การเตรียมผิวเอบีเอสด้วยสารละลายโคบอลต์และนิกเกิลสำหรับการชุบแบบไร้กระแส

นางสาว พิมพ์พรรณ เดชาสิทธิ์

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SURFACE TREATMENT OF ABS USING COBALT AND NICKEL SOLUTION FOR ELECTROLESS PLATING

Miss Pimpan Dechasit

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พิมพ์พรรณ เดชาสิทธิ์ : การเตรียมผิวเอบีเอสด้วยสารละลายโคบอลต์และนิกเกิลสำหรับการชุบแบบไร้กระแส (SURFACE TREATMENT OF ABS USING COBALT AND NICKEL SOLUTION FOR ELECTROLESS PLATING) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. วิมลรัตน์ ตระการพฤกษ์, 74 หน้า.

งานวิจัยนี้ศึกษาการกระตุ้นผิวของอะคริโลไนทริลบิวทาไดอีนสไตรีน (ABS) โดยใช้โลหะโคบอลต์และนิกเกิล ศึกษาปัจจัยที่มีผลต่อการกระตุ้นผิว คือ ชนิดและความเข้มข้นของสารกระตุ้นและสารรีดิวซ์ และเวลาในการเกิดปฏิกิริยา กระบวนการนี้สามารถแบ่งได้หลายขั้นตอน ขั้นตอนแรกคือกระตุ้นผิวเอบีเอสด้วยสารละลายของโคบอลต์และนิกเกิล ขั้นตอนต่อไปคือ รีดิวซ์ไอออนของโลหะให้เป็นอะตอมของโลหะโดยใช้สารละลายทิน(II)คลอไรด์และโซเดียมโบโรไฮไดรด์ พบว่าสารละลายโซเดียมโบโรไฮไดรด์มีประสิทธิภาพสูงในการรีดิวซ์ไอออนของโคบอลต์และนิกเกิล จากการศึกษาพบว่าเมื่อใช้สารละลายโซเดียมโบโรไฮไดรด์ความเข้มข้น 0.5 M ที่เวลาการรีดิวซ์ 60 วินาทีมีประสิทธิภาพในการรีดิวซ์ไอออนของโลหะให้เป็นอะตอมของโลหะได้ดีที่สุด ในขณะที่สารละลายทิน(II)คลอไรด์ไม่มีประสิทธิภาพ เมื่อจุ่มเอบีเอสที่ผ่านการกระตุ้นผิวลงในอ่างสารละลายนิกเกิล พบว่าโลหะโคบอลต์ (หรือนิกเกิล) สามารถเป็นตัวเร่งปฏิกิริยาเหนี่ยวนำให้เกิดการเคลือบติดของฟิล์มนิกเกิลบนเอบีเอส ทำการวัดปริมาณและความหนาของฟิล์มนิกเกิลด้วยเทคนิคSEM พบว่าเมื่อใช้สารละลายนิกเกิลอะซิเทตความเข้มข้น 3 g/L สารละลายโซเดียมโบโรไฮไดรด์ความเข้มข้น 0.5 M และเวลาการรีดิวซ์ 60 วินาทีให้ปริมาณและความหนาของฟิล์มนิกเกิลมากที่สุด พิสูจน์ลักษณะเฉพาะของเอบีเอสที่ถูกเคลือบโดยวิธี tape test ตามมาตรฐาน ASTMD3359 ซึ่งแสดงการยึดเกาะที่ดีระหว่างฟิล์มนิกเกิลและวัสดุเอบีเอส.

ศูนย์วิทยทรัพยากร
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สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต..

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5173417623: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: ELECTROLESS PLATING / COBALT CATALYST / SURFACE ACTIVATION / PLATING PROCESS

PIMPAN DECHASIT: SURFACE TREATMENT OF ABS USING COBALT AND NICKEL SOLUTION FOR ELECTROLESS PLATING. THESIS ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., 74 pp.

This research studied the surface activation of the acrylonitrile butadiene styrene (ABS) using Co and Ni metal. The parameters affecting the surface activation, namely types and concentrations of activator and reducing agent and reaction time, were studied. This process can be divided by many steps. The first step is to activate the ABS surface using Co and Ni solution. Next step is to reduce metal ions to metal using stannous (II) chloride and sodium borohydride solution. It was found that sodium borohydride solution was quite effective in the reduction of both Ni and Co ions. The results showed the most effective in reduction of metal ions into metals when using 0.5 M sodium borohydride solution at the reduction time of 60 seconds while the stannous (II) chloride solution was not effective. By immersing in a Ni plating bath the Co (or Ni) can then auto-catalytically deposit a Ni film on the ABS. The amount and thickness of Ni coating film was determined by using SEM. It was found that the amount and thickness of the Ni coating film were the highest when using 3 g/L of nickel acetate solution, 0.5 M sodium borohydride solution at 60 s of the reduction time. The characteristics of the coated ABS were checked by tape test according to ASTM D3359, which indicated good adhesion between Ni film and ABS substrate.

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Field of Study ...Petrochemistry and Polymer Science...... Student's Signature ....
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LIST OF ABBREVIATIONS

ABS	:	Acrylonitrile-butadiene-styrene
AAS	:	Atomic absorption spectroscopy
CTS	:	Chitosan, 98% deacetylation degree
°C	:	Degree Celsius
EDTA	:	Ethylenediamine tetraacetic acid
EDX	:	Energy-dispersive X-ray spectroscopy
FT-IR	:	Fourier-Transform Infrared Spectrometer
°F	:	Degree Fahrenheit
GPa	:	Giga pascals
KPa	:	Kilo pascals
MRN	:	Mineral-reinforced nylon
Mpa	:	Mega pascals
Ni/B	:	Nickel/boron
Ni/P	:	Nickel/phosphorus
psi	:	Pound per square inch
SEM	:	Scanning Electron Microscope
sec	:	Second
TCTN	:	Thermochemical treatment at nitrogen
TCTA	:	Thermochemical treatment at ammonia

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CHAPTER I

INTRODUCTION

1.1 Introduction

Acrylonitrile-butadiene-styrene (ABS) plastic is one of the most popular materials nowadays. It is an important engineering material which has been used in place of many materials. ABS plastic has high thermal stability, excellent mechanical strength, and good resistance to chemical reagents. Therefore, it has been widely used to produce parts in an automotive industry, such as car grill, mirror cover, logo and car architrave. However, its application is limited due to some drawbacks, since it is an easily fretted and non-conductive material. In order to enhance the ABS plastic property, metallization technique is normally applied for either decorative or functional purposes. Through metallization, the specific properties of plastic, such as light weight, design flexibility and low cost of manufacturing, can be usually improved by the addition of metal with associated properties. Moreover, metallization can help adjusting reflectivity, abrasion resistance, electrical conductivity and variety of decorative effect [1]. Examples of products produced from ABS plastic plated with chromium are shown in Figure. 1.

Figure 1. Examples of products produced from ABS plastic plated with chromium.

Metal-plated technique can be applied to various types of plastics if there is an appropriate etching system [2,3]. In particular, ABS is usually the plated plastic because of its excellent toughness, good dimensional stability, good processability, chemical resistance and cheapness. For many years, activation process for the metallization of non-conducting substrates has received many attentions.

Activation process employs the catalyst metal sites on the substrate to initiate oxidation of a reducing agent in an electroless plating solution. It is one of the pivotal steps because of its direct effect on the quality of the plating layer [4]. In the conventional activation process, a sensitizing-activating method of dipping the substrate into a stannous chloride bath employs the catalyst palladium cluster. This process consists of chemisorbing of the catalyst on the polymer surface. Then the Pd (II) species on a polymer surface was reduced to Pd (0). In recent years a tin-free method has been developed to attach the Pd (II) species on a polymer surface. This method has numerous problems, such as the high toxic stannous, waste of noble metal and high cost of palladium. Thus, it is necessary to develop a cost effective activation technique employing less expensive metals, such as Co and Ni. Performing the direct electroless metallization of insulating substrates without seeding their surface with Pd (0) catalytic clusters is a challenge which aims at reducing the cost of the metallization process [5].

1.2 Objectives of research

1. To study surface treatment (etching, activating, sensitising) of ABS.
2. To study parameters and suitable condition of activating process using Ni and Co complexes.
3. To perform electroless metallization (Ni) of ABS.

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1.3 Scope of research

1. Literature survey.
2. Etching of ABS surface by dipping in a mixed solution of CrO_3/H_2SO_4.
3. Characterization of ABS surface using scanning electron microscopy (SEM).
4. Catalyst formation on ABS surface.

    4.1 Sensitizing/activating steps.

    The following parameters were studied:

Parameter	Range
Concentration of sensitizing solution ($SnCl_2$)	0.1-1 g/L
Type of activating solution	$CoCl_2$, $[CoCl_2(en)_2]Cl$
Concentration of activating solution	1-5 g/L
Time of activation	5-300 second.

    4.2 Oxidizing and reducing steps.

    The following parameters were studied:

Parameter	Range
Type of oxidizing agent	$(CH_3COO)_2Ni$, $CoCl_2$, $[CoCl_2(en)_2]Cl$
Concentration of oxidizing agent	1-5 g/L.
Concentration of reducing agent ($NaBH_4$)	0.1-1 M.
Time of reduction	5-300 seconds.

5. Characterizaion of treated ABS using atomic absorption spectroscopy (AAS) and energy-dispersive X-ray spectroscopy (SEM-EDX).
6. Electroless metallization of ABS in nickel-plating solution.
7. Characterization of ABS plated with Ni film by titration method (with EDTA) and adhesion test using ASTM D3359 (scotch® tape test).
8. Summary of results and conclusion.

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CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polymer [6]

Polymer is a large molecular weight substance which is composed of many repeating structural units or monomers generally connected by covalent chemical bonds. Polymer can be categorized into three types.

1. Homopolymer is the polymer chain that contains only a single type of monomer such as polyethylene.

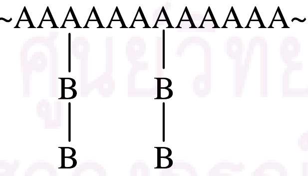
2. Copolymer is the polymer chain containing at least two types of monomers, and can be divided into 4 groups according to the chain rearrangement patterns.

- Random copolymer is the copolymer consisting of two different monomers with random length such as ~AABBBABA~

- Alternating copolymer is the copolymer with two different monomers joining along the chain in a manner such as ~ABABABABABAB~

- Block copolymer is the copolymer with two different monomers organizing into distince segments, or blocks such as ~AAABBBAAABBB~

- Graft copolymer is the copolymer comprising a group of monomers of which the main backbone chain of atoms has attached to side chains containing different atoms or groups from those in main chain such as



3. Terpolymer is the polymer consisting of three distinct monomers such as acrylonitrile-butadiene-styrene (ABS)

2.2 Properties of ABS plastic [7]

ABS can be fabricated in many grades. Each grade has different properties depending on the proportions of polybutadiene in relation to styrene and also acrylonitrile, molecular weight, molecular weight distribution, percentage of polymer grafting. The grafting can be performed by polymerization of acrylonitrile and styrene in polybutadiene latex. The structure of grafting and other properties of ABS are determined by this step. Table 2.1 shows the properties of ABS with various grades.

Table 2.1 Properties of ABS with various grades.

Property	ASTM method	Units	Low impact	Medium impact	High impact	Heat resistant
Izod impact	D 256	J/m	105-215	215-375	375-440	120-320
Tensile strength	D 638	MPa	41-52	41-47	33-44	41-52
Tensile elongation	D 638	%	5-30	15-50	15-70	5-20
Tensile modulus	D 638	GPa	2.2-2.6	2.1-2.4	1.7-2.1	2.1-2.6
Flexural yield strength	D 790	MPa	68-87	68-80	55-68	68-90
Flexural modulus	D 790	GPa	2.3-2.6	2.2-2.5	1.8-2.2	2.1-2.8
Rockwell hardness	D 785	R	105-110	95-105	88-100	100-112
Heat deflection temp at 1820 Kpa	D 648	^{o}C	94-100	96-100	98-104	105-121
Heat deflection temp at 455 Kpa	D 648	^{o}C	100-108	102-104	103-108	108-127
Coefficient of thermal expansion	D 696	x 10^{-5} cm/cm ^{o}C	7.0-8.8	7.8-8.8	9.5-11.0	6.4-9.3
Sp.gr.	D 792		1.05-1.07	1.04-1.05	1.02-1.04	1.04-1.06

Table 2.1 Properties of ABS with various grades. (cont.)

Property	ASTM method	Units	Flame retardant	Plating	Clear	ABS-PC
Izod impact	D 256	J/m	185-280	265-375	134	370-560
Tensile strength	D 638	MPa	40-50	38-44	43	45-60
Tensile elongation	D 638	%	45778	10-30	20-35	25-80
Tensile modulus	D 638	GPa	2.1-2.5	2.3-2.6	2.3	2.4-2.6
Flexural yield strength	D 790	MPa	69-86	69-80	72	79-90
Flexural modulus	D 790	GPa	2.3-2.8	2.3-2.7	2.4	2.2-2.6
Rockwell hardness	D 785	R	97-111	103-110	103	111-120
Heat deflection temp at 1820 Kpa	D 648	^{o}C	90-107	95-100	88	114-121
Heat deflection temp at 455 Kpa	D 648	^{o}C	96-111	99-104	92	117-124
Coefficient of thermal expansion	D 696	x 10^{-5} cm/cm ^{o}C	7.0-8.8	6.5-7.0	8.6	6.2-7.4
Sp.gr.	D 792		1.20-1.22	1.04-1.06	1.07	1.07-1.12

The chemical resistance property of ABS is attributed to acrylonitrile monomer in the polymer chain. The polarity of nitrile group can reduce the reaction between polymer and hydrocarbon solvent. Therefore, ABS plastic is proofed against minerals, vegetable oil, wax, organic compounds and weakly basic solvent. The resistance of ABS to chemical stress is shown in Table 2.2. However, the unsaturated polybutadiene made ABS quite active to some reactions such as oxidation, halogenation and sulfonation. **[8]**

Table 2.2 The resistance of ABS to chemical stress

Medium	Rate[a]	Medium	Rate[a]
Acetic acid, 50%	1	Ethyl alcohol, 50%	3
Glycerol	1	2-Propanol, 50%	3
Corn syrup	1	Kerosene	3
Hydrochloric acid, 25%	1	Propylene glycol	3
Potassium chloride, 25%	1	Acetone	4
Sodium hydroxide, 2%	1	Chlorobenzene	4
Camauba wax	2	Chloroform	4
Hexane	2	Ethyl acetrate	4
Nitric acid, 25%	2	Sulfur dioxide	4
Sulfuric acid, 25%	2	Toluene	4

[a]The rate of chemical resistance was obtained by leaving the polymer in the testing environment for 7 days continuously at 23 °C. These data present the behavior of general grade ABS.

Number 1 = excellent, no reactions or very small reactions observed
Number 2 = good, small reactions observed
Number 3 = fair, medium or high reactions observed
Number 4 = poor, very high reactions observed

2.3 Properties of ABS after plating [7]

Plating ABS with metal can induce the electrical conductive property of the polymer. Therefore, this technique is recommended for further metal electroplating. The final product of plating plastic would have five to ten times lighter weight comparing with the same product made of metal. Moreover, it also has better resistance to abrasion, heat, light, solvent and chemical resistance, including good appearance and mechanical properties.

a.) Heat resistance

Generally, plastic can be applied to applications under normal or not quite high temperature. However, after plating, the heat resistance of the plastic is 10-15 % increased since the metal coated on the plastic can help preventing the plastic deformation by heat. Therefore, the applications of plastic with metal-plating are increased up to 120 °C, while non-plating plastic is deformed under 75 °C. Moreover,

metal-plating can restrain the oxidation reaction between plastic and oxygen in the air, which is the main cause of plastic degradation.

b.) Mechanical resistance

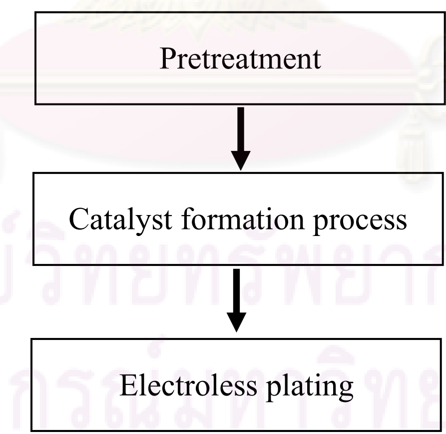
When the product ABS is coated with an appropriate layer thickness, the stiffness of the product will increase. Metal-plating layers will improve the strength of plastic, however, the impact strength is decreased.

c.) Corrosion resistance

Metal-plating plastic has better resistance to corrosion than metallic materials. The cracks or holes, occurred from corrosion, in the metallic coating layer on plastic is not widen as that on metals. Therefore, the appearance of metal-plating plastic is long-lasting than ordinary metallic materials.

2.4 Procedure of surface treatment of ABS for electroless plating [9,10]

The dielectric materials such as plastic cannot be metal-plated by electricity directly. Prior to electrical plating, the conductivity of the plastic surface must be prepared. The stepwise of the surface treatment is quite important. The surface treatment of ABS for electroless plating consists of three main steps as follows.



Pretreatment is to clean the plastic surface by eliminating oil on the surface with basic solvent. After that, the surface etching by acidic oxidizing agent is obtained to make holes in order to improve the attachment between plastic and metal layer. Next step is to treat the surface with the catalyst deformation process in order to obtain good dispersion of metallic particles on plastic surface. These particles could

catalyze or induce the metallic film formation on ABS surface in electroless plating. The last step is electroless plating, which is occurred by only the oxidation-reduction reaction without external energy such as electricity. The metal ions in the solvent are reduced into metal atoms attached on the plastic surface. Electroless plating provides more conductive surface than ordinary electroplating in the final product.

2.4.1 Pretreatment [9,10]

A. **Cleaning**

Cleaners are used for removing light soils such as fingerprints, dirt, and other debris from the parts. They are usually mild alkaline cleaners.

B. **Etching**

Etchants are usually strong oxidizing solutions that eat away the plastic surface to various degrees. There are two main purposes of etching. First, the surface area is greatly increased, making the part turned from a hydrophobic (water-hating) into a hydrophilic (water-loving) material. Second, the microscopic holes left in the surface of the plastic by the etchant provide the bonding sites for the deposited metal. These sites are needed for adhesion between the plastic and the metal.

When ABS is exposed to an etchant, the butadiene is selectively removed, thus leaving small holes or bonding sites as shown in Figure 2.1 **[9].**

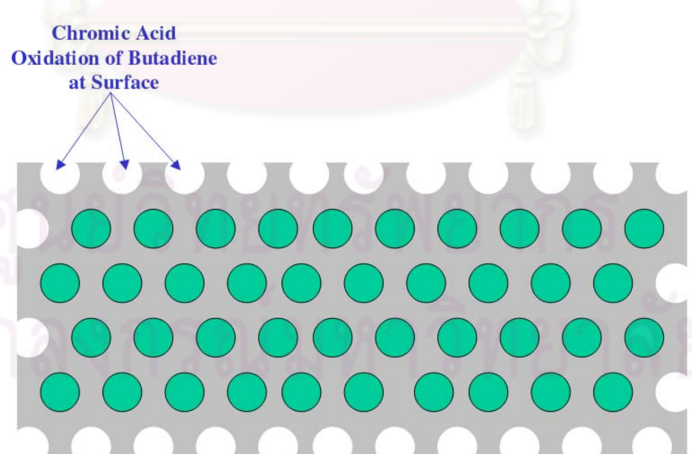


Figure 2.1 The porous surface or structure of the ABS surface after etching with chromic/sulfuric acid solution.

Commonly used etchants for ABS are Chromic/Sulfuric acid. It is also desirable to have about 40 g/L trivalent chromium in a new all-chrome bath to avoid over-etching the ABS surface. Etchants are generally operated at 60 to 71 ^{o}C for 4 to 10 minutes on ABS. Other plastics may require higher or lower temperatures and times. Polycarbonate, for example, uses an etchant at 77 ^{o}C for 10 minutes, while mineral-reinforced nylon (MRN) uses one at 40 ^{o}C for 2 minutes.

As the chrome-based etchants are used, the following reduction reaction occurs as the plastic is attacked as shown in Equation 1.

$$\mathbf{Cr^{6+} + 3e^{-} \longrightarrow Cr^{3+}} \qquad \mathbf{(1)}$$

After a certain build-up of Cr^{3+} (about 40 g/L in the “chrome-sulfuric’’ type etchant), the etchant starts to lose its ability to perform properly. Adding more Cr^{6+} in the form of chromium oxide extends the life of the etchant for a while, but it is better to eliminate the excess Cr^{3+}. This can be done in two ways:

- Decant part or all of the etchant and rebuild it. This method may cause a waste disposal problem if provisions for the spent material are not made.
- The excess trivalent chrome can be electrolytically regenerated.

The etchant is the most critical step in obtaining an acceptable finished part. An underetched part can result in poor adhesion and possible skip plate. Over-etching of a part can degrade the surface and cause poor adhesion and cosmetics **[11].**

C. **Neutralization**

After etching, the parts are thoroughly rinsed in water and then put into a neutralizer. These are materials such as sodium bisulfite or any of the proprietary products available that are designed to eliminate excess etchant from the parts and racks, usually by chemical reduction. Hexavalent chromium (Cr^{6+}) is harmful in the ensuing steps. Even with excellent rinsing, etchant may be trapped in blind holes. If this is not rinsed out or reduced to trivalent chromium (Cr^{3+}) “skip plate” can occur as a result of “bleed-out” of etchant in subsequent steps.

Neutralizers are generally cheap to make up and are usually dumped and remade on a regular basis. They are usually run at 21 to 43 ^{o}C for 1 to 3 minutes with air agitation.

D. **Pre-activator**

After neutralization and rinsing, a pre-activator may be employed for certain resins, such as polypropylene acrylonitrile butadiene styrene or polyphenylene oxide. These proprietary materials are designed primarily to enhance activator absorption. Generally they do not reduce hexavalent chromium. Pre-activators help making resins platable by conditioning the resin surface, such as forming a film or changing the surface charge. One must be careful in selecting a pre-activator, as excessive conditioning can lead to resistance overplating and rack plating. Typical parameters for these baths are 21 to 49 ^{o}C for 1 to 3 minutes.

2.4.2 Catalyst formation process [1,9]

A. **Sensitizing/catalyzing process**

The traditional approach of activation is a two step procedure. The first step is to adsorb the Sn^{2+} onto the plastic surface by immersion in a stannous chloride/hydrochloric acid solution. Then, the part is rinsed before immersed in the palladium chloride/hydrochloric acid solution. The oxidation-reduction between the Sn^{2+} and Pd^{2+} occurs. The Sn^{2+} can be easily oxidized to Sn^{4+}. The Pd^{2+} is reduced to Pd^{0} as shown in Equation (2) and Figure 2.2 **[7]**.

$$\mathbf{Sn^{2+} + Pd^{2+} \longrightarrow Sn^{4+} + Pd^{0}} \qquad \mathbf{(2)}$$

Palladium chloride, stannous chloride and hydrochloric acid are mixed as one solution called the palladium-tin hydrosol, which is a solution of complex ions and colloidal particles. The activity and stability of the palladium-tin hydrosol depend on the chloride and stannous ion concentrations.

B. **Oxidizing/reducing process**

This method takes advantage of the autocatalytic property of Ni. The first step uses nickel acetate in ethanol solution to deposit a thin organo-nickel film (Ni^{2+}) by its chemisorption on the substrate surface. Nickel ions adsorbed on the substrate surface are reduced by dipping in $NaBH_4$ solution. BH_4^- is a powerful reducing agent whose decomposition in basic solution yields 8 electrons according to the following Equation (3).

$$\mathbf{BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4H_2O + 8e^-} \qquad \textbf{(3)}$$

The redox potential E^o ($B(OH)_4^-/BH_4^-$) is equal to -1.24 V at pH value of 14 and the redox potential E^o ($Ni^{2+} + 2e^- \rightarrow Ni^0$) is equal to -0.25 V. Under these conditions, the overall redox reaction is shown in Equation (4).

$$\mathbf{4Ni^{2+} + BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4Ni^0 + 4H_2O} \qquad \textbf{(4)}$$

Furthermore, this operation maintains enough Ni (0) species on the substrate surface to allow immediate Ni deposition when the sample is immersed in Ni industrial plating baths.

2.4.3 Electroless plating [9,12]

Preplating consists of an electroless bath, which is used to deposit a thin adherent metallic film, usually copper or nickel, on the plastic surface by the chemical reduction. The electroless solution consists of main four components as follows:

1.) Metal salt

The source of metallic ions to be plating such as Cu or Ni salts. The salt can be prepared by dissolution of copper sulfate or nickel sulfate in the electroless solution.

2.) Reducing agent

This chemical substance can reduce the metallic ions into metallic atoms adsorbed on the plastic surface. Each electroless solution needs different reducing agent, for instance, formaldehyde and sodium hypophosphite for electroless copper and electroless nickel solutions, respectively.

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3.) Complexing agent

The complexing agent can react or combine with the metallic ions and forms a complex compound, which can be dissolved in the electroless solution easily. This agent can prevent the precipitation of the metal salt and the degradation of the solution. Moreover, it also helps improve the chemical reaction between the metallic ions and the reducing agent.

4.) Buffer and stabilizer

The buffer and the stabilizer are used to stabilize the pH level of the electroless solution. They help delay the pH change and maintain the suitable conditions for the system. The electroless solution remains stable in the bath until a palladium or nickel-bearing surface is introduced into the solution. A chemical reduction of metal occurs on the palladium or nickel sites, and through autocatalysis, continues until the part is removed. The basic reactions for nickel are shown in Equation (5) **[1,10].**

$$\mathbf{Ni^{2+} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni^0 + 2H_2PO_3^- + H_2 + 2H^+} \qquad \mathbf{(5)}$$

Phosphorus incorporation in the Ni deposit results from a secondary reaction due to hypophosphite disproportionation in acidic medium as show in Equation (6) **[1,10].**

$$\mathbf{3H_2PO_2^- + 2H^+ \longrightarrow 2P + H_2PO_3^- + 3H_2O} \qquad \mathbf{(6)}$$

For the electroless nickel solution, pH is adjusted to 9 by ammonium hydroxide.

2.5 Types of nickel solution [9,10,13]

Different types of plating solution have been developed to provide special properties, depending on the end-use requirement.

A. **Alkaline nickel-phosphorus**

These baths plate at a relatively low temperatures, around 24-60 ^{o}C, making them suitable for plating on plastics and other nonconductive materials or for use on zincated aluminum. In addition, because of the low phosphorus content deposited

(3-4%), they offer enhanced solderability and bondability, especially in electronic applications.

B. **Acid nickel phosphorus**

Deposits from these baths can be identified by phosphorus content, which, in turn, determines deposit properties. 2-5% = Low phosphorus; 6-9% = Mid phosphorus; 10-12% = High phosphorus. Low phosphorus deposits offer improved hardness and wear characteristics, higher temperature resistance, and increased corrosion resistance in alkaline environments. Mid phosphorus coatings are bright and aesthetically pleasing and have good hardness and wear resistance, along with moderate corrosion resistance. High phosphorus coatings provide very high corrosion resistance and a complete lack of magnetic response.

C. **Nickel-boron baths**

Low boron, nickel-boron coatings (less than 1%B), reduced with amine boranes, are most often used in electronic applications to provide high electrical conductivity, good solderability and good ultrasonic bonding characteristics. Deposits with higher levels of boron (2-3%) have high hardness values and better wear resistance than other coatings. In addition, the melting point of nickel-boron alloys is higher than that of nickel-phosphorus coatings. The chemical cost of amine borane reduced coatings is five to 10 times that of nickel-phosphorus deposits. Sodium borohydride reduced nickel-boron plating solutions, deposit higher levels of boron (3-5%) than amine borane baths and are usually co-alloyed with thallium. These coatings provide exceptionally high hardness and wear resistance, usually equal to hard chromium.

2.6 Properties of electroless nickel [9,10]

A. **corrosion resistance and corrosion protection**

One of the most common reasons for the use of electroless nickel coatings in functional applications is its excellent corrosion resistance. In highly corrosive conditions encountered in drilling and producing oil wells, for example, electroless nickel has shown its ability to withstand the combination of corrosive chemicals and abrasion.

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B. **Density**

The density of electroless nickel coatings declines with increasing phosphorus content. An electroless nickel deposit containing 3% phosphorus has a density of 8.5 g/cm^3, while that of a deposit with 11% phosphorus has a density of 7.75 g/cm^3. These values are lower than those of pure metallurgical nickel (8.91 g/cm^3).

C. **Melting temperature**

The final melting temperatures of electroless nickel deposits is depending upon the amount of phosphorus alloyed in the deposit. The initial melting point is about 1630 ^{0}F (890 ^{0}C) for all deposits.

D. **Adhesion**

Excellent adhesion of electroless nickel deposits can be achieved on a wide range of substrates, including steel, aluminum, copper and copper alloys. Typical bond strengths reported for electroless nickel on iron and copper alloys range from 50 to 60,000 psi (340 to 410 MPa). The bond strength on light metals, such as aluminum, tends to be lower, in the range of 15 to 35,000 psi (100 to 240 MPa). Low temperature, heat treatment is commonly employed to improve adhesion of electroless nickel on all metals, particularly on light metals such as aluminum or titanium. During this heat treatment diffusion can occur between the atoms of the coating and the substrate. The surface preparation and activation is one of the most important factors for producing excellent adhesion.

E. **Brightness**

The brightness and reflectivity of electroless nickel can vary significantly, depending on the specific formulation. The reflectivity of the deposit is also affected by the surface finish of the substrate. Thus, a very bright electroless deposit may appear dull if the substrate is rough. The appearance of most electroless nickel coatings is similar to that of electrodeposited nickel.

2.7 Application of electroless nickel

Electroless nickel coatings have many unusual properties, which make them very useful in a broad range of functional applications. Most applications take advantage of the hardness, lubricity, corrosion resistance, electrical and magnetic properties of electroless nickel, as well as its ability to cover complex geometries and internal as well as external surfaces.

2.8 Characterization of thin films [14]

2.8.1 Scanning electron microscopy with energy dispersive x-ray analysis

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

2.8.2 Atomic absorption spectroscopy

Flame atomic absorption spectroscopy (FAAS) is a very common technique for detecting metals and metalloids in solid and aqueous samples. It is very reliable and simple to use. The technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths.

2.8.3 Titration of nickel quantity [15]

Nickel is titrated with EDTA against murexide. At the beginning of the titration, the solution should have low ammonia concentration, then increasing as getting to the end point. This procedure enhances color change at the end point. The reaction between EDTA and Ni^{2+} ions is relatively slow, so titration should be carried out slightly slower than in other direct EDTA determinations. The reaction occurred during the titration is show in Equation (7).

$$\mathbf{Ni^{2+} + EDTA^{4-} \longrightarrow Ni(EDTA)^{2-}} \qquad (7)$$

2.8.4 Adhesion test [16]

Measuring adhesion by “Tape Test” (ASTM D 3359) is commonly used method for determining the adhesion of a coating system on a substrate. The ASTM D 3359 test method is quick, inexpensive, and relatively easy to perform, there are also several major limitation and potential procedural problem associated with its use.

2.9 Literature Reviews

ABS surface etching

In 2000, Chatchaweewattana **[7]** studied the effect of the concentration of the corrosive substance. This substance consists of chromic acid and sulfuric acid at the concentration of chromic acid 200, 420 and 600 g/L, while the bulk concentration is 800 g/L. The effects of etching time and temperature on the adhesion of metal coated layer on ABS part by electrical plating were also investigated. The results showed that the adhesion tended to increase when etching time increased, but the adhesion tended to drop at further etching. The adhesion was increased with increasing temperature.

In 2006, Wang et al. **[17]** investigated the plating of ABS with copper. The etching was done by chromic/sulfuric solution with 10mg/L of Pd solution. After etching, there were -OH, -SO_3H, -C=O and metal Pd left on ABS surface. Then the part was activated by Pd/$SnCl_2$ solution before dipping in metal copper solution by electroplating, which could form the copper layer on the plastic surface.

In 2007, Wang et al. **[11]** studied the effect of ABS surface etching by addition of Pd solution in etching chromic acid. After the etching by Pd mixed corrosive solution, it was found that less surface roughness was observed compared with the one using only chromic acid. Moreover, the oxidation was improved when the Pd concentration in chromic solution increased. This led to more hydrophilic groups on the surface, resulting in no effect on the adhesion of the metal layer in further plating.

ABS surface activation

In 1996, Maassen et al. **[2]** investigated the catalytic activity of palladium particles prepared upon thermal decomposition of Langmuir-Blodgett films of tris (4,4-diisopropyldibenzylideneacetone)palladium on ABS polymeric supports. It was found that long annealing time led to larger metallic palladium particles. The suitable annealing time was 30 minutes. Moreover, the Langmuir-Blodgett layers had no effect on the quantity of nickel film coated.

In 2006, Charbonnier et al. **[1]** investigated the nickel plating on various plastics by redox reaction between Ni^{2+} and strong reducer. The reduction of Ni^{2+} can be done either by chemical reduction of sodium borohydride or plasma reduction, in order to reduce Ni^{2+} to Ni^{0} deposited on substrate surface. Ni^{0} acts as the autocatalyst in electroless plating process by different nickel solution, namely high or low phosphorous nickel solution. The plasma reduction would provide the nickel film coated on the plastic after dipping in high phosphorous nickel solution only. The adhesion testing of nickel film defined that the chemical reduction by sodium borohydride had better adhesion strength than plasma reduction.

In 2007, Tang et al. **[18]** investigated the catalytic activity on ABS plastic film surface after etching with hydrogen peroxide/sulfuric solution. The etched part was activated by dipping into acetic acid solution containing chitosan and palladium chloride solution. The result showed that the palladium was fixed in chitosan film by chemical-sorption, of which the adhesive strength was higher than that of physical-sorption in the conventional surface activation method. Moreover, the nickel deposition started immediately after dipping the activated substrate (ABS-CTR-Pd) into the electroless solution.

In 2008 Tang et al. [5] studied the activation of the ABS surface for nickel electroless plating. The etched ABS was activated by acetic acid solution containing chitosan and nickel sulfate solution. Then the part was reduced in a solution of KBH_4. ABS-CTS-Ni was obtained. The electroless nickel deposition was catalytically achieved by dipping the activated substrates (ABS-CTS-Ni) into electroless nickel plating solution.

In 2009, Kanta et al. **[19]** investigated the nickel-boron coating on steel by electroless nickel plating and reduced by $NaBH_4$. Then the samples were either used heat treatment or thermochemical treatment at nitrogen atmosphere (TCTN) and ammonia (TCTA), respectively. The results showed that, after electroless nickel plating, a columnar structure of Ni-B film was formed on the steel surface. This film structure presented both nanocrystalline phases and amorphous phases. However, after heat treatment or thermochemical treatment, the corrosion resistance was

increased due to changing of the film structure into nanocrystalline phases. The film structure after thermochemical treatments (TCTA and TCTN) had higher corrosion resistance than that after heat treatment.

In 2009, Kanta et al. **[20]** studied two types of plating, Ni-B plating on steel and Ni-P/Ni-B on alumina, and investigated the wear and corrosion resistance. The film of Ni-P/Ni-B coated on alumina is more smooth than Ni-B coated on steel. Therefore, the corrosion resistance of Ni-P/Ni-B is higher.

In 2010, Wang et al. **[21]** investigated the electroless nickel plating process on wood veneers. Sodium borohydride was used as a reducer to create nickel(0) on the surface of wood veneers by hydrogen bond between hydroxyl group on wood veneers and hydrogen of the borohydride anion. When the concentration of sodium borohydride and dipping time in nickel solution increased, more nickel was formed as a film on the wood veneers surface.

CHAPTER III

EXPERIMENTAL

3.1. Material

Plastic ABS grade 3001 MB from TOYOTA company

3.2 Chemicals

Chemicals for cleaning

1. Sodium carbonate (Na_2CO_3), United excel chemical
2. Disodium metasilicate (Na_2SiO_3), United excel chemical
3. Sodium dodecylbenzene sulfonate ($C_{18}H_{29}NaO_3S$), United excel chemical

Chemicals for etching

1. Chromic acid (CrO_3), The East Asiatic (Thailand)
2. Sulfuric acid (H_2SO_4), S.T. Chemical Business

Chemicals for neutralization

1. Hydrochloric acid (HCl), RCI Labscan
2. Hydroxylammonium hydrogen sulphate (H_5NO_5S), United excel chemical

Chemicals for catalyst formation

1. Cobalt chloride ($CoCl_2$), Carlo Erba
2. Ethylenediamine ($C_2H_8N_2$), Panreac
3. Hydrogen peroxide (H_2O_2), Ajax Finechem
4. Hydrochloric acid (HCl), RCI Labscan
5. Methanol (CH_3OH), Ajax Finechem
6. Nickel(II) acetate ($(CH_3COO)_2Ni \cdot 4H_2O$), Carlo Erba
7. Sodium borohydride ($NaBH_4$), Ajax Finechem
8. Ethanol (C_2H_5OH), VWR International
9. Stannous Chloride ($SnCl_2$), Ajax Finechem

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Chemicals for electroless plating

1. Nickel chloride ($NiCl_2.6H_2O$), United Excel Chemical
2. Nickel sulfate ($NiSO_4.6H_2O$), United Excel Chemical
3. Phosphinic acid (H_3PO_2), United Excel Chemical
4. Citric acid ($C_6H_8O_7$), United Excel Chemical

Chemicals for tritration of Ni amount

1. Ammonium persulfate ($(NH_4)_2S_2O_8$,
2. Ammonium hydroxide (NH_4OH),
3. Murexide indicator ($C_8H_8N_6O_6$),
4. Ethylenediamine tetraacetic acid ($C_{10}H_{16}N_2O_8$),

3.3 Apparatus

1. Thermostat kit
2. Jig
3. Injection machine 350 tons (Toshiba, Model EC 160C), Japan
4. Scanning electron microscope (Model JSM-6380 with oxford EDX, JEO)
5. Atomic absorption spectrophotometer, AAS (Model GBC 932/933 AA)
6. Oven: 0-250 ^oC, (Model DHG-9070A), China
7. FTIR spectrometer (Perkin Elmer FTIR with Microscope Model i-series)

3.4 Experimental procedures

3.4.1 Sample preparation

The ABS samples were fabricated by injection molding by TOSHIBA injection machine. The injection condition is as follows:

Melting Temperature	230	^oC
Mould Temperature	45	^oC
Injection Pressure	85	kg/cm^2
Injection Time	4	seconds

3.4.2 Preparation of trans-dichloro bis(ethylenediamine) cobalt (III) chloride catalyst, $[CoCl_2(en)_2]Cl$ [22,23]

- Preparation of 10% ethylenediamine solution.

50 mL of DI water was added into a 100 mL volumetric flask, followed by 10 mL of ethylenediamine and DI water was added to make up 100 mL solution.

- Preparation of 10% hydrogen peroxide solution.

50 mL of DI water was added into a 100 mL volumetric flask, followed by 33 mL of hydrogen peroxide and DI water was added to make up 100 mL solution.

- Dichloro bis(ethylenediamine) cobalt (III) chloride solution.

1 g of cobalt(II) chloride hexahydrate was weighed in an evaporating dish followed by 2.5 mL of DI water. The dish was swirled until the cobalt compound had dissolved. Then, 4 mL of 10% ethylenediamine, 1.6 mL of 10% H_2O_2 and 3 mL of concentrated hydrochloric acid were added into the solution, respectively, while swirling. After that, the solution volume was reduced by placing the evaporating dish on top of the beaker containing boiling water. The solution was boiled until a thick layer of dark green crystal was formed. Finally, the crystal was dried and characterized by Infrared Spectroscopy (IR).

3.4.3 Surface cleaning

The ABS samples were immersed in the cleaning agent. The compositions and the conditions of the cleaning agent are as follows:

Sodium carbonate	50	g/L
Disodium metasilicate	35	g/L
Sodium dodecylbenzene sulfonate	3	g/L
Cleaning solution temperature	40	^{o}C
Dipping time	3	minutes

The surface cleaning step was applied to remove oils and dirts on the ABS surface. Then the samples were rinsed with DI water for 5 minutes.

3.4.4 Surface etching

Etching was be conducted by dipping the samples in chromic/sulfuric acid, 400 g/L each, at 68 ^{o}C for 10 minutes. Then the samples were rinsed with DI water. Finally, the ABS surface was characterized by SEM/EDX.

3.4.5 Neutralization

The neutralization was done by dipping the etched samples in the neutralizing agent. The compositions and the conditions of the neutralizing agent are as follows:

Hydrochloric acid	30	g/L
Hydroxylammonium hydrogensulphate	20	mL/L
Temperature	25	^{o}C
Time	1	minutes

The surface etching was carried out in order to balance the pH level of the sample surface by eliminating the trace chromic acid left on the sample. After that, the samples were rinsed with DI water.

3.4.6 Catalyst formation process

This process was applied in order to obtain good metallic particles dispersion on the plastic surface. These particles were meant to accelerate or induce the metallic film formation on the ABS surface in the electroless plating step. The catalyst formation process was done by two methods.

A. **Sensitizing/Activating method**

The neutralized ABS sample was immersed in the sensitizing solution, which consisted of tin (II) chloride ($SnCl_2•2H_2O•HCl$). The interesting concentration of sensitizing solution is 0.1, 0.5 and 1 g/L, reduction time is 3 minutes at 25 ^{o}C.

- Preparation of sensitizing solution

$SnCl_2$, 0.1 g (0.5 or 1 g), were dissolved in DI water at 60 ^{o}C and 40 mL/L of HCl was added into the $SnCl_2$ solution. The flask was swirled until homogeneous phase appeared. Then, DI water was added to make up 1 L solution.

After the sensitizing step, the part was immersed in the activator solution, which consisted of cobalt solution. The activator solution is $CoCl_2$ or $[CoCl_2(en)_2]Cl$ at the concentration of 1, 3, 5 g/L and different activation time of 5, 8 and 10 minutes.

- Preparation of activator solution

$CoCl_2$ or $[CoCl_2(en)_2]Cl$, 1 g (3 or 5 g), were dissolved in DI water. Then 10 mL/L of HCl was added into the solution. The flask was swirled until homogeneous phase was obtained. Then, water was added to make up 1 L solution.

The samples were dried and characterized by SEM and AAS to analyze the distribution and the quantity of the catalyst on ABS surface.

B. **Oxidizing/Reducing method**

The sample was dipped into the different oxidizing solution namely, nickel acetate in ethanol, $[CoCl_2(en)_2]Cl$ and $CoCl_2$ solution. The concentration of oxidizing solution is 1, 3, 5 g/L, for 3 minutes.

The metal(II) ions were adsorbed on the plastic surface in this step, when the samples were dried, they were characterized by SEM and AAS. After the oxidizing step, the sample was immersed into the reducing agent, which consisted of sodium borohydride ($NaBH_4$). The concentration of reducing solution is 0.1, 0.5 and 1 M at different reduction time of 5, 30, 60, 180 and 300 seconds.

3.4.7 The electroless plating

The activated samples from above step were electroless plated in nickel solution, which comprised of nickel chloride, nickel sulfate, citric acid and phosphinic acid at 38 ^{o}C for 10 minutes. The metallic ions in the solution were be reduced into metallic atoms on the plastic surface. The quantity, thickness and adhesion of the nickel film on ABS surface were performed by titration method, SEM and tape test (according to ASTM D3359), respectively.

CHAPTER IV

RESULTS AND DISCUSSION

The ABS surface was cleaned to remove oil. Then the ABS surface was etched by immersing into an acidic oxidizing agent. The pore structure was formed in this step, which helped increasing the adhesive strength between the metallic coating layer and the plastic. After that, the ABS surface was analyzed by scanning electron microscopy. The etched ABS substrate was activated with metal (Co or Ni) solution at various concentrations and activation times, in order to find the optimum condition for good dispersion of the metallic particles on the plastic surface. These particles played an important role in accelerating the metallic film formation on the ABS surface in the electroless plating. The amount of the catalyst (Co or Ni) and the catalyst dispersion on ABS after immersing in the activating solution were also investigated. After that, the activated samples were electroless plated in the nickel solution. The amount, thickness and the adhesion of Ni film on ABS substrate were characterized. The results in each step are reported as follows:

4.1 The characteristic of ABS surface after etching with acidic oxidizing agent

After cleaning the ABS substrate, the surface etching was done by dipping the parts into 400 g/L of chromic/sulfuric acid, each, at 68 ^{o}C for 10 minutes to form porous surface. Then the samples were rinsed with DI water. The ABS surface characterized by scanning electron microscopy (SEM) is shown in Figure 4.1. It can be seen that the surface possessed a porous structure.

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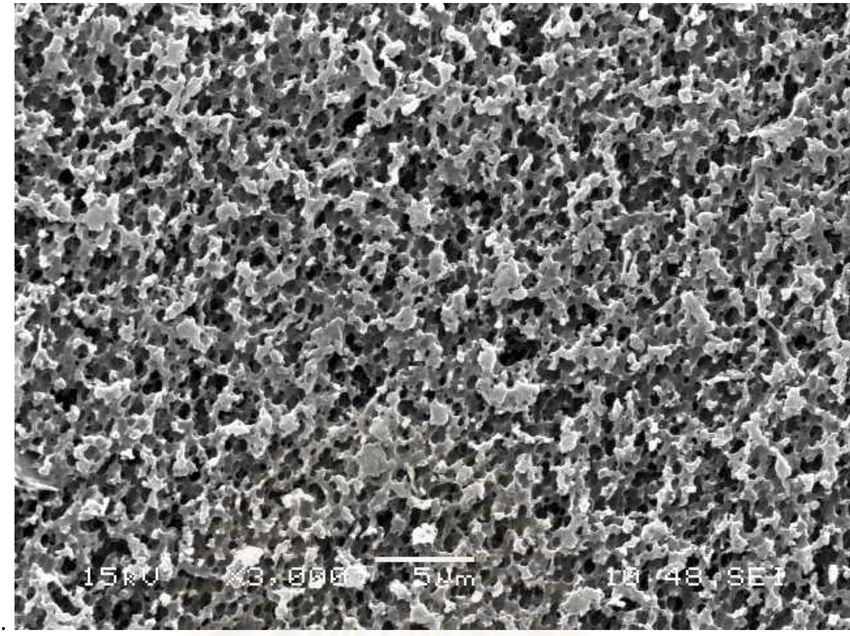

Figure 4.1 The porous surface or structure of the ABS surface after etching with chromic/sulfuric acid solution characterized by SEM.

4.2 Preparation and characterization of $[CoCl_2(en)_2]Cl$ [22,23]

The dichloro bis(ethylenediamine) cobalt (III) chloride in trans-configuration (trans-$[CoCl_2(en)_2]Cl$) was synthesized by the reaction of the cobalt(II) chloride, ethylenediamine, hydrogen peroxide and hydrochloric acid as in equation 1.

$$CoCl_2 \xrightarrow[H_2O,\ H_2O_2,\ HCl]{H_2N\text{–}CH_2CH_2\text{–}NH_2} \left[\text{trans-}CoCl_2(en)_2 \right]^+ \ Cl^- \qquad (1)$$

The synthesized catalysts were characterized by Fourier transform infrared techniques (FT-IR**).** The FT-IR spectrum of the compound is shown in Figure 4.2.

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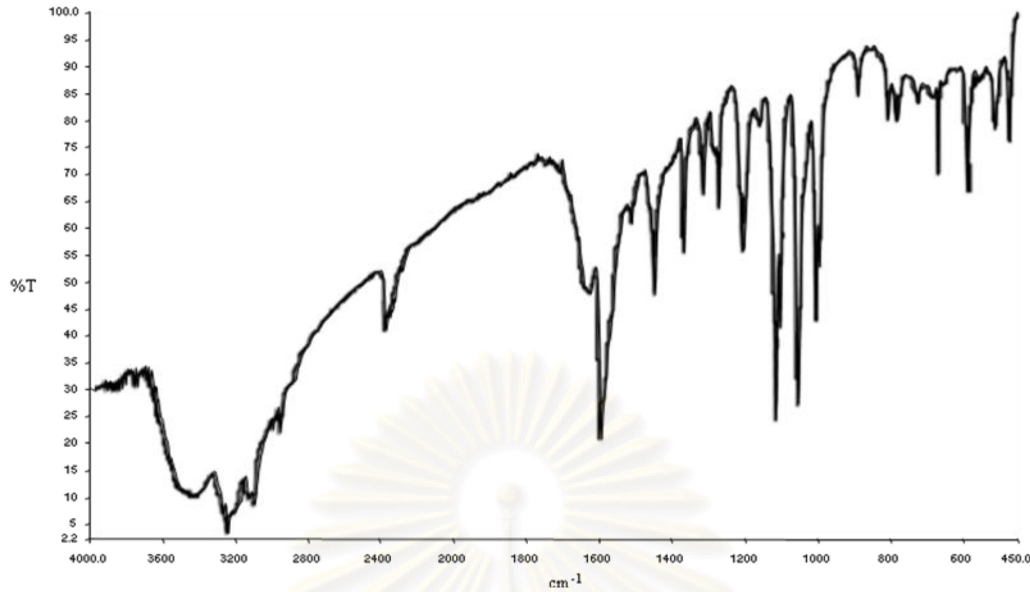

Figure 4.2 FTIR spectrum of $[CoCl_2(en)_2]Cl$.

The spectrum exhibited the characteristic absorption band of the N-H stretching vibration at 3290 cm^{-1}, the N-H bending vibration at 1620 cm^{-1} and the C-N stretching vibration at 1250-1020 cm^{-1} **[25,26].**

4.3 The amount and the dispersion of the catalyst on the ABS surface

The etched ABS samples were dipped into different catalyst namely, $CoCl_2$, $[CoCl_2(en)_2]Cl$ and $(CH_3CO_2)_2Ni$ at 25°C for 3 minutes. The amount of the catalyst on the ABS substrate were characterized by the atomic absorption spectroscopy (AAS).

Table 4.1 presents the amount of catalysts on the surface of the ABS substrate. It can be seen that, the amount of the $(CH_3CO_2)_2Ni$ on the ABS substrate was higher than $CoCl_2$ and $[CoCl_2(en)_2]Cl$ at the same concentration and he amount of the catalyst was increased with the increasing concentration of the catalyst solution.

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Table 4.1 The amount of the catalyst on the ABS substrate at various concentrations of the catalyst solution

catalyst	$(CH_3CO_2)_2Ni$			$CoCl_2$			$[CoCl_2(en)_2]Cl$		
	1 g/L	**3 g/L**	**5 g/L**	**1 g/L**	**3 g/L**	**5 g/L**	**1 g/L**	**3 g/L**	**5 g/L**
catalyst amount (ppm)	1.30	2.50	3.90	0.25	1.30	1.70	0.30	1.30	1.70

Table 4.2 display the dispersion of each sampling spot. The amount of catalyst at three points (P1, P2 and P3) on the ABS surface are quite close. This indicates good dispersion on the ABS substrate. At 1 g/L concentration of activating solution, the amount of $(CH_3CO_2)_2Ni$ at each point was higher than those using $CoCl_2$ and $[CoCl_2(en)_2]Cl$.

Table 4.2 The dispersion of the catalyst at 1 g/L catalyst solution

Catalyst	$(CH_3CO_2)_2Ni$			$CoCl_2$			$[CoCl_2(en)_2]Cl$		
	P1	**P2**	**P3**	**P1**	**P2**	**P3**	**P1**	**P2**	**P3**
% Atomic of catalyst	4.43	4.97	4.14	0.18	0.13	0.17	0.07	0.07	0.09

Table 4.3 displays the dispersion of catalyst on the ABS surface. At 3 g/L concentration of activating solution, the amount of Ni and Co at each point was higher than those using 1 g/L of activating solution.

Table 4.3 The dispersion of the catalyst at 3 g/L catalyst solution

Catalyst	$(CH_3CO_2)_2Ni$			$CoCl_2$			$[CoCl_2(en)_2]Cl$		
	P1	**P2**	**P3**	**P1**	**P2**	**P3**	**P1**	**P2**	**P3**
% Atomic of catalyst	13.07	12.79	12.07	2.18	2.10	1.97	0.34	0.35	0.45

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Table 4.4 display the dispersion of catalyst on the ABS surface. The amount of Ni at 5 g/L concentration of $(CH_3CO_2)_2Ni$ was close to that found at 3 g/L concentration of $(CH_3CO_2)_2Ni$. The amount of Co at each point was higher than those using 3 g/L concentration of $CoCl_2$ and $[CoCl_2(en)_2]Cl$. The amount of catalyst at each point was increased with the increasing concentration of the activating solution.

Table 4.4 The dispersion of the catalyst at 5 g/L catalyst solution

Catalyst	**$(CH_3CO_2)_2Ni$**			**$CoCl_2$**			**$[CoCl_2(en)_2]Cl$**		
	P1	**P2**	**P3**	**P1**	**P2**	**P3**	**P1**	**P2**	**P3**
% Atomic of catalyst	12.69	13.02	12.09	2.93	2.57	2.93	0.67	0.59	0.64

The amount of the catalyst found on the ABS surface can affect the induction of the electroless nickel plating, this result shows that $(CH_3CO_2)_2Ni$ yields the best performance in accelerating the electroless plating.

4.4 Ni metallization performed in electroless nickel bath on ABS substrate

The activated samples were electroless plated in the nickel solution, which comprised nickel chloride, nickel sulphate, citric acid and phosphinic acid at 38 ^oC for 10 minutes**.** The pH was adjusted to 9.[1] After plating the sample surface was grayish which demonstrated the adsorption of Ni on the ABS surface. The Ni amount and thickness of the plating Ni were determined. The variables that affect the Ni amount and thickness of Ni film were studied and the results are described in detail below.

4.4.1 Effect of $SnCl_2/CoCl_2$ and $SnCl_2/[CoCl_2(en)_2]Cl$ solution as the catalyst in electroless nickel plating

The etched ABS substrates were immersed in the different concentrations of $SnCl_2$ solution (0.1, 0.5 and 1 g/L) for 3 minutes at 25°C. It was found that Sn^{2+} ions were adsorbed onto the plastic surface in this step. Then the substrates were dipped in different concentrations of Co solution (1, 3 and 5 g/L) for 5, 8 and 10 minutes. Finally, the substrates were plated in the electroless nickel solution. After plating, no metallization was obtained. This indicated that $SnCl_2$ cannot reduce Co ion to Co(0).

Consequently, a new approach in activation the surface by oxidizing/reducing technique was investigated**.** The etched ABS substrate was immersed in the different oxidizing solution namely, $(CH_3CO_2)_2Ni$, $[CoCl_2(en)_2]Cl$ and $CoCl_2$ solution (1, 3 and 5 g/L) for 3 minutes. After the oxidizing step, the sample was reduced by $NaBH_4$ solution (0.1, 0.5 and 1 M) for 5 to 300 seconds. These particles were meant to accelerate or induce the metallic film formation on the ABS surface in the electroless plating step. The parameters affecting the activation were studied, and the results are described in topics 4.4.2 to 4.4.4.

4.4.2 Effect of $(CH_3CO_2)_2Ni$ solution as the catalyst in the electroless nickel plating

The ABS substrate was immersed in 1, 3 and 5g/L of $(CH_3CO_2)_2Ni$ solution for 3 minutes and dipped in 0.1, 0.5 and 1 M of $NaBH_4$ solution at room temparature for 5-300 seconds.

(1) The Ni film thickness and Ni amounts when using 1 g/L $(CH_3CO_2)_2Ni$ solution and different concentrations of $NaBH_4$ reducing solution: 0.1, 0.5 and 1 M for 5-300 seconds are presented in Figures 4.3.

In Figure 4.3 (a), for 0.1 M $NaBH_4$ reducing solution at 5 and 30 second reduction time and in Figures 4.3 (b) and (c), for 0.5 and 1 M $NaBH_4$ reducing solution at 5 second reduction time, the Ni film was not fully plated on all over the part, therefore the Ni film thickness cannot be measured.

In Figures 4.3 (a), (b) and (c), at 0.1, 0.5 and 1 M $NaBH_4$ reducing solution and 5-300 second reduction time indicate that after immersing the activated ABS substrate into the electroless nickel solution, the Ni amount of the plating Ni was increased with increasing reduction time. It was observed that at 60 second of reduction time the highest Ni amount and thickness of the Ni film was obtained.

However, Ni amount and thickness of the Ni film started to be decreased at 180 and 300 seconds due to a slight re-oxidation of metal after longer reduction time.

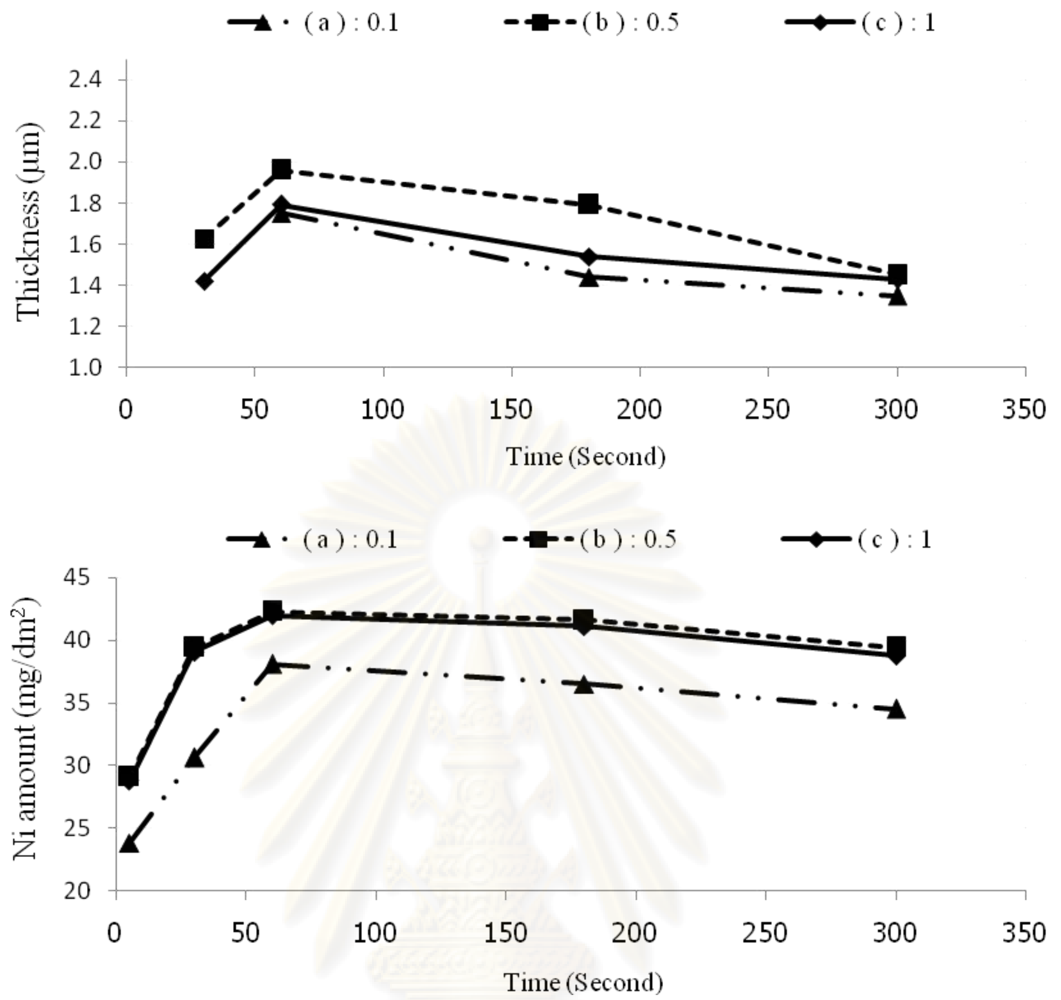

Figure 4.3 Ni film thickness and Ni amount when activated by 1 g/L $(CH_3CO_2)_2Ni$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$ (c) 1 M $NaBH_4$

(2) The Ni film thickness and Ni amounts when using 3 g/L $(CH_3CO_2)_2Ni$ solution and different concentrations of $NaBH_4$ reducing solution: 0.1, 0.5 and 1 M for 5-300 seconds are presented in Figure 4.4.

In Figures 4.4 (a), (b) and (c), for 0.1, 0.5 and 1 M $NaBH_4$ reducing solution at 5-300 second reduction time, it was observed that at 60 second reduction time the Ni film is the thickest and has highest Ni amount. However, the thickness of the Ni film and Ni amount started to be decreased due to a slight re-oxidation of metal after longer reduction time.

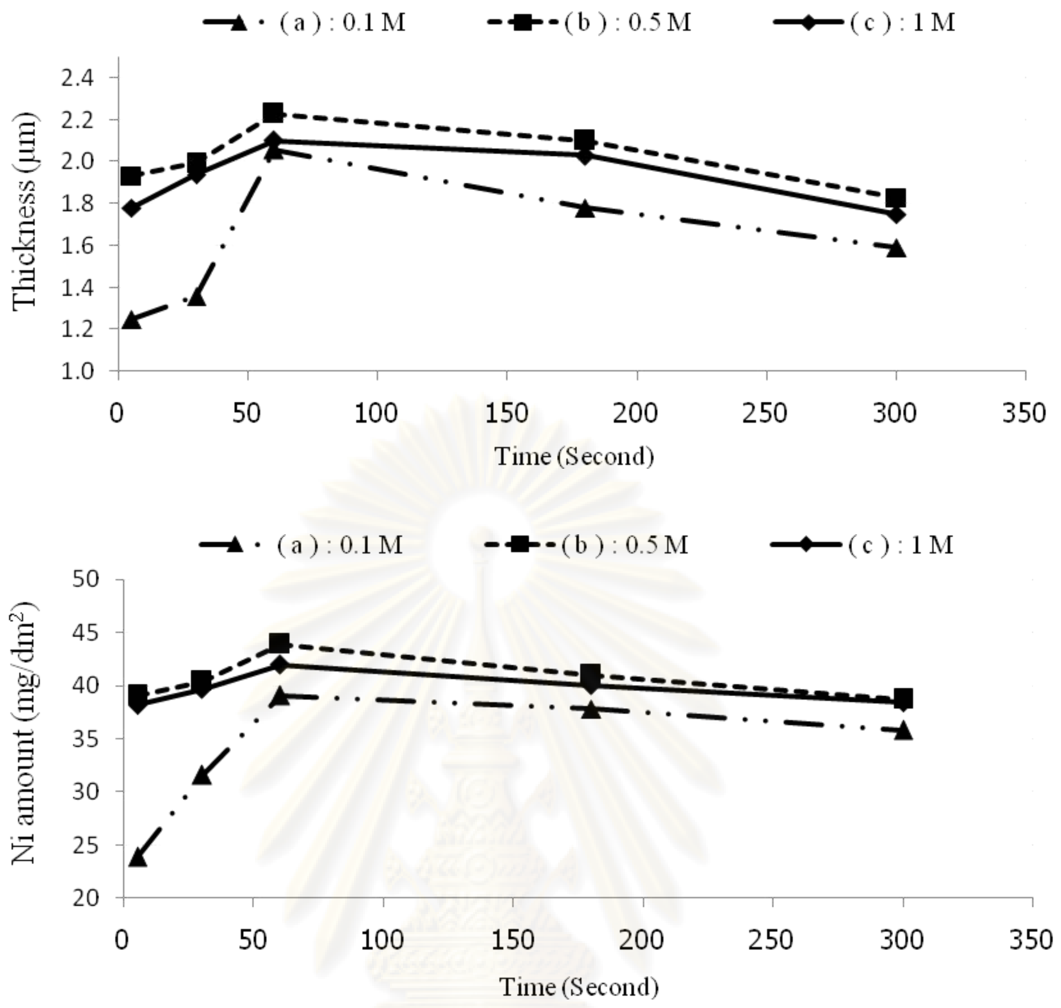

Figure 4.4 Ni film thickness and Ni amount when activated by 3 g/L $(CH_3CO_2)_2Ni$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$ (c) 1 M $NaBH_4$

(3) The Ni film thickness and Ni amounts when using 5 g/L $(CH_3CO_2)_2Ni$ solution and different concentrations of $NaBH_4$ reducing solution: 0.1, 0.5 and 1 M for 5-300 seconds are presented in Figures 4.5.

In Figures 4.5 (a), (b) and (c), it can be seen that the amount and thickness of the Ni film has similar trend to the results presented in Figures 4.4. It was observed that at 60 second of reduction time the thickest Ni film and highest Ni amount was obtained.

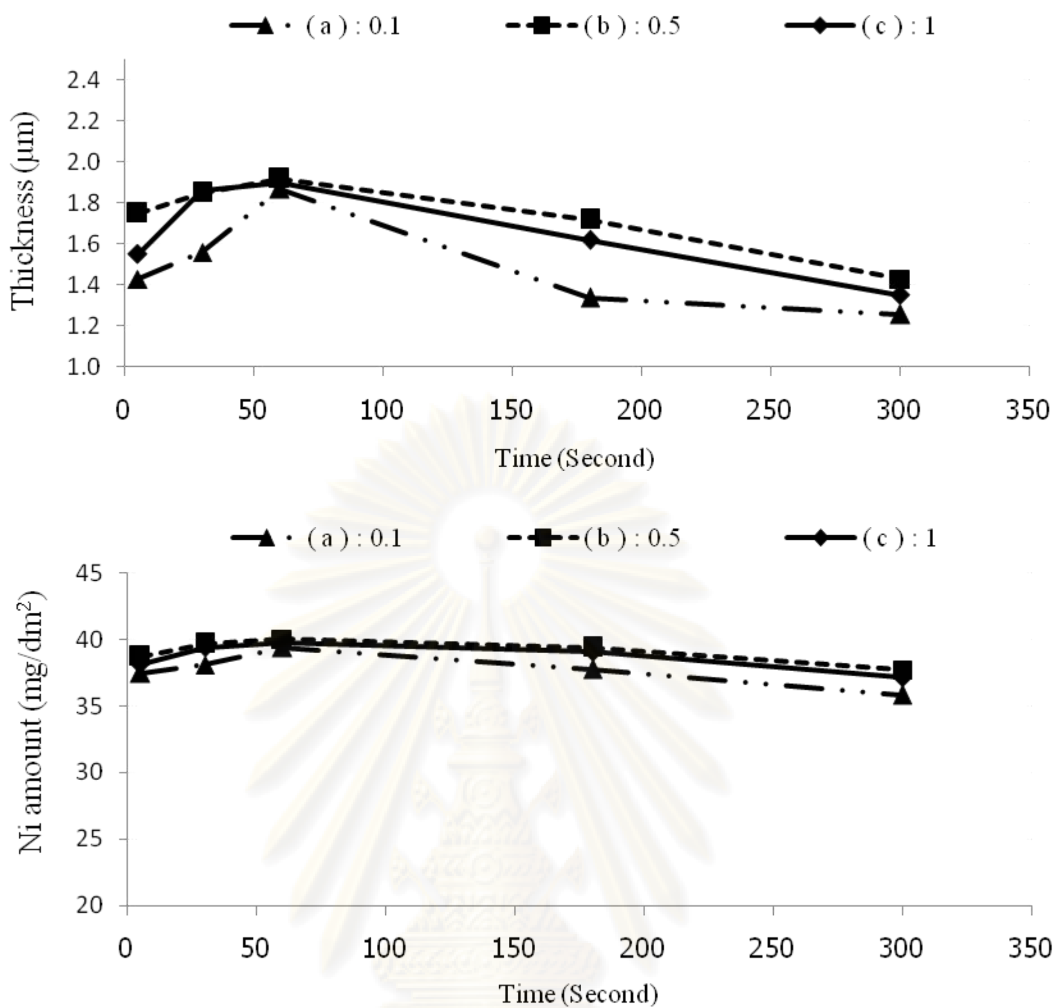

Figure 4.5 Ni film thickness and Ni amount when activated by 5 g/L $(CH_3CO_2)_2Ni$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$ (c) 1 M $NaBH_4$

4.4.3 Effect of $CoCl_2$ solution as the catalyst in the electroless nickel plating

When using $(CH_3CO_2)_2Ni$ solution as the catalyst, the plating was completed at the concentration of 3 g/L of $(CH_3CO_2)_2Ni$ solution and 0.5 M $NaBH_4$ solution. Therefore, for the next experiment using $CoCl_2$ solution, the conditions of 1 and 3 g/L of $CoCl_2$ solution and 0.1, 0.5 M $NaBH_4$ solution were used. The ABS substrate was immersed in 1 and 3 g/L of $CoCl_2$ solution for 3 minutes and dipped in 0.1 and 0.5 M of $NaBH_4$ solution at room temperature for 5-300 seconds.

(1) In Figure 4.6 (a), using 1 g/L $CoCl_2$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickness cannot be measured. Figure 4.6 (b), for 0.5 $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film was thickest at 60 second reduction time.

In Figures 4.6 (a) and (b), at 0.1 and 0.5 $NaBH_4$ reducing solution and 5-300 second reduction time. It was observed that at 60 second of reduction time the highest Ni amount was obtained. After 60 seconds a slight re-oxidation of metal occurred, resulting in decrease of the Ni amount and thickness.

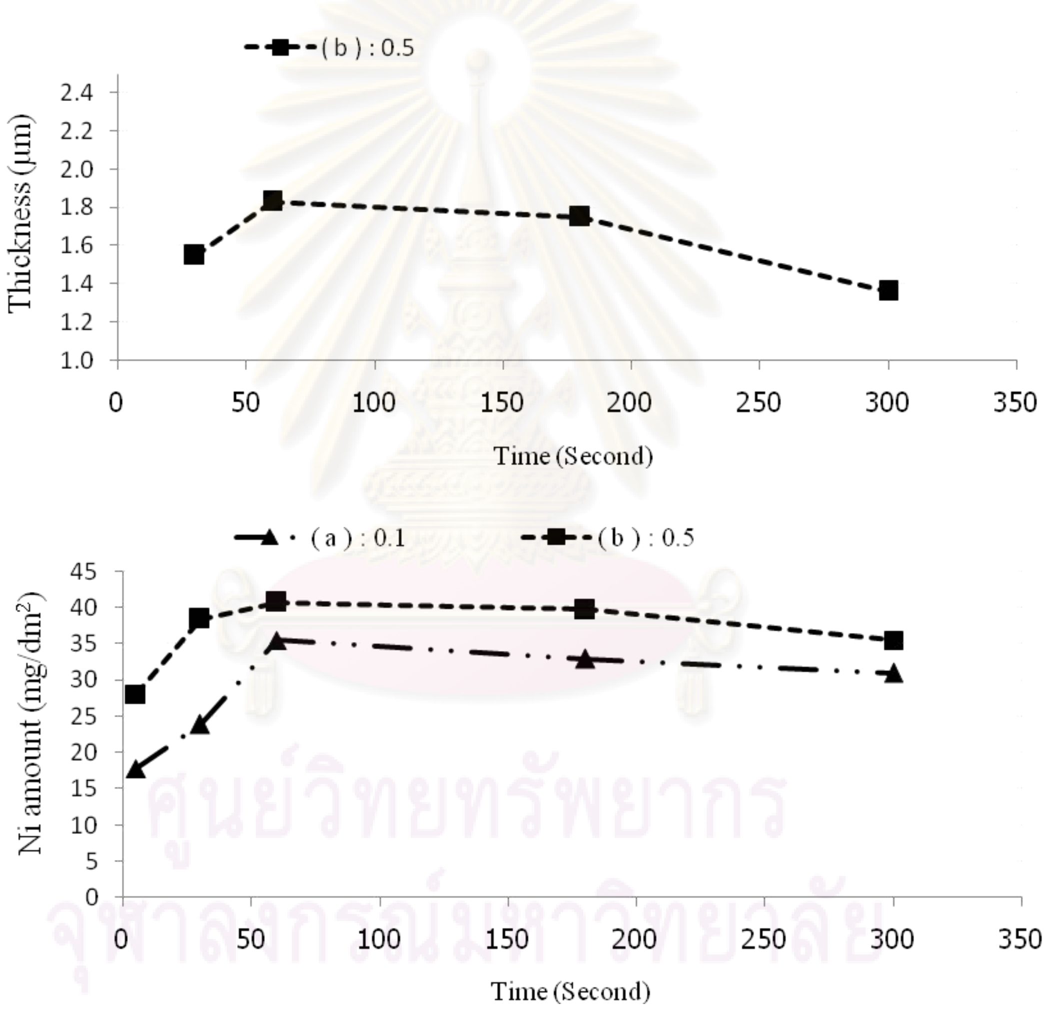

Figure 4.6 Ni film thickness and Ni amount when activated by 1 g/L $CoCl_2$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$

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(2) In Figure 4.7 (a), using 3 g/L $CoCl_2$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickness cannot be measured.

In Figure 4.7 (b), for 0.5 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film was the thickest at 60 second reduction time.

In Figures 4.7 (a) and (b), at 0.1 and 0.5 M $NaBH_4$ reducing solution at 60 second of reduction time the highest Ni amount was obtained.

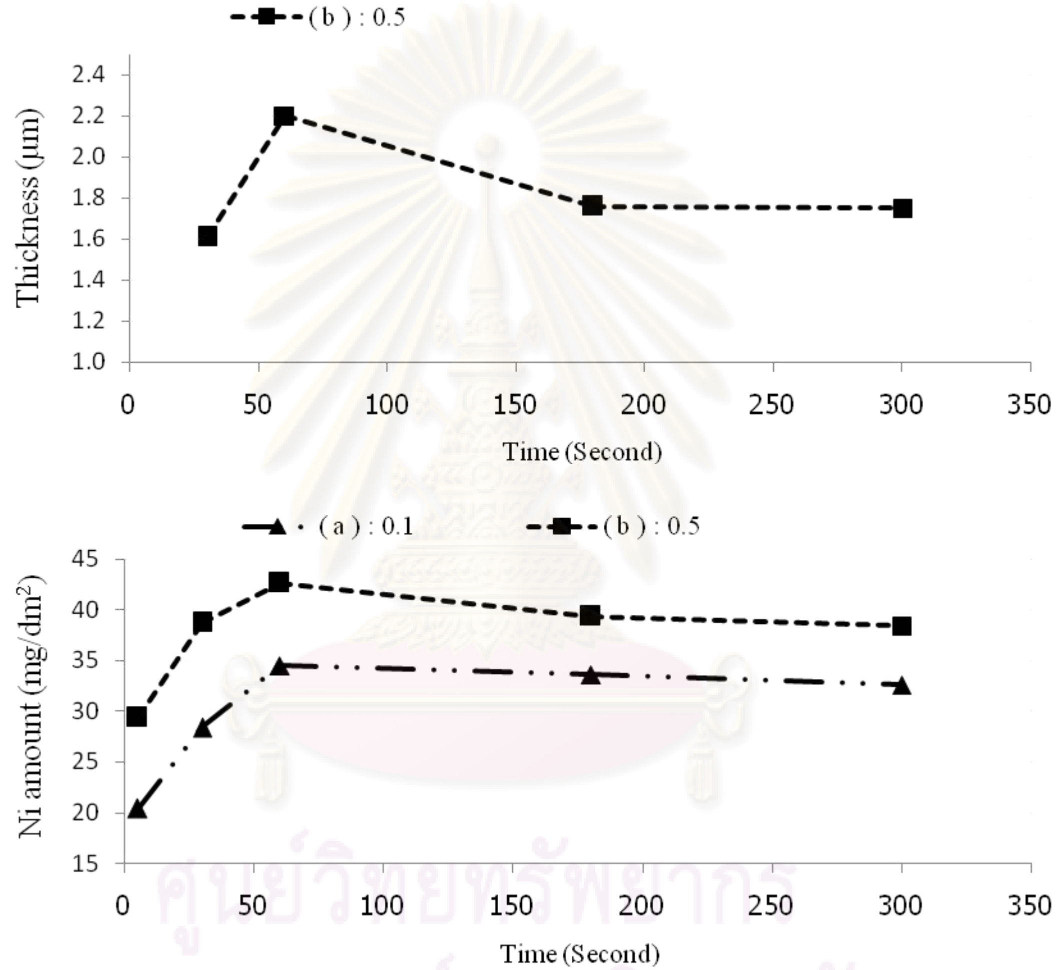

Figure 4.7 Ni film thickness and Ni amount when activated by 3 g/L $CoCl_2$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$

4.4.4 Effect of $[CoCl_2(en)_2]Cl$ solution as the catalyst in the electroless nickel plating

(1) In Figure 4.8 (a), using 1 g/L $[CoCl_2(en)_2]Cl$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickness cannot be measured. In Figure 4.8 (b), for 0.5 M $NaBH_4$ reducing solution the Ni film was thickest at 60 second reduction time.

In Figures 4.8 (a) and (b), at 0.1 and 0.5 M $NaBH_4$ reducing solution at 60 second of reduction time the highest Ni amount was obtained.

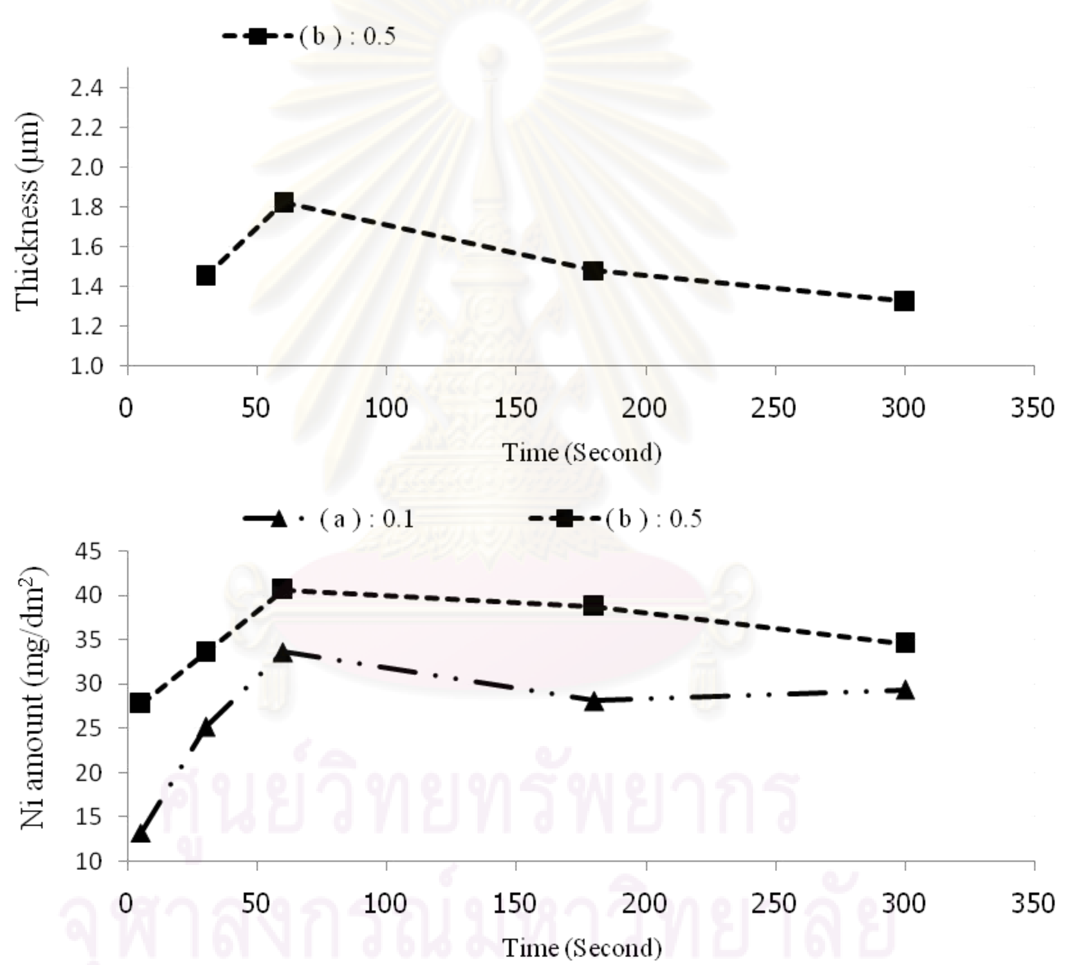

Figure 4.8 Ni film thickness and Ni amount when activated by 1 g/L $[CoCl_2(en)_2]Cl$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$

(2) In Figure 4.9 (a), using 3 g/L $[CoCl_2(en)_2]Cl$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickness cannot be measured. In Figure 4.9 (b), for 0.5 M $NaBH_4$ reducing solution the Ni film was thickest at 60 second reduction time.

In Figures 4.9 (a) and (b), the amount and thickness of Ni has similar trend to those found in Figures 4.7 (a) and (b)

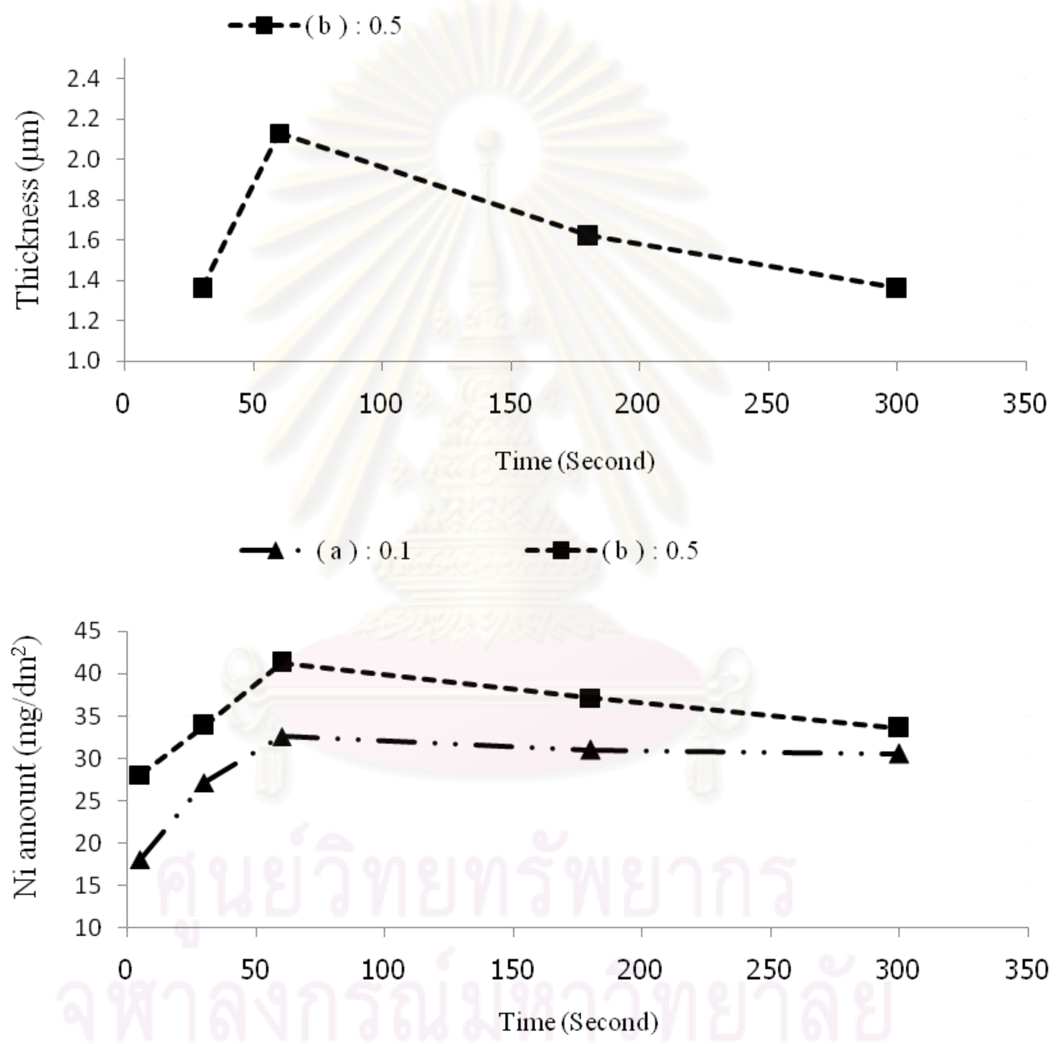

Figure 4.9 Ni film thickness and Ni amount when activated by 3 g/L $[CoCl_2(en)_2]Cl$ solution and reduced by (a) 0.1 M $NaBH_4$ (b) 0.5 M $NaBH_4$

4.4.5 Comparison of the efficiency of Ni and Co catalyst in electroless nickel plating

For 1 g/L of $CoCl_2$ or $[CoCl_2(en)_2]Cl$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film was not fully plated on all over the part, therefore the Ni film was thickness cannot be measured.

In Figure 4.10 for 1 g/L of $(CH_3CO_2)_2Ni$ and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickest at 60 second reduction time.

In Figure 4.10 the Ni amount show that $(CH_3CO_2)_2Ni$ solution was efficiently activating the surface of the ABS substrate more than $CoCl_2$ solution and $[CoCl_2(en)_2]Cl$ solution, respectively.

However, the amount and thickness of Ni started to be decreased due to a slight re-oxidation of metal after longer reduction time.

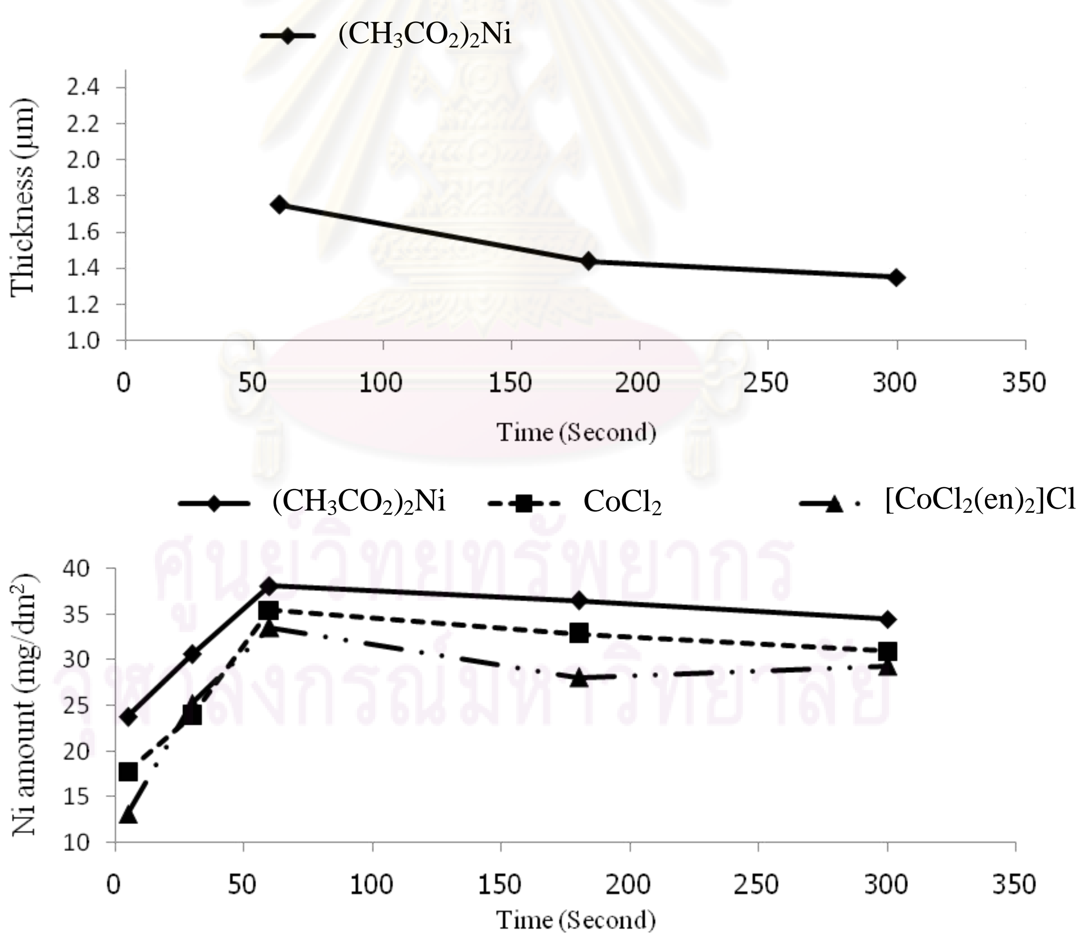

Figure 4.10 Ni film thickness and Ni amount after immersing into the electroless nickel solution when activated by (a) $(CH_3CO_2)_2Ni$ 1 g/L (b) $CoCl_2$ 1 g/L (c) $[CoCl_2(en)_2]Cl$ 1 g/L

For 3 g/L of $CoCl_2$ and $[CoCl_2(en)_2]Cl$ solution and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film thickness cannot be measured.

In Figure 4.11 for 1 g/L of $(CH_3CO_2)_2Ni$ and 0.1 M $NaBH_4$ reducing solution at 5-300 second reduction time, the Ni film was thickest at 60 second reduction time.

The results showed that $(CH_3CO_2)_2Ni$ solution was efficiently activating the surface of the ABS substrate more than $CoCl_2$ solution and $[CoCl_2(en)_2]Cl$ solution, respectively. After 60 seconds a slight re-oxidation of metal occurred, resulting in decrease of the Ni amount and thickness.

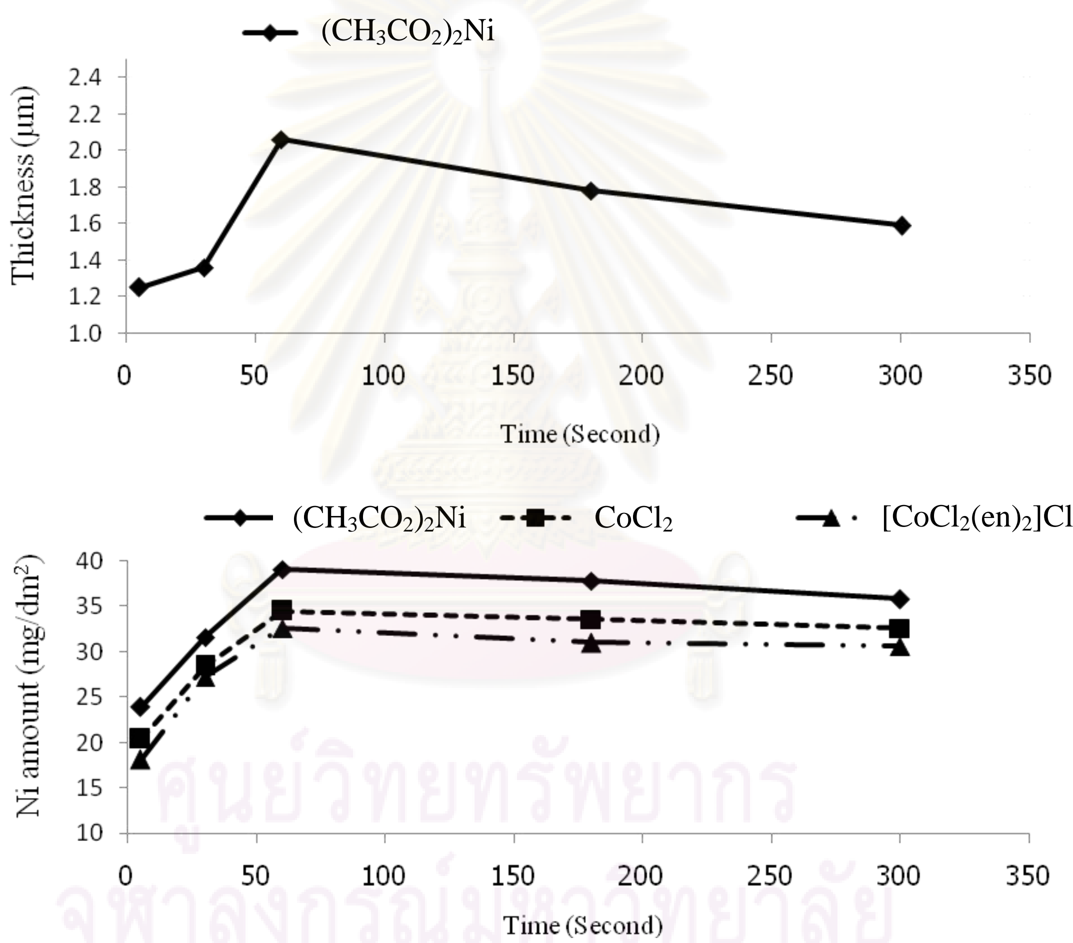

Figure 4.11 Ni film thickness and Ni amount after immersing into the electroless nickel solution when activated by (a) $(CH_3CO_2)_2Ni$ 3 g/L (b) $CoCl_2$ 3 g/L (c) $[CoCl_2(en)_2]Cl$ 3 g/L

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The comparison of Ni film thickness and Ni amount at 1 g/L of $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ solution and reduce by 0.5 M $NaBH_4$ solution at room temperature for 5-300 seconds are present in Figure 4.12

For 1 g/L of $(CH_3CO_2)_2Ni$, $CoCl_2$ or $[CoCl_2(en)_2]Cl$ solution and 0.5 M $NaBH_4$ reducing solution at 5-300 second reduction time, the results showed that $(CH_3CO_2)_2Ni$ solution as the catalyst, the amount and thickness of Ni was higher than using $CoCl_2$ solution and $[CoCl_2(en)_2]Cl$ solution, respectively.

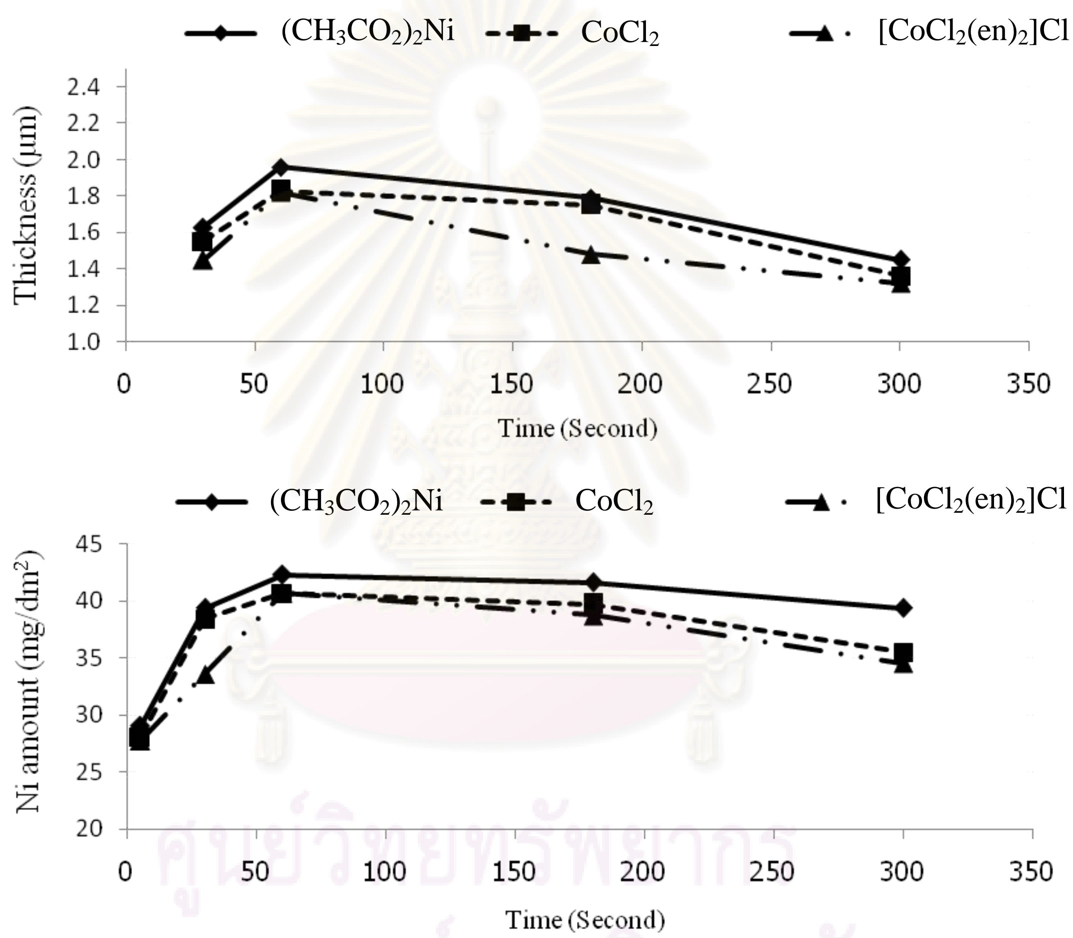

Figure 4.12 Ni film thickness and Ni amount after immersing into the electroless nickel solution when activated by (a) $(CH_3CO_2)_2Ni$ 1 g/L (b) $CoCl_2$ 1 g/L (c) $[CoCl_2(en)_2]Cl$ 1 g/L

The comparison of Ni film thickness and Ni amount at 3 g/L of $(CH_3CO_2)_2Ni$, $CoCl_2$ or $[CoCl_2(en)_2]Cl$ solution and reduce by 0.5 M $NaBH_4$ solution at room temperature for 5-300 seconds are present in Figure 4.13

In Figures 4.13 (a), (b) and (c), the amount and thickness of Ni has the same tendency as those found in Figure 4.12. When increasing the concentration of the activating solution from 1 to 3 g/L, the result showed higher amount of Ni and thicker film.

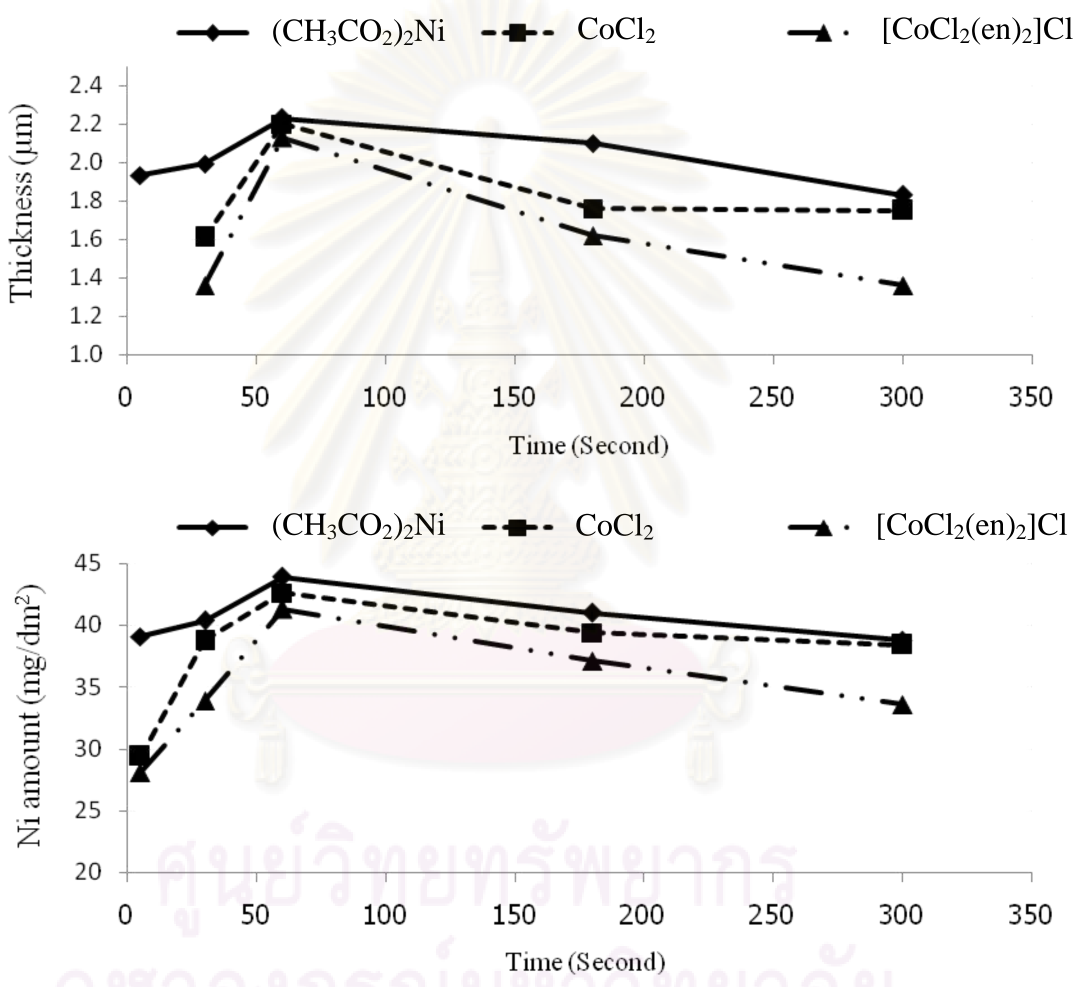

Figure 4.13 Ni film thickness and Ni amount after immersing into the electroless nickel solution when activated by (a) $(CH_3CO_2)_2Ni$ 3 g/L (b) $CoCl_2$ 3 g/L (c) $[CoCl_2(en)_2]Cl$ 3 g/L

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4.4.6 Evaluation of the adhesion of nickel films on ABS

The success of metallization depends on the substrate, catalyst formation process and plating bath nature. In this study, the Ni plating bath was supplied by Enthone company. After the electroless nickel plating, the sample surface was grayish, which indicated the adsorption of Ni film on the surface. After that, the characteristics of the coated ABS was checked by the tape test according to ASTM D3359. The results when using 1, 3 and 5 g/L $(CH_3CO_2)_2Ni$ and reduced by different concentrations of $NaBH_4$ reducing solution at room temperature for 5-300 seconds were shown in Tables 4.5-4.7.

Table 4.5 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $(CH_3CO_2)_2Ni$.

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M		Entry	$NaBH_4$: 1 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
1	5	*	6	5	*	11	5	5B
2	30	*	7	30	5B	12	30	5B
3	60	5B	8	60	5B	13	60	5B
4	180	5B	9	180	5B	14	180	5B
5	300	5B	10	300	5B	15	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

Table 4.6 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $(CH_3CO_2)_2Ni$.

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M		Entry	$NaBH_4$: 1 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
16	5	5B	21	5	5B	26	5	5B
17	30	5B	22	30	5B	27	30	5B
18	60	5B	23	60	5B	28	60	5B
19	180	5B	24	180	5B	29	180	5B
20	300	5B	25	300	5B	30	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

Table 4.7 Adhesive results of Ni film on ABS substrate at the condition of 5 g/L $(CH_3CO_2)_2Ni$.

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M		Entry	$NaBH_4$: 1 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
31	5	5B	36	5	5B	41	5	5B
32	30	5B	37	30	5B	42	30	5B
33	60	5B	38	60	5B	43	60	5B
34	180	5B	39	180	5B	44	180	5B
35	300	5B	40	300	5B	45	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

At 1 g/L of $(CH_3CO_2)_2Ni$ solution and reduced by 0.1 M $NaBH_4$ solution at 5 and 30 seconds and 0.5 M $NaBH_4$ solution at 5 seconds, the Ni film was not fully plated on all over the part, therefore the Ni film thickness cannot be measured. On the other hand, when Ni film was fully plated on the entire part, the Ni film was found to have good adhesion.

The results when using 1 and 3 g/L $CoCl_2$ or $[CoCl_2(en)_2]Cl$ and reduced by different concentrations of $NaBH_4$ reducing solution at room temperature for 5-300 seconds were shown in Tables 4.8-4.11.

Table 4.8 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $CoCl_2$

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
46	5	*	51	5	*
47	30	*	52	30	5B
48	60	*	53	60	5B
49	180	*	54	180	5B
50	300	*	55	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

Table 4.9 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $CoCl_2$

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
56	5	*	61	5	*
57	30	*	62	30	5B
58	60	*	63	60	5B
59	180	*	64	180	5B
60	300	*	65	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

Table 4.10 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $[CoCl_2(en)_2]Cl$

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
66	5	*	71	5	*
67	30	*	72	30	5B
68	60	*	73	60	5B
69	180	*	74	180	5B
70	300	*	75	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

Table 4.11 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $[CoCl_2(en)_2]Cl$

Entry	$NaBH_4$: 0.1 M		Entry	$NaBH_4$: 0.5 M	
	Reduction time(sec)	Scotch test		Reduction time(sec)	Scotch test
76	5	*	81	5	*
77	30	*	82	30	5B
78	60	*	83	60	5B
79	180	*	84	180	5B
80	300	*	85	300	5B

* Cannot be evaluated.
** Scotch® test result : (5B) None removed

At 1 and 3 g/L of $CoCl_2$ or $[CoCl_2(en)_2]Cl$ solution and reduced by 0.1 M $NaBH_4$ solution at 5-300 seconds and 0.5 M $NaBH_4$ solution at 5 seconds, the Ni film was not fully plated on all over the part, therefore the Ni film thickness cannot be measured. On the other hand, when Ni film was fully plated on the entire part, the Ni film was found to have good adhesion.

4.4.7 Surface treatment of ABS for electroless plating using Pd

The activation process is to employ the palladium catalyst sites on the substrate to initiate an oxidation of a reducing agent in an electroless plating solution. The activation method consists of a sensitizing-activation method of dipping the substrate into $SnCl_2/PdCl_2$ bath to obtain the catalyst palladium cluster.

Table 4.12 compares the prices of $PdCl_2$, $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ which are used as the catalyst for activating the ABS surface in electroless nickel plating. The etched ABS substrate was immersed in 1 g/L of oxidizing solution namely, $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ solution for 3 minutes and reduced by 0.5 M $NaBH_4$ solution at room temperature for 60 seconds. $PdCl_2$ solution was obtained from Marui Industry Thailand. The surface activation was performed by dipping the ABS substrate into $SnCl_2/PdCl_2$ solution at 28 ^oC for 3 minutes. The activated samples were electroless plated in the nickel solution at 38 ^oC for 10 minutes**.** The pH was adjusted to 9. After plating, the sample surface was grayish which demonstrated the adsorption of Ni on the ABS surface. The Ni amount and thickness of the plating Ni were determined and the results are described in detail below.

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Table 4.12 Effect of $PdCl_2$, $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ solution as the catalyst in the electroless nickel plating

Metal catalyst	Catalyst concentration	Ni film thickness (µm)	Ni amount (mg/dm^2)	Result of tape test	Cost (baht)
$PdCl_2$	6.5 ml/L	2.4	48	5B	39
$(CH_3CO_2)_2Ni$	1 g/L	2.0	42	5B	2.3
$CoCl_2$	1 g/L	1.8	40	5B	5.5
$[CoCl_2(en)_2]Cl$	1 g/L	1.8	40	5B	5.5

In Table 4.12, the results show that $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ solutions can be used as catalyst to activate the ABS surface in the electroless nickel plating as they can provide good adhesion of the Ni film. Considering about the cost of production, it was calculated that the prices of Ni or Co catalysts are much lower than that of $PdCl_2$.

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

This work has shown autocatalytically deposit Ni film on ABS surface without using the Pd conventional catalyst. To obtained thin layer of catalyst site, the catalyst must be deposited on the surface and reduced the corresponding metal(+2) ions to metal(0) using $NaBH_4$.

The activation process is to employ the Ni and Co catalyst sites on the substrate to initiate an oxidation of a reducing agent in an electroless plating solution. The parameters affecting the surface activation were studied. The results showed good catalyst property of $(CH_3CO_2)_2Ni$, since Ni(0) could provide better autocatalytic plating in the electroless plating compared with those from $CoCl_2$ and $[CoCl_2(en)_2]Cl$. When the concentration of the catalyst was increased, the Ni film on the substrate was thicker, due to increasing plating of Ni .

When increasing the concentration of the $NaBH_4$ reducing agent solution , the reduction of metal ion to metal(0) was higher. These metal(0) sites on the ABS surface act as the catalyst for electroless nickel plating. When increasing the reduction time, the effectiveness of the reduction of metal ions to metals(0) increased. At 60 seconds of reduction time, the Ni amount and thickness were the highest.

Among various catalysts tested in this work: $(CH_3CO_2)_2Ni$, $CoCl_2$ and $[CoCl_2(en)_2]Cl$ in electroless nickel plating, the results indicated that the $(CH_3CO_2)_2Ni$ solution gave the highest amount and thickness of the plated Ni film.

The results of the adhesion of the nickel films on ABS show that when Ni film was fully plated on the entire part. The Ni film has good adhesion with the substrate.

5.2 Suggestion for the future work

Future work should be the study of characteristic of Ni film plating between using low phosphorous and high phosphorous Ni plating baths because internal stresses in the Ni film strongly depend on the film composition therefore on the Ni plating bath used.

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APPENDICES

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Appendix A

Table A-1 The dispersion of the Ni catalyst on the ABS substrate at various concentrations of the activating solution.

Position	% Atomic of Ni		
	$(CH_3CO_2)_2Ni$ 1 g/L	$(CH_3CO_2)_2Ni$ 3 g/L	$(CH_3CO_2)_2Ni$ 5 g/L
1	4.43	13.07	12.69
2	4.97	12.79	13.02
3	4.14	12.07	12.09

Table A-2 The dispersion of the Co catalyst on the ABS substrate at various concentrations of the activating solution.

Position	% Atomic of Co		
	$CoCl_2$ 1 g/L	$CoCl_2$ 3 g/L	$CoCl_2$ 5 g/L
1	0.18	2.18	2.93
2	0.13	2.10	2.57
3	0.17	1.97	2.93

Table A-3 The dispersion of the Co catalyst on the ABS substrate at various concentrations of the activating solution.

Position	% Atomic of Co		
	$[CoCl_2(en)_2]Cl$ 1 g/L	$[CoCl_2(en)_2]Cl$ 3 g/L	$[CoCl_2(en)_2]Cl$ 5 g/L
1	0.07	0.34	0.67
2	0.07	0.35	0.59
3	0.09	0.45	0.64

Appendix B

EDTA - titration of nickel

Procedure.

1. Put the coated ABS into the flask.
2. Add 30 mL DI water to the sample and 2 g of ammonium persulfate.
3. The flask was placed on the heater until grayish color disappear.
4. Add 100 mL DI water and boiling for 30 minutes.
5. Cool the solution to room temperature.
6. Add 5 mL of ammonium hydroxide to obtain pH around 8 and add murexide indicator.
7. Titrate with 0.05 M EDTA until violet color as end point.

$$Ni^{2+} + EDTA^{4-} \rightarrow Ni(EDTA)^{2-}$$

Amount of nickel (mg/dm^2) = V x 2.93/0.45

: V = ml of EDTA

Table B-1 Ni film thickness and Ni amount obtained from different concentration of $(CH_3CO_2)_2Ni$ solution after immersed into the electroless nickel solution of Ni(+2) ion at different concentration of $NaBH_4$ reducing agent and reduction time

$(CH_3CO_2)_2Ni$ (g/L.)	$NaBH_4$ (Molar)	Reduction time (second)	Ni film thickness (µm)	Ni amount (mg/dm^2)
1	0.1	5	-	23
		30	-	30
		60	1.7	38
		180	1.4	36
		300	1.3	34
	0.5	5	-	29
		30	1.6	39
		60	2.0	42
		180	1.8	41
		300	1.4	39
	1	5	-	28
		30	1.4	39
		60	1.8	42
		180	1.5	41
		300	1.4	38
3	0.1	5	1.2	23
		30	1.4	31
		60	2.1	39
		180	1.8	37
		300	1.6	35
	0.5	5	1.9	39
		30	2.0	40
		60	2.2	43
		180	2.1	41
		300	1.8	38
	1	5	1.8	38
		30	1.9	39
		60	2.1	42
		180	2.0	40
		300	1.7	38

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Table B-1 (cont.) Ni film thickness and Ni amount obtained from different concentration of $(CH_3CO_2)_2Ni$ solution after immersed into the electroless nickel solution of Ni(+2) ion at different concentration of $NaBH_4$ reducing agent and reduction time

$(CH_3CO_2)_2Ni$ (g/L.)	$NaBH_4$ (Molar)	Reduction time (second)	Ni film thickness (µm)	Ni amount (mg/dm^2)
5	0.1	5	1.4	37
		30	1.6	38
		60	1.9	39
		180	1.3	37
		300	1.3	35
	0.5	5	1.7	38
		30	1.8	39
		60	1.9	40
		180	1.7	39
		300	1.4	37
	1	5	1.5	38
		30	1.9	39
		60	1.9	39
		180	1.6	39
		300	1.3	37

Table B-2 Ni film thickness and Ni amount obtained from different concentration of $CoCl_2$ solution after immersed into the electroless nickel solution of Ni(+2) ion at different concentration of $NaBH_4$ reducing agent and reduction time

$CoCl_2$ (g/L.)	**$NaBH_4$ (Molar)**	**Reduction time (second)**	**Ni film thickness (μm)**	**Ni amount (mg/dm^2)**
1	0.1	5	-	17
		30	-	23
		60	-	35
		180	-	32
		300	-	31
	0.5	5	-	28
		30	1.5	38
		60	1.8	40
		180	1.7	39
		300	1.4	35
3	0.1	5	-	20
		30	-	28
		60	-	34
		180	-	33
		300	-	32
	0.5	5	-	29
		30	1.6	38
		60	2.2	42
		180	1.8	39
		300	1.7	38

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Table B-3 Ni film thickness and Ni amount obtained from different concentration of $[CoCl_2(en)_2]Cl$ solution after immersed into the electroless nickel solution of Ni(+2) ion at different concentration of $NaBH_4$ reducing agent and reduction time

$[CoCl_2(en)_2]Cl$ (g/L.)	**$NaBH_4$ (Molar)**	**Reduction time (second)**	**Ni film thickness (µm)**	**Ni amount (mg/dm^2)**
1	0.1	5	-	13
		30	-	25
		60	-	33
		180	-	28
		300	-	29
	0.5	5	-	27
		30	1.4	33
		60	1.8	40
		180	1.5	38
		300	1.3	34
3	0.1	5	-	18
		30	-	27
		60	-	32
		180	-	31
		300	-	30
	0.5	5	-	28
		30	1.3	33
		60	2.1	41
		180	1.6	37
		300	1.4	33

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Appendix C

Adhesion test by Scott® tape test (ASTM D3359) [16]

Procedure

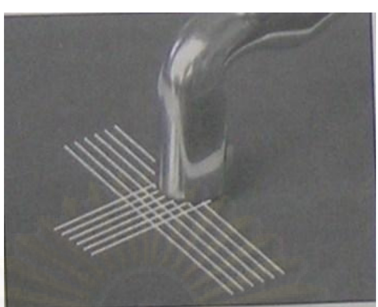

Figure C-1 second cut

1. Place the cutting tool on the sample. Gently press down and pull the tool towards yourself in one steady movement for 20 mm to create a series of parallel cuts. A sufficient pressure was required to ensure that the sample was cut right through the coating to the next layer of coating, or to the substrate. Then, place the cutting tool on the sample at 90° to the first cut and repeat the pulled-cutting to make a lattice pattern on the coating as presented in Figure C-1.

Figure C-2 Apply tape

2. Brush the area to remove debris. And place the adhesive tape over the center of the lattice, using finger or a pencil eraser to smoth the tape to the sample, as shown in Figure C-2.

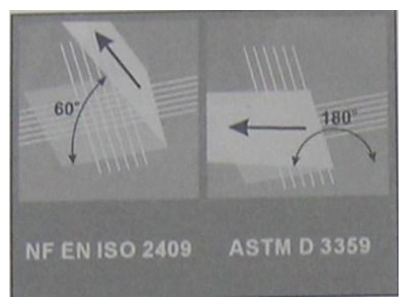

Figure C-3 Remove tape at 60^0 or 180^0

3. Remove the tape by pulling in a single smooth action at the angle of 60° or 180° as shown in Figure C-3

Table C-1 Standard ASTM D3359 [16]

Classification	% of Area removed	Surface of Cross-cut area from which flaking has occurred for 6 parrallel cuts & adhesion range by %
5B	0 % None	
4B	Less than 5 %	
3B	5 - 15 %	
2B	15 - 35 %	
1B	35 - 65 %	
0B	Greater than 65 %	

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Table C-2 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $(CH_3CO_2)_2Ni$ and 0.1 M $NaBH_4$ solution

$NaBH_4$: 0.1 M		
Reduction time (sec.)	Before	After
5	*	*
30	*	*
60		
180		
300		

* (cannot be measured)

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Table C-3 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $(CH_3CO_2)_2Ni$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

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Table C-4 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $(CH_3CO_2)_2Ni$ and 1 M $NaBH_4$ solution

$NaBH_4$: 1 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

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Table C-5 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $(CH_3CO_2)_2Ni$ and 0.1 M $NaBH_4$ solution

$NaBH_4$: 0.1 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

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Table C-6 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $(CH_3CO_2)_2Ni$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

Table C-7 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $(CH_3CO_2)_2Ni$ and 1 M $NaBH_4$ solution

$NaBH_4$: 1 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

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Table C-8 Adhesive results of Ni film on ABS substrate at the condition of 5 g/L $(CH_3CO_2)_2Ni$ and 0.1 M $NaBH_4$ solution

$NaBH_4$: 0.1 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

Table C-9 Adhesive results of Ni film on ABS substrate at the condition of 5 g/L $(CH_3CO_2)_2Ni$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

Table C-10 Adhesive results of Ni film on ABS substrate at the condition of 5 g/L $(CH_3CO_2)_2Ni$ and 1 M $NaBH_4$ solution

$NaBH_4$: 1 M		
Reduction time (sec.)	Before	After
5		
30		
60		
180		
300		

Table C-11 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $CoCl_2$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

Table C-12 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $CoCl_2$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

Table C-13 Adhesive results of Ni film on ABS substrate at the condition of 1 g/L $[CoCl_2(en)_2]Cl$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

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Table C-14 Adhesive results of Ni film on ABS substrate at the condition of 3 g/L $[CoCl_2(en)_2]Cl$ and 0.5 M $NaBH_4$ solution

$NaBH_4$: 0.5 M		
Reduction time (sec.)	Before	After
5	*	*
30		
60		
180		
300		

* (cannot be measured)

VITA

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