**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# DEVELOPMENT OF CHROME-FREE ETCHING FOR ELECTROLESS COATING OF POLYMERIC MATERIALS

**M.Sc. THESIS**

**Mehtap ARSLAN**

**Department of Metallurgical and Materials Engineering**

**Production Metallurgy and Technologies Engineering Programme**

**DECEMBER 2019**

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# DEVELOPMENT OF CHROME-FREE ETCHING FOR ELECTROLESS COATING OF POLYMERIC MATERIALS

**M.Sc. THESIS**

**Mehtap Arslan**
**(506171228)**

**Department of Metallurgical and Materials Engineering**

**Production Metallurgy and Technologies Engineering Programme**

**Thesis Advisor: Prof. Dr. İ. Servet TİMUR**

**DECEMBER 2019**

**ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# POLİMERİK MALZEMELERİN AKIMSIZ KAPLANMASINDA KROMİK ASİTE ALTERNATİF DAĞLAYICI GELİŞTİRİLİMESİ

**YÜKSEK LİSANS TEZİ**

**Mehtap Arslan**
**(506171228)**

**Metalurji ve Malzeme Mühendisliği Anabilim Dalı**

**Üretim Metalurjisi ve Teknolojileri Mühendisliği Programı**

**Tez Danışmanı: Prof. Dr. İ. Servet TİMUR**

**ARALIK 2019**

Mehtap Arslan, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student 506171228, successfully defended the thesis entitled "DEVELOPMENT OF CHROME-FREE ETCHING FOR POLYMERIC MATERIALS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

**Thesis Advisor :** **Prof. Dr. Servet İ. TİMUR** .............................
Istanbul Technical University

**Jury Members:** **Prof. Dr. Mustafa K. ÜRGEN** ............................
Istanbul Technical University

**Asst. Prof. Hatice Kübra AKBEN** ...........................
Gedik University

**Date of Submission : 15 November 2019**
**Date of Defense : 11 December 2019**

***To my all supporters, family and friends,***

# FOREWORD

First of all, I would like to serve my special thanks to my supervisor Prof. Dr. Servet Timur for his excellent guidance and support during my thesis studies. In addition, his precious knowledge shares, his experiences in science and his human and moral values, which I take as an example for my own attitude to life, gave me a support to finish this thesis.

I also want to thank to Prof. Dr. Mustafa Kamil Ürgen for his supports and helps in solving of problems, which I encounter during my experimental trials and sharing his magnificent knowledge.

A very special thanks to Assoc. Prof. Dr. Güldem Kartal Şireli for her support both in academic and real life. In addition, in laboratorty works, the team mates are very important and at this point, I would like to thank my friend Research Assistant Oğuz Kağan Coşkun for his supports. Also, I want to give my thanks to MSc. Yasin Kılıç for his precious academic sharings and technical supports and TORUN Innovation Center for their moral and material support.

I thank to AutoTech and Ecoplus companies for the materials they provided and my friend Nazlı Ersan in this manner.

Also, I want to thank to İTÜ BAP office for the contribution to my thesis with a project number of MYL-2018-41830.

I would like to thank to my dear friends Merve Seyyitoğlu, Yasemin Bahadır, and Esra Tanısalı for showing me that becoming a sister does not require blood connection.

And the most importantly, I want to thank to my family especially my mother Tülay Arslan .Their presence and support made me who am I, without them it would be impossible to reach this point.

A physicist Wolfgang Pauli said, **“*God created matter; surfaces were invented by devil.*”.** People who are dealing with the surface of the materials would understand what he means by this sentence and so do I. It was a difficult period for me and thank you for all who support me during this period.

December 2019 Mehtap ARSLAN

Metallurgical and Materials Enginneer

## TABLE OF CONTENTS

**Page**

## ABBREVIASIONS AND SYMBOLS

**ABS** : Akrilonitril Bütadien Stiren
**ELP** : Electroless Plating
**PA** : Polyamid
**PC** : Polycarbonate
**AAS** : Atomic Absoption Spectroscopy

## LIST OF TABLES

# LIST OF FIGURES

**Page**

# DEVELOPMENT OF CHROME-FREE ETCHING FOR THE ELECTROLESS COATING OF POLIMERIC MATERIALS

## SUMMARY

Coating process is a metallurgical surface development process that is used to improve the mechanical, physical and chemical properties of the materials, and shows the necessity for decorative or non-decorative (functional) reasons for every produced material. There are many types of coating available, and among all, electroless coating plays a key role especially in automative industry which is a remarkable sector.

In history, only metallic surfaces could have been coating, thereafter non-metalic surfaces such as ceramic and polymeric ones wanted to be coated. However, in order to apply electroplating on these surfaces, it is neccesary for substrate materials to have conductivity. This situation has led to development of electroless coating method to give non-conductive surfaces an opportunity for coating. In electroless coating, it is subjected to modify the ceramic or polimeric surfaces with metallic coating without using electical current. Depending on the application area, the materials whose surface are gained conductivity are exposed to electroplating to increase the thickness of the metallic film on them and take the final product shape.

In the content of this thesis, polymeric materias were selected as the substrate material and during the period, different polymer types such as ABS, PA and PC were studied. Electroless coating requires precision in pre-treatments before immersing the substrate materials into the coating bath. Non-conductive surfaces are required to etch, namely, it is necessary to distort the material surface in order to create reactive micro sites for further steps. The polymeric substrates were initially applied concentrated chromic acid solution using in industry very commonly for that purpose. Chromic acid is a chemical having extremely harmful nature for both environment and human health. Beside its carcinogenic effects, it can be only used for ABS type polymeric materials. For this reason, in theory electroless coating is solely applied for ABS type polymer.

This thesis involves the use of various organic chemicals as an alternative to chromic acid and the new compositions to be developed. After optimizing all the parameters in traditional method, new researches were conducted. The alternative method was studied and several organic solutions were tried. Each solution was used to etch the surface of the ABS type polymer and both as-etched and etched surfaces were characterized. After etching step, sensitization and activation were followed. In sensitization, $SnCl_2$ was used and Sn ions were adsorbed to holes that were created during etching. By using $PdCl_2$ solutions, the activation step was conducted and Pd ions give reaction with Sn ions. After this reaction, Pd was adsorbed into created holes and catalaytic sites were formed as places where the coating reaction takes place.

During and after experimental studies the necessary characterization methods were applied to check the physical and the mechanical poperties of the final product. At the end of the thesis, metal coated polymeric materials having the same physical properties with the materials prepared by traditional method in industy, were obtained without being exposed to the hazards of the chromic acid.

# POLİMERİK MALZEMELERİN AKIMSIZ KAPLANMASINDA KROMİK ASİTE ALTERNADİF DAĞLAYIILARIN GELİŞTİRİLMESİ

## ÖZET

Kaplama prosesi; her üretilen malzeme için dekoratif veya dekoratif olmayan sebeplerle gereklilik gösteren metalurjik bir yüzey geliştirme işlemidir. Birçok uygulama alanında kaplama uygulaması ile servis ömrü uzatılmış malzemeler kullanılmaktadır. Bu bağlamda kaplama uygulamasıyla, malzemelerin mekanik, fiziksel ve kimyasal özellikleri iyileştirilmektedir. Günümüzde birçok kaplama yöntemi kullanılmakta olup aralarından akımsız kaplama endüstrideki önemini katlayarak arttırmaktadır.

Kaplama tarihine bakılacak olunursa başlangıçta sadece metalik yüzeyler elektrolitik kaplama ile kaplanıyorken, akabinde seramik ve polimer gibi yüzeylere de kaplama prosesi uygulanmak istenmiştir. Fakat elektrolitik kaplama yapılabilmesi için altlık olarak kullanılacak malzemenin iletken olması şarttır. Bu durum elektrolitik kaplamaya uygun polimer ve seramik yüzeylerin hazırlanması için akımsız kaplama yönteminin gelişmesine ön ayak olmuştur. Akımsız kaplamada çözelti içine ilave edilmiş redüktan katkısı ile aktive edilmiş polimer ve seramik yüzeylerin metalik kaplanması amaçlanmaktadır. Akımsız kaplama ile yüzeyleri iletken hale getirilen malzemeler, uygulama alanına bağlı olarak elektrolitik kaplama işlemiyle üzerlerindeki kaplama kalınlığı arttırılarak nihai halini alırlar.

Bu tez kapsamında endüstriyel olarak en yaygın kullanım alanına sahip polimerik malzemeler altlık malzeme olarak seçilmiş ve süreç boyunca başta ABS olmak üzere PA ve PC gibi farklı polimer çeşitleri ile çalışılmıştır. Malzemelere ilk olarak sanayide yaygın olarak kullanılan konsantre kromik asit çözeltisi kullanılarak ön işlem uygulanmıştır. Sonrasında ise dağlanmış yüzey ilk olarak asidik kalay klorür çözeltisi kullanılarak sensitizasyon uygulanmış, akabinde asidik paladyum klorür çözeltisine maruz bırakılmıştır. Bu işlem sonrasında yüzeyde ki hatalı noktalarda adsorbe olan Pd atomları sayesinde iletken olmayan polimer yüzey katalitik hale dönüştürülmüştür. Sonrasında yüzey ön işlemi bitmiş malzemeler akımsız Ni kaplama işlemine tabi tutulmuştur.

Yüzey ön işlemleri sırasında, kromik asitin kullanım amacı, polimer yüzeyinde boşluklar ve hatalar oluşturup uygulanacak kaplama prosesi için aktif bölgeler yaratmaktır. Ancak kromik asitle yapılan bu işleme çoğunlukla doğası gereği ABS tipi polimerin yeterli cevap verdiği bilinmektedir. ABS tipi polimer yapısında bulundurduğu aktif butadiyen grubu sayesinde kromik asitle tepkime vermektedir. Sonuç olarak bütadiyen grubu reaksiyon sonrası yapıyı terk eder ve geride yüzeyde mkroskobik boşluklar bırakır. Bu boşluklara daha sonrasında Pd atomları adsorbe olup yüzeyi otokatalitik bir tepkime için yüzey hazır hale getiriler. Bilindiği üzere Cr (VI) kanserojen

olup, insan sağlığına ve çevreye son derece zararlı ve günümüzde kesinlikle alternatifine ihtiyaç duyulan bir kimyasaldır.

Tez kapsamında yapılmış olan deneylerin ikinci bölümünde, kromik aside alternatif bir kimyasal arama yoluna gidilmiş ve buna bağlı olarak, öncelikle ABS ile etkileşimi olan inorganik ve organik kimyasallar belirlenmiştir. Seçim aşamasında, çalışılmak istenilen kimyasalların kanserojen olmaması, insan sağlığını ve çevreyi tehdit etmemesi temel kriter olarak kullanılmıştır. Malzeme seçim işlemi tamamlandıktan sonra, kullanılacak polimerik numunenin, her bir kimyasal içerisinde yüzey dağlama deneyleri yapılmıştır. Ön deneysel çalışmalarda belirlenmiş çok sayıda kimyasal içerisinden seöilen amonyum karbonat, metil asetat ve hidrojen peroksit çözeltileri tez kapsamında kullanılmıştır. Seçilen organik ve inorganik reaktifler öncelikle ABS üzerinde denenmiş olup sonrasında PC ve PA üzerinde de çalışılmıştır.
Dağlama işlemi sonrasında yüzey karakterizasyonu optik mikroskop ve 3D optik profilometre, SEM kullanılarak yüzey pürürüzlülüğü hakkında hem niteliksel hem de niceliksel olarak veri elde edilmiştir.

Dağlanmış yani boşluk veya hata oluşturulmuş yüzeyleri, aktif hale geçirmek amacıyla, kalay klorür ve paladyum klorür çözeltileri kullanılıp, akımsız kaplama için uygun yüzeyler elde edilmiştir. Sensitizasyon ve aktivasyon işlemleri iki kademede yapılmış olup numuneler çözeltilere ayrı ayrı daldırılmıştır. Endüstride ise bu işlem yaygın olarak tek basamak halinde uygulanıyor olup, numunelerin kalay klorür ve paladyum klorürün kolloidal partiküllerinden oluşan çözeltisine daldırılması şeklinde yapılmaktadır. Bu tez çalışmasında, bütün bu yüzey hazırlama ön işlemlerinden sonra, akımsız kaplama banyosu olarak AutoTech adlı firmadan alınan ticari bir banyo kullanılmış ve akımsız nikel kaplama işlemi uygulanmıştır. Bu işlem ile birlikte malzeme yüzeyinde ince metalik bir film oluşturulmuştur. Elde edilmiş olan metallik film sayesinde bazı uygulamalarda direct kullanıma uygun iken, ihtiyaç duyulan endüstriyel uygulamalar için de malzeme yüzeyi elektrik akımını iletebileceği için akımlı kaplama için hazır hale getirilmiştir.

Elde edilen nikel kaplamaların renk ve parlaklık ölçümleri gerçekleştirilmiştir. Parlaklık seviyesinin belirlenmesinde kaplanmş yüzey önüne sabit mesafe ve açıda maket bir uçak yerleştirilerek fotoğraf çekimi ve elde edilen görüntü derinliğine bakılarak kaplamaların parlaklığı kendi içinde karşılaştırmalı olarak sınıflandırılmıştır. Tezin ilerleyen süreçlerinde optimize edilmiş dağlayıcı kullanarak mat ve saydam kaplama elde etmek için deneyler sürdürülmüştür. Bu bağlamda mat kaplama yapılabilmesi için numune yüzeyinde mekanik işlemlerle yüzey modifikasyonu sağlanmıştır, yüzey pürüzlendirmede kumlama işlemi tercih edilmiştir. Yüzeyn kontrolsüz aşınmaması ve elde edilen kadife görünüm için kumlama malzemesi olarak sertlik değeri düşük ve küresel tanecik yapısına sahip malzme kullanılmıştır. Kumlama işleminden sonra deneysel prosedür aynı şekilde uygulanmış ve sonuç olarak numune yüzeylerinde mat, kadife görünümlü özel kaplamalar elde edilmiştir.

Saydam kaplamalar; mevcut olan numunelerin yüzey özellikleri gereği sadece PC numunelere uygulanmıştır. Deneysel çalışmalarda nötralizasyon işlemi yapılmaksızın uygulamada başarı sağlamıştır. Bu koşullarda gerçekleştirilen kaplamalar hem parlak olup hem de saydam olma özelliği göstermektedir. Tez çalışmasının yüzey parlaklığı belirleme aşamasında yine maket bir uçak kullanılmıştır. Yüzeyde görüntüsü elde edilen maket uçağın görüntü derinliğinden yola çıkılarak kaplama parlaklığı sınıflandırılmıştır. Işık geçirgenliğine sahip bu kaplamalar maket uçak model numune arkasında kalacak şekilde yerleştirilmiş saydam olan yüzeyden arkadaki uçak gözlemlenmiştir.

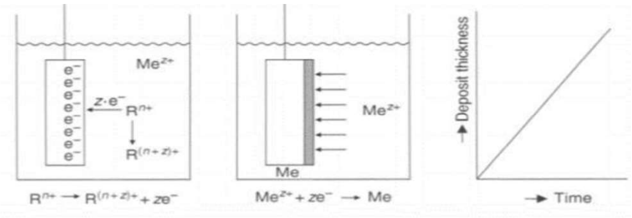
Bu tez kapsamında kromik asit kullanılmadan yapılmış olan kaplamaların sadece fiziksel özellikleri üzerinde deneysel çalışmalar gerçekleştirildiğinden kaplamaların mekanik özellikleri üzerinde çalışma yapılmamıştır. Uygulanan deneysel aşamalar, akımsız kaplama uygulamalarında kromik asitin zararlarına maruz kalınmadan hazırlanmış, fiziksel özellik anlamında pazarda standart metotlarla elde edilmiş kaplamalardan farkı olmayan ürünler elde edilmiştir.

Tez kapsamında kromik asit ile kaplamaya uygun hale getirilemediği için endüstriyel uygulamalarda kullanılamayan PA ve PC gibi farklı polimer çeşitlerinin de akımsız kaplanabileceği ortaya konmuştur. Tez çalışmaları sonucu PA ve PC üzerinde akımsız nikel kaplama uygulamaları bu alanda öncü çalışma niteliğindedir.

# 1. ELECTROLESS COATING

If an aqueous solution has enough electrons and belongs to a metal salt, the metal deposition can be obtained from that solution. Inside the solutions, the metal ions can be reduced to its metallic state. In practice, there are two main sources of electrons; each forms the basis of technologically important processes. The first of these technologies is the electrolytic deposition, where electrons are supplied externally The second is the electroless or chemical deposition, which does not include external power source [1]. Electroless coating involves autocatalytic[1] reactions, the metal ions from the solutions are reduced with the existence of the nuclei [2]. The anodic and cathodic reactions take place at the surface of one electrode and at the same interface [3]. The principles of eletroless coating is shown in Figure 1.1.

Electroless coating gives advantages to the user to plate all kinds of shapes and parts homogeneously [4, 5]. On the other hand, there exist limitations in substrate geometry. The limitations of electroplating in size and shapes are given in Figure 1.2. There is no limitation with those shapes in electroless coating.



a b c

**Figure 1.1:** Principle of electroless deposition: **a)** oxidation **b)** reduction of the metal ion, **c)** rate of deposition vs. time [1].

---

[1] *Deposition in autocatalytic way is described as forming a metallic film by controlled reactions catalysed by the metals which is wanted to be formed on the substrate surface. The reaction is given as following if the metal ions are reduced by reductant [19].*

$$M^{2+} + R^{n-} (catalyst) = M + R^{z-n} \qquad (1)$$

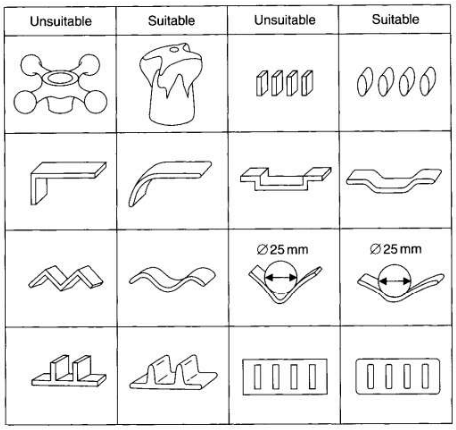


**Figure 1.2:** The limited geometries for the electroplating process [1].

Electroless coating was firsly tried by Brenner and Riddell in 1946 for electroless nickel plating. In order to proceed the electroless coating system, the coating bath consists of at least a metal salt and a reductant. In this type of coating, the reaction is autocatalytic and when thermodynamically stable catalytic surface is obtained, plating starts under optimal conditions and there is no external source needed to make the coating solution charged. [6].

Electroless coatingis a process in which the metallic or non metallic surfaces are plated either with the direct chemical reduction method or the reactions accelerated by catalytic surfaces [7]. The place of the electroless coating amoung the thin film deposition techniques is shown in Figure 1.3.

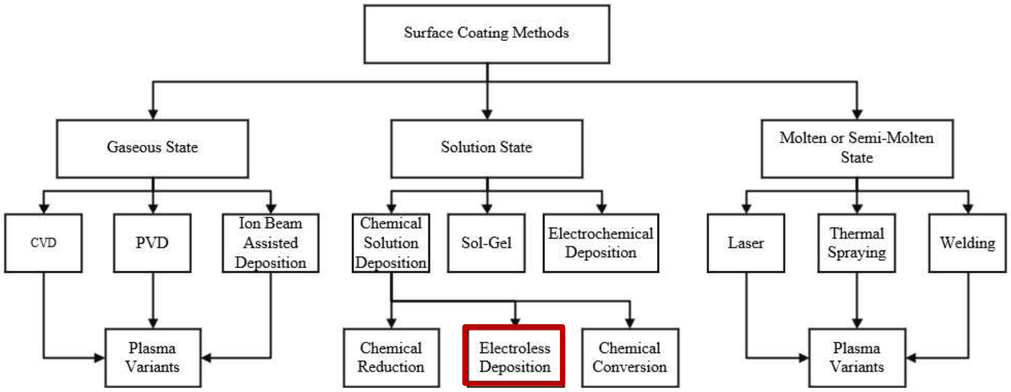


**Figure 1.3:** Surface coating methods [16].

Coating of nonmetallic surfaces with metals has been commonly used for years in several sectors to combine the properties of metals with substrate materials [8 -10] Especially, plating of polymeric materials takes part in many usage areas such as automotive industry and electrical industry [8]. The weight of the pieces and the production cost become lower by metalizing the non-conductive surfaces, while it gives an advantage to work with various parts to design [11]. Metalized plastics are gained properties in optical, electrical, mechanical and decorative aspects which make the final product better than the substrate material [12,13]. Electroless coating is the most commonly used method to metallize the nonconductive surfaces. Despite the fact that electroless coating is quite common, there is no huge number of polymer types coatable. Among the coatable polymers, ABS (acrylonitrile butadiene styrene) is the most commonly used one due to its features make it available for coating [12,14,15].

Metals that have been deposited by true electroless processes are shown in Figure 1.4. The metalloids, such as boron and phosphorus, have no technological importance as deposits in their pure form. However, they are significant just as parts of electroless deposited alloys [1].

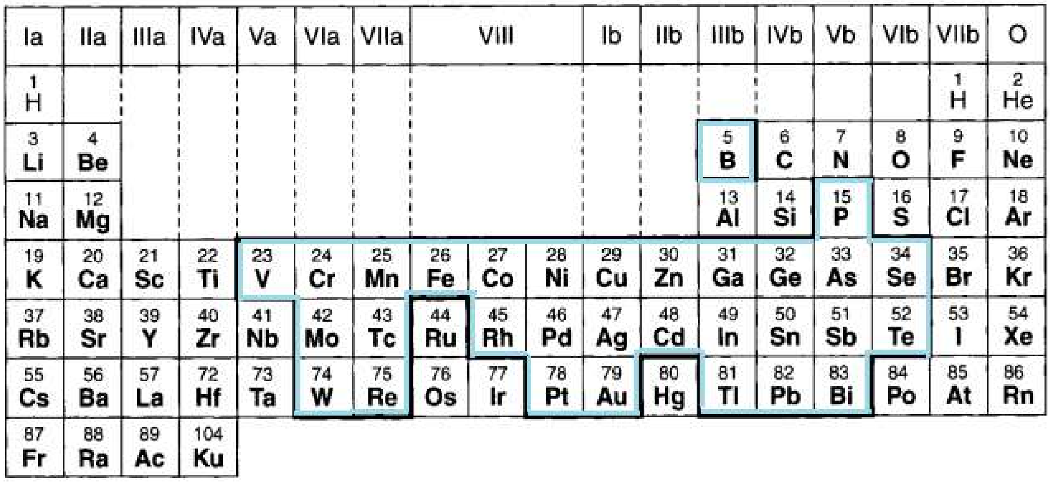


**Figure 1.4:** Metals and metalloids which can be deposited by electroless coating method [1].

### 1.1 Types of Electroless Coating

There exist several types of metals plated on metallic or non-metallic surfaces.These are nickel, copper, silver, chrome, tin and palladium. Among them, nickel, copper and gold are used in industrial scale. Ni-P plating is used to improve mainly the mechanical, electrical and physical properites and also for the decorative purposes. Ni-B alloy coating is also utilized to avoid oxidation films may be formed on the surfaces. gold and silver coating are mainly applied in electrical industry. In the case of copper electroless coating, the main purpose is to form the circuit in PCBs. Besides the electroless metal coating, there exist other options like alloy and composite coating [17]. The types of electroless coating is shown in Figure 1.5.

- Electroless Metal Coatings

In order to improve some mechanical properties and corrosion resistance of the materials, electroless metal coating is preferred as another option to electroplating. Several metals such as Ni, Cu, Au et. can be coated on the surfaces for these purposes [18].

- Electroless Alloy Coating

This type of electroless coating contains plating of the surfaces with alloys. There exists a relationship between the used reducent agent and the formed alloy. Based on the metal addition to the bath, the ternary and the quaternary alloys can be formed [18].

- Electroless Composite Coating

Composite coating comprises of codeposition ofsolid particles such as $SiO_2$ , $Al_2O_3$, TiC, $SiO_2$ etc. inside of the electroless coated metal matrix. This metal matrix is usually NiP and NiB. This kind of coating is utilized to enhance the properties like wear and corrosion resistance [19].

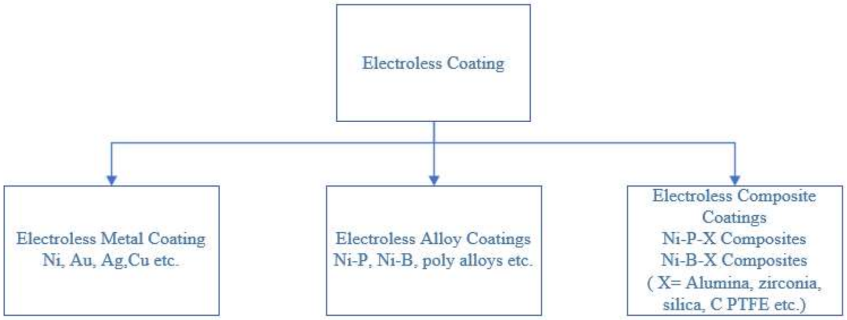


**Figure 1.5:** Types of Electroless Coating [19].

## 2. ELECTROLESS NICKEL COATING

Electroless Ni plating involves the reduction of Ni2+ ions from aqueous solutions by direct chemical reduction method and the most widely used reductant for this process is sodium hypophosphite [6,20]. Electroless nickel plating is the most frequently applied electroless coating type in the industry. In this type, pure nickel or Ni-P alloy is deposited on the substrate which can be either conductive or non-conductive (polymers) [19]. The aim of the electroless Ni plating is to enhance the mechanical properties and resistance to corrosion with forming a thin film which is compact and covering the surface of the substrate material uniformly. When it is compared with the electroplating, it allows to coat difficult to reach places and be able to cover the complex shapes and sizes [21,19]. Since there is no electricity usage in electroless coating, in all regions of the substrate the deposition rate is the same, thus the coating on the surface is uniform [20]. The surfaces coated with eletroplating and electroless plating are shown in Figure 2.1. Electroless nickel baths consist of nickel salts (nickel sulfate, nickel chloride), reducing agent (sodium hypophosphite), and additives [22].

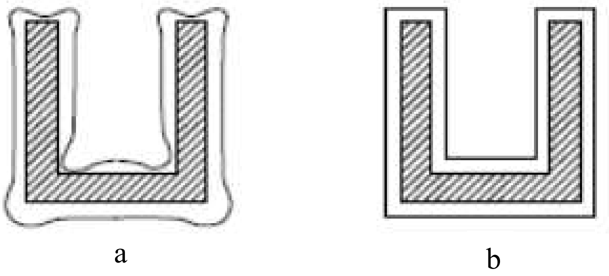


**Figure 2.1:** The comparison of a) electroplated surface and b) electroless plated surface [23].

Electroless nickel coating have sevaral advantages and disadvantages given in Table 2.1.

**Table 2.1:** The adventageous and disadventageous of electroless coating [24].

| **Advantages** | **Disadvantages** |
|---|---|
| Homogeneity | High cost of chemicals |
| Corrosion Resistance | Brittleness, |
| Wear Resistance | Low speed of the reactions compared to electroplating |
| Solderability<br>High Hardness, | |
| Resistivity,<br>Magnetic properties | |

## 2.1 The Usage Areas of Electroless Ni Coating

The application areas of electroless Ni coating is classified according to industrial sectors where it is used. Also, this classification can be done with the substrate material used in electroless Ni coating such as plastic, steel, stainless steel, aluminum copper, etc. Electroless nickel coating is mainly used in automotive, electric-electronic, chemical and white-good industries. Among all, automotive industry and electrical and electronical industry are the remarkable sectors which utilize from electroless coating. Especially plating of plastics is essential for automotive industry [25]. In Figure 2.2, the application areas of plated plastics is shown.

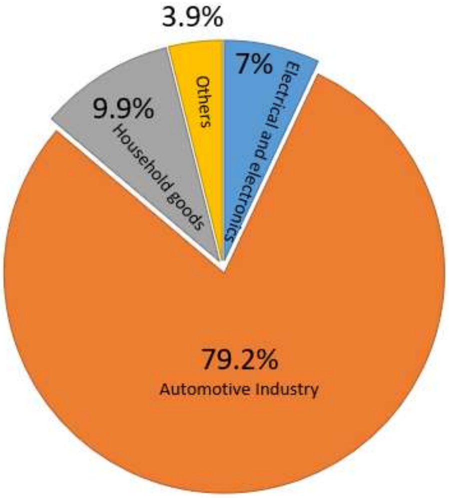


**Figure 2.2:** The dominant application areas of plated plastics [26].

## 2.2 Plating on Plastics

Polymeric materials provide advantages in the case of lightweight, easy manufacturing and handling with no design restriction. Due to these advantages, polymeric materials have been using as alternative to metals [12]**.** The sector which motivates plating of plastics is automotive sector. Usage of the plated plastics contributes decreasing fuel consumption by the help of low-density features of polymeric materials [28,29]. Besides it, if the properties of polymers can be combined with the properties of metals, the overall features of the final product become better. These features could be mechanical such as high hardness and abrasion resistance, electrical like electrical conductivity or decorative namely shiny appearance [30 - 32]. Polymers which can be plated are polypropylene, polysulfone, polyethersulfone, teflon and acrylonitrile-butadiene-styrene (ABS), etc. [32**]**. Among them ABS is considered as the best choice for coating since the dispersion of the butadiene group in acrylonitrile-styrene is homogeneous and it gives reaction and dissolves with the presence of concentrated oxidative solutions such as chromic acid [33]**.**

Plating of polymers differ from plating of metals in the case of bonding between the deposited metal and the substrate material. During metal deposition on metal substrate there exist chemical bonding. However, when the topic is metal deposition on a polymer substrate , the bonding would be only mechanical [34]. As the polymeric materials have the inert surface, in order to get the adhesion[2] between coating and polymers, the substrate surface is treated by chemical or mechanical ways [35].

### 2.2.1 Pre-treatment Methods in Plating of Plastics

Most of the time, the non-conductive surfaces firstly treated by etching solution [19,36, 37, 38]. The purpose is here to turn the surface into a hydrophilic form [2]. After making the surface hydrophilic, the etched surfaces are exposed to sensitization and activation steps. In these steps, the surfaces are exerted to $SnCl_2$ and $PdCl_2$

---

[2] *Adhesion is a term describes the bonding between the materials that are contiguous, and it is about the force needed to disconnect them from each other [44]. In the case of ABS polymer, the butadien group is selectively attacted by chemicals and as a consequence of this, pits are remained on the structure. These pits become the anchoring points between coating and the substrate material [45]. There exist several theories which claimed that adhesion depend on the chemical attraction of the coating and the substrate material, mechanical bondings, and the layer formation especially on the substrate [46]*

solutions containing HCl. During these steps, adsorption of ions takes place [2,37,39,40]. The following equation expresses the activation process:

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

The pre-treatment part involves degreasing, etching, sensitization and activation [12]. The pretreatment process begin with cleaning the surface, after forming holes for nucleation by etching, the surface is made catalytic with $SnCl_2$ and $PdCl_2$ treatments [12, 39, 40, 41].

#### 2.2.1.1 Degreasing

This step is required to get rid of oil, grease, dirt, fingerprint on the surface of the material [32,43]. The degreasing solution is typically alkaline solutions such as NaOH. The time, temperature and agitation are important factors affecting the cleaning properties [32]. The significance of the cleaning process cannot be underestimated. Many failures are considered to come from not well-cleaned surfaces [21, 25]. Inadequate cleaning of the surfaces leads to bad adhesion and flake and blister formation on coating [21]. Cleaning the surface is the main step to obtain proper coating on the surface [42, 47].

#### 2.2.1.2 Etching

Etching process is the must step in electroless plating (ELP), to attain strong adhesion and obtain nucleation sides [4]. The goal of the etching process is to turn the hydrophobic flat surface into the hydrophilic form [48, 49]. The connection between coating and substrate surface is increased due to rising in surface area of substrate material by etching [32]. The successful etching procedure of polymeric surface has a great effect on forming strong bonding between the substrate and the coating metal and it provides even deposition of the coating on substrate [49]. Chromic acid is the most commonly used etchant in this field. It is used as a mixture of sulfuric acid and chromic acid [50, 51]. This mixture contains about 40% chromic acid, 40% sulfuric acid and distilled water. The optimum concentration of each component is determined by the solubility diagram of $CrO_3$, $H_2SO_4$ and water shown in Figure 2.3.

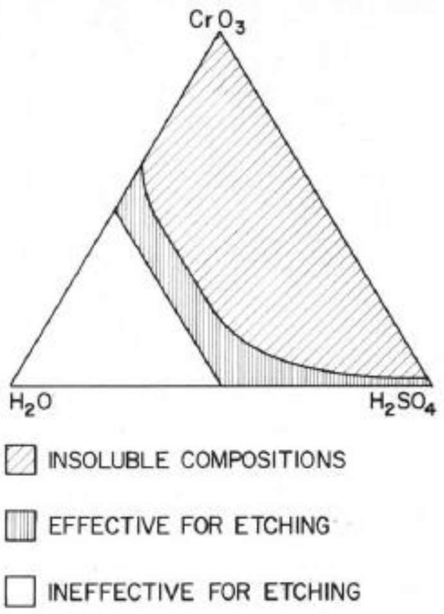


**Figure 2.3:** Solubility of $CrO_3$, $H_2SO_4$ and water [32].

The operation temperature and time are nearly 65-75 ˚C and 3- 10 minutes [52,6]. In etching step, a redox reaction between hexavalent chrome and the active part (butadiene) of the ABS realizes. As a result of this process, micro-holes are left on the substrate surface [33]. The surface structure of ABS after etching is given in Figure 2.4.

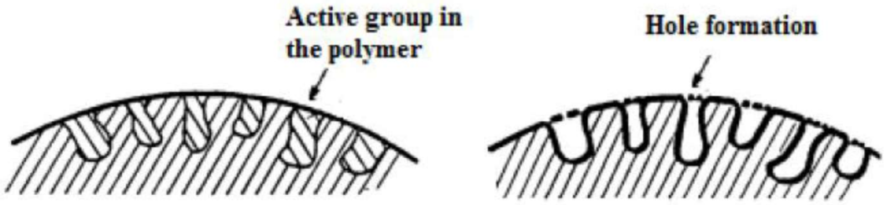


**Figure 2.4:** The schematic view of hole formation after etching [43].

The reaction taking place during etching process as in following :

$$2C_{15}H_{17}N + 81H_2SO_4 + 54CrO_3 \rightarrow 30CO_2 + 2NO_2 + 98H_2O + 27Cr_2(SO_4) \qquad (3)$$

From equation 3, it is seen that $Cr^{6+}$ is reduced to $Cr^{3+}$ [52]. $Cr^{6+}$ is defined as carcinogenic and toxic. It may cause respiratory irritation asthma and has a bad effect on livers and other organs [33,53]. Also, controlling hot chromic acid is difficult and dangerous. Since the neutralization of chromic acid is a problematic process, chrome can remain on the substrate surface and may cause problems in further processes [33]. There are several other trials in industry for ething, they will be examined in Chrome-free Etching Section.

### 2.2.1.3 Sensitization and activation

Before electroless coating, the nonconductive surfaces should be activated [3,34]. The activation is proceeded by forming catalytic nuclei on the surface of the substrate either by electrochemical or photochemical ways [3].

In the electrochemical method, the surface wanted to be coated is made catalytic by redox reaction shown in Equation 4.

$$\mathrm{Me}^{z+} + \mathrm{Red} \rightarrow \mathrm{M} + \mathrm{Ox} \tag{4}$$

Since the the standart electrode potential of $Sn^{4+}/ Sn^{2+}$ is lower than $Pd^{2+}/ Pd$, palladium ions can be reduced by $Sn^{4+}$ ions. In Table 2.2, it is seen that $Pd^{2+}/ Pd$ =0.951 V while $Sn^{4+}/ Sn^{2+}$ = 0.15 V [3].

**Table 2.2:** Stadart electrode potentials [3].

| **Metal/Metal Ion Couple** | **Electrode Reaction** | **Standart Value (V)** |
|---|---|---|
| **$Au/Au^{+}$** | $Au^{+} + e = Au_{(s)}$ | 1.692 |
| **$Au/Au^{3+}$** | $Au^{3+} + 3e = Au_{(s)}$ | 1.498 |
| **$Pd/Pd^{2+}$** | $Pd^{2+} + 2e = Pd_{(s)}$ | 0.951 |
| **$Cu/Cu^{+}$** | $Cu^{+} + e = Cu_{(s)}$ | 0.521 |
| **$Cu/Cu^{2+}$** | $Cu^{2+} + 2e = Cu_{(s)}$ | 0.3419 |
| **$Sn/Sn^{4+}$** | $Sn^{4+} +2e = Sn^{2+}_{(aq)}$ | 0.15 |
| **$Fe/Fe^{3+}$** | $Fe^{3+} + 3e = Fe_{(s)}$ | -0.037 |
| **$Pb/Pb^{2+}$** | $Pb^{2+} + 2e = Pb_{(s)}$ | -0.1262 |
| **$Ni/Ni^{2+}$** | $Ni^{2+} + 2e = Ni_{(s)}$ | -0.257 |
| **$Co/Co^{2+}$** | $Co^{2+} + 2e = Co_{(s)}$ | -0.28 |
| **$Fe/Fe^{2+}$** | $Fe^{2+} + 2e = Fe_{(s)}$ | -0.447 |
| **$Zn/Zn^{2+}$** | $Zn^{2+} +2e = Zn_{(s)}$ | -0.7618 |
| **$Al/Al^{3+}$** | $Al^{3+} +3e = Al_{(s)}$ | -1.662 |
| **$Na/Na^{+}$** | $Na^{+} + e = Na_{(s)}$ | -2.71 |

Accomplishing the catalyzation is a crucial step to obtain a homogeneous plating. Variety of metals such as Cu, Ni, Au, Ag and group 8B metals can be used as catalyst theoretically [6]. In practice, the most widely used solutions are acidic stannous chloride and palladium chloride solutions. When the substrate is immersed in $SnCl_2$ solution $Sn^{2+}$ ions are adsorbed on the surface and by this method the surface is sensitized.

After sensitization, the substrate surface is exposed to a palladium chloride solution and the following redox reaction takes place.

$$\mathbf{Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^{0}} \qquad (5)$$

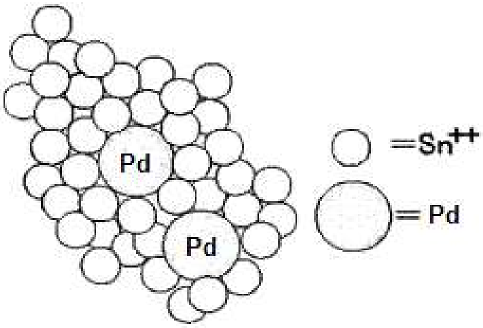


**Figure 2.5:** The surrounded Pd atoms with Sn ions [54].

During the activation step, Sn ions meet with Pd ions, and all the divalent Sn is removed and the palladium atoms are gathered on the substrate surface. The palladium atoms surrounded by $Sn^{2+}$ is shown in Figure 2.5.

After deposition of palladium atoms on the surface holes, reduction of the ions of the metal that will be deposited becomes possible [28].

This route of sensitization activation is known as *two-step immersion* and the traditional one in the industry [37]. In first immersion $Sn^{2+}$ is adsorbed on the holes created by etching step and in second immersion, as a result of redox reaction, Pd atoms are replaced by Sn ions and the surface becomes catalytic [54]. The schematic demonstration of sensitization and activation step by two-step electrochemical method is shown in Figure 2.6.

**Figure 2.6:** The adsorption Pd atoms on the holes [12].

Another type of sensitization and activation process is done in one step by using a palladium-tin colloid. The tin and palladium chlorides are mixed with an acidic solution. The colloidal particle consists of rich in palladium core and $Sn^{4+}$ cover. Extra tin (II) makes the solution sensitized.

As an alternative to palladium, copper is also used as catalytic metal because of the high cost of palladium. Another way to activate to surface of the substrate is *photochemical way*[3] [6].

### 2.3 Studies on Chrome-Free Etching

There many studies conducting in the world about chrome-free etching.

- Han et al. use $HNO_3$, $H_2SO_4$ and $NiSO_4$ for 20 minutes, at 50, 60, 70 ˚C respectively for etching and after etching, they applied NaOH 1-methyl-2 pyrroline and 2-Butoxy ethanol to make the surface rough [48].
- Gan et all. use $KMnO_4$ and $H_2SO_4$ mixture in the etching step and coates the PET fabrics electroless method [55].
- Wang et all. use the mixture of $MnO_4$ and $H_2SO_4$ solutions at 70 ˚C for 20 minutes to etch the ABS surface and than he neutralizes the surface by using $H_2C_2O_4{\cdot}H_2O$ and sulfuric acid at 50˚C for 3 minutes [31].
- Gui et all. apply acetic acid solution at 90 ˚C for 30 minutes to etch the surface of PA12 [35].
- Hiroshi et all. use sputtering method and the Pt/Pd catalyst is sputtred on the surface of the honeycomb structured PS film after that the electroless coating is applied [56].
- Lijeri et all. have a new environmentally friendly solution to take the place of the chromic acid and they can coat ABS surfaces without using chromic acid [28].
- Bruce P. has a patent of etching the polyarylene polyethers, polycarbonate or polyhydroxyethers with N, N dimethylformamide, pyridine, and its compounds [57].

---

[3] *Photochemical reactions are initiated by the absorbsion of light [62]. In this type activation, the process is started with photochemical reactions to get electrons neccessary to obtain a required reductant. And than in sequent electrochemical reactions the reductant is used to reduce palladium ions [3].*

- Teixeira et al. uses the mixture of $H_2SO_4$ and $H_2O_2$ in different concentrations to etch ABS [58].
- Zhang et al. use molecular grafting method to coat ABS with electroless coating [59].
- Zarnoch et all. have a patent on etching of aromatic polymers by using nitriding solution (the mixture of $HNO_3$ AND $H_2SO_4$) firstly and than applying hydroxlating solution like ammonium hydroxide [60].
- Pearson at all. have a patent on etching the plastic surfaces by applying the method in which the bath contains Mn(II) solution with 9 M of $H_2SO_4$ and 15 M of $H_3PO_4$ .After applying current Mn(II) ions turn into Mn(III) ions. These ions form a a sulfate complex. By using this complex the surface of the polymers is etched [61].

The reason for the limited number of studies about the metallization of polymeric materials is that while in the literature it is claimed that the surface of all polymeric materials can be metalized with electroless coating, in industry only ABS type of polymers is commercially available. The only company applying electroless coating in different types of polymers is located in the USA.

The limited number of studies about the chrome-free etching and electroless coating of different types of polymeric materials including ABS is the main motivation of this study.

## 3. EXPERIMENTAL PROCEDURE

### 3.1 Experimental Set-up

The set- up consists of a container that is filled with water, a heater that is placed into the container so that the water can be controlled heated to set temperature, a mechansim (to move the sample), a beaker, electroless nickel coating bath and an ABS specimen. The front and top views of the experimental set-up are shown in Figure 3.1.

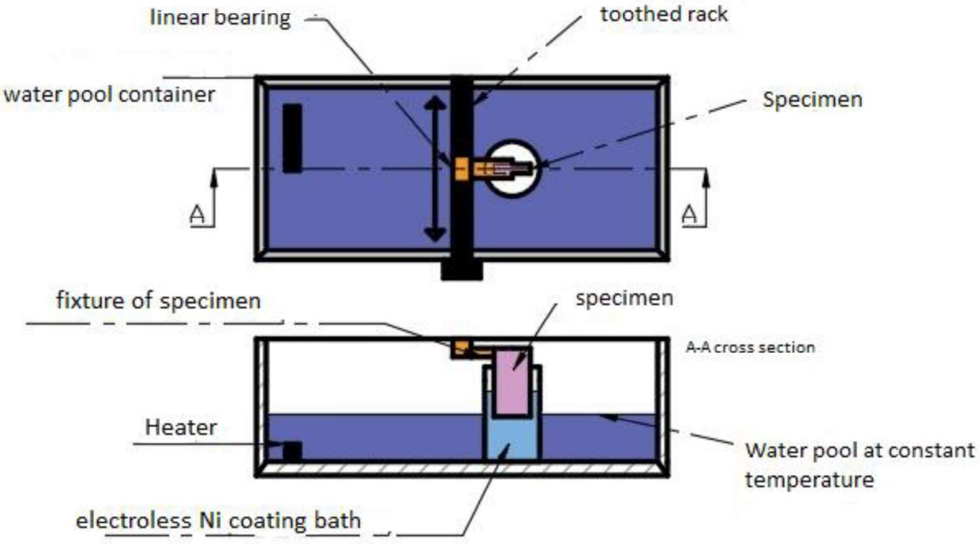


**Figure 3.1:** Front view and top view of experimental set-up.

A mechansim was assembled on the top of the container. There exist one toothed rack and one steel rod. These two were connected to each other and the toothed rack is assembled with a DC motor. The aim of this designed mechanism is to make the ABS specimen move forward and backward during coating. This was achieved by using an Arduino and L298N DC motor driver (2cm/sec). After finishing all the necessary connections between Arduino and motor driver, the code providing the forward and backward movement was written and the final connection with the DC motor was realized.

While the DC motor is making the toothed rack rotate, the rotating rack will move the steel road where the specimen is connected.

All the electronic devices (Ardunio, DC power supply, and power source) were placed into a box so that they can be protected from any external demages.

### 3.2 Electroless Coating with Chromic Acid Etching

The first experiments were conducted by using chromic acid in order to be sure whether the coating bath is working and to check if polymeric samples are suitable for electroless coating since most plastics are not suitable for electroless coating. In this chromic acid etching, the surface of the specimen was rinsed with distilled water. The rinsed surface was exposed to chromic acid solution for etching at 60˚C for 5 minutes. After etching, the substrate surface is applied $SnCl_2$ solution at 40-45˚C for 10 minutes and the same time and temperature were applied in $PdCl_2$ treatment. After each step, the specimen surface was rinsed with distilled water.

The pre-treated specimen was plugged into electroless nickel coating bath for 10 minutes and the coating was obtained on the surface of the specimen. After this trial, some areas on the sample were observed as non-coated. In order to solve this problem, ABS polymers were exposed to alkali cleaning with 1 M of NaOH solution in an ultrasonic cleaner for 15 minutes, and the operating time and temperature of the coating bath are optimized to 28 ˚C and 5 minutes.

### 3.3 Selection of Alternative Chemicals to Chromic Acid

At the end of the literature searches, 9 different types of etching reactives (dimethyl acetate, methyl acetate, ethyl acetate, acetone, chloroform, hydrogen peroxide, ammonium carbonate, and toluene) which are not carcinogenic and/or harmful to environment but be able to solve the specimens (ABS, PC, MA) were studied.

The ABS specimens were treated with these 9 different chemicals. Before using all chemicals, the MSDS' were checked to be sure that they are not carcinogenic and environmentaly hazardous. Each one was selected by looking at if they give a reaction with ABS or not.

At first, one rectangular specimen is marked to obtain for 4 regions on it and dimethyl acetate, methyl acetate, ethyl acetate, and acetone were applied for 30 seconds. After etching the specimen was exposed to sensitization and activation steps and plugged into the coating bath for 10 minutes. The same procedure was applied to another rectangular specimen, this time, chloroform, hydrogen peroxide, ammonium carbonate, and toluene were applied. The obtained coating is shown in Figure 3.2.

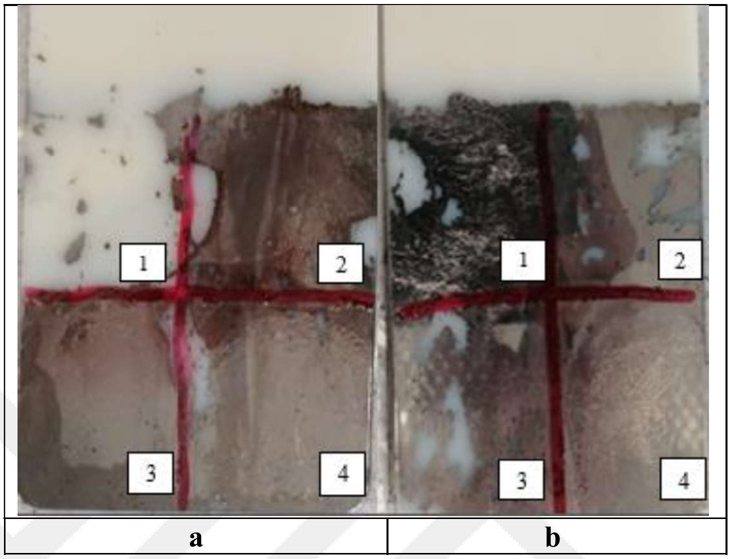


**Figure 3.2:** Electroless coating of ABS with a1)dimethyl oxalate, a2) methyl acetate, a3) ethyl acetate, a4) acetone, b1) chloroform, b2)hydrogen peroxide,b3) ammonium carbonate, b4) toluen etching. [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*]

As can be seen in Figure 3.2, the first region of the specimen one could not be coated, dimethyl oxalate did not work and it was eliminated. In both specimen, it is seen that second and third regions show proper coating. In forth regions, it is observed that there exist aggresive etching.

From these observations, it is selected to go beyond with methyl acetate, ethyl acetate, ammonium carbonate and hydrogen peroxide. Since acetone and toluene show more aggressive behavior compared to others, it was necessary to dilute them with proper agents if they are wanted to use in further experiments.

After making pre-experiments with four in one specimen, each solution was tried individually. Also, xylene was tried as a new etching solution excluding the 8 etchants tried before. Figure 3.3 shows the specimen surfaces after coating experiments.

| **Ethyl Acetate** | **Xylene** | **Ammonium Carbonate** | **Hydrogen Peroxide** | **Methyl Acetate** |
|---|---|---|---|---|
|  |  |  |  |  |

**Figure 3.3:** Ni coated ABS pieces exposed to different etchants, [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

As it is seen in Figure 3.3:

- Since the coating obtained with ethyl acetate etching is both uncontrolled and almost non-adherent, it cannot be used as a potential etchant.
- In xylene etching, some coated areas are seen and those areas are bright enough so it is worth studying with, however, xylene has a strong odor and it irritates the throat. In this work, xylene was not selected as the potential alternative etchant, by considering problems going to be faced with because of the excessive usage of the xylene in industrial applications.
- In the third picture, it is seen that there exists a bright, homogenous, smooth coating achieved via ammonium carbonate which was used as 0.1 M. Besides the successful coating, the concentration of ammonium carbonate can be diluted up to 0.1 M with distilled water. It means there is no need for high concentrations to etch the substrate surfaces when ammonium carboate is used as an etchant.
- In hydrogen peroxide etching, the coating is not as satisfactory as the coating obtained after ammonium carbonate etching. However, when it is compared to ethyl acetate and xylene, it was selected as the potential etchant to study.
- Lastly, the methyl acetate effect on coating is shown, the coating covers all the surface of the specimen. Although it does not show bright coating, this chemical was selected as a potential etchant for further studies to the observation of even coating on the surface.
- As a result of this study, methyl acetate, ammonium carbonate and hydrogen peroxide were selected as the potential etchant candidates to chromic acid.

## 3.4 Electroless Coating with Chrome-free Etching

Electroless coating with chrome-free etching trials firstly conducted on ABS polymers. The process steps consist of degreasing, neutralizing, etching (chrome-free), sensitization and activation.

### 3.4.1 Degreasing

Specimens were cleaned with 0.1 M of NaOH solution in an ultrasonic cleaner for 15 minutes. The cleaned surface were rinsed and neutralized into 0.1 M HCl solution and the specimen was rinsed with distilled water.

### 3.4.2 Chrome-free etching

After taking all the surface dirt, oils and fingerprints from the specimen surface with degreasing, the etching step proceeded. Three solutions including hydrogen peroxide, 0.1 M ammonium carbonate and 2% methyl acetate with 5% ethanol and 93% distilled water were prepared. After 10 minutes etching of each specimen, the surfaces were rinsed with distilled water.

### 3.4.3 Sensitization and activation

In sensitization and activation step, the conventioanal two-step immersing method was utilized. During acidic $SnCl_2$ solution preparation, 10g/L $SnCl_2$ was used with 3.5% HCl in distilled water . The operation temperature was arranged to 45˚C. The etched specimens were immersed into the solution and waited for 10 minutes. During this process, Sn (II) ions were adsorbed on the holes formed during the etching step. After sensitization, the specimens were immersed into an acidic palladium solution consisting of 1g/L $PdCl_2$ with 1% HCl in distilled water. The process was conducted at 45 ˚C for 10 minutes. No rinsing was applied in this section.

The reduction of Pd ions are clearly seen in this step. Obtained surface, after all, is catalytic and ready to be coated by autocatalytic way.

### 3.4.4 Electroless Ni coating

In the coating step, a commercial electroless nickel was supplied from AutoTech company and the bath was prepared in given ratios. The pH of the bath kept between 9-10 by using an ammoniac solution. The activated catalytic surfaces were immersed into coating bath after seconds chemical reduction of Ni ions was started. The bath temperature was fixed at 28˚C and coating was conducted about 5 minutes. The coating of ABS specimen is shown in Figure 3.4.

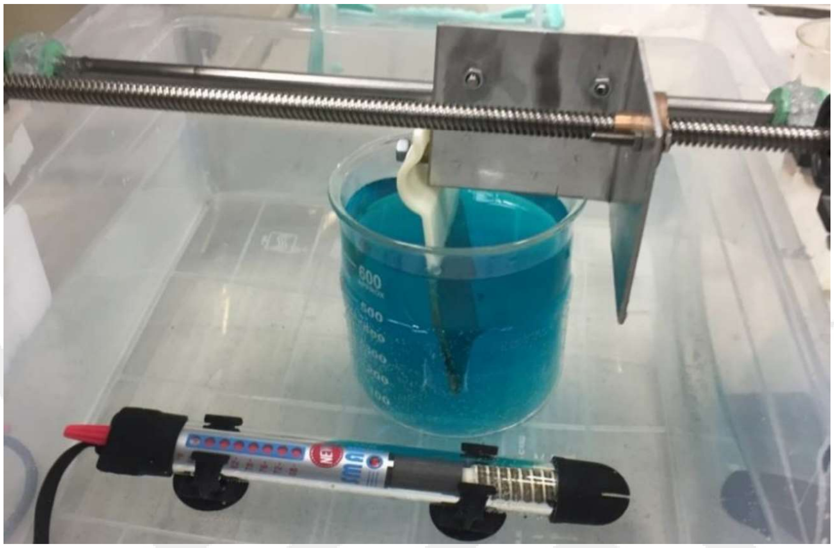


**Figure 3.4:** Electroless Ni coating of ABS.

The flow chart of ethe xperimental procedure is given in Figure 3.5.

### 3.4.5 Aging of ammonium carbonate and methyl acetate solutions

In this section of the experimental studies, the effect of the freshness of the etching solutions was investigated. Ammonium carbonate and methyl acetate solutions have first waited for 15 days and the experimental procedure was conducted to ABS, PA and PC specimens. The same solutions then waited for 30 days and the coating was applied to substrates. In this way, if the quality of the etchants changes with respect to passing time was controlled. At the end of this study, it was determined that there is no effect of passing time on the etchants. Therefore the freshness of the etching solution does not affect the coating quality.

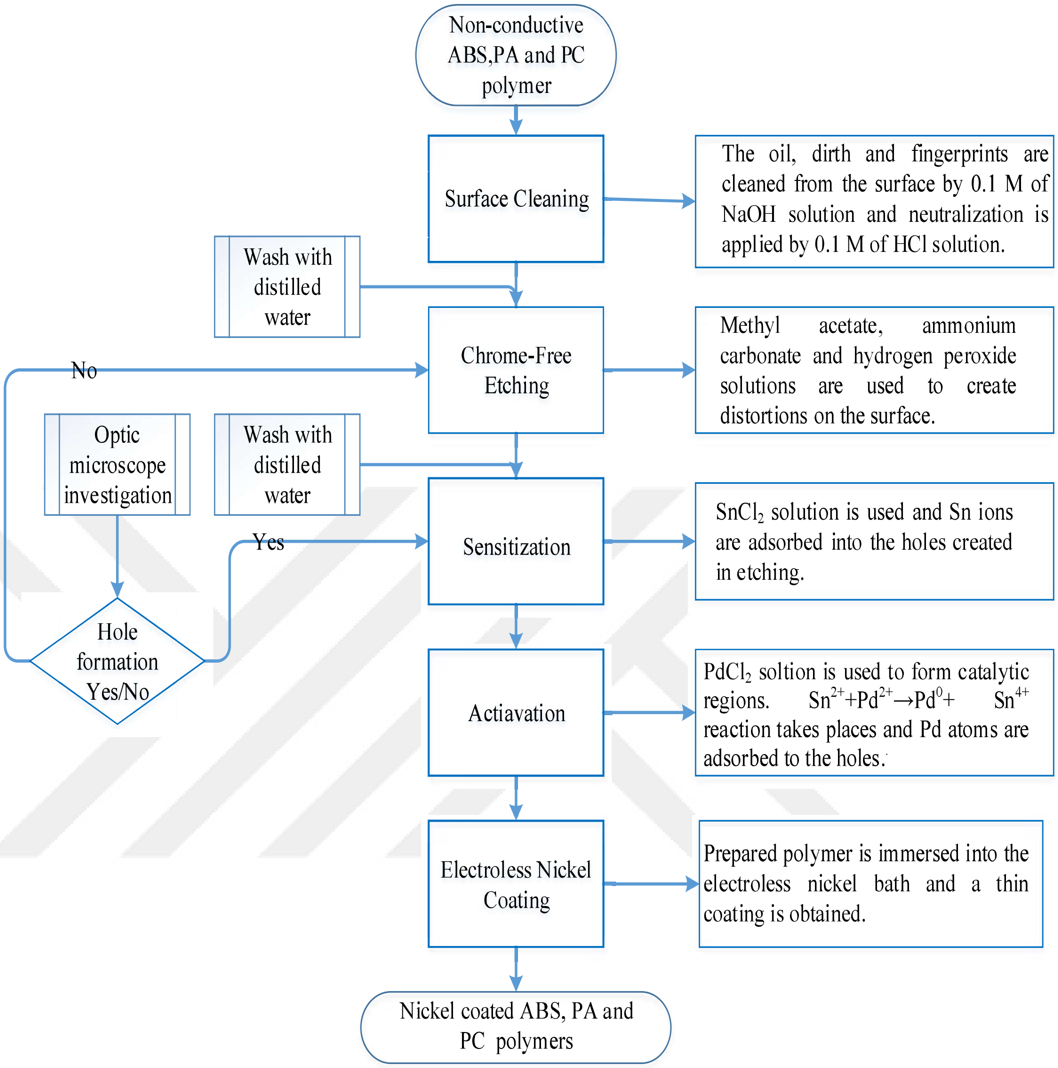


**Figure 3.5:** The flow chart of the experimental procedure.

# 4. RESULTS AND DISCUSSION

## 4.1 Electroless Ni Coating of ABS Specimens

The ABS specimens whose etching step was proceeded by methyl acetate, ammonium carbonate and hydrogen peroxide etching instead of chromic acid were coated by nickel by electroless coating with following the described experimental procedure. The brightness and colour features of the typical coatings obtained after experiments with constant and repeated conditions are given in Figure 4.1.

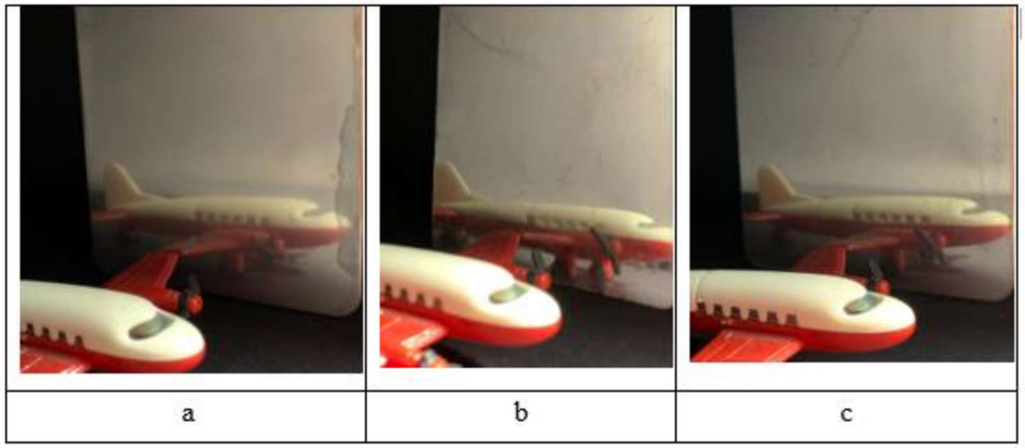


**Figure 4.1:** Visuals of brightness and colour properties of electroless Ni plated ABS specimens followed by standard **a)** methyl acetate etching, **b)** ammonium carbonate etching and **c)** $H_2O_2$ etching, [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

After coating of ABS samples, the topic investigated was if the ammonium carbonate and the methyl acetate solutions detorioate or not by time. Consequently, the time experiments were conducted. The prepared solutions were waited for 15 days. In 15th day, the experiment was repeated. In Figure 4.2, the coated samples are shown.

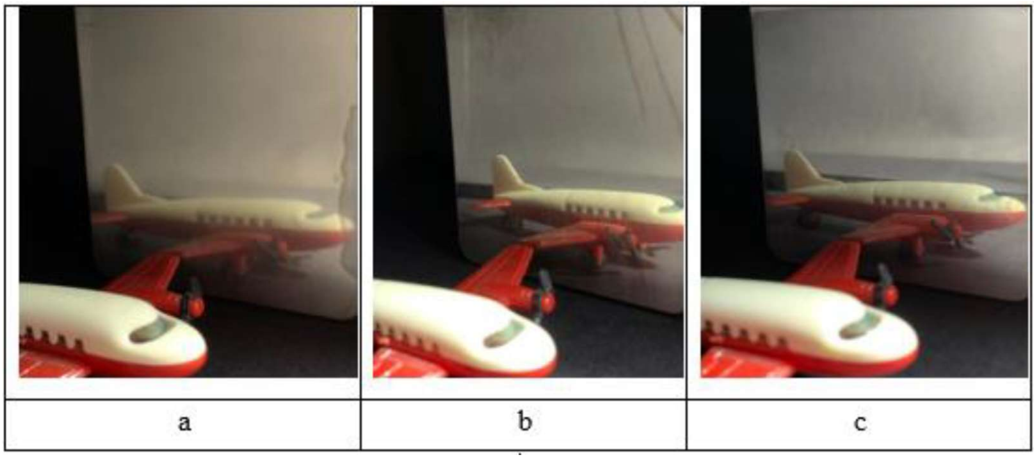


**Figure 4.2:** The coated ABS with a) fresh methyl acetate, b) altered methyl acetate (15th day), c) altered methyl acetate (30th day)
[*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*]

In 15th day experiments, it is obviously seen that there is no change in coating appearance and the etchants are still working.

After this experiment, the etchants were altered 15 more days, and the same procedure was conducted again. The coated ABS samples are shown in Figure 4.3.

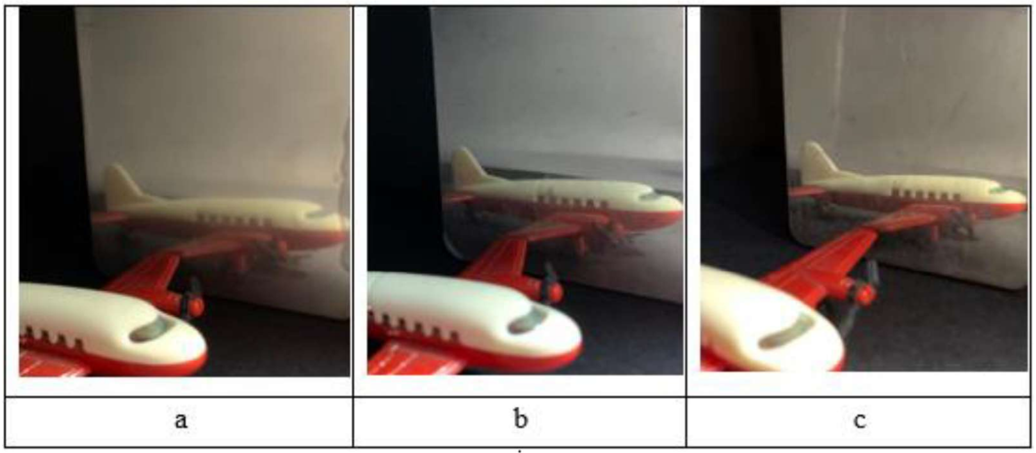


**Figure 4.3:** The coated ABS with a) fresh ammonium carbonate, b) altered ammonium carbonate (15th day), c) altered ammonium carbonate (30th day)
[*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*]

After 30th day experiment, it was understood that there is no effect on time in etchant life they can be used repeatedly like chromic acid. Hence the nature of the $H_2O_2$ is not suitable to use more than one time, these experiments were only made by ammonium carbonate and methyl acetate. $H_2O_2$ loss its active oxygen during time and it turns into a diluted solution with passing time.

## 4.2 Electroless Coating of PA and PC

After obtaining continuity in the electroless coating of ABS, it was decided to coat other types of polymer such as PA and PC. The same procedure conducted to ABS was also applied to these polymer types. Their surface were degreased with 1 M of NaOH in an ultrasonic bath and neutralized with 0.1 M of HCl for 30 seconds.After that, 3 samples were plugged into methyl acetate, ammonium carbonate and $H_2O_2$ solutions respectively. After 10 minutes of etching. the specimens exposed to sensitization and activation to make them catalytic. Lastly, each surface was applied electroless coating. After all electroless coating treatment, the coated surfaces were rinsed with distilled water and dried. The coated surfaces of PA and PC is are shown in Figure 4.4 and 4.5 respectively.

a b c

**Figure 4.4** Electroless Ni coated PA specimens a**)** $H_2O_2$ etching, **b)** Ammonium carbonate etching **c)** Methyl acetate etching, [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

Since the surface of the substrates was not smooth the coating obtained here is dull. If the surface of the specimens had been smooth enough, it would have been a bright coating on the surface and the plane could have seen on the mirror-like surface.

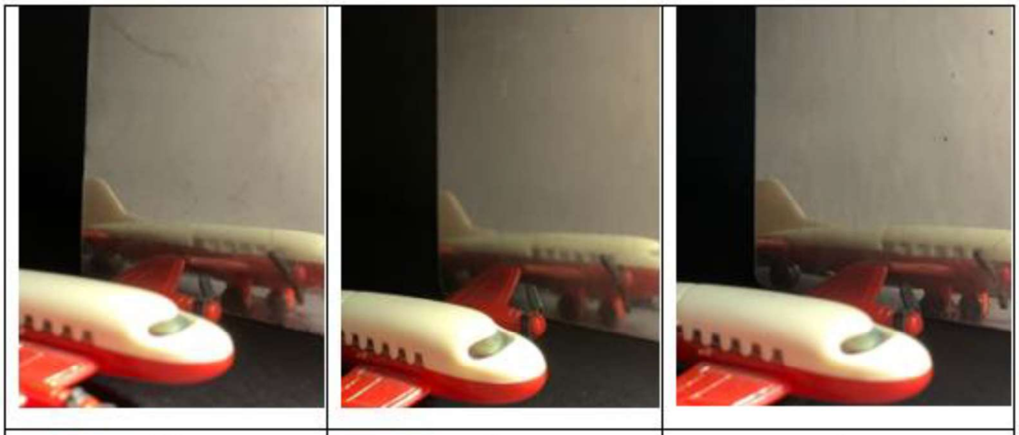

a b c

**Figure 4.5:** Electroless Ni coated PA specimens **a)** ammonium carbonate etching, **b)** $H_2O_2$ etching, **c)** Methyl acetate etching. [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

At the end of the experimental studies, it was observed that the surface roughness is so important for the coating brightness. Also, in the application of electroless coating on PC materials, it is inevitable to use mechanical pretreatments to obtain the ideal surface roughness on the substrates.

### 4.3 Sateen-Mat Plating

By using chrome-free etching pre-treatment ABS, PA and PC surfaces can be coated by electroless coating. There were mirror-like, bright coating formed on the surface of the ABS and PC.

In this experiment, it was tried to achieve a velvety surface by forming mechanical distortion with sand-blasting on the surface of the specimens. After this mechanical treatment, the smooth surface turns into a blurred rough form. The specimens were subsequently exposed to the same experimental procedure as in previous sections. The coated surfaces of ABS and PC polymer are shown in Figure 4.6 and Figure 4.7 respectively.

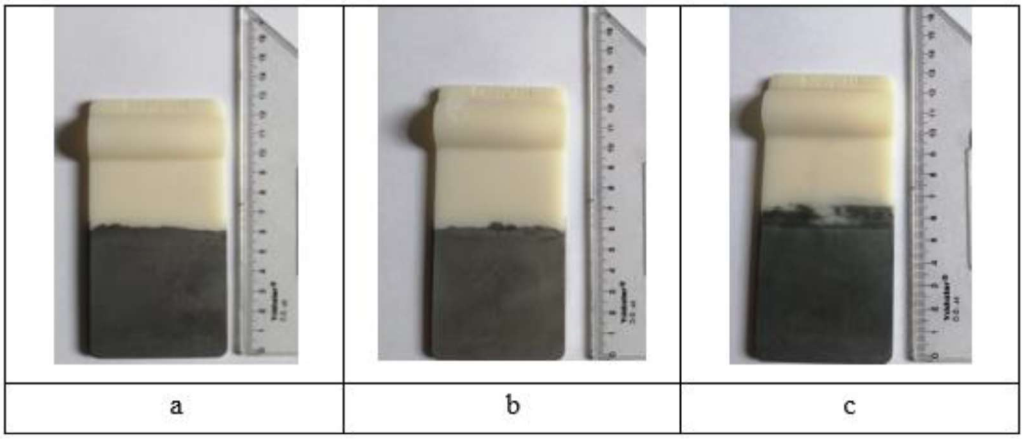


**Figure 4.6:** The sateen-mat plating on PC polymers with **a)** $H_2O_2$ etching, **b)** ammonium carbonate etching, **c)** Methyl acetate etching. [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

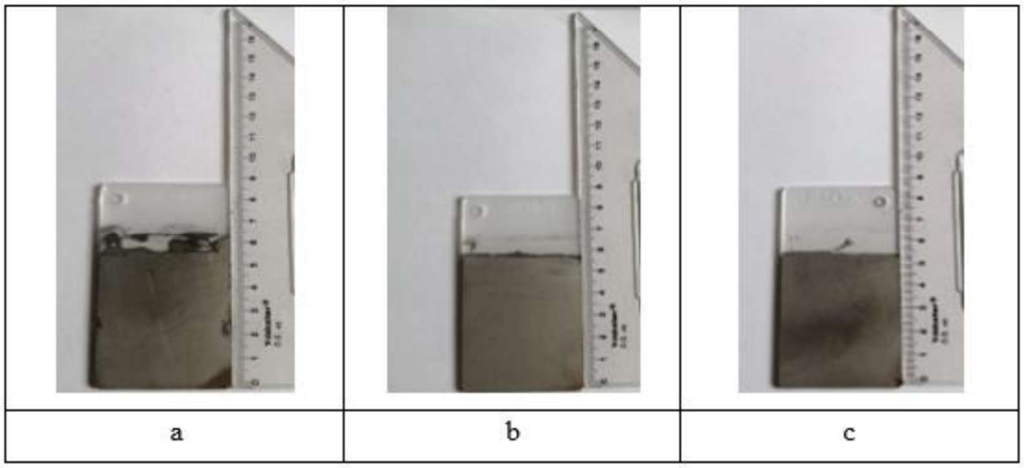


**Figure 4.7:** The sateen-mat plating on PC polymers with **a)** $H_2O_2$ etching

**b)** ammonium carbonate etching, **c)** Methyl acetate etching. [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

## 4.4 Transparent Plating of PC

The PC specimens were exposed to the same experimental procedure. This time, before pre-treatment, the surface is not applied a mechanical treatment and directly coated. After coating, it is observed that the coating formed on the surface is very thin and the surface is both bright and transparent. In Figure 4.8, the plane was placed in front of the sample and it can be seen on the mirror-like surface, when the plane was placed behind the sample like in Figure 4.9, it could be also seen, since the sample surface was transparent.

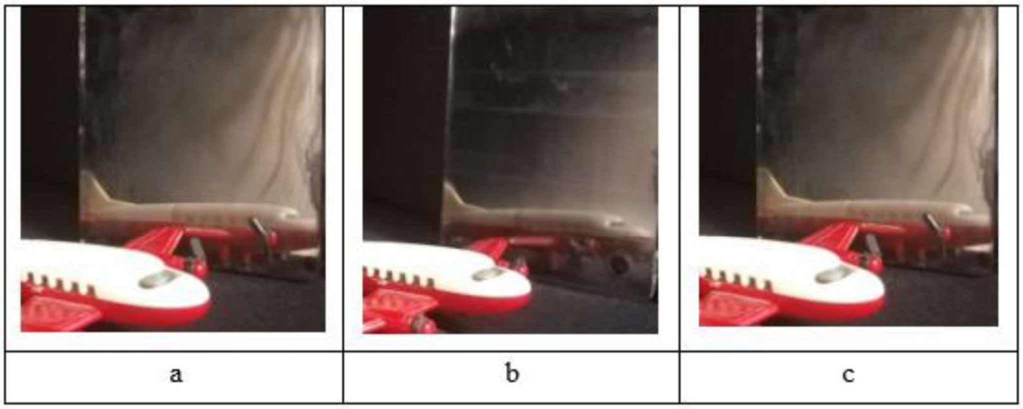

a b c

**Figure 4.8: a)** Ammonium carbonate etching, **b)** $H_2O_2$ etching **c)** Methyl acetate etching [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

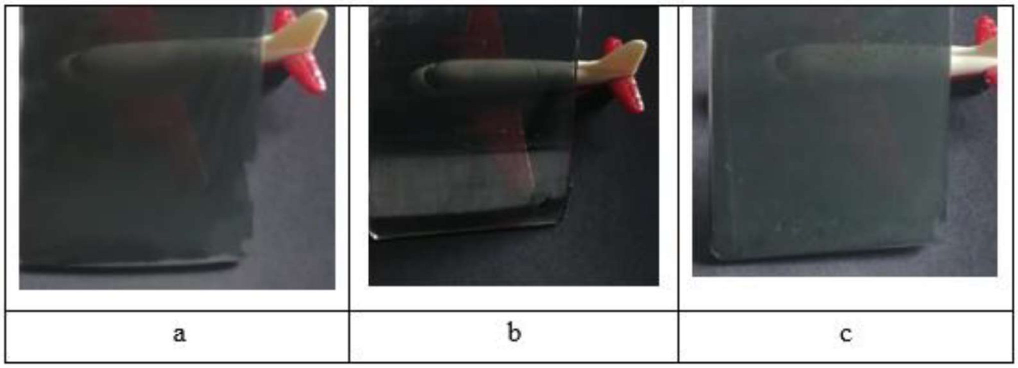

a b c

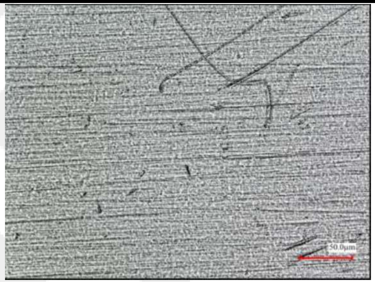
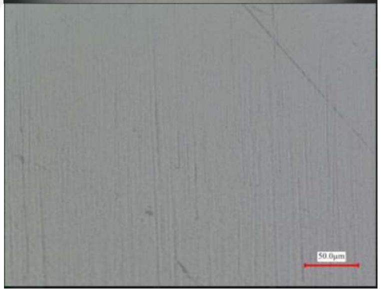
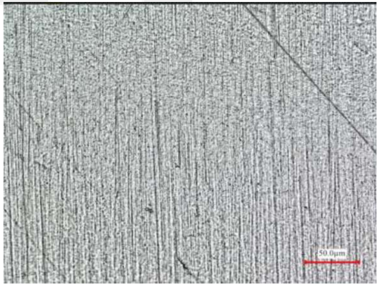
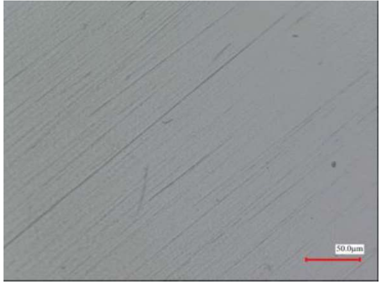
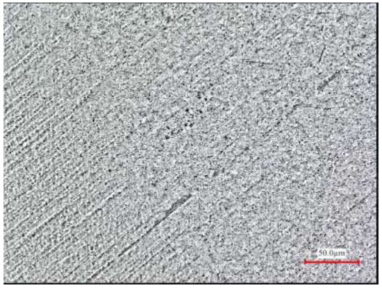
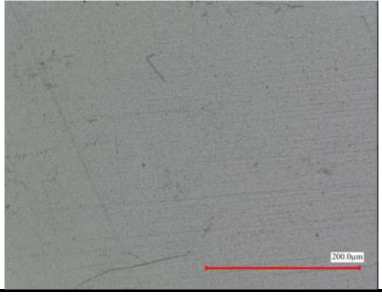
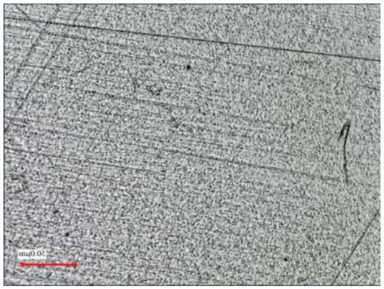
**Figure 4.9: a)** Ammonium carbonate etching, **b)** $H_2O_2$ etching **c)** Methyl acetate etching, [*28 ˚C, 250g/l Ni, pH 9-10, 3 min, movement 2 cm/sec*].

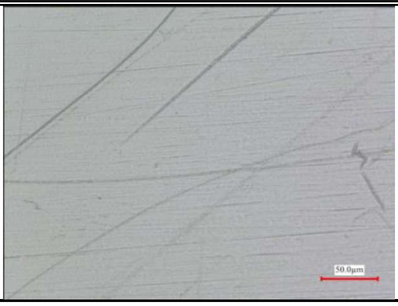
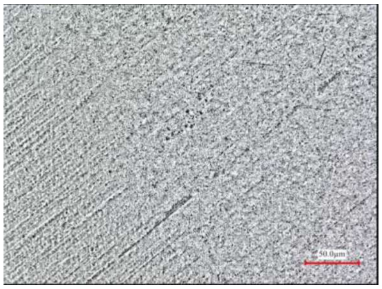
The usage of this kind of coatings could be beneficial in areas where the light transmittance is important to control. These areas are especially skyscraper windows, inner side of the office windows and greenhouse etc.

### 4.5 Optic Microscope Investigation

After etching ABS, PA and PC the distortion of the surface was investigated under an optical microscope. In Table 4.1, the micrographs belong to reference, chromic acid, ammonium carbonate, $H_2O_2$ and, methyl acetate etched ABS are shown respectively.

**Table 4.1:** The micrograhps belog to **a)** Reference, **b)** Chromic acid etched, **c)** Ammonium carbonate etched, **d)** $H_2O_2$ etched and **e)** Methyl acetate etched ABS.

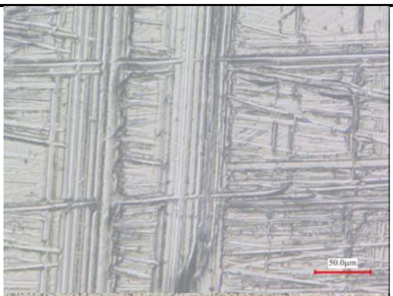
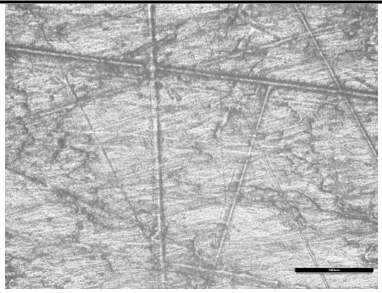
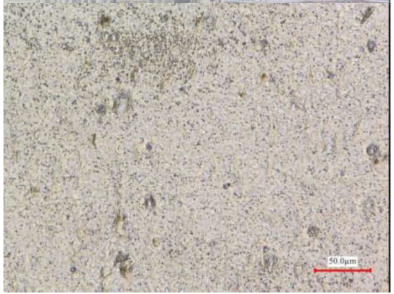
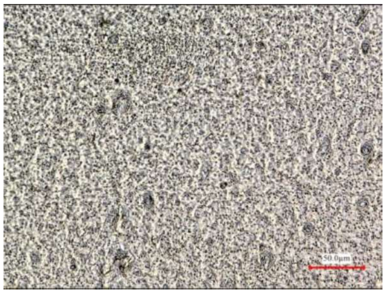
| Specimen Type | Optic Microscope Image | HDR Image |
|---|---|---|
| **Reference** |  |  |
| **Chromic-Acid Etching** |  |  |
| **Ammonium Carbonate Etching** |  |  |
| **Methyl Acetate Etching** |  |  |

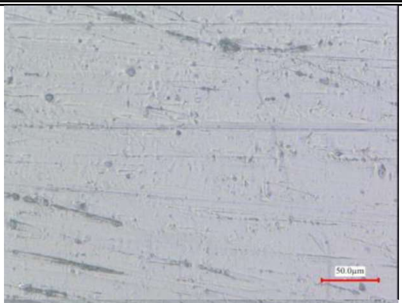
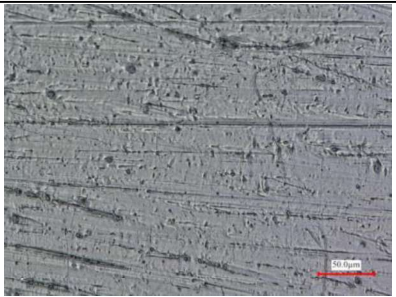
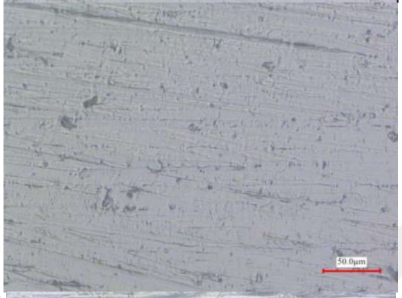
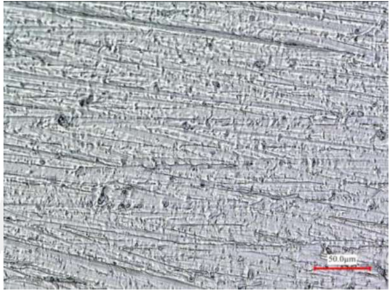
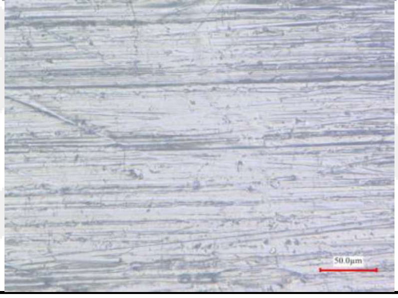
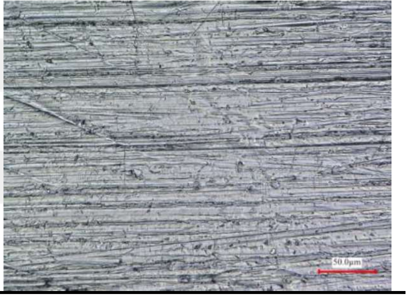
| | | |
|---|---|---|
| **$H_2O_2$ Etching** |  |  |

As it can be seen in these micrographs when the surfaces etched with methyl acetate, ammonium carbonate $H_2O_2$ are compared with the surface of the reference specimen, it is clearly seen that the etchants interact with butadiene group of ABS and it results in hole formation.

The same optic microsope investigation was done for PA, the results are given in Table 4.2. As it can be seen in the table, chromic acid attack inhomogeneously, on the other hand, ammonium carbonate, methyl acetate and, hydrogen peroxide create homogeneously distributed holes and/or distortions on the surface of the PA samples.

**Table 4.2:** The micrographs of PA.

| Specimen Type | Optic Microscope Image | HDR Image |
|---|---|---|
| **Reference** |  |  |
| **Chromic-Acid Etching** |  |  |

| | | |
|---|---|---|
| **Ammonium Carbonate Etching** |  |  |
| **Methyl Acetate Etching** |  |  |
| **$H_2O_2$ Etching** |  |  |

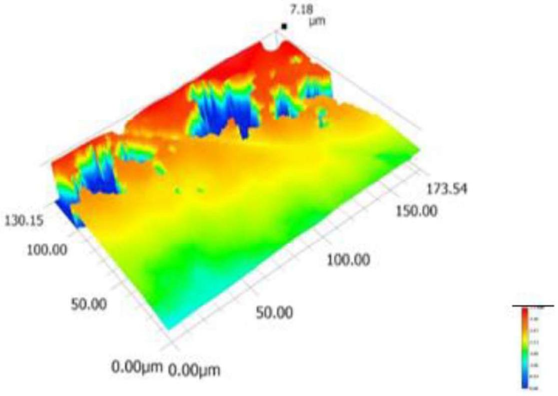
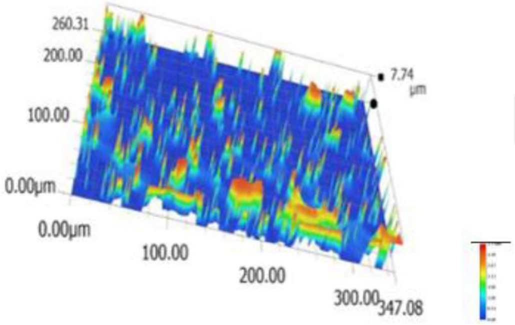
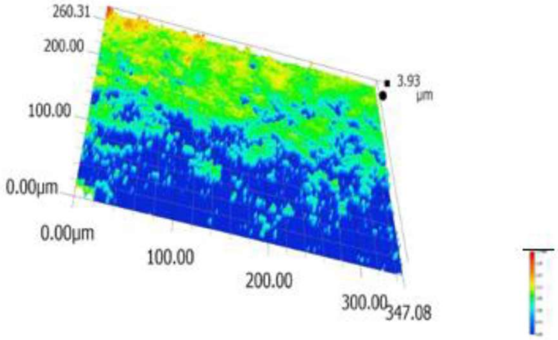
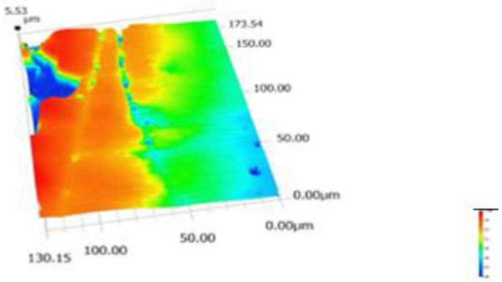
The formation of holes and/or chemical distortion on the surface of the substrate material plays a key role in the electroless coating process since the holes and distorted areas are the active sides for the adsorption of palladium atoms in activation step and reduction of nickel ions in coating step.

If there is no hole and distortion created on the surface of the substrate material, it means that there is no active side for the further steps namely, the process cannot be finalized. A successful etching step is inevitable for electroless coating of polymeric materials. In this thesis, the results show that hole and/or distortion formation on the surface can be achieved by methyl acetate, ammonium carbonate and hydrogen peroxide etching. This means that the most important step for electroless coating of polymeric materials is successfully conducted by the developed chrome-free etchants.

### 4.6 Surface Topography Investigation

The surface topography of ABS, PA was investigated by profilometry and the results are given in Table 4.4, 4.5.

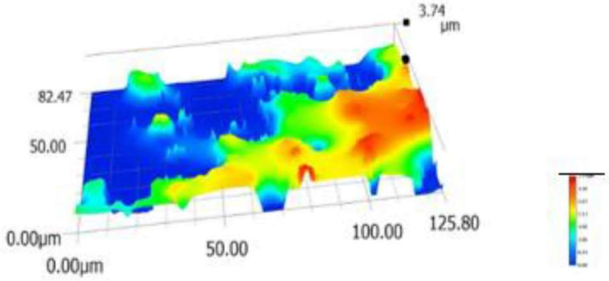
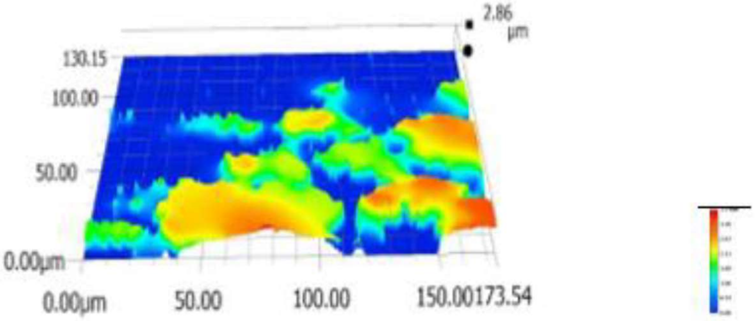
**Table 4.3:** Surface topography of ABS.

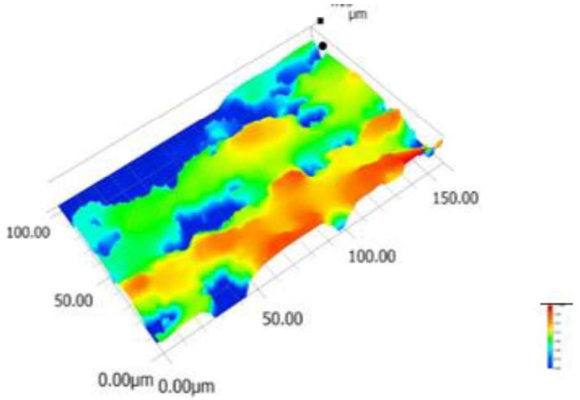
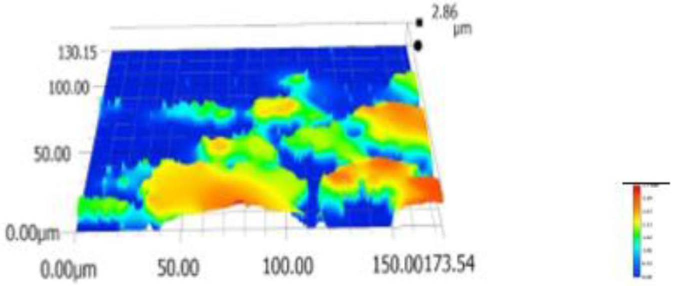
| Specimen Type | Surface Topography |
|---|---|
| **Chromic-Acid Etching** |  |
| **Ammonium Carbonate Etching** |  |
| **Methyl Acetate Etching** |  |
| **$H_2O_2$ Etching** |  |

As can be seen in the Table 4.3, in chromic acid etching wide holes are created on the surface of the substrate. It is expected behavior, hence chromic acid attacks the butadiene group of ABS. On the other hand, ammonium carbonate and methyl acetate have totally different etching mechanisms when they are compared to chromic acid. In ammonium carbonate etching, instead of creating big and wide holes, small pits are formed. However, the depth of the created holes and pits is the same. In methyl acetate etching, the mechanism is solving the hills on the surface of the substrate material, because methyl acetate is an organic solution like polymeric substrate. Since they have both organic structures, the attraction between them based on solving. While solving the hills, methyl acetate creates new active areas where the adsortion and reduction take place for further steps. In $H_2O_2$, there is no difference in etching mechanism when it is compared to chromic acid etching.

In Table 4.4, the surface topography results for PA (polyamide) are shown. It is obviously seen that the etching mechanism of chrome-free etchants are quite similar to each other and chromic acid. Every etchant attacks the surface of the polyamide and creates chemical distortion on it. This chemical distortion is seen as big and wide holes.

**Table 4.4:** Surface topography results for PA.

| **Specimen Type** | **Surface Topography** |
|---|---|
| **Chromic-Acid Etching** |  |
| **Ammonium Carbonate Etching** |  |

| | |
|---|---|
| **Methyl Acetate Etching** |  |
| **$H_2O_2$ Etching** |  |

## 4.7 Coating Thickness Measurement

The thickness of the coatings are measured by means of chemical analyzing methods. The nickel amount was measured by AAS (atomic absorption spectroscopy) machine. After that by looking at the nickel amount in the known areas, the height of the coating was calculated. The nickel amounts and coating thicknesses of the substrate materials (ABS, PA, and PC) are given in Table 4.5.

**Table 4.5:** The coating thickness of the substrate materials.

| Substrate Material | Nickel Amount(g/L) | Area ($cm^2$) | Coating Thickness (µm) |
|---|---|---|---|
| ABS | $5.3 \times 10^{-3}$ | 1.5 | 4 |
| PA | $1.63 \times 10^{-3}$ | 1 | 2 |
| PC | $1.2 \times 10^{-3}$ | 0.8 | 1.7 |

## 5. CONCLUSION

In the content of this thesis ABS, PA and PC types of polymers were used for the development of chrome-free etching for polymeric materials. For the alternative chemicals to chromic acid ethyl acetate, methyl acetate, ammonium carbonate, hydrogen peroxide, toluene, acetone, chloroform, dimethyl oxalate, and xylene were studied. Among all, ammonium carbonate, methyl acetate, and hydrogen peroxide were selected to conduct the experiments. The criteria of this selection was the quality of the coating formed on the substrate surface. the experiments were started with chromic acid etching to check whether the coating bath and the substrate materials are working or not. After achieving the continues results of repeated experiments, the experiments were continued with new etchants; methyl acetate, ammonium carbonate and hydrogen peroxide. After all experiments:

- ABS, PA, and PC were coated with electroless Ni coating by methyl acetate, ammonium carbonate and hydrogen peroxide etching.
- The effect of the etcant freshness was controlled 15 and 30 days periods for methyl acetate and ammonium carbonate and it was observed that there is no change in coating quality with changing in freshness of the ethants.
- Sateen-mat coating was obtained on PC, ABS and PA surfaces.
- Transparent coating was observed on the surface of PC specimens.

The brightness of the coating was investigated and the mechanical properties of the coating were examined. In the light of observations and obtained results, it can be said the coating quality in the physical manner is the same with the coatings obtained by chromic acid etching. However, in the case of mechanical properties such as adhesion behaviour, further studies should be applied.

As a result, ABS, PA, and PC can be coated with bright and mat nickel by using chrome-free etchant with electroless coating.

# REFERENCES

[1] **Kanani, N**. (2004). *Electroplating: basic principles, processes and practice*. Elsevier.

[2] **Barker, B. D.** (1981). Electroless deposition of metals. *Surface technology*, *12*(1), 77- 88.

[3] **M., & Schlesinger, M.** (1998). Fundamentals of electrochemical Paunovic deposition. *New York*.

[4] **Tarditi, A. M., Bosko, M. L., & Cornaglia, L. M.** (2017). 3.1 Electroless Plating of Pd Binary and Ternary Alloys and Surface Characteristics for Application in Hydrogen Separation.

[5] **Sha, W., Wu, X., & Keong, K. G.** (2011). *Electroless copper and nickel-phosphorus plating: processing, characterisation and modelling*. Elsevier.

[6] **Davis, J. R.** (Ed.). (2000). *Nickel, cobalt, and their alloys*. ASM international.

[7] **Roy, M.** (2017). Protective Hard Coatings for Tribological Applications. In *Materials Under Extreme Conditions* (pp. 259-292). Elsevier.

[8] **Bazzaoui, M., Martins, J. I., Bazzaoui, E. A., Albourine, A., Wang, R., & Hong, P. D**. (2013). A simple method for acrylonitrile butadiene styrene metallization. *Surface and Coatings Technology*, *224*, 71-76.

[9] **Dixit, N. K., Srivastava, R., & Narain, R.** (2017). Electroless Metallic Coating on Plastic Parts Produced by Rapid Prototyping Technique. *Materials Today: Proceedings*, *4*(8), 7643-7653.

[10] **Djokic, S.** (Ed.). (2011). Electroless Deposition Principles, Activation, and Applications. The Electrochemical Society.

[11] **Li, D., & Yang, C. L.** (2009). Acidic electroless copper deposition on aluminum-seeded ABS plastics. *Surface and Coatings Technology*, *203*(23), 3559-3568.

[12] **Garcia, A., Berthelot, T., Viel, P., Mesnage, A., Jégou, P., Nekelson, F., ... & Palacin, S.** (2010). ABS polymer electroless plating through a one-step poly (acrylic acid) covalent grafting. *ACS applied materials & interfaces*, *2*(4), 1177-1183.

[13] **Raja, K.** (2016). A review on Chemical Processes for Plastics substrates used in engineering industries. *International Journal of ChemTech Research*, *9*(7), 354-365.

[14] **Bazzaoui, M., Martins, J. I., Bazzaoui, E. A., & Albourine, A.** (2012). Environmentally friendly process for nickel electroplating of ABS. *Applied Surface Science*, *258*(20), 7968-7975.

[15] **McCaskie, J. E., & Tsiamis, C**. (1985). *U.S. Patent No. 4,520,046*. Washington, DC: U.S. Patent and Trademark Office.

[16] **Abegunde, O. O., Akinlabi, E. T., Oladijo, O. P., Akinlabi, S., & Ude, A. U.** (2019). Overview of thin film deposition techniques.

[17] **Sudagar, J., Lian, J., & Sha, W.** (2013). Electroless nickel, alloy, composite and nano coatings–A critical review. *Journal of alloys and compounds*, *571*, 183-204.

[18] **Loto, C. A.** (2016). Electroless nickel plating–a review. *Silicon*, *8*(2), 177-186.

[19] **Bockris, J. O. M., & Damjanovic, A.** (1964). *Modern Aspects of Electrochemistry, No. 3* (p. 224). London: Butterworths.

[20] **Parkinson, R.** (1997). Properties and applications of electroless nickel. *Nickel Development Institute*, *37*.

[21] **BALSEEAL engineering Inc.(nd)***Electroless nickel plating: A general description of electroless nickel plating and its effect on BAL Seal spring-energized seal performance in reciprocating and rotary service.* (report no: 100-63-4).USA. retrieved from https://www.balseal.com/wpcontent/uploads/2019/03/effects_of_electroless_nickel_plating_on_reciprocating_and_rotary_bal_sealTR_16.pd

[22] **Ahmad, Z.** (2006). *Principles of corrosion engineering and corrosion control*. Elsevier.

[23] **Soler Viladrich, L.** (2014). Estudio del proceso de biosorción del níquel de aguas residuales mediante residuos de raspo de uva.

[24] **Kaya, B.** (2015). *Nano kompozit kaplama* (Doctoral dissertation, Fen Bilimleri Enstitüsü).

[25] **Eraslan, S.** (2010). *Akımsız Ni-B Kaplama Sistemlerine W İlavesinin Kaplama Özellikleri Üzerindeki Etkisinin İncelenmesi* (Doctoral dissertation, Fen Bilimleri Enstitüsü).

[26] **Ahuja K., Singh S.**(2018) *Plating On Plastics (Pop) Market Size By Finish, By Application, Industry Analysis Report, Regional Outlook Application Potential, Price Trends, Competitive Market Share & Forecast, 2018 – 2024*. (report no: GMI366).USA. retrieved from https://www.gminsights.com/industry-analysis/plating-on-plastics-POP-market

[27] **Ijeri, V., Shah, K., & Bane, S.** (2014). Chromium-free etching and palladium-free plating of plastics. *NASF Surf. Tech. White Pepers*, *78*(12), 1-8.

[28] **Nigam, S., Mahapatra, S. S., & Patel, S. K.** (2017). Fabrication and study of properties in metallized ABS plastic. *Integrated Ferroelectrics*, *185*(1), 16-21.

[29] **Tsuji, K., Maeda, T., & Hotta, A.** (2015). Polymer Surface Modifications by Coating. In *Printing on Polymers: Fundamentals and Applications* (pp. 143-160). Elsevier Inc..

[30] **Xu, W., Zhuang, M., & Cheng, Z.** (2016). Environmentally friendly copper metallization of ABS by Cu-catalysed electroless process. *Rare Metal Materials and Engineering*, *45*(7), 1709-1713.

[31] **Equbal, A., Dixit, N. K., & Sood, A. K.** (2013). Electroless plating on plastic. *International journal of scientific and engineering Research*, *4*.

[32] **Olivera, S., Muralidhara, H. B., Venkatesh, K., Gopalakrishna, K., & Vivek, C. S.** (2016). Plating on acrylonitrile–butadiene–styrene (ABS) plastic: a review. *Journal of materials science*, *51*(8), 3657-3674

[33] **Hajdu, J.** (1990). Surface preparation for electroless nickel plating. *Electroless plating: fundamentals and applications*, 193-206.

[34] **Gui, C., Chen, Z., Yao, C., & Yang, G.** (2018). Preparation of nickel/PA12 composite particles by defect-induced electroless plating for use in SLS processing. *Scientific reports*, *8*(1), 13407.

[35] **Free, M. L., Moats, M., Houlachi, G., Asselin, E., Allanore, A., Yurko, J., & Wang, S.** (Eds.). (2012). *Electrometallurgy 2012*. John Wiley & Sons.

[36] **Viswanathan, B.** (1993). Metallization of plastics by electroless plating. *Current Science*, 537-543.

[37] **Margolis, J.** (Ed.). (2012). *Conductive polymers and plastics*. Springer Science & Business Media.

[38] **Popov, K., Grgur, B., & Djokić, S. S.** (2007). *Fundamental aspects of electrometallurgy*. Springer Science & Business Media.

[39] **Schaubroeck, D.** (2015). *Surface modifications of epoxy resins to improve the adhesion towards electroless deposited copper* (Doctoral dissertation, Ghent University).

[40] **Di Bari, G. A.** (2000). Electrodeposition of nickel. *Modern Electroplating*, *5*, 79-114.

[41] **Electroless Nickel Plating Quality Metal Finishing Guide**. (n.d).Retrieved October 22, 2019, from https://www.academia.edu/8866249/Electroless_Nickel_Plating_Quality_Metal_Finishing_Guide

[42] **Kuzmik, J. J. (**1990). Plating on plastics. In *Electroless Plating–Fundmentals and Applications* (pp. 377-399). William Andrew.

[43] **Mittal, K. L**. (Ed.). (2015). *Progress in adhesion and adhesives*. John Wiley & Sons.

[44] **Saubestre, E. B.** (1969). Plating on Plastics: Current Status of Processes and Standards. *Transactions of the IMF*, *47*(1), 228-236.

[45] **Logie, G. R., & Rantell, A.** (1968). The adhesion of electroless metal deposits to ABS and other polymers. *Transactions of the IMF*, *46*(1), 91-94.

[46] **Hanim, M. A.** (2017). 3.15 Electroless Plating as Surface Finishing in Electronic Packaging.

[47] **Han, X., Wang, G., He, Y., Wang, Y., Qiao, Y., & Zhang, L.** (2018). Surface modification of ABS with $Cr^{6+}$ free etching process in the electroless plating. *Journal of Adhesion Science and Technology*, *32*(22), 2481-2493.

[48] **Mallory, G. O., & Hajdu, J. B.** (1990). *Electroless plating: fundamentals and applications*. William Andrew.

[49] ***Elektrometal kaplama tekniği.*** *(n.d). Retrieved 25 October, 2019, from https://docplayer.biz.tr/1970688-13-ders-elektrometal-kaplama-teknigi-elektrolize-kaplama-vakum-ve-buharla-kaplama-yalitkan-kaplama.html*

[50] **Gui-Xiang, W., Ning, L., Hui-Li, H., & Yuan-Chun, Y.** (2006). Process of direct copper plating on ABS plastics. *Applied Surface Science*, *253*(2), 480-484.

[51] **Mandich, N. V., & Krulik, G. A.** (1993). On the mechanisms of plating on plastics. *Plat Surf Finish*, *80*(12), 68-73.

[52] ***Toxicology of Chromic Acid****.(n.d).Retrieved October 25, 2019, from https://www.nlm.nih.gov/toxnet/index.html*

[53] **Petro, R. A.** (2014). Modern Applications of Novel Electroless Plating Techniques.

[54] **Schlesinger, M.** (2000). Electroless deposition of nickel. *Modern electroplating*, *4*, 667-684.

[55] **Gan, X., Wu, Y., Liu, L., Shen, B., & Hu, W.** (2007). Electroless copper plating on PET fabrics using hypophosphite as reducing agent. *Surface and Coatings Technology*, *201*(16-17), 7018-7023.

[56] **Yabu, H., Hirai, Y., & Shimomura, M.** (2006). Electroless plating of honeycomb and pincushion polymer films prepared by self-organization. *Langmuir*, *22*(23), 9760-9764.

[57] **Barth, B. P.** (1970). *U.S. Patent No. 3,518,067*. Washington, DC: U.S. Patent and Trademark Office.

[58] **Teixeira, L. A. C., & Santini, M. C.** (2005). Surface conditioning of ABS for metallization without the use of chromium baths. *Journal of materials processing technology*, *170*(1-2), 37-41.

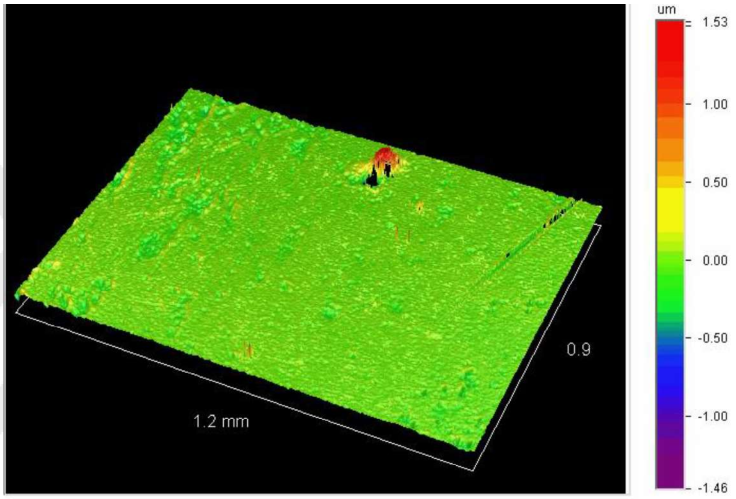
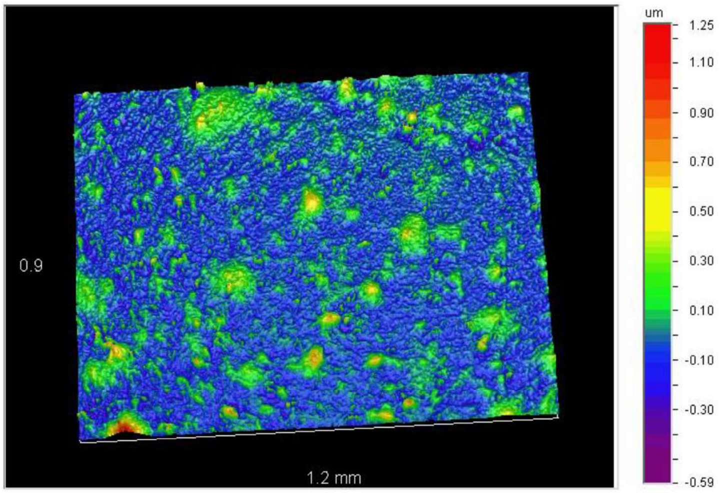
[59] **Zhang, H., Kang, Z., Sang, J., & Hirahara, H.** (2018). Surface metallization of ABS plastics for nickel plating by molecules grafted method. *Surface and Coatings Technology*, *340*, 8-16.

[60 **Zarnoch, K. P**. (1993). *U.S. Patent No. 5,180,639*. Washington, DC: U.S. Patent and Trademark Office.

[61] **Pearson, T., & Robinson, C.** (2019). *U.S. Patent No. 10,280,367*. Washington, DC: U.S. Patent and Trademark Office.

## APPENDICES

### **Appendix A:** 3D Optic Profilometer Images

| | |
|---|---|
| **Reference** |  |
| **Chromic Acid** |  |

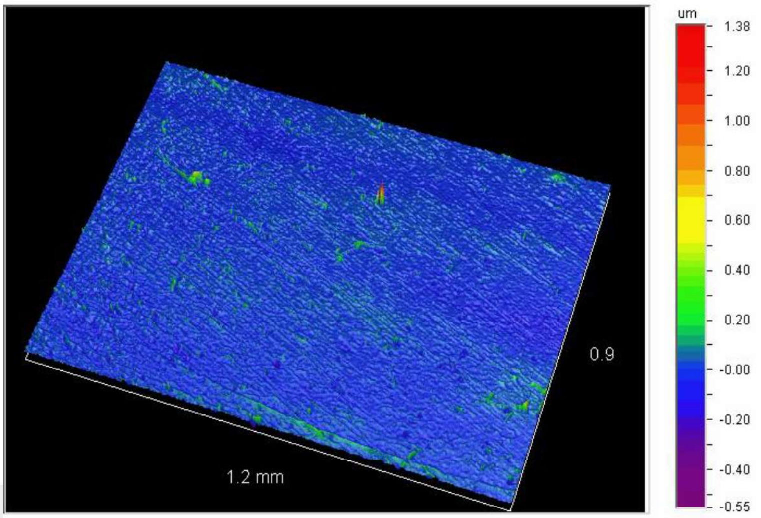
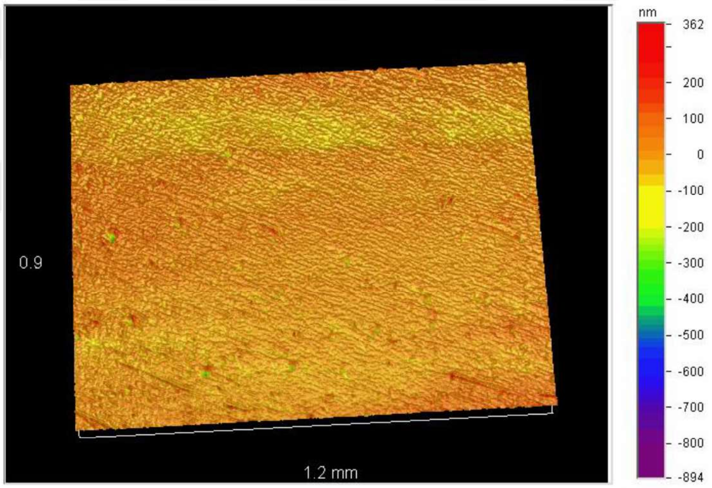
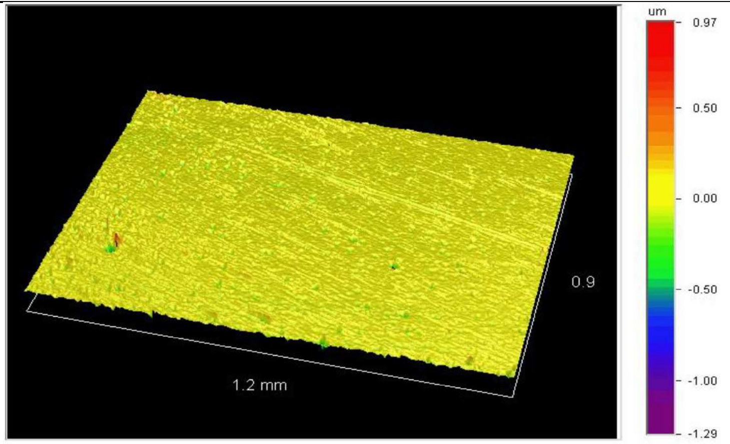
| | |
|---|---|
| **Ammonium Carbonate Etching** |  |
| **Methyl Acetate Etching** |  |
| **$H_2O_2$ Etching** |  |

**Figure A1:** The surface topography results of PC substrate

## CIRRICULUM VITEA

**Name- Surname** : Mehtap Arslan
**Place and Date of Birth** : Bakırköy/İSTANBUL – 05.06.1993
**E-mail** : arslanmeht@itu.edu.tr

### EDUCATION:

- **BSc** : 2017, İTÜ, Faculty of Chemical and Metallurgical Enginnering, Metalurgical and Materials Enginnering
- **MSc** : 2020, İTÜ, Production Metallurgy and Technologies Enginneering

### Professional Experiences and Rewards

- Researh Assistant (2019- )
- 2017 The Best Graduation Project