อิทธิพลของความหนาแน่นกระแสไฟฟ้าในการชุบสังกะสีด้วยไฟฟ้าต่อสภาพปรากฏของการเคลือบคอนเวอร์ชันไตรวาเลนท์โครเมตสีดำ

นางสาวนิรดา พินทุพีรโกวิท

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ปีการศึกษา 2557

THE INFLUENCE OF ELECTROPLATED ZINC COATING’S CURRENT DENSITY ON APPEARANCE OF BLACK TRIVALENT CHROMATE CONVERSION COATING

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Metallurgical and Materials Engineering

Department of Metallurgical Engineering
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Thesis Title	THE INFLUENCE OF ELECTROPLATED ZINC COATING'S CURRENT DENSITY ON APPEARANCE OF BLACK TRIVALENT CHROMATE CONVERSION COATING
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นิรดา พินทุพีรโกวิท : อิทธิพลของความหนาแน่นกระแสไฟฟ้าในการชุบสังกะสีด้วยไฟฟ้าต่อสภาพปรากฏของการเคลือบคอนเวอร์ชันไตรวาเลนท์โครเมตสีดำ (THE INFLUENCE OF ELECTROPLATED ZINC COATING'S CURRENT DENSITY ON APPEARANCE OF BLACK TRIVALENT CHROMATE CONVERSION COATING) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. ยุทธนันท์ บุญยงมณีรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร. ปฐมา วิสุทธิพิทักษ์กุล, หน้า.

เหล็กเป็นโลหะที่ใช้งานอย่างแพร่หลายในหลายภาคอุตสาหกรรม เช่น อุตสาหกรรมยานยนต์ อุตสาหกรรมเคมี อุตสาหกรรมโครงสร้าง เป็นต้น แต่ปัญหาหลักในการใช้งานของเหล็กที่เกิดขึ้นในอุตสาหกรรมคือปัญหาการกัดกร่อน ปัจจุบันจึงมีการพัฒนากระบวนการเพื่อลดปัญหาการกัดกร่อนอีกทั้งยังเพิ่มความสวยงามที่ผิว เช่น สีและความเงาหลากหลายรูปแบบเพื่อตอบสนองความต้องการของตลาดนอกเหนือจากสีโลหะทั่วไป เนื่องจากเหล็กเคลือบสังกะสียังไม่สามารถป้องกันการกัดกร่อนและตอบโจทย์ด้านสีสันได้เพียงพอ ทำให้มีการเพิ่มกระบวนการการนำเหล็กเคลือบสังกะสีมาผ่านการเคลือบอีกชั้นหนึ่ง ที่เรียกว่าการเคลือบโครเมตคอนเวอร์ชัน

ในงานวิจัยนี้จะทำการศึกษาถึงผลกระทบของตัวแปรในการเคลือบสังกะสีด้วยไฟฟ้าที่มีต่อลักษณะด้านสีของผิวเคลือบโครเมตสีดำที่ผลิตด้วยการชุบแบบใช้ไฟฟ้า หนึ่งในพารามิเตอร์หลักในการกระบวนการชุบสังกะสีด้วยไฟฟ้าคือความหนาแน่นของกระแสไฟ งานวิจัยนี้จึงมุ่งเน้นศึกษาผลกระทบจากความหนาแน่นกระแสไฟฟ้าที่ 0.5, 1.0, 2.0 และ 4.0 แอมแปร์ต่อตารางเดซิเมตร โดยมุ่งเน้นศึกษาสีจากการเคลือบโครเมตที่ให้ผิวเคลือบโทนสีดำ เนื่องจากสีดำเป็นสีที่ได้รับความนิยมมากที่สุดสีหนึ่งในตลาด การศึกษาได้ดำเนินการโดยการบูรณาการศาสตร์ทางโลหะวิทยา (Metallurgy) ไฟฟ้าเคมี (Electrochemistry) และวิศวกรรมทางแสง (Optical engineering) เพื่อหาความสัมพันธ์ของความหนาแน่นกระแสไฟที่มีต่อโครงสร้างและสมบัติด้านสีของผิวเคลือบ องค์ความรู้ที่เกิดขึ้นจะมีความน่าสนใจในเชิงวิชาการเป็นอย่างยิ่งเนื่องด้วยงานวิจัยเชิงลึกทางด้านนี้ยังมีอยู่โดยจำกัด โดยงานนี้มีการนำเครื่องมือในการตรวจวัดคุณภาพน้ำยาเคลือบของสังกะสีอย่าง Hull Cell เข้ามาใช้ผลิตชิ้นงาน เพื่อให้ได้ชิ้นงานที่ง่ายต่อการเปรียบเทียบสมบัติทางแสงและควบคุมผลกระทบจากตัวแปรอื่นๆได้ดีในการผลิตในครั้งเดียว อีกทั้งเครื่องมือการตรวจวัดสมบัติทางแสงอย่าง CCD spectrometer ได้นำมาใช้ประกอบกับข้อมูลทางแสงจาก Colorimeter และ การตรวจวัดด้วยสายตา เพื่อให้เห็นความสัมพันธ์และความชัดเจนของการวัดข้อมูลทางแสงของผิวเคลือบ

จากการศึกษาพบกว่า ไม่ใช่เพียงการควบคุมพารามิเตอร์จากชั้นเคลือบโครเมตคอนเวอร์ชันเท่านั้นที่มีผลต่อสีของผิวเคลือบ แต่พารามิเตอร์ในการผลิตของชั้นสังกะสีเองก็อาจมีผลต่อสีสุดท้ายของชั้นโครเมตคอนเวอร์ชันสีดำด้วย ดังเช่นที่ในงานวิจัยนี้ได้พบว่าความหนาแน่นกระแสไฟฟ้าจากชั้นสังกะสีมีผลให้สีดำของโครเมตคอนเวอร์ชันเปลี่ยน โดยบริเวณความหนาแน่นกระแสไฟฟ้าสูงจะทำให้การเคลือบชั้นสังกะสีมีความหนาสูงกว่าบริเวณที่มีความหนาแน่นกระแสต่ำ และสมบัติทางจุลภาคอื่นๆที่อาจเปลี่ยนเช่นกันจากผลกระทบของความหนาแน่นกระแสไฟฟ้าที่ไม่เท่ากัน เพราะฉะนั้นการควบคุมขั้นตอนการผลิตสีดำของผิวเคลือบโครเมตเพียงอย่างเดียวนั้นไม่เพียงพอ จึงจำเป็นต้องควบคุมขั้นตอนการผลิตของชั้นสังกะสีด้วย การตรวจสอบเบื้องต้นทางจุลภาคและทางเคมี เช่น กล้องจุลทรรศน์อิเล็คตรอนแบบส่องกราดกำลังขยายสูง, กล้องจุลทรรศน์แบบแสง, และเครื่อง เอ็กซ์เรย์ฟลูออเรสเซนซ์ ได้นำมาใช้เพื่อสร้างความเข้าใจเบื้องต้นเกี่ยวกับกลไกที่เป็นไปได้ที่ควบคุมการปรากฏสีของชั้นเคลือบ จุดเริ่มต้นของความเข้าใจจากงานวิจัยนี้จะเป็นประโยชน์ต่อภาคอุตสาหกรรมของประเทศเป็นอย่างสูงเนื่องจากผิวเคลือบประเภทนี้มีปริมาณการผลิตและการใช้เป็นอันดับต้นๆ และมีความต้องการในการวิจัยพัฒนาจากอุตสาหกรรมอย่างต่อเนื่อง

ภาควิชา วิศวกรรมโลหการ	ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมโลหการและวัสดุ	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ปีการศึกษา 2557	ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5570549621 : MAJOR METALLURGICAL AND MATERIALS ENGINEERING
KEYWORDS: ELECTROPLATING / ZINC / GALVANIZED STEEL / CHROMATE CONVERSION COAITNG / PASSIVATION / BLACK CHROMATE CONVERSION COATING

NIRADA PINTUPERAKOVIT: THE INFLUENCE OF ELECTROPLATED ZINC COATING'S CURRENT DENSITY ON APPEARANCE OF BLACK TRIVALENT CHROMATE CONVERSION COATING. ADVISOR: ASST. PROF. YUTTANANT BOONYONGMANEERAT, Ph.D., CO-ADVISOR: ASSOC. PROF. PATAMA VISUTTIPITUKUL, Ph.D., pp.

Steels are widely used in various field of industrial such as automotive, chemical and structural industries. Nevertheless the main obstacle of steel application in industries is the corrosion problems that diminish some desired properties. Recently there are developments of process to lessen the corrosion, additionally to improve aesthetic property for instance colors and glossiness to serve market needs except from ordinary colors. The zinc-coated steels cannot provide sufficient corrosion resistivity and aesthetic property. Thereby adding the second process of second coating on zinc-coated steel was introduced which is called Chromate conversion coating.

In this work, for the first time, a systematic study is carried out to correlate the electroplating parameters, mainly the current density, on the formation of the trivalent chromate conversion coating, and hence the color appearance of the top-coats. This work focused on the study of current density at 0.5, 1.0, 2.0 and 4.0 Ampere per square decimeter. Focusing on the black conversion coating, since the black coating is one of the most widely used color in the market. The study had been processed on the basis of metallurgy, electrochemistry and optical engineering to find the correlations that current densities have towards structural and optical property of the films. Also the first time Hull cell setup had been introduced to fabricate the samples in order to create more ease of distinguishing the color and have all controlled conditions in one setup in one bath. The color and optical properties are analyzed using a colorimeter and an optical CCD spectrometer. Also comparison to visual inspection had been implemented to see the relation and to obtain virtual optical data

The results notably show that, current density affects the optical properties in the visual spectrums. Not only the processing parameters from conversion coating that can affect appearance of it, but the processing parameters such as current density from zinc process also have influence towards conversion coating. It had been discovered that the current densities from zinc plating layer have the influence towards shade of black color on CCC layer changing, the high current density area exhibits darker blackness comparing to low current density area. Therefore controlling only process of conversion coating might not be sufficient. Controlling the process from first layer of zinc is also important in appearance wise. The basic microstructural and chemical characterization techniques, namely FE-SEM, OM, and XRF, are used to shed some light on the possible underlying mechanism that controls the color appearance. For further study, suggestions of investigation means had been advised to get more tangible and clearer microstructural data. The understanding developed in this study will impact the design and fabrication of the electroชgalvanizing products of desired color and esteemed functional performance.

Department:	Metallurgical Engineering	Student's Signature ....
Field of Study:	Metallurgical and Materials Engineering	Advisor's Signature ....
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Chapter 1

Introduction

1.1 General Introduction

One of the outstanding ways to improve the properties of steels is to employ some surface finishing on top of the products. The common obstacles of steel using are red corrosion products which pervades and create loss of based metal. Protecting the steel with more sacrificial, in another word : inert, metals is a good alternative for improving resistivity to corrosion, for instance, coating with zinc, nickel, chromium or other combination of metal coating such as aluminum-zinc, zinc-nickel coating etc. [1-4]

Electroplating zinc coating, in industrial generic term as electro-galvanized coating, is widely used by its prominent ease of use and fair protection. Method of this protection is the mechanism of Cathodic protection which Zinc sacrifices itself instead of steel due to its lower potentials. Even though electroplated zinc layer would protect the steel from rusting or corroded by environment[5], the zinc layer will be sacrificially corroded and lose overtime. Therefore, obtaining more protection means zinc coating should be thick enough to sacrifice for a period of time. In short, thickness of zinc layer affects dominantly on the ability to withstand the corrosion. However, coating the thick zinc on the surface is sometimes inapplicable and tedious. Thereby another so-called Chromate conversion coating (CCCs) had been utilized as the second layer of protection. Except from the prolonged lifetime benefit, CCCs had been developed to serve consumer with better functional properties and distinctively provide variety of coloring shades for products shown in Figure 1.1.

Figure 1.1 Schematic coating of electroplated zinc layer with CCC as top-coating on steel products

Not only lengthen their service lifetime, but CCCs can also improve the appearance of samples through color and glossiness. Depending on the chemistry and processing parameters of CCCs, application of CCCs could result in either a yellow, blue, iridescent, green or black tone color on the surfaces. The black color, in particular, recently receives several industries' interests, especially the automotive and the aviation[6]. Therefore it is chosen as the target study color in this project. Initially, the hexavalent chromium (Cr^{6+}) had been widely employed in coating solution because of their self-healing property with great protection and desired colors. Unfortunately, it had been lately found that the hexavalent chromium is carcinogenic; agent that can cause cancer. From the stringent requirements on environmental issues, the industries are replacing the conventional hexavalent chromate with the more environmentally friendly trivalent chromate (Cr^{3+}) for the production of coatings. Also, there are several types of zinc bath solution to create different identical properties of zinc layers, for example, Cyanide baths, non-cyanide alkaline baths and acid (Chloride) baths. Each type of baths exhibits uniqueness and advantages with drawbacks. To lessen the toxicity issue, Non-cyanide alkaline bath is the selected type of electroplating zinc used in this work.

The mechanisms of conversion film formation and growth had not been completely explained, nevertheless many valuable studies proposed some viral chemical reactions describing the oxidation reactions of zinc and the formation of cross-linked backbone developed by chromate ions in addition with anions such as sulfate ions [7] While there presents a fair amount of studies on the corrosion properties of the CCCs [8-11], an investigation on their appearance and optical property and how processing parameters control these features are rather limited [10-14]

There are some interesting works investigating on how processing parameters from CCCs itself affect of final color of the films (pH, temperature, additives etc.) to predict the optical model of the conversion layer, and also show that the higher pH of chromate bath leads to a formation of thinner films, which in turn affect the optical process assessed by spectroscopic Ellipsometry [15]. Also the former work showed that the chemical contained in zinc bath had the effect toward the colors [11]. Yet, the understanding about the relation between zinc layer and final color of the CCC layers is still limited. This leads this work to the drive to understand the relation between the underlying processing parameters of electroplating zinc process to the final black color of the CCC products. One of the outstanding parameter is current densities which is the starting point of the overall process.

It is indeed important to design the process of last layer which logically dominate in determining the color. Still, Zinc layer itself could act as underlying basic cause of color as well. Process to produce the zinc layer is varied by many parameters such as current densities, steps of post treatments before undergoing the CCC processes, Ratio of chemical compositions in electroplating bath etc. Particularly, current density used in each batch of production is initially starting point of processing parameter controlling. It is also known that different current densities used in electroplated zinc leads to different microstructures such as thickness,

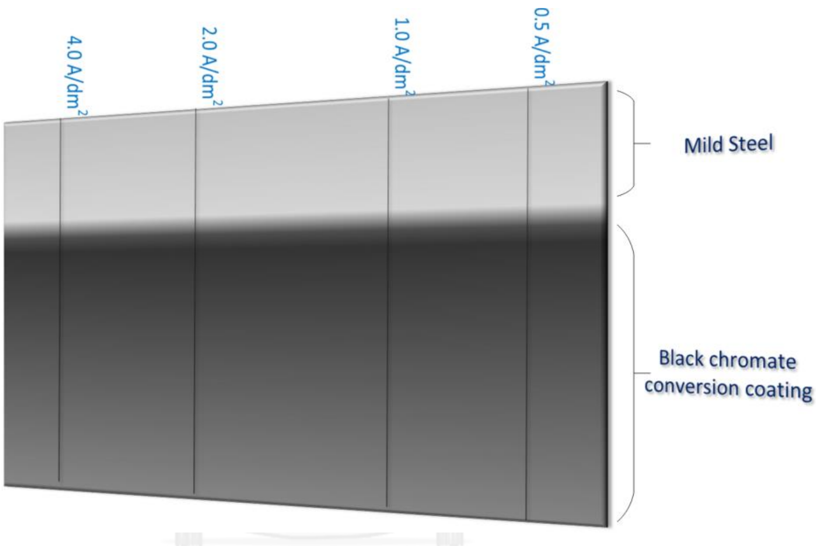


Figure 1.2 Four selected current densities created by Hull-cell electro-plating zinc bath

roughness or structures. This work helps identify the effect of current density changes that might determine blackness or shade of black color in CCC layers. Further guiding of the understanding of post-treatment processing parameter such as hydrogen elimination baking after electroplating had been introduced to shed some light of the effect of heat treating as well.

Additionally, to control the conditions of processing parameters, this works shows the first time of applying the fabrication of zinc-plating samples through Hull-cell setup. The identity of this setup is to provide different current densities of plating within one sample in one controlled condition. Therefore, in one setup it is certify that other processing parameters had been controlled and vary only current densities. The cathode side of Hull-cell plating is placed with plated sample aligned unparallelly with anode in the zinc bath. Current density distributions were generated by asymmetric insertion between unparalleled electrodes [16]. Four different current densities had been selected to study and investigate the correlation of the current density from zinc process that affect the final coating's color of CCCs (Figure 1.2)

Most of the studies mainly emphasized on corrosion properties of the products. Still, the blackness of the film plays the important role for industrial quality assuring of appearance. Acquiring the accurate data of blackness is thereby critical to industries. The characterization of the blackness in industrial wise had been done through visual inspection by inspectors. Hence, this work will introduce the method and results of obtaining optical data and study the relation between visual color and optical spectrum color.

The fabricated film colors had been investigated by detecting the reflected light from the surface. The reflected light from the film results from the film absorption and surface roughness. Based on the former studies of CCCs film characteristic, the CCC films contain metal oxides and trivalent chromium complexes, hence the optical assumption assumes that the CCCs thin films are dielectric hosts filled with some impurities. When the incoming visible light travels into the film, some spectrums are absorbed by the impurities and property of the host, some spectrums are allowed to travel through. Once it reaches the based metallic plated Zinc, which acts as bulk metal that allows very thin molecular-layer penetration of light, the incident light will bounce back into dielectric CCC film and then reflected back out of the film surface to the detectors. The colorimeter and CCD spectrometer had been utilized to precisely record the optical data, spectrum, reflected and scattered from the films. The results notably show that, current density from the first layer of zinc coating have the effect to the optical properties in the visual spectrums of CCC layer.

The microstructural and chemical characterization techniques, namely SEM, FE-SEM, OM, and XRF, are used to shed some light on the underlying mechanism that controls the color appearance. The understanding developed in this study will impact the design and fabrication of the electro-galvanizing products of desired color and esteemed functional performance.

1.2 Objective

To study the relationships from current density that affect the optical property of chromate conversion coating film on electroplated-zinc steel

1.3 Scope of Research

1. To study the effects of processing parameters of the coating on optical property
2. Current density of electroplated zinc (Zimex E-555) process : at 0.5, 1.0, 2.0, 4.0 A/dm^2
3. With or without Hydrogen elimination baking before black trivalent chromate conversion coating process
4. To observe thickness of Zinc layer by XRF, surface morphology by Optical microscope and field-emission scanning electron microscope , and optical property by spectrometer

1.4 Expected results

Understand shades of blackness of the coating that affected by processing parameters

Chapter 2

Background and Literature Reviews

Steps of fabricating products with electroplated zinc and conversion layer starts from preparation of Zinc bath with the desired type of bath and conditions. The samples will be cleaned with steps of work then undergo the process of electroplating. Some post-treatment after drying off the electroplated products might be applied to create specific properties such as higher wear resistance. Then the acid etching will be done to remove remaining oxides on zin surface followed by CCC process of coating and end up with last water rinsing and drying off the layers. Overall process flow is shown in

Figure 2.1

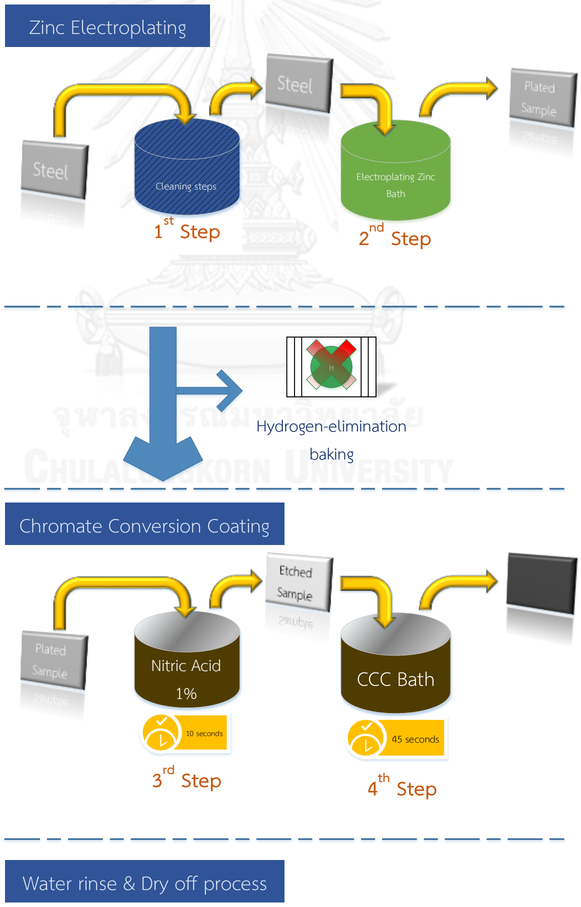


Figure 2.1 Overall steps of producing Chromate conversion coating on electroplated zinc steels

2.1 Electroplating Zinc

Electroplating, electrodeposited, or electrowinning zinc coating is the process of depositing metal, zinc, on the surface with the help of electro-driven force creating the attached zinc film on the cathode side or the plated materials. Using zinc coating is the most economical method of protecting steels [17].

2.1.1 Background of electro-plating zinc coating

In order to provide longevity property in corrosive environments for steels, coating had been plated as top-coatings. One of the most outstanding protective processes is electro-galvanizing. Electrogalvanized or electroplated zinc is the process that promotes the coating of sacrificial zinc layer on top of steel.

Electroplating process is the process that implements electrochemistry knowledge to deposit material as thin film on conductive metal in order to bestow desired properties such as corrosion resistance. In the circuit, the part to be plated is cathode while the metal to plate will be anode. Both electrodes will be submerged in electrolyte solution which contains several metal salts or ions with appropriate conditions that promote flow of current. On anode site, the metal will be oxidized after applying the direct current with positive pole. The anions will be dissolved in solution and driven towards negative electrode or cathode site. (eq.2.1) Reduction of metal ions will occur on the surface of Cathode, (eq.2.2) [18]

At Anode $M \rightarrow M^{z+} + ze^-$ eq. 2.1

At Cathode $M^{z+} + ze^- \rightarrow M^0$ eq. 2.2

Mechanism of this zinc passive film protection is based on the different potentials of plating metal, Zinc, and the metal to be coated, Steel. This potential difference will be the driving force for zinc to sacrifice itself instead of steel. In short, Zinc is more vulnerable to be corroded than steel. This protection can also be called as Anodic coating, or Cathodic protection coating.

2.1.2 Processing parameters

Before undergoing any process of plating, the sample preparation is needed. The process is listed in Table 2.1 Sample preparation helps provide more adhesive surface to promote better coating property.

Table 2.1 Sample preparation steps before electroplated zinc coating

Steps	Type of preparation	Details
1	Soak clean	50 °C
2	Water rinse	-
3	Electro-clean	Basic solution, 5.0 V, 30 seconds
4	Water rinse	-
5	Acid dip	pH 1.5-2.0
6	Deionized water rinse	-

As mentioned earlier in 2.1.1, there are several processing parameters during zinc plating procedures. Four viral processing parameters are listed below for the examples of most interested independent parameters concerning in industries that could cause dependent parameters difference afterwards. (Schematic diagram in Figure 2.2 shows the example of independent and dependent parameters during process of producing samples.) The independent processing parameters could cause the changing of dependent parameters and lead to shade of blackness changes.

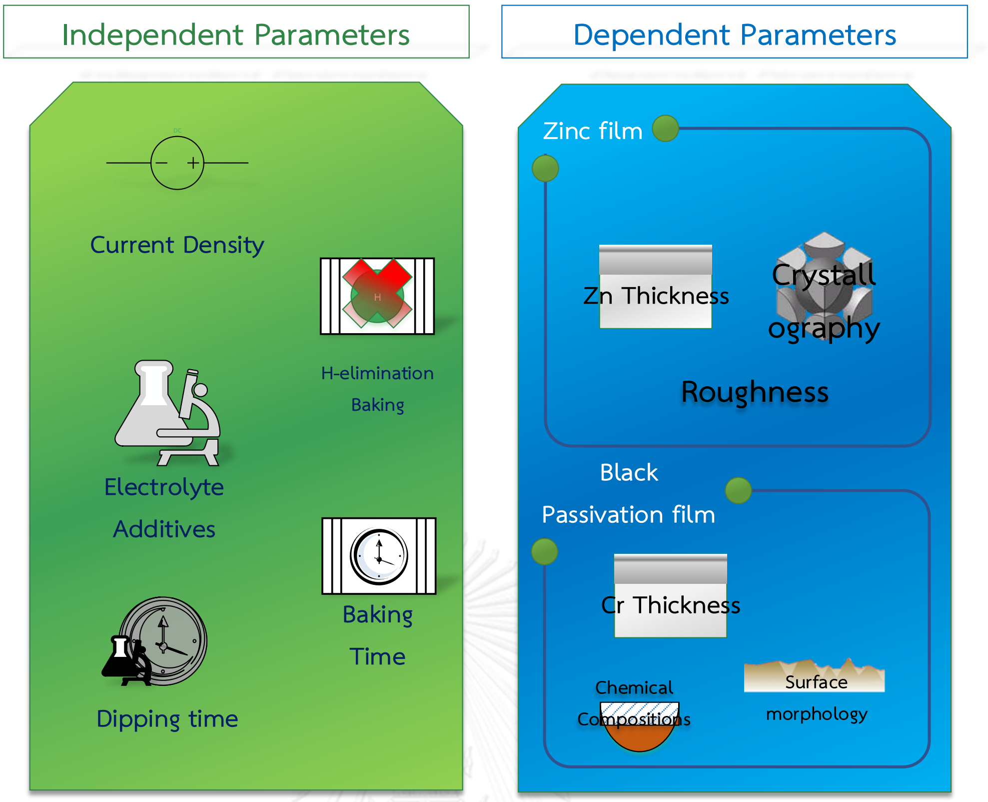


Figure 2.2 Schematic diagram of possible affective processing parameters that affect color appearance of CCC layers.

1. **Plating Solutions**

Chemical containing in the bath solution certainly defines chemical composition and chemical reaction during film formations. Most of former works compare different kind of plating solution with different conditions in order to optimize the range of each composition.

Various types of electroplating solution had been developed ad categorized. Three dominated categories that are recently used widely are listed below.

a. Cyanide bath (strongly alkaline solution/basic): This type of bathing solution contains Cyanide and Hydroxyl as complexing agents. The complexing agent means the agent that will bind with main plating component and help the reaction of film forming to occur. This type of solution exhibits good throwing power meaning that the ability of a bath to plate uniformly geometrically at non-uniform parts. Cyanide bath are well-known in terms of their high stability in performance in function of bath composition [19]

b. Non-cyanide alkaline bath: the plating mechanism is depending only on hydroxyl complexes and Zn^{--} ions. The drawback is its very-narrow optimum range of chemical composition.

c. Acid (Chloride) bath: Zinc exists in form of Zinc Chloride i.e. active species is Zn^{++} ions. This acid bath has the best leveling (micro-throwing power: ability to plate uniformly in molecular scale). This setup has low hydrogen evolution therefore it creates less in hydrogen embrittlement. Still, the setup requires a special tank or holder in order to withstand its high corrosiveness solution.

Several works focuses on the CCCs's solution or chemical compositions those results to different optical property of the coating. Still, stated in M. Tencer's work in 2005 that a cross-matrix study using different zinc plating techniques by different labs showed that the main deciding factor is the type of zinc plating bath used rather than the subsequent chromating process. [19]

2. **Current Density**

In the unit of Ampere per square decimeter or centimeter, current density is the parameter that states about how dense the current had been stored or put in a particular area. In the setup of plating bath, this current density is the first concerning in every industrial batch.

In McCOLM's work [16], it I stated about the shortcoming of using hull cell. It is the disability to do the microscopic analysis easily at specifies current density. Also, an exact current efficiency cannot be defined through current densities without knowing deposited mass.

In this work, the current density had been chosen as a major parameter to study the effect of color appearance of CCC based on different plating current densities.

3. **Immersion time**

Providing short or long immersion time promote the reaction to occur.

4. **Post heat treatment**

In some application of products, baking as post-treatment is required to yield better specific properties such as wear resistance. In general, Hydrogen-elimination baking at above 200 Degree Celsius is commonly applied after plating with zinc. Hydrogen gas aligned along the film can cause the wear weakness. This can cause a very big application drawback issue especially on components that needs to cope with wear and shearing force on surface such as bolts and nuts.

2.1.3 Hull cell setup

Hull Cell set up is the analytical electrochemical cell used in industrial laboratory scale to analyze the performance of the chemical bath. The trapezoidal geometric shape of the bath provides range of current densities along the plated sample. It was designed to examine electroplating rather than mass production processes [16]. Therefore, the fabrication of samples through hull cell is often empirical merely to do the virtual simulation of parameter effects.

Altering the Hull cell setup is accessible. Varying input current, time of immersion, ratio of zinc bath, type of zinc solution incorporate a range of current density all into single experiment.

There are various kinds of Hull cell setup; cylindrical, trapezoidal, modified shapes and modified setups, etc. The classic ones is Trapezoidal shape showed schematically in Figure 2.3.

Figure 2.3 Classic trapezoidal Hull cell bath of electroplated zinc process in this project.

One of the outstanding point of Hull cell identities is that it can create a wide range of interested current density in one setup. And that causes the controlled conditions other than current density. This work introduces the using of Hull cell setup to create representative samples to study about relations of single processing parameter at single experiment to its final optical property, appearance. Though Current density is the starting point of creating the coating layer, it is appropriate to examine and shed some light of the effect of underlying parameters from zinc plating layer to CCC appearance as a pilot study. Mass production scale or full-scale electroplating zinc scale needs further concerns.

2.2 Chromate conversion

'Chromate' had originated from the use of chromium anions in the process, while 'conversion coating' means parts of surface will be transformed or converted into film for better corrosion resistance and other functional properties [20]. The mechanism had been controlled by the oxidation-reduction equations shown in Table 2.2

Conversion coating can be undergoing in several methods. Two major categories of classifying the type are immersion and electrical. [20] The immersion type of CCC used in this work has been built from the understanding along developments of using trivalent chromate to get a homogeneous film on the surface based on the study of Winiarski [21] that tried to get the chromium-free conversion coating by adding Titanium in the solution. From the requirement and drive from industries, excessive demand of more protection on steel products had been developed by using CCC for many years some other treatments such as phosphate are used in order to provide more adhesion to the paint as well as increase ability to withstand more corrosion than zinc alone. Anyhow, in Zhang's work, it is stated that phosphate ability of corrosion resistance is not comparable to CCC [22].

Table 2.2 chemical reactions during CCC film formation

Types of reaction	Reactions	Equation	Reference
Oxidation	$Zn \rightarrow Zn^{2+} + 2e^{-}$	2.3	[11, 25]
Reduction	$2H^{+} + 2e^{-} \rightarrow H_2$	2.4	
Cr^{3+} Film formation	$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2$	2.5	[25]
	$Cr^{3+} + 3OH^{-} \rightarrow Cr(OH)_3$	2.6	
	$2Cr^{3+} + 6OH^{-} \rightarrow Cr_2O_3 + 3H_2O$	2.7	
	$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O$	2.8	[11]
	$Cr_2O_7^{2-} + 8H^{+} + 6e^{-} \rightarrow Cr_2O_3 + 4H_2O$	2.9	
	$CrO_4^{2-} + 2Cr^{3+} + 4OH^{-} \rightarrow Cr(OH)_3 \cdot CrOH \cdot CrO_4$	2.10	

The CCCs are mainly introduced to enhance corrosion property, appearance, strength and, in some case, wear resistance. The coating can be coated on various types of metals; electroplated-zinc steel, Aluminums, Zinc alloys. Initially most of CCCs are formed by hexavalent chromate (Cr^{6+}, Cr (VI)) due to their self-healing properties that exhibit to better protection [7, 20]. Nevertheless, hexavalent chromate is carcinogenic and toxic to environment [23]. Trivalent chromate had later widely developed to substitute hexavalent chrome content and simultaneously reduce the amount of other toxic contents in electrolytes. The chemical developments are to find best condition to coat trivalent chromate layer instead of hexavalent with comparable characteristic and properties. Some works for example the patent from 2006 [24] stated that the oxidizing agents contains in the CCC solution might cause transformation of trivalent back into hexavalent chromate which is hazardous such as peroxides or persulfates. Many developments in some works also avoid oxidizing agents in the solution.

2.2.1 Film formation

Cr^{3+} in the solution which then will be transformed into hydroxide compounds ($Cr(OH)_3$, $Zn(OH)_2$) or oxide of Zinc and chromium (Cr_2O_3) as shown in eq. 7,8,9 respectively. Chromium ions formation has similar mechanism as Sol-gel mechanisms in Figure 2.4

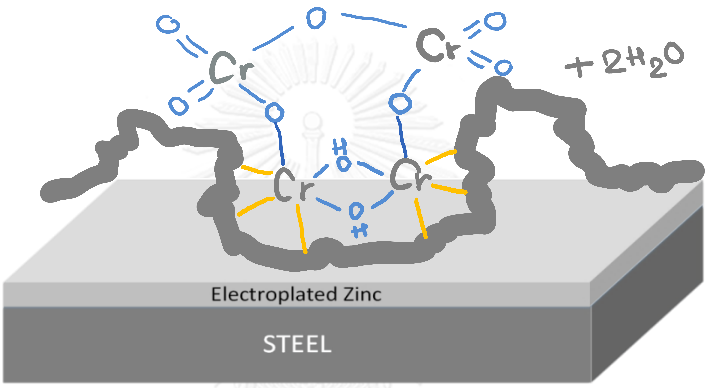


Figure 2.4 a) Formation of Cr^{3+} to $Cr(OH)_3$ in backbone shape b) Possible structure of Cr(III)/Cr(VI) oxide mixture in chromate film[1] and c) schematic picture chemical (reaction of Cr^{3+}

layer on the surface had been revealed. This work also show the role of each main anion usually used in black CCC solutions such as sulfate anions, acetate ions and the most important ion for black conversion coating are transition metal ions. The viral transition metals contained in the film had been found on the thin black oxide layer. And it is stated that those transition metals are essential factors to get black color of the film. It also showed that only the presence of chromium and zinc oxide and hydroxide are not enough to form black color. The schematic picture of CCC film in Gigandet's study had been showed in Figure 2.5 [11] it was formerly studied in Rozovski's work that containing cupreous oxide define the intensity of shading [26]

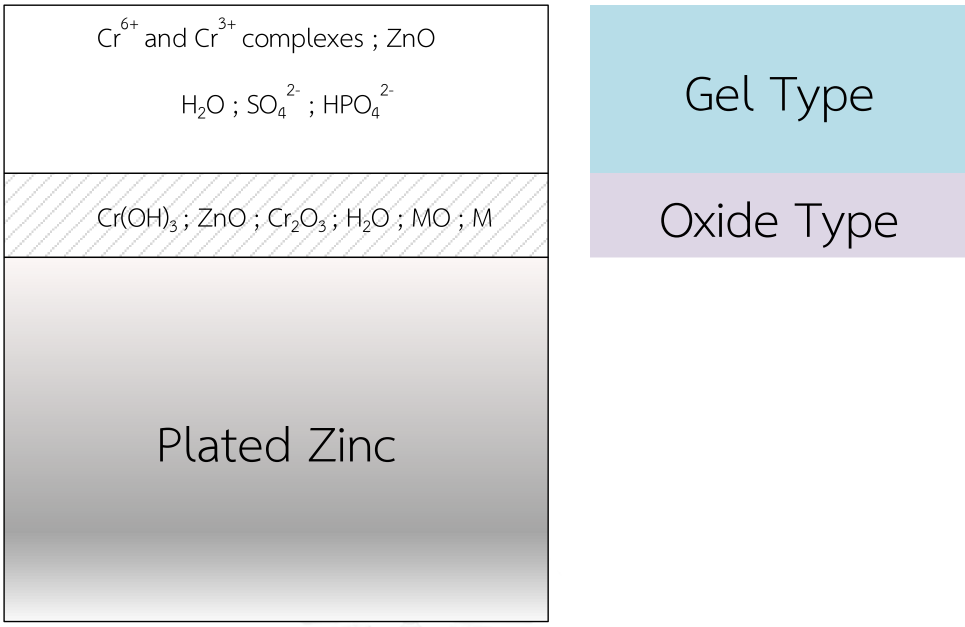


Figure 2.5 Gigandet's schematic proposing of sublayers in Chromate conversion coatings

As mentioned earlier, the usage of Cr (VI) had been concerned in environmental issue, changing the solution containing to trivalent chrome can sooth the situation and some non-chrome is also developed. In Zaki's work [27], the mechanism of film forming in CCC solution started from precipitation of trivalent chromium in the gelatinous film on the surface of zinc consisting of hydrated chromates, zinc, chromium hydroxide and other metal oxides.

However, using trivalent in substitution of hexavalent brought up some drawbacks, example from some works, thinner and lessen ability to design color [27], lessen ability of corrosion protection [10]

In Zhang's work [10] , it is stated that although the coatings formed in Cr(III) treatment solutions can be very thin, the electrochemical impedance of Cr(III)-treated surfaces is nevertheless many times larger than the impedance of untreated zinc surfaces. Therefore, even the trivalent can create thin layer of protection, it is still better than zinc coating alone. The ability to withstand corrosion in trivalent and hexavalent is different in two terms ; thickness and self-healing ability of hexavalent.

2.2.2 Categorizing CCCs

There are several types to categorize Chromate films. The simple and straightforward one is to differentiate them by their thickness. In Capper's work in 2012 the films had been claimed into three kinds of thickness, thin, thick and black [28].

The ones that contain less than 80 nm thickness of chromate film will be call as thin while 0.25-1.5-micrometer thickness had been claimed as thick film. Interestingly, the black films is also one of the thick films but different by its added chemical content such as Fe, Co and Ag.

Based on literature research from previous works published as patents, fifty patents had been chosen as the representative to see the development and point of interest from before 1980. In Figure 2.6, it distinctively shows three different point of interest in developing the chromate conversion solutions. Corrosion resistivity is the leading reason of developing this second coating layers followed by the environmental issues mentioned earlier such as restriction from REACH or RoHS that drives the development to avoid using hexavalent chromate and cobalt. The environment friendly conditions of solutions had been developed. For other properties, the development aimed to further properties than only corrosion resistance such as better wear resistance [29], low embrittlement in layer [30], workability [31], application with other base alloy [32] or more uniform color and finishing appearance [33].

The results show that corrosion property is the main property developed since before 1980 until recent period while it is gradually increased in developing more friendly solution such as lower cobalt and trivalent chromate replacing hexavalent. Not only the exponentially increased amount of patents concern about environment issue these days, but the appearance properties and other properties developments that need understanding of what parameters controls final properties had also been emphasized lately. Thereby, if we can ensure the underlying cause of final property such as colors and appearance, it would be very helpful in order to develop further properties in the future works.

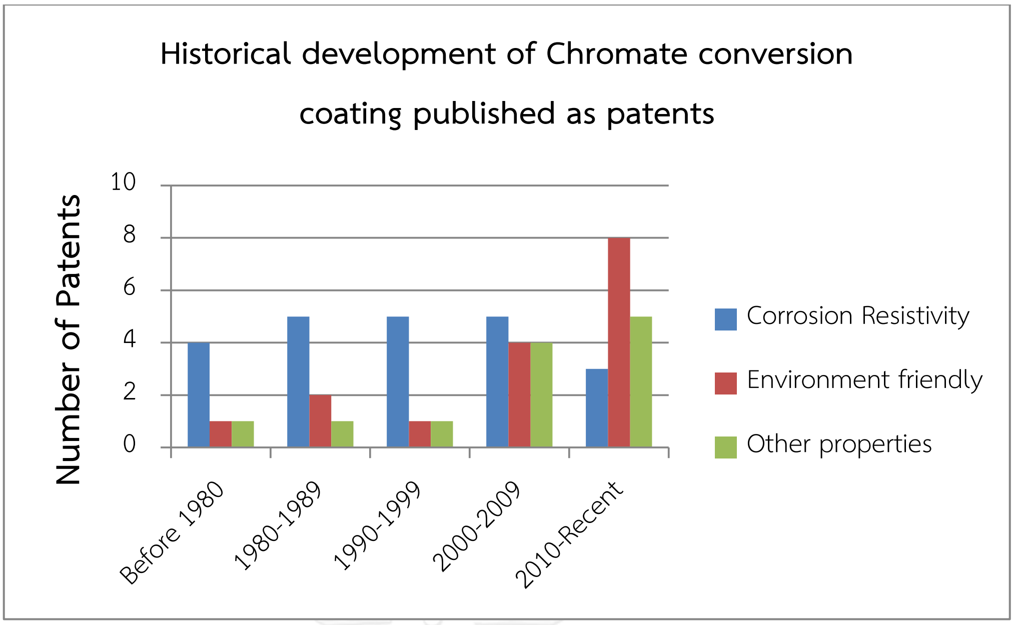


Figure 2.6 fifty patents of CCC development since 1942 showing the trend of developments [5, 7, 24, 28-32, 34-75]

2.3 Optical properties

Appearance is one of the most recent property customer encounter the first. To interpret the meaning behind colors, optical meaning should be simplified and explained in order to set the hypothesis about cause of color from the films.

2.3.1 Causes of color

Pigments and Dyes

Pigments and dyes are wavelength-selective reflecting and/or absorbing particles. Sample that contains blue pigment can exhibit high absorption pigment in yellow and red spectrums but does not absorb much in blue range of spectrum. The reflected spectrums create the appearing of colors. Meaning that part of light spectrum is absorbed while the rest reaches observer’s eyes. (Figure 2.7) [13]

Structural coloration

Butterflies' wing colors are very distinct example of how surface morphology effect directly on colors. Nano-scaled morphology of surface can be a main cause of color in terms of how the light scattered and reflected on the surface.

Peacocks' tail feather is originally brown in pigment. Nevertheless, structures and nano-scale surface roughness dominate over the brown pigment and express in various colors on butterflies' wings. (Figure 2.5) [76]

Bulk metals

Metals' atoms have free electron with metallic bonding between their neighbors, this leads to close packing of metal also high electrical conductivity. Their electrons are also 'free' to move along conduction bands which had been observed that most metals absorb light from infrared to ultraviolet range. This could imply the 'black' appearance of metals. However, metals can only be seen as black when they are in form of fine powder.

Bulk metals reflect lights due to its dense pack of structure. The shiny appearance of most metals is from the fact that the dense structure reflects light.

Colors from metals come from that fact that metals individually allow different type of wavelength to propagate through themselves such as gold and copper prefer long wavelength to reflect more than short ones. Yellow to red colors are then appear strongly to our eyes. On the other hands, bulk zinc reflects equally in visible range of spectrum. Thereby, the shiny greyish of reflection comes into observers' eyes. [76]

Thin films / Dielectric materials

Color can be caused by transmission of light. Gold thin film, even though gold is metal, beaten into thin film (less than 100 nm) exhibits differently in color from different spectrum of transmission and remission. Yellow color of gold came from the fact that gold emit or reflect light in red while it will allow blue spectrum to propagate through its layer. This leads to different color of gold. In short, The gold can be processed to have two mechanism of light reacting simultaneously, the bulk metal and the dielectric material.

Thin films can also be called as dielectric materials seeing that its main mechanism of light propagation is similarly the selective transmission obstructed by impurities. The color observed from thin film is the selected transmitted light. Dielectric materials are materials that allow selective frequencies or wavelengths of light to propagate in itself and the propagated wavelengths will be transmitted through the layer. Therefore, if we observed green color out of dielectric materials, that means the 550nm light is allowed to be mostly transmitted into the film and reflected back to our eyes. Metal oxides are categorized as dielectric materials.

In literature research, it is found that the work of Campestrini's tried to model the optical interaction between light source and yellow CCC film. As mentioned in [15], the study showed how pH of CCC coating process change the thickness of CCC layer on aluminum alloy. The spectrometry had also been used with range of light source as UV-Visible-infrared which is broader than our scope in this work. Although the optical model had been proposed to determine how light reacts with film thickness, the use of spectrometer had not yet been proposed to determine color. However, this can confirm that the spectrometer data can be interpreted and based on the collected data, the refractive index of chromate conversion layer can be called optically as dielectric film.

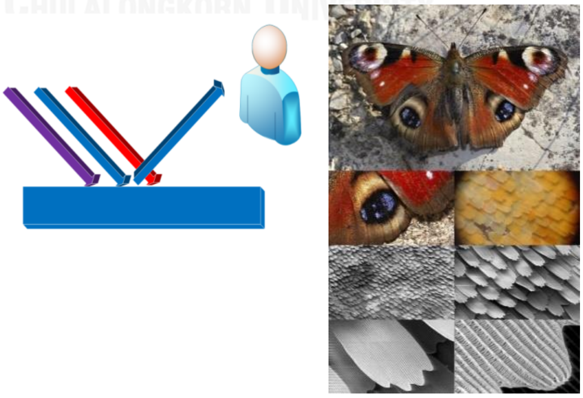


Figure 2.7 (Left) Observer detects blue spectrum from reflection of blue pigment (Right) Structural coloration on butterfly's wing

Figure 2.9 gold thin films (Left) gold color in normal ambient light (Right) gold color in light from behind the film.[13]

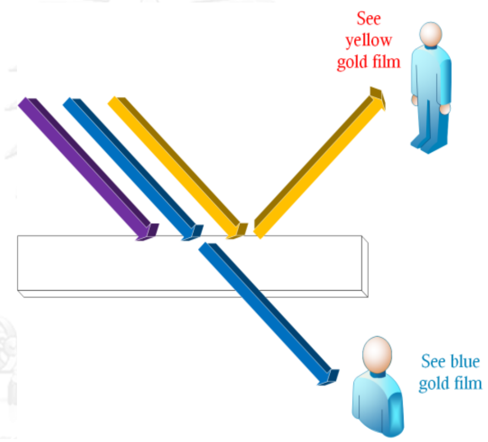


Figure 2.8 the upper man see the golden gold film from the mechanism of bulk metal while the lower person see the golf film through mechanism of dielectric materials

Another example for interfering effect from transmission caused by thin film is the oil on steels or metals. Oil on metal sheet can exhibit any of color on visible spectrum depending on condition of observers. Even though oil itself is liquid-like colorless, but light propagate through the thin film of oil and interact with metal base and the waves interfere among themselves before transmitted back into colors. (Figure 2.9 and Figure 2.7) [76, 77]

According to the optical theory, the first hypothesis applied for our film of CCC is that because literature works stated that the film contain metal oxides, the CCC film can act itself as dielectric host filled with impurities that can change propagation of light and yet change the final color of the film. Also under the CCC film, there is the ‘bulk metal’ film that mainly contains zinc atoms packed together as if it is a chunk of zinc bulk element. Then we expected to get the ‘molecular layer reflection’ when the light propagated from CCC and hit the bulk-metal film. Therefore, if the light cannot penetrate through the zinc film, the thickness of zinc should not affect directly on propagation. However, the investigation on how zinc thickness has effect on the color of CCC is still needed as well as the roughness on zinc surface that might affect the formation of the CCC layers. One possible mechanism on high-roughness zinc layer on the formation of the CCC is that it has more surface area to react with the solution. Thereby, the CCC might form easier on high roughness zinc layer and eventually CCC dielectric condition changed, appearance is also changed

Chapter 3
Experimental Procedure

The experimental had been divided into parts. Fabrication steps contain repeating samples to affirm the information obtained from the fabricated set of samples. The recorded data had been analyzed systematically through the averaging steps of particular areas.

3.1 Fabrication

Surface cleaning of product is needed in order to help enhance addicting ability of coating and degrease dirt before coating. General steps of surface cleaning are showed schematically in Figure 3.1.

Detergent cleaning or soak cleaning is usually applied at the first step to degrease the dirt and oils from samples. Following by alkaline cleaning with electricity and elevated temperature helps to extract some remaining unwanted impurities on surface. Acid etching or acid dip is normally applied to remove undesired oxides from surface as well as some intermetallic particles [6]. After the overall cleaning procedure, the sample will undergo the coating steps which are electroplated zinc with a second layer of black Chromate conversion coating.

3.1.1 Sample preparations

The test samples chosen for the investigation were prepared from mild steel with a dimension of 6.0 x 10.0 x 0.3 cm. Table 2.1 shows surfaces cleaning steps.

3.1.2 Electroplated Zinc

A standard-type Hull cell (Kolour setup) with 267 ml volume-under-immersion was employed to fabricate the electroplated zinc samples.

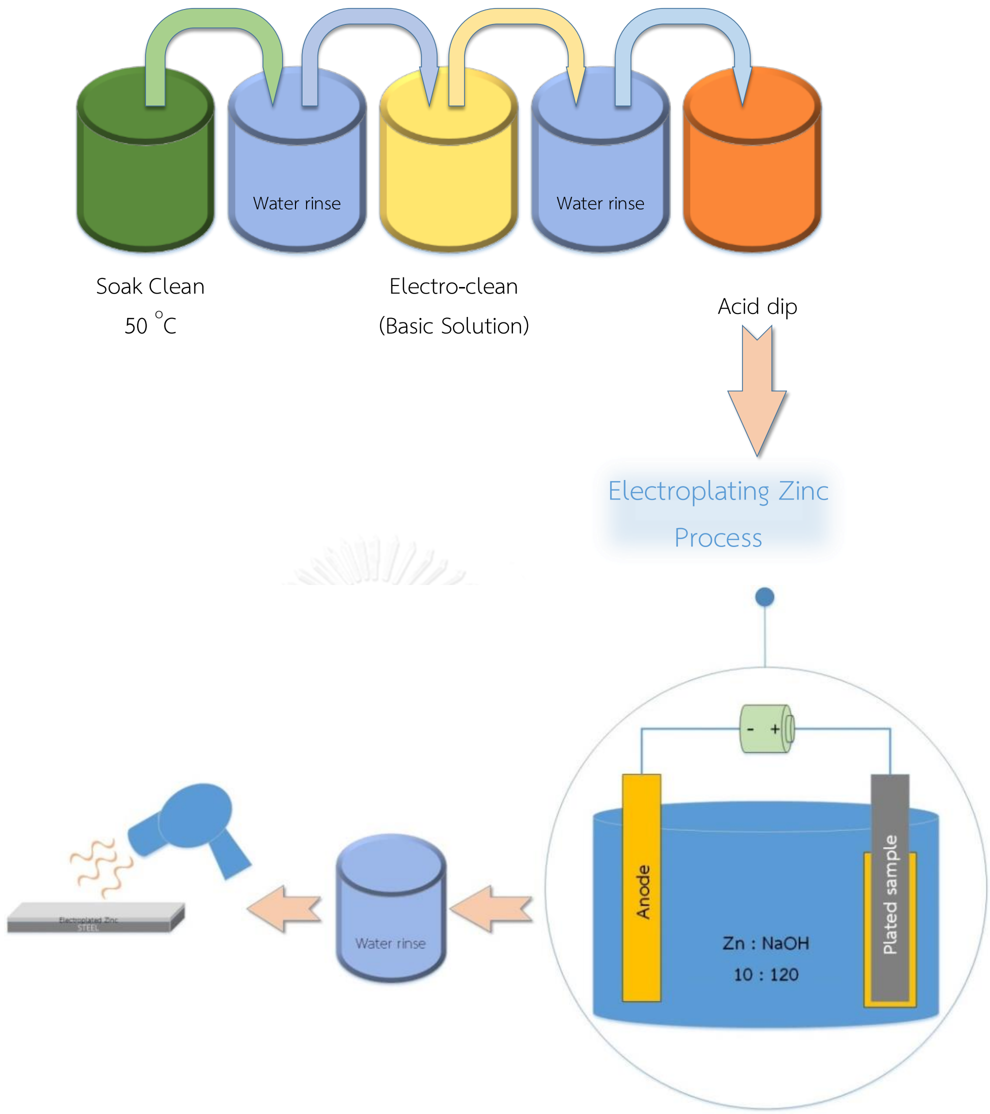


Figure 3.1 Surface cleaning steps and electroplated zinc process flow

With its unique trapezoidal shape, the Hull cell allowed deposition with a variation of imposed local current densities along the surface of each sample. The plating solution was of noncyanide-alkaline type containing Zn, NaOH, and a small amount of leveling additives. The ratio of Zn : NaOH was controlled at 10:120 by weight. The electrodeposition was carried out for 10 minute at room temperature, using the DC current of 1.0 A (Sanrex DC electrical source).

This provided local current densities ranging from 0.05 A/dm^2 to 5.0 A/dm^2 for each sample. After electroplating, the samples were dried at 60^o C until no water stain was found. Figure 2.3

3.1.3 Chromate conversion Coating

The electroplated zinc samples were then immersed in 1% Nitric acid to clean off any residuals from the plating solutions and organic additives, and immediately dipped into a black chromate conversion bath for 45 seconds. The chromating solution was of commercial type (ES Coat Black SOP by OKUNO) and was controlled at 30^{o}C+/- 1 ^{o}C with pH of 2.1 +/- 0.01. Such the strong acidic condition would help etching the zinc surface and enhance the chromating process [19] A newly-prepared solution of 3,500 ml was used for each sample. After chromating, the samples were water-rinsed and dried-off at 60 ^{o}C. Five main chemical compositions had been listed in

Table 3.1

Table 3.1 Main controlled chemical composition in CCC solution

Zinc	Chromium	Cobalt	Iron	Copper
5-10 g/L	2-3 g/L	0.8-1.4 g/L	0-60 mg/L	0-5 mg/L

Three fabricated samples (A, B, and C) are repeated with 1 A input, immersed for 10 minutes. Then instantly underwent black CCC coating. Two different batches of fabrication had been done in order to confirm the relationship we found in the first batch. The second batch of D, E and F had been fabricated with the same electricity input and immersion time but before undergo the CCC coating, it had been baked to eliminate hydrogen gas in zinc layer for 30 minutes at 200 degree Celsius then undergo the CCC coating. The last batch is X, Y and Z, which are different in immersion time. 1 A of input of electricity is still controlled but provide longer immersion time (creating thicker zinc layer) at 30 minutes. After electroplating they had been coating with black CCC without hydrogen elimination baking. Three conditions of the mentioned samples had been investigated by instruments but the first condition of 1 A- 10minute A-B-C is the main target of this work's scope. The other two conditions had been fabricated and characterized in order to give a guideline to further work.

Table 3.2 Fabricated samples with techniques of investigations. The characterization techniques with marks shows the samples had been investigated by that instrument.

Inspections		Visual	Colorimeter	spectrometer	SEM		FE-SEM		Confocal OM	XRF
					image	EDS	image	EDS		
1A	A	√	√	√	√	√	√	√	√	√
10mins	B	√	√	√	-	-	-	-	-	√
Unbaked	C	√	√	√	-	-	-	-	-	√
1A	D	√	-	√	-	-	-	-	√	-
10mins	E	√	-	√	-	-	-	-	-	-
Baked	F	√	-	√	-	-	-	-	-	-
1A	X	√	-	√	-	-	-	-	-	√
30mins	Y	√	-	√	-	-	-	-	-	√
Unbaked	Z	√	-	√	-	-	-	-	-	√

3.2 Characterizations

The Inspection of the result had been categorized in two parts, the optical and microstructure properties. In optical part, visual inspection and distinction of shades through instrument had both been applied in order to relate two data received from both sides of perceptions. The data collected from instruments had been repeatedly recorded three times. Each time at each condition had been done in three area controlled by the automated controller. (Repeating collection of data had been showed in Figure 3.2)

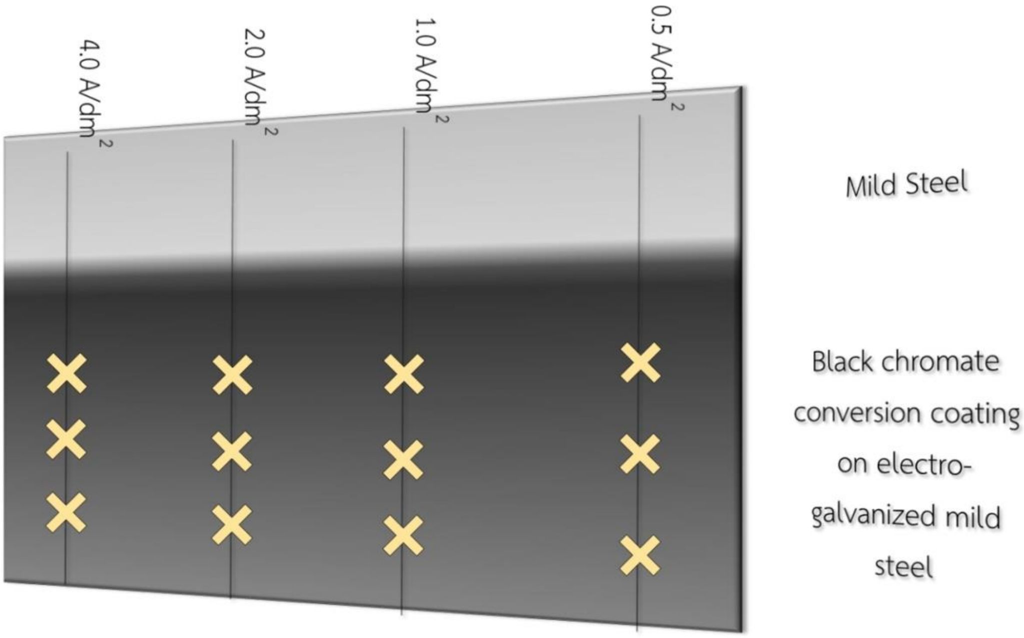


Figure 3.2 Average data at each current density had been recorded through three different area marked in the picture operated by automated controller of sample holder.

3.2.1 Optical characterization

Visual Inspection and colorimeter

The distinction of the color appearance between areas of low current densities and high current densities was characterized with visual inspection and colorimeter (Minolta CR-200). The colorimeter is the instrument normally used in the industrial scale to determine how much the color or appearance of the area deviates from the desired color. The instrument consists of a light source that applies light in a visible range onto a sample's surface, and a detector that retrieves the optical data and converts it to three standard indices.

Colorimeter is the instrument used to identify the amount of light absorption by the testing samples. Two major types of colorimeter are color densitometer and color photometer. The difference is that the first type can identify density of specific primary colors of interest while the later type translates the transmittance and reflectance of overall visible wavelengths of the sample into numbers. The colorimeter used in characterization in this work is the photometer type. This colorimeter can also be called as spectrophotometer which works similar way of CCD spectrometer applied in the coming up characterization of this study. The recorded reflected light intensity will be captured and grouped together in colorimeter and transform the data into three figure of merits; L, a and b. Most colorimeter works in the similar instruction. The incident light will be passed on the sample specimen. Reflections after the absorption of the sample property will be captured out from the surface. It is normally used to compare the desired sample color with the fabricated sample. In another words, it can also use to record the comparing shades of colors. From their small and portable size, many industries used the spectrometer to identify the thorough color of their products. It is claimed in Sugiura's work that value on metallic coating should be lower than 28 to produce black color [66].

Optical spectrometry

Compact CCD Spectrometer (Thorlabs CCS200) is applicable for wavelength range of 200-1000 nm. The instrument was connected to the detector with lens that receives the reflected light from the samples. The light source at visible range of LED source was set up with Fiber-coupled high-power LED (Thorlabs MCWHF) as a cold white light source. The setup is shown in Figure 3.4

The four selected points that were measured with CCD Spectrometer were the areas imposed by electroplating current density of 0.5 A/dm^2, 1.0 A/dm^2, 2.0 A/dm^2 and 4.0 A/dm^2 which are shown in diagrams of Figure 1.2. Four current densities measurements on each sample on four fabricated samples had been repeatedly observed to identify the optical properties in all four specimens which have the same controlled condition of processing.

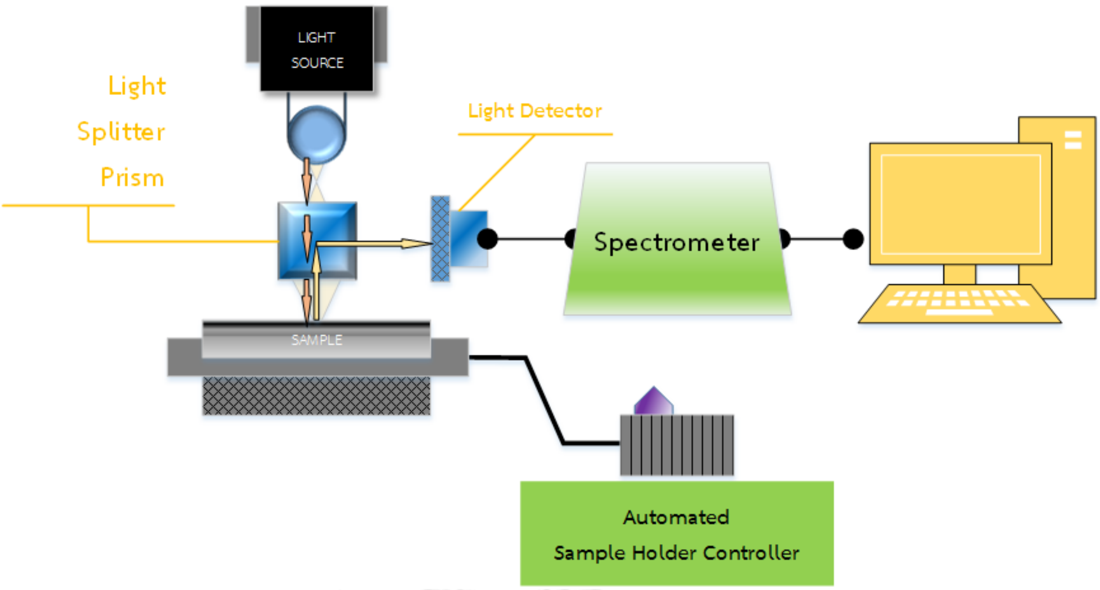


Figure 3.3 Spectrometer set up flow chart

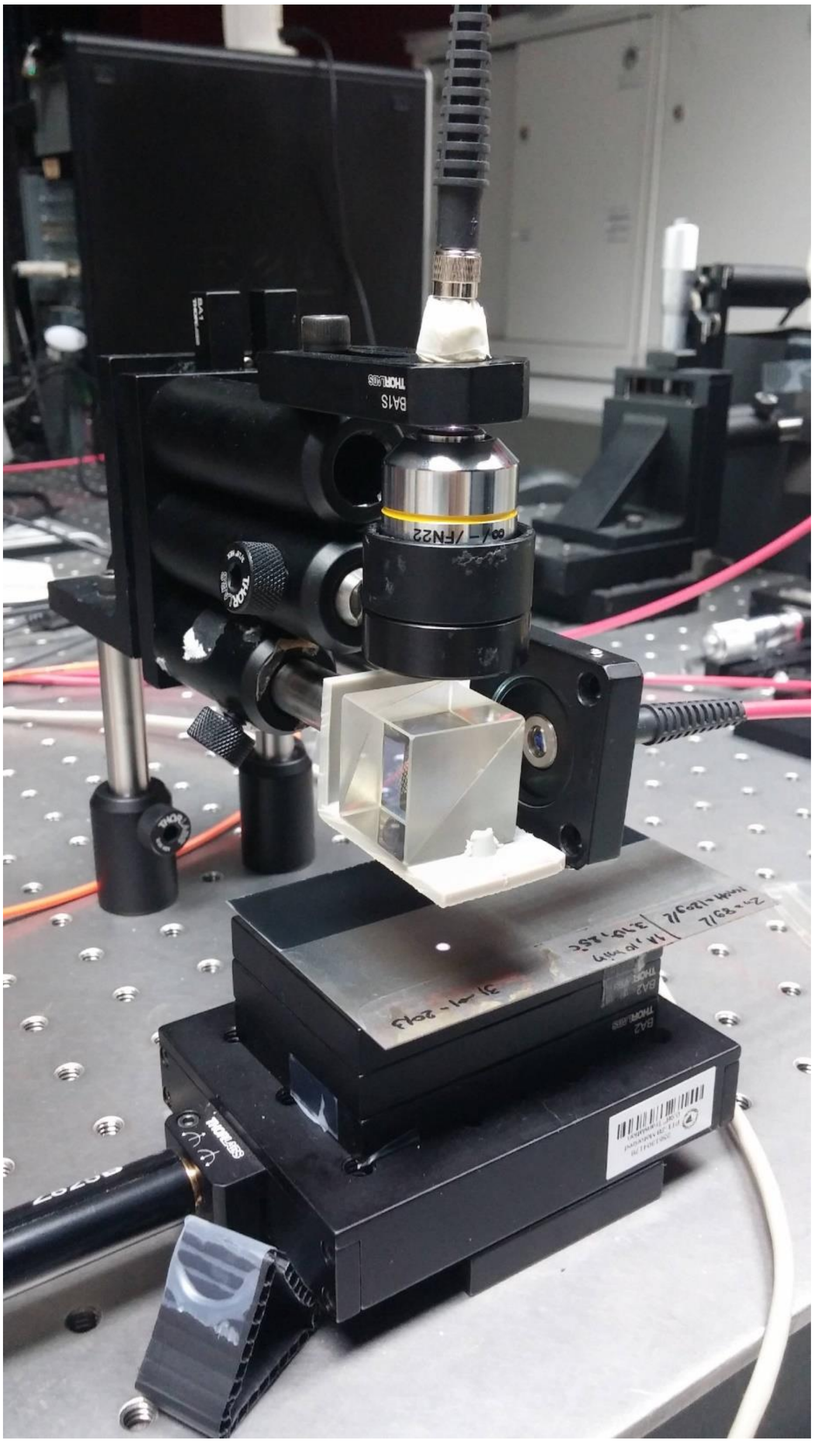


Figure 3.4 Alignment of sample below CCD spectrometer using white light source on top of the setup focused by lens with prism to reflect data back to detector

3.2.2 Film properties

3.2.2.1 Surface roughness

Roughness of the surface of each sample was observed through a confocal optical microscope (Olympus LEXT OLS4100). Due to the instrument's high resolution in the z-axis, the roughness was measured in terms of R_a or average roughness of the area. Four sets of average roughness data were collected from each sample to achieve statistically accuracy

3.2.2.2 Thickness

The thickness of the coating layers was characterized from optical micrographs obtained from a Field-Emission Scanning Electron Microscope (FE-SEM, Hitachi 8030). Energy-dispersive X-ray Spectroscopy (EDS) was employed to identify the phases in the coating layers.

3.2.2.3 Ratio of Chromium to Zinc

To obtain amount of chromium content contained within the film, one non-destructive approach is to use X-Ray Fluorescent to measure the ratio between Chromium and Zinc. Fischerscope X-ray XUV 773 had been utilized in order to get the mentioned records.

Chapter 4
Results and Discussion

As mentioned in earlier chapters, the appearance of final layer can cause from the very beginning processing parameters from electroplating zinc. In this work, analyzing the output data from characterization methods had been done under the construction of black box way of thoughts. Since it is very limited understanding of how light reacts within both layers, this work takes the zinc ad CCC layer as black box. The input of cold white light ranged from 450 - 750 nm had been used. At four different current densities, Zinc thickness and % of chromium per % zinc had been analyzed and compared in order to obtain relative dependent parameters from the experiments. Then the final analyzing of how much different in terms of photonic data had been done through averaging % reflectance of the transmitted light.

4.1 Optical results

As mentioned in Chapter 3, three different batch of sample had been fabricated to see how color changes with zinc condition changes. In this discussion, the first batch is our main scope of studying. Though the other two had been compared I some investigations. In short, first batch is 10-minute immersion with no further baking, second batch is 10-minute immersion with baking before CCC, and last batch is the batch where 30-minute immersion had done with no baking.

4.1.1 Color Appearance

The test samples from three batches were succesfully prepared with a smooth and uniform surface, using the Hull cell deposition setup. From visual inspections, the samples from three batches exhibits generally black color, but with different shades along the surface. Comparing between each batch, the first batch has the locations where black color shade is the darkest among other region. At the locations where high current densities were imposed (e.g., 4 A/dm^2), the surface appears to be darker than the areas where the lower current densities were applied (e.g., 0.5 A/dm^2). The other regions appear to be in almost a greenish tone. These results confirm that current density does influence color appearance of CCC coatings in all batch. Interestingly, last batch of X, Y and Z has the darkest black by visual inspection among other 6 samples, A, B, C, D, E and F.

The use of colorimeter provided the indices L, a and b, where L corresponds to the level of black/white tones, with a lower value refers to a higher degree of blackness. The results of the measurements from the colorimeter, illustrated in Table 2, are generally in agreement to the visual observation in that the darker shades of coating surface are observed at the high-current regions, and vice versa. The L values obtained from different areas however cannot state much about how different the color in each area deviate from other areas.

Table 4.1 Average L Value from colorimeter measurements at selected current density areas

Current Density	Average L value	Standard Deviation
4.0 A/dm2	22.47	0.40327
2.0 A/dm2	24.63	0.61119
1.0 A/dm2	25.64	0.62059
0.5 A/dm2	24.73	0.56739

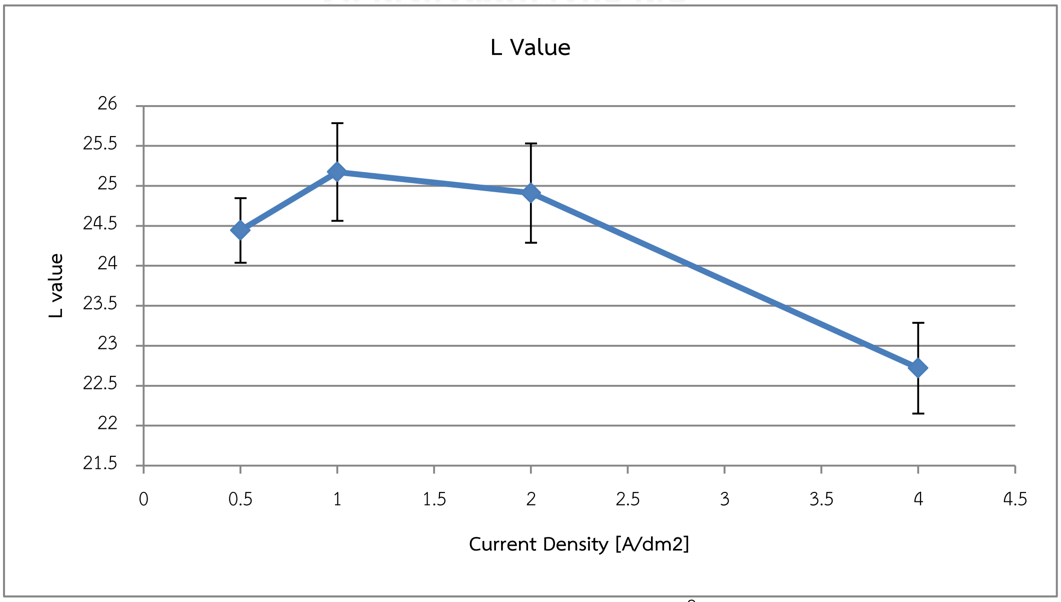


Table 4.2 L Value of Sample A shows that at 4 A/dm^2 has the lowest L Value but cannot specify the difference between the other three current densities

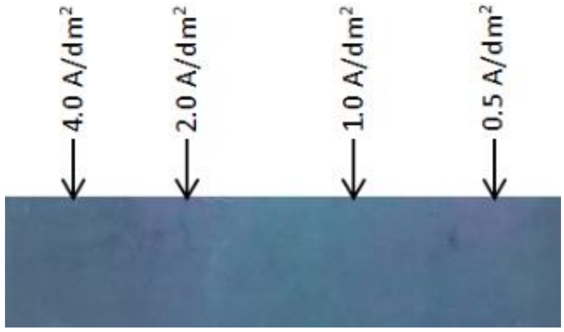


Figure 4.2 Color apperance was investigated at four points of interests on the surface of the specimens fabricated from the Hull cell setup

Figure 4.1 Model of dielectric host filled with impurities (black layer)

4.1.2 Reflectance

To better quantify and understand the formation of color appearance, a CCD spectrometer was employed to measure spectrums of the reflectance of light imposed to the samples' surfaces. Figure 4.3 exemplifies the reflectance spectrums as obtained from the CCD spectrometer. Flat and low reflection means that the surface exhibits optically black appearance.

The bare steel without coating had been used as our reference. To receive precise data, deduction of background spectrum is needed. Every measurement had been calibrated through reference and background deduction to receive the data from transmission of the film layer. The origin of the optical profiles in reflectance-wavelength graphs can be explained by a dielectric model, whereby selective transmission occurs as incident light passes through a dielectric layer that is filled with impurities. Once it reaches the optically bulk metal layer, it reflects back to a dielectric film and then propagates to the detector, as schematically shown in Figure 4.1

Three black CCC coated samples were undergone the measurement. Similar trending of the optical data was received. The high current density, 4.0 A/dm^2, exhibits the most flat and low percentage of reflection. All of the samples also exhibit the high reflection along the green range of 550 nm wavelength. Matching the visual observation with optical measurement through CCD spectrometer shows the similar outcome. The film colors are black with greenish reflection in three regions, 0.5, 1.0 and 2.0 A/dm^2.

While, as mentioned earlier, the outcome from L value of colorimeter cannot state much about color difference of four interested regions. And the visual inspection alone cannot give actual figure of color on the surface. Therefore we introduced the use of CCD Spectrometer to navigate to the relation between color we detect by visual and virtual optical data.

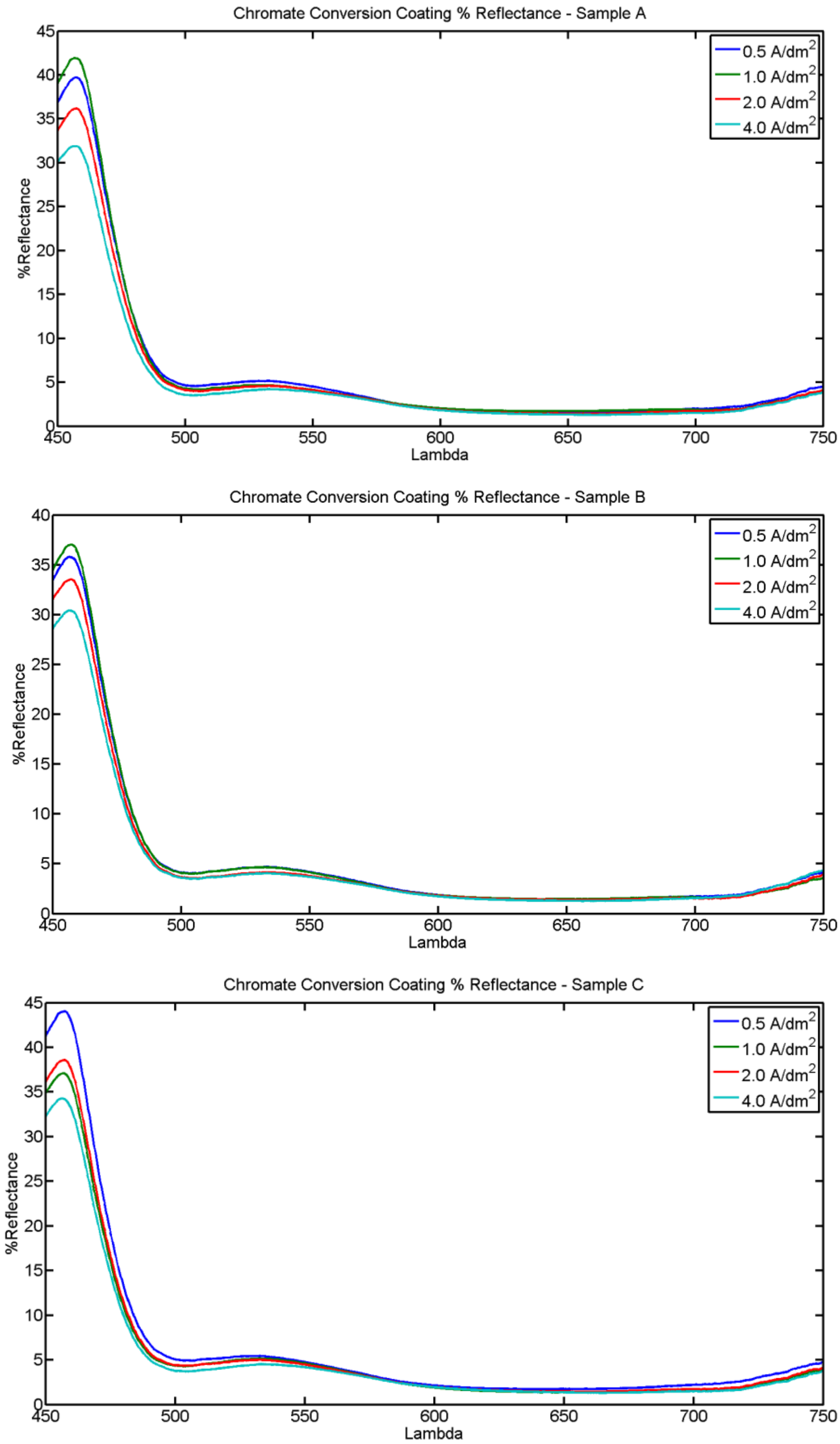


Figure 4.3 Reflectance of three repeating 1.0-Ampere-10-minute electroplated in on steel with back chromate conversion coating as the second layer.

The received data of optical spectrum had also been calculated in terms of Red, Green and Blue visible wavelengths in order to create actual color from the received data and compare to other characterization. The calculation had been done through averaging overall reflectance with specific range of Red, Green, and Blue. (Details had been shown in appendix)

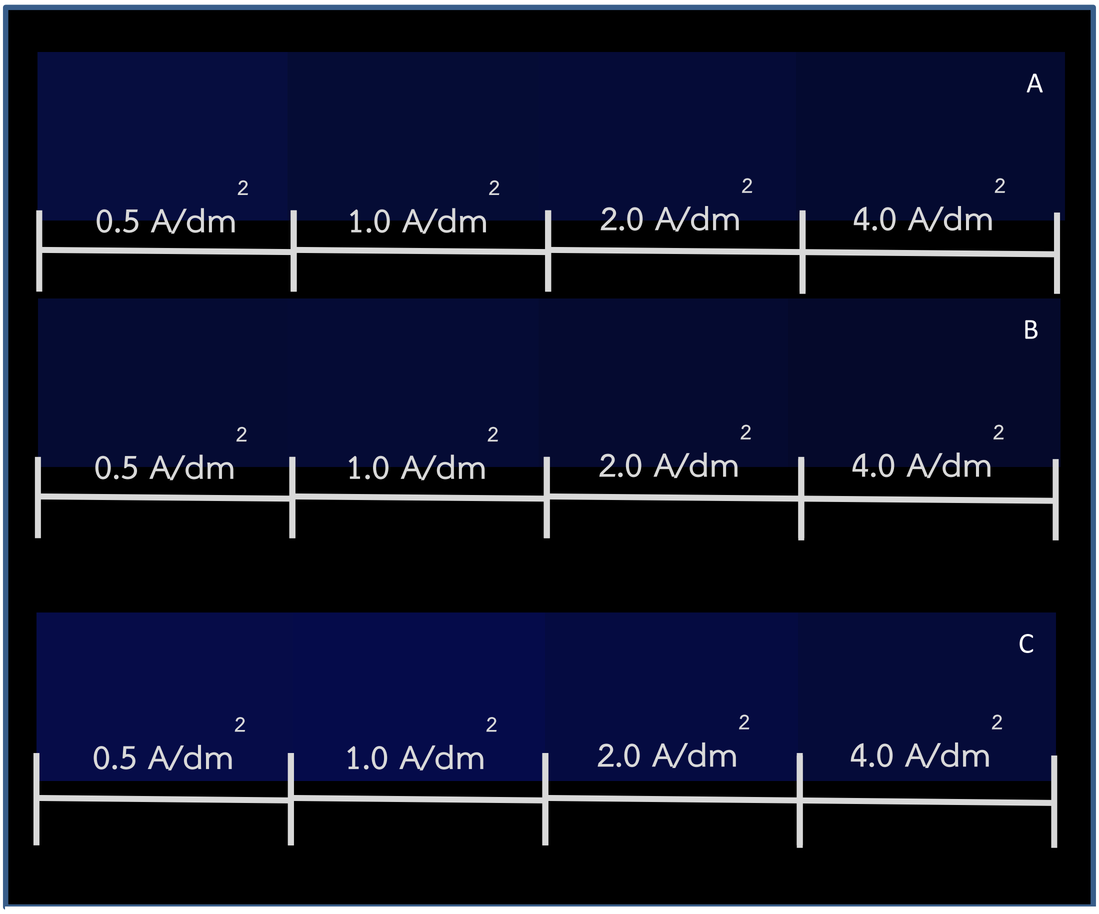


Figure 4.4 RGB interpretation from reflectance recorded from spectrometer shows highest blackness at high current density in all three fabricated samples.

From the average data, rounding up number after multiplication to 255 will result with numbers of RGB. Filling in the numbers result in these following shades of blackness is shown in Figure 4.4.

The colors confirmed that the darkness of black at 4.0 A/dm^2 is highest in comparison with 0.5 A/dm^2. Shades of each area are shown in Figure 4.4.

4.1.3 Average reflectance

Providing figure of merit or point of reference to the actual application in production line, rather than comparing the color with eyes, optical data received from spectrometer can give a sense of average reflectance in the range of 450-750 nm. Comparing three repeating samples A, B and C, the blackest areas are all at 4.0 A/dm^2. The average reflectances of three samples at high current density are 5.058%, 4.661% and 4.800%. Visualized by inspector from industry, all samples contain desired black for industry in 4.0 A/dm^2. Therefore, it could be suggested that for this condition of 10-minute plating time with unbaked condition, the desire black color can be obtain if it is at least 5.058% in reflectance.

Acquiring the figure of merit similar to L value in colorimeter is also another obstacle from academic wise to industrial wise. One possible way to sum up the received data is to convert the frequency (or wavelength) into RGB value (Red, Green, and Blue). To change the coordinate from frequency VS reflectance into RGB VS reflectance, it needs the understanding of the nature of Red, Green and Blue. However changing coordinates is out-of-scoped in this study. Thus the averaging done in this work is to sum the percentage of reflectance at each wavelength together and divide that summation with number of data collected. The result will show the average reflectance that the collected wavelengths behave.

As mentioned earlier, the 10-minute is the scope to see relation of black color and the current densities from electroplating zinc. Still, guiding fabrication had been investigated in order to confirm that other processing parameters from zinc plating can affect the color of CCC black coating as well. The baking and more immersion time had been investigated by visual and CCD Spectrometer.

Introduction to the actual conditions in industrial production line had also been fabricated. The condition is that the controlled input of immersion time during electroplating zinc should be 30 minutes to produce roughly 10 microns thickness of zinc layer before undergoing the CCC process. Three repeating samples (X, Y, Z) had been produced to replicate the conditions of processing and confirm the results. From visual inspection, the difference of blackness between 2.0 and 4.0 A/dm^2 are not distinctively different as well as the comparison between 0.5 and 1.0 A/dm^2. This can be confirmed by optical data from Spectrometer that the reflectance at 4.0 and 2.0 are similar. However the 0.5 and 1.0 have distinct difference that eye detection cannot distinguish.

The difference of collected data from three batches could be the effect from the theory in Figure 4.1 that the CCC film is dielectric host filled with impurities. The changing of processing parameters from zinc can affect the ability of dielectric film formation or affect the impurities in the CCC film. This causes color or shades of blackness change.

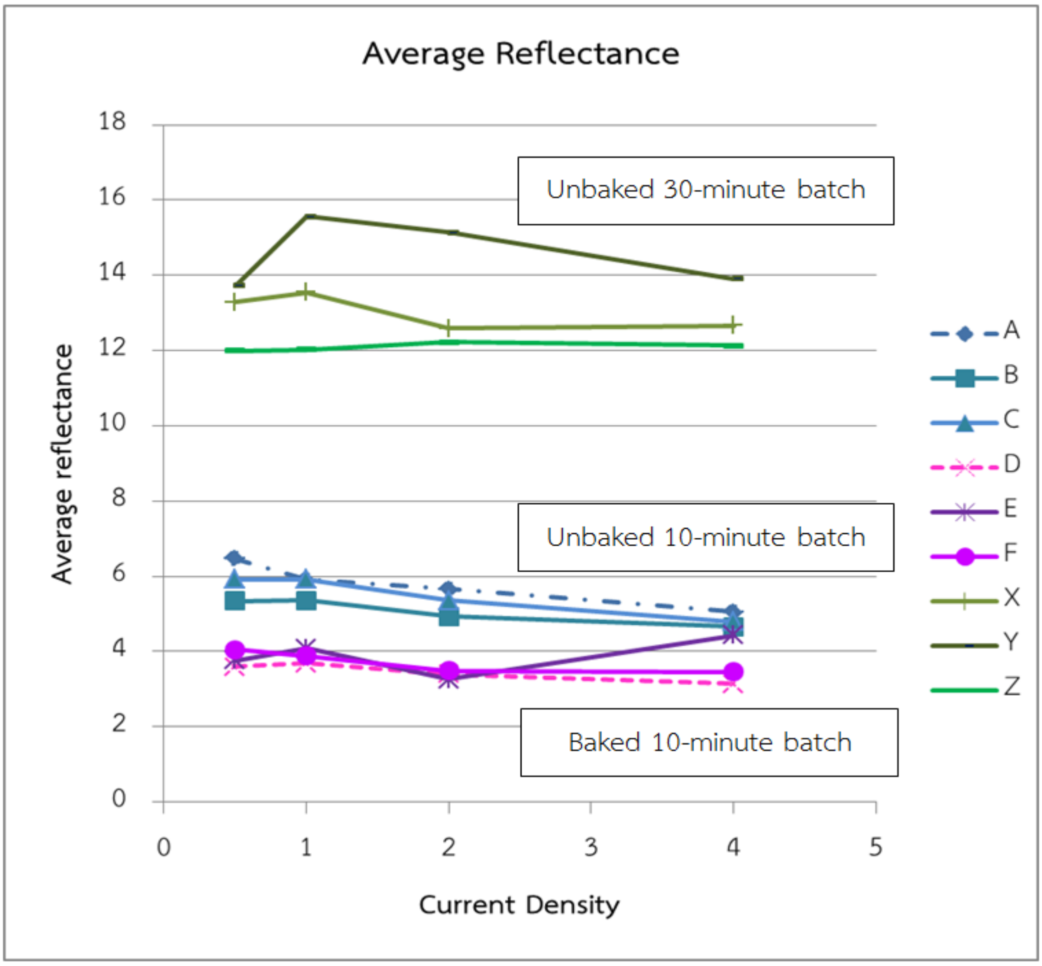


Figure 4.5 average reflectance of both 10-minute (sample A, B and C) and 30-minute (sample D, E and F) samples at each current density

4.2 Microstructure

4.2.1 Roughness

Figure 4.7 (Top) presents the surface morphology of the as-deposited specimens in different areas, namely those being imposed by current densities of 0.5, 2, and 4 A/dm^2. (Sample A) Using the confocal OM, the average roughness (R_a) of the surface can be measured.

Comparing the R_a values of the as-deposited and as-passivated specimens at different areas along the samples' surface, it can be observed that surface roughness measured at different regions are comparable. This should be mainly attributed to the effectiveness of the leveling additives employed in the electroplating bath. Furthermore, it is found that surface roughness is slightly reduced following the process of conversion coating.

Roughness from confocal optical microscope shows similar in three current densities. However, because the method of averaging R_a in confocal optical microscope is summation of minimum and maximum peaks of surface and average. This method of averaging can mislead the understanding because high surface area with high peaks can also exhibit the similar R_a value to the low surface area with small peaks as explained in Figure 4.6

. Thereby the R_a Value alone from confocal area cannot conclude that the low current density and high current density are similar in surface area or not.

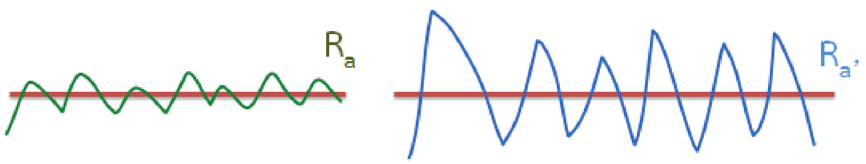


Figure 4.6 (Left) Low surface area and (Right) high surface area are having the similar R_a Value (R_a=$R_{a'}$)

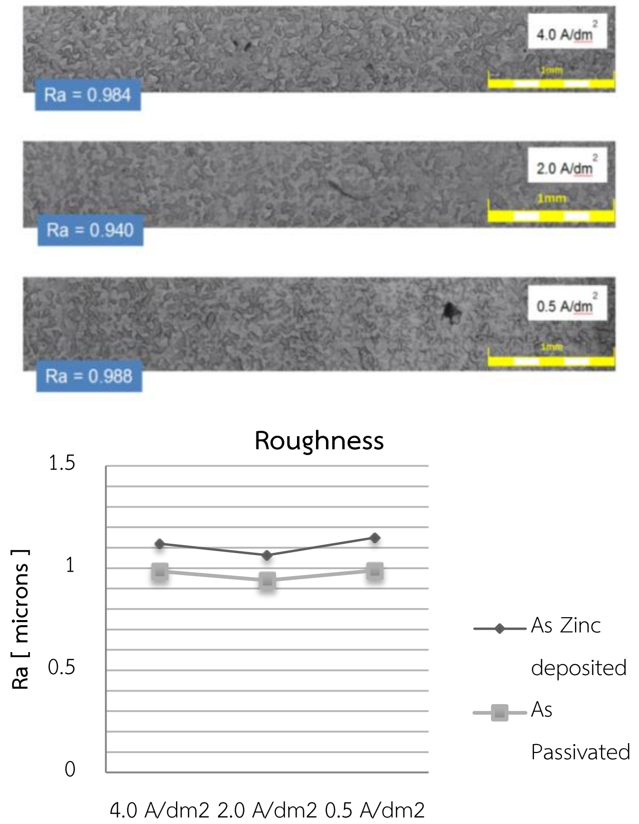


Figure 4.7 A comparison of average roughness of zinc layer and chromate conversion layer (sample A)

4.2.1 Thickness

Figure 4.8 shows the FE-SEM cross-sectional micrographs of the specimens at different current-density regions. While the zinc layer and the steel substrate can be viewed clearly from the micrographs, the thin CCC layers cannot be detected clearly. However, using the EDS-SEM, chromium can be detected on the top surface of the specimens, signifying that the CCC layer is present (Figure 8). From the micrographs, it is determined that the average thickness of the zinc layer is 0.6, 1.4, and 1.5 microns for the areas imposed with the local current density of 0.5, 1.0, and 4.0 A/dm^2, respectively.

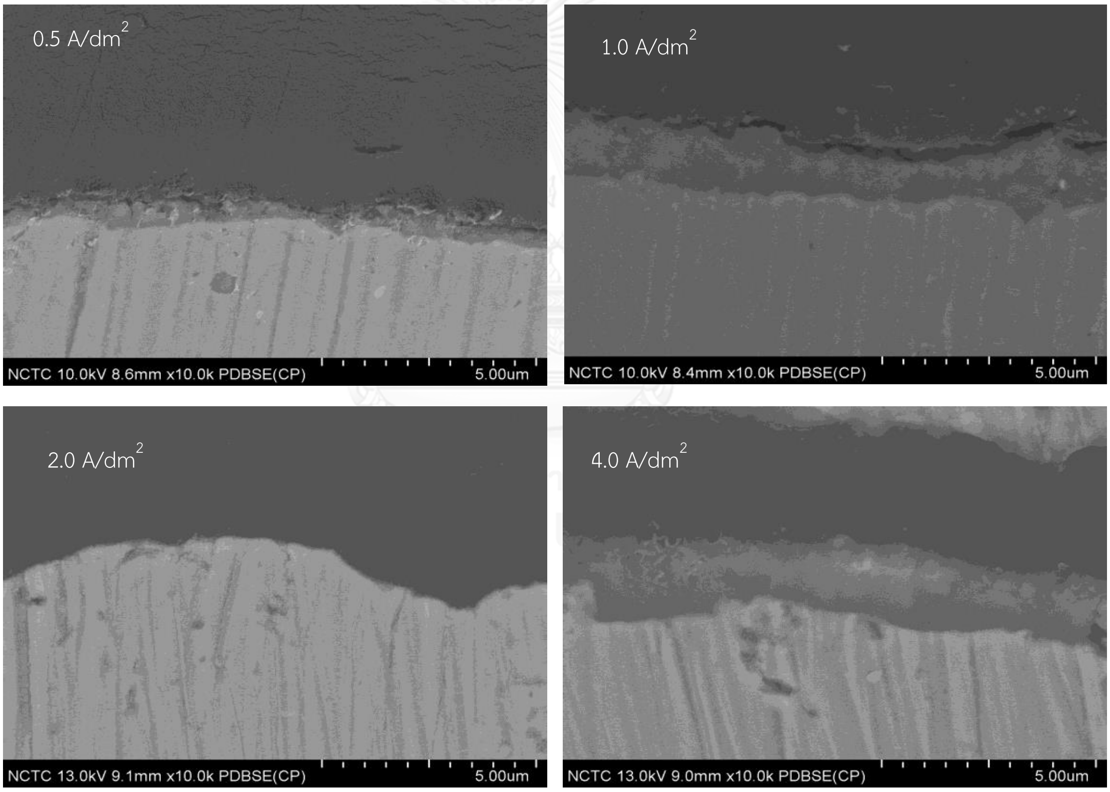


Figure 4.8 FE-SEM cross-sectional images of specimens at four different areas, which were imposed by different current densities.

4.2.2 Ratio of Chromium to Zinc

As mentioned earlier that the CCC layer had direct effect toward how light propagates. From optical theory implementing within this work, thicker zinc layer should not affect how light propagate and eventually not affect the color of product, as the light will bounce back into dielectric layer immediately after hitting the bulk metal layer of zinc. And we controlled to have similar roughness in all areas; the roughness should not be the cause of color difference. While the thicker layer of this dielectric host cause direct effect to color and appearance.

Therefore one possible reason why colors at different current densities are not similar could be the effect of content of chemical composition within the layers. Since the dielectric host filled with impurities that can cause colors, chromium is the major content in the CCC layers; investigating % chromium to % zinc should help understand the effect from major elements towards color. XRF had been used to investigate this effect.

The results from X-ray Fluorescent show the difference of ratio between %Cr and %Zn at particular current densities. Figure 4.9 represent the decreasing trend of %Cr per %Zn with increasing current density area. The result can hint the fact that this ratio caused by the processing parameter from zinc even though the roughness of underlying zinc layer at all current density areas are similar, the amount of zinc converted into chromate layer is not the same as roughness. This might cause by other dependent parameters such as thickness or structures. The higher blackness at higher current density area have lower ratio between Chromium and zinc.

Comparing the 10-minute samples with 30-minute ones also shown trend of decaying ratio of Chromium to Zinc from low current density to high current density shown in Figure 4.10. The results also reveal the fact that higher immersion time provides lower ratio of Chromium to Zinc. Although three repeating samples exhibit similarly in ratio wise, the XRF investigation alone is not enough to confirm the dependent parameters behind colors. Higher immersion time (30-minute) can cause lower ratio because zinc thickness is increased. Interpreting records of Cr/Zn ratio also need confirmation from chromium content alone in order to affirm that higher content of chromium in film can cause shade different in black.

As mentioned, these records can as well leads to further works to study that the current density of zinc layer has effect to the dependent parameters such as thickness and structure.

In 30-minutes case, the thickness of zinc might be high enough to yield saturation point of film formation in conversion film. The CCC film itself will act as a barrier to conversion reactions. Therefore once it is thick enough to reach its saturation thickness, the film will not grow thicker. This understanding can be implement to the result from 30-minute samples that has somewhat linear decreasing in ratio of Cr/Zn. Once the chromium layer cannot grow more, the ratio should be linearly decreasing.

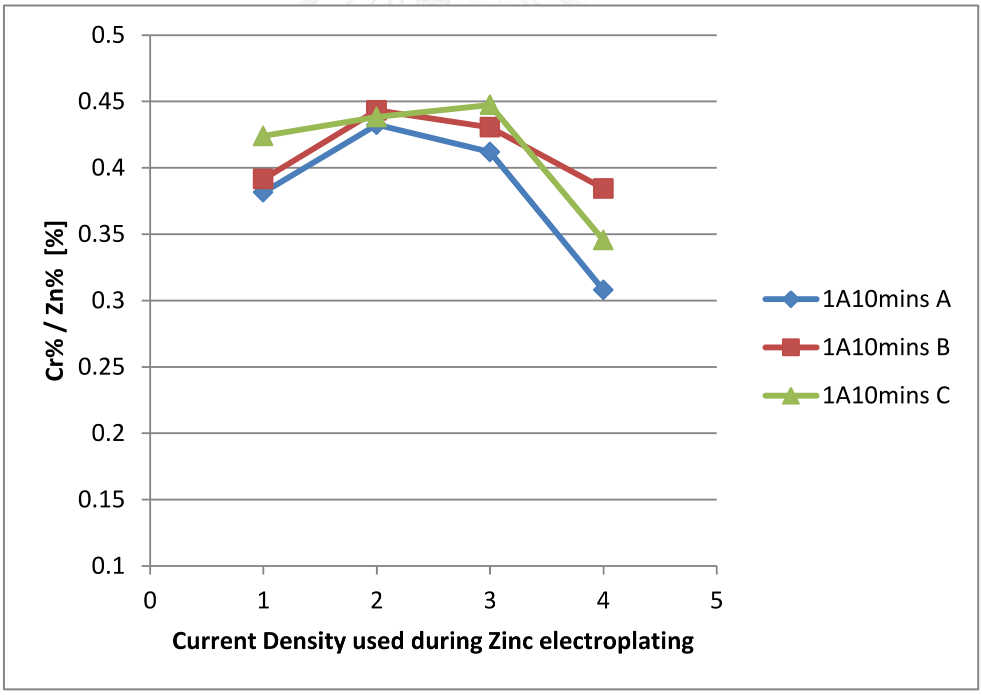


Figure 4.9 Ratio of % Cr to % Zn from XRF at each current density from 10-minute electroplated zinc with Black CCC layer

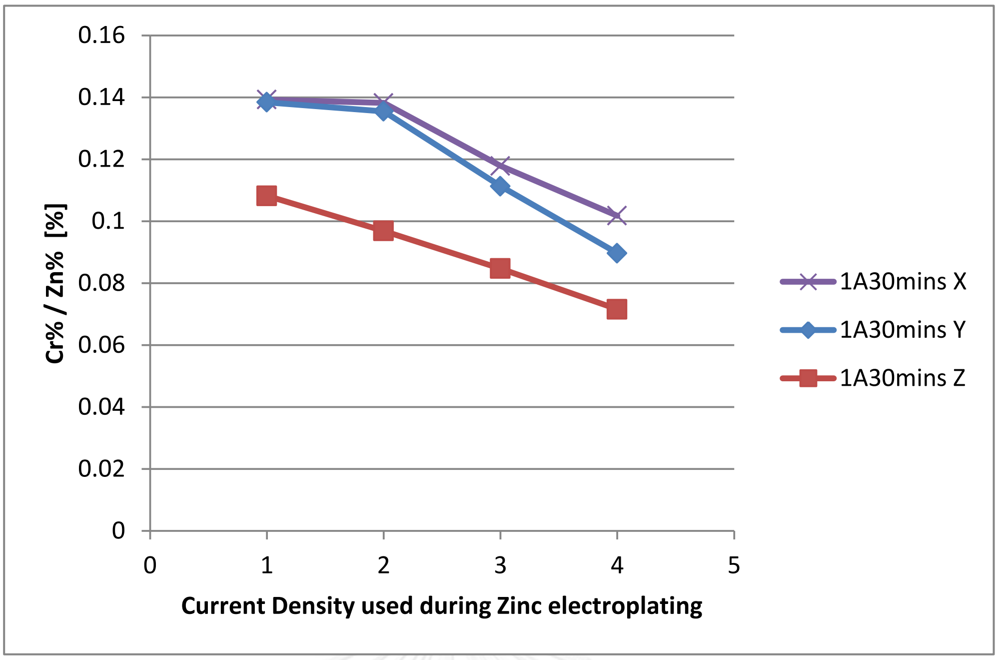


Figure 4.10 Ratio of chromium to zinc from XRF in three repeating samples produced with 30-minute process in electroplating zinc

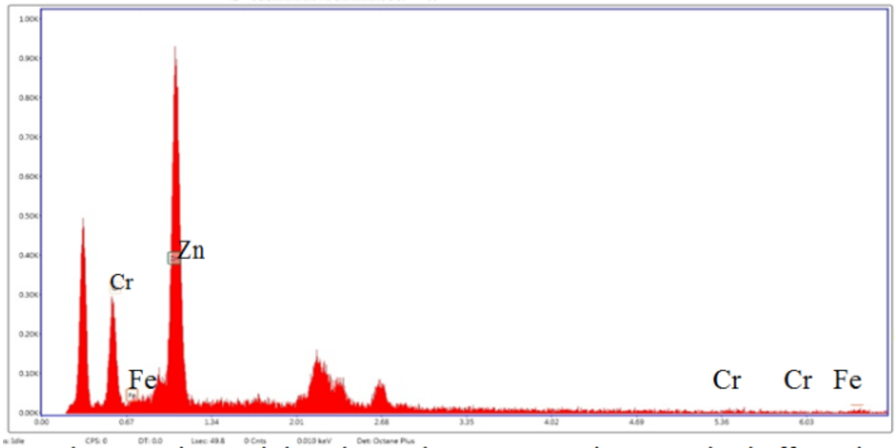


Figure 4.11 EDS-SEM shows the Cr peak on the surface of cross-sectioned samples (Sample A)

4.3 Relations of plating processing parameters and color appearance

From the results, it is observed that electroplating current density indeed affects the final color appearance of CCC coatings. The high current densities generally lead to the optically darker shades of color. This may be rationalized by understanding the effects of current density that would have on the zinc layer and in turn on the formation of the chromate conversion coatings. From the analysis, it is evident that the roughness of zinc deposits is approximately equivalent at all regions in the samples, so the effect of this parameter could be insignificant. As for thickness, clearly increasing current density leads to thicker zinc deposits, in agreement with Faraday's law. The low current densities, on the other hand, may attract some carbon residue contaminations into the deposits. These influences could subsequently affect the formation of the CCC coatings and hence the characteristics of the films, especially thickness and chemical composition, which control optical properties of the oxide dielectric. The investigation of ratio between Chromium and Zinc content, the major element in both films, shows that decreasing ratio causes more blackness. This can result from the fact that higher thickness of zinc carries dependent parameters such as structure that cause different surface reaction during conversion. In case that the ratio started to decrease linearly, it can imply that the saturation point of CCC film had reached.

Further study can affirm that not only the current densities that can affect color appearance of the CCC films, but also other processing parameters such as immersion time in plating bath, post-treatment before undergoing CCC process. These studies show that the CCC film formation should be controlled with both processing parameters of CCC bath and plating bath.

Chapter 5

Conclusion

Hull-cell fabricated samples had been done within the controlled processing parameters in order to provide all-in-one set up and very only particular interested parameter which in this case is current density used in electroplated zinc step. The outcomes of the samples are satisfying. The shading of blackness can be compared with ease. The breakthrough from this work is also included the ability to use Hull-Cell set up to predict the compatibility between zin solution and CCC bath.

The optical data obtained from most instruments and calculations shows that the highest current density at 4.0 A/dm^2 exhibits the most blackness out of other with the least ratio between chromium to zinc. The thickness of each layer cannot be determined through optical image. Comparing three repeating samples A, B and C, the blackest areas are all at 4.0 A/dm^2. The average reflectances of three samples at high current density are 5.058%, 4.661% and 4.800%. Visualized by inspector from industry, all samples contain desired black for industry in 4.0 A/dm^2. Therefore, it could be suggested that for this condition of 10-minute plating time with unbaked condition, the desire black color can be obtain if it is at least 5.058% in reflectance.

5.1 Relations of processing parameters and color appearance

Electrogalvanized specimens with different imposed current densities along their surface were successfully prepared from a Hull cell setup and were subsequently dipped into the black chromating solution to obtain conversion coatings. The colorimeter and the optical CCD spectrometer all indicate that the electroplating current density affects the color appearance of the conversion coatings. Particularly, the high current densities generally lead to optically darker shades of color. It is suggested that current density affects thickness and possibly a contamination level of zinc deposits, and correspondingly influences the formation of chromate films, and thus their color appearance.

Also, current densities is not the only influence to the appearance change of CCC films, also other processing parameters , baking and plating time, from plating conditions that should be controlled and take for granted as well as parameters during CCC coatings.

The microstructural study should concern about roughness,, thickness and composition in dielectric film, CCC. The roughness of based steel should be measured in order to affirm the effect of the virtual roughness. To obtain the nature and character of the zinc film and CCC film, surface area on the film should be one of the interesting points to investigate. While thickness of CCC can be one of the causes of light propagation change and yet leads to shade of color change. While chemical composition can also be one of the causes that directly linked to the impurities that diffract light in dielectric film and causes change of color.

5.2 Contributions

This work can give a distinct distribution towards both academic and industrial. In Academic, The hypothesis of dielectric host with impurities had been introduced to interpret and link the relation of color to the underlying film's processing parameters. While, industrial wise, the hull cell setup had been used to fabricate the CCC on zinc samples and diversify the method of color inspection to use CCD spectrometer to obtain more-detailed optical data.

5.2.1 Experimental procedures

Hull cell is a good alternative to fabricate the sample. However, some further concern of the microstructure is needed. From its fluctuation of the current, exact one-point measurement of microstructure cannot be executed with ease. Average of compiled data is needed to confirm the detection. Thickness measured optically by SEM or FE-SEM are not easy to obtain the information. This technique is good to product samples that will be compared with the preferred reference. Introducing hull cell to fabricate black CCC coating on electroplated zinc steel leads us to the pilot work of the linkage between current density effects to the color. Further work can be done in terms of full-scale production motivated by the relation from this pilot study for instance of comparing the effect of colors by fabricating the sample at only single current density in order to confirm the underlying effect from processing parameter of each type of solution and condition.

5.2.2 Optical implications

Theoretically black in optical science is to obtain the reflection data as flat and low as possible. From the baked products, it had proved that the desired black color in industrial wise sometimes requires not only low in average % of reflection during visible range but also other

5.2.3 Industrial application

This work simulated the controlled conditions based on industrial application through systematic testing of current density effect to appearance of color, emphasizing only on the reflected photonic data from the film.

The underlying processing parameters from electroplating zinc process are essential in concerns of producing desired color or surface appearance of the chromate conversion coating films. One of the parameters that had been showed within this work is the current density during the plating of zinc. The appearance of final color on the surface by visual inspection is the reflection from the incident light that had been traveled within the dielectric host film filled with impurities of metals. Scattering might play role in terms of appearance, but the color exhibit mainly from the light that transmitted back to detectors.

5.3 Further work guidance

1. To determine the microscopic thickness relation to the color through optical imaging, longer time of plating is needed in order to provide thicker zinc layer.
2. To confirm that chromium content had effect towards color, Glow Discharged Sputtering instrument can be used to identify amount of chromium content and zinc content from surface.
3. Possible dependent parameters that should be investigated further are CCC surface structure and thickness.

4. The darker shade of black from visual inspection is not enough to determine optical ability such as thermal absorption. Darker black from the film alone, neglecting the reflected from light source, might be able to store or absorb more energy and used in terms of thermal properties.

REFERENCES

[1] Lin, C.J. and He, J.L., Cavitation erosion behavior of electroless nickel-plating on AISI 1045 steel. Wear, 2005. 259(1–6): p. 154-159.

[2] Tang, P.T., Watanabet, T., Andersen, J.E.T., and Bech-Nielsen, G., Improved corrosion resistance of pulse plated nickel through crystallisation control. Journal of Applied Electrochemistry, 1995. 25(4): p. 347-352.

[3] Pushpavanam, M., Natarajan, S.R., Balakrishnan, K., and Sharma, L.R., Corrosion behaviour of electrodeposited zinc-nickel alloys. Journal of Applied Electrochemistry, 1991. 21(7): p. 642-645.

[4] Kendig, M.W. and Buchheit, R.G., Corrosion Inhibition of Aluminum and Aluminum Alloys by Soluble Chromates, Chromate Coatings, and Chromate-Free Coatings. Corrosion, 2003. 59(5): p. 379-400.

[5] T, C.W.J., *Method of and composition for preventing "white rust" formation*, 1969, US3477882.

[6] Hughes, A.E., Harvey, T.G., Birbilis, N., Kumar, A., and Buchheit, R.G., 7 - Coatings for corrosion prevention based on rare earths, in Rare Earth-Based Corrosion Inhibitors, M. Forsyth and B. Hinton, Editors. 2014, Woodhead Publishing. p. 186-232.

[7] Tomachuk, C.R., Elsner, C.I., Di Sarli, A.R., and Ferraz, O.B., Morphology and corrosion resistance of Cr(III)-based conversion treatments for electrogalvanized steel. Journal of Coatings Technology and Research, 2010. 7(4): p. 493-502.

[8] Dingwerth, B., Trivalent passivates need trivalent post-dips. Surface finishing guidebook, 2011. 109.

[9] Bibber, J., An overview of nonhexavalent chromium conversion coatings—Part II: Zinc. Metal Finishing, 2002. 100(2): p. 98-102.

[10] Zhang, X., van den Bos, C., Sloof, W.G., Hovestad, A., Terryn, H., and de Wit, J.H.W., Comparison of the morphology and corrosion performance of Cr(VI)- and Cr(III)-based conversion coatings on zinc. Surface and Coatings Technology, 2005. 199(1): p. 92-104.

[11] Gigandet, M.P., Faucheu, J., and Tachez, M., Formation of black chromate conversion coatings on pure and zinc alloy electrolytic deposits: role of the main constituents. Surface and Coatings Technology, 1997. 89(3): p. 285-291.

[12] Frąckowiak, E. and Skowroński, J.M., Passivation of zinc in alkaline solution effected by chromates and CrO_3–graphite system. Journal of Power Sources, 1998. 73(2): p. 175-181.

[13] Di Sarli, A.R., Culcasi, J.D., Tomachuk, C.R., Elsner, C.I., Ferreira, J.M., and Costa, I., A conversion layer based on trivalent chromium and cobalt for the corrosion

protection of electrogalvanized steel. Surface & Coatings Technology, 2014. 258: p. 426-436.

[14] Esfahani, S.L., Ranjbar, Z., and Rastegar, S., An electrochemical and mechanical approach to the corrosion resistance of cathodic electrocoatings under combined cyclic and DC polarization conditions. Progress in Organic Coatings, 2014. 77(8): p. 1264-1270.

[15] Campestrini, P., Böhm, S., Schram, T., Terryn, H., and de Wit, J.H.W., Study of the formation of chromate conversion coatings on Alclad 2024 aluminum alloy using spectroscopic ellipsometry. Thin Solid Films, 2002. 410(1–2): p. 76-85.

[16] McColm, T.D. and Evans, J.W., A Modified Hull Cell and its Application to the Electrodeposition of Zinc. Journal of Applied Electrochemistry, 2001. 31(4): p. 411-419.

[17] D. C. H. Nevison, ASM Handbook. ASM International,
Materials Park, Ohio 1987. 9th ed.

[18] Ken Osborne, e.b.J.P., metal protection limited.

[19] Tencer, M., Electrical conductivity of chromate conversion coating on electrodeposited zinc. Applied Surface Science, 2006. 252(23): p. 8229-8234.

[20] G.E.Thompson, U., Manchester, conversion coatings. 1994: p. 9.

[21] Winiarski, J., Masalski, J., and Szczygieł, B., Corrosion resistance of chromium-free conversion coatings deposited on electrogalvanized steel from potassium hexafluorotitanate(IV) containing bath. Surface and Coatings Technology, 2013. 236(0): p. 252-261.

[22] X. Zhang, T.B., A.Hovestad, E.P.M. van Westing, J.H.W. de Wit, Electrochemical Behaviour of Chromate and Phosphate
Conversion Coatings on Zinc.

[23] Li, J., Yao, C., Liu, Y., Li, D., Zhou, B., and Cai, W., The hazardous hexavalent chromium formed on trivalent chromium conversion coating: The origin, influence factors and control measures. Journal of Hazardous Materials, 2012. 221–222(0): p. 56-61.

[24] Diaddario, L.L. and Marzano, M., *Trivalent chromate conversion coating*, 2006, US7029541.

[25] Rosalbino, F., Scavino, G., Mortarino, G., Angelini, E., and Lunazzi, G., EIS study on the corrosion performance of a Cr(III)-based conversion coating on zinc galvanized steel for the automotive industry. Journal of Solid State Electrochemistry, 2011. 15(4): p. 703-709.

[26] Rozovsky, V.S. and Sarmaitis, R.R., Plating and Surface Finishing 68,54,No.10,1981. 1982(16): p. p67-69.

[27] Zaki, N., Trivalent chrome conversion coating for zinc and zinc alloys. Metal Finishing, 2007. 105(10): p. 425-435.

[28] Lee Capper, A.N., AQUEOUS REACTION SOLUTION AND METHOD OF PASSIVATING WORKPIECES HAVING ZINC OR ZINC ALLOY SURFACES AND USE OF A HETEROAROMATIC COMPOUND. Sep. 11, 2012.

[29] *Scratching-resistant and wear-resistant color-coated steel sheet*, 2012, CN101659175.

[30] Tran, L.M., Schriever, M.P., and Jones, J.H., *Low hydrogen embrittlement zinc/nickel plating for high strength steels*, 2011, US8048285.

[31] Suda, A. and Ogino, T., *Composition and method for chromating treatment of metal*, 1992, WO1992003594A1.

[32] Bhatia, P., *Corrosion resistant trivalent chromium phosphated chemical conversion coatings*, 2006, US7018486.

[33] *Novel galvanizing and chrome-free passivating technology*, 2013, CN103014688A.

[34] Bishop, C.V., Thomay, M.J., and Page, B.J., *Black chromium-containing conversion coatings on zinc-nickel and zinc-iron alloys*, 1995, US5415702.

[35] Bradley, J.L.D., *Composition for forming a black, adherent coating on a metal substrate*, 1999, US5931993.

[36] Miyoshi, T., Kubota, T., Sagiyama, M., Sugimoto, Y., and Yamashita, M., *Manufacturing process on chromate-coated lead-containing galvanized steel sheet with anti-black patina property and anti-white rust property*, 2001, US6280535.

[37] Thompson, J.S., *Process of coating*, 1942, US2276353.

[38] Akira, K. and Yuzuru, M., *Conversion coating zinciferous surfaces to resist blackening and white rust*, 1999, WO1999018257A1.

[39] Kuezynski, J., Splittstoesser, K.A., Tofil, T.J., and Vermilyea, P.A., *Methods for Reducing Hexavalent Chromium in Trivalent Chromate Conversion Coatings*, 2009, US20090014094.

[40] Maiquez, J.A.O., *Process for sealing chromate conversion coatings on electrodeposited zinc*, 1993, US5178690.

[41] Reichgott, D.W. and Chen, F., *Method and composition for treatment of galvanized steel*, 1994, US5282905.

[42] Tang, X., Bhatia, P., Parkos, J.J., Lomasney, G.M., and Jaworowski, M., *Stability additive for trivalent chrome conversion coating bath solutions*, 2003, US6648986.

[43] Sabata, A., Douthett, J.A., and Winkle, S.E., *A precoated chromium alloyed steel with good paint adhesion for exhaust applications*, 2006, EP0876849B1.

[44] Sobata, T. and Ushio, A., *Coating type, chromate conversion coating composition*, 1989, EP0322984A2.

[45] Richard, B.K., *Conversion coating solution*, 2003, WO2003083171A1.

[46] Da Fonte, B., *Trivalent chromium passivate solution and process for yellow passivate film*, 1982, US4359346.

[47] Archer, H.L., Powell, W.J., and Menke, J.T., *Method for deposition of steel protective coating*, 2010, US7803428.

[48] Murphy, J.E., *High Temperature Conversion Coating on Steel and Iron Substrates*, 2014, US20140251503.

[49] E, P.W., *Protective coating*, 1962, US3053692.

[50] L, N.I. and A, W.E., *Method of coating zinc surfaces*, 1963, US3097978.

[51] Kulkarni, A.S., Ponkshe, S.R., Kulkarni, J.S., Mahendiran, R., Kulkarni, S.V., Mahajan, S.S., and Bhoite, G.S., *Corrosion resistance passivation formulation and process of preparation thereof*, 2014, US20140017409.

[52] P, H.F., *Method of forming a chromate conversion coating on magnesium*, 1960, US2961358.

[53] C, J.W., *Method of controlling chromate conversion coating baths*, 1964, US3162207.

[54] Otrhalek, J.V. and Gerard, D.R., *Method of forming chromate conversion coatings on aluminum surfaces and the coating formed thereby*, 1985, US4531978.

[55] Kramer, K. and Salet, L., *Composition and processes of a dry-in-place trivalent chromium corrosion-resistant coating for use on metal surfaces*, 2012, US8092617.

[56] Buchheit, R.G., Guan, H., and Laget, V.N., *Corrosion resistant coating with self-healing characteristics*, 2006, US7135075.

[57] Greene, J.L., *Chromium-free or low-chromium metal surface passivation*, 1981, US4298404.

[58] Goodrich, G.D. and Colahan, P.J., *Chrome coating composition*, 2006, US7150923.

[59] Sazanov, Z., Bedrnik, L., Thom, K., and Dingwerth, B., *Treatment solution for producing chrome and cobalt-free black conversion coatings*, 2011, WO2011036058A1.

[60] Crotty, D.E., *Non-peroxide trivalent chromium passivate composition and process*, 1986, US4578122.

[61] Bishop, C.V., *Iridescent chromium coatings and method*, 1995, US5407749.
[62] Terada, H., Fukuda, A., and Oho, Y., *Treatment of galvanized steel*, 1988, US4756805.
[63] Oshima, K., Tanaka, S., Inoue, M., and Yamamoto, T., *Processing solution for forming hexavalent chromium free and corrosion resistant conversion film on zinc or zinc alloy plating layers, hexavalent chromium free and corrosion resistant conversion film, method for forming the same*, 2005, US6858098.
[64] Preikschat, P., Jansen, R., and Hulser, P., *Chromium(VI)-free conversion layer and method for producing it*, 2008, US7314671.
[65] Crotty, D.E., *Stabilized trivalent chromium passivate composition and process*, 1982, US4359348.
[66] Sugiura, T. and Ishikawa, S., *Composition for chemical conversion treatment and process for production of member having black coating by using the composition*, 2011, EP2336390A1.
[67] Izaki, T., Fuda, M., Nakamura, M., Kawakami, K., and Mizuno, K., *Hexavalent chromium-free surface-treating agent for sn- or al-based coated steel sheet, and surface treated steel sheet*, 2002, WO2002020874A2.
[68] Inoue, M. and Yuasa, S., *Treatment solution for forming of black trivalent chromium chemical coating on zinc or zinc alloy and method of forming black trivalent chromium chemical coating on zinc or zinc alloy*, 2007, WO2007094496A1.
[69] Inoue, M., Watanabe, K., NAGATA, G., Nakatani, M., Ishizu, K., and Inomata, T., *Corrosion-resistant trivalent-chromium chemical conversion coating and solution for trivalent-chromium chemical treatment*, 2014, US20140124099.
[70] *Passivation formula of zincification trivalent chromium*, 2012, CN101812681B.
[71] BHOITE, G.S., KULKARNI, A.S., KULKARNI, J.S., KULKARNI, S.V., MAHAJAN, S.S., MAHENDIRAN, R., and PONKSHE, S.R., *Corrosion resistance passivation formulation and process of preparation thereof*, 2012, WO2012143934A2.
[72] Ernst-Walter, H., *Passivation method for zinc-nickel layers*, 2001, WO2001012877A1.
[73] Urban, T. and Jordan, M., *Cobalt-free passivation solution and method for depositing cobalt-free passivation coatings on zinc and zinc alloy surfaces*, 2012, EP2492371A.
[74] YAMAMOTO, T.D.C.C.L., YOSHIDA, M.D.C.C.L., and SHIMAMUNE, S.D.C.C.L., *Agent for reducing coating film overall friction coefficient for trivalent chromate treating solution, trivalent chromate treating solution and method for production*

thereof, and trivalent chromate coating film reduced in overall friction coefficient and method for production thereof, 2006, EP1734152A1.

[75] Yoshimi, N.N.C., Watanabe, T.N.C., and Yamashita, M.N.C., *Weldable colored steel sheet*, 1992, US5556715.

[76] https://www.itp.uni-hannover.de/~zawischa/ITP/pigments.html.

[77] http://www.webexhibits.org/causesofcolor/9.html.

APPENDIX

Appendix

CCD Spectrometer Probe diameter : 1.0-4.0 mm (nominal 2.0 mm – in this project)

RGB measurements

Red color wavelengths : 620-750 nm

Green Color wavelength : 495-570 nm

Blue color wavelength : 620-750 nm

Average reflectance calculated from wavelength range of 450-750 nm

Sample A, B and C : 10 minutes immersion time during electroplated zinc

Sample D,E and F : 30 minutes immersion time during electroplated zinc

Raw data averaged from spectrum of spectrometer 10-minute samples (Table 0.1)

Table 0.1 sample A, B and C RGB value and sample D, E and F RGB value

current density	Avarage reflectance			
A	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	2.3486	4.9242	24.7225	6.474
1	1.8386	4.5801	20.6208	5.4991
2	1.9272	4.4993	21.5267	5.6639
4	1.7195	4.0473	18.9601	5.058
B	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	1.9143	4.214	20.1143	5.347
1	1.8036	4.1703	20.6498	5.3646
2	1.7676	3.7528	18.6693	4.928
4	1.8036	3.6698	17.0477	4.6612
C	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	2.1868	4.7801	28.1685	5.9129

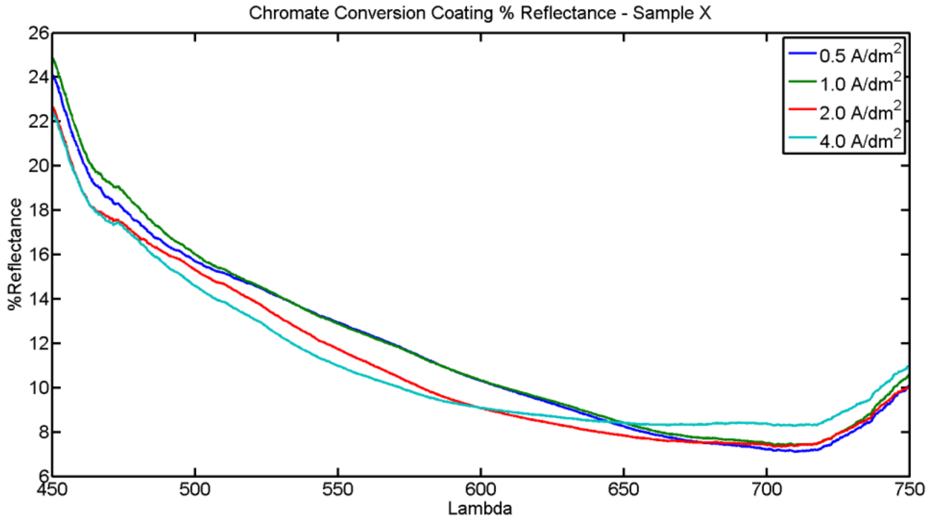
1	2.136	4.3808	29.1936	5.9216
2	1.9647	4.2771	25.5266	5.3569
4	1.7961	3.9165	22.3906	4.7998

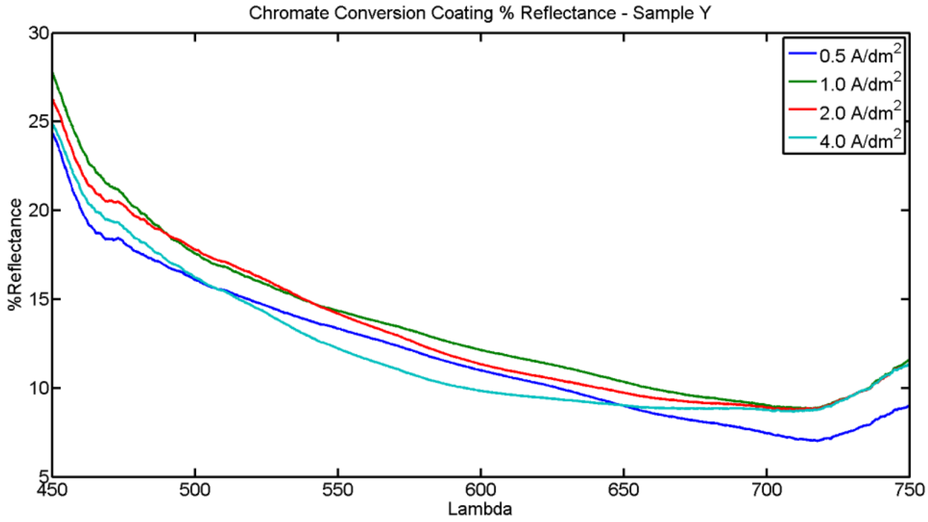
current density	Average reflectance			
D	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	0.9233	2.9142	14.3788	3.598
1	1.1585	2.8838	14.3747	3.6881
2	1.09	2.6765	13.0912	3.399
4	0.958	2.555	11.8174	3.1343
E	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	0.9788	2.9736	15.2176	3.7694
1	1.5184	3.079	15.5128	4.0804
2	1.0236	2.6245	12.3228	3.265
4	1.9888	3.6043	14.9175	4.4311
F	R (620-750 nm)	G (495-570 nm)	B (620-750 nm)	AVG (450-750 nm)
0.5	1.3812	3.154	15.6052	4.0505
1	1.2166	3.0069	15.2656	3.8833
2	1.1258	2.705	13.5429	3.491
4	1.2304	2.7466	12.8129	3.4559

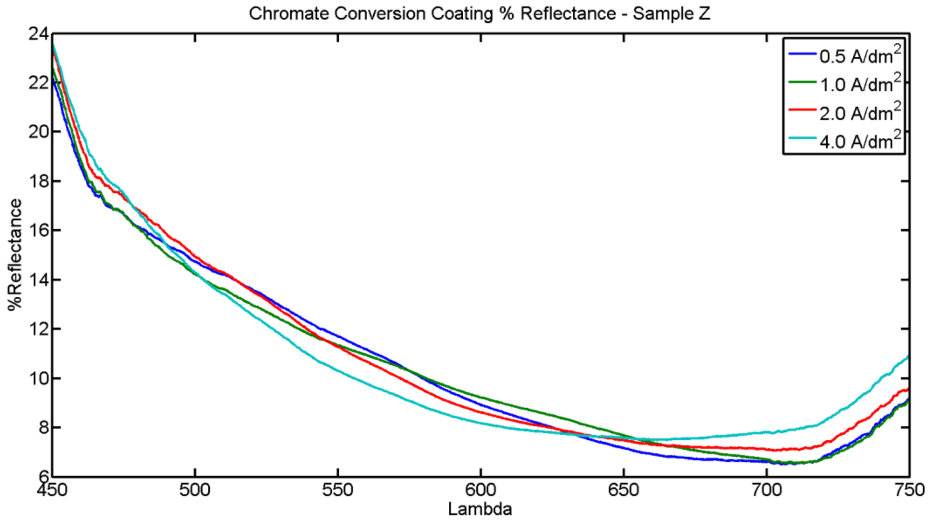
current density	Translation		
A	R	G	B
0.5	6	13	63

1	5	12	53
2	5	11	55
4	4	10	48
B	R	G	B
0.5	5	11	51
1	5	11	53
2	5	10	48
4	5	9	43
C	R	G	B
0.5	6	12	72
1	5	11	74
2	5	11	65
4	5	10	57
current density	Translation		
D	R	G	B
0.5	2	7	37
1	3	7	37
2	3	7	33
4	2	7	30
E	R	G	B
0.5	2	8	39
1	4	8	40
2	3	7	31
4	5	9	38
F	R	G	B
0.5	4	8	40
1	3	8	39
2	3	7	35
4	3	7	33

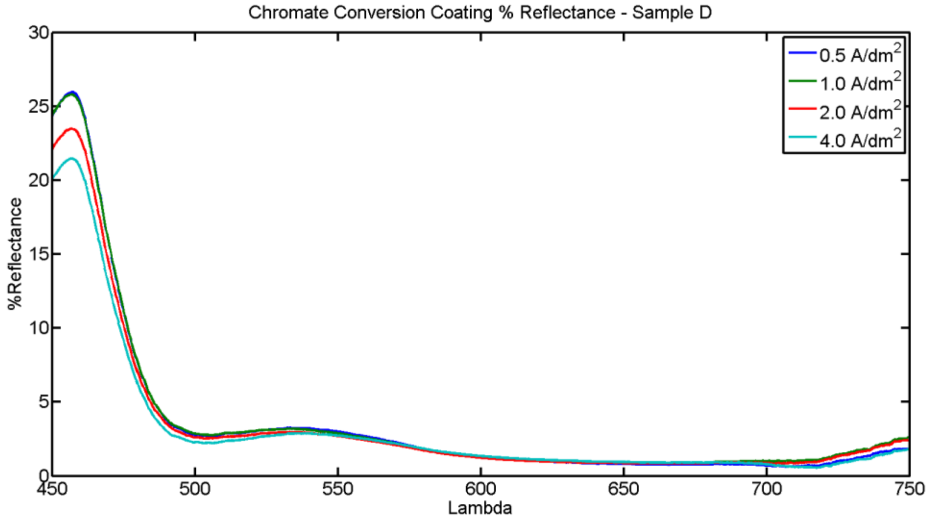
Reflectance of 30-minute unbaked samples

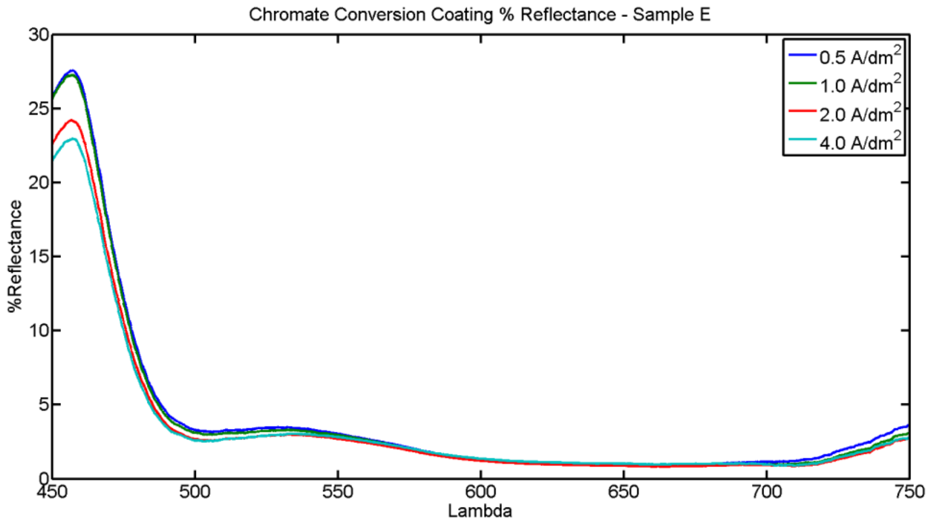


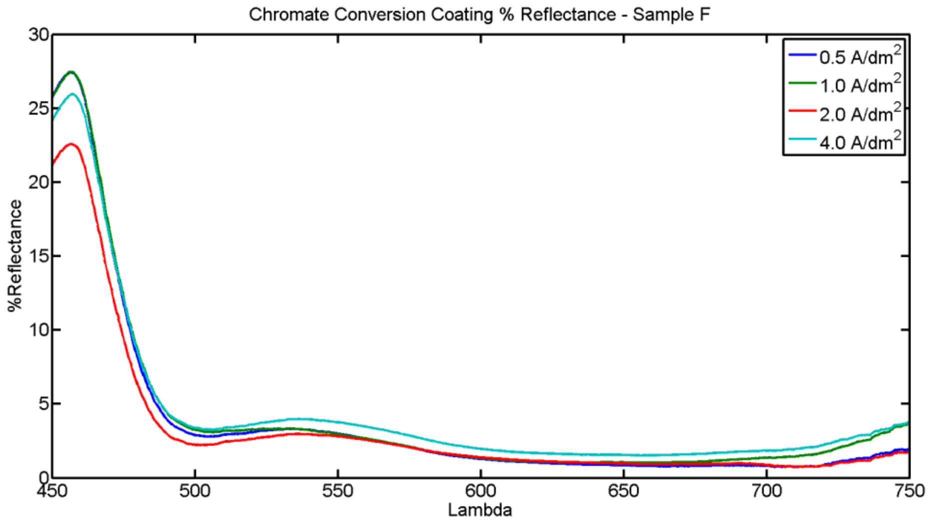




Reflectance of 10-minute baked samples







VITA

Miss Nirada Pintuperakovit was born on April 4th, 1990 in Bangkok, Thailand. She completed high school at Amatyakul School. In 2012, she received the Bachelor’s Degree from Department of Nano Engineering,International School of Engineering, Faculty of Engineering, Chulalongkorn University. After graduation, she pursued her graduate study for a Master’s Degree in Engineering at Department of Metallurgical and Materials Engineering, Faculty of Engineering, Chulalongkorn University in November, 2012. In August 2014, she became a full-scholarship student funded by Nstda-University-Industry Research Collaboration (NUI-RC) to pursue her degree in her expertise. During December 15th-16th, 2014 she was awarded with best oral presentation prize in the 8th Thailand Metallurgy Conference (TMETC-8) in processing session with the her work of "The Influence of Black Trivalent Chromate Conversion Coating’s Parameter on The Color Appearance of Electroplated Zinc Coatings" endorsed by POSCO-Thainox Public Company Limited held at Bangkok, Thailand.