and pigment concentrate in a water-based solution [Cotell et al. 1994]. The substrate to be coated acts as the cathode and an inert material such as graphite is used as the anode, forming an electrolytic cell with an applied voltage in the system. The charged pigment and resin particles in the bath are deposited onto the substrate due to the electrophoretic migration of the particles and form a paint film strongly bonded to the surface. The film is cured at a higher temperature to obtain optimal coating quality. The electrophoretic painting process addresses the issue of line of
sight deposition encountered in PVD and the powder coating process and enables uniform coatings for large complex shapes including the inside of tubular components. However, the decorative coating consists of a resin-pigment matrix that does not provide the strength and hardness equivalent to that of a metallic coating.

As described above, each respective decorative coating process has its limitation and drawbacks that need to be addressed and improved in order to deposit a strong decorative metallic coating. There is a need to find and develop a simple coating process that is not limited by line of sight deposition and deposits a metallic coating, in this case nickel which provides both durability and decorative properties. A promising method for such a coating could be the electroadeposition process, which enables the deposition of nickel while simultaneously co-depositing pigment particles.

1.3 Objectives

Electrodeposition is a versatile process that enables the synthesis of nickel coating for many different industrial applications. However the need for a decorative component in such coatings motivates this research to explore possibilities of further develop the electroadeposition synthesis process by incorporating pigments to produce nickel coatings with different colour and surface appearance.

The objectives of the thesis are as follows:

i) To develop a one step co-deposition process to synthesize nickel-pigment composite coatings by incorporating pigment into the nickel metal matrix via electrodeposition.
To obtain a decorative colour effect in the electrodeposited nickel-pigment composite coating

The structure of this thesis is as organized in the following way. Chapter 2 will introduce relevant background information to this thesis. The section will first start by explaining how we see colour followed by elaborating on the basic mechanisms for electro-deposition, electrophoretic deposition, and co-deposition, all of which play a crucial role in synthesizing nickel-pigment composite material. Current literature related to the synthesis of nickel-pigment composite material will be discussed.

Chapter 3 will outline and describe the experimental procedures performed to synthesize and characterize the nickel-pigment composite coatings.

In Chapters 4 and 5, results and discussion will be presented. Chapter 4 will focus on the synthesis aspect of the composite coatings. Characterization of the pigment particle in a colloidal system as well as plating parameters will be discussed in detail. In Chapter 5, the focus will shift to characterizing the colour of the nickel-pigment composite coating.

Chapter 6 and 7 will summarize the thesis and present recommendations for future work that will help to improve the synthesis and characterization of the nickel-pigment composite as well as help better understand the colour phenomena observed in this thesis.
Chapter 2
Literature Review

2 Literature Review

2.1 Light and Colour

The main objective of this thesis is to produce a nickel composite material that exhibits colour by incorporating pigments. Therefore, before elaborating on the synthesis aspects of the composite material, a brief section will first be dedicated to help understand the background on how light and matter interact with each other to produce colour in the particular organic pigment which will be used in this study.

Electromagnetic radiation consists of electric and magnetic fields oscillating out of phase perpendicular to each other, and also perpendicular to the direction of propagation [Serway 2005]. As can be seen from the electromagnetic spectrum in Figure 2.1, electromagnetic radiation can be classified by wavelength into several different types: gamma rays, X-rays, ultraviolet radiation, visible light, infrared radiation, microwaves, and radiowaves [Tilley 2011]. The visible spectrum, or what we call visible light, comprises a small section of the spectrum in

![Electromagnetic Spectrum](image)

**Figure 2.1 – Electromagnetic Spectrum [Tilley 2011]**
the range of wavelengths between 400nm and 700nm. This is the range of wavelengths which the human eye is able to detect and perceive as different colours.

Colour is the result of the human brain’s interpretation of light at different wavelengths or energies that our eyes can detect. It is an attribute we use to describe the appearance of an object. Colour arises from the interaction of light and the object. In the case of a pigmented surface of a coating, the coating appears as a specific colour under sunlight due to the selective absorption of specific wavelengths on the surface. The pigment absorbs or scatters the incoming light and causes certain wavelengths from the visible spectrum to be missing or reduced as it is being reflected into the observer’s eye. The human eye detects the reflected light and interprets it as a specific colour. The colour we see represents the corresponding complementary colour of the absorbed region and is derived from the remaining portion of the spectrum [Walter 1997]. For instance, the appearance of red can arise from reflected sunlight in which the green-blue component (wavelength below 600nm) has been absorbed by the pigment.

The reason why organic pigment molecules absorb specific ranges of wavelength is due to the molecular orbitals and the associated energy during electron transitions. For the purpose of explaining the energy levels in molecules, light can be regarded as a stream of photons with the energy of each photon being defined as

$$E' = \frac{hc}{\lambda}$$

(eq. 2.1)

where h is the Planck constant, c is the speed of light, and λ is the wavelength of the equivalent light wave. The absorption of light in the pigment induces an excitation of the electrons
occupying a series of molecular orbitals assigned of a specific energy from the ground state to an excited state. The two molecular orbitals that are of interest in determining the colour of a molecule are the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital). During light absorption, electrons are excited from HOMO to LUMO and the energy difference between the two states, also referred to as the HOMO-LUMO gap, translates into the specific wavelength that is being absorbed during this transition. As the energy (E) and the wavelength (\(\lambda\)) have an inverse relationship in Eq (2.1), the smaller the energy difference between the two states, the longer the wavelength of absorption.

Figure 2.2 – Schematic diagram of the molecular energy levels showing the HOMO and LUMO a) in ground state, and b) in an excited state [Tilley 2011]

Coloured organic molecules often consist of conjugated bonds (alternating single and double bonds) between carbon atoms. In such molecules, the HOMO is a \(\pi\) molecular orbital which is derived by the overlap of \(p\) orbitals between two carbon atoms while LUMO is the antibonding \(\pi^*\) molecular orbital. The electronic transition from \(\pi\) type HOMO to \(\pi^*\) type LUMO, the so-called \(\pi - \pi^*\) transition, gives rise to the intense absorption band responsible for the colour we observe. An example in which conjugated bond structure give rise to colour can be found in
phthalocyanines. Phthalocyanine is a class of compounds in which conjugated bonds circle a centre metal atom, typically Cu, Fe, Al, Ni, Co, etc. The molecular structure is shown in Figure 2.3. The colour of these compounds is mainly blue and green/blues due to the $\pi - \pi^*$ transition in the phthalocyanine ring system. Copper phthalocyanine, one of the derivatives of the phthalocyanine compounds exhibits a vivid blue colour that is only slightly changed when the Cu centre atom is replaced by an alternative metal. This reveals that the colour is not due to copper but the organic structure of the conjugated carbon rings around the centre metal atom.

![Molecular structure of Copper Phthalocyanine](image)

**Figure 2.3 – Molecular structure of Copper Phthalocyanine [Christie 1994]**

### 2.2 Electrodeposition of Nickel

Electrodeposition of nickel is a versatile surface finishing process that involves the deposition of a nickel coating on a desired substrate material for functional or decorative applications (e.g. Di Bari 2010). The advantageous combination of mechanical properties such as strength, hardness, and workability as well as its corrosion resistance makes nickel a desirable metal to electrodeposit in nanocrystalline form for various functional purposes [Erb 2011]. For decorative application, nickel can be electrodeposited in combination with chromium to create a coating of mirror-bright finish, which also results in an improved corrosion resistance. Development and
improvements of the nickel electroplating process for different applications have been on-going for more than 200 years and continue to do so as a commercially viable and practical surface finishing process. The ability to produce fully dense nickel metal-matrix composites in a single step process by simple modification of electrolyte composition and electrical plating parameters makes electrodeposition a suitable method to create nickel composite coatings (e.g. Robertson 1999).

Electrodeposition of nickel involves immersing two electrodes (anode and cathode) in an aqueous solution of nickel salts. A schematic diagram an electrodeposition setup is shown in Figure 2.4.

![Diagram of Electrodeposition Setup]

**Figure 2.4 - Schematic diagram of the electrodeposition setup**

By applying an over-potential through an external power supply between the two electrodes, the flow of the current causes the anode, in this case metallic nickel, to dissolve in the solution as positively charged nickel ions. Subsequently, the nickel ions dissolved in the solution react with
the electrons being supplied at the cathode surface and are deposited as metallic nickel. The flow of the current between the two electrodes enables the anode to dissolve and replenish nickel ions that are being depleted when being deposited at the cathode. An additional unwanted reaction that occurs simultaneously at the cathode is hydrogen evolution, which lowers the efficiency of electrodeposition process.

Anodic Reaction: \( \text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \)

Cathodic Reactions: \( \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \)
\( 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \)

The amount of nickel deposited at the cathode given 100% current efficiency can be calculated from the expression derived from Faraday’s law of electrolysis

\[
m = \frac{AIt}{nF}
\]

where \( m \) is the amount of nickel deposited, \( A \) is the molecular weight of nickel, \( I \) is the current flow, \( t \) is the time in hours, \( n \) is the number of electrons in the electrochemical reaction, and \( F \) is Faraday’s constant. As seen from equation 2.2, the deposition rate of nickel (\( m/t \)) is proportional to the current flow and can therefore be controlled by varying the current density at a given cathode area. However, in conventional DC plating, there is a limiting (maximum) current density that is governed by the mass transport limitation of the depositing nickel ions near the cathode surface. The limiting current density \( I_L \), is

\[
I_L = \frac{nFD}{\delta} \zeta_b
\]

(eq. 2.3)
where $D$ is the diffusion coefficient, $\delta$ is the thickness of Nernst diffusion layer, and $C_b$ is the bulk concentration of the metal ions in the solution.

Figure 2.5 - Concentration profile of the depositing metal ion species near the cathode surface; $C_b$ is the bulk concentration of metal ion in solution; $C_{(x)}$ is the concentration at the surface of the electrode [Schlesinger et al. 2010]

Figure 2.5 is a diagram of the Nernst diffusion layer model that shows the concentration profile of the depositing metal ion species near the surface of the cathode. $\delta$ is the thickness of the Nernst diffusion layer while $C_b$ is the bulk concentration of the depositing metal ion. The model assumes that the solution maintains a bulk concentration of $C_b$ up to a distance $\delta$ away from the cathode. At distances less than $\delta$, the concentration starts to decrease down to 0 as it reaches the surface of the cathode. When a current density higher than the limiting current density is applied, other reduction reactions such as the hydrogen evolution will be dominant and affect the quality of the metal deposits [Schlesinger et al 2010]. This limitation can be overcome by using pulsed
current where current is turned on and off in short intervals, enabling the metal ions to be replenished near the cathode surface during the off time [Erb 2011]

2.3 Electrophoretic Deposition

Synthesizing a composite material involves not only the deposition of metal but also includes secondary particles that are to be embedded in the metal matrix. While the electrodeposition process accounts for the deposition of metals, an additional process that allows the incorporation of secondary particles must be identified. A process by which secondary particles can be deposited on a substrate is electrophoretic deposition.

Table 2.1 - Comparison Table between Electrodeposition and Electrophoretic Deposition

<table>
<thead>
<tr>
<th>Deposition Technique</th>
<th>Electrodeposition</th>
<th>Electrophoretic Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moving Species</td>
<td>Metal Ions</td>
<td>Solid Particles</td>
</tr>
<tr>
<td>Charge Transfer on Deposition</td>
<td>Ion Reduction</td>
<td>None</td>
</tr>
<tr>
<td>Preferred Liquid Medium</td>
<td>Water</td>
<td>Organic</td>
</tr>
<tr>
<td>Required Conductance of Liquid Medium</td>
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<td>Low</td>
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</tbody>
</table>

Electrophoretic deposition (EDP) is a colloidal process in which charged particles suspended in a liquid medium are electrostatically attracted and deposited onto a conductive substrate of opposite charge under an applied electric field [e.g. Bersa and Liu 2007]. This process is used to deposit various materials such as polymers, ceramics, or organic materials into coatings. EDP is not to be confused with the electroplating process. In electroplating, as is the case for the deposition of nickel metal, the ions are the moving species and undergo reduction on deposition as metal [Miracle and Donaldson 2001]. On the other hand, in EPD, the particles migrate with no charge reduction on deposition. Therefore EPD is based on the suspension of particles in a
solvent whereas electroplating is based on the solution of salts or ionic species. Table 2.1 shows a comparison between electroplating and electrophoretic plating.

Figure 2.6 is a schematic diagram of the EPD process that shows the two main steps involved during the process: electrophoresis and deposition. The EPD involves two electrodes immersed in a suitable liquid medium with suspended charged particles. In the first step, an electric field is applied between the two electrodes causing the charged particles suspended in the liquid to move towards the oppositely charged electrode. In the second step, the particles accumulate at the electrode and create a compact and homogenous film [Corini et al 2008]. The EDP process exploits the surface electrostatic charge characteristic of the particles [Miracle and Donaldson 2001]. Therefore, a stable suspension of non-agglomerated dispersed charged particles is essential in providing them the mobility to migrate towards the electrode.

Figure 2.6 - A schematic diagram of the electrophoretic deposition process with two electrodes and charged particles in solution [Sarkar and Nicholson 1996]
2.4 Electro-codeposition Mechanism

Electro-codeposition involves the incorporation of inert particles in an electroplating bath in order to codeposit the particles with metal. Therefore it involves both the electrodeposition of the depositing metal as well as electrophoretic migration of the inert particles towards the cathode simultaneously. Particles are deliberately added to produce metal matrix composites with improved physical properties compared to pure metal deposits (e.g. Hovestad and Janssen 2005). For instance, SiC particles are often codeposited with nickel to improve its wear resistance. To achieve the objective of this thesis, pigment particles will be incorporated to obtain coloured nickel-pigment composites.

There exist many models explaining the mechanisms involved in the electro-codeposition process. The two common processes in the various models for incorporating particles into metallic coatings are the physical dispersion of particles in the electrolyte and the electric field assisted (electrophoretic) migration of the particles. The mechanism proposed by Guglielmi in 1972 has been largely adopted and is the basis for various other models [Guglielmi 1972].

![Figure 2.7 – Schematic diagram of the two-step deposition process proposed by Guglielmi](Gluglielmi 1972)
As the schematic diagram in Figure 2.7 shows, Guglielmi’s model is based on two consecutive adsorption steps. In the first step, the particles are loosely adsorbed on the surface of the electrode with the coverage following the classical Langmuir adsorption isotherm. The ionic cloud (ie. formed by metal/salt ions) surrounding the particles screens the particles from interacting with the electrode, only enabling a weak adsorption on the surface. The second step involves a stronger electric field assisted adsorption. The ionic cloud surrounding the particle is no longer present and the particles become strongly adsorbed and progressively submerged by the growing metal. Although Gugliemi experimentally verified his model for Ni-Ti and Ni-SiC composites, it is somewhat limited, as it does not consider important process parameters such as hydrodynamic effects, bath constituents, or particle types [Low et al. 2006].

In 1987, Celis et al. proposed a codeposition mechanism involving 5 stages and subsequently used a probability concept to describe the amount of particles that can be codeposited at a given current density [Celis 1987]. Figure 2.8 illustrates the 5 stages in a schematic diagram.

Figure 2.8 – Proposed codeposition mechanism involving 5 stages by Celis [Celis 1987]
The first step involves the formation of ionic cloud around the particles when dispersed in the plating solution. The particles then move towards the hydrodynamic boundary layer at the cathode surface through convection and pass the diffusion double layer through diffusion. Upon contact with the cathode surface, the particle is adsorbed with its ionic cloud still intact. Finally, the adsorbed ionic species, specifically metal ions, are reduced to metallic deposit by which the particles become irreversibly incorporated into the metal matrix. Celis further takes a statistical approach to develop a mathematical expression to determine the amount of particles that are codeposited in the metal matrix. He verified his model with experimental work involving the codeposition of Al₂O₃ particles with copper and gold.

Additional studies have been done to establish a relationship between the quantity of particles embedded and the hydrodynamic condition during the codeposition. Vereecken et al. in 2000 described a model based on the kinetics of the particles taking into account the influence of particle gravitational force and hydrodynamics during the convective diffusion of the particles (Vereecken et al. 2000). Bercot in 2002 incorporated a correction factor to Guglielmi’s model to account for the hydrodynamic effects during the codeposition using a rotating disk electrode [Bercot 2002].

Although numerous theoretical models have been proposed over the past few decades, they are usually restricted to specific conditions and cannot always be applied universally to different electroplating systems. Extensive numbers of interrelated variables such as particle characteristics (type, size, and concentration), operating parameters (temperature, current density, and pH), and electrolyte composition make the mechanism of codeposition complex and difficult to idealize [Low et al. 2006].
2.5 Colloidal System of the Electrolyte and the Effect of Surfactants on Co-deposition

A major aspect during the co-deposition of secondary particles is the dispersion and the suspension of the particles in the electrolyte during the electrodeposition process. An understanding of a colloidal system is required in order to study the effect of surfactants that are used to disperse the particles (pigments in this study) in the electrolyte.

2.5.1 Electric Double Layer and DVLO Theory

The electric double layer model is used to describe the distribution of ions and charge near the particle surface [Besra and Liu 2006]. The double layer consists of the Stern layer and the diffuse layer. When a particle is initially suspended in an ionic solution, ions of opposite charge (counter-ions) are attracted towards the surface and are strongly bound to form an inner layer called the Stern layer. However, as the Stern layer is formed, it starts to repel additional counter-ions from approaching the particle while ions of the same charge (co-ions) are attracted towards the particle. As a result there is an outer region where the counter and co-ions are loosely bound and distributed broadly in a layer called the diffuse layer. The charge density (and the potential energy) is the greatest near the surface where the counter-ions are highly concentrated and gradually decreases with distance and diminishes to zero in bulk solution. A schematic representation of the potential drop is shown in Figure 2.9.

The DVLO (Derjaguin, Laudau, Verwey, Overbeek) theory describes the stability of a colloidal system by assuming that the stability of a particle in a solution depends on the balance between
attractive and repulsive forces between charged particles. The attractive contribution comes from the van der Waals forces while the repulsive contribution comes from the electrical double layer forces that exists between particles. The theory proposes that the repulsive force produced by the electrical double layer prevents two particles from approaching and adhering to each other and thus prevents flocculation of particles, forming a stable colloidal system.

Electrostatic stabilization allows repulsive forces to remain dominant in a stable colloidal system: it utilizes the repulsion interaction between charged species in the colloidal system. If the particles in a colloidal solution carry the same electrical charge (both positive or both negative), the electrostatic repulsion between adjacent particles effectively separates them into discrete colloids, given that the particles have high enough magnitude of electrical charge. This can be achieved, for example, by using ionic surfactants.
2.5.2 Zeta Potential

When there is a relative movement between the charged interface and the adjacent electrolyte solution, some part of the double layer charge moves with the particle while another part moves with the bulk liquid [Elimelech et al 1995]. The boundary that separates such phenomena within the double layer is called the shear plane. The potential that is measured at this plane is called zeta-potential (ζ), and becomes a useful parameter in determining the electrokinetic behaviour of the particles. A colloid is considered stable when the zeta potential value is above 25mV in magnitude [e.g. Duhkin and Goetz 2010]. Colloidal stability is achieved through dispersion force acquired through surface charge that exceeds thermal forces for separations between particles [Mewis and Wagner 2012].

2.5.3 The Effect of Surfactants

Surfactants are typically molecules with a polar hydrophilic head and a hydrophobic tail consisting of a long hydrocarbon chain group. They can be classified as either non-ionic or ionic depending on the charge present at the head group. Non-ionic surfactants often contain long polymeric chains that form a barrier between particles when adsorbed onto the surface. In the case of ionic surfactants, they can be categorized as anionic if they contain a negatively charged head group or cationic if they contain a positively charged head group. Surfactants are often used to disperse micron or sub-micron sized particles that tend to agglomerate into large packed particles due to strong inter-particle electrostatic attraction [Wang 2004]

The addition of ionic surfactants in the electrolyte during the electrodeposition process helps modify the surface charge of the particles that are to be co-deposited and decrease their tendency to agglomerate when suspended in the plating solution. Not only do the adsorbed ionic surfactants provide an electrostatic repulsion between particles due to their charges and hence
deter agglomeration but they also promote electrophoretic migration of the particles towards the cathode in the case of cationic surfactant. This can help more particles to become embedded in the coating during the electrodeposition process.

Many studies report the usage of ionic surfactants to assist the co-deposition of particles during the electrodeposition process. For example, Khameneh studied the influence of anionic sodium dodecylsulfate (SDS) and cationic hexadecyltrimethylammonium bromide (HTAB) surfactants on the incorporation of barium hexaferrite nanoparticles in electrodeposited CoFe alloy [Khameneh 2014]. Figure 2.10 shows the barium hexaferrite content in the electrodeposited CoFe alloy as a function of the amount of surfactants used in the electroplating bath. The addition of surfactants in both cases of SDS and HTAB resulted in an increase of the barium hexaferrite content from 6 to 9.5 at% for SDS and from 6 to 12 at.% for HTAB, respectively.

![Graph showing barium hexaferrite content vs surfactant concentration]

**Figure 2.10 – Effect of anionic SDS and cationic HTAB surfactant concentration on the barium hexaferrite content in CoFe electrodeposits [Khameneh 2014]**

The author attributed this to the effective dispersion of particles with the presence of surfactants. The author also stated that the cationic HTAB surfactant was more effective than the anionic
SDS surfactant as the cationic charge on the particles makes it more suitable to be attracted to the cathode.

F. Kilic further examined the effect of adding Cetyl trimethylammonium bromide (CTAB), a cationic surfactant, in the electrolyte while co-depositing SiC nano particles in a nickel matrix during electrodeposition [Kilic 2013]. The author stated that the addition of CTAB resulted in a non-agglomerated dispersion of particles and increased the amount of Si-C particles deposited in the composite coating. This is shown in the cross sectional SEM micrographs in Figure 2.11 where increased concentration of CTAB in the electrolyte during plating resulted in a higher volume percentage of SiC particles deposited in the composite. Also, as Figure 2.12 shows, the addition of CTAB resulted in a higher zeta potential of SiC particles as the positively charged CTAB molecules are adsorbed onto the particles. The positive zeta potential value leads to the separation of SiC particles due to electrostatic repulsion and effectively disperses the particles. The author also states that positive zeta potential provides a stronger adhesion force between the particle and the negatively charged cathode surface due to electrostatic attraction, resulting in an increased amount of SiC particles being embedded in the composite (up to 11.5 vol.%).
Figure 2.11: SEM micrographs of distribution of SiC particles in the cross sections of nickel composite coatings prepared at the following CTAB concentrations; (a) 0mg/L, (b) 100mg/L, (c) 200mg/L, (d) 300mg/L, and (e) 400mg/L [Kilic 2013]
2.6 Coloured Nickel Composite Coatings

Codeposition of various fine particles into a metallic matrix has been studied extensively to achieve composite materials with improved physical, chemical, and optical properties. However, very few studies have reported specifically on coloured nickel-pigment composite coatings. Shrestha and Saji reported on a nickel-organic pigment composite film that can be prepared in two steps [Shrestha and Saji 2000]. The first step involves preparing a thin film of organic pigment on a nickel substrate by electroless plating of the pigment by reduction of a nonionic azo-surfactant (AZPEG). Copper phthalocyanine blue was one of the pigments used as an organic pigment. The pigment particles in the thin film are arranged according to their shape and size, yielding porous holes in between the particles. The bare surfaces of the substrate exposed underneath the film by the porous holes become an active site for nickel ions to deposit during the subsequent step of electrodeposition. The deposited nickel grows continuously on the pigment film covered substrate during the electrodeposition and eventually results in a nickel-pigment composite. Shretha and Saji reported a blue colour for the pigment film itself and a highly reflective purple tone colour for the Ni-CuPc composite. However, there were no
available coloured images of the composite samples in the paper and it is very difficult to identify the pigment particles in the cross sectional SEM images due to the low resolution and magnification of the images. Also the two-step process can potentially increase the complexity of the manufacturing process as well as the cost of production of the final material.

Kowase et al. followed Shrestha and Saji’s study by preparing coloured pigment-nickel composite films using immersion plating over a zinc surface [Kowase et al. 2006]. The composite film was synthesized by immersing a zinc substrate in an aqueous solution containing nickel ions and pigment particles dispersed with a surfactant mixture containing AZPEG and n-sodium dodecyl sulfate (SDS). The electrochemical redox activity of the AZPEG molecules assists in the deposition of the pigment film on the substrate surface. At the same time, deposition of nickel on the zinc substrate takes place by displacement reaction ($\text{Zn} + \text{Ni}^{2+} \rightarrow \text{Ni} + \text{Zn}^{2+}$). Therefore pigment particles and nickel are deposited on the zinc substrate and form a composite film until all the active sites of zinc substrate are covered with the film. Figure 2.13 shows optical photographs of as-deposited nickel pigment composite films using immersion plating on a zinc substrate. Each sample, (a) Ni-CuPc (Copper Phthalocyanine Blue), (b) Ni-DAR (Dianthroaquinonyl Red), and (c) Ni-PG (Phthalocyanine Green), showed their respective pigment colour on the composite film.

Figure 2.13 - Photographs of as-deposited (a) Ni-CuP), (b) Ni-DAR, and (c) Ni-PG composite films on a zinc substrate [Kowase et al. 2006]
In both studies by Shrestha & Saji and Kowase et al., the photographs of the composite films lack resolution and detail to quantify the colour of the film. They also lack detailed top and cross-sectional SEM images that confirm the presence of pigment particles in the electrodeposited nickel matrix. It is difficult to determine whether the colour exhibited by the prepared sample is only a top surface phenomenon due to the residue of thin film pigments remaining on the top surface. More detailed microscopy and surface characterization are required to investigate the contribution of the pigments embedded in the nickel matrix to the colour of the film.

More recently, Saji’s group proposed a new approach in preparing coloured metallic coatings by incorporating photolithography and electrodeposition (e.g. Kibayashi et al. 2012). The preparation process (Figure 2.14) first involves spin coating of color photoresists on a nickel substrate, followed by patterning of micrometer-sized coloured dots using photolithography, and finally electrodeposition of nickel on the exposed substrate area that is not covered by the coloured microdots. The diameter and the spacing of the microdots were 120µm and 30µm with a thickness of 1µm. The height of the surrounding nickel walls was approximately 2µm, which protects the coloured dots from physical damage and result in an increase in hardness and durability of the film. Figure 2.15 shows a photograph and the reflectance spectra of the blue, green, and red coloured films that were prepared. The film exhibits a metallic luster and a glossy colour.

Although the film exhibits the desired colour, it is to be noted that the film is not a nickel-pigment composite where the pigment particles are embedded in the nickel matrix. It is rather a microdot-patterned coloured film separated by nickel walls that are electrodeposited in order to protect the microdots from physical damage. In addition, photolithography is an expensive
process mostly accessible in a small laboratory scale, making this process economically challenging for industry large-scale production.

Figure 2.14 – Illustration of preparation process for obtaining coloured films: (a) spin-coating of colour photoresist, (b) micropatterning by photolithography, and (c) electrodeposition of Ni walls [Kibayashi et al 2012].

Figure 2.15 – (a) Optical photograph of the blue, green, and red coloured film. (b) Reflectance spectra of the (i) blue, (ii) green, and (iii) red coloured films [Kibayashi et al. 2012].
The limited number of studies on synthesizing coloured nickel coatings suggests that there is a need to further explore the potential of incorporating pigment particles into the nickel matrix to achieve coloured nickel coating. Also, more research is needed to improve and modify the electrodeposition process, as it is a viable platform in which there may be great potential to achieve codeposition of pigment particles with nickel.
Chapter 3
Experimental Procedures

3 Experimental Procedures

This chapter outlines the experimental procedures performed throughout this study. These procedures can be divided into three different groups. The first group involves the characterization of the CuPc pigment particles that are to be co-deposited in the Ni-CuPc composite. Particle shape and size distribution, as well as its colloidal behaviour in solution will be studied. Then, the electrodeposition process which is used to synthesize the Ni-CuPc composite will be described in detail. After the synthesis of the Ni-CuPc composite, different characterization techniques will be used to study the co-deposition of the CuPc pigment particles within the nickel matrix as well as to study the resulting colour of the composite samples.

3.1 Particle Size Characterization

As mentioned in the previous section, the pigment that was used in an attempt to introduce colour to the electroplated nickel composite is Copper Phthalocyanine (CuPc) Blue 15:3, received from AArbor Colorant Corp located at Brighton, Michigan. However, no information regarding the pigment particle’s shape or size distribution was provided from the manufacturer/supplier of the pigment. In order to obtain such information, SEM (Scanning Electron Microscope) images at different magnifications were first obtained using a Hitachi S-4500 field emission SEM.

For sample preparation, some of the pigment powder was sprinkled on a small piece of carbon tape (5mm x 5mm) and any excess loose particles were removed with compressed air. The pigment powders were then carbon coated to avoid charging and help acquire better quality SEM
images. The SEM images were captured at an acceleration voltage of 1.5 kV, using a probe current of 20\(\mu\)A. The lower detector was used and images were captured at magnifications of 10,000x and 40,000x, respectively.

With the help of Image J software, the major and minor axes of the individual pigment particles were measured. A histogram was subsequently created with the measurements to acquire a statistical representation of the particle size distribution.

3.2 Colloidal Behaviour of the CuPc Pigments with added surfactants

An important aspect during the co-deposition of secondary particles during the electrodeposition process is the colloidal behaviour of the particles within the electrolyte. A stable colloidal suspension of the pigment particles in the electrolyte solution is required for a successful co-deposition of secondary particles within the nickel matrix as composites. However, the hydrophobic nature of the CuPc pigment particles and their tendency to form agglomerates poses a challenge in dispersing these particles as fine particles in solution. As discussed previously in the literature review cationic surfactants assist in breaking down these agglomerates into smaller sized particles. Therefore the colloidal behaviour of the particles was studied by first visually observing the colour change of the solution, and then measuring the particle size distribution and zeta potential as a function of the amount of cationic surfactant CTAB added to the solution.

3.2.1 Visual Colour Inspection

A simple experiment was set up to observe the dispersion behavior of the pigment through visual inspection of the solution, in particular the change of colour of the solution. Five test tubes were prepared with a fixed concentration of pigments of 10g/L dispersed in de-ionized (DI) water.
CTAB surfactant was added incrementally to each test tube from 0.25g/L up to 1g/L. As shown in Figure 3.1 these test tubes were placed side by side to inspect and compare the colour change of the solution for each CTAB concentration. The test tubes were inspected immediately after agitation as well as after 24 hours to allow settling of the pigments. The experiment was repeated in the nickel Watt’s electroplating bath which will be described in section 3.3.

![Figure 3.1 - Series of test tubes with CuPc pigment particles suspended in D.I. water with varying CTAB concentration after 24 hours](image)

### 3.2.2 Particle Size Distribution (PSD) and Zeta Potential Measurements

While the visual inspection of the solutions can yield a qualitative analysis mainly through change of colour, a more quantitative method was needed to study the colloidal behaviour of the pigment particles. Therefore an acoustic spectrometer, DT-1200 was used to acquire accurate particle size distribution and zeta potential measurements of the CuPc pigment particles suspended in solution.
As aforementioned, the addition of surfactants in the solution plays a crucial role in determining how well the particles disperse within the solution. Therefore PSD and zeta potential measurements were performed when the pigments were dispersed in D.I. water and Watt’s bath separately.

Table 3.1 – Concentration and Ratio of CuPc pigment and CTAB surfactant for PSD measurement

<table>
<thead>
<tr>
<th>CuPc Conc.</th>
<th>CTAB Conc.</th>
<th>CuPc : CTAB Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10g/L</td>
<td>0g/L</td>
<td>-</td>
</tr>
<tr>
<td>10g/L</td>
<td>0.25g/L</td>
<td>40:1</td>
</tr>
<tr>
<td>10g/L</td>
<td>0.5g/L</td>
<td>20:1</td>
</tr>
<tr>
<td>10g/L</td>
<td>0.75g/L</td>
<td>13:1</td>
</tr>
<tr>
<td>10g/L</td>
<td>1g/L</td>
<td>10:1</td>
</tr>
</tbody>
</table>

As shown on Table 3.1, PSD and zeta potential measurements were performed as a function of the concentration of the surfactant (CTAB) added to the solution. The solution was first prepared.
by dispersing a fixed pigment concentration of 10g/L in D.I. water. Subsequently, CTAB surfactant was added incrementally from 0.25g/L up to 1g/L while the PSD measurements were recorded after each increment of the surfactant concentration. The ratios between the CuPc pigment and the CTAB surfactants concentration are indicated in Table 3.1 to use as a reference for the relative amount added. This series of measurements was repeated in Watt’s bath.

### 3.3 Synthesis of the Ni-CuPc Composite

The Ni-CuPc composite materials were synthesized through an electrodeposition process. The experimental set up is shown below in Figure 3.3. The set up includes a stirring hotplate with a magnetic stir bar to heat up and agitate the electrolyte, and a DC power supply. The cathode and the anode are immersed in the electrolyte and the circuit is connected to an ammeter to monitor the current.

![Figure 3.3: Schematic diagram (left) and picture of electroplating experimental set-up (right)](image)

For the electrolyte, a Watt’s type nickel electroplating bath was used. The chemical composition is listed in Table 3.2. First, D.I. water was heated up to 60°C in a 350mL beaker on a hotplate
and the chemicals for the Watt’s bath were added while agitating it with a magnetic stir bar. Pigment powder and CTAB surfactant were added subsequently and the solution was agitated longer until the pigment was dispersed in the electrolyte. The concentration of the pigments added varied from 0g/L up to 20g/L while the concentration of the surfactant varied from 0.25g/L up to 2g/L. A series of Ni-CuPc composites were synthesized at various concentrations of pigment and surfactant in order to determine the ideal ratio between the two. 2cm x 2cm copper coupons with a nominal thickness of 1.55mm were used as cathodes. The exact dimension of each copper coupons were measured in order to calculate the current needed from the power supply. The copper coupons were polished using a 1200 grit abrasive paper and further ultrasonically cleaned in ethanol prior to electroplating. The backside of the cathode was covered with non-conducting electrical tape, allowing only the front side facing the anode to be electroplated. Inco nickel R-Rounds were used as anodes, which were contained in a titanium mesh basket.

Table 3.2 - Chemical composition of Watt’s type nickel electroplating bath with varying CuPc pigment and CTAB concentration

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄ • 6H₂O</td>
<td>300g/L</td>
<td>Temperature</td>
<td>60°C</td>
</tr>
<tr>
<td>NiCl₂ • 6H₂O</td>
<td>45g/L</td>
<td>Agitation</td>
<td>350RPM</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>45g/L</td>
<td>pH</td>
<td>2.8-3.5</td>
</tr>
<tr>
<td>CuPc</td>
<td>0-20g/L</td>
<td>Time</td>
<td>20 min</td>
</tr>
<tr>
<td>CTAB</td>
<td>0-2g/L</td>
<td>Current Density</td>
<td>100mA/cm</td>
</tr>
</tbody>
</table>

The electroplating conditions are summarized in Table 3.2. The agitation rate, temperature, and current density were held constant while the pigment and surfactant concentrations were
varied. The plating time was 20 minutes, which yields roughly a 30um thickness of Ni-CuPc composite samples. The samples were then rinsed in water and ultrasonically cleaned in ethanol to remove any loosely adhered particles on the surface.

3.4 SEM Image Surface Analysis

Both the top and the cross sectional surfaces of the electrodeposited samples were analyzed using the images captured by Scanning Electron Microscopy. For the top surface, a Hitachi S-4500 field emission SEM was used to capture secondary electron images at different magnifications. Secondary electron imaging is surface sensitive and thus gives topographical information of the samples with high resolution. The images were captured at an acceleration voltage of 20 kV, a probe current of 20uA, and at a working distance of 7mm. The lower detector was used and the magnification of the image captured varied from 1,000x to 40,000x. Images captured at lower magnification were used to determine the area coverage of the CuPc pigments while higher magnification images yielded information regarding the interface between the pigment particle and the nickel metal matrix. Utilizing the contrast observed in the image between the pigment particles and the nickel matrix, ImageJ software was used to determine the percentage area coverage of the CuPc pigment particles.

In order to capture cross section images of the electrodeposited samples, the samples were cut using a Struers Minitom with diamond blade. The cut samples were mounted in epoxy resin and polished using 1200 grit SiC polishing paper, 1um alumina suspensions, followed by 0.3um alumina suspensions in order to remove areas of deformation and defects caused by the diamond blade during cutting. The polished sampled were carbon coated to reduce charging during image capturing at the interface between the epoxy and the sample. A Hitachi S-3500 was used to capture cross sectional images using backscattered electrons. Backscattered electron imaging
suffers loss in topographical resolution but is more sensitive to atomic mass of the elements present on the surface and thus, gives more distinct contrast between the pigment and nickel.

Energy Dispersive X-Ray Spectroscopy (EDX) in the Hitachi S-4500 was performed to obtain elemental composition of the samples. However due to the close proximity between the copper and the nickel peaks in the EDX spectrum, it was difficult to determine the presence of copper in CuPc. Therefore as an alternative method, X-Ray Photoelectron Spectroscopy, which will be discussed in section 3.5, was performed instead to obtain elemental composition and chemical bonding information of the samples.

In order to get a cross sectional image of higher resolution and magnification, a micro-sample was prepared using Focused Ion Beam using the Hitachi NB-5000 instrument. The first step involved depositing a tungsten layer on the top surface of the sample in order to protect the sample from ion beam damage as well as to prevent re-deposition of other materials. A small micro-sample was acquired from the top surface by making multiple trenches using a liquid gallium source focused ion beam. The ion beam used was 40kV with aperture size varying from 550\( \mu \)m to as small as 30\( \mu \)m for finer beam size (Figure 3.4). The micro-sample was mounted on a separate grid where it was further thinned down to less than 200nm using a fine focused ion beam setting. The cross sectional SEM images of the final prepared sample were captured using the Hitachi NB-5000.
Figure 3.4 - Micro-sample prepared using the Hitachi NB-5000 instrument: trenches are cut on the top surface of the sample using a focused ion beam.

3.5 X-Ray Diffraction (XRD)

XRD measurements were performed to characterize the texture and the crystallography of the Ni-CuPc composite coating as well as to confirm the presence of the CuPc pigment particles in the composite coatings.

A Rigaku Mini Flex 600 was used to perform the XRD analysis on the as-received CuPc pigment, electrodeposited nickel, and the Ni-CuPc composite coating. Cu-Kα (λ = 0.1542nm) was used as the X-ray source, operating at 40kV and a current of 15mA. The angular scan range for the 2θ measurements was 5°-100°, covering the crystalline phase of the CuPc pigment as well as the first 5 plane orientations of the face centered cubic nickel. The coated samples were cut into dimensions of 2cm x 0.5cm using the diamond blade wheel so that they fit in the XRD specimen holder.
3.6 X-Ray Photoelectron Spectroscopy (XPS)

The XPS analyses were carried out with the Thermo Scientific K-Alpha Instrument using a monochromated Al K$_\alpha$ X-ray source. The area that was analyzed was 400µm × 400µm. The background from each spectrum was subtracted using a Shirley type background [Shirley 1972]. A survey scan was first conducted to examine the surface chemical composition of the samples in atomic percentage. High resolution spectra were then obtained for specific elements of interest, particularly nickel and oxygen, as well as the constituent elements of the CuPc pigment: copper, nitrogen, and carbon. The step size was 0.10eV.

Four samples were prepared for the XPS analysis. The first sample was CuPc in powder form that was sprinkled on to a small piece of carbon tape. Another sample was the blue CuPc film that is formed on the surface of the electrodeposited Ni-CuPc composite during the pigment co-deposition process. Also, electrodeposited nickel with no additives as well as the Ni-CuPc composite coating, with no CuPc surface layer was analyzed.

3.7 UV-Vis Spectrum

A UV-Vis spectrometer was used to characterize the optical properties of the Ni-CuPc composite samples, see Figure 3.5. The measurements were performed near the visible spectrum (wavelength of 350nm to 750nm) to look for any preferential reflectance of specific wavelengths of colour. A Lambda 1050 UV/Vis/NIR Spectrometer instrument was used with a 150mm integrating sphere system. A tungsten lamp light source was used with a monochromator to disperse the light into selective wavelengths ranging from 350nm to 750nm. The integrating sphere system is capable of both specular and diffuse reflectance measurements and therefore allows an accurate measurement of the total reflectance of the sample. In the integrated sphere set-up, there are two incident beams of selected wavelength reaching the sphere chamber:
reference beam and the sample beam. The reference beam is used as a reference to subtract background signal. The sample beam traverses through the sphere chamber and reaches the sample. Since the interior of the integrating sphere is coated with a highly reflective fluropolymer material, all light that is reflected or scattered by the sample will eventually be collected by the detector, yielding a total reflectance spectrum for the visible wavelength spectrum range.

Figure 3.5 - Schematic diagram of the UV-Vis Spectrometer with 150mm Integrated Sphere system
Chapter 4 :  
Results and Discussions I

4 Synthesis and Surface Characterization of the Ni-CuPc Composite

The following section will discuss mainly the results pertaining to the process of the electrodeposition of Ni-CuPc composites. Characterization of the pigment powder and its behaviour in the electrolyte solution, as well as the varying plating parameters during the electrodeposition will be discussed in detail. Also, the top and the cross sectional structures of the electrodeposited Ni-CuPc composite will be examined through scanning electron microscopy to observe the co-deposition of the CuPc pigment particles.

4.1 CuPc Pigment Particle Characterization

4.1.1 Particle Size Measurements

SEM images of the as-received CuPc pigment particles were taken at different magnifications using a Hitachi S-4500 instrument. Figure 4.1 A) shows an image captured at a low magnification in which the pigments are found as porous agglomerates with sizes in the micrometer scale ranging from 1 \( \mu \text{m} \) – 10 \( \mu \text{m} \). Figure 4.1 B) is an image captured at a higher magnification in which the individual pigment particles can be resolved.

The SEM image at higher magnification shows that the pigment particles are mainly rod shaped with a fairly homogenous distribution of size and shape. The dimensions of the particles were measured for a set of 50 particles and are shown in a histogram in Figure 4.2 for major and minor axes. The average major axis length was 186nm ± 37nm and the minor axis length was 61nm ± 15nm. SEM images therefore showed that the individual CuPc pigment particles are submicron
in size less than 200nm in length but with a tendency to agglomerate into micrometer sized particles up to 15µm.

Figure 4.1 SEM images of CuPc pigment powders at magnification of A) 5000x and B) 30,000x.

Figure 4.2 – Histogram of the major and minor axis lengths of as-received CuPc pigment particles
4.2 Colloidal Behaviour of CuPc Pigment Particles with Added Surfactants

An understanding of the colloidal behaviour of the CuPc pigment particle is necessary prior to the electrodeposition process. As mentioned earlier, the tendency of the particles to agglomerate poses a challenge in achieving a stable colloidal system in the electrolyte during the electrodeposition process. The addition of cationic surfactant helps overcome this challenge. In this study, a cationic surfactant, cetrimonium bromide (CTAB), was used to disperse the pigment particles in the electrolyte. As shown in Figure 4.3, when CTAB is dissolved in solution, Br\(^{-}\) ions are dissolved while the remaining CTA\(^{+}\) gains a positive charge on its head group. The following section examines the colour change of the solution with the addition of CTAB, and measures the particle size distribution and zeta potential as a function of the surfactant concentration.

![Molecular structure of the cationic surfactant, CTAB](image)

**Figure 4.3 - Molecular structure of the cationic surfactant, CTAB**

4.2.1 Colour Change of Colloidal Solution

Figure 4.3 shows a simple experimental set up where we can observe the change in colour of the solution in which the CuPc pigment particles at concentration of 10g/L are suspended in de-ionized water as the concentration of CTAB surfactant is increased. Figure 4.3 A shows the solution right after mixing while Figure 4.3 B shows the solution after a settling time of 24 hours. In Figure 4.4 A, at CTAB concentrations of 0.25g/L and 0.5g/L, a dull dark blue colour of the solution is observed. At 0.75g/L CTAB, (13:1 CuPc to CTAB ratio) the colour changes to a more vivid and bright blue colour. The dispersion and breakdown of CuPc pigment particles, from bigger agglomerates to smaller primary particles can attribute to the more intense and vivid
blue colour observed starting at 0.75g/L CTAB concentration. Smaller particle sizes result in larger surface area given the same quantity of pigment particles. The larger surface area with which light can interact allows for more light absorption and scattering at the pigment surface and hence a more prominent and vivid blue colour of the solution. Figure 4.3 B shows the test tubes 24 hours after agitation, allowing sedimentation to occur for the pigment particles. We can see that for 0.25g/L CTAB, the pigment particles have completely settled and separated from water. For 0.5g/L CTAB, the colour of the solution is an opaque blue but the sedimentation is still evident at the bottom of the test tube. For both 0.75g/L and 1g/L, the solution maintains a bright vivid blue colour, suggesting a good stability of the colloidal solution.

![Test tubes](image)

**Figure 4.4** Series of test tubes with CuPc pigment particles suspended in D.I. water with varying CTAB concentration. The concentration at the bottom of the test tubes indicates the CTAB concentration (A) right after mixing and (B) after 24 hours.
Figure 4.5 - Series of test tubes with CuPc pigment particles suspended in Watts bath with varying CTAB concentration. The concentration at the bottom of the test tubes indicates the CTAB concentration (A) right after mixing and (b) after 24 hours.

A similar trend was observed in the Watts electroplating bath. A more vivid blue colour past 0.75g/L CTAB (Figure 4.4 A) is observed. Upon allowing sedimentation, segregation between the Watts bath solution and the pigment particles for 0.25g/L and 0.5g/L CTAB can be seen. As was the case in water, 0.75g/L of CTAB concentration (CuPc to CTAB ratio of 13:1) seems to be a critical point where there was a prominent change in colour from dark blue to a vivid blue with the particle dispersion remaining stable even past 24 hours after agitation. This colour change can be associated with the large agglomerate particles breaking down to smaller individual particles with the addition of the CTAB surfactant to the solution.
4.2.2 Particle Size Distribution Measurements

In addition to observing the colour change of the solution, particle size distribution measurement was used to quantify the effect of the surfactant in dispersing the CuPc pigment particles within the aqueous solution.

Figure 4.6 – Cumulative particle size distribution graph of CuPc particles dispersed in A) D.I. water and B) Watts Bath. CuPc concentration was 10g/L while CTAB concentration varied from 0g/L to 1g/L plotted in different colours.
Table 4.1 – Table of particle median size for the CuPc pigment particles as a function of CTAB concentration dispersed in water (left) and Watts bath (right)

<table>
<thead>
<tr>
<th>CTAB conc.</th>
<th>D.I. Water</th>
<th>Watts Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Particle Median Size (µm)</td>
<td>Particle Median Size (µm)</td>
</tr>
<tr>
<td>0g/L</td>
<td>52.7</td>
<td>107.5</td>
</tr>
<tr>
<td>0.25g/L</td>
<td>40.8</td>
<td>109</td>
</tr>
<tr>
<td>0.5g/L</td>
<td>26.2</td>
<td>96</td>
</tr>
<tr>
<td>0.75g/L</td>
<td>3.3</td>
<td>0.73</td>
</tr>
<tr>
<td>1g/L</td>
<td>0.27</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Figure 4.6 shows cumulative particle size distribution graphs for the CuPc pigment particles dispersed in D.I water and Watt’s bath respectively acquired using the acoustic spectrometer DT-1200. The average median particle sizes obtained from the plotted graphs are summarized in Table 4.1.

The graph shows a trend where the median particle size decreases with increasing CTAB surfactant concentration in the solution, indicating the breakdown of agglomerates into smaller particles. For particles suspended in water, the median particle size with no surfactant added is 52µm and gradually decreases down to 26µm at 0.5g/L CTAB. There is a significant decrease in median size down to 3.3µm at 0.75g/L CTAB, which is also the concentration where a change in colour of the from dark blue to vivid blue was observed as previously shown in Figures 4.3 and 4.4. Pigment to CTAB ratio of 13:1 seems to be the critical ratio where the dispersement of the pigment into smaller particles becomes more prominent. Also a wider particle distribution range at this CTAB concentration can be observed. The median particle size at 1g/L CTAB is 0.27µm which is close to the actual size of the individual particle measured in the SEM images (Figure
4.1 B). A narrower distribution range in the graph can be seen at this concentration, within the range of 0.1µm and 1µm. This indicates that at 1g/L CAB concentration, the pigment particles are suspended as submicron particles within the solution.

A similar trend for CuPc particles suspended in Watt’s bath is observed. With no surfactant added, the median particle size is 100µm, larger than when they were dispersed in water. At 0.25g/L and 0.5g/L, there is a very slight decrease in the median particle size but the distribution range becomes wider. The wider distribution indicates that the agglomerates are breaking down to different sizes. A more abrupt decrease in the median particle size is observed down to 0.73µm at 0.75g/L of CTAB at 13:1 CuPc to CTAB ratio. This measurement is similar at 1g/L CTAB concentration. The dispersion behaviour of the CuPc pigment particles in Watt’s bath is slightly different from when dispersed in water. The decrease of the agglomerate size with increasing CTAB surfactant concentration was more gradual when dispersed in water. The median size in Watts bath was also slightly larger 0.73µm compared to 0.27µm.

It should be noted that for both DI water and Watts bath, the particle sizes for pure solution and solutions with CTAB concentrations were larger than observed in the SEM micrographs of the as received powder (Figure 4.1A). This suggests that adding the powder to DI water and Watts bath initially results in powder agglomeration. Upon adding CTAB surfactants, these larger particles are broken up into smaller particles.
4.2.3 Zeta Potential Measurements

Zeta potential was measured for the CuPc particles dispersed in D.I. water with increasing CTAB concentrations. The results are shown in Figure 4.7. Zeta potential is a means to measure the electrostatic repulsion between particles and predict the colloidal stability of particles in solution. If the particles in suspension have higher magnitude of zeta potential, they will tend to repel each other and resist formation of aggregates [Lee et al. 2006].

![Graph showing zeta potential measurement values plotted against CTAB concentration]

<table>
<thead>
<tr>
<th>CTAB Conc. (g/L)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-9.6</td>
</tr>
<tr>
<td>0.25</td>
<td>9.7</td>
</tr>
<tr>
<td>0.5</td>
<td>12.3</td>
</tr>
<tr>
<td>0.75</td>
<td>16.2</td>
</tr>
<tr>
<td>1</td>
<td>24.5</td>
</tr>
</tbody>
</table>

Figure 4.7 – Zeta potential measurement values plotted against CTAB concentration

As seen from Figure 4.7, there is an increasing trend for the zeta potential value from -9.6mV with no addition of the CTAB surfactant up to 24.5mV with 1g/L CTAB added to the solution. A colloid is considered stable when the zeta potential value is above 25mV in magnitude [Duhkin and Goetz 2010]. Therefore it can be seen that the addition of CTAB surfactant assists in dispersing and stabilizing the pigment at smaller particle size, which can be correlated to the
decreasing particle size trend observed in the particle size measurements. Also the positive charge zeta potential indicates that the cationic surfactant CTAB imposes a positive surface charge when adsorbed onto the surface of the pigment particle. Overall the zeta potential measurements agree well with the colour changes observed in Figure 4.4.

### 4.3 Electrodeposited Samples

Figure 4.8 A is an example of an electrodeposited pure nickel on a copper substrate. This sample was produced as a reference and comparison point without the addition of any pigment particles to the Watts solution. Figure 4.8 B is a sample that was electrodeposited at a pigment concentration of 15g/L and 1g/L of CTAB surfactant. The figure shows the sample immediately after it was taken out of the electrolyte after 20 minutes of electrodeposition, and prior to any cleaning procedure. A blue film of pigment with thickness of roughly 20µm is visible on the top layer of the sample. This blue film is a dense layer of the CuPc pigment particles adsorbed onto the cathode due to electrostatic attraction (electrophoretic deposition). The electrostatic attraction comes from the positively charged pigment particles due to the cationic CTAB surfactant used to disperse the pigment and the negatively charged cathode. Upon ultrasonic cleaning in ethanol for 10 to 15 minutes, the pigment film is removed from the surface and the underlying Ni-CuPc composite reveals a rather unexpected metallic copper colour (Figure 4.8 C).

**Figure 4.8** - Optical photographs of A) Electrodeposited nickel B) Blue pigment electrophoretic film formed on the top surface of electrodeposited Ni-CuPc composite C) Ni-CuPc composite after ultrasound cleaning in ethanol.
Through incorporating blue CuPc pigment in the Watt’s type nickel bath and CTAB surfactants to help disperse the pigment particles during the electrodeposition process, a Ni-CuPc composite that displays a metallic bronze colour on the surface was produced. This will be further discussed in Chapter 5.

4.3.1 Surface Characterization: SEM images

Further surface analysis was performed by examining SEM images of ultrasonically cleaned samples in order to confirm the co-deposition of the pigment particles with the nickel matrix. Figure 4.9 shows SEM images of the top surface of the electrodeposited Ni-CuPc composite captured at different magnifications. The sample was electrodeposited at a CuPc pigment concentration of 15g/L and was ultrasonically cleaned in ethanol. At low magnification (Figure 4.9 A), dark submicron sized particles are seen to be evenly distributed throughout the surface. Higher magnification images (Figures 4.9 B and C) reveal more clearly, the presence of the rod shaped particles well embedded and in intimate contact with the nickel matrix. The SEM images confirmed a successful co-deposition of the CuPc pigment particles with the nickel matrix during the electrodeposition process.

Figure 4.10 shows cross sectional SEM images of the electrodeposited Ni-CuPc composite at different magnifications. Figure 4.10A captures the top electrodeposited Ni-CuPc composite layer of about 25um thickness as well as the copper substrate below the composite layer. Again, evenly distributed sub micron particles throughout the entire thickness of the deposit can be seen. Higher magnification images (e.g. Figure 4.10B) confirms the presence of CuPc pigment particles embedded within the nickel matrix.
Figure 4.9 – SEM images at three different magnifications of the top surface of electrodeposited Ni-CuPc composite at different magnifications.

Figure 4.10 – SEM images of the cross section of electrodeposited Ni-CuPc composite at A) low magnification and B) higher magnification. The dotted line indicates the interface between the composite coating and the Cu substrate.

In order to get better cross sectional images of higher resolution and magnification, a micro-sample was prepared using a Focused Ion Beam (FIB) system for additional SEM imaging in the
Hitachi NB-4000 instrument. The micro-sample was obtained from the Ni-CuPc composite sample electrodeposited at the pigment concentration of 15g/L. Figure 4.11 captures an overview image of the micro-sample that was prepared using the FIB. The dimensions of the micro-sample prepared using the trench method are around 15 microns in width and 6 micron in thickness. The brighter topmost layer is the tungsten layer deposited during the FIB process. Underneath the tungsten layer, we can see the Ni-CuPc composite with the rod shaped pigment particles again dispersed evenly throughout the entire coating. At higher magnifications of 35,000X and 45,000X (Figure 4.12), the individual pigment particles of 200-300nm in length present in the composite coating can be clearly resolved. The coverage area percentage of the pigment particles for this coating was 35% for the cross sectional SEM images obtained using the FIB. Therefore through both top surface and cross sectional SEM images, it can be confirmed that CuPc pigment particles are successfully co-deposited throughout the entire composite during the electrodeposition process.

Figure 4.11 – SEM cross sectional image of the Ni-CuPc composite.
Figure 4.12 – SEM cross sectional images of the Ni-CuPc composite at A) 35,000X and B) 45,000X magnification

4.3.2 X-ray Diffraction (XRD) Measurements

X-ray diffraction patterns for the CuPc pigment, electrodeposited pure nickel coating, and the CuPc composite coating were obtained. The purpose of XRD measurement was to confirm the presence of the CuPc pigment particles in the composite coatings.

Figure 4.13 shows an overview of the XRD patterns for all three materials: CuPc pigment, electrodeposited pure nickel, and the Ni-CuPc composite. To examine the diffraction patterns in more detail, Figure 4.14 A shows the measured XRD pattern for the as-received CuPc pigment powder (top) and the XRD pattern from the database of PDXL, an integrated X-ray powder diffraction software (bottom). It can be seen that the as-received CuPc is a crystalline material with distinct diffraction peaks occurring in the 2θ range, 5°-40°, corresponding to the characteristic XRD patterns in the database. Figure 4.14 B shows the measured XRD pattern over the 2θ diffraction angle range of 5°-100° for the electrodeposited nickel again in comparison with the database pattern. The diffraction pattern shows typical peaks for the first five plane orientation in a FCC material, namely the (111), (200), (220), (311), and (222) planes.
The diffraction pattern of the Ni-CuPc composite is shown in Figure 4.15. Three sets of characteristic peaks can be identified in this diffraction pattern: nickel, CuPc, and copper. The most prominent characteristic diffraction peaks are from nickel, followed by a set of diffraction peaks of smaller intensity corresponding to copper. The diffraction peaks of copper are likely due to the copper substrate exposed near the edges of the samples where the composite coating has chipped off during the cutting for sample preparation. More importantly, CuPc peaks with a relatively lower intensity are also detected in the 5°-40° range. For better comparison, the XRD patterns for CuPc pigment and the Ni-CuPc composite were re-plotted in Figure 4.15B specifically for the 2θ diffraction angle range of 5°-40°. It can be seen more clearly that the diffraction peak for CuPc is present at the Ni-CuPc composite diffraction pattern, indicating that the CuPc pigment is embedded in the nickel matrix with its crystallinity intact.

![Diffraction pattern](image)

**Figure 4.13 – Overview of the XRD patterns for the as-received CuPc pigment powder, electrodeposited pure nickel, and the Ni-CuPc composite**
Figure 4.14 – XRD patterns for the A) as-received CuPc pigment powder and B) electrodeposited pure nickel coating.
Figure 4.15 – XRD patterns for the A) Ni-CuPc composite and B) compared with CuPc XRD pattern at 2θ range of 5° - 40°.
4.4 Effects of Pigment and Surfactant Concentrations

Important parameters during the electrodeposition process are the concentrations of the pigments and the surfactant added to the electrolyte. It was noted earlier that without the addition of any surfactant, the pigment does not disperse into smaller primary particles within the solution as measured through particle size distribution measurement (Figure 4.5, Table 4.1) and the dark blue colour observed in the electrolyte (Figure 4.4). Further acoustic measurements showed that a pigment to surfactant ratio of 13:1 (see section 4.2.1) was a ratio at which the agglomerated particles started to break up significantly when dispersed in solution. To further study the effect of particle size distribution of the CuPc particles in the electrolyte bath and the resulting composite coatings, a series of samples were produced with fixed concentration of the pigment and varying the concentration of the surfactant in the electrolyte bath.

![Figure 4.16](image)

**Figure 4.16** – Ni-CuPc composite coatings electrodeposited at a fixed CuPc pigment concentration of 10g/L but with varying CTAB concentrations (starting from the left 0g/L, 0.25g/L, 0.5g/L, 0.75g/L, and 1g/L CTAB concentration). All coatings are shown after ultrasonic cleaning in ethanol

Figure 4.16 shows the samples electrodeposited at a fixed CuPc pigment concentration of 10g/L but with varying CTAB concentrations. Starting with the sample on the left, the composite was first electrodeposited without any addition of the surfactant. Subsequently, the concentration of the surfactant was increased by increments of 0.25g/L up to a maximum of 1g/L. As observed from the particle size distribution measurement in Figure 4.5, higher concentration of surfactant
in the plating bath result in the breakdown of the agglomerated CuPc pigment particles into smaller particles. The addition of surfactant helps modify the surface charge and decrease particle agglomeration, and thereby enhances their electrostatic adsorption on the cathode surface, facilitating the co-deposition process of the pigment particles [Narasimman et al. 2012]. By increasing the concentration of the surfactant, we therefore induce a favorable plating environment and co-deposit more pigment particles. Meanwhile, as seen from Figure 4.16, upon increasing the concentration of the surfactant there is a progressive change in colour from a light tint of bronze at lower concentration to a stronger metallic bronze colour at higher concentration. Therefore smaller average particle size of the pigment in the electrolyte due to increasing amount of surfactant during the electrodeposition process can be correlated to the outcome of the colour that is observed on the Ni-CuPc composite. By increasing the surfactant concentration in the electrolyte, a stronger and more intense bronze colour is observed on the Ni-CuPc composite coatings.

However, as can be noted from the sample on the right in Figure 4.16, excessive amount of surfactant can result in the deterioration in the mechanical quality of the coating. At and 10g/L CuPc and 1g/L CTAB (10:1 ratio) the coating becomes brittle as can be seen from the cracks present in the sample. Also the coating partially delaminated from the substrate, indicating a weak adhesion strength at the interface between the substrate and the coating and for increasing internal stress. This indicates that there is an optimal balance between the amount of pigment and surfactant added to the plating bath in order to achieve both colour and structural integrity of the coating. A noticeable change in the quality of the coating occurs starting from the sample electroplated at 0.75g/L of CTAB (13:1 CuPc to CTAB ratio) where a rough surface is apparent.
Therefore the maximum ratio between CuPc and CTAB for acceptable coatings was established as 13:1. Excessive CTAB surfactant results in brittleness and degradation of the coating quality.

Figure 4.17 – Ni-CuPc composite coatings electrodeposited at a fixed concentration ratio of 13:1 between the CuPc pigment and the CTAB surfactant. The concentrations of CuPc starting from the left: 0g/L, 5g/L, 7.5g/L, 10g/L, 15g/L. All coatings are shown after ultrasonic cleaning

After establishing the ideal ratio between the concentration of pigment and the surfactant, another series of samples were electrodeposited to study the effect of the pigment concentration on the colour of the composites. Figure 4.17 shows the set of samples where the CuPc concentration was increased while maintaining the CuPc to CTAB ratio at 13:1. Starting from the left, the concentrations of pigments in the electrolyte were 0g/L, 5g/L, 7.5g/L, 10g/L, and 15g/L, respectively. A correlation can be seen that with increasing concentration of pigments in the electrolyte, again, a stronger metallic bronze colour is observed for the Ni-CuPc composites.

Figure 4.18 shows SEM images of the top surfaces of the Ni-CuPc composites electrodeposited at different CuPc pigment concentrations. The images correspond to the samples that were electrodeposited at pigment concentrations of 5g/L, 7.5g/L, 10g/L, and 15g/L. From Figure 4.18 A to D, we can see an increase in the coverage of the submicron particles that were confirmed to be the rod-shaped CuPc particles.
Figure 4.18 – SEM images of the top surfaces of Ni-CuPc composites at a magnification of 1,000x electrodeposited at different CuPc pigment concentrations: A) 5g/L, B) 7.5g/L, C) 10g/L, and D) 15g/L.

ImageJ software was used to determine the area coverage percentage of the pigment particles for SEM images at different concentrations. The percentages of the area coverage of the CuPc pigment determined by the analysis were 20%, 25%, 33%, and 36%, respectively. Image analysis confirms that higher concentration of CuPc pigment in the electrolyte during the electrodeposition process yields higher area coverage of pigments on the top surface, which in turns results in a stronger metallic bronze colour. Therefore there is a correlation where increasing the CuPc pigment concentration in the electrolyte results in an increased content of
the particles co-deposited in the composite coatings. Also, the intensity of the bronze metallic colour is increased with increasing amount of CuPc pigment particles being co-deposited.
Chapter 5
Results and Discussion II

5 Understanding the Copper Colour of the Ni-CuPc Composite

In the previous section, the CuPc pigment and its colloidal behaviour were characterized and the varying plating parameters during the electrodeposition process when synthesizing Ni-CuPc composite coatings were described. In addition, successful co-deposition of the CuPc pigment particles in the nickel matrix was confirmed through SEM images both on top surface and in cross sectional view. However the question still remains why the Ni-CuPc composite reveals an unexpected metallic copper colour rather than the blue colour of the pigment itself. The following sections focus on the additional surface analysis used to further study the resulting colour of this composite, as well as a tentative explanation as to why this phenomenon was observed.

5.1 UV-Vis Spectrum

Since the perception of colour is subjective to the human eye, a UV-Vis spectrometer was used to quantify the colour through the reflectance spectra of the samples. The reflectance was measured in the visible wavelength range (400 to 700nm) for the electrodeposited pure nickel (Fig 4.6A), the electrophoretic blue surface film that is formed during the electrodeposition of Ni-CuPc (Fig 4.6B), as well as the final ultrasonically cleaned Ni-CuPc composite (Fig 4.6C). Figure 5.1 shows the reflectance curves for these three samples and a schematic colour chart corresponding to the wavelengths below the graph. The reflectance curve for nickel is rather flat with no characteristic peak, indicating no preferential reflectance for a specific wavelength. This corresponds to the metallic silver colour we observe for many metals including nickel. The
reflectance curve for the CuPc film shows a characteristic peak at around 460nm. This range of wavelength corresponds to the colour blue, which is the colour we indeed observe on the electrophoretic CuPc film. The reflectance curve for the ultrasonically cleaned Ni-CuPc composite shows a broad peak at around 620nm, which corresponds to the colour orange that resembles the colour of copper.

Figure 5.1 – Reflectance spectra of electrodeposited pure nickel, electrophoretic pigment film, and the ultrasonically cleaned Ni-CuPc composite

From this figure, it can be seen that the reflectance curve for the Ni-CuPc composite is not a cumulative response from the nickel and the CuPc film reflectance curves. The reflectance peak of 460nm observed in the CuPc reflectance curve is no longer present for the Ni-CuPc composite despite the incorporation of the CuPc pigments within the composite. Instead we observe a new broad peak with maximum of 620nm. This leads to the speculation that the CuPc pigment particles do not contribute their blue colour when embedded in the composite. Rather there may
be an additional layer forming or a change on the surface that is responsible for the copper colour, which corresponds to the peak at 620nm.

5.2 Removal of the surface layer: The colour of the Ni-CuPc composite

To further investigate whether copper colour is a surface effect or is present throughout the entire thickness of the composite coating, the outer most surface layer of the Ni-CuPc composite was removed through argon ion milling. Figure 5.2 shows the sample that was ion milled with the Hitachi Ion Milling System, IM-4000 operated at an acceleration voltage of 6kV for 10 minutes to remove roughly 500 nm of the surface layer on the left half of the coated sample.

![Image](image.png)

**Figure 5.2 - Ni-CuPc composite after ion-milling**

Upon argon milling the left half side of the sample, the copper colour on the surface disappeared and the metallic silver colour similar to the colour of electrodeposited pure nickel appeared. In other words, there is an additional thin layer only on the surface of the sample of different composition compared to the underlying bulk Ni-CuPc composite that is deposited during the electrodeposition process. Therefore it was speculated that a thin layer of copper-rich material only on the surface may be contributing to the copper colour that was observed on the samples.
In Figure 5.3, backscattered electron images are shown for the Ni-CuPc composite before (Figures 5.3 A and C) and after ion milling (5.3 B and D). Figures 5.3 A and B are at 10,000X magnification while C and D are at 20,000X magnification, respectively. In both images, the dark rod shaped pigment particles are distributed evenly throughout the brighter nickel matrix. Comparing the two images, the area coverage percentage of the CuPc pigment particles remains relatively the same before and after the sputtering off the surface layer. However, after ion milling, even with the distribution of the blue CuPc pigment particles within the nickel matrix on
the surface, no visible blue colour is observed from the composite. The blue colour of the CuPc pigment does not seem to contribute to the colour we see on the surface of the composite surface. Rather the colour we observe is metallic silver, similar to the colour of any plain electrodeposited nickel coatings. This lead to a further investigation with regards to i) the surface layer responsible for the copper colour and ii) why a coloured nickel composite cannot be achieved even with pigment particles co-deposited in the nickel matrix as seen from the sputtered sample.

5.3 X-ray Photoelectron Spectroscopy (XPS) Analysis

Assuming that another layer of different chemistry or composition has formed on the surface of the Ni-CuPc composite, X-ray Photoelectron Spectroscopy (XPS) was performed to further investigate the surface chemistry of the composite sample.

XPS is a useful surface analysis technique that reveals information regarding the surface chemistry of the sample surface. The XPS spectrum of the Ni-CuPc composite was closely examined and compared with that of the CuPc pigment itself to see if there are any indications of chemical change within the pigment during the electrodeposition process. The spectral range of around the Cu2p peak was closely examined. Copper is the central atom for the CuPc pigment molecule and the colour that was observed on the surface of the composite was a metallic copper colour. Therefore a break of the copper bond within the CuPc pigment was suspected that allows the central copper atom to leach out from the pigment and deposit onto the surface of the composite as metallic copper. The spectral range around the Ni2p peak was also examined to see if there were any changes in the chemical bonds for nickel when in contact with the pigment particles.
5.3.1 Cu2p 3/2 Spectrum

The Cu2p binding energy region was examined in detail to observe any significant shifts in the binding energy peaks that may indicate a change in the chemical state of copper within the CuPc pigment. Figure 5.4 shows the XPS spectra of the Cu2p signals for a) CuPc pigment in as-received powder form, b) electrophoretic CuPc film, and c) Ni-CuPc composite sample, after removing the electrophoretic layer to expose the copper coloured surface.

Figure 5.4 A is the XPS spectrum for the as-received CuPc pigment powder prior to any exposure to the electrolyte for the electrodeposition process. The spectrum shows the characteristic shape of Cu2p 3/2 peak as well as the satellite peaks typical of a stable CuPc film layer. There is a distinct main peak at 935eV and broad satellite peaks around 945eV. This spectrum closely resembles the ones reported in other studies. For instance, Figure 5.5 shows the Cu2p spectra obtained from a thermally deposited layer of CuPc film on a Si (111) substrate in a study of the doping impact on the CuPc film and its stability [Krzywiecki et al. 2008]. In another study on CuPc film on Si (111) substrate, Ottaviano reported a similar peak binding energy of 935.7eV for the main peak and 945eV for satellite peaks for Cu2p spectrum [Ottaviano and Santucci 1998]. Comparing the two spectra, Figures 5.4 A and 5.5, the same characteristic peaks at 935eV and 945eV are observed for the main peak and satellite peaks, respectively.

Figure 5.4 B is the Cu2p spectrum acquired from the electrophoretic CuPc pigment film that is formed on the top surface of the electrodeposited prior to ultrasonic cleaning. It can be seen that there are no significant changes in the spectrum when compared to Figure 5.4 A. Therefore it can be concluded that exposure to the electrolyte in the plating condition did not drastically alter the chemical state of copper within the bulk of the pigment being deposited as an electrophoretic
film. The pigment remained stable in the acidic (~pH<3.0) and high temperature (T=60°C) environment during the electrodeposition process.

Figure 5.4 – Cu2p 3/2 XPS Spectra for A) CuPc pigment in powder form, B) electrophoretic CuPc film, and C) Ni-CuPc composite sample
Figure 5.5 Cu2p 3/2 XPS peak obtained for 16nm CuPc film evaporated on n- and p-type Si/SiO2 substrate [Krzywiecki et al. 2008]

Figure 5.4 C is the Cu2p spectrum acquired from the Ni-CuPc composite after removing the electrophoretic layer, i.e. the copper coloured deposit. In this spectrum, we can observe a noticeable difference in the Cu2p peaks. The same main peak and the satellite peaks are still present in the spectrum. However there is an additional shoulder peak at 933eV adjacent to the main peak. This additional peak indicates that there is a change in the binding energy for copper during the electrodeposition process as the CuPc pigment particles become co-deposited within the nickel matrix. The binding energy of the additional shoulder peak, 933eV is close to that of metallic copper. In one of the studies done by Adolphi, XPS spectra were collected for heat-treated CuPc films [Adolphi et al. 2001]. The author performed a series of heat treatment at temperatures ranging from 250°C to 350°C to observe any change in the chemical state of the CuPc film. For the films that were heat treated at 350°C, the Cu2p spectrum showed an additional peak at 932.5eV forming adjacent to the main peak (935eV), similarly to the spectrum seen on Figure 5.4 C. The author observed this new peak after 1 hour of heat treatment at 350°C which is the temperature where the CuPc pigment starts to lose its stability. The Cu2p spectrum
from Figure 5.6 shows that after 3 hours, the main peak at 935eV diminished while the additional peak at 932.5eV became stronger. This binding energy is similar to the additional peak that was observed in Figure 5.4 C. The author attributed this change to a breakdown of chemical bonds in the CuPc during the heat treatment as the copper detaches itself from the chemical bonds in the CuPc molecule and thus, detecting the binding energy that corresponds to metallic copper.

![Figure 3. Cu2p peak after different heat treatments, take-off angle 45°.](image)

**Figure 5.6 - Cu2p 3/2 spectrum for thin CuPc film after different heat treatments**

[Adolphi et al. 2001]

Therefore the new shoulder peak in the XPS spectrum of the composite coating may be due to a formation of additional surface layer of metallic copper originating from the CuPc pigment.

### 5.3.2 Ni2p 3/2 Spectrum

The matrix metal in which the CuPc pigment particles become embedded into is nickel. Therefore the Ni2p 3/2 spectrum was also examined in detail to observe any potential changes in the chemical bonding state of nickel due to the possible interaction with the CuPc particles.
during the co-deposition process. Figure 5.7 shows the Ni2p 2/3 spectra that were acquired from electrodeposited pure nickel and Ni-CuPc composite material.

**Figure 5.7 – Ni2p XPS spectra for A) electrodeposited nickel and B) Ni-CuPc composite sample**

Figure 5.7A is the spectrum acquired for the electrodeposited pure nickel sample. The spectrum closely resembles that of the Ni 2p spectrum for nickel metal surface covered by a thin NiO film as shown in Figure 5.8. The binding energy of the main peak is 852.6 eV which agrees with the literature value range of 852.7 ± 0.4 eV for the Ni metal 2p3/2 peak position (Biesinger, 2009).

Figure 5.7 B is the XPS spectrum for the Ni-CuPc composite sample. As was the case for the Cu2p spectrum, there is a change in the spectrum for the composite sample. A significant increase in the intensity is observed for the peak to the left of the main peak at the binding energy of 855.6 eV.
Figure 5.8 - Ni2p spectrum from a Ni metal surface covered by a thin NiO film [Biesinger 2009]

Interestingly, it is noted that this peak is comparable with the binding energies of the Ni2p peak for Nickel Phthalocyanine (NiPc), in which the central metal atom is nickel instead of copper. Petraki characterized a NiPc thin film deposited on a polycrystalline gold substrate and found the Ni2p peak to be 855.9eV [Petraki et al. 2005]. Ottaviano reported the value of 855.4eV for the Ni2p3/2 peak after characterizing a thin film of NiPc on a graphite substrate [Ottaviano et al. 1997]. Figure 5.9 shows the XPS spectrum of Ni2p3/2 acquired by Ottaviano’s group.

Figure 5.9 – Ni2p XPS spectrum for NiPc for film thickness of E) 5Å and B) 130Å [Ottaviano et al. 1997]
If the newly formed shoulder peak at 855.6eV for the Ni-CuPc composite sample is indeed due to the formation of NiPc compounds, then there is a possibility that upon co-deposition process, an interchange between nickel and copper atoms is occurring at some stage during the co-deposition process.

The additional peaks that forms adjacent to the characteristic peak of a CuPc molecule in the XPS spectrum for both copper and nickel indicates that there may be a change in the molecular structure of the CuPc on the surface of the Ni-CuPc composite. More specifically, the bonding energy of metallic copper detected on the Cu2p spectrum suggests that the copper from the CuPc molecule may be depositing on the surface while the bonding energy corresponding to NiPc detected on the Ni2p spectrum suggests the presence of NiPc molecules.

5.4 Proposed Mechanism for Copper Colour Formation

In the previous section, it was shown that the binding energy of the additional shoulder peak observed from the Cu2p spectrum for the composite sample could be attributed to the presence of metallic copper. The appearance of metallic bronze colour that resembles copper, and the presence of the additional peak corresponding to metallic copper suggest that there may be metallic copper being deposited on the outermost surface of the composite sample. A possible explanation for this could be a galvanic displacement reaction occurring at the interface between the porous electrophoretic CuPc pigment layer and the Ni-CuPc composite after the composite sample is removed from the electroplating cell and before the porous electrophoretic layer is removed. This section will elaborate more on the speculation that a galvanic displacement induced ion exchange occurs on the Ni-CuPc composite surface based on the information from the additional XPS and EDS spectra acquired.
Figure 5.10 – Schematic diagrams of the Ni-CuPc composite illustrating the galvanic displacement induced ion exchange

Figure 5.10 A is a schematic diagram of the Ni-CuPc composite with the electrophoretic CuPc film attached on the surface before ultrasonic cleaning. The Ni-CuPc composite part in this figure resembles the FIB cross-sectional image captured earlier in Figure 4.12A. It is suggested that a galvanic displacement occurs on the surface of the Ni-CuPc composite. Galvanic displacement occurs when the depositing metal is more noble than the substrate material. The depositing metal in this case would be copper, which comes from the CuPc pigment particles in the porous electrophoretic top and the upper layer of the Ni-CuPc composite while the substrate material would be nickel from the Ni-CuPc composite. At the interface between the CuPc film
layer and the Ni-CuPc composite, copper can be deposited onto nickel by galvanic displacement due to its favorable reduction potential. The reduction potential for copper and nickel are

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E = 0.34 \text{ V}$$

$$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \quad E = -0.23 \text{ V}$$

Copper, with a relatively higher standard potential than nickel is the noble metal and nickel is the base metal. Thus, Cu$^{2+}$ metal ions can be reduced by the electrons derived from the valence band electrons of the substrate material, nickel. This results in the deposition of metallic copper on the interface of the substrate accompanied by the dissolution of the metallic nickel. Thus, the cathodic reaction is Cu$^{2+} + 2e^- \rightarrow \text{Cu}$ and the anodic reaction, Ni \rightarrow Ni$^{2+} + 2e^-$. The potential difference, $\Delta E$ between copper ($E=0.34\text{V}$) and nickel ($E=-0.23\text{V}$) is 0.57V, which is the driving force that enables this reaction to occur.

Figure 5.10C is a schematic diagram showing where XPS analysis was performed after the electrophoretic layer was removed from the coating. It was noted earlier in section 5.3.2. that an additional peak with binding energy that corresponds to NiPc was detected on the Ni2p spectrum for the Ni-CuPc composite sample. If indeed NiPc molecules are present on the outermost top surface of the Ni-CuPc composite, additional anodic and cathodic reaction can be considered: 

CuPc \rightarrow Cu^{2+} + Pc^{-2} and Pc^{-2} + Ni^{2+} \rightarrow \text{NiPc}. The ion exchange between copper and nickel for the CuPc pigment molecules and the nickel matrix is driven by their potential difference and can result in the formation of NiPc and the deposition of copper layer on the surface. The result of this process is schematically represented in Figure 5.10 B. The CuPc pigment close to the top surface becomes NiPc as the pigment replaces the copper (which subsequently become galvanically deposited on the surface) with nickel. If we incorporate the ion exchange between
the CuPc pigment and the nickel, a simplified version of the overall anodic and cathodic reactions is as follow:

\[
\text{Cathodic Reaction:} \quad \begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} \\
\text{Pc}^{2-} + \text{Ni}^{2+} & \rightarrow \text{NiPc}
\end{align*}
\]

\[
\text{Anodic Reaction:} \quad \begin{align*}
\text{Ni} & \rightarrow \text{Ni}^{2+} + 2e^- \\
\text{CuPc} & \rightarrow \text{Cu}^{2+} + \text{Pc}^{2-}
\end{align*}
\]

Figure 5.11 shows the cross-sectional image of the microsample prepared using the FIB with the Hitachi NB-5000 system and a EDS spectrum acquired for below the surface of the Ni-CuPc composite. The area of the sample in which the spectrum was required is marked with a yellow box on the cross sectional image; an area analysis was selected in the cross section. The spectrum confirms the presence of copper K-alpha X-ray near 8 keV. This indicates that the CuPc pigment particles below the top surface do not participate in the galvanic displacement reaction while the pigment embedded directly on the surface do. Therefore it can be assumed that a galvanic displacement induced ion exchange is occurring only near the top surface of the Ni-CuPc composite and is responsible for the metallic copper colour observed. This displacement reaction occurs during the time period between removing the coating with the electrophoretic cover and the actual removal of the electrophoretic coating by ultrasonic cleaning. During that period (typically 5-10 minutes), galvanic displacement can occur because i) there is sufficient electrolyte left in the porous electrophoretic layer to make this reaction possible and ii) there is no external potential applied as during the electrodeposition process.
Figure 5.11 – Cross-sectional microsample image of the Ni-CuPc composite and the corresponding EDS spectrum

5.5 Speculations on the Absence of Blue Colour

While the previous section focused on investigating the copper colour observed on the Ni-CuPc composite after the removal of the electrophoretic layer, it did not give insight to the metallic silver colour observed after the removal of the copper coloured surface layer. In the following section, additional experiments and simulation were performed to further investigate why blue colour is not observed despite the distribution of the blue CuPc pigments in the nickel matrix after the removal of copper coloured layer.
As was seen in section 5.2, it was observed through SEM images (Figure 5.3) that in an electrodeposited Ni-CuPc composite, the CuPc pigment particles are well embedded within the composite with intimate contact with its surrounding nickel matrix. A tight interface between the pigment and the nickel matrix is achieved. An attempt was made to mimic a similar environment for the CuPc pigment particles to see if the same colour diminishing effect of the pigment can be achieved when embedded in another metal matrix. This was done by performing experiments using first gallium and then consolidated silver powder to mimic the metal matrix.

### 5.5.1 Liquid Gallium Experiment

Gallium was first chosen to mimic the metal matrix environment due to its low melting temperature ($T_m = 29.7$ °C). This unique low melting point of gallium allows the metal to be mixed in its liquid state near room temperature with the pigment particles and solidify upon rapidly lowering the temperature. Gallium was heated up indirectly in a hot water bath beaker up to 60°C to ensure that gallium is in liquid state. CuPc pigment particles were then added and vigorously agitated and stirred using a glass rod. However, after numerous attempts to mix the pigment particles into liquid gallium, the pigment particles continued to be rejected and remained on the surface of the gallium, both during the mixing and after the cooling. The difference in density between gallium (5.91 g/cm$^3$) and the CuPc pigment (1.6 g/cm$^3$) results in the pigment to separate and remain on the top surface. The surface tension between the liquid gallium and the pigment particles was too high and is thus the particles were rejected from the gallium. Due to the immiscibility of the two materials, an alternative method to create the metal matrix environment was necessary.
5.5.2 CuPc - Silver Powder Experiment

Figure 5.12 – A) Nickel powder and CuPc pigment before mixing, B) Nickel powder and CuPc pigment after mixing, C) Nickel powder and CuPc pigment after mixing and compressing

Figure 5.7A shows the two powders that were mixed: silver powder acquired from Johnson Matthey & Mallory Limited on the left and the CuPc pigment powder on the right. Silver powder was used as it does not oxidize in air and maintains its shiny metallic colour in powder form. Powders were mixed to create a mixture of 70vol% Ag and 30vol% CuPc. Upon mixing the two powders, the mixture displayed a blue colour as seen in figure 5.7B. The powder mixture was then compressed between two aluminum coupons to consolidate into a more closely compacted state. The consolidated Ag-CuPc solid is shown in figure 5.7C. It can be seen that the consolidated Ag-CuPc solid has lost the original blue colour and instead shows a silver metallic colour. Near the edge of the compacted area where compaction is less severe than in the centre,
the blue colour can still be seen. Therefore a somewhat similar phenomenon can be observed where the colour of the pigment is being diminished by the silver colour of the metal upon creating a tight interface between the powder particles.

The state in which the CuPc pigments are embedded in is not exactly the same for the case of the consolidated Ag-CuPc powders when compared with the electrodeposited Ni-CuPc composites. However, this simple experiment does give an insight to indicate that the colour of the pigment can indeed be diminished with tight interfaces and intimate contact with metal is created.

5.6 Simulation Modeling

A Finite Difference Time Domain (FDTD) simulation software, FDTD Solutions was used to simulate the conditions that resemble the electrodeposited Ni-CuPc composite with comparable pigment particle sizes embedded in the nickel matrix. Finite-difference time-domain (FDTD) is a method for numerical analysis that solves Maxwell’s equations to predict the interaction between light and structural features on the wavelength scale. With the input of the optical constants $n$ and $k$ for the nickel matrix and the CuPc pigment particles, the reflectance response was obtained for the visible wavelength range of 400nm -700nm. The optical constant values were obtained from the database of the software and reported values from literature [Wojdyla et al. 2006] for nickel and CuPc, respectively. The CuPc pigment particle was simulated as a spherical shape surrounded by the nickel matrix while the diameter of the sphere and the spacing between adjacent CuPc particles were varied when obtaining the reflectance responses. Figure 5.13 shows a series of reflectance curves with varying diameter ($D$) of the CuPc particle (indicated on the right side of the curves: 20nm, 50nm, 100nm, 400nm, 800nm, and 1600nm) and the interparticle spacing (indicated in the legend for each curve in nm). The reflectance curve that was measured
with the UV-Vis spectrometer for the CuPc pigment (Figure 5.1) is indicated as the blue curve for each of the graphs.

Looking at Figure 5.13, it can first be seen that the reflectance curve at very small particle size (i.e. D = 20 nm), does not have a distinct peak regardless of the spacing distance values. In the case of particle diameter size of 20nm, the reflectance curves are rather flat and resemble the reflectance curve for the electrodeposited pure nickel sample. At larger diameter sizes (i.e. 50nm, 100nm), a very broad peak is observed near the wavelength of 550nm but only when the interparticle spacing is small enough. The peak becomes more distinct with increasing particle diameter. Looking at the reflectance curve for the largest diameter (D=1600nm), a more distinct peak at the wavelength of 500nm is observed while the height of the peak becomes higher with decreasing interparticle spacing.

With increasing particle diameter size, a more distinct peak that corresponds to the blue colour wavelength was observed on the reflectance curves. In addition, given the same particle diameter size, smaller particle spacing distance yielded more reflectance response.

The simulated reflectance curves are preliminary and require further investigation and modification of the parameters to reflect the actual sizes and geometries in the experimental composite materials. However, the preliminary simulation results seem to indicate that the colour we observe is dependent on the size of the pigment particles embedded and the interparticle spacing between the particles. As seen from the cross-sectional FIB images for the Ni-CuPc composite coating, the pigment particles were embedded in small submicron size (200nm) particles, with intimate contact at the interface between the CuPc pigment particles and the
nickel. This suggests the need to use larger particle sizes with closer interparticle spacing in order to achieve the desired colour for nickel-pigment composite coatings.

The main result from the silver powder and simulation studies presented in this section are as follows.

i) Embedding pigment particles into a metallic matrix to produce colour is not as straightforward as embedding the same pigment into an organic matrix, for example paints and lacquers. The CuPc pigment used in the current study is mainly used for paint application in which smaller particles produce more brilliant colours. In contrast, when embedded in a metallic matrix, intimate contact between the metal and pigment particles results in a “colour quenching” effect.

ii) For the purpose of producing colour in metallic matrices, the pigment particles should likely be larger and more closely spaced as suggested by the FDTD results. In other words, any future work on producing coloured nickel electrodeposits should focus on using larger pigment particles, perhaps in the micronmeter range.
Figure 5.13 – Reflectance response curves for the visible spectrum range (400nm to 700nm) for spherical CuPc particles surrounded by a nickel matrix acquired using the Lumerical FDTD simulation software.
Chapter 6
Conclusions

The objectives of this thesis were to i) synthesize a nickel composite coating through the codeposition of pigment particles with nickel in a one-step electrodeposition process and ii) to obtain a decorative colour effect from the resulting nickel-pigment composite coating.

The synthesis of the composite coating was achieved by incorporating CuPc (Copper Phthalocyanine) Blue as the pigment and using a Watt’s type bath as the electrolyte for the electrodeposition process. CTAB, a cationic surfactant was used to help disperse the CuPc pigment particles within the electrolyte and assist their co-deposition within the nickel matrix. The optimal ratio between CuPc to CTAB was found to be about 13:1. Insufficient concentration of the surfactant lead to agglomeration of pigment particles while excessive concentration resulted in poor adhesion strength of the coating and deterioration of its mechanical properties. Top surface and cross-sectional SEM images and XRD patterns confirm that the CuPc pigment particles were embedded throughout the entire Ni-CuPc composite coating. A direct correlation between the pigment bath concentration and the amount of pigment deposited in the composite was found. Image analysis showed that the area coverage of the pigments on the top surfaces of the coatings for the concentrations of 5g/L, 7.5g/L, 10g/L, and 15g/L were 20%, 25%, 33%, and 36% respectively.

While the codeposition of particles was successful, an interesting and unexpected colour effect was observed for the Ni-CuPc composite coatings. Upon removing the outer electrophoretic pigment film that forms on the surface of the composite coating after the electrodeposition process, instead of the blue colour of the pigment itself, a metallic copper colour was observed. X-ray Photoelectron Spectroscopy was performed to further investigate the surface chemistry of
the coating causing the copper colour. The spectral range around the Cu2p copper peak revealed the presence of metallic copper. This lead to the proposed mechanism that the copper atom from the CuPc pigment in the composite top layer has leached out from the pigment and deposited on the surface of the composite as metallic copper through a galvanic displacement reaction.

The metallic copper colour was found to be only a superficial surface coating on the top layer of the Ni-CuPc composite coating. The copper colour disappeared upon removing about 500nm via ion milling and turning into a metallic silver colour similar to the colour of a pure electrodeposited nickel. The blue colour of the pigment was not observed despite the even distribution of the pigment particles throughout top surface of the ion-milled composite coating.

Silver powder and the CuPc pigment particles were mixed and compacted to mimic a similar environment in which the pigment particles are surrounded by the metal matrix. The blue colour of the pigment disappeared upon consolidating the mixed powders to form a dense composite. Further FDTD simulation results indicated that the colour observed on a pigment-nickel composite is dependent on the size of the pigment particles embedded and the interparticle spacing between the particles. These results showed that both the particle size and volume fraction in the composites produced in this thesis are likely too small to produce a significant colour effect. Future work should focus on a larger pigment particle size and even higher volume fractions of pigment in the deposits.
Chapter 7
Recommendations for Future Work

There are several areas in which further investigation is needed to improve the synthesis process of viable coloured nickel-pigment composite coatings.

It was noted earlier that some of the composite coatings showed brittleness and poor adhesion to the substrate. A more detailed study is needed on the relationship between the concentration of surfactants and pigment volume fraction in the electrolyte and the mechanical properties of the resulting composite coatings. Micro-hardness and wear resistance measurements would be a good indicator of the mechanical integrity of the composite coatings.

The XPS spectra were acquired only for the top surface of the Ni-CuPc coatings. Additional XPS measurements using depth profiling for the Ni-CuPc composite could help determine the uniformity or change in elemental composition of the composite throughout the coating. Compositional information at different depths of the coating could help determine whether the proposed mechanism of galvanic displacement is responsible for the copper colour.

Based on the preliminary simulation results, pigment of larger particle size and smaller interparticle spacing are required to achieve colour for the composite coatings. To confirm this speculation, it is suggested that pigment of larger size be used at a higher concentrations to co-deposit higher volume% of larger pigment particles in the nickel-pigment composite coatings. Crude CuPc pigment has an average particle size of 15-25µm and may be suitable for this purpose. Another promising alternative would be to use pigment-resin particles that are often used for powder coatings. These particles are in the micrometer range (30-50µm) and can likely be electrostatically charged, making them suitable for codeposition.
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