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INVESTIGATIONS OF CONDUCTIVE POLYMER COATINGS FOR
CORROSION PROTECTION OF ALUMINUM ALLOYS

BY

ROBERT JAMES RACICOT

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DOCTOR OF PHILOSOPHY DISSERTATION
OF
ROBERT JAMES RACICOT

APPROVED:

Dissertation Committee

Major Professor Sze Chay Gao

Richard B. M.

Chris B. M.

Angela L.

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

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ABSTRACT

It is well known in the aircraft industry that the Environmental Protection Agency (EPA) has set guidelines for the eventual elimination of chromate conversion coatings for corrosion protection of aluminum alloys. The implications of these guidelines are serious and far reaching. They have initiated urgent development of a suitable replacement for chromate conversion coatings. Given the well known and documented excellent performance of the Alodine 600 and 1200 industrial chromate conversion coatings under cyclic polarization, impedance spectroscopy and ASTM B-117 salt spray tests, this is a difficult goal. To date nothing seems to be able to perform better or at least as equally as well as the chromates and have the same ease in applying the coating to the metal's surface.

However, conductive polymer coatings have the potential to perform as well as the chromates with further development work and offer an easy application method to the metal surface.

Around the mid 80's, the idea of using conductive polymer coatings for corrosion protection on steels started to surface in the literature. In fact, the first commercial application of conductive polymers was as a coating on the space shuttle launch pad under the guidance of Bernard Wessling at Zipperling Kessler. However, the information in the literature and our own testing has shown that the single strand polyaniline coatings are not effective in environments above a pH of 3.0. The polymer transforms to a less effective non-conductive blue colored form via the loss of a proton. Research

conducted in the Chemistry Department at the University of Rhode Island has shown that the polymer coating must remain conductive to be effective in protecting the metal surface, for both steel and aluminum alloys. One suggested mechanism for protection is the polymer's conductive nature provides for an electroactive interaction with the metal surface to form a passivation layer between the metal surface and the polymer coating. This mechanism is the hypotheses for this dissertation. Therefore, its function is not as a barrier coating, as other polymer type coatings, but as a surface conversion agent, similar to the chromate coatings. Although these early results offer some interesting and useful applications in adverse acidic conditions, it is not helpful for more general applications, especially in marine environments where the pH is much higher, approaching a pH of 8.0.

The research towards this endeavor started with the development of a new conductive polymer compound, a double strand complex of polyaniline with a full range of different polyelectrolytes. This new compound is in the form of a twisted double helix, similar to DNA. The drive for this development was to improve the stability of the electroactive green colored form of polyaniline under heat, solvents and pH environments and improve the solubility characteristics of the polymer. Single strand polyaniline is not soluble except in strong acids and loses conductivity in solutions with a pH above 3.0. The double strand polyaniline complex can be modified with a large number of different functional groups to render it soluble in any polar or non-polar solvents. Additionally, the double strand polymer remained

conductive in solutions with pH's as high as 9.5. Unfortunately, this solution did not provide the best wetting, adhesion or corrosion protection as other coatings developed. The best protective coating developed to date has remained conductive at a pH of 6.0, which is at the boundary of the testing solutions pH's, a 0.5 N NaCl solution. The polymer coating changes slowly from the green color to the blue color over several weeks time frame. The polymer was shown to protect the metal surface via cyclic polarization, electrochemical impedance spectroscopy and salt spray testing prior to this color change. With the right chemical modifications, it is quite feasible to develop a conductive polymer coating that will remain conductive at higher pHs and still offer suitable wetting, adhesion and corrosion protection. When tested in salt environments with a pH below 4.0, the double strand coating offered excellent protection. In fact, the impedance data showed a one order of magnitude higher charge transfer resistance over Alodine 1200 on the AA2024-T3 aluminum alloy. This is to be expected as the chromate's oxide coating is soluble below a pH of 4.0. However, X-ray diffraction and XPS analysis on the conductive polymer coated samples show no formation of aluminum corrosion products on the alloy's surface after several months exposure to the acidic salt solutions and, upon removal of the film after testing, there is no evidence of pit formation on the alloy's surface.

These developments offer some exciting possibilities. The performance of the conductive polymer coatings, when maintained in the green conductive state, warrants further investigations into these types of coatings. If a double strand complex can be

developed that will remain conductive at higher pHs and offer the performance demonstrated at pHs below 4.0, then it is very reasonable to assume that an effective replacement for the chromate conversion coatings on aluminum alloys can be developed. As well, the double strand conductive polymer coating can be applied to the metal surface in an easy and industrially accepted method. Our research team at the University of Rhode Island is actively pursuing several approaches to solve the pH limitations. There are currently two approaches under way. The first is a chemical modification of the polyaniline backbone thorough substituted groups on the benzene ring of polyaniline. The goal of this work is to try to increase the pKa of the polyaniline strand. The other approach is to blend the conductive double strand complexes with various epoxies to slow down the de-protonation process of the polyaniline. This work could lead to a new primerless epoxy coating technology.

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PREFACE

This dissertation is written in the Manuscript form according to guidelines of the Graduate School of the University of Rhode Island. Five manuscripts are written in the appropriate format for the submission to journals. An Introduction chapter was written to present the purpose of research, background information and experimental techniques employed in the study.

Chapter II presents results of the double strand conductive polymer coating applied to aluminum alloys and tested with cyclic polarization, electrochemical impedance spectroscopy and high temperature, high humid salt spray exposure for corrosion protection. Comparison of protection performance are made with the industry standard method of chromate conversion coatings. Results show the conductive polymer coating is offering protection to the aluminum alloy surface from pitting corrosion and near equivalent protection to the Alodine 600 industry standard chromate conversion coating for several weeks. Long term studies show the polymer coating losing the ability to protect the alloy surface. This loss in ability to protect is believed attributed to the change in the polymer coating over time. Results show the polymer film changing color, from the green conductive emeraldine salt state to the blue non-conductive emeraldine base state after several weeks exposure to a 0.5N NaCl solution.

Chapter III presents results of a contrast study between the conductive state of the double strand polymer and a non-conductive form of the same polymer. Results show the polymer film must be

in the conductive green colored state to offer protection to the alloy surface. The current polymer film will change from the green colored conductive state to the blue colored non-conductive state if exposed to solutions above a pH of 6.0.

Chapter IV presents results of corrosion protection when the polymer film is kept below a pH of 6.0. Results from low pH environment testing show the polymer film performing better than the best chromate conversion coating on the most corrosive aluminum alloy, AA2024-T3. Evidence is presented of the polymer film not performing as a barrier type polymer coating but as chemical conversion agent to the alloy's surface.

Chapter V presents the model and experimental evidence to support a mechanism model of the protection provided by the conductive polymer coating. A theory for protection mechanism is presented with support from scanning electron microscope (SEM) analysis, X-ray photoelectron spectroscopy (XPS) depth profile data and electrochemical impedance spectroscopy (EIS) modeling.

Chapter VI presents results of corrosion testing of the conductive polymer coating as an undercoat pretreatment system. EIS and salt spray chamber tests are performed with various overcoat epoxy layers.

Most of this work was presented at international conferences and were published as attached in the Appendix.

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CHAPTER 1

INTRODUCTION

INTRODUCTION

This dissertation presents the results from research investigating the use of a novel double strand conductive polymer based on polyaniline as a corrosion protection coating for light-weight, high-strength aluminum alloys used in the aircraft industry. The electrochemical analytical techniques of electrochemical impedance spectroscopy (EIS) and cyclic polarization were employed to investigate the corrosion protection properties of the conductive polymer films and compare this performance against the industry standard chromate conversion coatings. Additionally, long term salt spray exposure tests operating under standard conditions set forth in ASTM B-117 were carried out. Finally, surface analysis of tested samples were conducted using scanning electron microscopy, x-ray photoelectron spectroscopy and x-ray crystal diffraction to help ascertain the electroactive interaction mechanism of the conductive polymer to the metal surface.

Aluminum alloys do not corrode in a manner similar to other common metals, such as rusting of steels in sea water. 1-15 The alloys do not corrode uniformly, but instead, form pits on the surface, these pits have a unique chemistry inside the surface walls of the aluminum. 1-2, 7 The formation of pits is prevalent in marine environments where the chloride ions can attack and dissolve, through an anion exchange mechanism, the native oxide layer. 6 Once the underlying surface is exposed to the salt electrolyte

solution, micro-galvanic cells are setup between the different reduction-oxidation potentials of the atomic constituents on the alloy's surface. 4, 10 For the copper rich alloys used in the aircraft industry, this galvanic coupling essentially sets up a mini-battery with the aluminum atoms being the anode and Cu_2Al as the cathode. The aluminum atoms become oxidized to Al^{+3} cations and the surface begins to dissolve. There is a localized pH lowering at the aluminum dissolution site which prevents the re-formation of the native oxide and accelerates the dissolution process at that site and thus, begins the formation of a pit. 1-2, 7 Pits are a more dangerous corroding phenomena in that it is a non-uniform process that is unpredictable in location and rate of growth into the alloy. Secondly, a pit offers more serious structural failure problem due to the eventual creation of a hole in the alloy's bulk material.

The impetus behind this investigation is to find a suitable replacement for the currently used corrosion protection method for aluminum alloys. The industry standard employs a chromate conversion coating pretreatment. 16-19 The chromate conversion coating is based on dipping the aircraft parts in an acidic chromium trioxide bath. 16,18 The chromate conversion coatings work by first forming a strong, tight native oxide layer of Al_2O_3 on the alloy surface. The oxide layer formed is a hexagon shaped structure that grows from the alloy's surface with a narrow circular hollow channel in the center of the hexagon. 17 The chromium atoms reduced to the plus three oxidation state in this process can enter this channel and essentially seal the pores. The chromium atoms will get further

oxidized to the plus six oxidation state in a corrosive environment. This type of pretreatment is the best known to date for protection of aluminum alloys. In the aircraft industry, the chromate conversion layer is further sealed with a primer and an urethane topcoat.

A major problem currently facing industry is the known carcinogenic properties of the hexavalent and trivalent oxidation states of chromium. There is considerable interest in industry to find a suitable, yet more environmentally safe replacement for these type of anti-corrosion films. The EPA has set guidelines for the eventual elimination of all chromate based conversion coatings used for corrosion protection of aluminum alloys by 1998.¹⁷ The aim of this research is to investigate the applicability and feasibility of recently developed double strand conductive polymers as a new chemical conversion agent to replace the chromate conversion coatings.

The idea of using conductive polymer coatings for corrosion protection was first suggested in 1985.^{20,21} There have been a number of significant results published over the last several years on the corrosion protection of mild steels and stainless steel with coatings of polyaniline²⁰⁻³² and other conductive polymer coatings.³³⁻³⁷ These studies indicate the protection of the steel surface is a result of the electroactive interaction of the polymer coating with the metal's surface that forms a passive oxide layer through an anodization process. Even more significant findings have shown that if two steel samples are coated with a clear epoxy, one with a conductive polymer undercoat, the other without, and then

scratched to expose the underlying metal surface and exposed to a corrosive environment, the scratch of the sample with the polymer undercoat will not rust as fast as the sample without the undercoat. 25-27 The polymer film adjacent to the exposed scratch seems to have the ability to repair the exposed surface. One theory on this is the polymer can passivate the exposed metal area via an electroactive galvanic coupling mechanism. The attachment of the polymer near the surface of the scratch offers an electroactive coupling to the exposed area and essentially keeps the exposed metal area at a more noble potential than if no conductive pathway were present. 25-27 These results seem to indicate that the conductive form of the polymer is the key to offer any corrosion protection for metals. It makes sense that an electroactive interaction is needed to offer protection to metals in marine environments, since most metals do not passivate in chloride environments, a change to the metal surface is needed to passivate the surface.

The most promising results for an anti-corrosion coating comes from the conductive polymer, polyaniline. Of all the different conductive polymers available, polyaniline offers the most chemical stability, although it still has some difficulties with processing and long term conductive stability. These limitations will be discussed in the following paragraphs.

Polyaniline has the structures shown in figure 1 with four different oxidation states as shown. Only the emeraldine salt green

colored state is conductive, all of the other oxidation states are insulators. The control of these states is governed not only by reduction-oxidation reactions but also by the pH of the environment. Therefore, polyaniline has its own Pourbaix diagram for stability of the conductive state.³⁸ The Pourbaix diagram for polyaniline is shown in Figure 2. Therefore, conductive polymers can be thought of in a similar way to metals with different electroactive reduction-oxidation states and environmental sensitivity.

The development of conducting polymer based anti-corrosion coatings has been slow. This is attributed to three main problems: (1) difficulty in coating polymers on non-noble metals, (2) material instability, and (3) non-amenability to industrial manufacturing processes. Most previous techniques required electrochemical polymerization of the polymer to the metal surface. The chemistry of electrochemical polymerization of polyaniline dictates that the electroplating solution needs to be highly acidic (0.1M HClO₄) and the applied potential highly anodic (1.0 V vs. standard calomel electrode). These conditions limited the type of metal surfaces that could be studied to only carefully passivated stainless steel samples and thus limited its usefulness and further development.^{23, 29-32}

The difficulties with the conventional conducting polymers of material instability and lack of processability are associated with two of their properties. The material instability comes from the ease in losing the anionic dopants (Cl⁻, or molecular anions) and thus a loss in electrical conductivity. The anionic dopants are lost due to

heat, moisture, rain water, etc. The lack of processability comes from the fact that the conducting polymers are pi-conjugated polymers. 39 The delocalized pi electronic structure results in a stiff polymer chain and a strong inter-chain attraction. 40-44 Thus the conventional conducting polymers can not be easily dissolved, melted or blended with other polymers. Because of this lack of processability, previous researchers were not able to use the conducting polymer as a paint and were forced to use the difficult electroplating technique on a limited range of metals. 30, 33-35 The electroplating of organic polymers is a much less attractive technology for coating as compared to a painting or spraying application of the active ingredient.

There have been recent developments to improve the processability of polyaniline so that one can avoid the troublesome electroplating process. These techniques only succeed in improving the ability to apply the conducting polymer onto the metal surface. 28, 35 They are still deficient in the other two aspects: (1) the material is not stable enough for long term corrosion protection, and (2) the material has difficulty in manufacturing directly as a paint. There have been efforts to chemically modify the conducting polymer by attaching functional groups onto polyaniline. These attempts were not successful because the substituent group interferes with the conformation of the conducting polymer backbone and decreases its electrical conductivity. 23, 31-32, 45

Recently, a German company (Zipperling Kessler) developed a formulation that incorporates a hydrochloric acid (HCl) doped polyaniline structure for anticorrosion coatings.⁴⁶ A paintable formulation was made by mixing fine powders of polyaniline with a lacquer, thus bypassing the problem involved with electroplating the polymer film. Although this is an improvement it has not solved the more fundamental problem of material instability. The dopant HCl in polyaniline is easily lost due to heat induced evaporation or by rain water wash out. This prior art material may be only used in the special application for NASA because the shuttle's acidic booster fumes help to replenish the lost dopant. Without the dopant the polymer becomes non-conductive and it is believed will not protect the surface.

The new double strand conductive polymer system used in the studies in this dissertation was developed at the University of Rhode Island. Numerous publications, thesis's and dissertations have already given sufficient detail to the development of this new class of material.⁴⁷⁻⁵³ The work presented in this dissertation is for the development of a new application for the double strand polymer system and as such only a brief description is given below.

This new polymer is a novel double strand polymer complex fabricated with a template guided synthesis technique. This technique allows for the development of a polymer system that is soluble in water or simple organic solvents. This property significantly eases the use of operation for applying polymer films to

the metal surface. Now the polymer can be applied like a paint, either sprayed on or brushed on; currently the solution is dropped onto the surface, allowing the solvent to dry in air, whereby the polymer film is attached to the metal surface.

An illustration of the double strand polymer system is shown in figure 3. The double strand conducting polymer allows for structural designs that can solve the problems with material stability and processability. The anionic functional groups are now covalently bound to the second strand. The material stability is improved because the polymeric dopant is strongly coupled with the polyaniline chain thus the dopants are not lost with heat, water or solvent. This renders the complex stable in ambient environments and has shown thermal stability up to 290 °C. The presence of the second strand provides ample opportunity to modify its structure by attaching appropriate functional groups. This leads to complexes that can be rendered soluble in water and simple organic solvents allowing for easy processing and use as a coating material.

The objectives of this research for this dissertation was to extend the earlier successes with corrosion protection of a conductive polymer coating on steels to the application of high-strength, light-weight aluminum alloys used in the aircraft industry.

EXPERIMENTAL TECHNIQUES

Several electrochemical and surface analysis experimental techniques were employed in this study. The electrochemical techniques involved using cyclic voltammetry or cyclic polarization, as referred to in the corrosion field, and electrochemical impedance spectroscopy (EIS). Long term exposures to high temperature, high humid salt spray were performed according to the standardized operating procedures set forth in ASTM B-117. Finally, surface analysis of coated samples was performed using a scanning electron microscope, x-ray photoelectron spectroscopy and x-ray diffraction analysis. These surface studies were conducted to try and obtain an understanding of the interactive nature of the conductive polymer with the aluminum alloy's surface. This type of data is crucial to ascertain the possible mechanisms involved with any corrosion protection of the metal surface.

Cyclic Polarization

The first electrochemical corrosion testing technique used is called cyclic polarization. This technique is essentially the same as a one cycle voltammetry experiment, as it is commonly referred to in chemistry, except the scan rate is greatly reduced to usually 0.1mV per second and the data is presented opposite to voltammetry with the measured current as the x-axis and the applied potential as the y-axis. In these tests the electrochemical behavior of coated, uncoated and chromate conversion coated

aluminum alloys are compared. The test environment is 0.5N NaCl solutions made from double distilled deionized water. The tests are run from open circuit potential up to 0 volts vs. SCE and then reversed back down to the open circuit voltage. The scan rate is 0.1mV/sec. The potential range is far greater than any possible coupling with common engineering metals and well above the potentials when extremely high corrosion rates in the uncoated aluminum alloys are found. In this testing the passive current densities for different formulations of the coatings can be measured. From the passive current density a calculation of the Al^{3+} ion interface between the conductive polymer and the substrate can be calculated. The passive current density will also be the criterion used to initially identify the most corrosion resistant coatings. Also the shift in open circuit voltage or current density at open circuit can indicate whether an anodic or cathodic inhibitor is present to produce the passive response. This technique is rather simple to perform and only requires a potentiostat, computer and the appropriate software. The results of cyclic polarization can help to identify the protection mechanism as a passivation mechanism and can identify the protection range for the coating.

Cyclic polarization was used as the first test for screening and mechanistic purposes of new coatings. If the coating's failed in this tests, then they generally were not investigated closer in EIS or salt spray exposure, as this meant the coating were not showing a passivation capability. The samples were placed into an electrochemical cell that allowed a 1cm² area of the sample to be

exposed to a 0.5N NaCl solution. The sample acted as the working electrode, with a platinum counter electrode and saturated calomel (SCE) reference electrode as the other electrodes in the cell.

Potentiodynamic measurements using an EG&G Princeton Applied Research Model 273 potentiostat were performed. The voltage was scanned from -50mV below the measured open circuit potential to 0 volts with a scan rate of 0.1mV/s while the resulting current was measured and recorded. Data of interest was the open circuit potential, whether a passive range is formed, the breakdown potential, the passive current and the voltage-current behavior upon reversal of the potentiostat at high current densities.

Electrochemical Impedance Spectroscopy

Impedance spectroscopy (EIS) is a recent tool in corrosion laboratories that is slowly making its way into the service environment as units are decreased in size and become portable. 54-69 In impedance spectroscopy, a small sinusoidal voltage is placed on the sample over a wide frequency range, from 10^5 to 10^{-3} Hz. The system measures the magnitude of the current induced by the potential and the phase angle relationship between the applied potential and induced current maxima. A modified Ohms law is applied:

For direct current (DC) conditions: $V=IR$

For alternating current (AC) conditions: $V=IZ$

where Z is the impedance of the system. From this modified Ohms Law for AC conditions the impedance can be calculated by setting

the input potential and measuring the induced current. When the phase angle between the voltage applied and the current induced is zero, then a pure resistance is present. When a phase angle of 90° is measured between the voltage and current at the same frequency, a pure capacitance is present. Angles between these values can mean a combination of a capacitor and a resistor are present. It is therefore important to plot the impedance, usually the log of the impedance magnitude as a function of frequency and in addition the phase angle as a function of frequency. These are known as Bode plots.

An example of a Bode plot is shown in Figure 4 for a simple electrical circuit called a Randles circuit. It consists of a resistor and a capacitor in parallel. This circuit simulates the type of data found for a simple corroding interface, such as steel in seawater. When the circuit has a maxima in the phase angle as shown in this case, it is caused by a combination of a resistance and a capacitor in parallel and is called an RC circuit. It also leads to models of electrochemical interfaces. One simple model is called the double layer model. In this the interface for a metal in electrolyte is envisioned as a layer of ions adjacent to the electrode surface with a further layer of solvated ions further away from the surface. The two layers of ions leads to a capacitor as they store charge, called the double layer capacitance, C_{dl} . It also leads to a resistor as charge leaks across the capacitor, called the charge transfer resistance, R_t . Therefore the models of electrochemical interfaces are represented as a capacitor and resistor in parallel. In series with this is a resistor representing

the solution resistance, R_s . A typical interface is shown in figure 5 along with its electrical analogs.

By using the electrical circuit analog approach, the data can be modeled to provide quantitative values for R_s , C_{dl} and most importantly R_t . R_t is proportional to corrosion resistance of the electrode. The higher this value the more resistant to corrosion. Typical values for R_t are 10^4 ohms/cm² for steel in seawater and 10^6 for titanium. Metals which will tend to pit are below the 10^5 region.

A more complex analysis is available for paints on steel and other coated samples. In this case the circuit involves two parallel capacitors and resistors in series along with a solution resistance. In this case the parameter of importance is the pore resistance or R_p shown in figure 6. This value extracted from models is often around 10^{10} , but if it decreases below 10^6 it implies that corrosion is occurring below the paint film and the paint system is generally non-protective. This is commonly used in paint and coatings development work to determine the most effective protection scheme.

To conduct an impedance test a glass tube is clamped onto the surface to be tested and then filled with the test solution. The surface exposed is then the working electrode. A counter electrode, a piece of platinum foil, and a saturated calomel electrode as a reference electrode are placed in the solution. The connections from

these electrodes firstly go into a frequency response analyzer. This has the capability to impose on a voltage signal a small sinusoidal potential over a wide frequency range. It also can detect the phase angle and magnitude of the induced current in the sample. The impedance is directly calculated in the frequency response analyzer. This data is transmitted back through the potentiostat to the controlling computer and can be stored and plotted.

Generally a 5mV potential is imposed on the sample and the current measured. However for very resistive samples such as thick paints and very low resistive solutions a higher potential amplitude is used. Values up to 100 mV were reported in the literature. The reason for increasing the potential is to produce a reasonable signal to noise ratio so that the data is meaningful, especially for highly resistive coatings. It should be noted that the potential cannot be too high otherwise the sample is polarized and anodic and cathodic reactions are initiated. The idea of the small potential is to avoid major current flow and so maintain the technique as non-destructive.

Long term studies can be done by this technique to determine the behavior of coatings for example. In addition, quantitative information is available which cannot be determined by salt spray (ASTM B117) or other techniques. For example if several coatings pass the salt spray test, the best one is still not known. However impedance testing can determine the best coating. In addition the long term measurement capability along with the non-destructive

and quantitative nature of the test will sometimes indicate important information, such as the coating with the highest resistance at the initiation of a test will degrade very quickly and not last as long as a coating which started at a lower value and did not decrease as much. Using commercial software the data can be modeled and values extracted.

Salt Spray Tests

Long term salt spray tests are performed according to a standard set of operating conditions specified in ASTM B-117 or ISO 9227. ⁷⁰ A large chamber is heated to 95°F and a 5% by weight sodium chloride solution is sprayed into the chamber. Samples are scribed with a knife edge in a cross pattern and placed inside the chamber. The corrosion is monitored over time and periodically samples are removed to conduct EIS studies or record their condition with photographs.

Surface Analysis

Several surface analysis techniques were employed to investigate the corrosion protection mechanism and try to understand the electroactive interaction of the conductive polymer coatings to the metal's surface. The most useful technique is scanning electron microscopy. With this technique, samples can be screened at a very high magnification for evidence of corrosion on

scratched areas of the sample or under the film, after it is removed from the metal.

Depth profiling studies using X-ray photoelectron spectroscopy (XPS) were conducted on coated samples. The objective is to determine the thickness and ionic state of the interface between the conductive polymer and the metal substrate. This information is important to help ascertain the protective mechanism involved with a conductive polymer coating.

X-ray diffraction studies are conducted on the corrosion products formed from marine environment exposure testing to also help determine the mechanism of protection for the conductive polymer coating.

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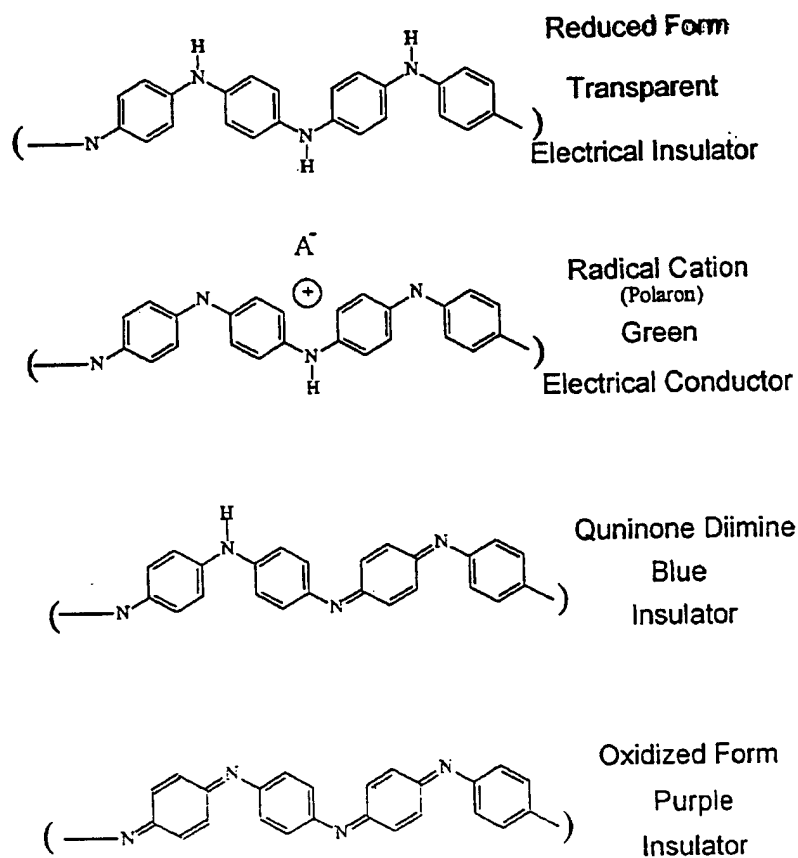


Figure 1. The four oxidation states of polyaniline.

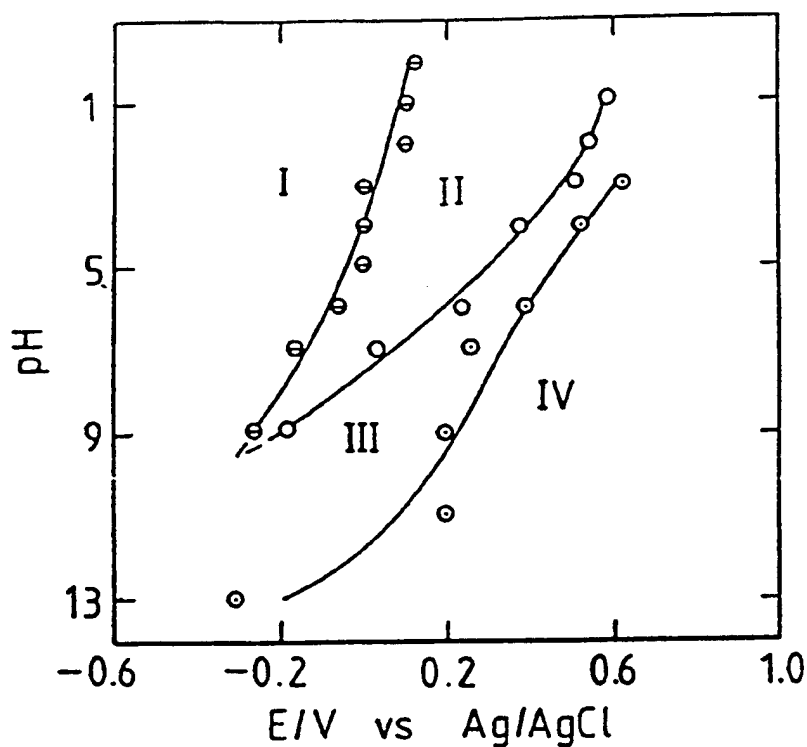


Figure 2. Pourbaix type pH-potential diagram for polyaniline that shows the range of stable regions for the protonation states and oxidation states. The state labeled I is the transparent reduced form of polyaniline that is an electrical insulator. State II is the radical cation green colored emeraldine salt form that is electrically conductive. State III is the oxidized blue colored emeraldine base insulator form and state IV is the completely oxidized purple colored insulator form.

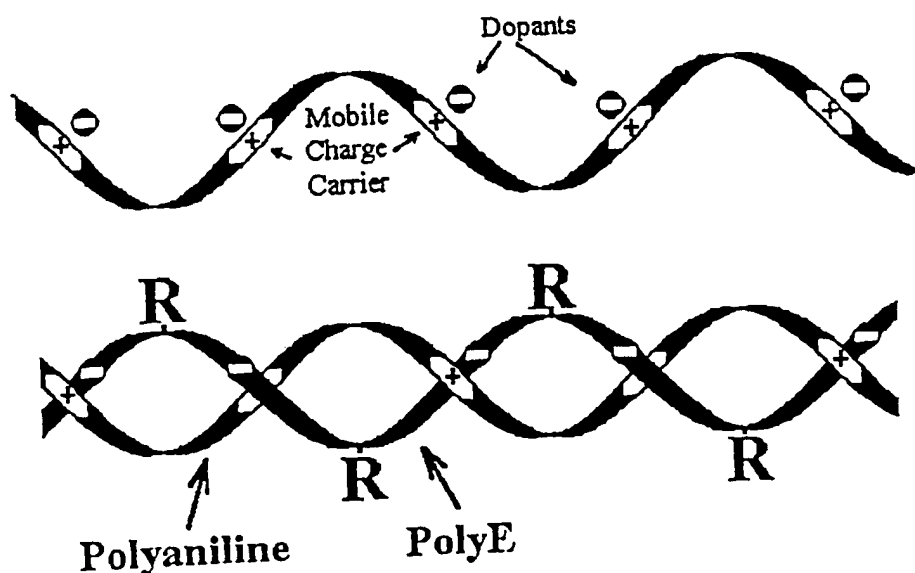


Figure 3. Traditional conductive polymer (top) and new double strand conductive polymer (bottom). The single strand remains conductive with the anionic dopants. The PolyE serves as the anionic dopant for the double strand. Functional groups on the second strand, represented as R groups, offer flexibility in the polymers solubility.

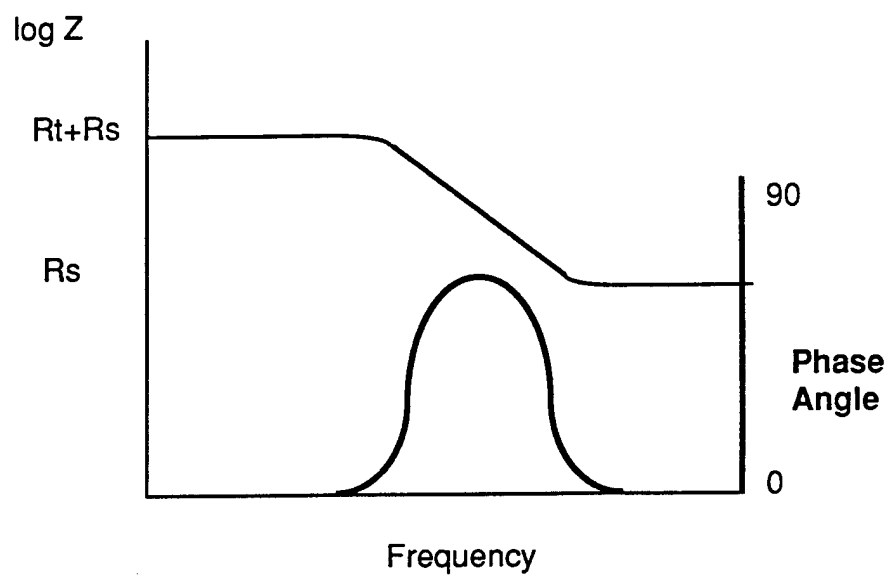


Figure 4. Typical plot of data acquired from EIS, represented in a Bode plot as frequency versus impedance and frequency versus phase angle.

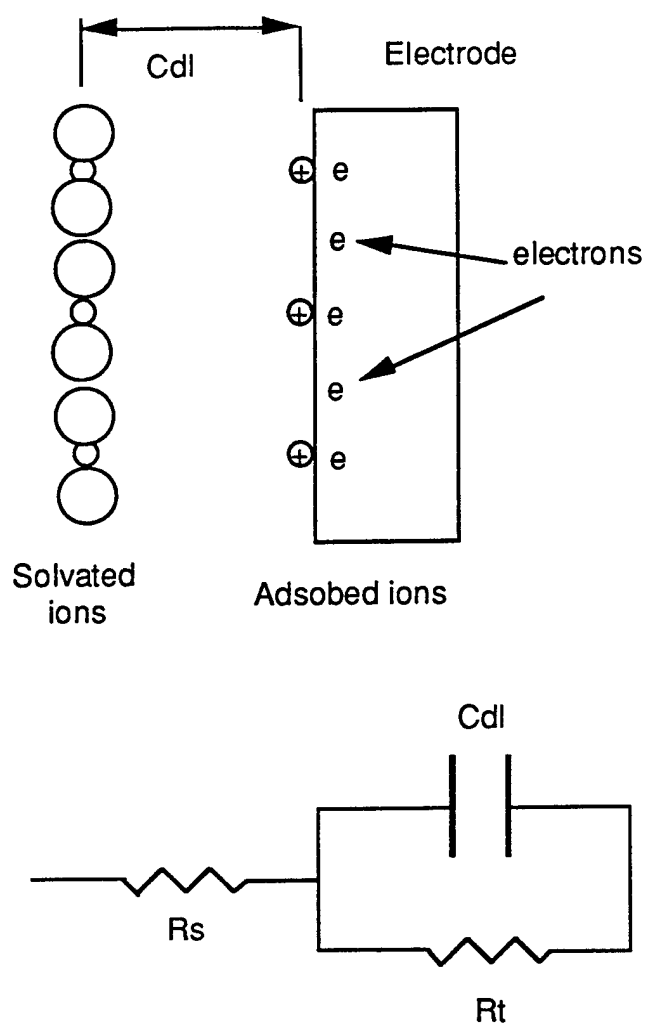


Figure 5. Simple Randles circuit that describes the electrochemical interface shown above. C_{dl} is the double layer capacitance setup from the difference in charge of the solvated ions and the adsorbed ions of the metal's surface. R_s is the solution resistance and R_t is the charge transfer resistance.

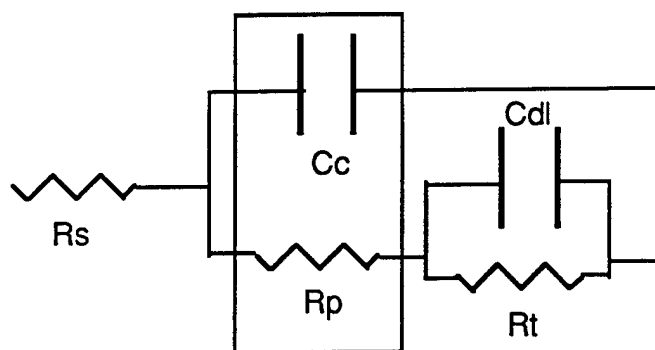


Figure 6. Electrochemical equivalent circuit model of a coated metal electrode, for example epoxy paint on a steel. R_p is the pore resistance of coating, C_c is the capacitance of coating, R_t the charge transfer resistance of the coating substrate interface and C_{dl} is the double layer capacitance of interface.

CHAPTER II

CORROSION PROTECTION PERFORMANCE EVALUATION OF DOUBLE STRAND CONDUCTIVE POLYMER COATINGS COMPARED TO CHROMATE CONVERSION COATINGS ON ALUMINUM ALLOYS

ABSTRACT

Comparison of the corrosion resistance performance of the polyaniline based double strand conductive polymer coating with a chromate conversion coating, based on the industrially accepted Alodine 600 process was made. Potentiodynamic scans, electrochemical impedance spectroscopy (EIS) in 0.5N NaCl solutions and ASTM B-117 salt spray tests were performed on coated samples of AA7075-T6 and AA2024-T3 aluminum alloys. Results show the conductive polymer film offers, at the least, an equivalent protection performance as the Alodine 600 chromate coating for several weeks with a two order of magnitude reduction in corrosion current densities in cyclic polarization tests, near equivalent impedance values and less undercutting of a scribed area in salt spray test samples.

Long term testing shows a color change of the conductive polymer film from green to blue. This color change is associated with a measured decrease in corrosion protection performance of the coating. Implications of this change are discussed.

INTRODUCTION

Double Strand Polymer Coating

The double strand conductive polymer system used in these tests consisted of one strand of polyaniline and the other polyelectrolyte strand was polyacrylic acid. The strand loading ratio was 2:1, polyacrylic acid to polyaniline. Other complex's with different polyelectrolytes and different loading ratios were tested during this research, but the best corrosion protection came from a modified 2:1 loaded polyacrylic acid to polyaniline system. This complex is referred to as PAA in this dissertation.

The polymer complex was first synthesized employing the previously reported template guided method,^{1,2} then dried, yielding a black powder which is soluble in water or an alcohol based solvent. Solutions of the polyaniline/polyacrylic acid complex in methanol were tested as coatings for the aluminum alloys but did not reveal any evidence of a good protective coating. There are two suspected reasons for this coating's poor performance. The first reason is that the solution pH was very low at approximately 2.5. The very acidic nature of the coating corroded the aluminum alloys upon application of the solution to the surface. When the solution was treated to a neutral pH with a mild base the coating still did not perform well. This suggested the most probable reason for poor performance was the highly hydrophilic nature of the coating. These coating are readily soluble in water and as such will start to dissolve upon application to the alloy surface. As presented in chapter 1, it is suspected that the part of the protective nature of a

conductive polymer coating is an electroactive interaction of the polymer with the metal surface after immersion in the test solution. The conductive polymer is best thought of as a chemical conversion coating similar in nature to the chromate conversion coatings. If the polymer dissolved upon immersion in the test solution, then an adequate interaction can not take place with the alloy surface to offer the formation of protective passive layer. This protection mechanism is discussed further throughout the dissertation with supporting evidence. As a consequence of this, the PAA coating will not be presented further in this dissertation.

The polyaniline/polyacrylic acid complex was further processed with esterification of the acrylic acid group on the second strand with methanol to manufacture a polyaniline strand with a methylated polyacrylate ester complex. This complex is referred to as PMA in this dissertation. This complex gave, to date, the best corrosion protection results and offered the best wetting and adhesion of the polymer to the aluminum alloy's surface. The results presented in this dissertation will focus on the further investigations of this esterified polyacrylic acid/polyaniline coating as a candidate for a chromate conversion coating replacement.

Aluminum Alloy Samples

Five square centimeter samples of 6061-T6, 7075-T6, 2024-T3 aluminum alloys were then coated with these solutions. The different alloy series have different alloying compositions and are used for different applications. The percentage of alloy

compositions for each is shown in Table 1. ³ The aircraft industry uses mostly the AA7075-T6 and AA2024-T3 alloys, as these have the highest percentage of copper, which offers a higher strength-to-weight ratio for the alloy. However, the draw back to these stronger alloys is their increased susceptibility to pitting due to the greater difference in reduction-oxidation potentials of aluminum and copper atoms. Because of this, the studies presented in this dissertation will only focus on the experimental results of these two alloys.

EXPERIMENTAL PROCEDURES

The aluminum alloy samples are first ground with 600 grit silicon carbide paper, cleaned with a degreaser and de-ionized water prior to coating application. The soluble polymer is then applied to 5.0 centimeter square samples of AA7075-T6 or AA2024-T3 aluminum alloys by dropping from a pipette and allowing the solvent to evaporate from the surface leaving a thin uniform layer of polymer coating. Other coating processes consisted of painting with a brush or dropping solution for a pipette and spin coating. The drying process was used the most, as it succeeded in leaving a uniform polymer film on the metal surface.

Coating thickness determination was a technique which involved simply knowing both the amount of polymer in solution and the amount applied to the surface, then calculating the thickness based on the area of the sample's size and the volume of polymer present in the solution. The film thickness ranged from 1.0 to 10.0 microns

with this technique. There was an observed thickness effect to the performance of the polymer that showed the thicker coatings gave better performance in lowering the corrosion current density in cyclic polarization and impedance spectroscopy. This effect will be presented and discussed in further detail later.

The chromate conversion coating used in this study was based on the Alodine 600 coating process. Samples were placed in the standard solution of chromium trioxide, phosphoric acid and sodium hydrogen fluoride. This solution is an industrially and militarily accepted pretreatment chromate conversion process. It is specified by the military in the specification MIL-C-5541 for the chromate conversion process and MIL-A-8625 for the chromic acid anodized surface treatment.^{4,5} The alloys were dipped in this solution for 5 minutes to form a uniform green colored sealed oxide coating on the metal surface. Other samples were treated with the Alodine 1200 process. This is the best industrial chromate conversion pretreatment for aluminum alloys. This pretreatment process was performed to military specifications by Microfin Corporation of Providence, RI.

For cyclic polarization testing, the samples were placed into an electrochemical cell that allowed a 1 cm² area of the sample to be exposed to a 0.5N NaCl solution. The sample acted as the working electrode, a platinum counter electrode and saturated calomel (SCE) reference electrode were placed in the cell. Potentiodynamic measurements using a potentiostat were performed. The voltage was scanned from -50 mV below the measured open circuit

potential up to 1.0 volt versus SCE at a scan rate of 0.1 mV/s while the resulting current was measured and recorded.

Samples were also tested using the electrochemical impedance spectroscopy (EIS) technique. Samples were clamped with a 1 cm² hollow tube cell and filled with a 0.5N NaCl solution, a platinum counter electrode and SCE reference electrode were placed in the cell. The electrodes were connected to a potentiostat and a frequency response analyzer. A 5.0 mV alternating current (AC) perturbation signal was applied at the open circuit potential. The AC frequency was scanned from 0.003 Hz to 100 kHz. The resulting current and impedance were measured and recorded.

Other samples were exposed to a stagnant 0.5N NaCl solution in closed tubes for several months, with and without scribed surfaces. Still other samples were placed in a salt fog chamber operated at the ASTM B-117 conditions.⁶ An X mark was scribed to one side of the samples with a razor blade to expose the underlying metal prior to testing.

EXPERIMENTAL RESULTS

Performance versus Uncoated Alloys

Cyclic Polarization

Figure 1 shows cyclic polarization results of a double strand conductive polymer coated onto an AA7075-T6 aluminum alloy. Included in this figure is a potentiodynamic scan of an uncoated 7075 sample. The potentiodynamic curves of figure 1 show that the polymer coating reduced the open circuit current density by

two orders of magnitude. The open circuit current density is considered to be the corrosion current density for metals that corrode uniformly, such as steels. However, for metal that passivate, such as the aluminum alloys, the main corrosion event is pitting. As discussed previously, pitting is a non-uniform process that cannot not be accurately measured from current density measurements. The current density measurements are a measure of the overall surface current density and do not reveal information about a specific pit site or the corrosion rate in a pit. However, the determination of the open circuit current density was still conducted to be complete in the analysis and was used as an overall screening tool for different complexes tested. A more useful measurement is the determination of the passivation current obtained by potentiodynamic testing. These results are presented later.

The open circuit current densities are obtained by extrapolation of the linear regions of the cathodic and anodic curves with Tafel plots. This technique can be observed when the linear regions of the anodic and cathodic curves from figure 1 are enlarged to reveal their linear portion. Figure 2 shows the expanded regions of the anodic and cathodic curves from Figure 1. Extrapolation of these curves along the linear region to the point where they cross gives the open circuit current density of the sample. The open circuit current density is the corrosion current density. The open circuit current densities for the conductive polymer coated and uncoated 7075 aluminum samples are found to be 5×10^{-2} and 5×10^0 microamps/cm², respectively. It is seen that

by applying a polymer coating on 7075 surfaces, the open circuit current density is reduced by two orders of magnitude.

The open circuit potential, E_{corr} , for the conductive polymer coated sample is also found to be slightly more anodic (at -0.724 V) relative to that of the uncoated sample (-0.775 V). The open circuit potential is found by extending the linear portion of the cathodic and anodic curves to the intersection at the axis. This shift toward a more noble surface is the first indication of an electroactive interaction of the conductive polymer with the metal surface. There is a similar type of open circuit shift associated with the application of conductive polymer coatings on steels presented by other researchers.⁷⁻¹⁴

As mentioned above, the passivating current is a useful measure of a coatings effectiveness on metals that tend to pit. This current is measured at the point when the current density stops and the driving potential increases with no further increase in current density. This can be observed in figure 1 a approximately 0.8 microamps/cm². The important data is that the conductive polymer coated sample does passivate in a salt water environment. As is evident for the uncoated sample data in figure 1, aluminum alloys do not passivate in salt water environments. This is the first piece of evidence that the conductive polymer coating has an interaction with the alloy surface to form a passive layer.

At a potential of 0.0 volts the current density is 5.0 microamps/cm² for the coated sample in figure 1. Upon reversal of the potential towards more negative values, the current density was similar to the forward data. This behavior indicates little

propensity for pitting of the underlying aluminum substrate and shows no breakdown pitting up to 0.0 volts versus SCE. The uncoated sample did not show any formation of a passivating protective film, even though the surface of aluminum is covered with a somewhat protective native aluminum oxide layer. The scan was stopped when the potential reached 0.0 volts versus the SCE.

Previous scans of this complex were able to reach up to 1.0 volt which exceeded the oxidation breakdown potential of water and started the formation of oxygen gas. The oxygen penetrated the film and formed a bubble on the surface of the sample, degrading the adhesion of the film and giving erratic behavior of the data upon reversal of the potential scan. When the potential is intentionally set to stop below the oxidation of water, which is approximately 800 mV at the solution pH of 6.0, no bubble is formed and the film remains intact on the surface after the scan test.

Adhesion of the polymer coating to the alloy was very strong and passed the scotch tape test on a wetted sample. Therefore, the film could not be easily removed from the surface after testing. The samples were exposed to solutions of ethyl acetate in an ultrasonic bath to try and remove the polymer film from the surface, this did not prove to be an effective method to remove the film. In fact, to date, there is still not an effective method to remove the polymer film from the surface for analysis of the underlying aluminum surface. The film can only effectively be completely removed from the aluminum surface with a high grit number silicon carbide paper treatment.

After some of the film is removed, the underlying layer is still very shiny and free of any discoloration or evidence of corroding. Figure 3 shows a photograph of the sample, after cyclic polarization testing, after the film is removed. The photo shows no evidence of pitting on the alloy's surface. Figure 4 shows a photograph of the uncoated 7075 sample after cyclic testing. The uncoated sample visibly showed evidence of corrosion with pitting and discoloration.

Cyclic polarization results for a conductive polymer coated AA2024-T3 aluminum alloy sample are shown in Figure 5 compared to an uncoated 2024. The AA2024-T3 alloy is the most difficult aluminum alloy to protect from pitting corrosion, as it has the highest copper content of all the alloys. This difficulty can be seen with a higher current density (1×10^{-1} microamps/cm²) and lower passivation level (350mV vs. SCE) from the double strand coated sample than the AA7075-T6 alloy results. However, the coated sample still shows a one half order of magnitude lower open circuit current density and over the uncoated sample from the Tafel extrapolations.

A thickness effect on the open circuit current density was observed with the polymer coated samples under cyclic polarization testing. This effect can be observed in Figure 6, which shows the open circuit current density versus film thickness. Film thickness is related to the number of coats applied from a pipette. One coating was roughly equivalent to a 1.0 micron thick film. As can be seen from figure 6, the thickness of the film plays a role in lowering the open circuit current density, but only to a certain point. After thicknesses approaching 5 to 10 microns, no further lowering was

observed. However, as mentioned above, the open circuit current density might not be the best parameters to monitor during these test. The more important issue is the effect of film thickness on passivation current density. An effect of the passivation current versus with film thickness is not observed. There are small changes with passivation current for different film thicknesses but these changes are within the same order of magnitude and it cannot be concluded that any real effect is seen. There was however a two order of magnitude passivation current difference between the PAA complex and the PMA complex. This was another reason for the continued study of the PMA complex for this dissertation. An explanation of this behavior will be discussed in chapter five. This behavior will be used to support other theories on the protective mechanism of the conductive polymer coatings.

Long Term Exposure to Salt Solution

Cyclic polarization tests are not a true measure of the long term environmental performance of the polymer coatings. Actual exposure tests were performed to get a true measure of the polymer's performance. The industry standard for these types of test involve first exposing part of the coated sample's metal simply by scribing a scratch on the metal surface. Two inch squares of aluminum alloy AA7075-T6 were coated with the polymer complex and then scratched with a sharp knife edge to expose the underlying metal's surface. The samples were then clamped to closed glass tubes filled with a 0.5N NaCl solution for 3.5 months exposure.

Photographic data shows that the polymer protects the aluminum alloy surface with reduced pitting of the surface as seen in comparing figures 7 and 8. Figures 7 and 8 compare the surface conditions after three and a half months exposure to a 0.5N NaCl solution of uncoated and conductive polymer coated AA7075-T6 samples, respectively. The marked ringed area is where the o-ring and tube were clamped to the samples surface, so the area inside this ring is the exposed region. Importantly, even the area scratched prior to immersion does not show any evidence of pitting, versus the uncoated sample which has a large number of pits and large size pits.

Scanning electron microscope (SEM) photos were taken of the coated scratched area and the uncoated surface. Figure 9 is a 620 times magnification of the conductive polymer coated scratched area . The scratched surface is seen in the under two-thirds of the photo with the bottom third showing the polymer film. The white flakes are pieces of the polymer film. The scratch area is still seen to be smooth and free of any pitting and there is no evidence of undercutting or peeling of the polymer film from the alloy's surface. The uncoated SEM photo in figure 10 shows formation of pits on the surface along the scribe.

Performance Versus Chromate Conversion Coatings

Cyclic Polarization

Figure 11 shows cyclic polarization scans in 0.5N NaCl solutions of a conductive polymer coated sample versus a chromate conversion coated sample of AA7075-T6 aluminum alloys. The Tafel extrapolation of the cathodic and anodic lines from the scans show a two order of magnitude lower open circuit current density at 5.0×10^{-2} microamps/cm² for the conductive polymer coated sample over the chromate conversion coated sample at 5.0 microamps/cm². Additionally, the conductive polymer coated sample shows a significant decrease in the open circuit current density upon a further increase in the driving voltage on the forward scan. This data indicates passivation of the aluminum surface has occurred from the polymer coating. Furthermore, upon reversal of the potential, the reverse scan follows the path of the forward scan indicating a lack of film breakdown nor any propensity for pitting of the surface. Additionally, and more importantly, the chromates do not show passivation in the salt water environment as the conductive polymer. Although these results are promising, cyclic polarization is not the best testing technique for comparison with chromate conversion coatings., It is well known that the chromate are the best protection available for aluminum alloys, yet the results form cyclic polarization would indicate otherwise. A more reasonable testing technique is presented next.

Electrochemical Impedance Spectroscopy

Figure 12 shows the impedance and phase angle data, respectively, from the EIS tests on the AA7075-T6 alloy coated samples of the conductive polymer and the chromate conversion coatings. These samples were exposed to a 0.5N NaCl solution for two weeks prior to this test. The low frequency impedance values, at 0.1 Hz and lower, show an almost one order of magnitude higher impedance for the conductive polymer sample over the chromate conversion sample. The shape of the phase angle data in Figure 12 shows that it can be fitted with a three RC circuit. It is believed that the third circuit represents a third passive interface layer formed between the conductive polymer coating and the alloy surface. The modeling results and implications are discussed further in chapter five. Studies have shown the conductive polymer coating is not a barrier coating but can slightly swell and allow the permeation of water and ions in the test solution.^{15, 16} Previous results indicate that the polymer coating has the ability to oxidize the aluminum surface and form a passive layer on the alloy's surface.¹⁷⁻¹⁹ It is believed this passive layer is seen in the phase angle data showing a higher capacitive behavior at approximately 0.1 Hz.

The open circuit current density can also be determined from the charge transfer resistance value of the Bode plot of figure 12. Because the potential excitation perturbation of the system is small, at only 5mV, we can assume the anodic and cathodic reactions

behave close to linear. With this assumption it is easy to calculate the open circuit current density from equation 1 as;

$$R_t = (R)(T)/(n)(F)(i) \quad 1$$

where R_t is the charge transfer resistance, either determined from the Bode plots as the log impedance at low frequency or modeled with an equivalent circuit model. R is the gas law constant, T is the operating temperature, n is the moles of electrons in the reaction, F is Faraday's constant and i is the current density. For our test results from figure 12 and using n equal to 3, the open circuit current density is calculated to be 8.5×10^{-2} microamps/cm². This is compared to the Tafel extrapolation determination from the cyclic polarization curves of figure 1, which was 5×10^{-2} microamps/cm². There is a close match from the two electrochemical testing techniques.

Figures 13 are EIS results for the coated AA2024-T3 alloy samples. In these samples the conductive polymer and chromate conversion samples have near equivalent low frequency impedance values. However, the phase angle data of Figure 13 shows a remarkable different result for the conductive polymer sample over the chromate sample. In this data, the capacitance behavior at 0.1 Hz is very pronounced for the conductive polymer. As well, there is an increase in phase angle at the very high frequency end. It is believed that this high frequency capacitance behavior is due to the conductive nature of the polymer itself and the 0.1 Hz capacitance

behavior is due to the passive layer formed between the polymer and the alloy's surface.

Salt Spray Exposure

Long term exposure to a salt fog environment under the ASTM B-117 conditions. Figures 14 shows an AA7075-T6 sample coated with the double strand conductive polymer after 200 hours exposure in the salt fog chamber. Figure 15 shows a chromate conversion coated AA7075-T6 sample after exposure for the same amount of time in the salt fog chamber. The polymer sample in Figure 14 shows less undercutting at the scribed area and a decreased amount of white corrosion product formed at the scratch than the chromate sample in Figure 15. Figure 16 shows a photograph of an uncoated 7075 sample after 200 hours in the salt spray chamber as a control sample. The uncoated sample shows severe corrosion along the scribed area.

Long Term Results

As the tests continued into longer terms, a change in the performance of the polymer coatings was observed. The interesting data observed during the tests was the change in color of the polymer film while immersed in the test salt solution. Approximately two hours after immersion of the sample the polymer film at the edges of the scratch or at the edges of the clamped o-rings began turning from its natural oxidation state color

of green to blue, a higher oxidation state. Over the course of several weeks the entire film would turn completely blue. When the film was removed from samples, the exposed metal areas were recessed from the remaining sample surface and of a darker oxidized color, indicating that some oxidation and corrosion had started at these areas. The samples exposed to the test salt solutions for long periods of time under EIS testing eventually did not show any protection after 2 months. Figure 17 shows the EIS results of a PMA coated sample in EIS testing for 2 months compared to the Alodine 600 and an uncoated sample. The figure shows the PMA coated sample has reached a charge transfer level equivalent to the uncoated sample, yet the chromate has remained one order of magnitude higher. It is believed this decrease in long term performance is attributed to the change in color and conductivity of the film, from the green colored conductive state to the blue colored non-conductive state. It is proposed that the conductive state forms a passive protective layer on the aluminum surface when applied to the surface. This passive layer can self repair under attack from chloride ions. However, when the film turns blue, it no longer can repair the thinned passive layer and eventually the passive layer dissolves leaving the alloy surface unprotected.

The double strand polyaniline has four oxidation states that are controlled by pH environment and redox condition. The esterified double strand is only conductive up to a pH 6.0. This was confirmed twice with tests of glass samples coated with the esterified double strand of polyacrylic and polyaniline immersed in

various solutions of differing pH. Below a pH of 6.0, the polymer complex remained green on the glass slides. The polymer system was experiencing deprotonation of the proton on nitrogen of the polyaniline backbone which renders the polymer non-conductive and changes the color from green to blue. The typical test solutions used for corrosion or pitting studies for the aluminum alloys is a 0.5N NaCl solution which typically has a pH greater than 6.0.

The polymer was made soluble in ethyl acetate by performing an esterification of the acrylic acid in methanol with an acid catalyst of benzo-sulfonic acid. This adds to the carboxylic sites on the polyacrylic acid strand a methyl group and changes the polarity of the molecule to more non-polar in nature. One possible problem with this is that now the bonding of the second strand of the polyaniline could change and be a less attractive bond since the anodic sites of the acrylic acid do not have a negative charge density to attract to the polaron of polyaniline.

DISCUSSION

These early test results indicate the conductive polymer coating does protect aluminum alloys from corrosion. This is confirmed from three different independent corrosion tests, cyclic polarization, EIS and salt spray exposure. The salt spray results indicate that the conductive polymer coating offers less undercutting of a scratched area on the surface. This performance is better than the Alodine 600 chromate conversion coating. These polymer

coatings are permeable to salt, water and oxygen, yet still provide sufficient protection from corrosion to the aluminum surface. Additionally, the coherency of the coating after exposure shows that the polymer is strongly adherent to the aluminum surface. This data suggests there is a passive protection mechanism on aluminum alloys involved with the conducting polymer complex film.

All experimental observations are consistent with a reactive interaction between the conductive polymer and the aluminum alloy. The electrochemical potential of the conductive polymer solution (0.3V vs. SCE) is sufficiently anodic to oxidize aluminum. The rate of the interfacial reduction-oxidation or the charge transfer reaction could be relatively high comparing with other solid coatings because the material is electrically conductive. The possible consequences of such an oxidative interaction is dissolution of aluminum to aluminum ions and the build up of an oxide or oxide like interfacial layer between the polymer and the metal surface. If this chemically converted interfacial layer is stable against corrosive anions, such as chlorides, it may limit the corrosion current. Additionally, the functional groups on the second strand of the double strand polymer structure can chelate with aluminum ions or aluminum metal on the surface of the alloy. The passive layer could possible be a chelated oxide type structure.

There is certainly a similarity between the function of a chromate conversion agent and the soluble polyaniline. Both are oxidizing agents or oxidation catalysts that chemically convert the

aluminum surface into a protective layer that is somewhat resistant to aggressive anion attack. Both have multiple and reversible oxidation states to facilitate the regeneration of oxidation power in an oxidative environment. The experimental data suggest that the soluble polyaniline is, like the chromates, a chemical conversion agent for aluminum alloys.

CONCLUSION

The double strand polyaniline was shown to exhibit corrosion protection for aluminum alloys AA2024-T3 and AA7075-T6 in salt-spray and in salt immersion tests. Electrochemical monitoring of the polyaniline treated surface shows resistance to corrosion is equivalent to an Alodine 600 chromate conversion coating in salt environment for periods of time under 2 months if the polymer film is kept in the conductive green colored state. These results show that the conductive property of the polymer film plays a role in the corrosion protection mechanism. Therefore, the stability of the polymer's conductive state, especially in water, is an important aspect for corrosion control. The mechanisms for protection appears to be a polyaniline induced surface chemical conversion to form a passive layer at the interface of polymer and aluminum alloy. The advantage of the double stand polyaniline is in its ability to be formulated as a good surface wetting paint and the offer good adhesion to a metal surface.

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TABLE 1: Minor Alloying Elements for Al Alloys (wt. %)

<u>Element</u>	<u>AA2024-T3</u>	<u>AA6061-T6</u>	<u>AA7075-T6</u>
Cu	3.8 - 4.9	0.15 - 0.40	1.2 - 2.0
Si	<0.50	0.4 - 0.8	<0.40
Fe	<0.50	<0.70	<0.50
Mn	0.3 - 0.9	<.15	<0.30
Mg	1.2 - 1.8	0.8 - 1.2	2.1 - 2.9
Zn	<0.25	<0.25	5.1 - 6.1
Cr	<0.10	0.04 - 0.35	0.18 - 0.28
Ti	<0.15	<0.15	<0.20

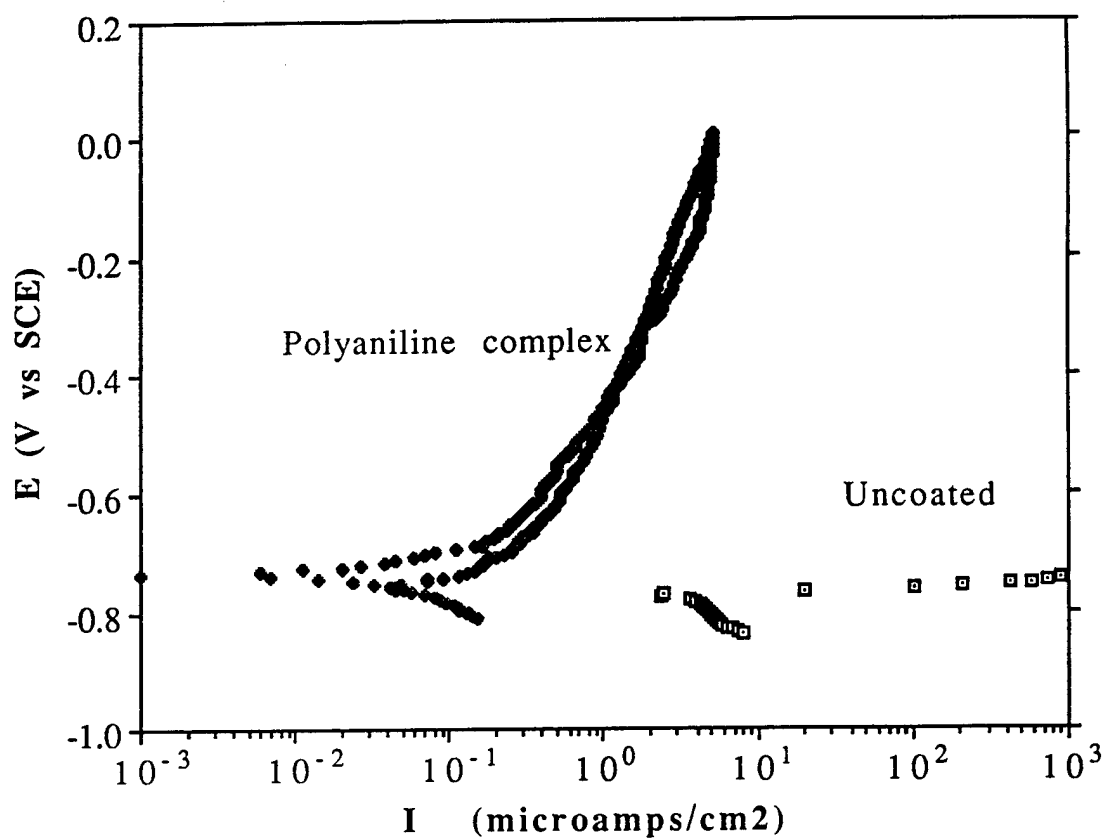


Figure 1. Potentiodynamic scan of 7075-T6 aluminum alloy samples coated with the double strand conductive polymer (PMA) versus an uncoated 7075 sample. Tests were performed in 0.5 N NaCl solutions.

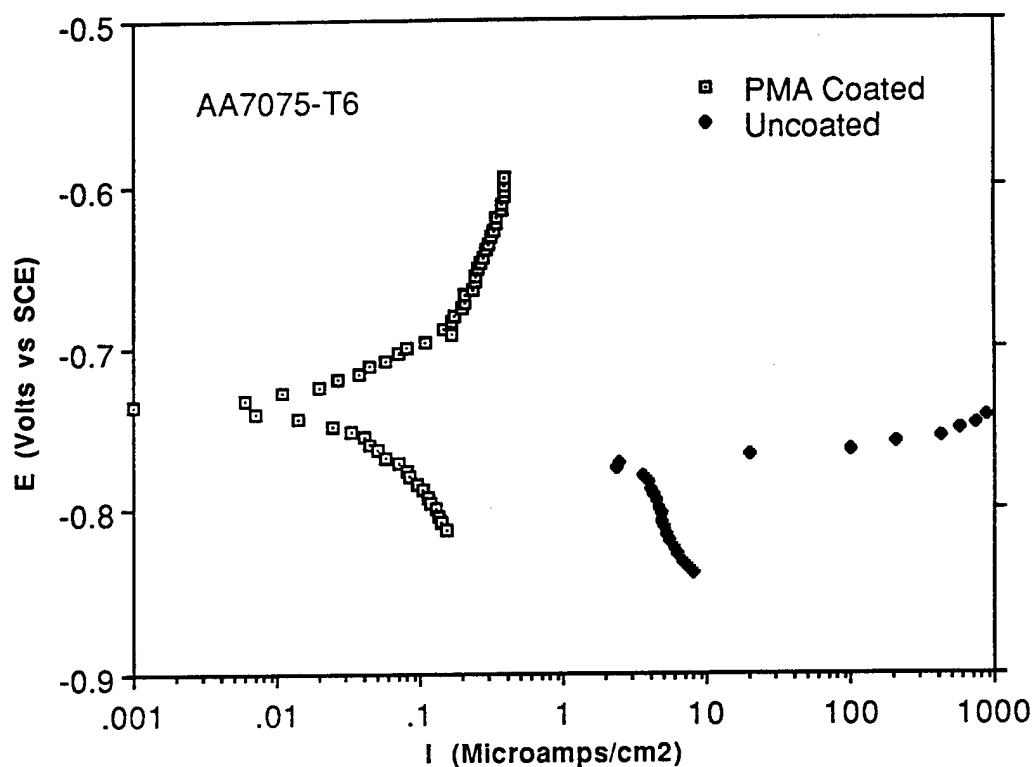


Figure 2. More detailed graph of figure 1 showing the cathodic and anodic curves for the PMA coated 705 and the uncoated 7075 samples. A line is drawn thorough the linear portions of the curves and extrapolated to were the cathodic and anodic lines cross. the point of crossing is the corrosion current density of the sample.

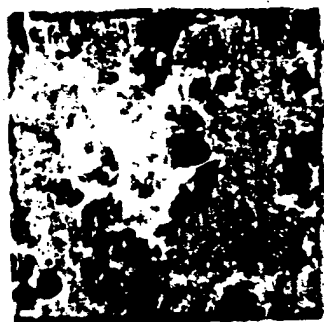


Figure 3. Photograph of a PMA coated 7075 sample after cyclic polarization with the film removed from the test site.



Figure 4. Photograph of an uncoated 7075 sample after cyclic polarization.

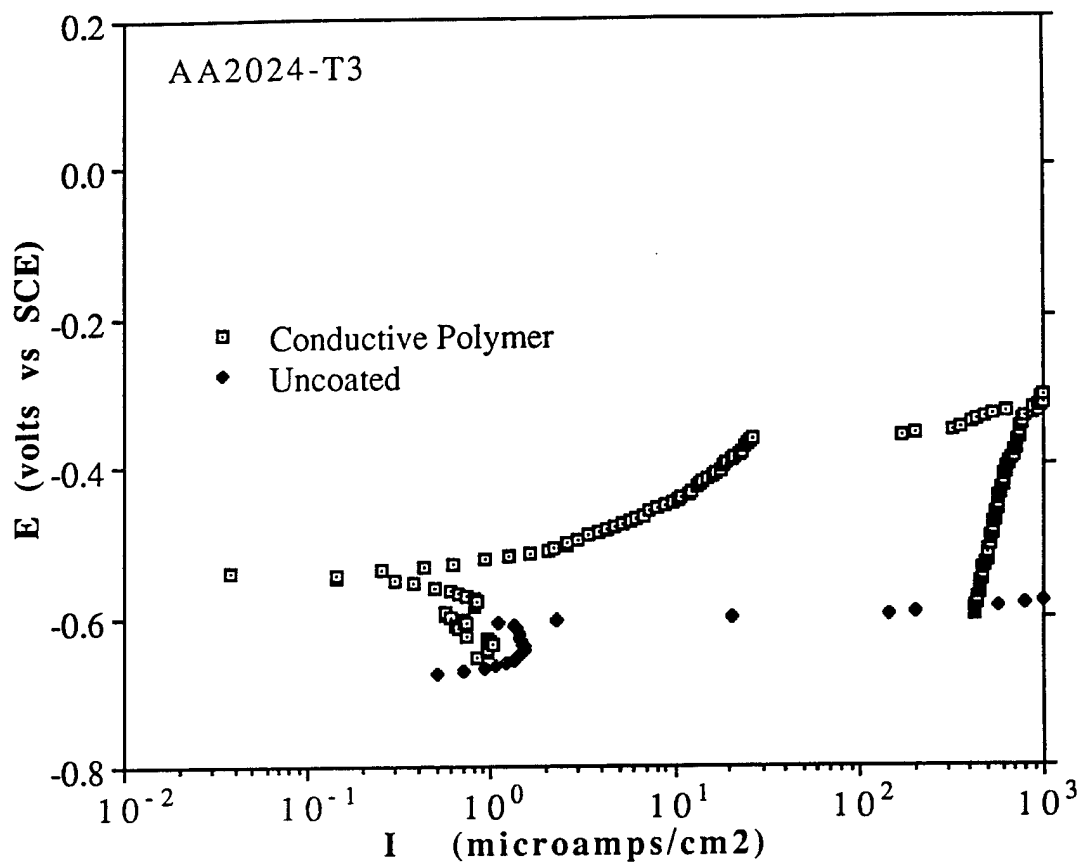


Figure 5. Cyclic polarization of PMA coated AA2024-T3 versus an uncoated sample in 0.5N NaCl.

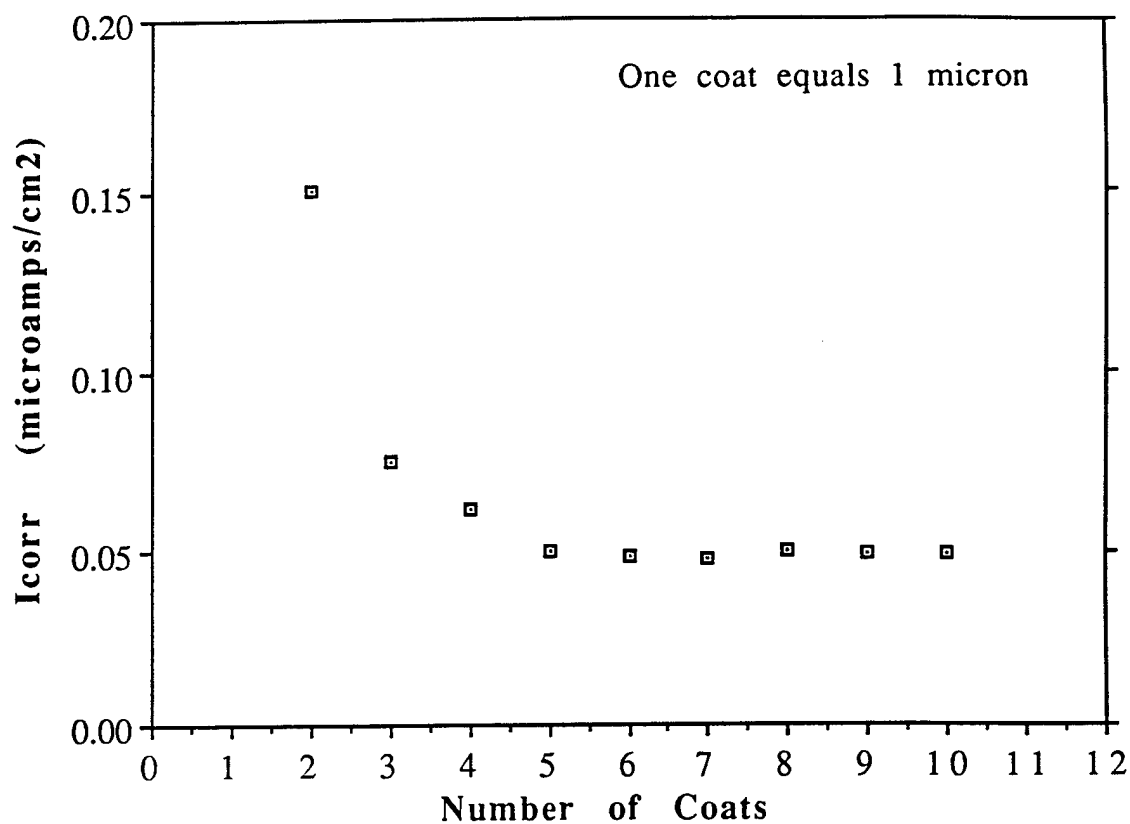


Figure 6. Number of conductive polymer coatings applied to a 7075 alloy prior to cyclic polarization testing showing the resulting corrosion current density from the Tafel extrapolations of the anodic and cathodic curves.



Figure 7. Photograph of a conductive polymer coated AA7075-T6 sample after exposure to a 0.5 N NaCl solution for 3.5 months with the film removed to reveal the aluminum surface. The photos are magnified to 1.75" on the photo being equal to 1" of the actual sample.

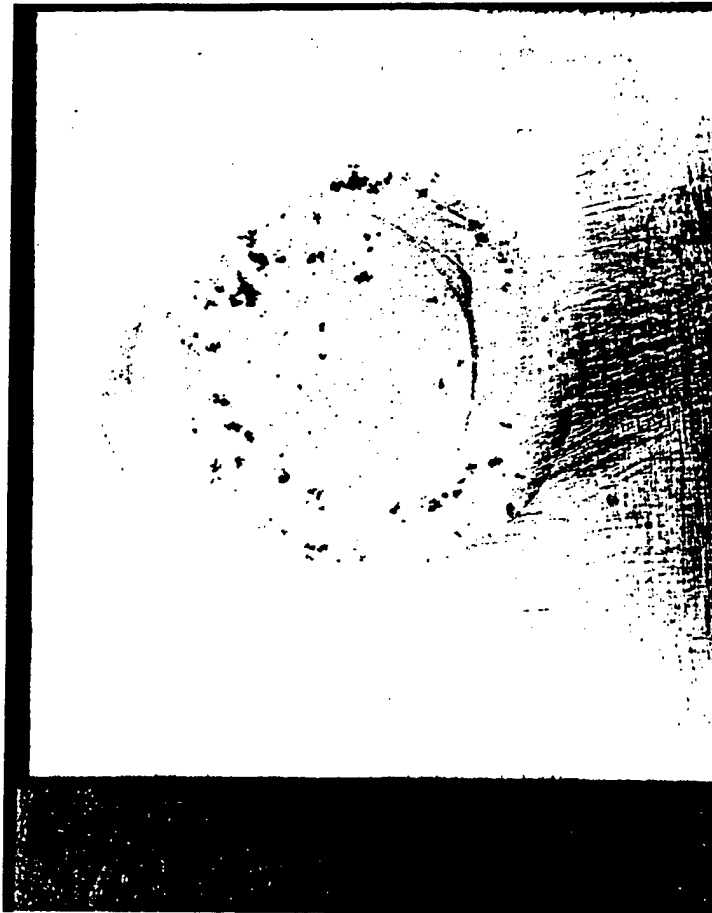


Figure 8. Photograph of pit density on an uncoated 7075 sample.

Figure 8 shows an uncoated AA7075-T6 sample exposed to 0.5N NaCl for 3.5 months. The photos are magnified to 1.75" on the photo being equal to 1" of the actual sample.

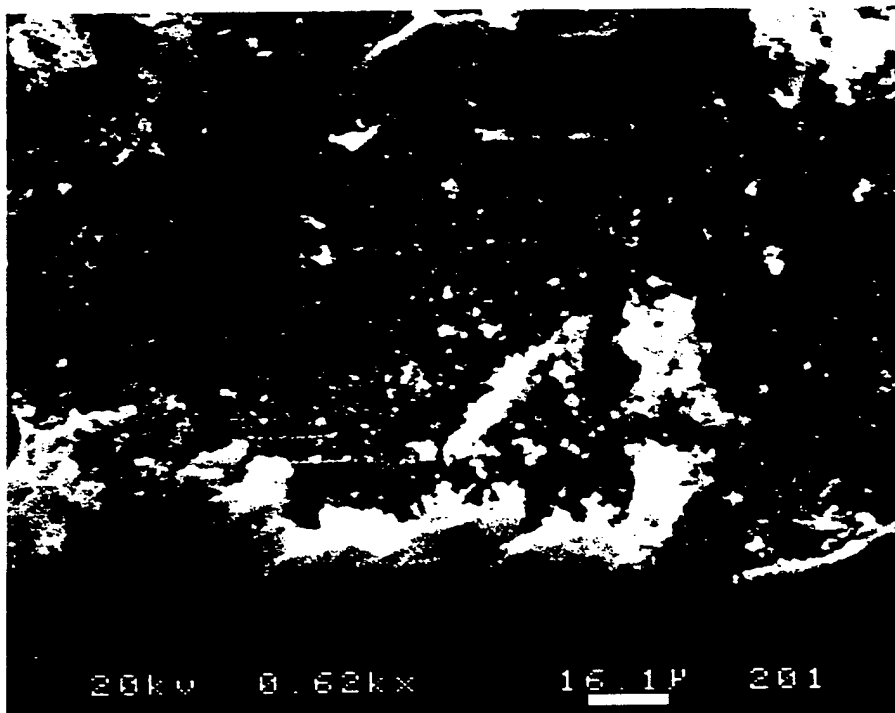


Figure 9. Figure 9 is a 620 times magnification of a PMA coated 7075 sample at the scratched area. The scratched surface is seen in the under two-thirds of the photo with the bottom third showing the polymer film. The white flakes are pieces of the polymer film. The scratch area is still seen to be smooth and free of any pitting.

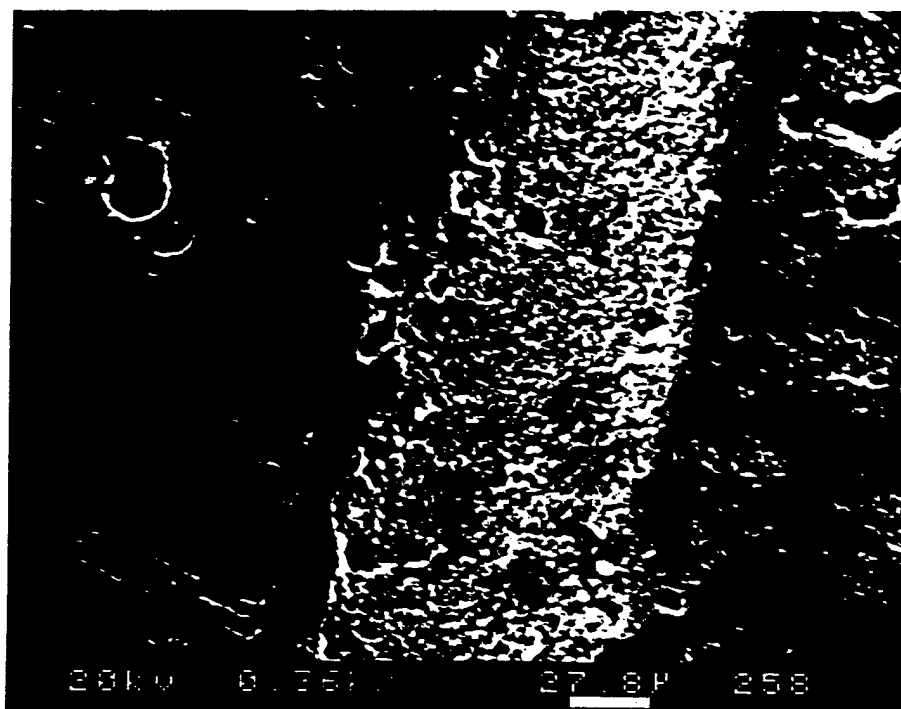


Figure 10. Figure 10 is a 360 times magnification of an uncoated 7075 sample at the scratched area after exposure to a 0.5N NaCl for several weeks. The holes along the edge of the scratch are pits in the aluminum alloy surface.

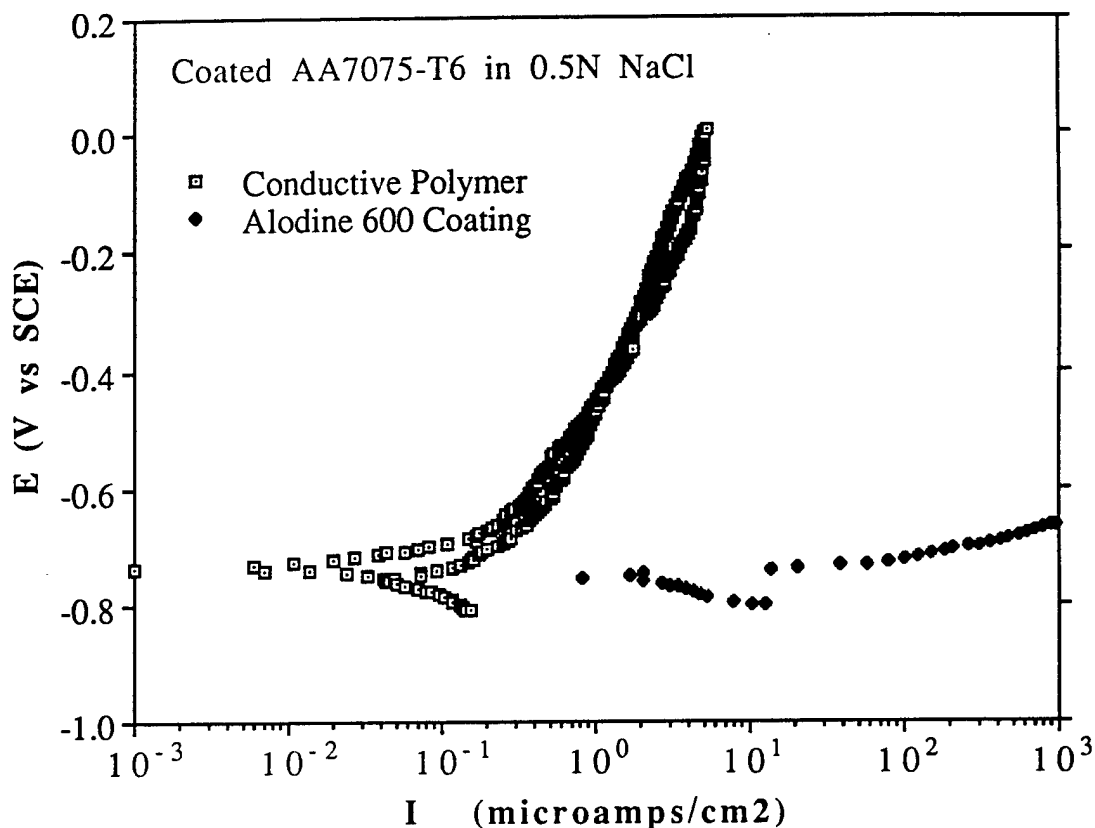


Figure 11. Potentiodynamic scans of a conductive polymer coated 7075 sample and an Alodine 600 chromate conversion coated 7075 sample in 0.5N NaCl. The data shows a lower corrosion rate from a Tafel extrapolation of the anodic and cathodic curves for the conductive polymer sample versus the Alodine 600 chromate sample. The conductive polymer sample also offers a passivation up to 0 volts (vs. SCE), the Alodine 600 shows minimal passivation.

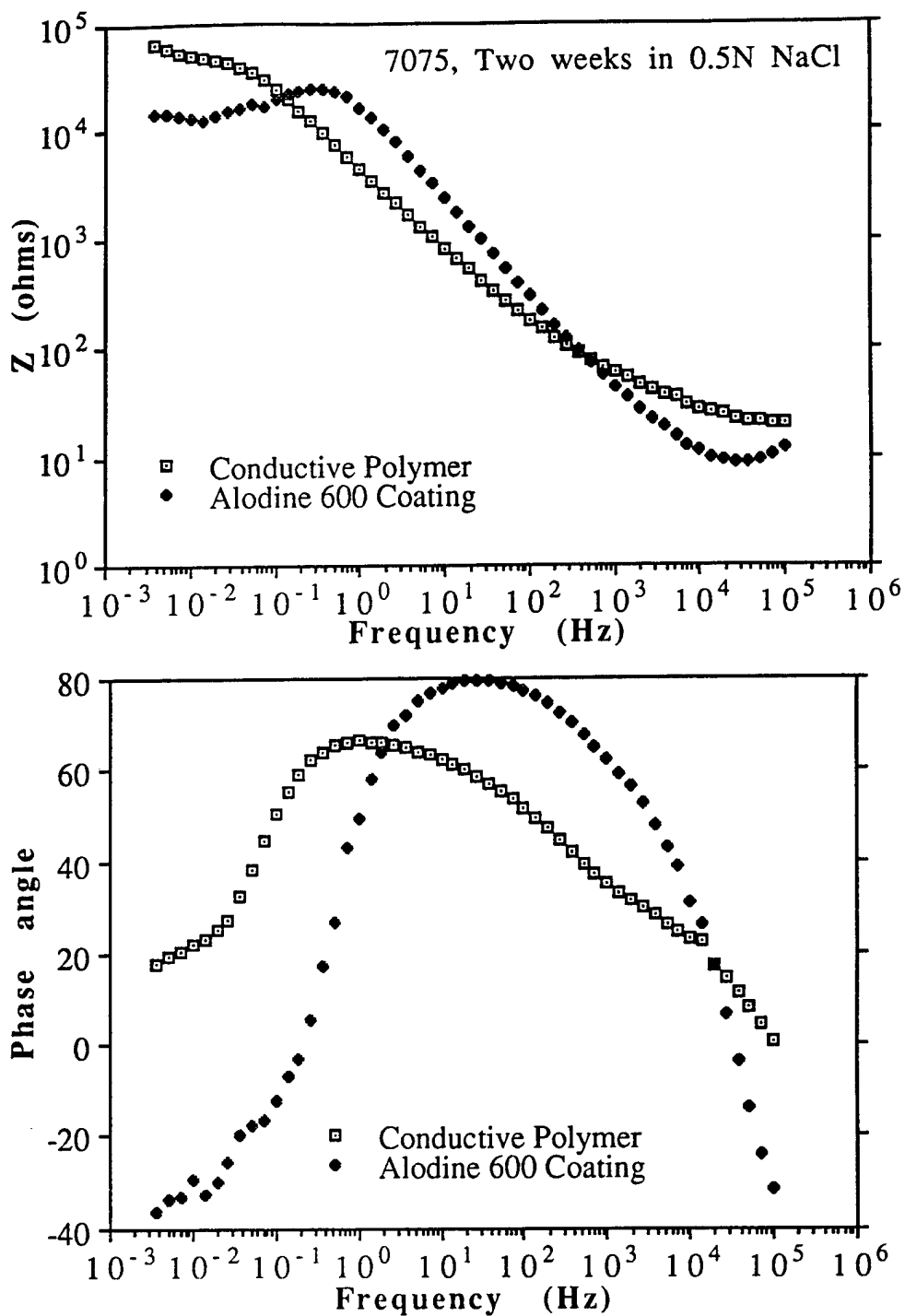


Figure 12. Impedance spectroscopy results (log impedance and phase angle versus frequency) of a conductive polymer coated 7075 sample and an Alodine 600 chromate conversion coated 7075 sample after two weeks in 0.5N NaCl.

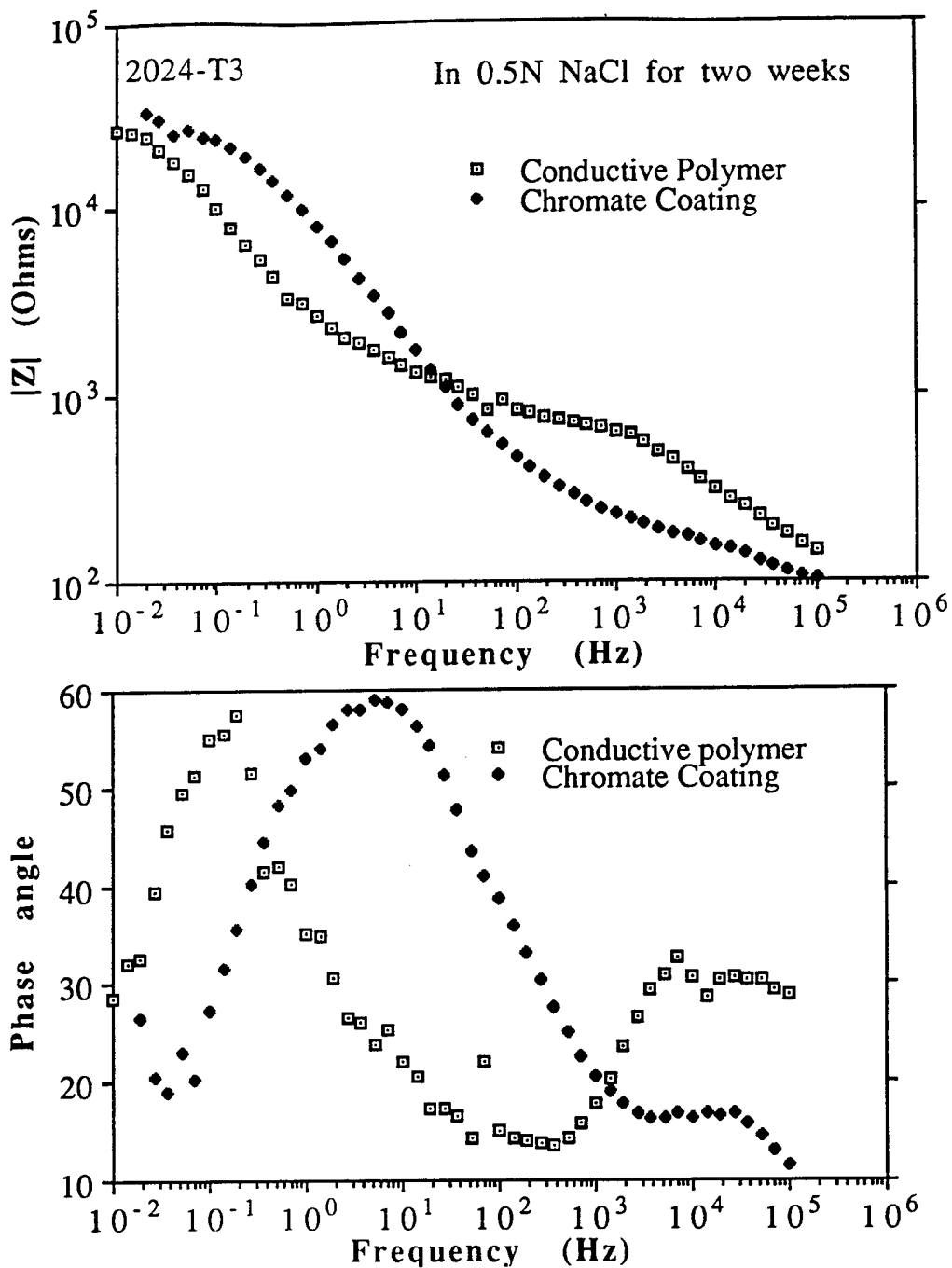


Figure 13. Impedance spectroscopy results (log impedance and phase angle versus frequency) of a conductive polymer coated 2024 sample and an Alodine 600 chromate conversion coated 2024 sample after two weeks in 0.5N NaCl.

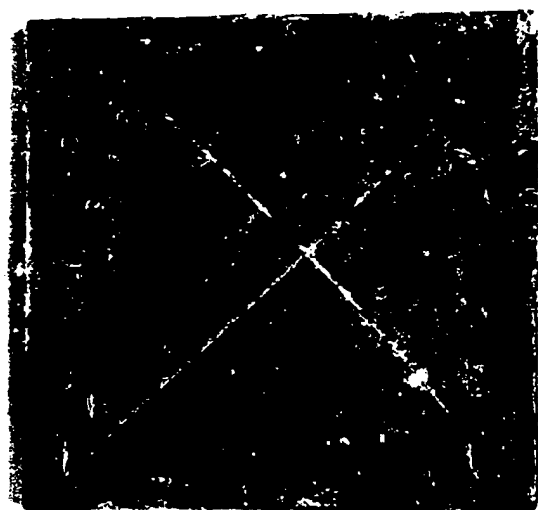


Figure 14. Photograph of scribed PMA coated 7075 alloy after 200 hours in the salt spray chamber.



Figure 15. Photograph of scribed Alodine 600 coated 7075 alloy after 200 hours in the salt spray chamber.



Figure 16. Photograph of uncoated 7075 alloy after 200 hours in the salt spray chamber.

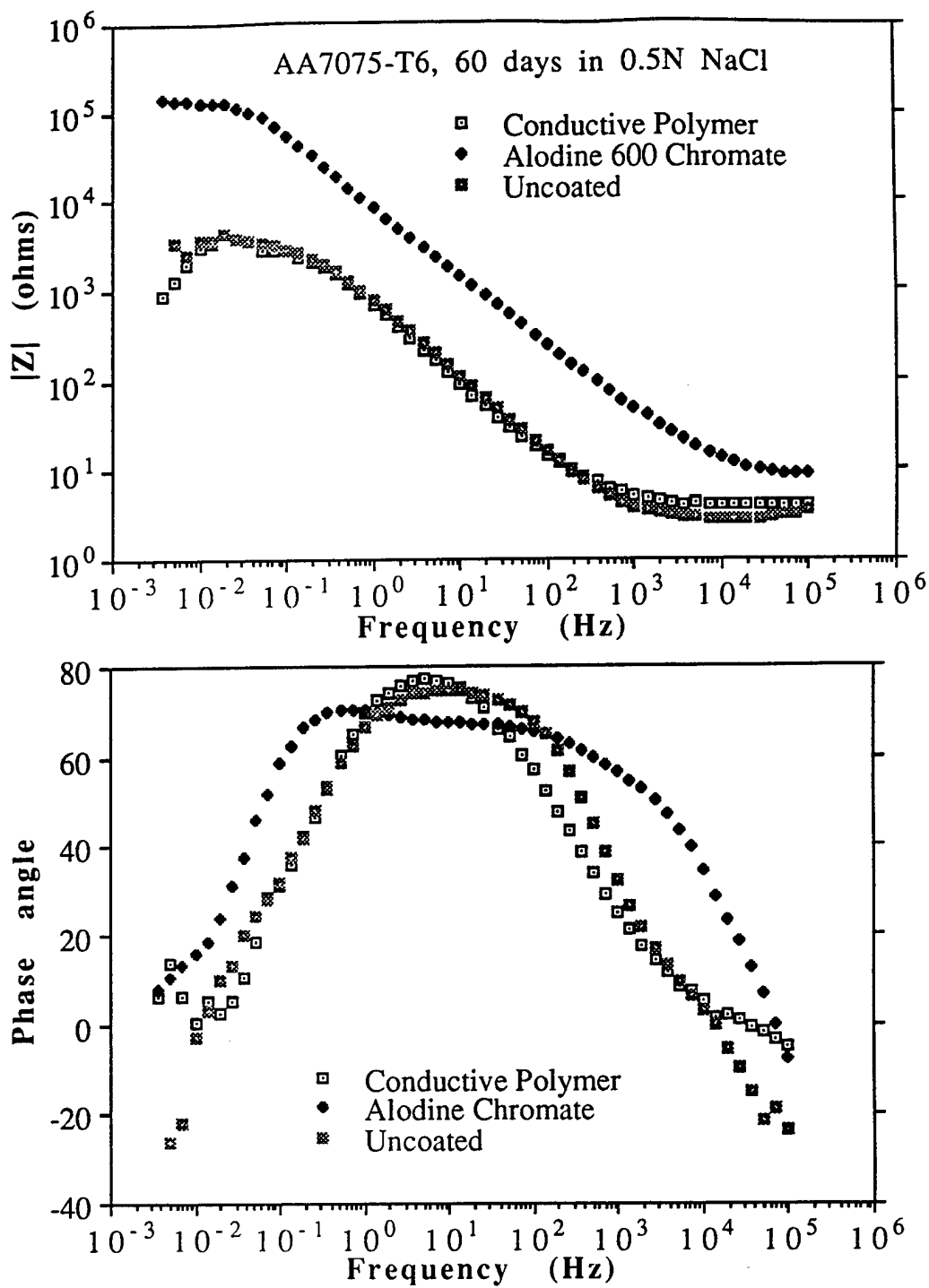


Figure 17. 60 Day EIS results of conductive polymer, Alodine 600 and uncoated 7075 samples in 0.5N NaCl.

CHAPTER III

COMPARISON OF CONDUCTIVE WITH NON-CONDUCTIVE STATES OF DOUBLE STRAND POLYANILINE FOR CORROSION PROTECTION OF ALUMINUM ALLOYS

ABSTRACT

Electrochemical testing was conducted on two oxidation states of the double strand polyaniline coating on AA7075-T6 aluminum alloys. Results show the green colored emeraldine salt conductive state is required to offer improved protection for aluminum alloys over an uncoated sample. Samples coated with the non-conductive blue colored emeraldine base form of the double strand polyaniline did not show any improved corrosion protection over an uncoated sample. Implications for these result are discussed.

INTRODUCTION

The long term EIS results presented in chapter 2 suggest that the conductive polymer coating must remain in the conductive, green colored, emeraldine salt state to protect the aluminum alloys. The experiments conducted in this chapter were performed to finally prove and quantify these results. Observations throughout experiments show a color change of the coated polymer from green to a non-conductive state of blue after immersion in aqueous solutions above a pH of 6.0. This was confirmed with tests of glass samples coated with the esterified double strand of polyacrylic and polyaniline immersed in various solutions of differing pH. Below a pH of 6.0, the polymer complex remains green colored on the glass slides. The polymer system is experiencing deprotonation of the proton on the polyaniline backbone which renders the polymer non-conductive and changes the color from green to blue. The typical test solutions used for corrosion studies of aluminum alloys is a 0.5N NaCl solution, which typically has a pH greater than 6.0. Therefore, over time the polymer coating changes from the conductive green state to the non-conductive blue state during the tests. This change in oxidation states of the polymer film can also be observed in the EIS Bode plots. Figure 1 shows the Bode plots of a PMA coated 7075 alloy at progressively longer exposure times. The change in shape of the phase angle data corresponds exactly with the color change of the polymer film. The film after two weeks was completely blue, yet it still offered some protection over an uncoated alloy sample with a one order of magnitude higher charge transfer resistance.

The complete explanation of this behavior is better saved for chapter 5, however, it suffices to say at this point, that it is believed the polymer film has formed a passive protective layer when applied to the surface in the green conductive form and, even though this film has turned to the blue non-conductive form, the passive layer is still present on the surface. This passive layer will eventually become dissolved through, it is suspected, chloride ion attack, and can not be reformed since the polymer is now in a non-interactive state to further repair the thinned passive layer. After two months exposure, the passive layer is completely removed, as evidenced by figure 17 from chapter 2. Therefore, the reason for concern of this change in conductive state of the coating is because the results of potentiodynamic scans and electrochemical impedance spectroscopy show that the non-conductive state does not show sufficient protection in the lowering of the corrosion current density.

The objectives of the experiments performed for this chapter were to quantify the performance of the conductive polymer through a rather simple contrast study of the conductive green state and the non-conductive blue state films coated on 7075 alloys. Examinations under cyclic polarization and EIS to record a difference in corrosion protection performance of the two oxidation states and confirm the previous observations were performed.

EXPERIMENT

The conductive polymer PMA coatings were compared against PMA coated samples whose double strand polymer coating was rendered non-conductive by either dipping a coated aluminum alloy sample in a mild basic solution (non-conductive state 1) or solution cast in the non-conductive state (non-conductive state 2) by mixing the polymer solution in a mild ammonium hydroxide solution and then applying the solution to the alloy's surface. Cyclic polarization and EIS test were performed for corrosion current density comparisons.

RESULTS and DISCUSSION

Figure 2 shows cyclic polarization results for the conductive coating versus the two non-conductive coatings and an uncoated AA7075-T6 alloy. Tafel extrapolations were performed on the cathodic and anodic curves for each sample in figure 2 to determine the corrosion current densities. The results of the Tafel extrapolations are shown in Table 1. The potentiodynamic results illustrate a significant reduction in the corrosion current density over the uncoated (two orders of magnitude) and non-conductive coatings (one order of magnitude) for the conductive state. What is more significant are the shapes of the potentiodynamic scans. The uncoated and non-conductive scans show no ability to form a protective passivating layer. The slightest perturbation above the open circuit potential results in a drastic increase in the corrosion

current. What is also interesting from the data in table 1 is that the non-conductive state 1 was applied to the alloy surface in the conductive state and then changed to the blue colored state within under a minute, yet this film offers more protection than the film that was applied directly to the surface in the non-conductive state. The implication is that sufficient time might have been available to start the formation of passive layer when the conductive state was applied. Over time this non-conductive state 1 sample eventually degraded down to a level equivalent to an uncoated sample. The data indicates that the conductive form of the polymer starts a passive layer formation and can repair this passive layer from chloride ion attack if maintained in it's conductive state. However, when the film becomes non-conductive, it cannot further repair the passive layer and becomes thinned form the chloride ion attack and can no longer offer protection to the surface

Results from EIS tests are shown in Figure 3 for the conductive coating versus the uncoated and non-conductive state 1 coating after two weeks exposure to the 0.5N NaCl test solution. Figure 3 is a Bode plot and graphs the log of the experimentally measured impedance versus the log of the AC signal's frequency and the phase angle of the measured signal versus the log of the frequency. The high frequency impedance value in figure 3 measures the electrolyte solution resistance. The low frequency impedance value is the solution resistance plus the charge transfer resistance at the working electrode's surface. The charge transfer resistance is inversely related to the corrosion current of the working electrode, in our experiments the working electrode is the

aluminum alloy sample. Therefore, the higher the impedance value the lower the corrosion current density of the sample. A two orders of magnitude higher charge transfer resistance for the conductive coating over the uncoated sample and over a one order of magnitude higher charge transfer resistance over the non-conductive polymer film after two weeks was found. The non-conductive state 1 coating was initially at a higher impedance value but quickly decreased to a value equivalent to an uncoated sample. This behavior is shown in figure 4. The charge transfer resistance for the initial test at zero hour of non-conductive state 1 approaches a $\log 10^5$ impedance value, yet it quickly drops to $\log 10^4$ within one week and below this value after two weeks. This type of behavior again supports the idea that the film had originally formed a passive layer on the alloy's surface yet could not maintain that passive layer under ion and water attack. The conductive state is still offering protection after two weeks even though this film is also turning blue during the test, the change is much slower and allows the formed passive layer to still protect longer than the blue colored non-conductive state 1 film. The non-conductive state 2 film was not displayed in figure 3 because the data was even worse and exhibited a large amount of scatter, again indicating that the film applied in the non-conductive state will not be able to form any passive layer for protection of the alloy's surface. This extreme scatter at low frequencies can be seen in figure 5 which displays a comparison between the non-conductive states 1 and 2. Figure 5 shows non-conductive state 2 having very low log impedance values and the phase angle data shows a large amount of scatter. Other researchers

have attributed a large amount of scatter in the phase angle data with crevice corrosion phenomena in aluminum alloys. Again, this comparison shows the polymer film that was applied first in the conductive state then converted to the non-conductive state (state 1) offers an order of magnitude higher charge transfer resistance than the film applied directly in the non-conductive state (state 2). PMA, which is the esterified double strand conductive polymer coating, will eventually turn to a blue colored non-conductive state over several weeks to two months time when exposed to an environment with a pH higher than 6.0.

The next question to address is what happens if the film stays in a conductive state. This can be accomplished by buffering the test solution to a pH below the stability point of the coating. The next chapter presents results from this type of testing.

CONCLUSION

The results of this study show that the double strand conductive polymer film must remain in the conductive state to offer any corrosion protection to aluminum alloys. The double strand conductive polymer coating used in these studies will remain conductive when exposed to solutions below a pH of 6.0. To further confirm these results, the next chapter is a study with EIS testing of the conductive polymer coating versus chromate conversion coatings in a pH 3.6 buffered 0.5N NaCl solution.

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#. Crevice Corrosion references

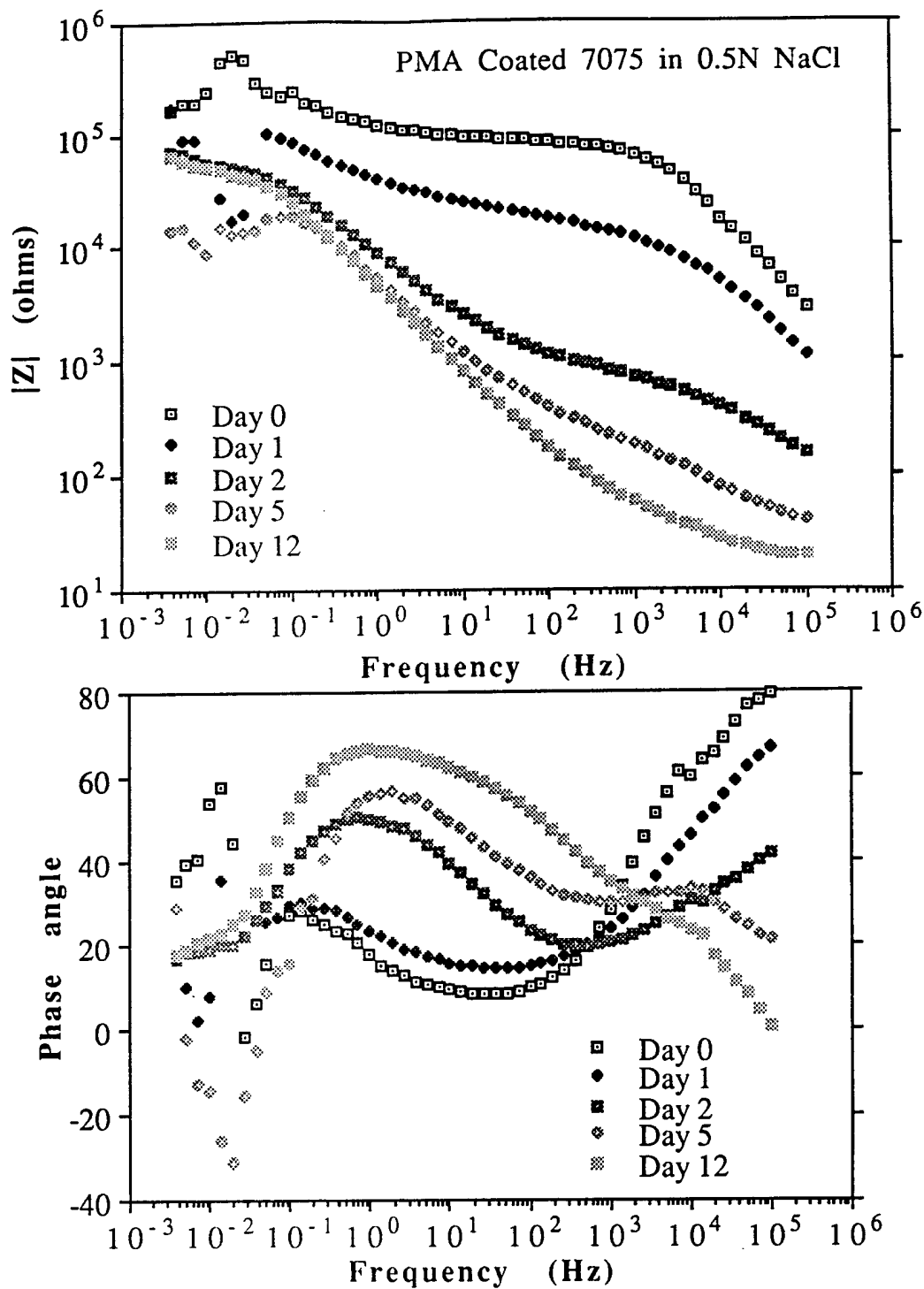


Figure 1. Bode plots of PMA coated 7075 from day one to day twelve showing the change in impedance and the change in shape of the phase angle data over time.

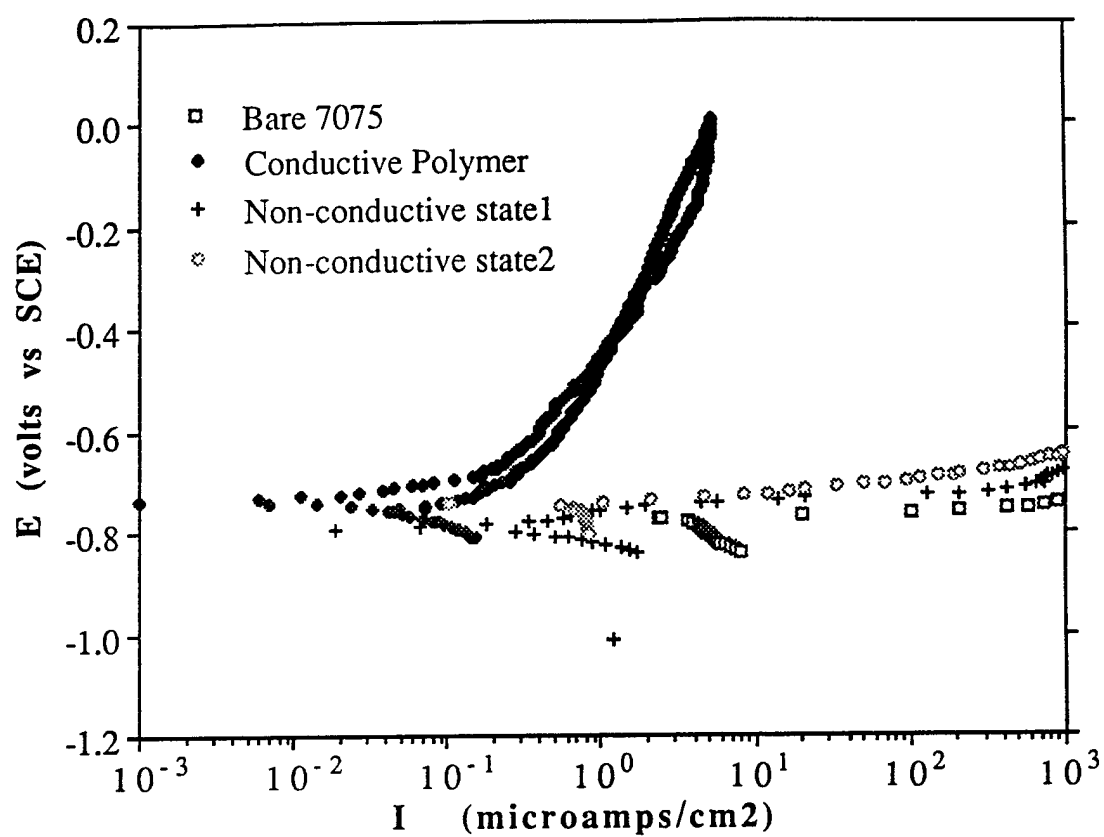


Figure 2. Cyclic polarization results of the conductive and non-conductive states of the double strand polyaniline complex in 0.5N NaCl.

Table 1. Cyclic Polarization I_{corr} Values from Figure 2
Different States of PMA Coated on AA7075-T6

Sample -----	I _{corr} (microamps/cm ²) -----
Conductive State	5 x 10 ⁻²
Non-conductive State 1	4 x 10 ⁻¹
Non-conductive State 2	7 x 10 ⁻¹
Uncoated AA7075-T6	5 x 10 ⁰

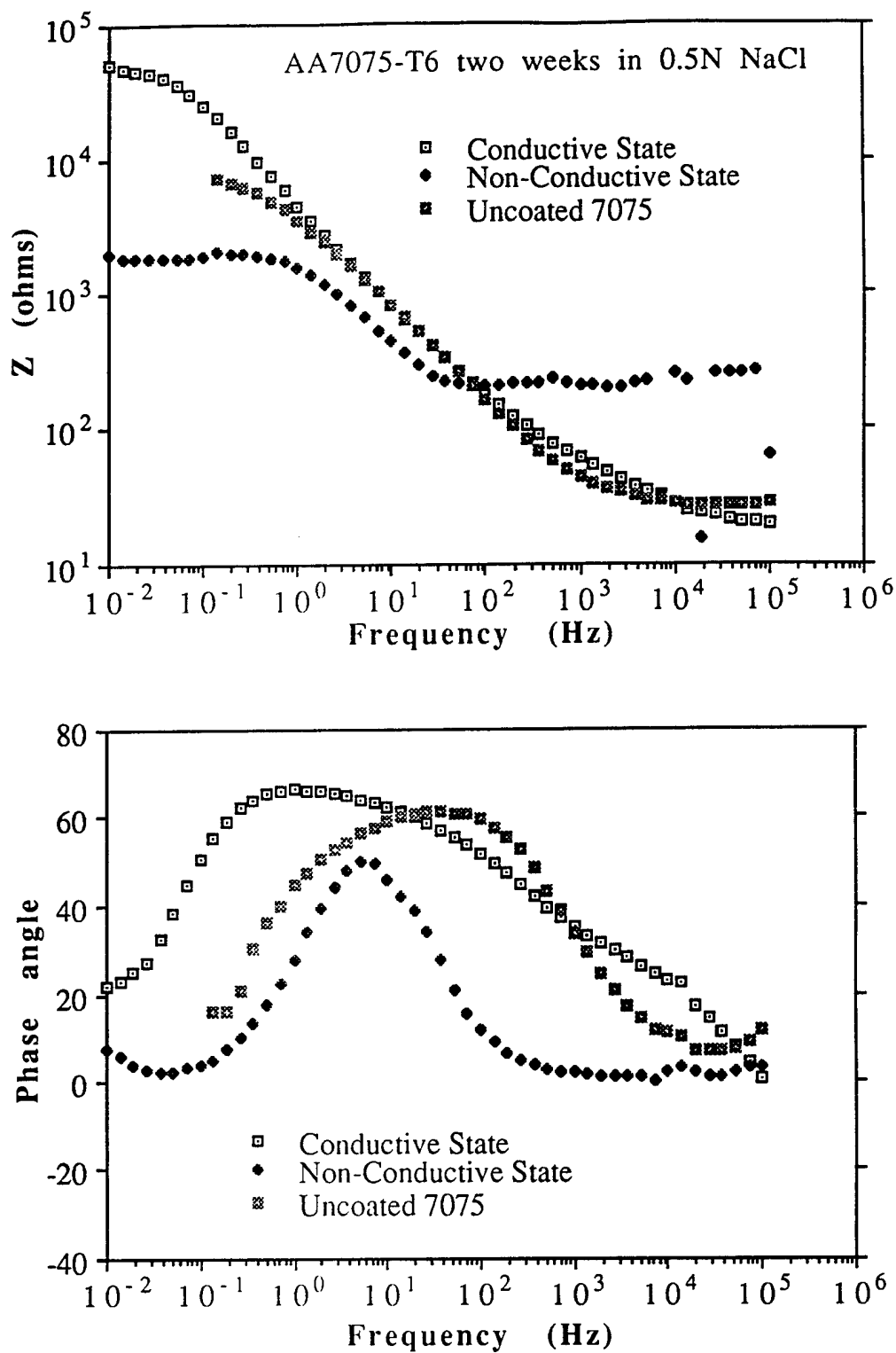


Figure 3. EIS results of conductive and non-conductive states of the double strand polyaniline complex after two weeks in 0.5N NaCl.

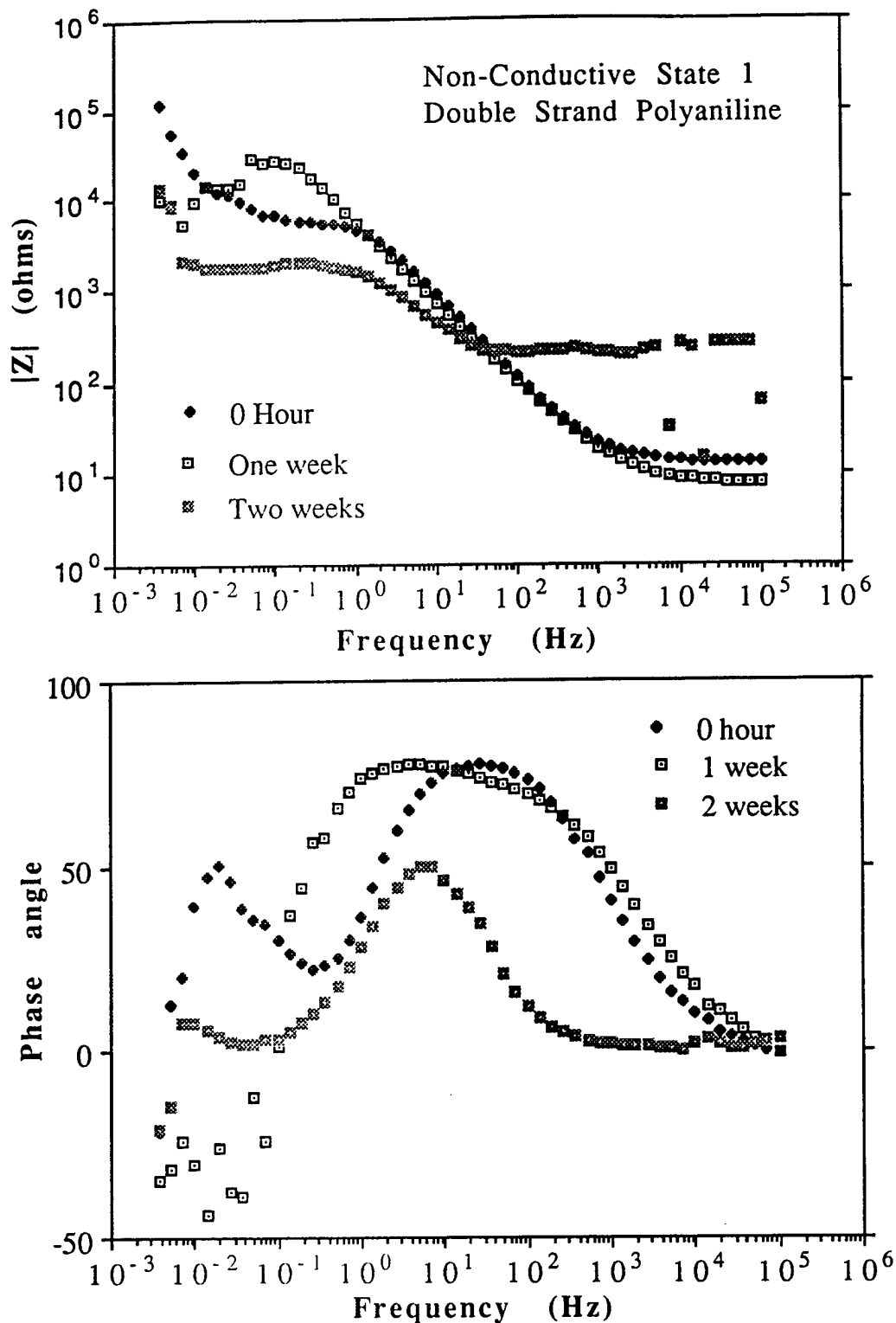


Figure 4. EIS results of the double strand polyaniline in the non-conductive state 1 over two weeks time frame.

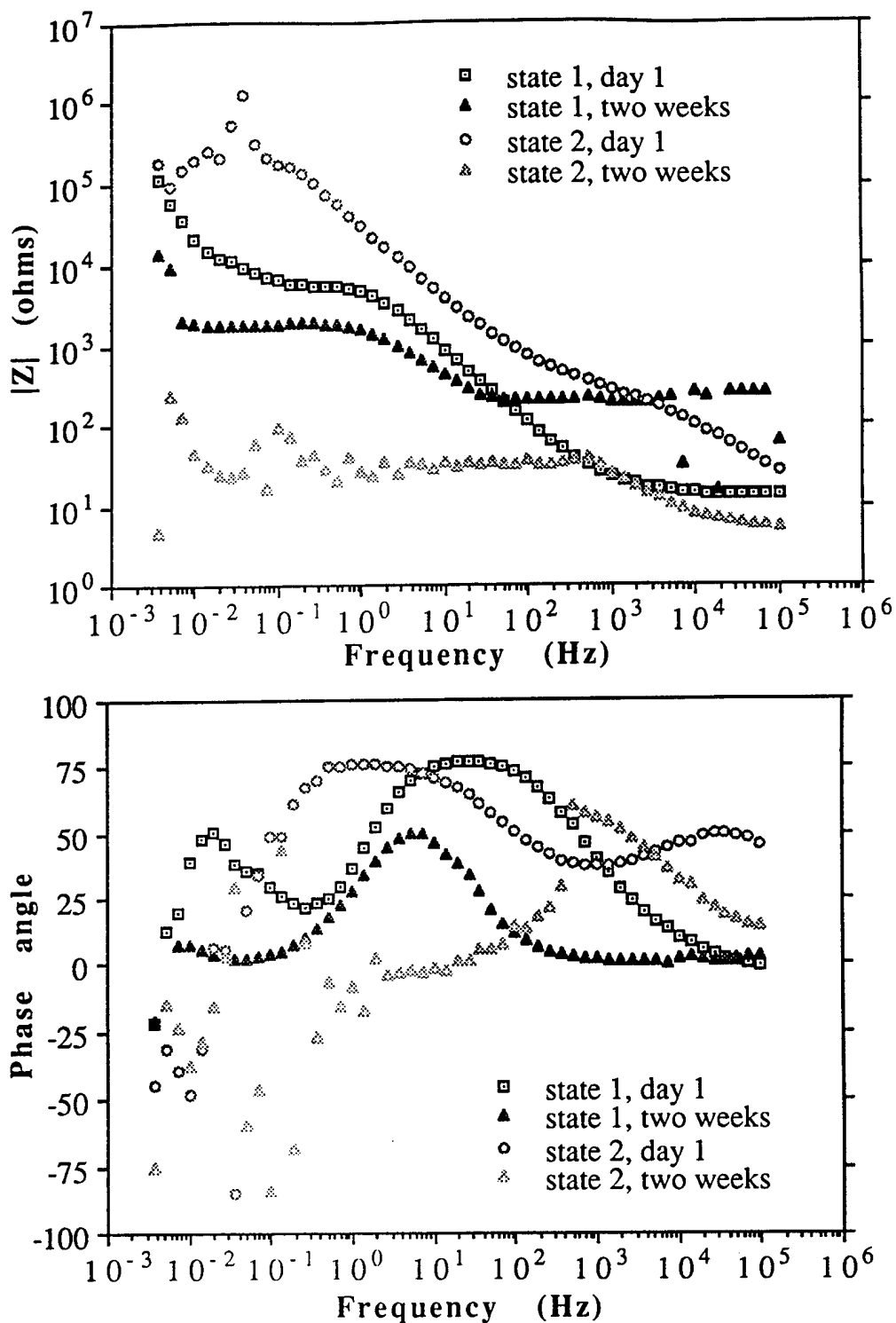


Figure 5. EIS results of the non-conductive states 1 and 2 of the double strand polyaniline on AA7075-T6 in 0.5N NaCl solution.

CHAPTER IV

THE EFFECT OF ACIDIC ENVIRONMENTS ON CORROSION PROTECTION OF ALUMINUM ALLOYS COATED WITH CHROMATE CONVERSION AND CONDUCTIVE POLYMER COATINGS

ABSTRACT

Electrochemical impedance spectroscopy (EIS) results are presented for a polyaniline double strand conductive polymer coating applied to aluminum alloys. EIS tests were performed in a 0.5N NaCl solution buffered at pH 3.6 for several months. Results are compared to Alodine 600 and 1200 chromate conversion coatings. EIS results show at least a one order of magnitude higher charge transfer resistance for the conductive polymer coating over the Alodine coatings on AA2024-T3 and AA7075-T6 aluminum alloys. Implications for this improved performance of the conductive polymer coating in acidic environments is discussed.

INTRODUCTION

The results of the comparative studies between the conductive and non-conductive states of the double strand polymer coating from chapter 3 show that the conductive form must be maintained to offer any corrosion protection for aluminum alloys. The next issue to answer is the performance of the polymer coating when it is maintained in the conductive state. As discussed before, the transition point for the stability of the conductive state of the esterified double strand complex is at a pH of 6.0. If we can keep the test solution is maintained below this pH point, then the film should remain conductive. The objective of this research is to investigate the role of lower pH environments on the corrosion protection properties of the double strand conductive polymer on aluminum alloys.

As discussed in previous chapters, there have been several very interesting results presented over the past several years of conductive polymer coatings offering corrosion protection on steels. 1-10 The results of these studies suggest that the conductive polymer coating's protective nature is not a barrier type coating. Permeability and ionic transport studies have shown that the chemical nature of the conductive polymer coating offers little resistance to the passage of water and ions through the film. 11,12 This ionic transport property is one reason for conductive polymers potential usefulness as solid state rechargeable batteries. 13 Therefore, the ability to show corrosion protection to the metal surface must come from a different mechanism. One idea behind

the mechanism for the protective nature of these coatings is a chemical conversion of the metal surface via an oxidation process from the electroactive nature of the coating. It has been suggested that this electroactive interaction of the polymer with the metal surface forms a passive layer on the surface which provides resistance to corrosion. 2-4 This implies that the conductive polymer must remain in a conductive state to offer any protection to the metal surface. If in a non-conductive state, the polymer is at best a very poor barrier layer.

The results of these past efforts show the conductive polymer offers an improved protection from corrosion in low pH environments. 5-8 These results can be explained by the fact that the conductive nature of the polymer coatings is highly dependent on pH environment. Polyaniline based conductive polymers have four oxidation states, of which one is conductive, the green colored emeraldine salt state. Single strand polyaniline will change to a non-conductive, blue colored, emeraldine base state above a pH of 4.0. It is possible to increase the pH stability point of polyaniline with chemical modifications of the polymer. One type of modification led to the development of a double strand conductive polymer complex. The synthesis of double strand polyaniline was previously reported. 14-16 The double strand polyaniline is a molecular complex of two polymers: (1) polyaniline and (2) a polyanion. These two linear polymers are bonded non-covalently in a side by side fashion to form a stable molecular complex which is structurally similar to DNA. The advantages of the double strand complex are the following: (1) In the conductive state the polymer

is very stable as the polymeric dopant is covalently bonded to the polyaniline strand. (2) With the proper choice of the polymeric dopant, the conductive polymer can be dispersed in solvents to be used as a coating material. To date, the most stable double strand complex developed is a polyaniline strand with polyacrylic acid as the second strand. This complex remains in the conductive state up to a pH of 9.5. However, the best coating developed to date, in terms of adhesion, wetting and corrosion resistance ¹⁷ has a pH stability point of 6.0. This is still not acceptable for any general coating use. Experiments continue to improve on the pH conductive stability point with chemical modifications of the polyaniline strand or the second polyelectrolyte strand and blending of the double strand complex with different epoxy coatings.

The goal of this paper is two fold. First, to present evidence for corrosion protection of aluminum alloys with the double strand conductive polymer coating when it is maintained in the conductive green colored state, this is accomplished by performing the EIS tests in a buffered solution below a pH of 6.0. Second, to present further evidence that the double strand conductive polymer coating is not a barrier type polymer coating and the protection mechanism is not from a barrier type mechanism.

EXPERIMENTAL

The polymer complex was first synthesized employing the previously reported template guided method ¹⁴, then dried, yielding a black powder which is soluble in water or an alcohol

based solvent. The polymeric dopant used for this study is a copolymer poly(methylacrylate-co-acrylic acid). Further processing of the complex can change the polarity of the second strand's functional groups to render the complex soluble in an organic solvent, such as ethyl acetate. The samples are first polished with 600 grit silicon carbide paper, cleaned with a degreaser then de-ionized water prior to coating application. The soluble polymer is then applied to two inch square samples of AA7075-T6 or AA2024-T3 aluminum alloys by dropping from a pipette and allowing the solvent to evaporate from the surface leaving a thin uniform layer of polymer coating. Coating thicknesses range from 1.0 to 10.0 microns.

The chromate conversion coatings used in this study were based on the Alodine 600 and 1200 coating processes. For the Alodine 600 samples, coupons were placed in a standard solution of chromium trioxide, phosphoric acid and sodium hydrogen fluoride. The alloys were dipped in this solution for 5 minutes to form a uniform green colored sealed oxide coating on the metal surface. The Alodine 1200 samples were commercially prepared by Microfin Corporation of Providence , RI.

EIS has become one of the methods of choice for the study of corrosion on metal surfaces. We use this technique to compare the performance of the double strand conductive polymer coatings against the industry standard chromate conversion coatings in acidic environments on aluminum alloys. Samples were clamped with a 1 cm² hollow tube cell and filled with a 0.5N NaCl solution that was buffered to a pH of 3.6. A platinum counter electrode and saturated

calomel (SCE) reference electrode were placed in the cell. The electrodes were connected to a EG&G Model 273 potentiostat and a Solartron 1255 frequency response analyzer. A 5.0 mV alternating current (AC) perturbation signal was applied at the open circuit potential. The AC frequency was scanned from 0.003 Hz to 100 kHz. The resulting current and impedance were measured, recorded and displayed in Bode plot format. Equivalent circuit modeling was performed with a non-linear least squares Boukeamp software package.

RESULTS AND DISCUSSION

Figure 1 shows Bode plots of impedance and phase angle versus frequency for a 7075-T6 coated alloy, an Alodine 600 chromate conversion coating and an uncoated 7075 as a reference sample after 3 days exposure to a 0.5N NaCl solution buffered at pH 3.6. The Alodine 600 sample originally had a charge transfer resistance close to 10^5 ohms, measured as the log impedance at low frequency, yet quickly dropped to the value approaching a typical uncoated aluminum alloy after only one week. This drop in charge transfer resistance is to be expected for a surface converted to an aluminum oxide structure, as the Pourbaix diagram for aluminum shows its oxide is soluble in solutions with a pH below 4.0. 18-19 However, the conductive polymer coated sample does not show a drop in charge transfer resistance after exposure to the acidic environment. In fact, continuously run samples have remained above 10^5 for greater than 60 days at this time. Figure 2 shows the

charge transfer resistance fitted from an equivalent circuit model versus time for the polymer coated and chromate coated samples for up to 60 days. The conductive polymer sample maintains a one order of magnitude higher charge transfer resistance than the chromate sample. Figure 3 shows a similar type EIS Bode plot for the conductive polymer coating on the more corrosive AA2024-T3 alloy versus the Alodine 1200, a better chromate conversion coating, after 50 days exposure to the 0.5N NaCl solution buffered at 3.6. Again, even for the more difficult 2024 alloy, the conductive polymer maintains an order of magnitude higher charge transfer resistance over the better Alodine 1200 sample under long term testing. The removal of the conductive polymer film from the alloy, after testing, revealed no discoloration or evidence of pitting on the surface. Figure 4 is a photograph of a double strand coated 7075 sample after 30 days exposure to the low pH salt solution under EIS testing after the film is removed from the test site. The aluminum surface is free of pits or any discoloration from a corrosion process. In contrast, figure 5 is a photograph of an Alodine 1200 coated 7075 sample after 30 days exposure to the same solution under EIS testing. The figure shows the sample has started the formation of pits. Figure 6 is an uncoated 7075 exposed for 30 days to the same solution showing severe corrosion of the aluminum alloy surface. X-ray diffraction studies were performed on the coated films and white products formed on their surface for the three samples shown in figures 4 through 6. The results show that the Alodine 1200 and uncoated samples had aluminum hydroxide products formed from

corrosion and the PMA coated sample only had sodium chloride crystals in the film.

Clearly, it seems evident that the protective nature of the conductive polymer coating is different than a natural aluminum oxide surface. As discussed earlier, the conductive polymer coating slightly swells in solution and, more importantly, allows the passage of ions and water through the coating. Therefore, it is unlikely that the protection is coming only from a barrier protection mechanism. Any 'barrier type' polymer coating, at the thicknesses used in these tests, would give extremely high impedance values in EIS testing. A gradual decrease in charge transfer resistance and increase in capacitance of the coating would occur as the barrier film absorbs the test solution.²⁰ The conductive polymer coatings do not give high impedance values compared to barrier coatings. A constant capacitance over time was found, in comparison barrier films will show an increase in capacitance over time as water adsorbs into the film and changes the dielectric constant of the film. Since it is well known that the conductive films readily adsorb water^{11,12}, the constant capacitance of the conductive polymer film can also indicate that the film has rapidly adsorbed water and the capacitance data is from the film and water dielectric constants. In fact, they maintain the same level of charge transfer resistance as a typical chromate conversion coating when exposed to neutral salt solutions, $\log 10^5$ at low frequencies.²¹ These results have led us to believe that the conductive polymer has formed a protective passive layer that clearly does not dissolve in lower pH environments and must be of a different type than the chromate's

protection layer. Furthermore, studies previously published and presented in chapter 3 show that the double strand conductive polymer coating must remain in the green colored emeraldine salt state to offer any protection to an aluminum alloy.²² This data further supports the idea that the conductive nature of the polymer is playing a role in the protection mechanism.

If a barrier type mechanism was involved, then you would not expect to see a difference in performance from the conductive emeraldine salt and the non-conductive emeraldine base coatings.

The results also give a hint into the mechanism of a passive layer formation. The lower pH environment not only prevents deprotonation of the polymer film but also facilitates the formation of aluminum ions at the alloy's surface, these ions could play a role in the passive layer formation and the composition of this layer. Chapter 5 presents experimental evidence for this passive layer and discusses possible composition of this layer.

CONCLUSION

The double strand polyaniline coating on AA7075-T6 and AA2024-T3 aluminum alloys was shown to exhibit a one order of magnitude higher charge transfer resistance over the Alodine chromate conversion coatings under EIS testing in a 0.5N NaCl solution buffered at pH 3.6. The mechanism of protection appears to be a polyaniline induced surface chemical conversion to form a passive layer at the interface between the conductive polymer and the aluminum alloy. This passive layer is not susceptible to low pH

dissolution as the aluminum oxide passive layer form the chromate conversion coatings.

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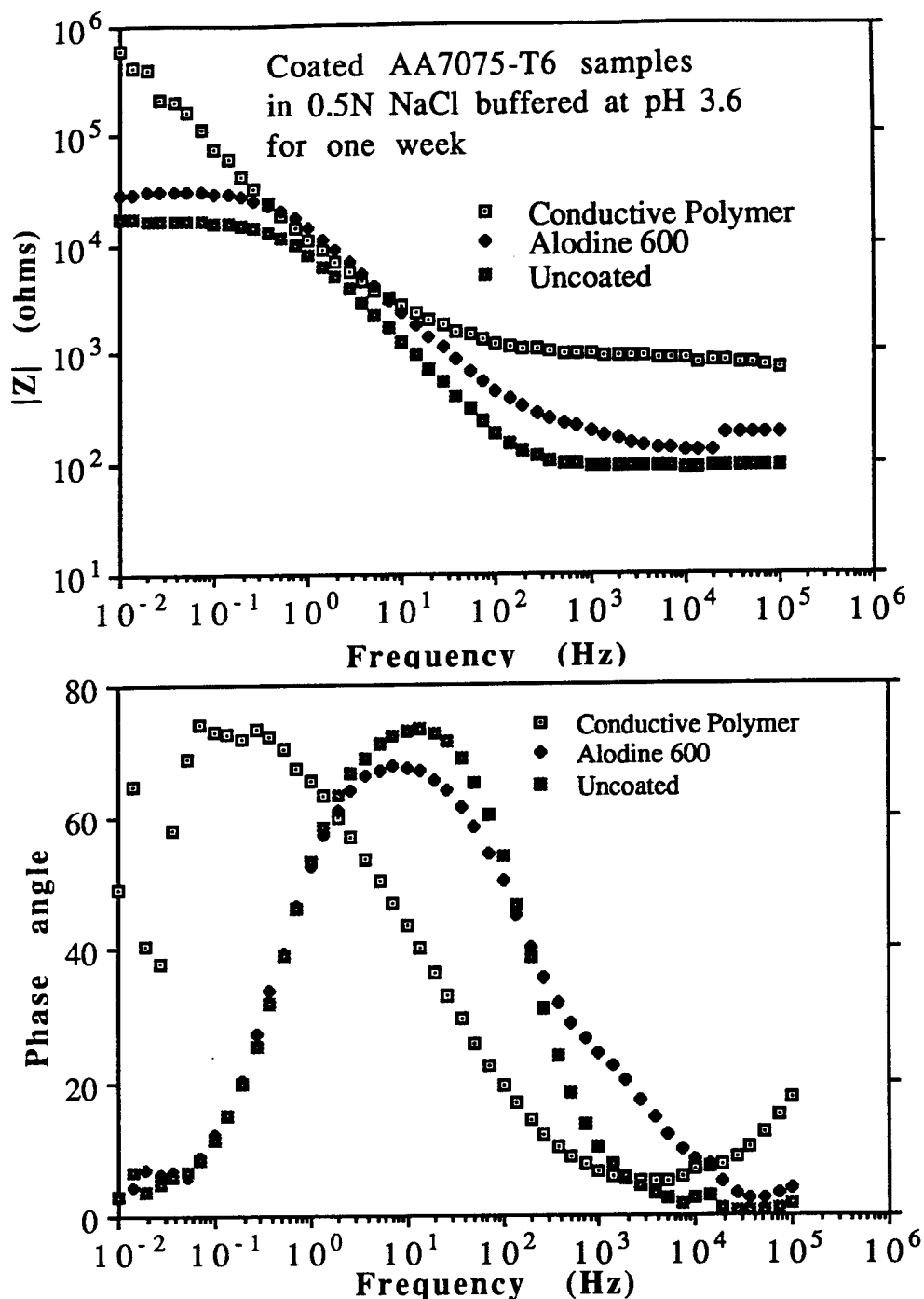


Figure 1. Electrochemical impedance data comparing a PMA coated 7075 sample and a chromate conversion coating using the Alodine 600 process tested in an acidic salt solution (0.5N NaCl solution buffered at pH 3.6) The samples have been immersed in the acidic salt solution for one week at the time of measurement.

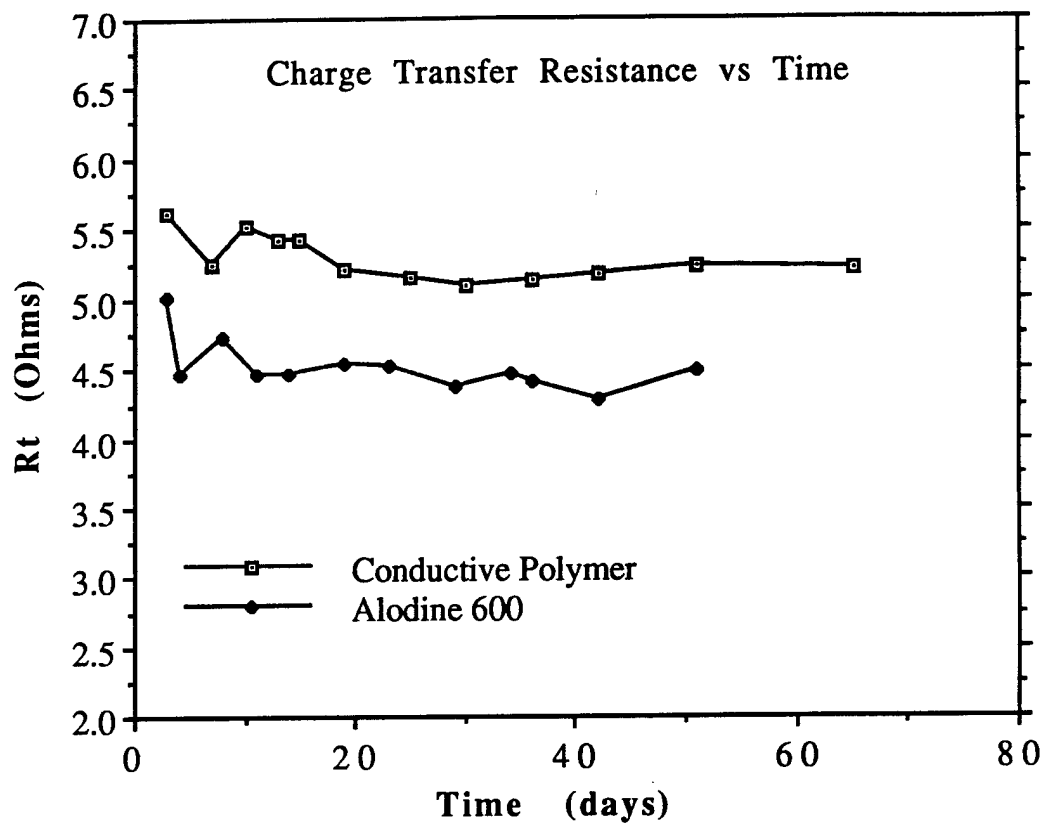


Figure 2. Charge transfer resistance versus time for a double strand conductive polymer coated AA7075-T6 alloy compared with an Alodine 600 coated sample.

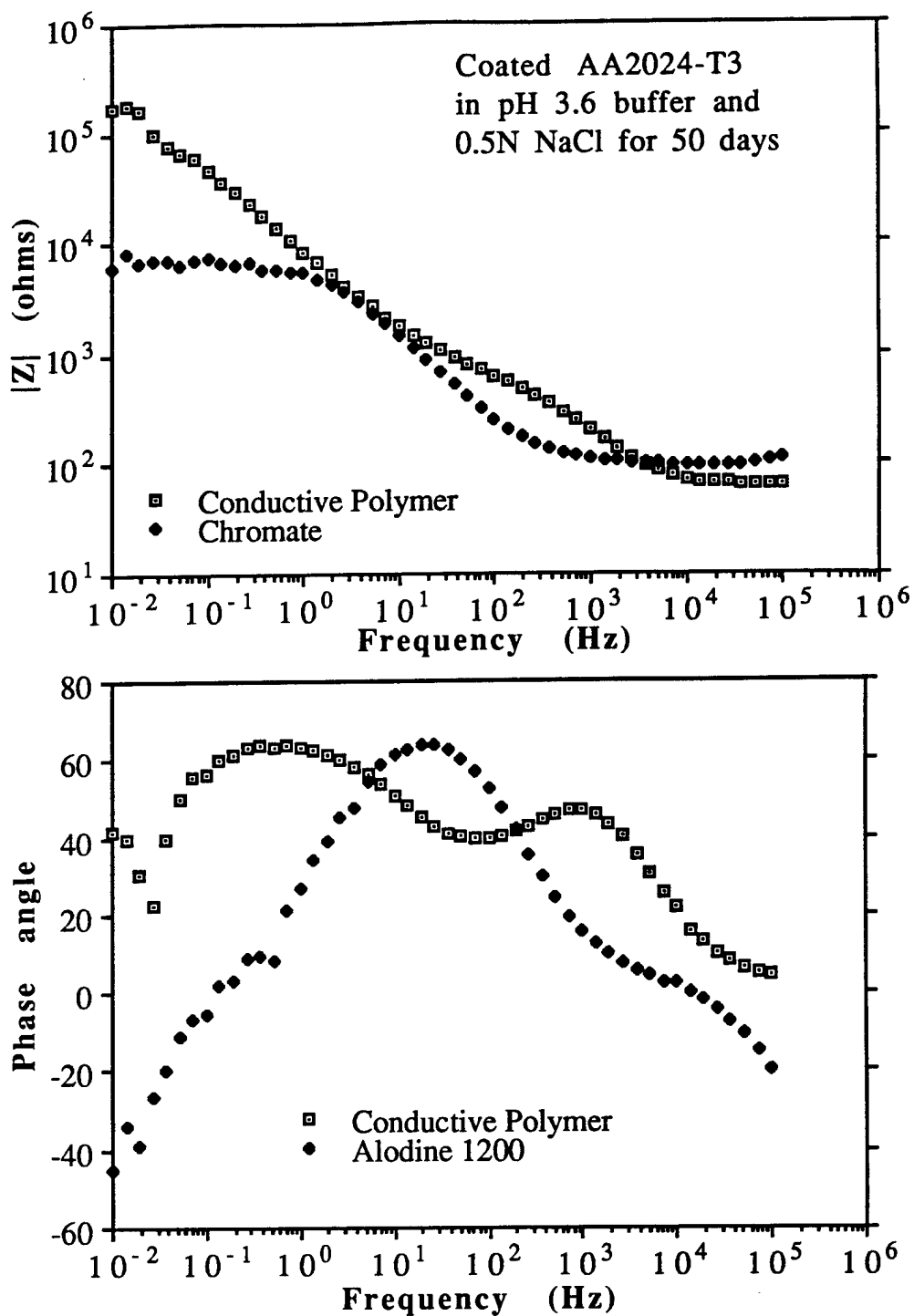


Figure 3. Bode plots comparing the double strand conductive polymer coated 2024 sample and an Alodine 1200 chromate conversion coated 2024 in acidic salt solution of 0.5N NaCl buffered at pH 3.6 for 50 days.

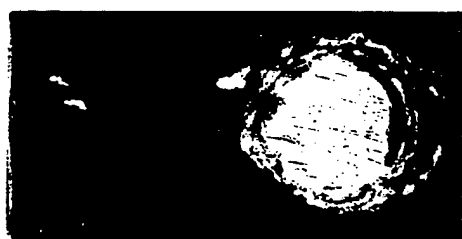


Figure 4. Photograph of PMA coated 7075 alloy after EIS testing in a pH 3.6 buffered 0.5N NaCl for 30 days. The film was removed from the test site.



Figure 5. Photograph of Alodine 1200 coated 7075 alloy after 30 days exposure to a pH 3.6 buffered 0.5N NaCl solution during EIS testing.

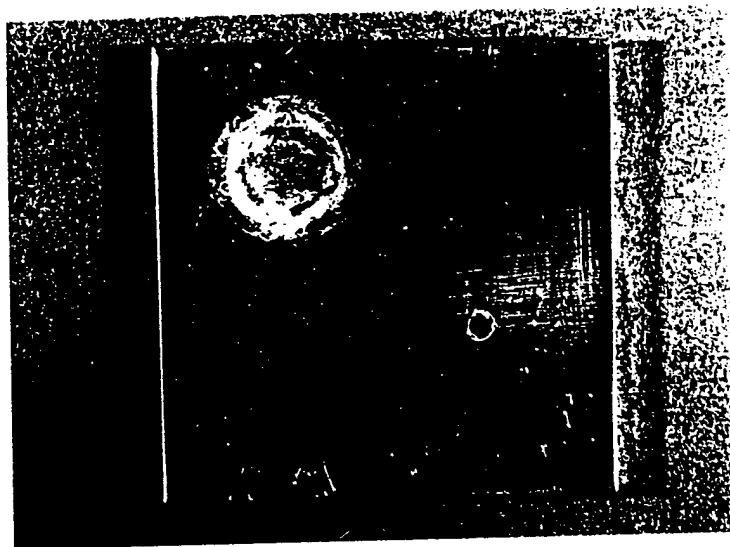


Figure 6. Photograph of an uncoated 7075 alloy after 30 days exposure to a pH 3.6 buffered 0.5N NaCl solution during EIS testing.

CHAPTER V

EXPERIMENTAL EVIDENCE FOR THE FORMATION OF PASSIVE LAYER FROM A DOUBLE STRAND CONDUCTIVE POLYMER COATING ON ALUMINUM ALLOYS

ABSTRACT

Experimental results from electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) on aluminum alloys coated with a novel double strand conductive polymer coating based on polyaniline reveal the evidence for the formation of a passive layer. The key results are: (1) Modeling of EIS data is best fit with a three RC circuit, indicating a third interface between the polymer coating and the alloy's surface; (2) EIS testing in acidic salt solutions shows the conductive polymer coating performs differently and better than a typical anodized or chromate conversion coating indicating a possibly different interface layer than a typical aluminum oxide, (3) SEM studies of the aluminum surface, after the polymer film is removed, indicates that this interfacial layer has a dense and smooth "oxide type" surface morphology and (4) XPS results show a different valence form of the aluminum atoms of the alloy's surface, not the typical aluminum oxide surface structure. The experimental results are consistent with a mechanism in which the conducting polymer serves as a surface conversion agent that oxidizes the aluminum metal surface to form a protective passive layer. The proposed model for this mechanism is presented and the possible chemical composition of the passive layer is discussed.

INTRODUCTION

The overall goal of this research is to investigate the applicability and feasibility of a new double strand conductive polymer to replace the chromate conversion coatings on aluminum alloys for corrosion protection. One important and obvious objective of this research effort is to investigate the mechanism of protection provided by the conductive polymer coating on aluminum alloys. This chapter explains the results presented and phenomena observed in the previous three chapters of this dissertation. A proposed model for the mechanism of protection with experimental evidence to back up this model is presented.

As discussed in chapter one, the past efforts by other researchers with conductive polymer coatings on steel showed results indicating the conductive polymer coating performed much better in acidic environments.¹⁻⁹ The reason for this is due to the polymer's conductive stability in different pH and solvent environments. Conductive polymer coatings based on polyaniline are susceptible to deprotonation in an environment with a pH of more than 3.0.¹⁰⁻¹³ This de-protonation process renders the polymer non-conductive in a blue colored form. It has been shown for aluminum alloys this non-conductive blue form of the polymer does not protect from corrosion in salt environments.¹⁴ Therefore, it seems clear that the electroactive nature of the conductive form is required to offer any protection from corrosion to a metal surface.

PROPOSED MODEL

There are several important properties of a conductive polymer thin film that offer clues to a possible mechanism of protection from corrosion on metal surfaces. The first clue is the realization that a conductive polymer coating is not a barrier type coating. It has been reported for numerous studies that a conductive polymer film is very permeable to the passage of ions and water when exposed to aqueous solutions. ^{15,16} The esterification of our double strand conductive polymer complex used in these studies only changes the hydrophobicity of the film slightly by rendering the polymer soluble in an organic solvent, usually ethyl acetate. These films are still very permeable to ions and water.

Another important property is the experimentally proven fact that the non-conductive blue colored emeraldine base form of the complex does not offer any protection from corrosion to a metal surface. This was supported by our own experiments and presented on chapter three. Since the conductive form is required, then clearly the electroactive nature of the polymer must play a role in the protection mechanism.

The proposed model for the mechanism of protection is best explained with an illustration. Figure 1 is an artist drawing of the conductive polymer complex coating on an aluminum alloy. Figure 1

illustrates an interfacial electron transfer between the polymer and the aluminum surface. Thermodynamically it is feasible for the polymer to oxidize the aluminum surface. The rest potential of the conductive polymer measures at 0.3 volts and the aluminum alloy's is approximately -0.75 volts versus SCE. Clearly the polymer being conductive can accept electrons from the metal surface to facilitate this oxidation process. The polyaniline complex has a stable reduced state as was presented in chapter 1 in figures 1 and 2. It is proposed that this oxidation process is similar to a chemical conversion of the surface, such as an acid anodization process with the chromate conversion coatings. This oxidation process forms a passive protective layer on the aluminum surface as illustrated in figure 2. The objective of this chapter is to present the experimental evidence that supports this proposed model and to present further discussion on the nature and composition of this proposed passive layer.

EXPERIMENTAL EVIDENCE FOR PASSIVE LAYER

Impedance Measurements and Modeling

The first evidence for a passive film being formed on the surface is seen from the EIS results and the subsequent equivalent circuit modeling of this data. It is commonly known that a typical barrier type polymer coated metal surface can be closely modeled with a double RC circuit model.¹⁷ The two RC circuits account for the solution/polymer layer and the polymer/metal layer. However,

the modeled data of the conductive polymer coating can only accurately be represented by a three RC circuit model. The third RC component in the circuit model shown in figure 3 may be interpreted as a third layer formed between the polymer/solution layer and the polymer/metal layer. Table 1 shows the equivalent circuit component values used to best match the EIS data. A comparison of the polymer coated EIS data and the circuit model of figure 3 is shown in the Bode plot of figure 4. This third circuit can also be seen in the three "hump" shape of the phase angle in the Bode plot of figure 4.

Impedance Measurements in Acidic Solutions

The second evidence for a protective layer formed on the aluminum surface can be seen from the EIS tests performed in acidic salt solutions as was presented in more detail in chapter 4. Figure 5 shows Bode plots of impedance (top) and phase (bottom) versus frequency for a 7075-T6 coated alloy and an Alodine 600 chromate conversion coating after one week exposure to a 0.5N NaCl solution buffered at pH 3.6. The Alodine 600 sample originally had a charge transfer resistance greater than 10^5 , measured as the log impedance at 0.1 Hz, and had quickly dropped to a value approaching a typical uncoated aluminum alloy of 10^4 . This drop in charge transfer resistance is to be expected for a surface converted to an aluminum oxide structure, as the oxide is soluble in solutions with a pH below 4.0.^{18,19} However, the conductive polymer coated sample does not show a drop in charge transfer resistance after exposure to the

acidic environment. In fact, continuously run samples have remained above 10^5 for two months now. Clearly, it seems evident that the protective nature of the conductive polymer coating is different than a typical aluminum oxide surface. This result has led to a suspicion that the conductive polymer has formed a protective passive layer that performs differently than the natural aluminum oxide.

Scanning Electron Microscopy Images

The next evidence for the formation of modified passive layer under the conductive polymer film is the SEM photograph shown in figure 6 of a polymer coated sample after removal of the polymer layer. This sample had been exposed to a 0.5N NaCl solution for two weeks prior to SEM analysis. The material's morphology appears similar to a crystal "oxide type" structure. The original surface was crack free, the cracks seen in the figure were formed during analysis under the SEM. The credence for this data is not as high as the other techniques presented. The removal of the film from the alloy surface was difficult and required immersion of the sample into an ultrasonic bath of ethyl acetate for several days. It is quite possible that the layer seen in the photograph is from the formation of an oxide layer during this bath exposure. However, when an uncoated alloy sample is exposed to an aqueous salt solution for two weeks and observed under SEM, no crystal "oxide like" layer is seen as observed in figure 7. Figure 7 shows an uncoated alloy after two weeks exposure to a 0.5N NaCl solution. The photograph only shows

corroded areas with white corrosion products formed and pitting of the surface. There is no evidence of a crystal "oxide like" structure seen on the surface.

X-ray Photoelectron Spectroscopy

Initial XPS results presented in figure 8 show that this passive film is not an aluminum oxide film but possibly a complex with the aluminum metal at a different oxidation state. The exact composition of this passive layer is still not known at this point. Preliminary results of depth profiling using XPS do indicate that oxygen is present under the polymer film, as would be expected. However, the energy spectrum of the aluminum layer is not typical of bohemite or an aluminum oxide. An uncoated sample under XPS depth profile analysis shows a strong peak at 76 eV associated with a native aluminum oxide layer of aluminum in the tri-valent oxidation state and the standard aluminum metal valent state at 72.5 eV of the underlying aluminum metal.

The conductive polymer coated sample's depth profile analysis did not show any native aluminum oxide peak after sputtering through the polymer film. However, a different aluminum valent peak is evident at 74 eV, on the shoulder of the aluminum peak. This new peak might be associated with a mono-valent aluminum state associated with a different complex of the aluminum and the conductive polymer film. Two theories for the chemical composition of this passive layer are discussed further in the next section.

DISCUSSION

The data presented above shows evidence from separate analysis techniques that the protective mechanisms for the conductive polymer coated samples involves the formation of a protective layer between the conductive polymer and the metal surface. It is suggested that the polymer layer facilitates the formation of this protective passivating layer due to it's conductive property. This mechanism is not possible for uncoated aluminum alloys in salt water as indicated from the cyclic polarization data presented on chapter 2.

There are several possible explanations of the polymers role in the protection process. The simpler explanation is that the polymer is acting as a non-sacrificial anode, which allows the electrons from the metal to pass through the polymer and reduce the water on the solution side of the polymer film. This process would then separate the anode and cathode reactions from the metal surface. The polymer can then form a complex with the aluminum ions formed in the oxidation process to form a passive layer. However, this mechanism would facilitate the dissolution of aluminum and simply corrode the surface faster.

Another postulated theory from researchers working with steel samples involves the conductive polymer raising the redox potential of the metal surface to a more noble value through a galvanic coupling to the polymer with the metal surface. The cyclic polarization result of chapter 2 do not support this theory for aluminum alloys. A change in rest potential is not observed for

conductive polymer coated samples. The change in rest potential would be observed if the redox potential of the metal was being raised to amore noble value.

A more plausible theory proposed involves a more complicated process involving the reversible nature of polyaniline from an oxidized conductive state to a reduced non-conductive state and back again with the formation of a different passive layer on the alloy's surface than a natural oxide. The reversible property of polyaniline has been extensively studied for reversible battery and electrochromic window applications. ²⁰ This reversible property could explain a repairing mechanisms of the passive film as it is thinned by chloride ion attacks or from film damage or pin hole exposure of the metal surface. This theory can be further explained by examining Figure 9.²¹ Figure 9 shows the reaction network of polyaniline showing the different reduction-oxidation states of the polymer. State II(2S) is the conductive form of the polymer and is green in color. The other states are all non-conductive forms, state I is transparent in color, state III is blue and state IV is purple. The stability of these states is governed by the pH environment and the applied potential to the polymer. If the polymer accepts electrons from the metal surface, during an oxidation of the metal, it is possible for the polymer film to change states, to the reduced state of I(1S), called the Leuco salt, shown in the upper left hand corner of figure 8. In this reduced state, the polymer film is no longer conductive, yet it has been readily demonstrated in electrochromic applications of polyaniline that the polymer can be re-oxidized from

two possible mechanisms. ²⁰ This re-oxidation process can change the polymer film at the metal surface back to the conductive state, II(2S), and the polymer film is now available to reform or repair the passive layer and start the cycle over again.

The first possible mechanism for re-oxidizing the film at the metal surface is due to dissolved oxygen in the test solution. It has been shown that oxygen can selectively penetrate a polyaniline film and oxidize the polymer. ²² The second possible mechanism for re-oxidation is an electron transfer process from the underlying Leuco salt, I(1S) layer attached to the metal to a layer of polymer film in the II(2S) state above it towards the solution surface. It is known that the transparent, non-conductive I(1S) state can transfer electrons to the green conductive II(2S) state even though the I(1S) form is not conductive. ²³ This electron transfer process will change the polymer attached to the metal surface back to the conductive green state.

What is also evident when examining this reaction network is that if the polymer becomes de-protonated from the green II(2S) state it will change to the blue non-conductive form represented as III(2A) in figure 8, called Emeraldine base, or it can also become de-protonated when in the I(1S) state and change to the Leuco base state of I(1A). The key here is that once the polymer de-protonates to the Emeraldine base or Leuco base it becomes permanently non-conductive and cannot be recycled back to the green conductive form unless placed in a solution with a pH below its de-protonation

stability point. Therefore, the polymer cannot further repair the surface via this reversible reduction-oxidation process. The key idea behind this theory, for long term protection in salt environments, is to maintain the polymer film in the reversible salt states of the green conductive II(2S) state and the transparent non-conductive I(1S) state. This can only be achieved by having a polymer system with a high pH stability point to prevent deprotonation of polyaniline coating or testing the films below this pH stability point as evidenced from the results of chapter four.

The composition of the passive layer is unknown at this point, although we have two theories as to its possible chemical structure. It is believed, as presented in the sections above, that the passive layer is of a different chemical structure than a typical native aluminum oxide layer. The two key results that have led us to believe this are, first, the acid solution EIS data showing the passive layer does not dissolve below a pH of 4.0 and , second, the XPS results showing a different valence for the aluminum under the polymer film. The first possible chemical structure is a chelated complex of the polyacrylic acid groups from the second strand with aluminum ions in the plus one oxidation state. The functional groups of the second strand polymer are of a chemical nature to readily chelate and form complexes with the aluminum ions formed in the oxidation process or oxygen atoms dissolved in the solution can react at the surface to form a modified protective oxide layer. Several inhibitor study results have shown that similar type compounds as the carboxylic acid groups have provided increased

protection of aluminum alloy surfaces through adsorption onto the surface to form an inhibitor type passive layer.^{24, 25} The preliminary results of depth profiling using XPS does indicate that oxygen is present under the polymer film, as would be expected. However, we do not see a shift in change in the energy spectrum of the oxygen present from a PMA coated sample versus an uncoated sample, which could indicate a different oxygen compound than the typical aluminum oxide. What is clear is that the energy spectrum of the aluminum layer is not typical of a bohemite or an aluminum oxide structure under the conductive polymer film from the different energy spectrum of the aluminum peaks.

The second possible chemical structure of the passive layer is from attachment of the nitrogen group from the polyaniline strand to the aluminum surface. There have been extensive studies done of nitrogen containing compounds that shows them to be effective cathodic inhibitors of aluminum alloys.²⁶⁻³⁰ It is beyond this dissertation to discuss all of the work done in this area. The overall key point of these studies is that the nitrogen atom of these compounds can readily adsorb onto the surface of the alloy and decrease the corrosion current density and reduce the amount of pitting on the alloy's surface through a cathodic inhibitor mechanism. It is quite possible to expect that the nitrogen in polyaniline to be able to adsorb onto the alloy's surface and serve a similar purpose. The role of the coating's electroactive property is to first slightly etch the alloy's surface with an oxidation process,

thereby preparing the surface with easier adsorption sites for the nitrogen groups. The computer identifying the XPS depth profiling peaks does pick up a small amount of nitrogen over the background noise. What is extremely interesting is that the nitrogen is only identifies on the samples that have not been exposed to the 0.5N NaCl test solution or that have been exposed to the lower pH test solution, meaning the film as still in the conductive state at the time of profiling. This could be one of the key clues that explains why the conductive polymer films work in the lower pH environment when they stay green colored and not after they turn blue. This needs to be confirmed with more XPS and Auger testing and possibly correlated with IR or Raman spectroscopy. However , the initial results seem to show that nitrogen is present adsorbed on the alloy's surface for only samples that have a conductive film or a film that was not exposed to chloride ion medium, It might be possible the chloride ions are displacing the adsorbed nitrogen sites to stop an inhibitor protection mechanism.

CONCLUSION

Evidence was presented from several electrochemical and surface analysis techniques that shows proof for the formation of a conductive polymer modified protective layer formed on the surface of aluminum alloy samples. The results are for a novel double strand conductive polymer system based on polyaniline. These results suggest that the conductive polymer coating is acting as a

surface conversion agent by facilitating the formation of this passive layer on the aluminum surface. It is suggested that the polymer layer facilitates the formation of this protective passivating layer due to its conductive property as a surface conversion agent.

The exact composition of this protective film is still unknown at this point, but it is possible that the layer is either a polymer modified oxide layer or a chelated complex of the polymer film to aluminum ions or the aluminum metal surface atoms with the carboxylic acid groups of the second strand or the nitrogen groups of polyaniline to form an inhibitor type passive layer.

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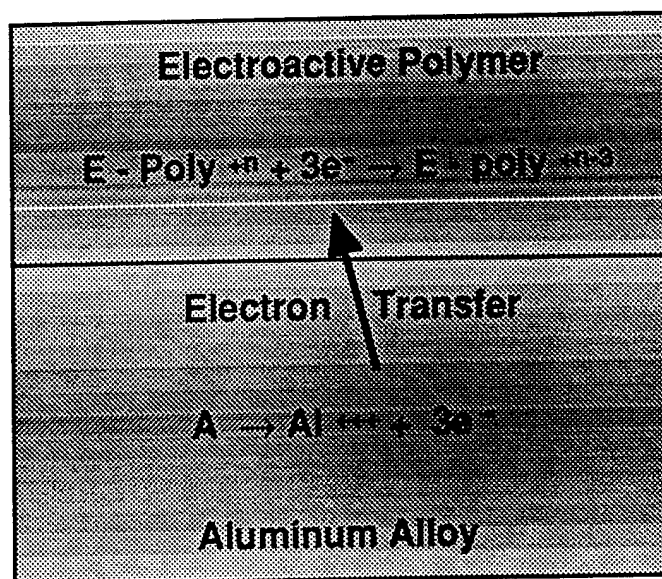


Figure 1. Illustration of a double strand conductive polymer coating on an aluminum alloy with an interfacial electron transfer between the electroactive polymer and the metal surface.

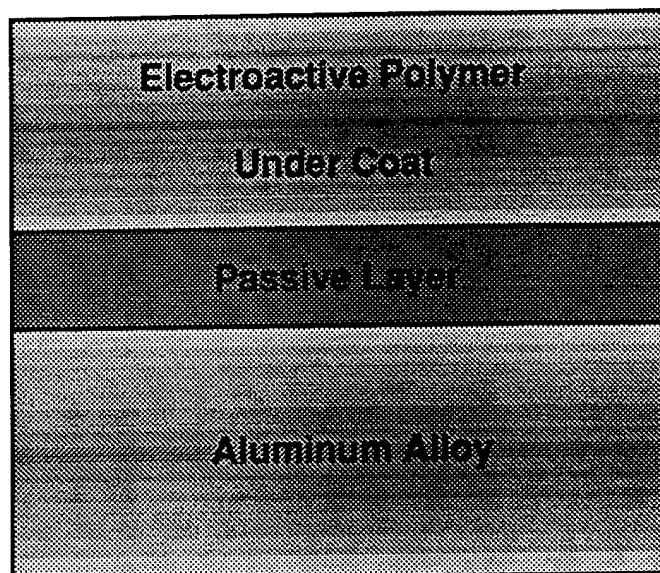


Figure 2. Electron transfer reaction (oxidation) of figure 1 leads to a passive layer formation. This thin and tight layer protects the underlying metal.

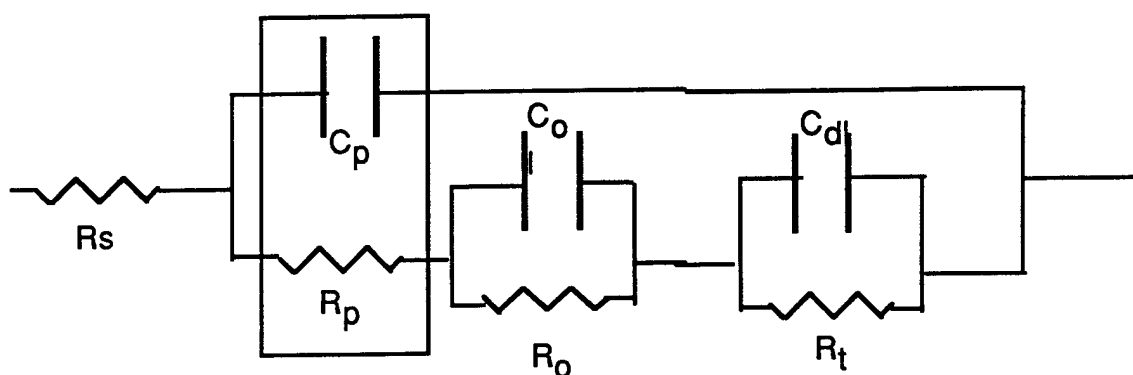


Figure 3. Equivalent circuit model for a PMA coated 7075-T6 aluminum alloy sample with circuit elements. R_s is the solution resistance, R_t and C_d represent the charge transfer resistance and the double layer capacitance at the metal surface, C_p and R_p represent the polymer layer's circuit and R_o and C_o represent the third layer possibly associated with a passive layer between the polymer and metal surface.

Table 1. Equivalent circuit element values for the three circuit model of figure 3 describing the impedance behavior of a PMA coated 7075-T6 aluminum alloy after exposure to a 0.5 N NaCl solution for two weeks. Model results matched to the impedance data is shown in figure 4.

<u>Element</u>	<u>Physical Description</u>	<u>Value</u>
R_s	Solution Resistance	1.69×10^1 Ohms
R_t	Charge Transfer Resistance	2.52×10^3 Ohms
C_c	Double Layer Capacitance	1.94×10^{-4} F
R_o	Passive Layer Resistance	4.97×10^4 Ohms
C_o	Passive layer Capacitance	5.24×10^{-5} F
R_p	Polymer Coating Resistance	2.1×10^4 Ohms
C_p	Polymer Coating Capacitance	4.41×10^{-3} F

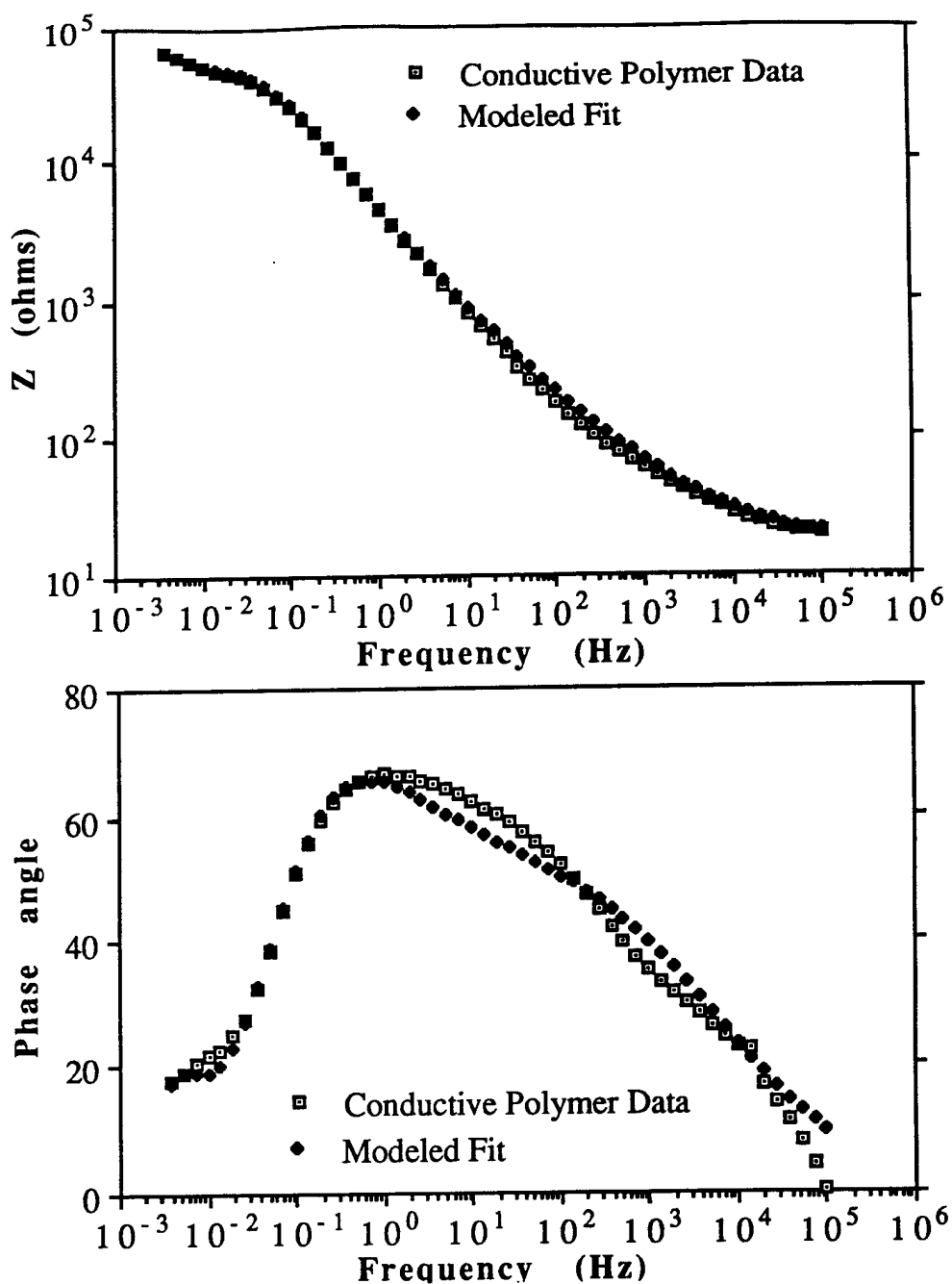


Figure 4. Bode plots of impedance (top) and phase (bottom) for a PMA coated 7075-T6 sample exposed to 0.5N NaCl solution for two weeks overlaid with the equivalent circuit model results using the values from Table 1.

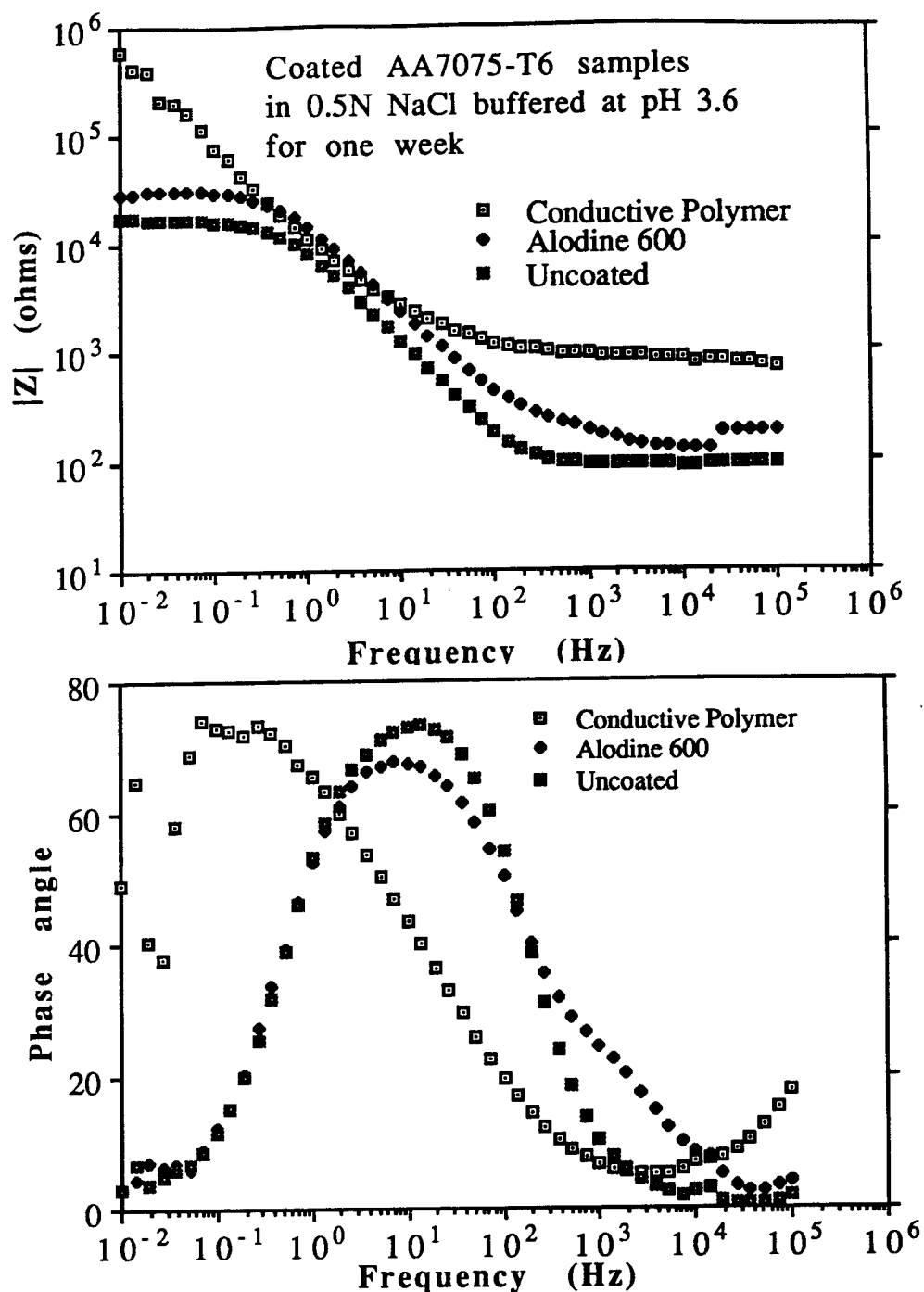


Figure 5. Electrochemical impedance data comparing a PMA coated 7075 sample and a chromate conversion coating using the Alodine 600 process tested in an acidic salt solution (0.5N NaCl solution buffered at pH 3.6) The samples have been immersed in the acidic salt solution for one week at the time of measurement.

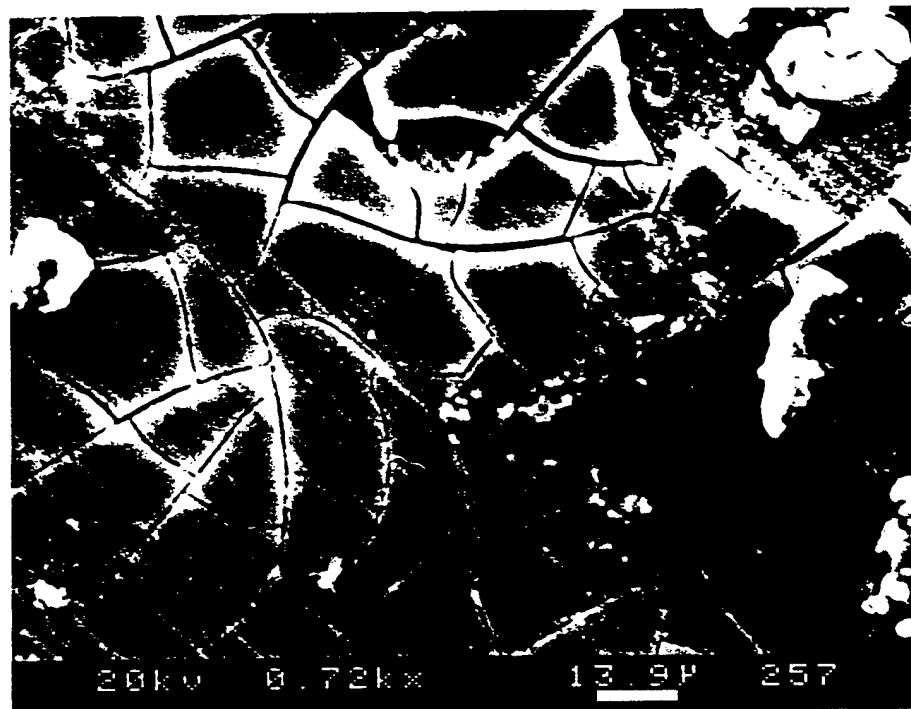


Figure 6. SEM photograph at 720 times magnification of a PMA coated 7075 alloy after the polymer film has been removed from the surface. Photograph shows a crystal "oxide like" structure. The sample was originally crack free, the cracks formed under exposure the electron gun.

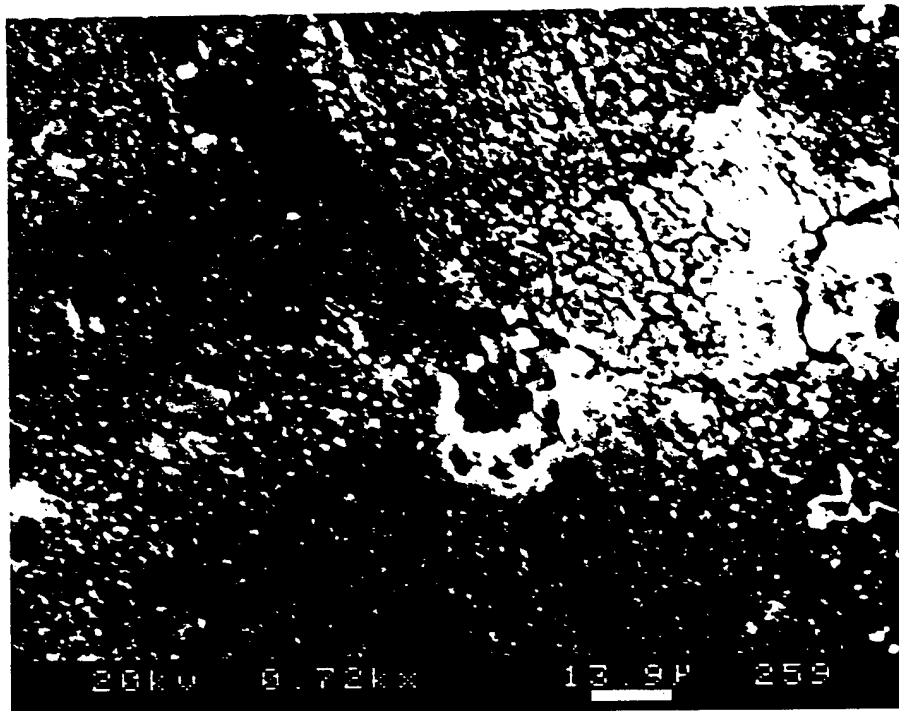


Figure 7. SEM photograph at 720 times magnification of an uncoated 7075 alloy. Photograph shows the formation of corrosion products and surface pitting

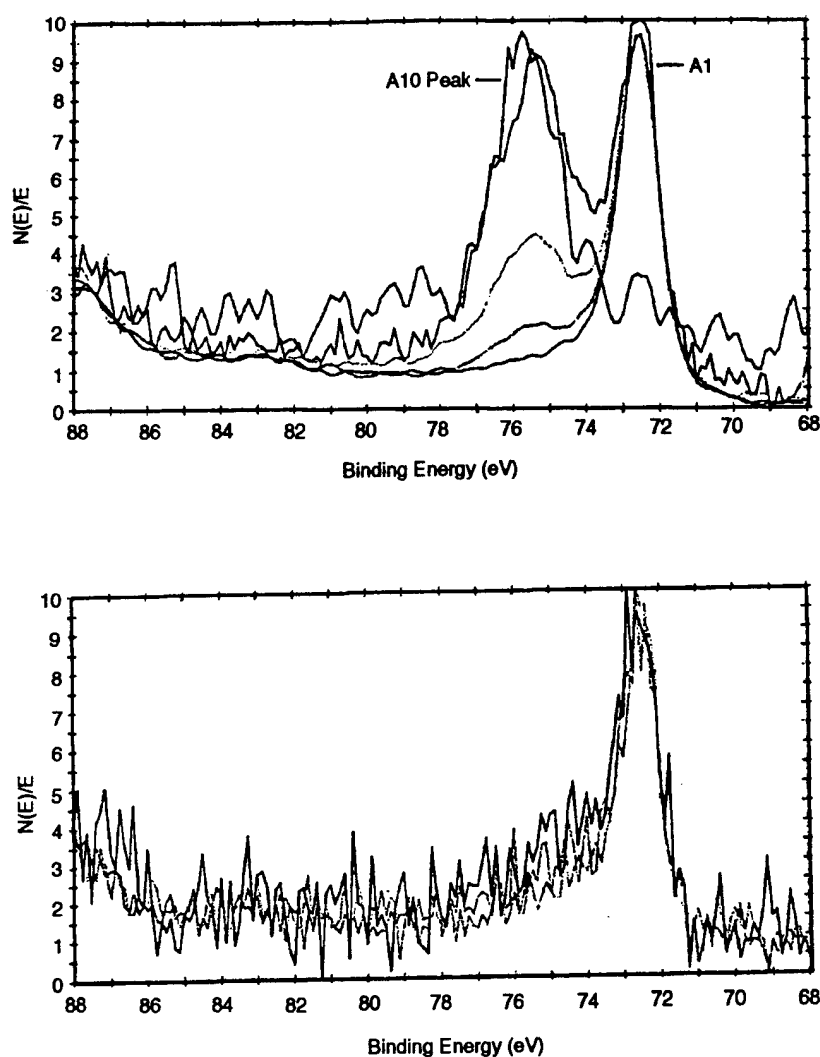


Figure 8. XPS depth profile results of an uncoated 7075 sample (top) and a conductive polymer coated (bottom) sample after sputtering through the polymer layer. The uncoated sample shows a strong peak at 75 eV associated with a native aluminum oxide layer. The conductive polymer coated sample did not show any native oxide peak after sputtering through the polymer film. However, a new peak is evident at 74 eV, on the shoulder of the aluminum peak.

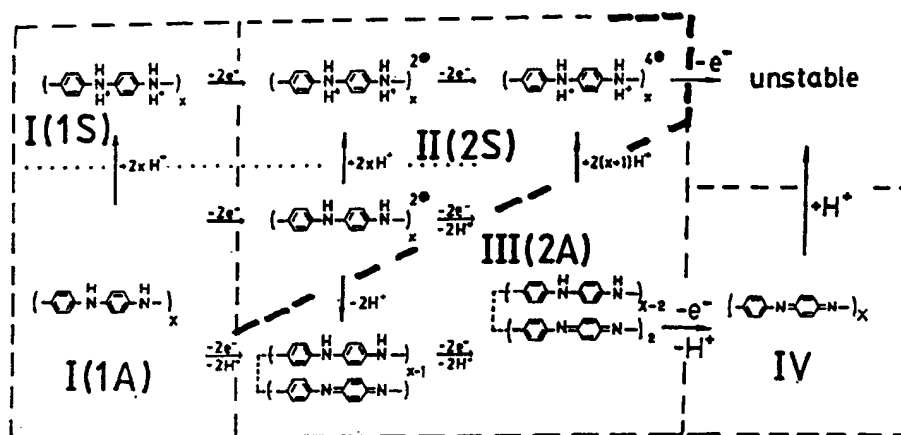


Figure 9. Reaction network of polyaniline showing the different oxidation states. State II(2S) is the green colored emeraldine salt form of the polymer. The other states are non-conductive forms. The states stability is governed by the pH environment and the applied potential to the polymer.

CHAPTER VI

DOUBLE STRAND CONDUCTIVE POLYMER PRIMERLESS COATING SYSTEM

ABSTRACT

A complete coating system employing a double strand conductive polymer undercoat with an epoxy spray paint overcoat was tested against epoxy overcoat samples without a polymer undercoat. Test techniques included both EIS and salt spray exposure tests. Results for equivalent thickness coatings show a higher charge transfer resistance for the conductive polymer undercoat compared to no conductive polymer undercoat after four months exposure.

Salt spray results show the conductive polymer undercoat samples have no blistering or delamination of the film along a scribed area while the samples with no conductive polymer undercoating have evidence of blistering on the film off the alloy's surface along the scribed area.

INTRODUCTION

There is considerable searching in the aircraft industry for a new coating system applicable to all new and existing airplanes. This is particularly true in the Air Force, which recently published recommendations for a new coating system from a Blue Ribbon Advisory Panel (BRAP) study. ¹ The BRAP was established to identify the research needs for such a large area of emphasis. The panel consisted of three people with recognized expertise in coatings technology together with two Air Force liaison personnel. The report highlighted five areas of emphasis, summarized as follows; (1) Mechanisms of aluminum corrosion and chromate inhibition and consequent inhibitor replacement technology for coated and uncoated systems, (2) Degradation mechanism of polymers in matte coatings and consequent performance prediction capability, (3) Synthesis/structure/property relationships for matte top coatings, (4) Advanced material (polymers, additives, pigments, inhibitors) and (5) Undercoating and coating property inspection.

The AF's approach to any new coatings development is to look at the coating as a whole system. Aircraft coating systems are multi-functional and provide three main attributes; (1) survivability, (2) corrosion protection, and (3) cosmetic appearance. Current coating systems consist of a surface pretreatment, a paint primer layer and paint topcoat. The surface pretreatment provides passivation of the metal surface, which includes inhibitors and is currently being performed by chromate conversion coatings. These eventually that need to be replaced as by 1998 they will not be

permitted. The pretreatment creates surface topography for maximum coating adhesion. The paint primer layer incorporates corrosion inhibitors and serves as an adhesive between the treated metal substrate and the topcoat layers. The paint topcoat layers provide signature control and protection against erosion and mechanical abrasion, in addition to acceptable cosmetic appearance.

With this type of system in mind, a small scale coatings system study was conducted using the double strand conductive polymer as the chemical conversion pretreatment, with an epoxy spray paint topcoat, without a primer layer. Figure 1 depicts a drawing of this primerless coating system. The objective was to investigate the protection provided by the conductive polymer pretreatment compared to no pretreatment but with a top coat. This chapter presents results from EIS testing and salt spray testing of 7075 aluminum alloy samples coated with the double strand conductive polymer coating and an epoxy spray paint overcoat. These results are compared against samples with just an epoxy spray paint coating. Care was taken to ensure the coating thicknesses were equivalent and the test results confirm the coating thicknesses were equal.

EXPERIMENTAL

AA76075-T6 aluminum alloys squares were coated with the esterified complex double strand polymer, then coated with a commercial white epoxy spray paint. Other samples were coated with only the white epoxy spray paint. EIS testing was conducted in

0.5N NaCl solution for up to four months. Additionally other samples were placed in the salt spray chamber for long term exposure to the simulated high temperature, high humid marine environment.

RESULTS AND DISCUSSION

Figure 2 shows the initial EIS Bode plot results for a PMA undercoat sample and a sample with only an epoxy overcoat on the first day of the test. The low frequency log impedance values are near equivalent, indicating that the film thicknesses were equivalent at the start of the test. Figure 3 shows the Bode plot results for the same samples in figure 2 after four months exposure to the test solution. The sample with a conductive polymer undercoat has a higher charge transfer resistance than the sample without, indicating better protection to the aluminum surface. Figure 3 also shows an increase in capacitance for the no undercoat sample, indicating the uptake of water into the film over time. This is observed by extrapolating the impedance line to the y-axis. This intercept point is represented as the inverse capacitance. These results indicate that the higher transfer resistance is coming from the presence of the conductive polymer undercoat. However, as discussed in previous chapters, it is believed this protection is not from adding another barrier coating but from a passive layer formation on the alloy's surface.

Even more significant results are from the salt spray testing. Figure 4 shows a photograph of a scribed sample with the polymer

undercoat after 7 days exposure in the salt spray chamber. Figure 5 shows a scribed sample without the polymer undercoat. The sample in figure 5 shows the formation of bubbles and lifting up of the epoxy overcoat from the alloy's surface. This can be seen from the bumps visible in the photograph along the scribed area. Figure 4 has no evidence of film lifting or bubbling in the same areas along the scribe.

CONCLUSION

These results are still very preliminary tests and it will take many years to effectively develop a new coating system. However, the result are promising. It appears the conductive polymer undercoat has stopped the propagation of the salt solution under the overcoat film from the scribed area and has improved the adhesion of this film to the alloy's surface. Additionally, the EIS results seem to show that the undercoat provides a longer term protection than without the conductive polymer undercoat with a higher charge transfer resistance over four months of testing. The next test needed are to compare these result with a chromate undercoat and an epoxy overcoat system.

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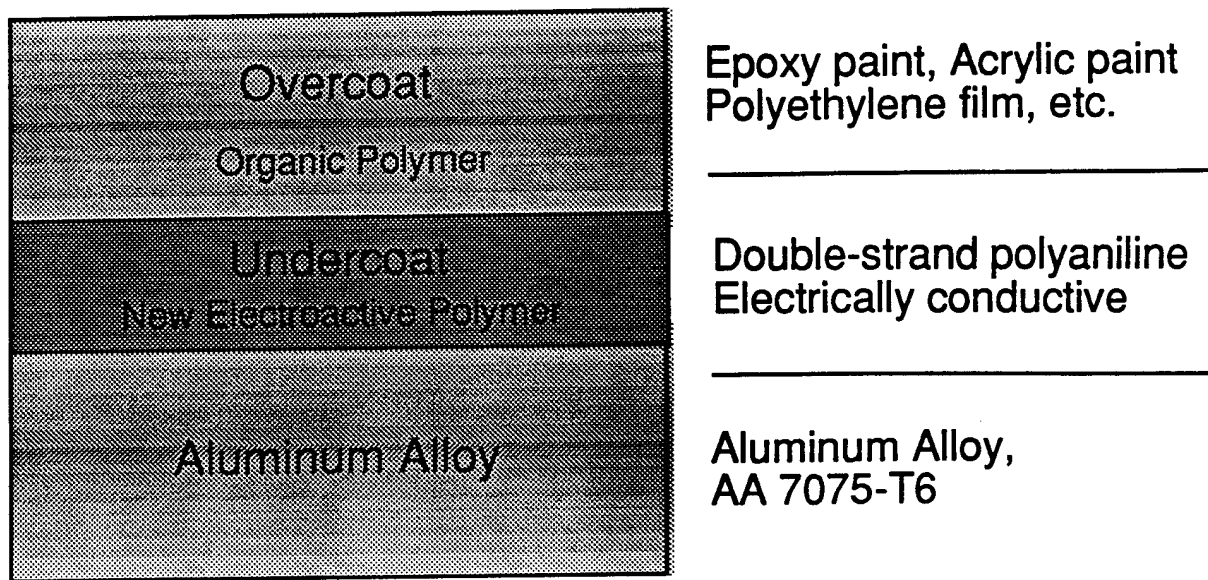


Figure 1. Artist drawing of a new primerless coating system with a double strand conductive polymer undercoat and an organic coating overcoat on a 7075 aluminum alloy.

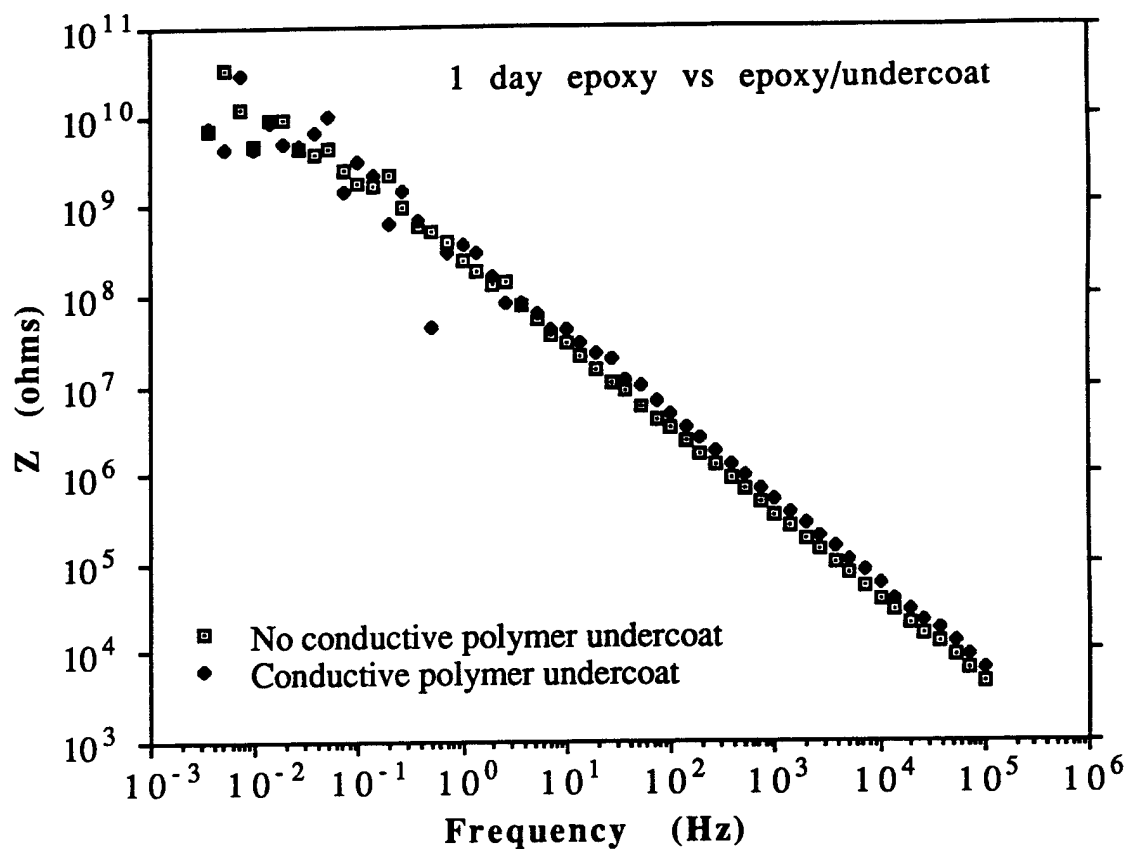


Figure 2. Bode plot results of conductive polymer undercoat with epoxy overcoat 7075 sample versus just an epoxy overcoat 7075 sample after one day under EIS testing in 0.5N NaCl.

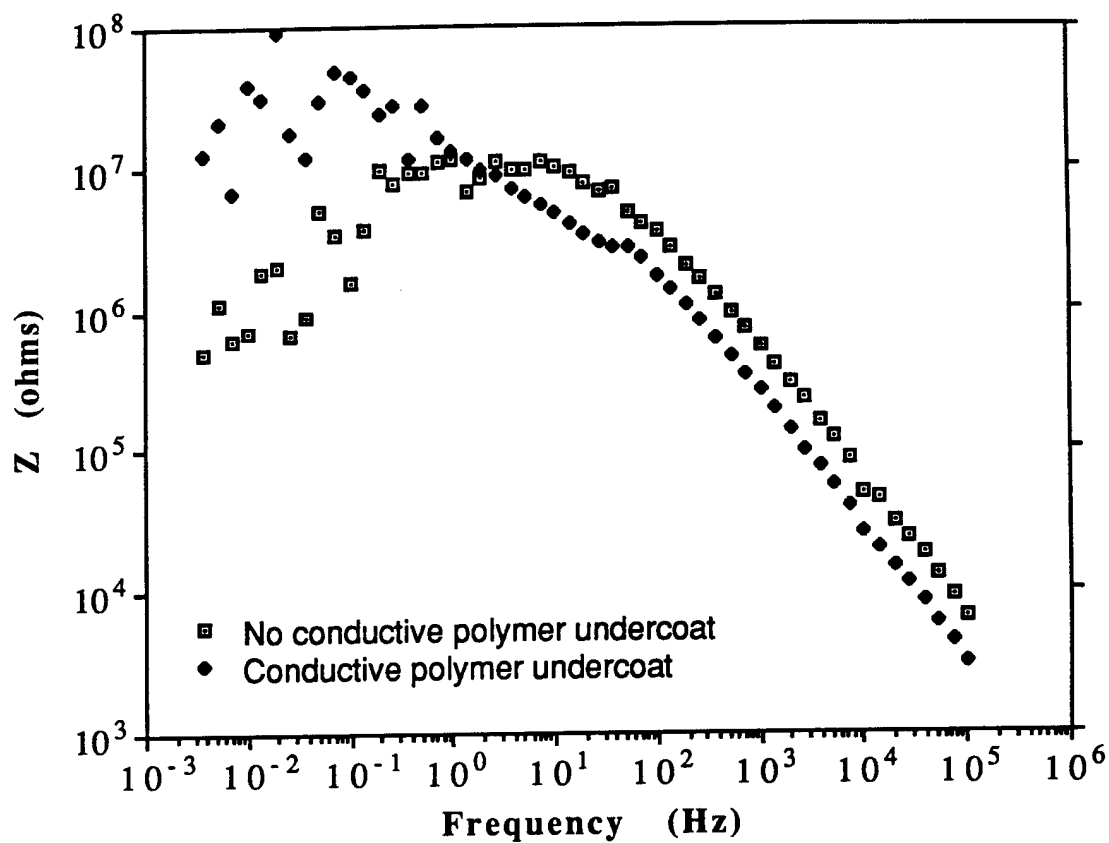


Figure 3. Bode plot results of conductive polymer undercoat with epoxy overcoat 7075 sample versus just an epoxy overcoat 7075 sample after four months under EIS testing in 0.5N NaCl.

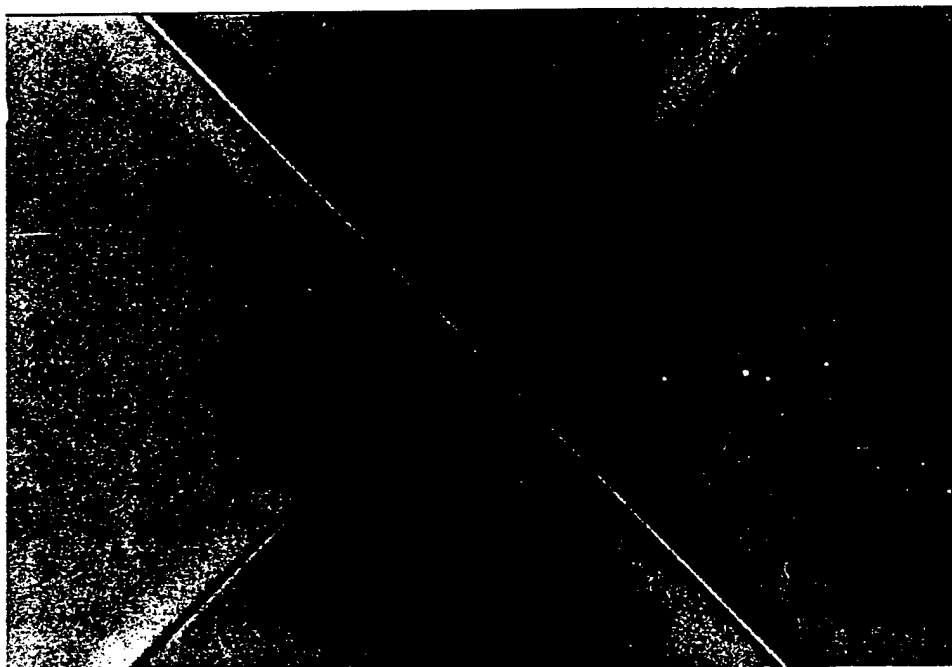


Figure 4. Scribed 7075 alloy with a double strand conductive polymer undercoat and a white epoxy spray paint overcoat after seven days in the salt spray chamber.

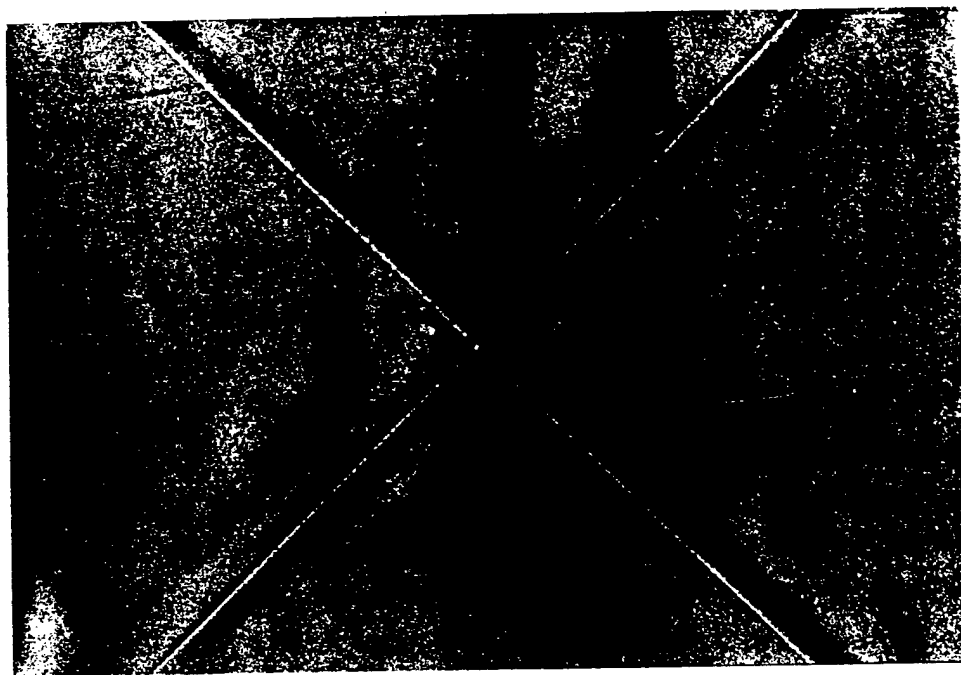


Figure 5. Scribed 7075 alloy with a white epoxy spray paint overcoat after seven days in the salt spray chamber.

CHAPTER VII

FUTURE WORK

Future work involves blending the double strand complex with various epoxies to develop a combined effect primerless coating system. Blends with the esterified complex and bisphenol A co epichlorohydrin glycidyl or polydiallyl isophthalate epoxies have been made. Initial tests under EIS and slat spray exposure have shown some promising results. The epoxy blends remain conductive after mixing with the conductive polymer and have shown to stop the de-protonation process of the double strand in pH environments higher than 6.0.

CHAPTER IX

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ABSTRACT

It is well known in the aircraft industry that the Environmental Protection Agency (EPA) has set guidelines for the eventual elimination of chromate conversion coatings for corrosion protection of aluminum alloys. The implications of these guidelines are serious and far reaching. They have initiated urgent development of a suitable replacement for chromate conversion coatings. Given the well known and documented excellent performance of the Alodine 600 and 1200 industrial chromate conversion coatings under cyclic polarization, impedance spectroscopy and ASTM B-117 salt spray tests, this is a difficult goal. To date nothing seems to be able to perform better or at least as equally as well as the chromates and have the same ease in applying the coating to the metal's surface.

However, conductive polymer coatings have the potential to perform as well as the chromates with further development work and offer an easy application method to the metal surface.

Around the mid 80's, the idea of using conductive polymer coatings for corrosion protection on steels started to surface in the literature. In fact, the first commercial application of conductive polymers was as a coating on the space shuttle launch pad under the guidance of Bernard Wessling at Zipperling Kessler. However, the information in the literature and our own testing has shown that the single strand polyaniline coatings are not effective in environments above a pH of 3.0. The small dopants will evaporate and the molecular dopants will segregate from the polyaniline backbone

upon aging. The polymer transforms to a less effective non-conductive blue colored form via the loss of a proton. Research conducted in the Chemistry Department at the University of Rhode Island has shown that the polymer coating must remain conductive to be effective in protecting the metal surface, for both steel and aluminum alloys. One suggested mechanism for protection is the polymer's conductive nature provides for an electroactive interaction with the metal surface to form a passivation layer between the metal surface and the polymer coating. This mechanism is the hypotheses for this dissertation. Therefore, its function is not as a barrier coating, as other polymer type coatings, but as a surface conversion agent, similar to the chromate coatings. Although these early results offer some interesting and useful applications in adverse acidic conditions, it is not helpful for more general applications, especially in marine environments where the pH is much higher, approaching a pH of 8.0.

The research towards this endeavor started with the development of a new conductive polymer compound, a double strand complex of polyaniline with a full range of different polyelectrolytes. This new compound is in the form of a twisted double helix, similar to DNA. The drive for this development was to improve the stability of the electroactive green colored form of polyaniline under heat, solvents and pH environments and improve the solubility characteristics of the polymer. Single strand polyaniline is not soluble except in strong acids and loses conductivity in solutions with a pH above 3.0. The double strand polyaniline complex can be modified with a large number of

different functional groups to render it soluble in any polar or non-polar solvents. Additionally, the double strand polymer remained conductive in solutions with pH's as high as 9.5. Unfortunately, this solution did not provide the best wetting, adhesion or corrosion protection as other coatings developed. The best protective coating developed to date has remained conductive at a pH of 6.0, which is at the boundary of the testing solutions pH's, a 0.5 N NaCl solution. The polymer coating changes slowly from the green color to the blue color over several weeks time frame. The polymer was shown to protect the metal surface via cyclic polarization, electrochemical impedance spectroscopy and salt spray testing prior to this color change. With the right chemical modifications, it is quite feasible to develop a conductive polymer coating that will remain conductive at higher pHs and still offer suitable wetting, adhesion and corrosion protection. When tested in salt environments with a pH below 4.0, the double strand coating offered excellent protection. In fact, the impedance data showed a one order of magnitude higher charge transfer resistance over Alodine 1200 on the AA2024-T3 aluminum alloy. This is to be expected as the chromate's oxide coating is soluble below a pH of 4.0. However, X-ray diffraction and XPS analysis on the conductive polymer coated samples show no formation of aluminum corrosion products on the alloy's surface after several months exposure to the acidic salt solutions and, upon removal of the film after testing, there is no evidence of pit formation on the alloy's surface.

These developments offer some exciting possibilities. The performance of the conductive polymer coatings, when maintained

in the green conductive state, warrants further investigations into these types of coatings. If a double strand complex can be developed that will remain conductive at higher pHs and offer the performance demonstrated at pHs below 4.0, then it is very reasonable to assume that an effective replacement for the chromate conversion coatings on aluminum alloys can be developed. As well, the double strand conductive polymer coating can be applied to the metal surface in an easy and industrially accepted method. Our research team at the University of Rhode Island is actively pursuing several approaches to solve the pH limitations. There are currently two approaches under way. The first is a chemical modification of the polyaniline backbone thorough substituted groups on the benzene ring of polyaniline. The goal of this work is to try to increase the pKa of the polyaniline strand. The other approach is to blend the conductive double strand complexes with various epoxies to slow down the de-protonation process of the polyaniline. This work could lead to a new primerless epoxy coating technology.