

**THE INFLUENCE OF INORGANIC AND ORGANIC
COATING LAYERS ON THE CORROSION
BEHAVIOUR OF COIL COATED ALUMINUM
SUBSTRATES**

**A Thesis Submitted to the
Graduate School of Engineering and Science of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of**

MASTER OF SCIENCE

in Chemical Engineering

**by
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**May 2020
İZMİR**

ACKNOWLEDGEMENTS

First, I would like to thank my supervisor Assist. Professor Dr. Ali Can KIZILKAYA, for his support, guidance and patience during my studies. He continually and convincingly inspired me to writing the thesis with his deepest knowledge.

I present my gratitude to Assist. Professor Dr. Bařar AĐLAR for the technical support and assistance he provided during the electrochemical experimental processes I conducted in the chemistry laboratory of Yařar University.

I would like to thank Akzo Nobel Kemipol for the material supply and technical support during the thesis studies.

Also, I would like to thank Mine BAHECİ, Adem YAVUZ, Mutlu Devran YAMAN, Zehra Sinem YILMAZ and Duygu OĐUZ KILI for their help and discussions during the material characterization I have performed in the IZTECH material research laboratory.

During my thesis study, I am always grateful to my teammate YaĐmur DAĐA. Her support was very important to me. Thank you girls, Nilsu İSKEMAN and Glin GMŐBULUT for always being friendly and helpful. Also, I would like to send my love to Ahmet Mert AKIR and YaĐmur BİLGİN from my heart. They always empowered me and made me move forward firmly.

Finally, I would like to extend my deepest thanks to my dear family for supporting me spiritually and always believing in me throughout my life.

ABSTRACT

THE INFLUENCE OF INORGANIC AND ORGANIC COATING LAYERS ON THE CORROSION BEHAVIOUR OF COIL COATED ALUMINUM SUBSTRATES

Organic coil coated aluminum substrates are one of the most widely used materials for construction industry. These coated substrates typically consist of 4 separate layers, the aluminum substrate, the inorganic conversion coating (resulting from the pretreatment application), and the organic coating layers that are called the primer and the topcoat. From industrial experience, it is not clearly and quantitatively determined how these layers contribute to the different processes that occur during corrosion, such as water uptake (diffusion of water through the coating) and the corrosion reactions that take place on the substrate. In this thesis, the formation of the inorganic conversion coating as a function of the pretreatment application parameters, immersion time, temperature and pH, and the individual effects of inorganic and organic coating layers on corrosion are investigated. The structure of the various surfaces formed after coating application and after corrosion testing by Neutral Salt Spray Test (NSST) is investigated by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Fluorescence Spectrometer (XRF) and Atomic Force Microscopy (AFM) analysis, while their anticorrosive properties are determined by Electrochemical Impedance Spectroscopy (EIS). The results indicate that the formation of the pretreatment layer is enhanced continuously as function of temperature and immersion time, within the values investigated, while for pH an optimum is observed. The investigation of the corrosion resistance of substrates coated with different coating layers reveal that without organic coating layers, the substrates corrode much faster, indicating the importance of water diffusion on the corrosion reactions.

ÖZET

İNORGANİK VE ORGANİK KAPLAMA KATMANLARININ BOBİN KAPLAMALI ALÜMİNYUM SUBSTRATLARIN KOROZYON DAVRANIŞINA ETKİSİ

Organik bobin kaplamalı alüminyum substratlar inşaat sektöründe oldukça yaygın kullanılan malzemelerdir. Bobin kaplama sistemi, alüminyum metali, önışlem uygulaması sonucunda oluşan dönüşüm kaplaması (inorganik kaplama), astar ve sonkat (organik kaplama) olarak adlandırılan kaplama katmanlarından oluşur. Endüstriyel çalışmalardan, bu katmanların, su alımı (suyun kaplamadan difüzyonu) ve substrat üzerinde meydana gelen korozyon reaksiyonları gibi korozyon sırasında meydana gelen farklı proseslere nasıl katkıda bulunduğu açıkça ve niceliksel olarak belirlenmemiştir. Bu tezde, önışlem uygulama parametreleri olan daldırma süresi, sıcaklık ve pH değerinin bir fonksiyonu olarak inorganik dönüşüm kaplamasının oluşumu ve inorganik ve organik kaplama katmanlarının korozyon üzerindeki bireysel etkileri araştırılmıştır. Kaplama uygulamasından ve tuzlu sis korozyon testinden (NSST) sonra oluşan çeşitli yüzeylerin yapısı, Atomik Kuvvet Mikroskobu (AFM), Taramalı Elektron Mikroskobu (SEM), Elektron Dispersif X-Işını Spektroskopisi (EDX) ve X-Işını Flüoresans Spektroskopisi (XRF) kullanılarak, korozyon önleyici özellikleri ise Elektrokimyasal Empedans Spektroskopisi (EIS) kullanılarak belirlendi. Sonuçlar, önışlem katmanının oluşumunun, sıcaklık ve daldırma süresinin fonksiyonu olarak, araştırılan değerler dahilinde sürekli olarak geliştirildiğini, pH için ise bir optimum değer gözlemlendiğini göstermektedir. Farklı kaplama katmanları ile kaplanmış substratların korozyon direncinin araştırılması, organik kaplama katmanları olmadan, substratların çok daha hızlı korozyona uğradığını ve korozyon reaksiyonlarında su difüzyonunun önemini göstermektedir.

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To my dear family,

CHAPTER 1

INTRODUCTION

In this section, literature information about corrosion, corrosion protection methods and coating process is summarized to understand the studies and results made during the thesis research.

1.1.Coating Industry

Coatings are one of the most important methods for metallic materials to protect against corrosion¹. They play an important role in providing both a specific point and an overall corrosion control. The coatings do not have a clear classification as it contains many meanings. However, it can basically be divided into four classes. This classification is in the form of organic, inorganic, conversion and metallic coatings.² Generally, it can be said that a material (usually liquid) applied to a substrate will dry and form a protective film.³ Theoretically, coatings are used in various ways to slow down, select and use the corrosion reaction.⁴ Most of the coatings are applied to the outer surface. The reason for applying outer layer is to protect the metal from natural atmospheric corrosion and atmospheric pollution. In some cases, it may also be necessary to protect the property from sudden spills and splashes. It is important that the metal was coated at this time.² Coatings are a very complex total of raw materials. It must be carefully prepared and properly applied to the substrate. In addition, it must be properly dried to achieve maximum efficiency. Although the application methods and contents are different, in general term, an ideal coating should provide the following properties;⁵

- should be continuous for every surface on it is applied
- should be impermeable against components and have a low environmental reactivity
- should be resistant to mechanical and physical effects
- should the desired function, i.e. aesthetics expectations or corrosion resistance
- should be low cost and consistent with the product
- should have reduce the energy loss through the environment.
- should have stable over years

1.1.1. Organic Coatings

Organic coatings are thin protective layers applied on metal. The main task of organic coatings is to improve the surface properties of the material and protect it from the influence of environmental factors. Such coatings act as a barrier while providing protection on the surface, trying to prevent the passage of oxygen, water and ion. However, as stated in the literature, barrier properties are limited. The reason for this is that not all organic coatings can prevent the passage of water and oxygen to some extent. It is known that the average velocity of water from a coating to the material surface is 10 to 100 times higher than that of a free-flowing surface. These types of coatings ensure the resistance of metals and resist physical and chemical factors such as weather, abrasion, toughness, humidity. It also responds to aesthetic concerns. Additionally, the efficiency of organic coatings depends on the mechanical properties of the coating system, the type and concentration of the inhibitors contained in the coating, the pretreatment process used before application and its adhesion to the metal surface.²⁻⁴

A paint system consists of two or more layers combined. Thus, in addition to providing specific protection of the layers, the coating thickness is increased. In addition, the pores are discontinued to prevent the reaching of moisture and water from the coating through the substrate as shown in Figure 1.⁶

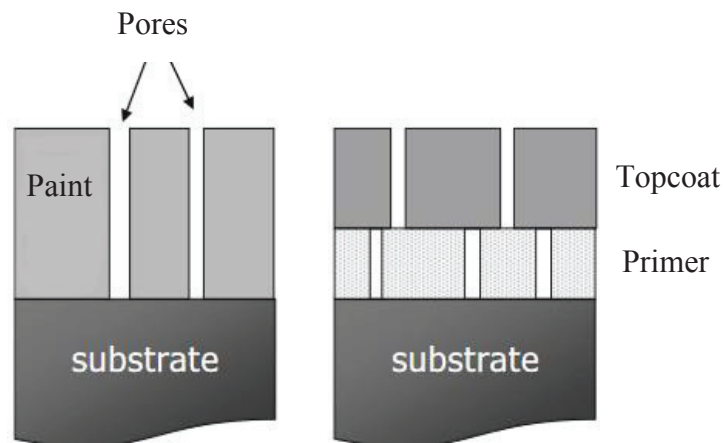


Figure 1. Schematic of different layer effect on pore structured coating⁶

Organic coatings have a complex structure and contain four essential ingredients as additives, pigments, solvents and binders.

- Binders: Binder is basically a component that provides the cohesive forces of the paint layers and structure and increases the continuity of the paint.⁶ Polymeric organic molecules or non-polymeric organic molecules can be used as binders. However, since the binders that are polymerized and used are of large molecule structure, they form a hard and solid layer on the surface. Binders with small molecules are also hard but may not be of sufficient hardness. Therefore, they can be hardened by using additive components or drying in ovens in order to increase their durability. Non polymeric binders are hardened using UV rays. The most commonly used binders are oleoresinous, alkyds, aminoresinous, phenolic resins and epoxide resins.^{3,7,8}
- Pigments: Pigments are an insoluble composition group in solvents and binders used for coloring organic coatings. Pigments are dispersed homogeneously in the organic coating medium as stable solid suspended agents. Pigments are divided into three groups as coloring pigments, anticorrosive pigments and fillers according to their function. However, the essential purpose of pigments is to provide color and opacity to the coating film. The common name of pigments is color pigments. This group includes red / yellow / black iron oxide colorants and whitening pigments such as titanium dioxide.

The properties of pigments vary according to the particle size. The size of the pigments is usually below 1 μ m. As the particle size of the pigments consisting of the same chemical material increases, their transparency decreases, the color intensity decreases and the endurance increases. Although the important majority of coatings contain pigment, there are also coatings that do not contain pigments or contain very little pigments. These coating groups are also called clear coats.^{2,3,7,8}

- Additives: Additives is a coating component that is applied in a small amount in a coating. However, despite their small amount, they affect the coating function, film formation and mechanical properties of the coating. In addition, they have great contributions in increasing film resistance. Stabilizers and flow modifiers are commonly used additions.^{3,7-9}
- Volatile Components: Volatile components are highly effective in the coating application process. The main purpose of using these components is to adjust the viscosity of other coating components to ensure homogeneous mixing of the paint. Thus, an effective wetting of the surface on which the formation of the continuous layer takes place is ensured. Such liquids evaporate during and after application.

In order to reduce VOC emissions, the use of solvents is tried to be reduced. For this, it is ensured that most of the volatile components are formed from water. Today many coatings contain volatile solvents. It contains not only solvent-free liquid coatings, powder coatings and radiation curable coatings.^{2,8,10}

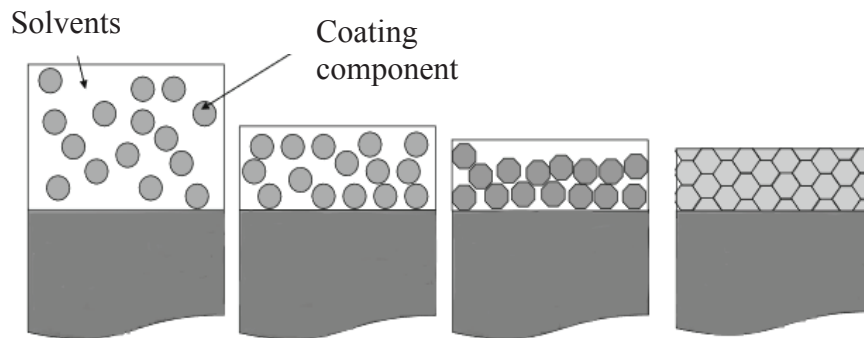


Figure 2. Mechanism of film formation with volatile components ⁶

1.2. Principles of Corrosion Protection

Corrosion resistant coatings are usually divided into three category according to the protection mechanism of the metal substrate. These categories are barrier protection coatings, inhibitive coatings and zinc-rich coatings. Barrier protection provide an impermeable barrier to water and corrosive ionic species while inhibitive coatings utilizing corrosion inhibition by using corrosion inhibitors. The type of coating used in this study is included in the class of barrier protection coating and inhibitive coatings. In addition, the coating system in this study is a multilayer coating system. In these systems pretreatment and primer interlayers can apply to increase the adhesion and corrosion resistance of the substrate metal. Additionally, topcoat can be used for aesthetic reasons and environmental resistance. ¹¹

1.2.1. Barrier Protection Coatings

Barrier coatings act as an impermeable barrier against moisture and corrosive ions, providing ideal protection of the substrate metal. In order to the corrosion process to begin, the environment must contain moisture. Therefore, if the coating that acts as a barrier is intact, no corrosion is observed in the inner layer. However, it initiates with the

passage of moisture and water from deformations on the coating. It is possible to use barrier coatings to control and prevent both oxygen permeability and the permeability of ionic components. Preventing oxygen from reaching the metals prevents the formation of a cathodic reaction. The ionic transfer resistance of the film shows every moisture reaching the substrate as much as it prevents the current transfer between the anodic and cathodic parts.^{3,12} The mechanism of barrier coating is shown in Figure 3. These coatings can be made to have high electrical resistance using non-hydrophilic materials. This ensures high adhesion, even in wet conditions.^{13,14}

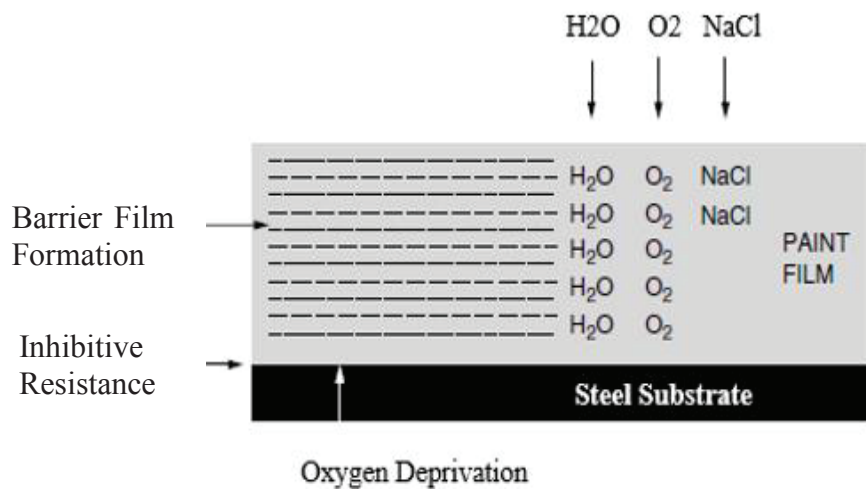


Figure 3. Barrier Coating of Steel Substrate⁴

Barrier coatings can be used combined with cathodic protection systems that impressed current. In this case, they provide smaller exposed cathode areas and thus reduce the cost of required electricity that maintains the current flow direction. One use of barrier coatings is to minimize the cathode-anode area ratio found in complex metal systems that are not conducive to insulation.

Organic coatings are structurally prone to water permeability, retaining moisture and maintaining the water concentration by trying to balance with the humidity in the atmosphere. In this case, if the coating adheres well to the substrate, the water molecules remain within the molecular structure of the coating. Thus, the coating does not accumulate at the substrate interface. If the coating adhesion is not good enough due to contamination on the substrate surface, the water molecules in the coating will react with the surrounding components and accumulate in the substrate interface forming blisters in the coatings, which could cause the corrosion.¹⁵ Inorganic coatings are generally more resistant to moisture due to their natural structure, but they have a fragile.

Inorganic coatings can crack and wear out. Some inorganic coatings can be applied directly on the metal substrate by chemical or electrochemical processes. Anodized coatings applied on aluminum are examples of this group. These coatings can be porous, depending on the application parameters.¹¹ Corrosion inhibitors can be added to the coating requirements to increase corrosion resistance to overcome situations where barrier coatings are insufficient.

1.2.2. Inhibitive Coatings

Corrosion inhibitors are chemical components that control the rate of electrochemical reactions in order to reduce the corrosion. These substances reduce the corrosion rate by chemically change the interfacial conditions against the metal. This process can be achieved by adding pigments that take the oxidizer ions formed in the intermediate layer and other passivating parts into the aqueous phase. Inhibitors are often used at low concentrations.^{9,14}

When the paint components are considered, the paint component that exerts a slowing resistance to the paint is usually pigments. With the use of pigment, passive films are formed on the metal under the coating. These passive films reduce the required electrolytic oxygen level. The choice of both binders and inhibitors is crucial to minimize blister formation on the coating and to provide long-term passivation without rapidly consuming pigment ions. PVC/CPVC control is also important in maintaining to coating permeability. Because in this way, enough moisture is stuck to break down the slowing ions in the pigment in the film. But many areas of the film may become porous. Highly porous films will allow absorption ion species (chlorides and sulphates) to be transmitted to the film and metal, where they compete with inhibitory ions for adsorption and prevent passivation.^{3,4,9}

Inhibitive coating mechanism for steel substrate is shown in Figure 4. In this case, the controlled porosity film allows the water to leak inhibitory ions from the soluble pigment, which makes it inhibitory. The formed film is less porous against corrosive ions outside the film. Therefore, the ratio of preventive ions to corrosive ions on the surface of the steel becomes conducive to passive surface formation. In this case, the surface of the steel substrate consists of a passive layer. Due to the passive formation, dissolved ions penetration is prevented through the metal surface.⁴

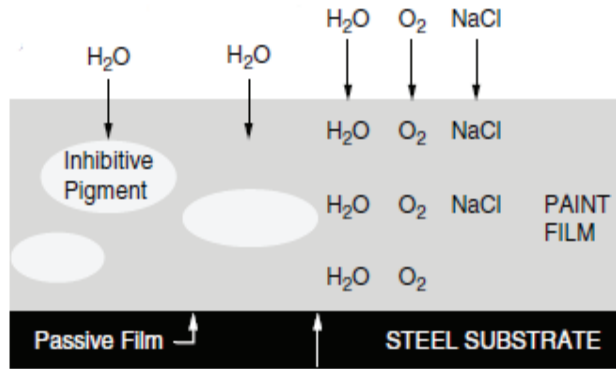


Figure 4. Schematic of Inhibitive Corrosion⁴

It is usually accomplished by incorporating inhibitors into the structure of the pretreatment solution and primer in the coating systems. One of the most important corrosion inhibitors is chromium. Although it is a strong inhibitor that increases the efficiency of the systems as an inhibitor, industrial usage is gradually reduced due to its carcinogenic properties. Therefore, searches for less toxic inhibitors that can replace them have begun.¹¹

Oleoresins, oils, alkyls, epoxy esters, and phenolic varnishes are most commonly used as a inhibitive coating components. In addition, epoxies and latex primers are also included in this group. Inhibitive coatings are usually used for light to change duty atmospheric service, although they may be part of relatively high performance systems. Automotive primers, aircraft coatings, and coil coating primers are kind of inhibitive coatings. However, they are often unsuitable for continuous use in long-term freshwater immersion, high temperatures or very humid conditions.⁴ Basically, organic compounds containing oxygen, sulfur and nitrogen and having multiple bonds are used as effective inhibitors for many metals and metal alloys. In different environmental conditions, for a given metal, the effect of the inhibitor depends on different parameters. These parameters are that the inhibitor molecule has centers that can attach to the metal surface and form bonds by means of an electron transfer. In addition, the stability of the complex formed is also important.¹⁶

1.3.Metal Surface Preparation and Coating Operation

The process of preparing the metal surface is one of the most important steps for

each coating process. It is also important to determination of metal substrates before preparing metal.

There are many different metal substrates in industry and research laboratories. The most preferred and used metal panels are galvanized steel, nickel, cold rolled steel, iron and aluminum. Metal substrate type can vary according to the demands and usage areas. During this study, standard aluminum test panels was used as substrate.

The main reason for using aluminum substrate is the suitability of these test panels for coating. Aluminum is lighter than many metals and has a lower exposure to corrosive attacks. While preparing aluminum metal, many alloys can be added. This strengthens the metal against external influences such as breakage, impact and makes it compatible for most pretreatment processes.⁴

Preparation of metals includes two stages as metal cleaning and pretreatment application. Another name for this process is conversion coatings. However, it is commonly called pretreatment in the field of industry. This applied stage is a main essential stage due to increasing compatibility with paint system and increasing the corrosion resistance of the general surface.^{2,17} In order to increase the adhesion of the coating to the surface, the surface must be cleaned before pretreatment application.

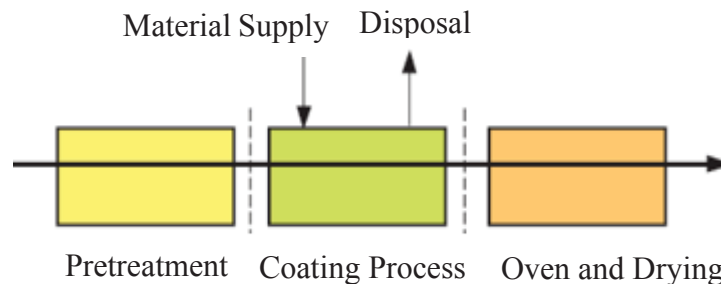


Figure 5. Application steps for coating process⁸

Different materials require different pretreatment steps. In case of wooden surfaces, it is necessary to fill the nail cavities and lining the knots. Acid pretreatments are effective in breaking down poorly bounded contaminations on the surface when cementitious and wall surfaces will be covered. On the other hand, a single pretreatment application may not be sufficient to increase adhesion throughout the plastic surfaces. Therefore, additional pretreatments can be applied. In this way, mold release is decreased or removed. When the metals are coated, metal surfaces are cleaned using aqueous

chemicals or solvents. This can be done by brushing or sanding and polishing. The structure, shape and size of the substrate are important in the choice of application.

Before coating a metal product, the mechanical and physical properties of the substrate need to be improved. Thus, the substance with increased chemical and corrosion resistance gains value by giving decorative properties. An effective pretreatment application eliminates cracks, deformations and contaminations of the metal surface, allowing the coating to spread to the surface more homogeneously and adhere to the surface in a compact way. If the metal substrate contains deformations such as pores, cracks etc. on the surface, the coating gets filled by these deformations and begins to spread as shown in Figure 6. Thus, a mechanical bond is formed in between substrate and coating. As a result of researches and analysis, it has been confirmed that the coating on these deformed surfaces penetrates and creates a mechanical bond between the coating and the surface.



Figure 6. Illustration of mechanical interaction between the coating and substrate²

When all these situations are taken into account, the compatibility of cleaning, pretreatment and coating stages with each other determines the quality of a coated finished product as shown in Figure 7. In order to obtain maximum efficiency from the coating to be applied to the metal surface and to improve corrosion resistance and adhesion, the pretreatment step should include the following properties;

- Activating the bare metal surface by removing its natural oxides, organic soils and contaminations.
- Pretreatment of the surface provide the prevent reformation of oxides, maintain surface stability and make the surface inert. Additionally, ensure the better adhesion of the coating and the surface.

- Avoid the risk of under-film corrosion when the coating is damaged.

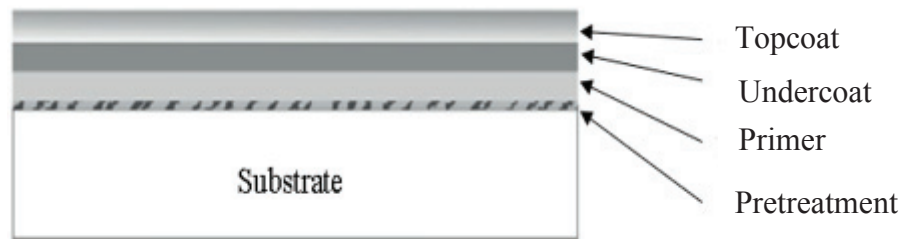


Figure 7. Schematic of coated final product¹⁸

1.3.1. Cleaning of Metal Surface

Coating application begins with the cleaning of the metal surface. The cleaning stage required for metal strips is cleaning where the surface oils and particles causing pollution are removed. Effective cleaning is a very important parameter for the life service of the coating. Oily soil particles should be cleaned before surface treatment. There is a risk of spreading to the surface if it is not cleaned. In addition, these soils are likely to contaminate abrasive cleaning environments and vehicles. This type of pollution, agitated immersion containers can be cleaned quickly. For contamination types such as dirt, grease, salts and pollutants, solvent clean substances may be appropriate. These cleaners are for use at high temperatures to be more effective.²

Cleaning can consist of one step or multiple steps. These stages can be applied with different application techniques. Abrasive brush application, immersion technique or brushing techniques are some of these techniques. Some of these applications are more suitable for easy pollution removal and some are more suitable for general surface cleaning.

While applying the cleaning solution, care should be taken not to expose substrates such as aluminum and zinc, excessive alkaline solutions. The high chemical attack can negatively affect the conversion coating, which will be applied after cleaning operation. It may cause staining on the surface and trigger the formation of corrosion product. Nowadays, with developing technology, low concentrated alkaline clean solutions are used. These new solutions are available with surfactant technology, which has excellent dirt removal and degreasing capability.

Besides the alkaline cleaning solution, aluminum surfaces can also be cleaned with an acidic solution. When cleaning aluminum, the most important point is to be able to etch the minimum amount of aluminum from the surface while the surface cleaning process is carried out. As a result of the researches, the optimum removal rate is 0.2-0.3 g/m². At values below this value, a homogeneous cleaning may not be achieved on the surface. This causes contamination residue on the surface.

In cleaning solution applications, it is also necessary to apply rinses. In this way, residual cleaning solution residues on the surface are prevented from proceeding to the next reaction steps. This process is necessary to remove residues on the surface and make the surface more inert.

1.3.2. Pretreatment of Metal Surface

After cleaning and rinsing, the pretreatment application stage comes. This stage is applied to ensure good adhesion, increase corrosion protection and achieve a relatively smooth surface.

Corrosive, acidic cleaning solutions can also be used as pretreatment solutions. Because the effect of multiplication of blasting media and the use of brush and abrasive pads improves adhesion by increasing the roughness of the surface in the substrate. However, this step is still a very important step for coating, as the acidic or alkaline cleaning process does not completely clean the substrate.²

The chemical pretreatment stage is one of the essential steps for a coating system, as it contributes to the compatibility between the topcoat and primer applications and the metal and increases the overall electrochemical resistance of the system and effect the ionic migration through the metal. The use of pretreatment application in the industry is very common and the commercial pretreatment reference is quite high. However, not all pretreatment systems are suitable for all metal substrates. The pretreatment option differs depending on the type of metal to be applied. The selection criteria for pretreatment depends on the quality of the metal substrate, the end-use application and its compatibility with the metal substrate.^{17,19}

The principle of corrosion prevention by conversion coating depends on the structure, composition and thickness of the coating solution. These parameters are effective in the formation of chemical bonds at the metal and coating interface. These

chemical bonds affect the permeability by controlling the passage of water, oxygen and ion to the metal surface.^{20,21}

Chemical pretreatment application methods can be classified as two basic groups as film forming and non-film forming methods. The film forming group is the method of flame cleaning thermal reduction of oxides, which involve the pickling of the metal surfaces with acids and bases. The second group are pretreatments that applied non film forming, are inorganic conversion layers.⁸

The most commonly used conversion coatings are phosphate conversion coatings and their use in industry is quite high. Phosphate pretreatments are commonly used in the automotive industry. In addition, it is preferred because it is economical in agriculture and white goods industries. However, phosphate conversion coatings have increased the tendency to other conversion coatings, although they are economical due to environmental causes and energy losses. Discharge after use of concentrated phosphate baths during surface pretreatment creates a fatal risk for living creatures in groundwater resources. In addition to these situations, sometimes chromic acid is added to its content to strengthen the function of phosphate conversion coatings. In this way, the roughness is reduced and this causes an increase in corrosion resistance. As chromic acid is a dangerous and toxic substance, its use is inconvenient. Due to such disadvantages, more environmentally friendly alternatives such as organosilanes, titanium and zirconium based conversion coatings have begun to take their place. Organosilanes are one of the highly effective conversion coatings in adhesion enhancement, but their use is limited as they are used for certain paints.^{22,23} Chromate conversion coatings are one of the most efficient coatings in terms of providing high corrosion resistance, application simplicity and provide better adhesion. Among the chromatic conversion coatings, the hexavalent chromium pretreatments are the ones that provide the best protection. The reason for the highest efficiency from chromated conversion coatings is that it provides resistance to corrosion by self-healing method.¹⁷

The self-healing mechanism is based on the principle of reducing Cr^{6+} to Cr^{3+} when the conversion coating occurs due to the high oxidation potential of the hexavalent chromium, chromates migrate to the areas where the coated metal surface gets damaged and corrosion begins. In this way, the chrome goes to the sacrificial anode state. The sacrifice of chromium ensures that metal corrosion is largely prevented. Thus, self-healing mechanism is realized. Cr-free conversion coatings are less effective than chromate conversion coatings because they do not have this mechanism. However,

research has recently increased for conversion coatings that can replace chromate. Instead, by providing barrier protection, ions and oxygen are prevented from reaching the metal. Due to the toxic and carcinogenic effect of chromate, the use of chromate conversion coatings has been banned. Therefore, conversion coatings with barrier mechanisms are used. The coating group that provides the best protection in this coating group is hexafluorotitanic acid and hexafluorozirconic acid groups.^{24,25} These conversion coatings are acidic solutions that contain manganese phosphate, titanium, zirconium, hexafluoride and organic polymer.

Pretreatments are generally applied to the metal surface with the help of immersion and spraying techniques. In addition, there are different pretreatment types that can be applied with roll coaters. Metals are pretreated by choosing different application technique that is suitable for the structure of the pretreatment solution and this pretreatment solution's application techniques. One of the traditional application methods, the rod coating method is shown in the Figure 8. ²⁶

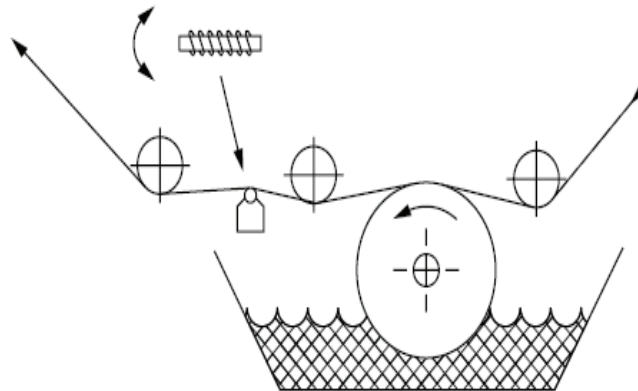


Figure 8. Schematic example of typical application. ²⁶

When the surface of bare aluminum metal comes into contact with air or water, it forms a protective oxide layer on it. Although this oxide layer helps provide corrosion protection against corrosive attacks, it can cause various problems when it is applied to the surface. This natural oxide layer formed on the aluminum metal surface prevents the adhere of the conversion coating to the surface since it is not evenly distributed on the surface. If the metal has a surface that affects its homogeneous distribution, it can negatively affect the corrosion resistance. Also, the oxide layer on the surface can dissolve when the pH value changes.

Researches show that it reduces the corrosion resistance when the pH value is below 4 or by dissolving above 10. Therefore, conversion coatings must be applied to the aluminum surface. ⁴

Studies have shown that the dispersion of titanium phosphate is highly effective in order to make the film formation on the aluminum surface is uniform. In addition, manganese ions support the formation of the film, increasing the homogeneity. In addition, fluorides are used so that aluminum ions do not dissolve and remain stable in the system. In addition, silicates can be applied as they do not see any inhibitors. ⁸

1.3.3. Primer Application

Primer application is the intermediate layer that can be applied to metals before the topcoat application. The main purpose of this mezzanine application is to ensure that the cleaned and pretreated metal surface adheres better to the finishing application. Primers can be applied directly to the pretreated surface to protect the metal substrate from corrosion. To increase the corrosion resistance of the primer layer, anticorrosive pigments are added. This layer is also applied to protect the finish of the coating from the acidic or basic properties of the pretreatment application. The primer can be considered as a preparatory step applied to the surface before the topcoat is applied and the metal is coated. It is also more economical than topcoat application in terms of cost savings in the long run. After the primer is applied to the metal surface, the primer can be applied to the surfaces after it ensures proper drying. ⁴

1.3.4. Topcoat Application

The topcoat application is a transparent or colored topcoat applied on the underlying material. Considering the coating system, it provides sealing feature for intermediate layers and metal surfaces. Topcoat application may not be single stage. Generally, the first topcoat application is effective in providing an impermeable surface for the intermediate layers. It is the primary defense layer of many coatings against an aggressive environment. The second finishing application is effective in increasing the mechanical resistance of the coating against external factors, providing corrosion resistance and meeting aesthetic expectations. ⁸

Considering all coating processes, effective and corrosion resistant coatings depend on different parameters. In order to apply the parameters adequately and properly, a good understanding of the corrosion mechanism is required.

1.4. Electrochemical Mechanism of Corrosion

Corrosion is the process that a material deterioration as a result of electrochemical and chemical reactions with its environment. Corrosion is an important problem that must be prevented because it can cause natural disasters, destructions and significant economic losses.²⁷

The main reason for the occurrence of corrosion is that the metals are stable in their own state in nature. The natural form in which metals are stable are ore forms. Energy is transferred from the ore when metals are taken from the ore states and processed. After this energy transfer, metals intent to become thermodynamically stable state. Metals react with the surrounding elements to reach their more stable nature. These reaction products are usually oxides, sulphates, halides and other corrosion products. During these reactions, metals gradually degrade.

If the oxides formed by the compound have a porous structure or do not adhere well to the surface of the metal substrate, the metal is actively corroded. If oxides on the surface form a compact and impermeable layer with the surface of the metal substrate, the oxides adhere well to the surface, passivating the metal and providing corrosion resistance. If the perimeter of the metal contains aggressive ions, the passive film may deteriorate and local corrosion may occur on the metal surface. Therefore, metals that do not form passive film naturally or where this film is inadequate and where there are many corrosive ions in the environment should be coated.¹¹

The corrosion process of metals is based on the principle of electrochemical and chemical reactions. An electrochemical, also called galvanic reaction, occurs when two different metal parts are connected together with a conductive wire and put into contact with the electrolyte. This electrolyte is usually water containing dissolved salts. The corrosion potential of metals can vary depending on the electromotive series. Compared to this electromotor series, metals with a more positive potential are electrochemically more noble or stable and the more negative potential are more active or unstable state as shown in Table 1.

The more negative single potential means that the metal is more active. This is because when the free energy of gibbs is less than zero, the environment becomes kinetically stable condition. The electrochemically more stable side oxidizes less and acts as a cathode. However, since polarization processes can change the characteristics of the metal, it can also change its electrochemical potential. Therefore, in some cases (adsorption of hydrogen gas, thin corrosion layer accumulation on the metal surface, etc.) potentials can change. In general, when looking at the basic elements, it can be listed as magnesium, aluminum, zinc, iron, tin and copper according to the decreasing degree of oxidation.⁴

Table 1. Standard electrode potentials of metals.⁴

Electrode Reaction		Potential (volts)	
Active			
Na	↔	$\text{Na}^+ + \text{e}$	-2.71
Mg	↔	$\text{Mg}^{+2} + 2\text{e}$	-2.38
Al	↔	$\text{Al}^{+3} + 3\text{e}$	-1.66
Zn	↔	$\text{Zn}^{+2} + 2\text{e}$	-0.76
Fe	↔	$\text{Fe}^{+2} + 2\text{e}$	-0.44
Pb	↔	$\text{Pb}^{+2} + 2\text{e}$	-0.13
H	↔	$\text{H}^+ + \text{e}$	0.00
Cu	↔	$\text{Cu}^{+2} + 2\text{e}$	0.34
Ag	↔	$\text{Ag}^+ + \text{e}$	0.80
Pt	↔	$\text{Pt}^{+2} + \text{e}$	1.2
Au	↔	$\text{Au}^{+3} + 3\text{e}$	1.4
Noble (Passive)			

The corrosion process consists of electrochemical reactions involving oxidation and reduction reactions. Oxidation reactions are anodic reactions, reduction reactions are cathodic reactions. Since metal dissolution occurs as a result of oxidation reaction, it is an anodic reaction. Therefore, corrosion occurs on the anode. The higher the voltage occurs between the anode and the cathode, this high voltage allows high resistance to be applied to aggressive ions.²⁸

The reactions that take place in a standard corrosion cell are as follows,^{2,11}

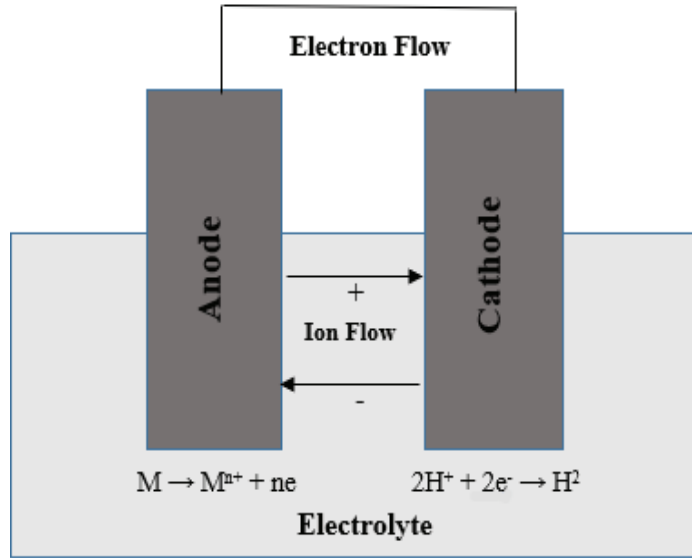
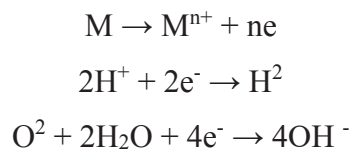


Figure 9. Schematic of electrochemical corrosion cell³

If the anodic reaction (M=metal) is as follows, the cathodic reactions take place in acidic and alkaline conditions respectively given in Equation 1.



Equation 1. Corrosion reactions occur on acidic, neutral and alkaline conditions²

The cell potential of the overall corrosion reaction must be positive for the corrosion process to occur. This positive E_{cell} indicates that gibbs free energy is decreasing. The potential of overall corrosion reaction is the difference in the equilibrium potentials of cathodic and anodic half reactions.¹¹ For example, according to equation 1., in general, during the dissolution of an acidic solution of a metal and the formation of hydrogen evaluation of a cathodic reaction in this cathodic half cell, general corrosion can be calculated as follows;

$$E_{cell} = E_{H^{+}/H_2} - E_{M^{n+}/M}$$

Equation 2. General corrosion equation²

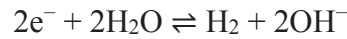
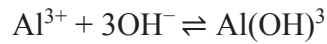
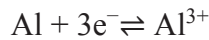
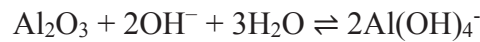
According to this given equation, the equilibrium potential can be calculated according to the equation given below. This equation is called the Nernst equation.

$$E = E^0 - (RT/nF) \ln(a^{\text{reactants}}/a^{\text{products}})$$

Equation 3. Nernst Equation²

In this equation, E^0 is standard potential, R is universal gas constant, T is absolute temperature, n is number of electrons that transferred during the half-cell reaction in the cells, F is Faraday constant, $a^{\text{reactants}}$, activity of reactant on the reaction and a^{products} is activity of products on the reaction.

If we consider corrosion reactions for aluminum substrate in alkaline conditions, the equations are as follows;



Equation 4. Corrosion reactions for aluminum substrate in alkaline condition²⁹

As stated in the previous sections, the task of the coating is to protect the metal substrate from the environment by protecting itself. The coating performs this process according to two basic properties of the coating material. The first of these features is that the coated coating becomes a continuous after it is applied correctly and the corrosion resistance that occurs during this time. Electrochemical behavior of the coating material when the coating is exposed to wear and faults. Given these two conditions, the mechanism of the corrosion cell can explain the behavior of the coating. Therefore, these coating and corrosion events complement each other.²

The potential difference between anode and cathode half cells is also a degree of the thermodynamic behavior of the metal surface against the environment. Therefore, the potential difference of reactions in the half cells directly affects the rate of corrosion. In order to make the surface of the active metal more stable, it is necessary to coat the surface with more stable metals. When exposed to the natural environment, the reactants of the

cathodic reactions in the cathode of the metal are dissolved oxygen and hydrogen ions, so they act as natural oxidants, and their potential values remain almost constant. Therefore, while choosing the coating material, a more stable metal should be chosen, taking into account the potential of this metal substrate.²

1.4.1. Effective Parameters on Corrosion Rate

The corrosion rate has dynamic parameters. These parameters are basically pH, temperature and immersion time. Because the change of these parameters can change the coating thickness, homogeneity and components. Therefore, they are directly effective on corrosion.

One of the most important parameters affecting the corrosion rate is the conductivity of corrosive ions and water on the metal surface. This is because conductivity varies with dissolved salts. Dissolved salts increase conductivity. However, at high salt concentrations, the corrosion rate decreases due to the decrease of the solubility of oxygen.³⁰

The other parameters affecting corrosion is the pH change. For metals that are soluble in high acidic solutions even if there is no electrochemical effect, the corrosion rate is higher at low pH values. Therefore, the optimum pH value that reduces the corrosion rate differs for each metal. When the corrosion of iron is considered, it decreases between Ph 4 and Ph 10. Because among these values, the start of iron corrosion causes the formation of iron hydroxides on the surface. Therefore, speed varies depending on oxygen dissolution and dispersion. Aluminum metal, on the other hand, is known to be stable in the range of pH 4 to pH 9 due to the passive layer formed on the aluminum caused by the oxide layer. Aluminum shows high corrosion rate at pH values above pH 10.³¹

Another important factor against corrosion protection is temperature. Electrochemical reactions occur faster at higher temperatures. Therefore, it has been observed that the corrosion rate increases as the temperature increases. However, as the temperature increases, the corrosion rate decreases as the solubility of oxygen in the water decreases. This situation leads to different progression of corrosion rate for closed and open systems. For closed systems, the increase in temperature increases the corrosion rate, while in open systems, the corrosion rate decreases with the increase in temperature.

This is because oxygen interacts with the air. This varying amount of oxygen differs according to the system. Therefore, depending on the temperature, the change of corrosion rate changes according to the system.

1.4.2. Corrosion Type

Corrosion is an important problem in the worldwide. The formation mechanism of these types of corrosion varies depending on the material used, the areas of use and the environment. According to recent studies, it has been reported that the estimated annual direct corrosion cost worldwide is almost \$4 trillion.⁴ This value does not include environmental damage, loss of production, misuse of resources, and personal injury caused by corrosion. Corrosion experts shows it is possible to clearly protect 25% of the annual cost by applying existing corrosion techniques. In addition, it is possible to increase this value up to 35% by developing and renewing smart coatings.²⁷ Therefore, developing a suitable coating for the type of corrosion is an important factor. Corrosion can come in many forms and types. Therefore, there is no clear boundary between the types of corrosion. However, the main corrosion classification is as follows;³

- **Uniform Corrosion:** Uniform corrosion is the most common type of corrosion. This type of corrosion is seen when substances are exposed to the atmosphere, aqueous solutions, in short, to the environment. Materials affecting the uniform corrosion are materials that have a uniform chemical component and can provide access to corrosive solutions with a homogeneous microstructure. Corrosion products are formed close to the metal surface.³²
- **Crevice Corrosion:** This type of corrosion occurs due to the accumulation of impurities such as dust, soil, mud that have accumulated on a metallic surface. These impurities are local corrosion types as they cause cavities, bumps and curves at the point where they form on the metal surface.
- **Pitting Corrosion:** Pitting corrosion is a type of corrosion that progresses when the area of its spread is limited and most of the passivated surface has not been degraded. This corrosion type is also one of the local types of corrosion. Pit corrosion is a type of corrosion that removes obvious gaps on metallic surfaces and the corrosion progression inside the pits is uniform. Pitting corrosion is a very common type of corrosion that can easily form on metal surfaces.

- Galvanic Corrosion: When two different metal substrates are interacted with each other by immersing them in an electrolyte, an electrochemical difference arises between the two metals. As a result of this potential difference, the metal with high potential is corroded and thus the other metal is protected from corrosion. This type of corrosion is called galvanic corrosion. The appearance of galvanic corrosion is similar to that of uniform corrosion. As the potential difference increases, the corrosion rate increases accordingly. By examining the electrochemical potentials of metals, it is possible to select the metal that will corrode first.³²

CHAPTER 2

LITERATURE SURVEY

2.1. Corrosion Resistant Coating Investigations and Related Problems

In the coil coating industry, corrosion protection provided by inorganic conversion coatings and organic coating systems are quite important. Although the importance of the coating in corrosion prevention is known, the formation mechanism of the conversion layer on the metal substrate and the effects of the organic layer on the corrosion resistance is an important question. The organic coating system is a whole with its metal, inorganic and organic coating layers. Therefore, research for the metal coating industry includes both the surface morphology of metals and coating layers and the study of their electrochemical behavior. Scanning Electron Microscopy and Electrochemical Impedance Spectroscopy has recently been used as an advanced tool for determining protective properties.

Many researches are under way to investigate the corrosion prevention properties with use of alternative protective coatings. These studies will be shown by classifying according to the analysis methods depending on the mechanism of action.

2.1.1. Surface Morphology, Structure and Electrochemical Properties of Aluminum

Lunder et al. examined the change in aluminum surface and electrochemical structure when Ti based pretreatment solution was applied on AA6060. During the investigation, SEM analysis was performed to see the surface morphology. During the SEM analysis, crystal particles were observed on the surface. As a result of EDX analysis on these crystal particles, they found that there were particles rich in Ti,Zr and Si at that point. As a result of the XPS analysis performed to measure the change in coating thickness, it was observed that the particles on the surface increase the coating thickness. The author considers that this situation is due to oxygen reduction and hydrogen formation at the point where the particles are, while the conversion coating occurs, and

the accumulation of matter on the surface as a result of the cathodic reaction. In addition, according to the experiments, it was observed by the author that the accumulation on the surface increases as the pH increases as shown in Figure 10, increasing the coating thickness. Therefore, pH change controls surface homogeneity. The author and colleagues observed that layer deposition and distribution on the surface formed by the conversion coating slowly reduced the cathodic activity of the surface.³³

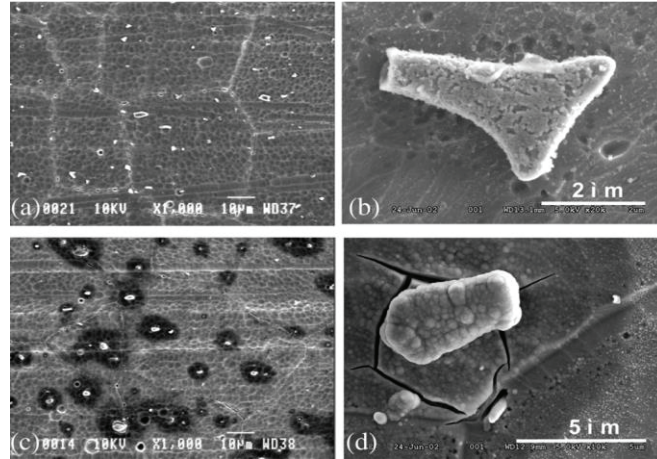


Figure 10. SEM images of AA6060 after 90 s of immersion in conversion solution of a)pH=2.9 b)pH=2.9 c)pH=4.0 d)pH=4.0³³

Yi et al. experienced the addition of tannic acid to the Ti containing conversion coating. In this study, they observed changes in the surface caused by dipping aluminum with different immersion times using this new coating. During this process, they used SEM to observe the surface morphology, XRF for determination of the composition on the surface and XPS devices for the measurement of the coating thickness formed on the surface.³⁴

According to SEM micrographs given in the Figure 11, they showed that with the increasing immersion time, the size of the spherical particles on the surface increased and spread over the surface.³⁴

As a result of their EDX analysis, they observed that their elemental contents did not change with increasing immersion time, but coating thickness increased with XPS analysis. The reason for the increase in coating thickness has shown that Na_3AlF_6 and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ components can be detected on the surface as a result of XRF analysis. The authors suggest that main components in the coating is Na_3AlF_6 , followed by the organic complex of Ti and Al, with small amount of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, TiO_2 and fluoride titanium.

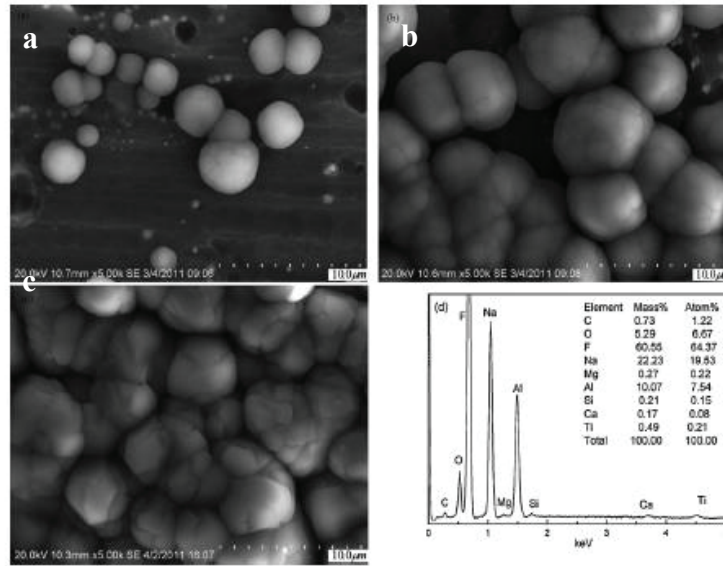


Figure 11. Sem micrographs and EDX spectrum of treated in conversion bath for a) 7 min b)15 min c)25 min³⁴

In line with this information, the authors have suggested that the formation mechanism of the coating layer containing tannic acid is the metal-organic complex interaction and the growth of spherical particles on the surface.

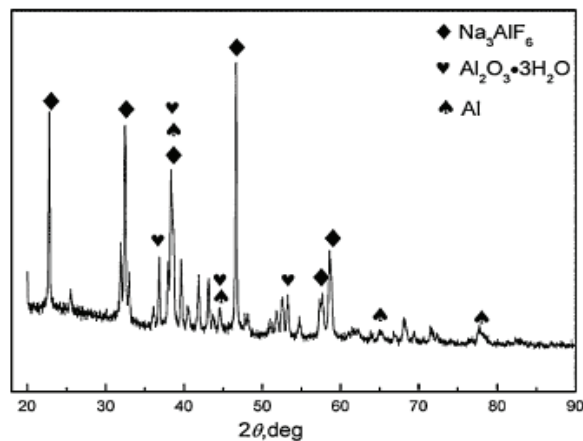


Figure 12. XRF spectrum of treated sample³⁴

Visser et al. conducted surface analyzes to investigate the passive layer formed by the corrosion inhibitor lithium salts on the aluminum alloy AA2024-T3. They observed that the protective layer formed by the lithium inhibitor on the surface at 80 seconds and 4h immersion times to the Li2CO3-NaCl solution. Figure 13a shows oxide thinning due to deoxidation after alkaline cleaning. In Figure 13b, it was observed that a layer formed

on the surface after 4 hours. It was observed that there were large crystals and a porous outer layer on the surface. Figure 13c is the cross-sectional SEM image of the 4 hour image. This image showed that there is a dense inner layer and a porous outer layer at the metal/oxide interface. Author and coworkers have demonstrated that when lithium salts are used, the coating defect provides passivation by forming two protective layers externally, the amorphous inner layer and the crystalline layer.²⁹

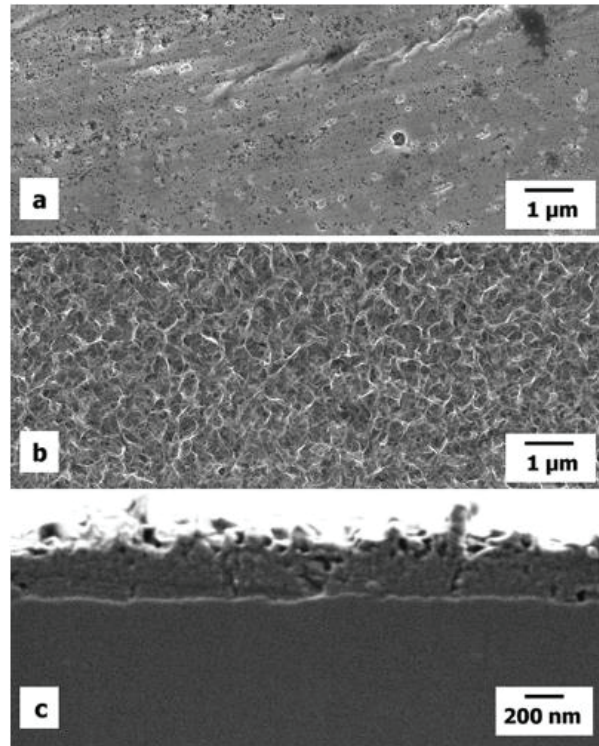


Figure 13. SEM micrographs of AA2024 -T3 a) for 80 sec b) for 4h immersion time to $\text{Li}_2\text{CO}_3\text{-NaCl}$ solution²⁹

Bastos et al. observed the coating quality of coil coated samples by examining their surface morphology. During this study, phosphate containing pretreatment, polyester primer and polyurethane midcoat coated sample were used. For this reason, the surface was observed by SEM analysis from five different regions of the coated sample as shown in Figure 14. As a result of the images, paint defects in the form of pinholes were found around the paint matrix. In addition, it has been found that the surfaces contain a large number of round shapes. They observed that this was a result of water penetration through the holes and puffing of the polymer matrix. The fact that these defects are present in every image shows that the barrier properties of the coating are weak as a result of increased oxygen and ion transfer from the coating through the metal substrate.³⁵

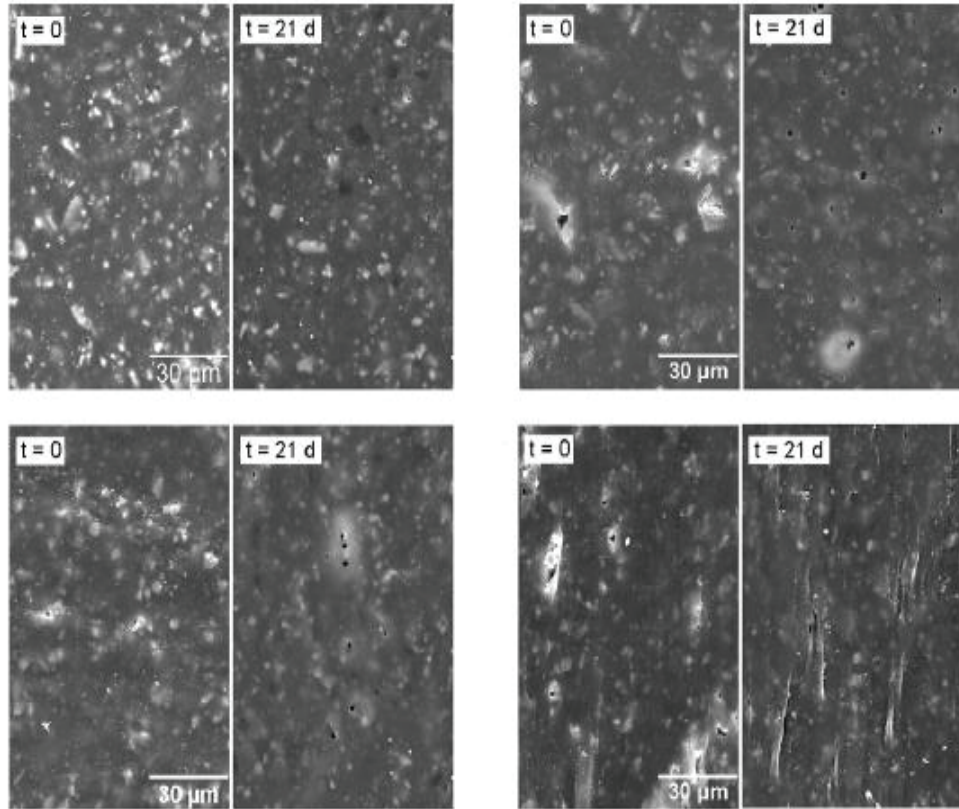


Figure 14. SEM micrographs of the coated substrate surfaces before ($t = 0$) and after immersion ($t = 21$ days)³⁵

Oki et al. examined the changes in the surface morphology and corrosion resistance of aluminum conversion coatings containing permanganate, with reference to conversion coatings containing chromate. During the research, they performed SEM and EDX analyzes. The reaction rate of aluminum, which is immersed in two different pretreatment solutions containing chromate and permanganate, is given depending on the time. According to this graph, they observed that the conversion coating with chromate content formed faster than the conversion coating containing permanganate and the coating weight changed less. After exposure of lacquered coated samples to sodium chloride solution, the conversion coating of chromate containing shows higher resistance against pitting than the conversion coating containing permanganate. Conversion coating application containing permanganate increased paint adhesion and corrosion resistance of aluminum substrates. However, for both conversion coatings, high corrosion resistance was observed compared to bare aluminum substrate. They said this is because the permanganate solution is almost neutral, while the chromated pretreatment is acidic bath conditions.³⁶

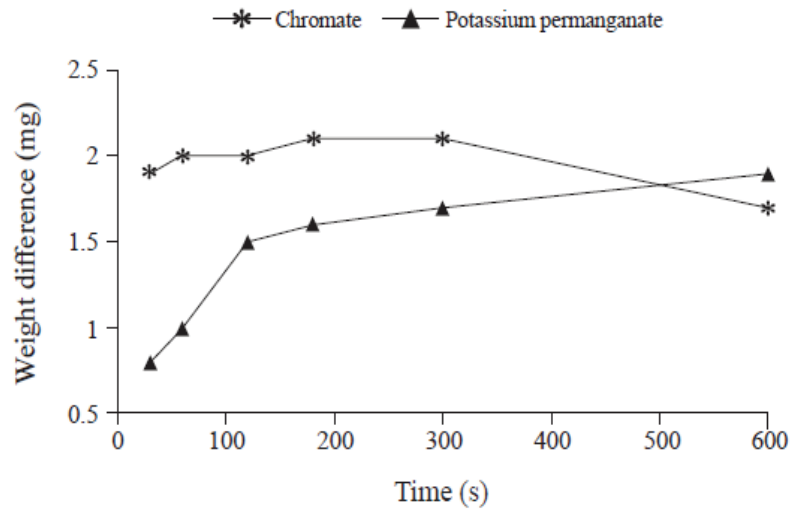


Figure 15. Weight differences permanganate and chromate pretreated aluminum specimens³⁶

The surface morphology of the conversion coating containing permanganate is as shown in the Figure 16. The authors observed a cracked structure on the surface of aluminum and, accordingly, stated that the coating metal interface had a micro-rough structure. This situation caused the exposure of the metal to the coating solution as the immersion time increases, thus increasing the coating thickness. It has been observed by the authors that the reason for this cracked structure is due to the shrinkage stress occurring in the drying process after coating.

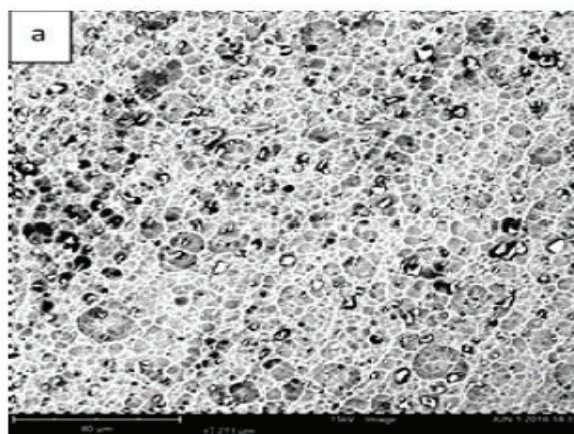


Figure 16. SEM micrograph of permanganate pretreated aluminum for 180 s.³⁶

In another study by Visser et al., they examined the effects of lithium oxalate and lithium carbonate inhibitors on protection of AA2024-T3 aluminum. During this study,

the surfaces exposed to neutral salt spray test for 168 hours were examined by SEM analysis. As can be seen in Figure 17, the use of both pigments resulted in the formation of textured structure and flat regions at some points on the surface. When the cross-sectional points of the surface were examined, three different layers were observed. These layers were found to be dense inner layers, porous middle layers and textured outer layers for both samples. By observing that lithium is distributed uniformly to these layers, the author and colleagues have said that protective activity is increased in this way.²⁹

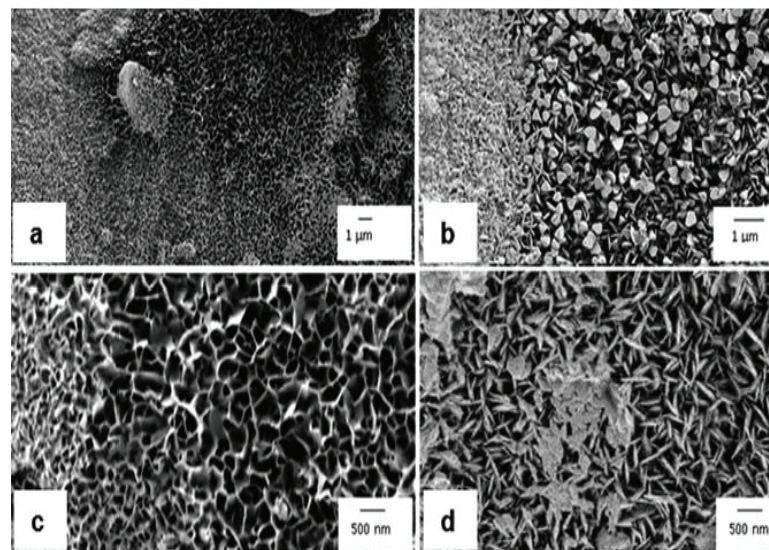


Figure 17. SEM micrographs after 168h NSST a,c)lithium carbonate
b,d)lithium oxalate³⁷

2.1.2. Electrochemical Impedance Measurements of Different Aluminum Alloys

Visser et al. examined the passive formation on the surface of the aluminum alloy exposed to alkaline lithium carbonate solution containing sodium chloride and how electrochemical properties change. They used electrochemical impedance spectroscopy during this review.

As can be seen from the Bode diagram, the authors have shown that impedance modules start to increase at low frequency values, the increase in medium frequency range continues, reaching the highest impedance values after four hours of exposure. However, they also observed two time constants in the phase angle diagram, one in the low and one in the middle frequency range. It is thought by the author that the first time constant is

thinning the oxide layer, and the second time constant is the electrochemical activity in aluminum metal. In addition, it is believed that during the oxide thinning, the time constant first contracts and decreases, but as time goes on, in the middle frequency range, a passivation layer begins to form on the surface of the alloy.^{29,35,38}

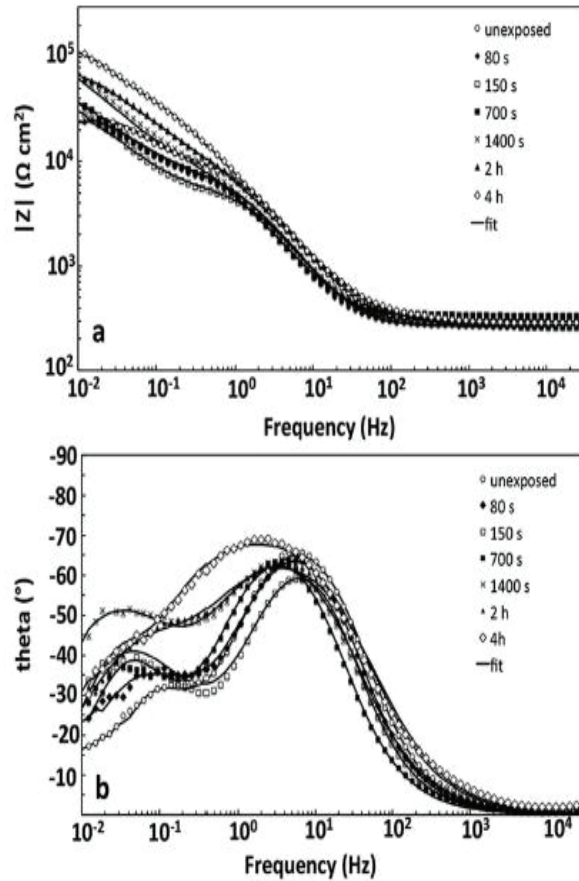


Figure 18. Bode Plot of the aluminum alloy before and after exposure to the $\text{Li}_2\text{CO}_3\text{-NaCl}$ solution²⁹

Liangliang Li and his colleagues, who mentioned the surface morphology study in the previous section, examined the corrosion resistance of 5200 conversion coatings for metal alloy in the same study. While making this examination, they benefited from EIS. The Figure 19 shows the Bode diagram for the aluminum alloy, which is coated with a special coating type 5200 coating and has not been applied. It was stated by the authors that the reason for having the same potential values for both applied and not applied conversion coating substrates in the high frequency range is the electrolyte resistance they have at that value. In the low frequency range, there is no significant difference between aluminum alloys with and without conversion coating applied.^{39,40}

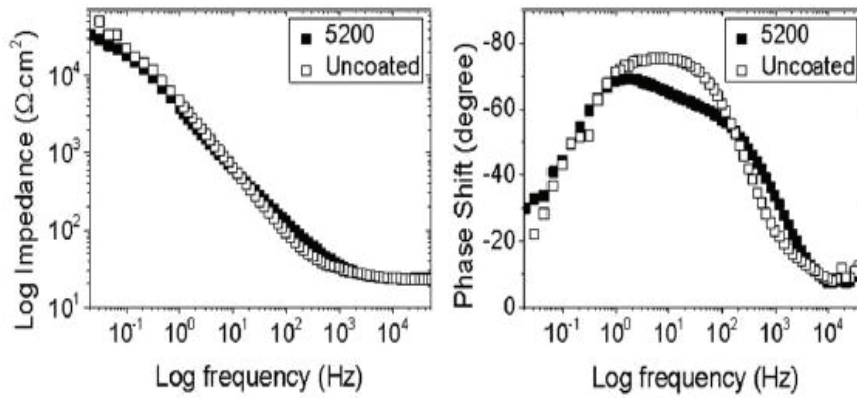


Figure 19. Bode Plot of 5200 coated and bare aluminum alloys⁴⁰

According to the Bode diagram, in aluminum alloys subjected to a salt spray test in the 168 hour time band, they observed that the impedance values of lithium inhibitor-containing coatings at high and medium frequency were higher and increased compared to lithium-free coatings, and the reason for this increase was the corrosion of lithium ions against the oxide layer formed in the damaged area. They stated that the application of resistance is the reason.

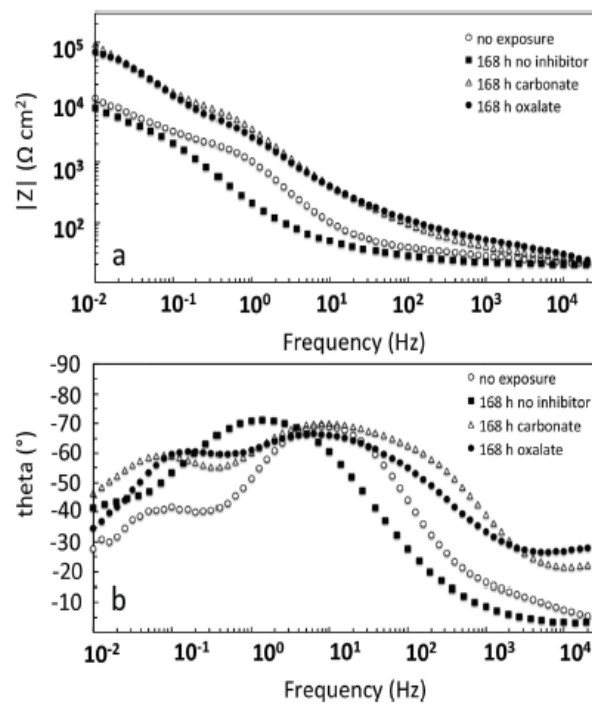


Figure 20. Bode Plot of defect areas on the coatings with and without lithium salts before and after NSST. ⁴¹

Phase angle graphs before and after exposure to the inhibitor-free coatings contain two time constants, which is thought to be due to oxide thinning at these points and to produce corrosion products in these areas. Although there is no significant difference between the electrochemical behavior of lithium-containing coatings, the authors who suggested that the phase angle values of these coatings are asymmetrical and widened at low frequency values have associated with an improved corrosion resistance because of the fact that two time constants overlap at those points. As a result, they stated that the use of lithium salts has an effect on the corrosive slowing for aluminum alloy.^{38,41,42}

Rodriguez et al. studied the AlMgSi alloy when exposed to a corrosive environment, altering the change of corrosion depending on the time. During this research, they used Electrochemical Impedance Spectroscopy. In the Bode diagram shown in the Figure 21 by the authors, time constants at medium and low frequencies were observed, and these time constants are thought to be solution resistance and charge transfer resistance.

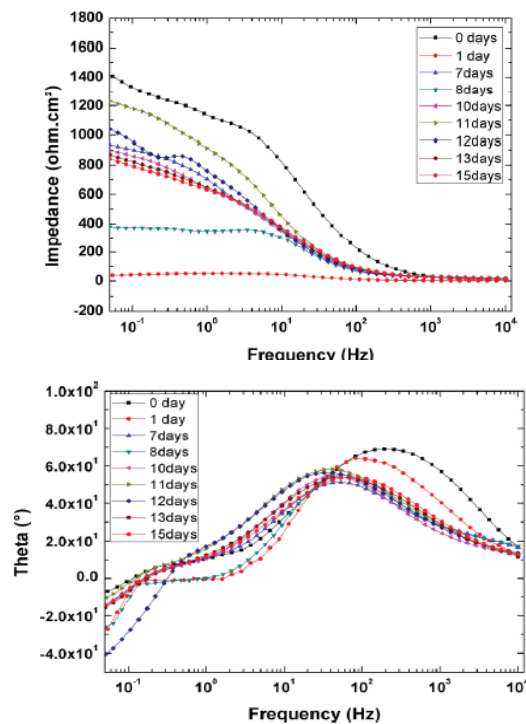


Figure 21. Bode Plot of AlMgSi alloy corroded in corrosive environment for 15 days⁴³

As a result of the fact that the peaks observed in the phase angle graphs can be seen more clearly with the help of the Nyquist graph, the authors stated that the time constants in the low frequency regions are intermediates formed as a result of the anodic

dissolution of the magnesium, which is the corrosion formation reaction. As a result, it has been shown that the protective properties of hydroxide and oxide layers on the surface for aluminum are low.^{43,44}

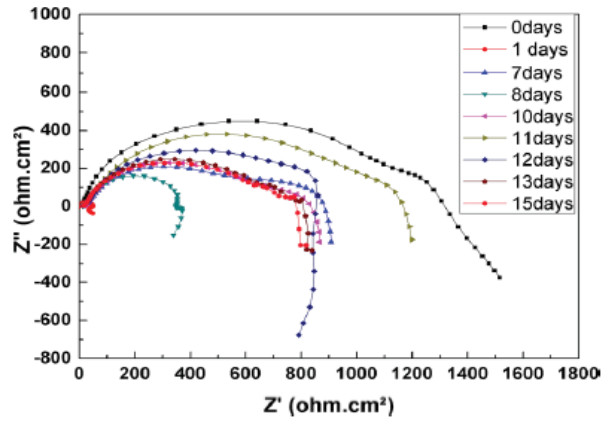


Figure 22. Nyquist Plot of the AlMgSi alloy corroded in corrosive environment for 15 days⁴³

2.2. Aim of The Study

As mentioned in the Literature Survey, one of the current challenges in the corrosion research of organic coated metal substrates is to understand the different contributing parameters to the overall corrosion resistance of the coated system. A typical industrial coated aluminum substrate, mainly used in the construction industry, consists of an aluminum substrate, covered with an inorganic coating, which is called a conversion coating that results from the pretreatment application, and further coated with organic coating (layers) that are called the primer and the topcoat. Up to now, to the best of our knowledge, there has not been significant research efforts to quantify how these layers contribute to the corrosion resistance of the overall system. Furthermore, the effect of the pretreatment application and the resulting inorganic conversion coating, which is essential for the upper organic coating layers to adhere to the substrate, has not been studied with industrially used substrates and solutions. The determination and better understanding of the parameters that affect the surface structure and corrosion resistance of the pretreatment applied to the metal surface, and the contribution of the upper organic coating layers can contribute to making new anticorrosive coating research more effective and reliable. Therefore, the main purposes of the study are;

- i) to investigate the effect of pretreatment application conditions on the structure of conversion coating formed
- ii) to investigate how organic coating layers on top of the conversion coating, namely the primer and topcoat applications contribute to the corrosion resistance of the overall coated metal system

During this study, the structural changes that occur on the surfaces coated with various layers were investigated using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray (EDX) Spectroscopy, Atomic Force Microscopy (AFM) and X-ray Fluorescence Spectroscopy (XRF). In addition, the anticorrosive behaviour of coated metal after being corroded by Neutral Salt Spray Test (NSST) is evaluated using Electrochemical Impedance Spectroscopy (EIS).

CHAPTER 3

EXPERIMENTAL METHODS

3.1. Material and Sample Preparation

In the first part of the experimental stage, the effects of three parameters, temperature, pH and immersion time were examined. The aluminum substrate used during this thesis research is type AA3003 aluminum alloy. Its main ingredient is the manganese element and its content varies between 1-1.5%. The cleaning chemical used in the experimental process of all three parameters is Bonderite C-AK C72. This chemical is a NaOH-based alkaline liquid solution containing surfactants, dense phosphates and silicates. The pretreatment solution is known as Bonderite M-NT 1455T (Granodine 1455T), which is an acidic chemical, the main ingredients are hexafluorotitanic acid (H_2TiF_6), Mn salts, phosphoric acid (H_3PO_4), hexafluorotitanate ($\text{F}_6\text{H}_2\text{Ti}$), Propylene glycol propyl ether ($\text{C}_6\text{H}_{14}\text{O}_2$), and methanol (CH_3OH). Epoxypolyester was used as a primer and polyester as a topcoat. These solutions and layers are supplied by the company Akzo Nobel Kemipol and according to the factory privacy policy, the amount of components in the solution is not shared. The thickness of the primer applied on these substrates is 5 μm and the thickness of the topcoat layer is 20 μm . Industrial samples are commercial coil bare aluminum available from QLAB, but aluminum thickness, surface treatment and finishing types have not been investigated further. Samples were used in the desired sizes by using metal cutting scissors during the experiments. GN 1/9-65 acid pools were used as pretreatment solution and cleaning solution baths. Controlled heaters were used for the heating process.

During the experiment carried out to observe the formation and changes of the pretreatment solution on the surface at different immersion times, the cleaning chemical was first heated to 60 °C. Aluminum panels that cut in 8x3 cm dimensions was immersed in 50 ml cleaning chemicals heated to 60 °C for 10 seconds with the help of forceps. Then, the panel taken in the cleaning solution was immersed for 60 seconds in 50 ml deionized water, which was also heated to 60 °C, and rinsing was performed. Then, using the zero applicator, excess water on the surface was removed with the help of pressure. The rinsed panel was dried in the drying oven set at 60 °C for 60 seconds. Then, the metal sample

taken from the drying oven was immersed in the pretreatment solution of 20% by volume and pH value 2.8 for 10 seconds. Then, the panel taken from the acidic bath was dried in a 60 °C drying oven for 5 minutes. This process was repeated for the immersion times in the acid bath for 20, 30 and 40 seconds, respectively.

In the experiment to observe the effect of the pretreatment solution at different pH values, the panels cut in size 8x3 cm into the cleaning chemical, which was also heated to 60 °C, were immersed for 10 seconds and then immersed in 50 ml deionized water heated to 60 °C for 60 seconds. Then, excess water accumulating on the surface was taken with the help of a zero applicator. In order to dry the rinsed sample, the sample was kept in the drying oven set at 60 °C for 60 seconds. Subsequently, the panel was immersed in the pretreatment solution with a pH value of 2.42 for 10 seconds. Then the panel was dried at 60 °C in the drying oven for 5 minutes and dried. This process was repeated for pH values of 2.66, 2.77 and 2.98 of the pretreatment solution, respectively.

In the experimental stage, where the effect of the change of the temperature parameter on the pretreatment solution was examined, metal panels cut in 8x3 cm size were immersed in 50 ml cleaning solution at room temperature for 10 seconds. Then, the panels were rinsed by immersing in 50 ml of deionized water at room temperature for 60 seconds. Then, for removal of excessed water on the panel, zero applicator is used. The rinsed panels were held for 60 seconds in the drying oven set at 60 °C. Then, the panels were immersed for 60 seconds in a pretreatment bath of 30 °C with a pH value of 2.80. Panels taken from the bath were taken to the drying oven set at 60 °C and dried for 5 minutes. This process was repeated for pretreatment baths of 40, 50 and 60 degrees respectively.

3.2. Surface Characterization of Aluminum Substrates

The working principle of the Scanning Electron Microscope is to determine the efficiency of secondary electrons and backscattered electrons, which is depending on the location of the primary beams, as a result of the high energy electron beam being sent to the metal surface. In this way, the morphology, topography and elemental information of the surface of a metal can be determined. It is a very suitable analysis method for surface examination of coated metals. To better understand its mechanical structure, the illustration of scanning electron microscopy is shown below.⁴⁵

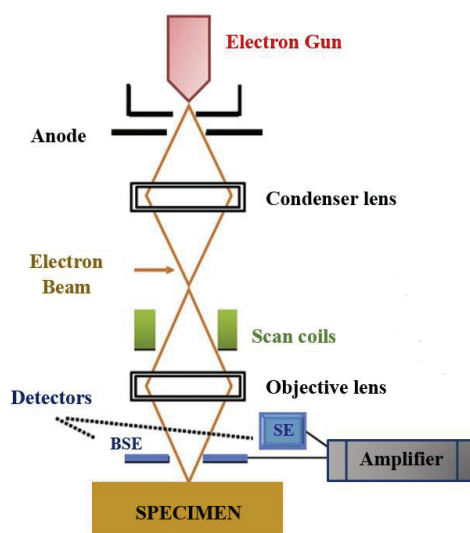


Figure 23. Schematic Illustration of Scanning Electron Microscopy ⁴⁶

In order to characterize the surface structure and components of the metal panels before and after coating application, SEM analyses are done using FEI QUANTA 250 FEG in a concentrated back scatter (CBS) mode, at a 15-20 Kv penetration density. In order to perform SEM analysis, metals were cut in 1x1 cm size before the analysis and metal surfaces were cleaned with isopropanol to remove impurities from the surface.

Atomic force microscope (AFM) is a characterization device included in the scanning probe group. With the help of this technique, surface roughness can be determined by taking local topography of the surfaces. The principle of determining the surface roughness is based on the atomic resolution obtained as a result of the interaction between a sharp tip called cantilever and the surface as shown in the Figure 24.

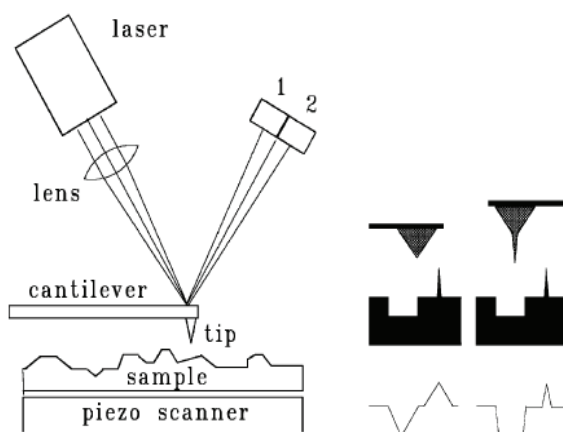


Figure 24. Schematic illustration of Atomic Force Microscopy ⁴⁷

The reason for using the piezo scanner is because it can create an oscillation. Laser beams reflected on cantilever create different signals due to different height on the surface and different chemical and physical structure, and these signals provide information about surface topography. The AFM device has three main modes. During this study, 15x15 micrometer areas were scanned in contact tapping and scan asyst modes with using Bruker-MMSPM Nanoscope 8. For bare panels measurement contact tapping mode with budget-sensors diamond-like carbon coated Tap300DLC and for coated panels scan asyst mode with nano world silicon point probe are used. During the measurements, the force constant is 42 N/m for all samples.

X-Ray Fluorescence Spectrometer (XRF) device was used to perform elemental identification of bare and coated metal panels. The XRF device is based on the principle of producing secondary X-rays or fluorescence as a result of scattering high-energy X-rays by the sample to be tested. Because each element produces a different characteristic X-ray, thus the chemical structure of the material can be determined by X-rays captured by the XRF spectrometer.

During this study, XRF analysis was carried out using SL FB method for alloys of 32 mm sized and 8 g weight samples using Spectro X-Lab Pro.

3.3. Electrochemical Measurements

Electrochemical Impedance Spectroscopy (EIS) was used to make electrochemical measurements. During this investigation, three electrode cells were used. In this system, Ag/AgCl solution used as reference electrode, carbon rod used as counter electrode and coated and bare aluminum substrates are used as working electrode. Additionally, %5 wt. NaCl solution was used as an electrolyte. In this way, the metal was contacted to the corrosive environment. During the analysis, Faraday Cage is used for the aging set-up, thus magnetic field was isolated and the measurement accuracy was paid attention.

The device used during EIS measurements is the Gamry Interface 1010B Potentiostatic EIS. During the measurements, EIS was performed 5 mV AC potential for bare panels and 10 mV AC potential for coated panels, with a frequency range of 0.1-10000 Hz. In order to obtain more reliable results, the device was operated in low noise mode.

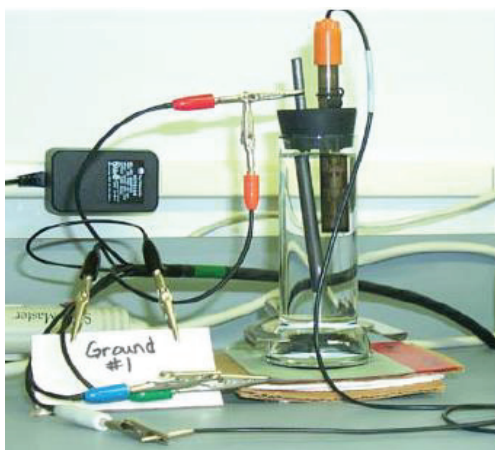


Figure 25. Experimental Set-up of Electrochemical Impedance Spectroscopy⁴⁸

3.3.1. Determination of Corrosion Mechanism with Using EIS

EIS provides an appearance that reveals the details more easily in the degradation process by corroding the coating system and enables the corrosion to be detected in the early stages. It also models the behavior of the overlays, providing objective information. Therefore, it is a suitable method for investigating coating properties.⁴⁹

The basis of measurement with the EIS method is based on Ohm's law. Ohm's Law defines the concept of resistance, which is the endurance ability of the electrical element in the circuit against electrical current, with the expressions of current and voltage as shown in Equation 5.

$$R = E/I$$

Equation 5. Ohm's Law⁵⁰

However, Ohm's Law applies to ideal resistance. Ideal resistance is a value that complies with Ohm's Law and is independent of frequency for all current and voltage values. However, due to the fact that real electrical circuits contain complex elements, impedance is used instead of ideal resistance. The impedance is a frequency-dependent value and it is a sinusoidal function that receives an AC current signal as a result of applying AC potential to the circuit.⁵⁰

If a stable system is perturbed, it becomes a new steady state. The analyses of the transition taken to this new steady state gives information about the system. The ratio of

system response to perturbation is known as the transfer function. If the perturbation applied is alternative current or alternative potential, the transfer function is impedance.⁴⁹ Electrochemical impedance measured with small excitation signals so that the cell response become pseudolinear. This creates a sinusoid at the same frequency when sinusoidal potential is applied in the system, but phase shift occurs.⁵⁰ In such systems, the potential of the system at time t according to the excitation signal is expressed as given in the following equations.

$$E_t = E_0(\sin\omega t)$$

$$\omega = 2\pi f$$

$$I_t = I_0(\sin\omega t + \phi)$$

$$Z = E_t/I_t = E_0(\sin\omega t)/I_0(\sin\omega t + \phi) = Z_0 (\sin\omega t)/(\sin\omega t + \phi)$$

Equation 6. AC perturbation and measured value formulations⁵⁰

In these equations, E_t is the potential at time t, E_0 amplitude of signal, ω radial frequency, f frequency, phase shift ϕ and Z impedance.

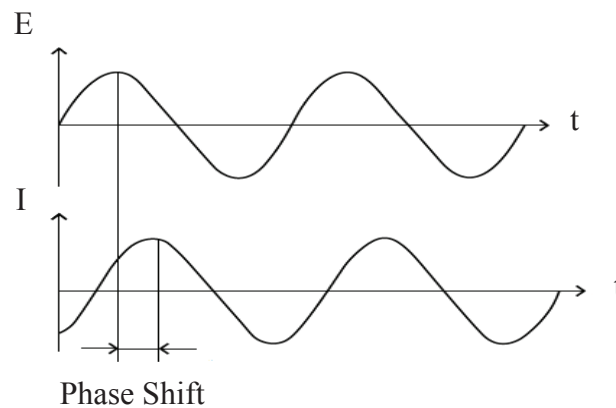


Figure 26. Sinusoidal Current Response in a Linear System⁵⁰

The potential also be expressed using complex interpretation with the help of Euler's relationship as shown in Equation 7.

$$\exp(j\phi) = \cos\phi + j\sin\phi \text{ (Euler's Relationship)}$$

$$E_t = E_0 \exp(j\omega t)$$

$$I_t = I_0 \exp(j\omega t - \phi)$$

$$Z(\omega) = Z_0 \exp(j\phi) = Z_0 (\cos\phi + j\sin\phi)$$

Equation 7. Euler's Relationship and complex interpretation of Impedance

The given EIS data can be transferred to the graph in two ways. If it is defined as impedance magnitude and phase angle, as Bode Plot, Complex quantity, $Z_{total} = Z_{real} + Z_{img}$, is expressed as Nyquist Plot. Both plots are different expressions of the same mathematical expression.⁵¹

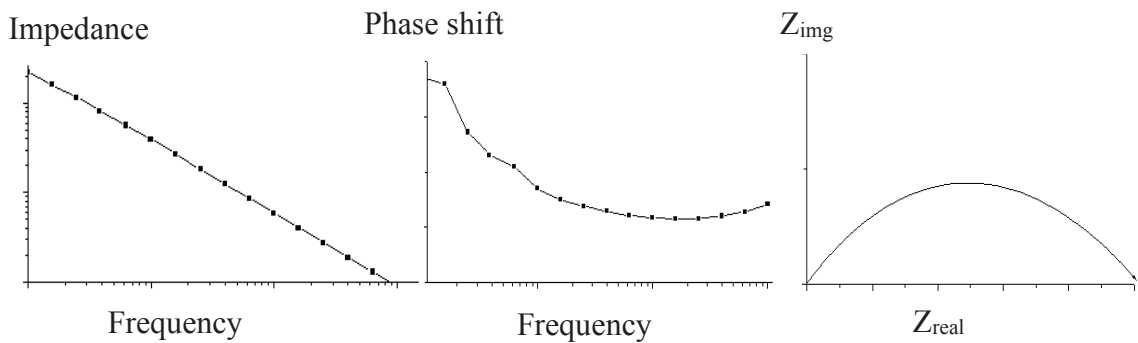


Figure 27. EIS data representations as a) impedance magnitude of Bode Plot b) Phase shift of Bode Plot c) Impedance magnitude of Nyquist Plot

3.3.2. Data Analyses of Coated Samples

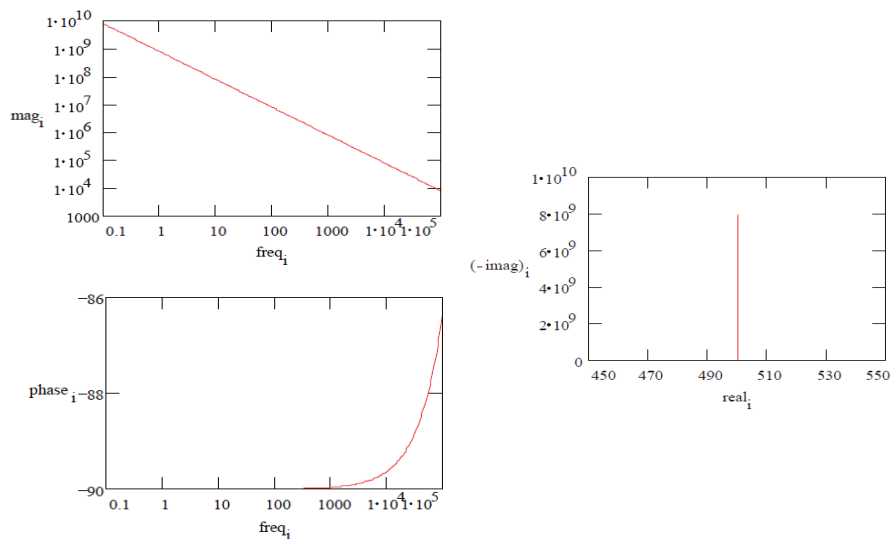


Figure 28. a) Impedance magnitude b) Phase shift of Bode Plot c) Nyquist Plot of Perfect Coating⁵⁰

The impedance values of the coatings that are not damaged and whose corrosion process has not started are high. The highest impedance value seen on the graphs is $10^{10} \Omega\text{cm}^2$. The impedance values of $10^{10} \Omega\text{cm}^2$ and above are expected for a perfect coating.⁵⁰

In order to understand the changes that occur while the coating is corroding, some circuit elements have been developed. These circuit elements are used for better understand the behavior of graphics. The five steps that occur in the coating during a corrosion process in general are shown below.

1) Step 1:Capacitive

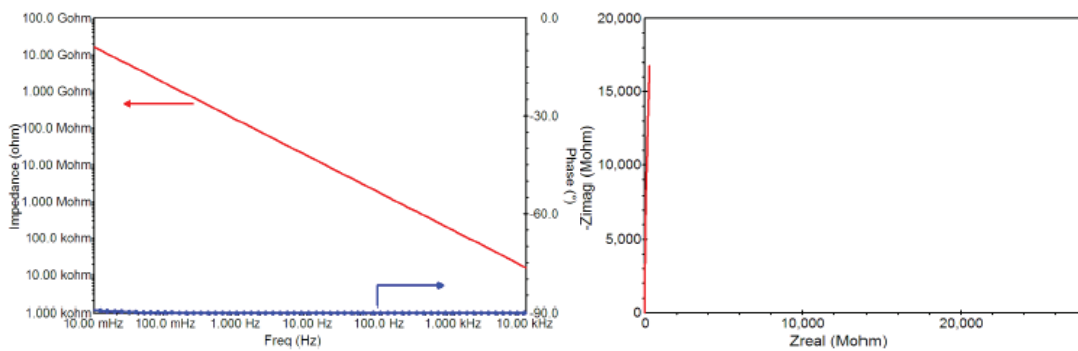


Figure 29. EIS data of Capacitive Coating Behaviour⁵²

The perfect coatings that are not damaged are capacitors. A capacitive acting coating also contains a resistor because it is in contact with the electrolyte. However, even at the highest frequency for these coatings, the resistance of the coating is more than the resistance of the solution. An increase in film capacitance occurs after water uptake into the coating.

2) Step 2:Water Uptake

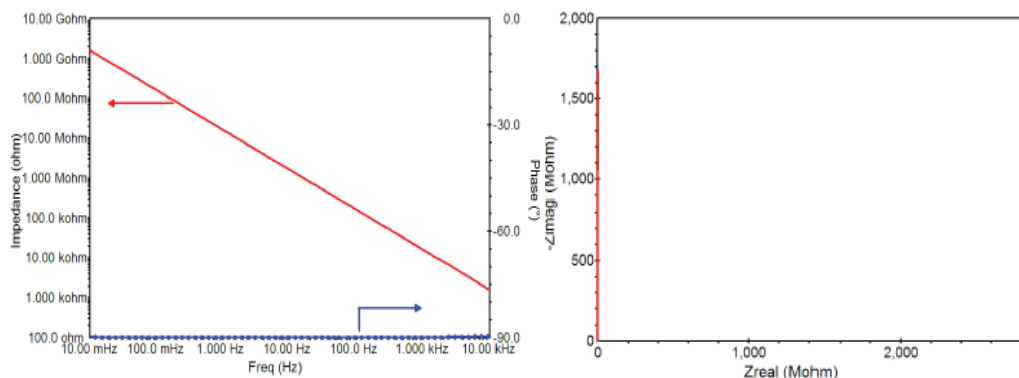


Figure 30. EIS data of Water Uptake Behaviour⁵²

The model developed for capacitance can be used to measure water uptake. This model, called The Brasher-Kingsbury, is as follows. According to this model, $C_c(0)$ is the initial capacitance, $C_c(t)$ is the coating capacitance at exposure time t . ϕ is the amount of water penetrating that depending on the free pore volume in the coating.⁵⁰

$$C_{\text{coat}} = \epsilon \epsilon_0 \frac{A}{d}$$

$$\phi = \frac{\log \frac{C_c(t)}{C_c(0)}}{\log \epsilon}$$

Equation 8. The Brasher-Kingsbury Expression⁵⁰

Since water uptake depends on the free pore volume in the coating, pore resistance may occur with increased water uptake.

3) Step 3 : Pore Resistance

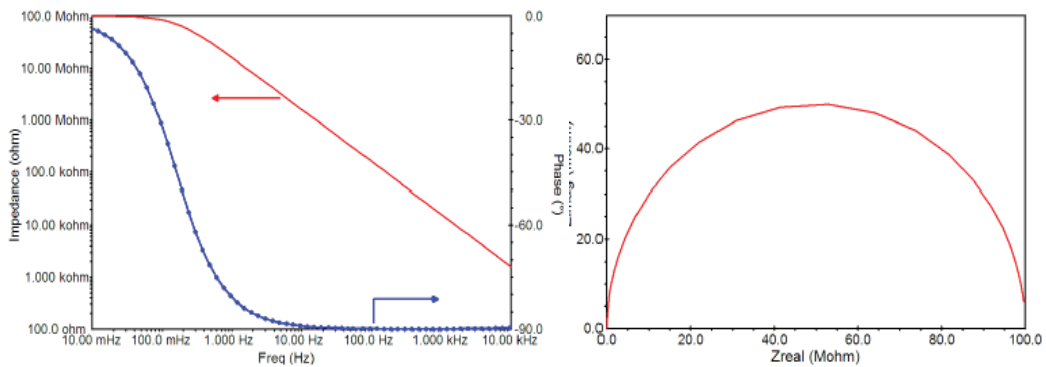


Figure 31. EIS data of Pore Resistance Behaviour⁵²

Pore resistance is the resistance caused by the ions that try to enter the coating through the roads. These pathways are physical pores filled with electrolytes. As a result of the passage of electrolytes through the pores, delamination occurs on the metal surface. Thus, corrosion initiation is seen. At this stage, the formation of semicircle is observed. It represents a time constant with each semicircle. Time constants, on the other hand, show that a different process occurs in coating degradation. Therefore, interpretations can be made about the processes occurring in coating according to time constants and provide the better understand for different processes.

4) Step 4 : Corrosion Initiation

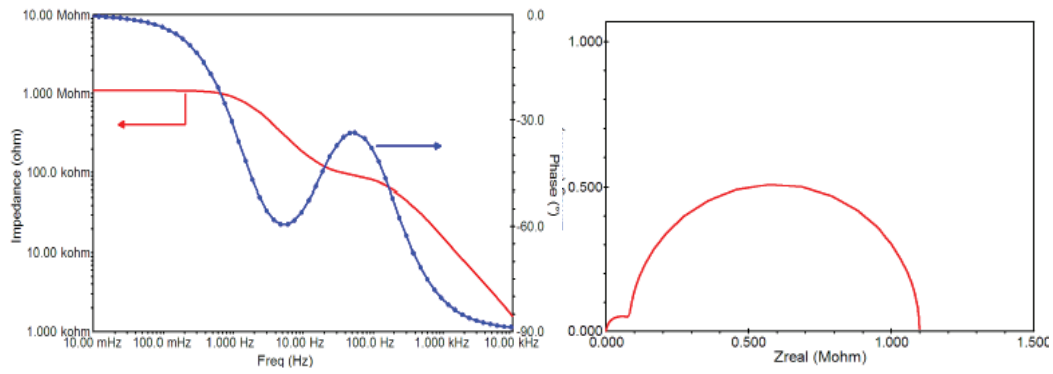


Figure 32. EIS data of Corrosion Initiation Behaviour⁵²

Charge transfer resistance occurs due to ion transfer from the pores between bare metal and coating. Instead of a single time constant, two time constants appear at the beginning of corrosion.

5) Step 5 : Major Damage

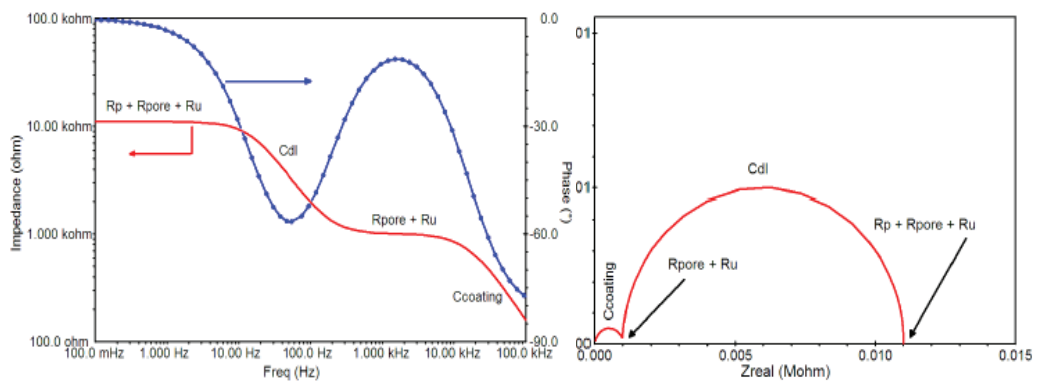


Figure 33. EIS data of Major Damaged Coatings⁵²

Corrosion resistance is the sum of the barrier properties of the system. This system is the stage where circuit elements such as coating resistance, electrolyte resistance, pore resistance and double layer capacitance can be observed.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Effect of Pretreatment Application Conditions on The Structure of Conversion Coating Formed on Aluminum Substrate

Under laboratory conditions, pretreatment was applied on bare aluminum panels supplied from QLab company (AA3003 type, mainly Al and around 1% Mn) after cleaning. In order to observe the changes on the metal surface with respect to immersion time, temperature and pH, SEM,EDX and XRF analysis were performed.

4.1.1. Effect of Immersion Time

SEM micrographs made after different immersion time are shown in Figure 34.

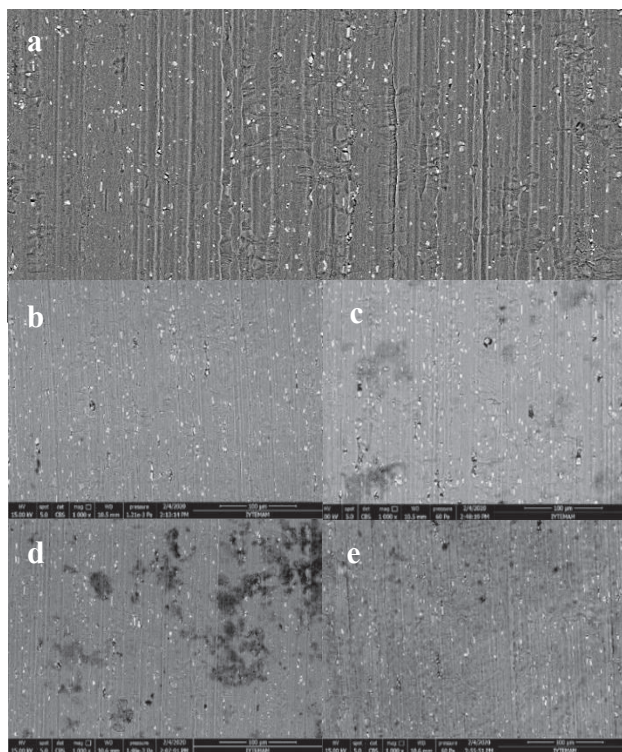


Figure 34. SEM micrographs of a) bare (cleaned) aluminum and aluminum immersed in pretreatment solution for b) $t = 10$ sec c) $t = 20$ sec d) $t = 30$ sec e) $t = 40$ sec

Figure 34 indicates that in the bare (cleaned) state, before the pretreatment application, the aluminum substrate consists of a continuous aluminum alloy, separated by rolling lines dividing the surface into microscale valleys and hills with different height values, plus impurities seen as whiter particle-like accumulations on the surface. These findings are in accordance with a previous study performed on the same type of aluminum substrate. The application of the pretreatment solution with increasing immersion time, results in the formation of darker structures, as clearly seen in Figure 34d and Figure 34e, while the white impurity particles are retained in similar concentration and size. These images indicate that the darker areas formed are the conversion coating layers, which seem to have a more porous structure compared to the bare aluminum substrate.

In order to understand the change of elemental composition of the pretreated aluminum according to the immersion time, the results of EDX and XRF analysis from the aluminum substrate are shown in Table 2. The amount of fluorine, titanium and phosphorus, which are the main ingredients of the pretreatment solution, were determined. In addition, the manganese element, which is present both in the aluminum alloy and the pretreatment solution was also identified.

Table 2. EDX analyses of aluminum with respect to different immersion time

Element weight %	10s	20s	30s	40s
F	0.15	0.41	0.44	0.98
P	0.13	0.41	0.20	0.63
Ti	0.16	0.12	0.11	0.65
Mn	0.69	0.96	0.89	0.98

Table 3. XRF analyses of aluminum with respect to different immersion time

Element	Concentration %			
	10 s	20 s	30 s	40 s
P	0.1157	0.5606	0.6859	0.7795
Ti	0.00051	0.0586	0.0724	0.105
Mn	0.9199	0.9094	0.9046	0.9808

EDX analyses in Table 2 show that F content increases with immersion time, while P and Ti concentration shows a less-clear correlation with immersion time, although their concentration increases with pretreatment application. XRF analyses in Table 3 indicate that P and Ti increases linearly with immersion time, while Mn content stay roughly constant. Elemental F could not be detected with XRF analysis.

However, due to the heterogeneous and non-uniform structure of the surface, more reliable information about surface chemistry was obtained by performing local SEM-EDX analyzes, as shown in Figure 35. The elemental composition obtained from different areas on the surface shown in Figure 36 is summarized in Table 4.

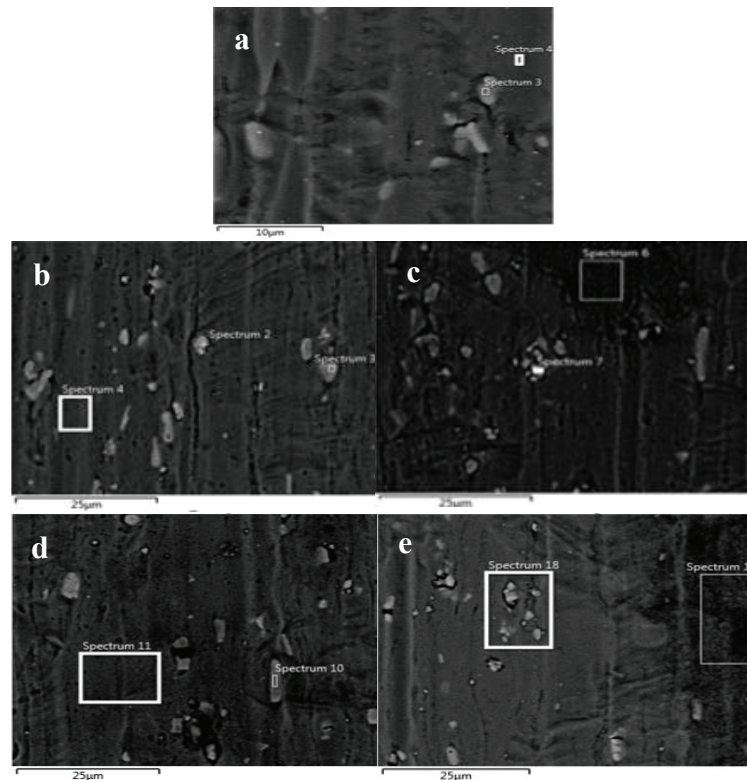


Figure 35. SEM images showing the location of EDX spectrums obtained for a) bare aluminum and aluminum immersed in the pretreatment solution for b) $t = 10$ sec c) $t = 20$ sec d) $t = 30$ sec e) $t = 40$ sec

An analysis of Figure 35a and Table 4 indicates that the white impurity particles are rich in Mn, which is probably in the form of an Al-Mn alloy, in line with a previous study performed by. Table 4 also indicates that as the immersion time increases, the concentration of F, P and Ti generally increases in the darker areas shown in Figure 36, which indicates that darker, porous areas are indeed the conversion coating formed as a

result of the pretreatment application. The white Mn-rich impurity particles do not increase in F, P and Ti concentration as high as the darker areas, which indicates that the conversion coating layer as a result of pretreatment application does not proceed sufficiently on Mn-rich impurities. Figure 36 and the elemental compositions in Table 4 also clearly show the highly non-uniform structure of the aluminum surface.

Table 4. EDX analyses results according to different spectra obtained from the pretreated aluminum substrates as a function of immersion time

Element	Concentration %									
	Bare		10 sec		20 sec		30 sec		40 sec	
	Spec.	Spec.	Spec.	Spec.	Spec.	Spec.	Spec.	Spec.	Spec.	Spec.
	3	4	3	4	6	7	10	11	17	18
F	0.00	0.00	0.20	0.20	0.85	0.00	0.86	0.21	1.36	1.01
P	0.00	0.00	0.06	0.0	1.09	0.00	0.57	0.23	1.01	0.43
Ti	0.00	0.00	0.63	0.06	0.76	0.45	0.49	0.25	0.98	0.25
Mn	12.42	0.00	0.48	0.63	0.77	2.24	5.43	0.36	1.07	1.55
Al	73.30	100	61.33	90.25	46.74	69.80	59.64	73.09	52.25	79.51
C	0.00	0.00	7.12	9.40	36.33	15.57	17.79	19.12	30.65	10.56

4.1.2. Effect of Temperature

The structure of the pretreated surface as a function of temperature is investigated by SEM analysis and shown in Figure 36.

Figure 36 shows that as the application temperature is increased, darker, porous structure of the surface becomes more visible and spread all over the surface. This situation indicating a denser formation of the pretreatment layer. To better understand the structure of the surface as a function of temperature, the SEM images are shown in the below. Additionally, the location of areas shows where EDX analyses are performed are shown in Figure 37 and the elemental composition obtained from EDX analyses are shown in Table 5.

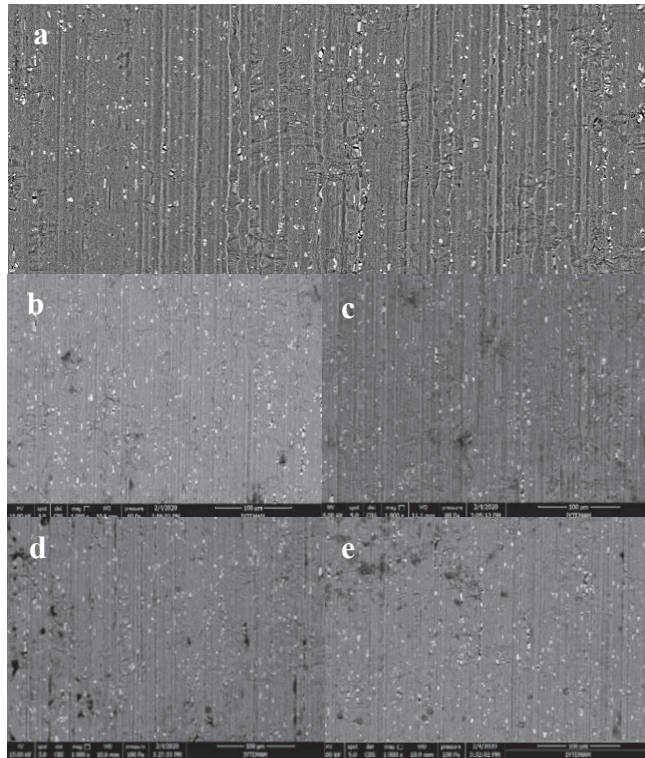


Figure 36. SEM micrographs of a) bare(cleaned) aluminum and aluminum immersed in pretreatment solution at various temperatures b) T = 30 °C, c) T = 40 °C, d) T = 50 °C, e) T = 60 °C

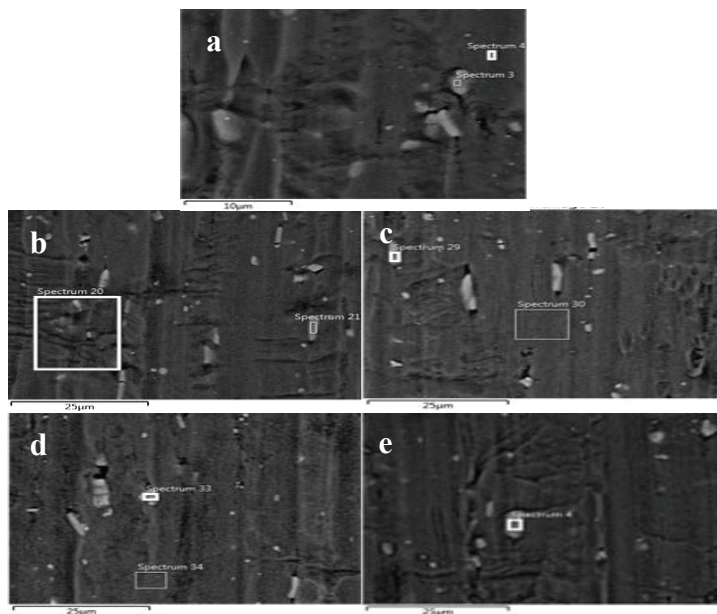


Figure 37. SEM images showing the location of EDX spectrums obtained for a) bare aluminum and aluminum immersed in the pretreatment solution at various temperatures b) T = 30 °C, c) T = 40 °C, d) T = 50 °C, e) T = 60 °C.

Table 5. EDX analyses results according to different spectra obtained from the pretreated aluminum substrates as a function of temperature

Element	Concentration %								
	Bare		30 °C		40 °C		50 °C		60 °C
	Spec. 3	Spec. 4	Spec. 20	Spec. 21	Spec. 29	Spec. 30	Spec. 33	Spec. 34	Spec. 4
F	0.00	0.00	0.00	0.00	0.34	0.21	0.33	0.15	0.72
P	0.00	0.00	0.08	0.16	0.07	0.09	0.19	0.35	0.36
Ti	0.00	0.00	0.27	0.03	0.33	0.12	0.31	0.66	0.38
Mn	12.42	0.00	1.02	7.79	8.30	0.33	7.43	0.19	5.05
Al	73.30	100	83.43	76.61	73.61	89.78	70.92	84.32	70.16
C	0.00	0.00	11.35	5.70	7.42	6.92	8.33	9.82	11.60

Table 5 shows that in general as temperature increased, the elemental concentration of the pretreatment solution contents, F, P and Ti increase. Comparing these results with the structures in Figure 37, it is seen that the increase is less pronounced for some temperatures and areas, which is considered to be due to the highly inhomogeneous structure of the aluminum substrate. In order to understand the average (bulk) trends in elemental composition on the surface as a function of temperature, XRF analyses are given in Table 6.

Table 6. Elemental composition of the pretreated aluminum substrate as a function of pretreatment application temperatures

Element	Concentration %			
	30 °C	40 °C	50 °C	60 °C
P	0.1082	0.3728	0.5075	0.6208
Ti	0.00051	0.022	0.084	0.1169
Mn	0.8919	0.9899	0.9413	0.9414

XRF results indicate that P and Ti concentration increases as a function of temperature, while Mn concentration stays around the same value.

4.1.3. Effect of pH

The structure of the pretreated surface as a function of pH is investigated by SEM analysis and shown in Figure 38.

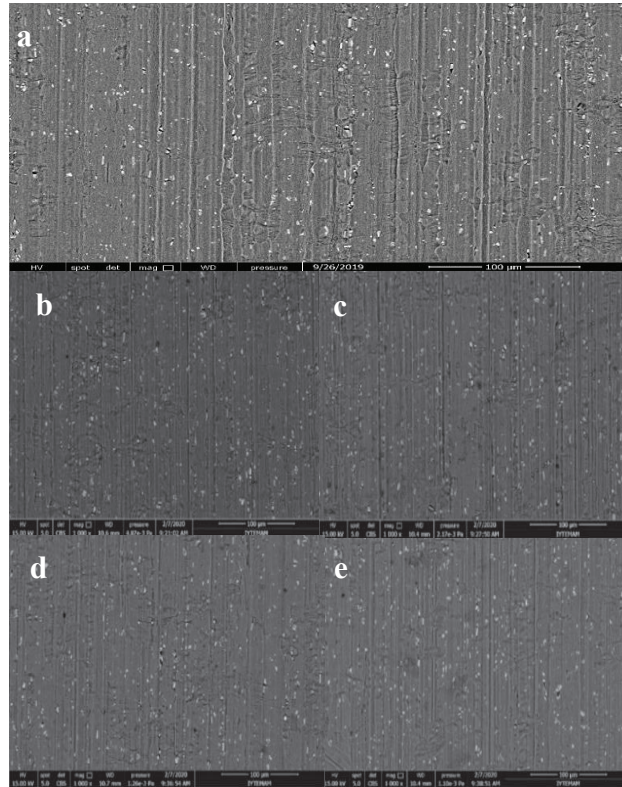


Figure 38. SEM micrographs of a) bare(cleaned) aluminum and aluminum immersed in pretreatment solution at b) pH = 2.42, c) pH = 2.66, d) pH = 2.77, e) pH = 2.98

Figure 38 shows that the darker, porous conversion coating is formed on the surface at different concentrations for varying pH levels, as indicated by the varying contrast in Figure 39a-39e. The darkest, densest conversion coating is formed for a pH of 2.66, while further increase in pH value results in a less optimal formation of the conversion coating. At the 2.66 pH value, the formations on the surface are the most obvious. Unlike other surfaces, spherical particles were observed on the surface at this pH value. SEM images showing different areas where the EDX spectra are obtained are shown in Figure 39, while the elemental composition from the EDX analyses are shown in Table 7. For a better comparison, the bulk elemental composition of the pretreatment contents, as determined by XRF analysis are given in Table 8.

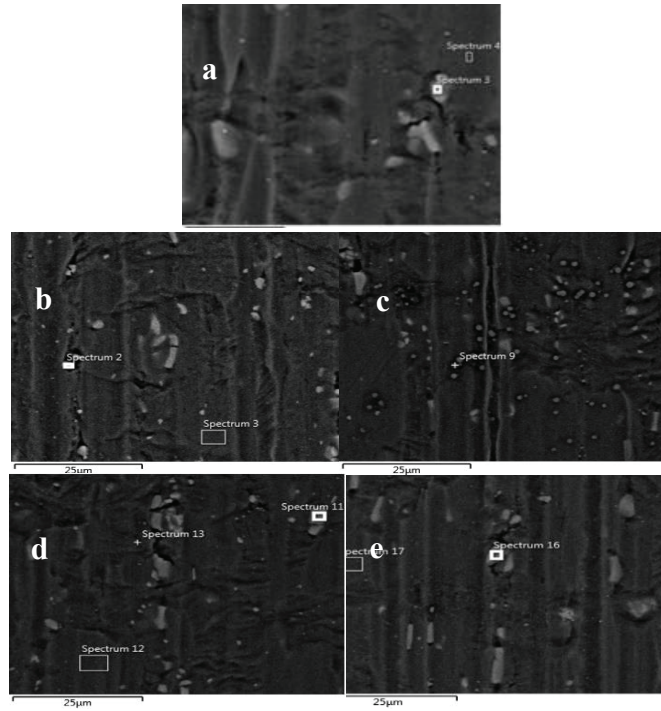


Figure 39. SEM images showing different areas of the aluminum substrate for EDX analyses, as a function of pH, a)bare aluminum b)pH=2.42 c)pH=2.66 d)pH=2.77 e)pH=2.98

The representation of elemental compositions is as in the table.

Table 7. Elemental composition of aluminum substrate obtained from EDX analysis, as a function of pH

Element	Concentration % of pH								
	Bare		2.42		2.66	2.77		2.98	
	Spec. 3	Spec. 4	Spec. 2	Spec. 3	Spec. 9	Spec. 11	Spec. 13	Spec. 16	Spec. 17
F	0.00	0.00	0.73	0.28	12.06	0.1	0.22	0.00	0.08
P	0.00	0.00	0.19	0.24	1.33	0.08	0.01	0.06	0.16
Ti	0.00	0.00	0.30	0.16	0.59	0.16	0.00	0.14	0.00
Mn	12.42	0.00	7.68	0.41	1.24	10.72	6.80	12.16	0.51
Al	73.30	100	70.16	91.15	59.56	69.39	76.15	69.02	93.97
C	0.00	0.00	10.43	6.35	17.24	6.48	6.25	4.16	3.85

Table 8. Elemental composition of aluminum substrate obtained from XRF analysis, as a function of pH

Element	Concentration %			
	2.42 pH	2.66 pH	2.77 pH	2.98 pH
P	0.162	0.733	0.206	0.126
Ti	0.0173	0.041	0.0005	0.00051
Mn	0.987	0.985	0.906	0.953

The results indicate that although, there are variations in pretreatment elemental contents F, P and Ti, as a result of the non-homogenous surface structure including Mn-rich impurities, their concentration reaches maximum for a pH value of 2.66. Also, local EDX analyses show that at 2.66 pH value surface have spherical structures. The results of spectrum 9 shows that this structures are F rich particles. Cerezo et. al says that because of pretreatment solution dissolve the metal substrate, surface ion exchange occur between F and O which leads to AlF complex.⁵³ Also, Yi. Et al stated that hydrolyses of hexafluorotitanates leads to formation of titanium oxides and fluorides the surface.³⁴ These findings are more clear for bulk concentrations of P and Ti from XRF analysis, as shown in Table 8.

4.2. Effect of Various Coating Layers on The Corrosion Behavior of Aluminum Substrates

As indicated in Introduction, under industrial use, substrates are coated with organic coating layers which are called primer and topcoat, on top of the conversion coating, the inorganic coating formed as a result of the pretreatment application. In order to understand the effect of these individual layers on the magnitude and the mechanism of corrosion of aluminum substrates, the following procedure is used. The industrial test for assessing the anticorrosive properties of coated metal substrates, Neutral Salt Spray Test (NSST) is applied on aluminum substrates coated with various layers for different amount of time. These coated panels are obtained from the company AkzoNobel Kemipol (ANK) and the NSST test is also performed in the company. Different panels are corroded in the NSST test for different amounts of time. For example, the substrates that contain

no coatings or the conversion coating are subjected to corrosion up to 8 days, while the substrates that also contain the protective primer and topcoat are corroded up to 40 days. This is because the protective abilities of the coatings increase as the number of layers increase, so they should be subjected to corrosion longer to observe changes occur in their structure. At certain days during the NSST test, the changes in the structure of panels are measured by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and Atomic Force Microscopy (AFM) analysis, while their anticorrosive properties are measured by Electrochemical Impedance Spectroscopy (EIS). The layers and the test time of the investigated coatings are given in Table 9.

Table 9. The layers and measurement days of coated aluminum panels obtained from ANK company

	Panel Type 1	Panel Type 2	Panel Type 3	Panel Type 4
Layers	Al substrate (No coating) (Bare aluminum)	Al substrate + Pretreatment layer (Pretreated aluminum)	Al substrate + Pretreatment layer + Primer layer (Primered aluminum)	Al substrate + Pretreatment layer + Primer layer + Topcoat layer (Topcoated aluminum)
Test measurement day numbers	1,2,3,4 and 8	1,2,3,4 and 8	1, 15, 30 and 40	1, 15, 30 and 40

4.2.1. The Corrosion Behavior of Al Substrate With No Coating (Bare Aluminum, Panel Type 1) vs Al Substrate With Conversion Coating (Pretreated Al, Panel Type 2)

The changes in the morphology of Panel Type 1 (bare aluminum, no coating) vs Panel Type 2 (pretreated aluminum, with conversion coating) as a result of Neutral Salt Spray Test (NSST) are investigated with SEM and AFM analyses as shown in Figure 40 and Figure 41. With these analysis methods, the morphology of the surface and the surface roughness were clearly seen. The roughness values obtained from the AFM analyses are given in Table 10.

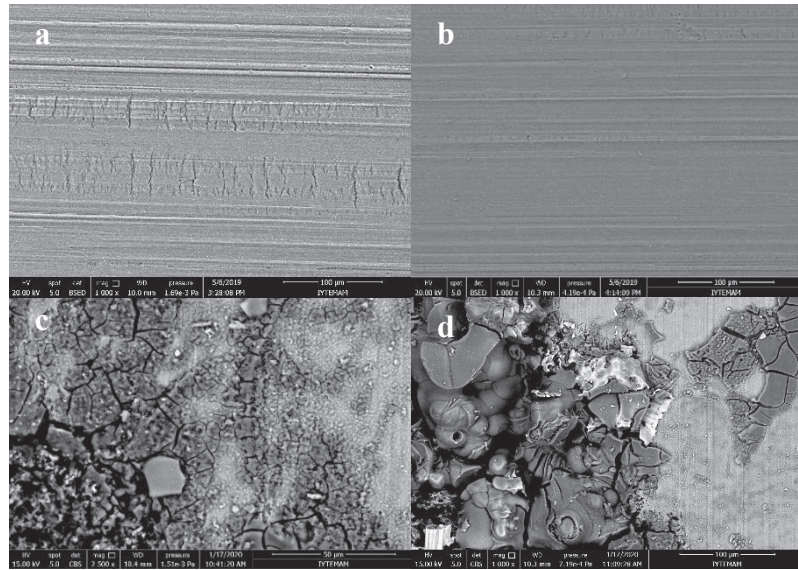


Figure 40. SEM micrographs of a)bare aluminum and b)pretreated aluminum (t=0, Before NSST test) vs c)bare aluminum and d) pretreated aluminum after exposed to NSST for 8 days.

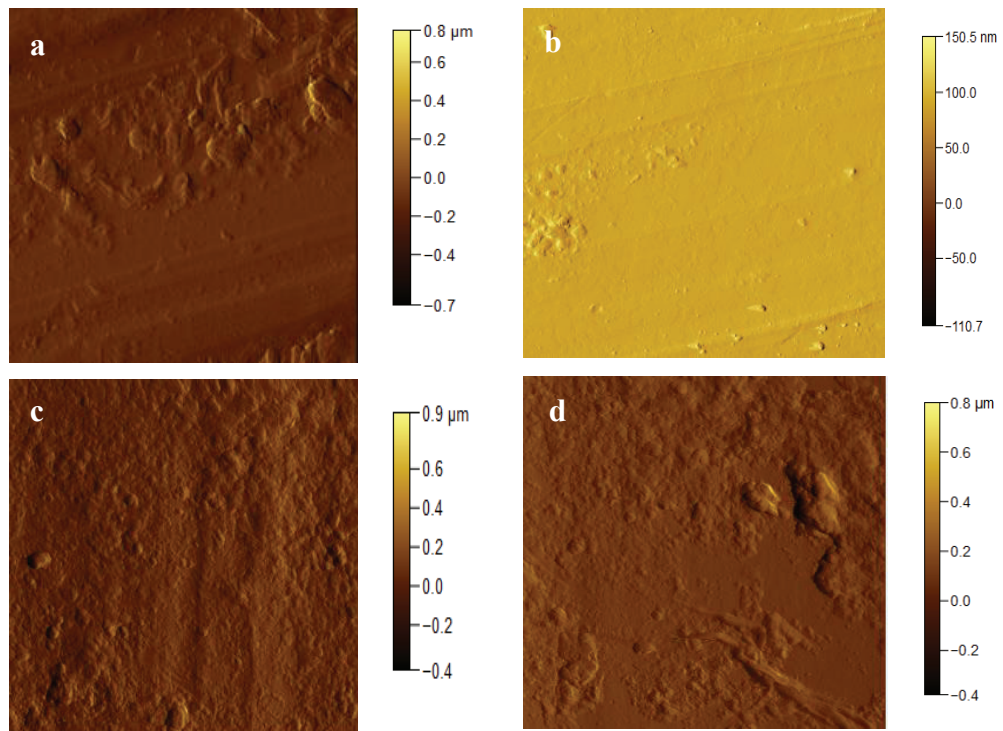


Figure 41. AFM images of a)bare aluminum and b)pretreated aluminum (t=0, Before NSST test) vs c)bare aluminum and d) pretreated aluminum after exposed to NSST for 8 days.

Table 10. Roughness values of bare and pretreated aluminum panels before and after exposed to NSST for 8 days.

Samples	Bare (t=0)	Pretreated (t=0)	Bare 8th day	Pretreated 8th day
Z range (nm)	1.427 μm	261.2	1.319 μm	1.177 μm
Rq (nm)	222.4	31.97	229.6	185.4
Ra (nm)	175.5	23.75	189.0	142.4

Figure 40 shows that on both bare and pretreated surfaces significant amounts of corrosion products are formed. These results indicate that conversion coating resulting from the pretreatment application, does not introduce a measurable, additional anticorrosive property to the substrate, as far as the surface morphology is concerned.

Figure 41 and Table 10 indicate that before exposure to corrosive environment in NSST, the surface roughness is reduced evenly by applying pretreatment, compared to the bare aluminum substrate. However, after exposure to corrosion by NSST, the roughness of the pretreated surface has increased significantly and has achieved the roughness value of the bare surface. The anticorrosive behaviour of the bare and pretreated surfaces are also compared by EIS to have an understanding of the corrosion mechanism differences for bare vs pretreated aluminum. The results of EIS measurements are shown in Figure 42.

Figure 42 indicates that during the 1st day of NSST, both the bare and pretreated panels have around $10^6 \Omega\text{cm}^2$ impedance values at 0.1 Hz. The impedance value at 0.1 Hz is considered as the most important parameter from the EIS measurements which show the anticorrosive property of the coated surfaces⁵². Although the bare panels lose their protective properties faster compared to the pretreated panels, at the end of the 8 day test, the impedance of both panels at 0.1 Hz decreases to around $10 \Omega\text{cm}^2$, indicating that the panels are completely corroded. The Nyquist plot is useful to understand the number of time constants, which are indicative of the process that are necessary for corrosion to take place, such as water diffusion and surface reaction.⁵⁰ The pretreated panel clearly shows two time constants, which indicate paint failure or significant progress in surface corrosion reactions. First time constant related with penetration starts through the conversion coatings because of heterogeneous surface and nonuniform distribution. Second time constant shows as Visser et al said, corrosion products occur on the surface.⁴¹

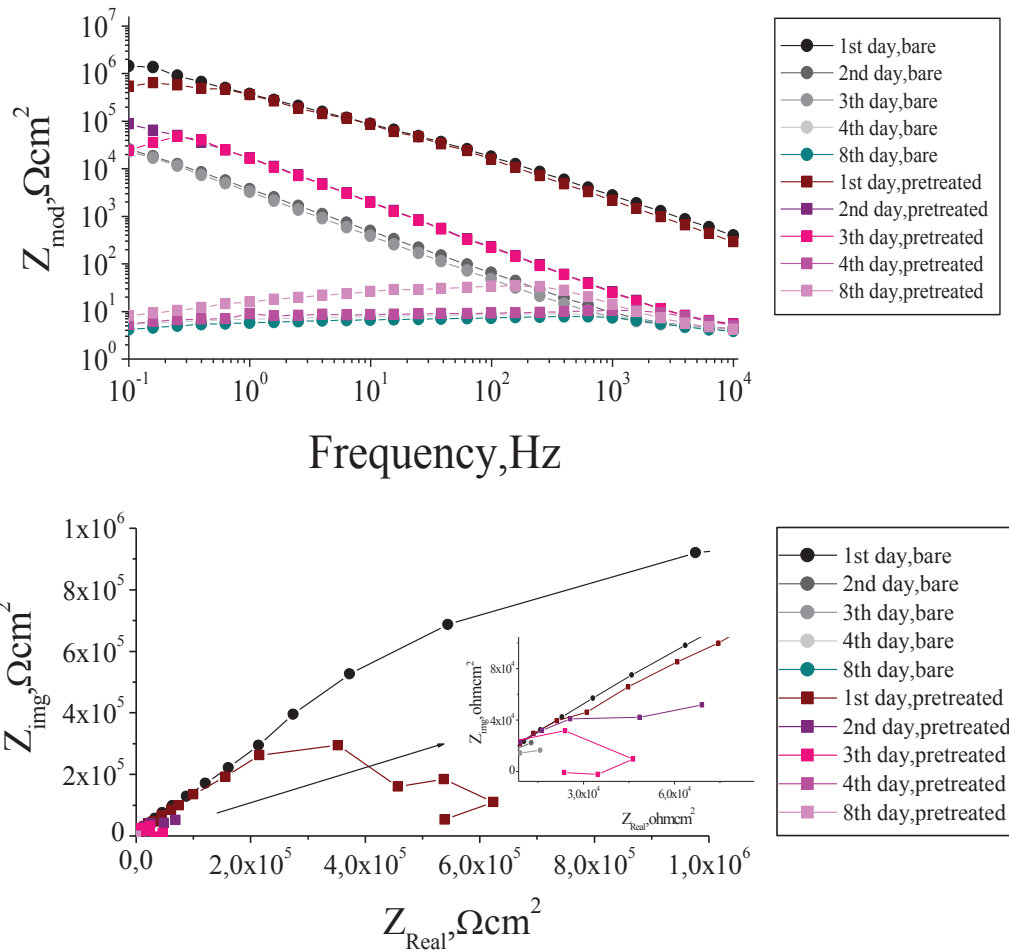


Figure 42. EIS measurements of bare and primed panels obtained during different days of the NSST

Bare panel have no time constant probably because there is no resistance against ion transfer and lower impedance values. For the bare panel, no time constants are observed, which is most probably due to very small impedance values measured.

4.2.2. The Corrosion Behavior of Al Substrate With Primer (Panel Type 3) vs Al Substrate With Topcoat (Panel Type 4)

To investigate the corrosion behaviour of the aluminum panels when the primer and topcoat are also applied, primed (Panel Type 3) and topcoated (Panel Type 4) aluminum panels are corroded with NSST for 40 days. The SEM micrographs of the panels after 40 days of aging under NSST is shown in Figure 43.

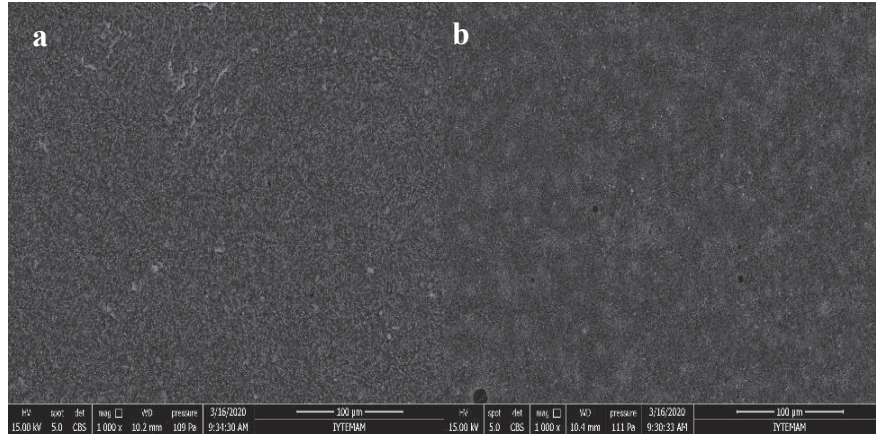


Figure 43. SEM micrographs at 100 μm scale of a) primed b) topcoated aluminum panels exposed to NSST for 40 days

Figure 43 shows no clear degradations in the organic coating layer for both primed and topcoated panels. In order to evaluate the corrosion behavior of both types of panel, EIS measurements are made at different days during NSST. The results of EIS measurements are shown in Figure 44.

Figure 44 indicates that the impedance values at 0.1 Hz of the primed and topcoated panels are around $10^6 \Omega\text{cm}^2$ and $10^7 \Omega\text{cm}^2$ at the 1st day of the test. These results indicate that organic coatings can increase the impedance value, thus the anticorrosive properties of the substrates, 1-2 orders of magnitude compared to the non-organic coated substrates. These results also indicate that anticorrosive properties also depend significantly on the water diffusion properties of the coating layers. At the end of the 40 day test, the EIS measurements as shown in the form of Bode plot in Figure 45a, indicate that the topcoated panel retains its initial impedance value at 0.1 Hz, thus its protective abilities. The Nyquist plot showing a single time constant also indicate that the coating does not have under film corrosion, but just the water uptake process. For the primed substrate, the Bode plot shows a decrease in 0.1 Hz impedance from $10^6 \Omega\text{cm}^2$ to $10^5 \Omega\text{cm}^2$ while, the Nyquist plot shows two time constants, indicating the occurrence of under-film corrosion on the aluminum substrate. As Fedrizzi et al said the first time constant shows the water uptake cannot prevented through the coating because of themicroporous structure of coating layer.⁵⁴ Second time constant shows the under film corrosion initiation as a result of water uptake through the coating. For topcoated panel, there is one time constant at the 30th day of NSST.

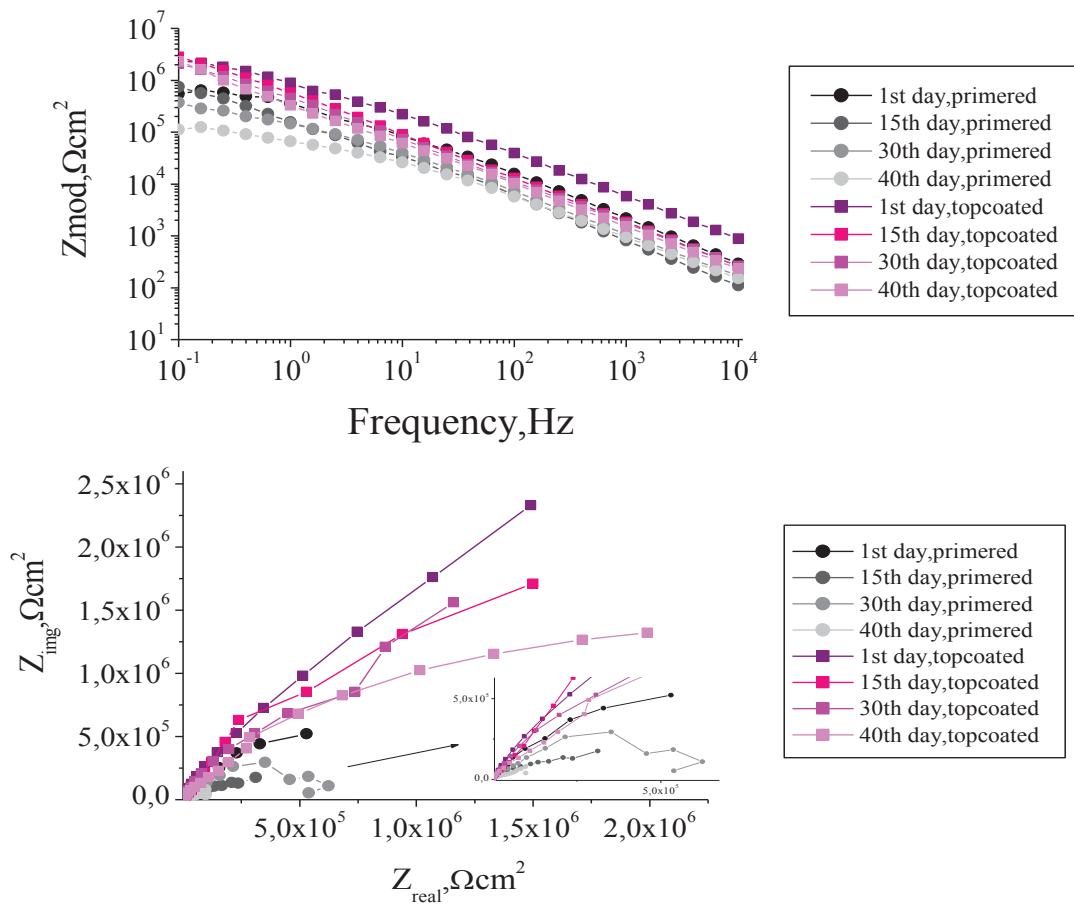


Figure 44. EIS measurements of primered and topcoated panels obtained during different days of the NSST

Additionally, as Bastos et. al said it shows there is no under film corrosion but water uptake occur from the coating due to black holes on the topcoat as a result of weaker barrier properties³⁵. These results indicate that, water permeability of the film is the main driving force for the substrates, which are coated with various layers.

CHAPTER 5

CONCLUSIONS

In this thesis, the effect of pretreatment operating conditions on the structure of the conversion coating formed on the aluminum substrate and the individual contributions of conversion coating and the organic coating layers, primer and topcoat, are investigated to get a more detailed understanding of the anticorrosive properties of coated aluminum substrates that are used in construction industry. This study is performed in collaboration with the AkzoNobel Kemipol, paint company and the aluminum substrate, the pretreatment solution and the organic coating layers used in this study are obtained from commercial suppliers, in order to investigate the industrially relevant systems. In the first part of the study, the aluminum substrates (AA3003 type) are cleaned and pretreated with the industrial solutions Henkel Bonderite C-AK C72 and Henkel Bonderite M-NT 1455T in the university laboratories. The standard operating conditions for the pretreatment application were an immersion of time of 10 seconds, temperature at 25°C and pH at 1.9-2.9 range. The effect of these operating conditions on the conversion coating formed were investigated by using various values for the immersion time, temperature and pH. The resulting inorganic conversion coating was investigated by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and X-Ray Fluorescence Spectrometer (XRF) analysis. For the temperature and immersion time, it was found that increasing the temperature (from 30 °C to 60 °C) and the immersion time (from 10 sec to 40 sec), resulted in a denser formation of the conversion coating, as indicated visually by SEM micrographs and from increasing elemental concentration of the pretreatment elements F, P and Ti obtained from XRF analysis. The SEM analysis also indicated that the surface is highly heterogeneous. Therefore, the elemental concentration of the pretreatment elements did not show a clear correlation with the parameters of temperature and immersion time for some areas on the surface. For the pH, it was found that there was an optimum value of 2.66, which resulted in the densest formation of the conversion coating. For the second part of the study, the effect of coating layers on the corrosion behavior of the coated aluminum substrate by an investigation of SEM and Electrochemical Impedance Spectroscopy (EIS), after the panels have been subjected to corrosion by the industrially used Neutral Salt Spray Test (NSST). It was

found that the bare and pretreated surface both have impedance values of $10^6 \Omega\text{cm}^2$ at 0.1 Hz at the beginning of the test. Both of these panels lost their protective properties completely after 8 days in NSST, as shown by the decrease of their impedance value to around $10 \Omega\text{cm}^2$, seen in Bode plot and the appearance of two time constants in the Nyquist plot. For the primered and topcoated panels, the initial impedance value at 0.1 Hz was measured as $10^6 \Omega\text{cm}^2$ and $10^7 \Omega\text{cm}^2$ respectively, indicating that the application of organic coating on top of the conversion coating increased the anticorrosive properties of the aluminum substrate by 1-2 orders of magnitude. At the end of the 40 day NSST, the impedance of the primered coating at 0.1 Hz decreased to $10^5 \Omega\text{cm}^2$, and the appearance of two time constants indicated that corrosion reaction has initiated under organic coating. For the topcoated aluminum substrates, the impedance at 0.1 Hz did not show a significant decrease and only a single time constant was observed indicating the process of water uptake by the coating. These results indicate that water resistance of the organic coatings may be the major important factor in protecting the aluminum substrate. Combined with the results from the pretreatment application and the NSST results of the bare and pretreated layers, it can be concluded that the porosity of the pretreatment layer. The findings also indicate that the water resistive properties of the conversion coating are at least as important as the interfacial resistance between the aluminum substrate and the conversion coating formed after the pretreatment application.

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