I, Zhangzhang Yin, hereby submit this original work as part of the requirements for the degree of:
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Development of an Environmentally Benign Anticorrosion Coating for Aluminum Alloy Using Green Pigments and Organofunctional Silanes

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This work and its defense approved by:
Committee Chair: William Vanooij, PhD

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William Vanooij, PhD

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Development of an Environmentally Benign Anticorrosion Coating for Aluminum Alloy Using Green Pigments and Organofunctional Silanes

A dissertation submitted to the Graduate School of the University of Cincinnati

In partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY (Ph.D.)

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By

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Aerospace aluminum alloys such as Al alloy 2024-T3 and 7075-T6 are subject to localized corrosion due to the existence of intermetallics containing Cu, Mg or Zn. Current protection measurement employs substantial use of chromate and high VOC organics, both of which are identified as environment and health hazards. The approach of this study is to utilize a combination of organofunctional silanes and a compatible inhibitor integrated into high-performance waterborne resins. First, an extensive pigment screening has been done to find replacements for chromates using the testing methodology for fast corrosion inhibition evaluation and pigment. Zinc phosphate and calcium zinc phosphomolybdate were found to have the best overall performance on Al alloys. Some new corrosion inhibitors were synthesized by chemical methods or modified by plasma polymerization for use in the coatings. Low-VOC, chromate-free primers (superprimer) were developed using these pigments with silane and acrylic-epoxy resins. The developed superprimer demonstrated good corrosion inhibition on aluminum substrates.

The functions of inhibitor and silane in the coating were investigated. Both silane and inhibitor are critical for the performance of the superprimer. Silane was found to improve the adhesion of the coating to the substrate and also facilitate corrosion prevention. Addition of zinc phosphate to the coating improved the resistance of a scratched area against corrosion. The microstructure of the acrylic-epoxy superprimer coating was studied. SEM/EDAX revealed that the superprimer has a self-assembled stratified double-layer structure which accounts for the strong anti-corrosion performance of the zinc phosphate pigment. Zinc phosphate leaches out from the coating to actively protect the scratched area. The leaching of pigment was confirmed in the ICP-MS analysis and the leaching rate was measured. Coating-metal interface and the scribe of coated panels subjected to corrosion test was studied. ToF-SIMS studies confirmed the presence of silane at the interface and the hydrolysis of the
silane. The abundant presence of silane was believed to improve the adhesion and also facilitate the corrosion prevention.

The protection mechanism of the acrylic-epoxy superprimer was proposed. The self-assembled double-layer structure of the acrylic-epoxy superprimer consist of a less-penetrable hydrophobic layer (epoxy-dominated) on the top and a hydrophilic layer (acrylic-dominated) accommodating the inhibitors underneath. This unique structure of the acrylic-epoxy accounts for the good protection of the coating. Furthermore, the inhibition mechanism of zinc phosphate was explored and compared to those which have been reported. Based on the protection mechanism of the superprimer, electrodeposition was explored in order to achieve a more organized coating with a better engineered metal/coating interface. The electrodeposited coatings were found to have higher barrier property and anticorrosion performance.
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Chapter 1 Introduction

1.1 Aluminum alloys and corrosion

Aluminum alloys are widely used in aerospace engineering because of their high strength and light weight. Aluminum alloy 7075-T6 (AA7075) and aluminum alloy 2024-T3 (AA2024) are the two most widely used alloys in aerospace. Like other common metals, aluminum alloys are susceptible to corrosion.

1.1.1 Susceptibility to corrosion of aluminum alloys

Pure aluminum is highly corrosion resistant because of the very rapid formation of a thin, compact and adherent oxide film on the surface that limits further corrosion. Alloying additions improve mechanical performance, however, reduce resistance to corrosion [1]. In an Al-Zn-Mg-Cu alloy such as AA7075, localized corrosion, e.g., pitting, is the major corrosion problem because the existence of Cu and Fe rich intermetallics. The most abundant intermetallics in AA7075 are Al$_7$Cu$_2$Fe and (Al,Cu)$_x$(Fe,Cu). Mg$_2$Si intermetallics are the third intermetallics in order of abundance [2]. Fig. 1.1 shows the intermetallics in AA7075. The intermetallics containing Cu and Fe are cathodic with respect to the matrix, while the intermetallics rich in Mg are anodic with respect to the matrix [3].

In an Al-Cu-Mg alloy like AA2024-T3, there are two major types of intermetallics particles. One is Al-Cu-Mg with an Al$_2$CuMg nominal composition. The other is Al-Cu-Fe-Mn with more complex and varying compositions which are principally (Cu, Mn, Fe) Al$_6$ and/or Cu$_2$FeAl$_2$. These two intermetallics, especially the Al$_2$CuMg particles (S phase), mainly attribute to the pitting corrosion of 2024-T3 alloy[4].
1.1.2 Corrosion of aluminum alloys

The Corrosion of a metal involves the dissolution of metal

\[ M \rightarrow M^{n+} + ne^- \]

and hydrogen or oxygen reduction depending on the pH of the electrolyte. The cathodic reactions occurring in specific condition are listed below:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] (Oxygen reduction in acid solution)
\[ 2H^+ + 2e^- \rightarrow H_2 \] (Hydrogen reduction reaction)
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] (Oxygen reduction in basic and neutral solution)
\[ M^{3+} + e^- \rightarrow M^{2+} \] (Metal ion reduction, e.g. Fe^{3+} + e^- \rightarrow Fe^{2+}) \[4].

Depending on how and where the metal is used corrosion can occurs in different forms. As a heterogeneous metal, aluminum alloys are susceptible to the following forms of corrosion:

- Uniform corrosion
- Pitting corrosion
- Crevice corrosion
- Filiform corrosion
- Intergranular corrosion
- Exfoliation corrosion
- Stress corrosion cracking
- Galvanic corrosion

In a neutral environment such as on the aircraft, pitting corrosion is one of the most common forms of aluminum alloy corrosion. Pitting corrosion is a localized form of corrosion that causes destructive pits. Pitting corrosion may be initialized when breakdown of a protective film (passive oxide film or organic coating) occurs [5]. There are three mechanisms proposed for the breakdown of passivity: the penetration mechanism, the film breaking mechanism and the
adsorption mechanism [6]. According to the penetration mechanism anions transfer through the oxide film to the metal surface where they start their specific action, as shown in Fig 1.2a. The film breaking mechanism requires the passive film to break to allow anions, e.g. Cl', to access the unprotected metal surface. The adsorption mechanism involves the adsorption of aggressive anions at the oxide surface which catalytically enhances the dissolution of metal anions from the oxide to the electrolyte and finally attenuates or even removes the protective oxide film.

Micro-flaws in the oxide film exist at the heterogeneity sites and potential differences exist between the intermetallics particles and the Al matrix [4]. These micro-flaws and the galvanic couples increase the vulnerability of aluminum alloys to pitting corrosion. Fig 1.3 shows the SEM image and the illustration of pitting of on Al-Li alloy.

1.2 Corrosion prevention by organic coatings and current industrial coating system

1.2.1 Protection of metal by coatings

In order for corrosion to occur all the following elements are imperative [7]:

- Water
- Oxygen or another reducible species
- A dissolution process at the anode
- A cathode site
- An electrolyte path between the anode and cathode

Without any of the above corrosion will not occur. All corrosion prevention measures are based on this mechanism. One or more elements listed above were suppressed in corrosion prevention. Specifically, the corrosion protection by using organic coating serves the following functions [7]:
• Acting as an effective barrier blocking corrosion reactants water and oxygen
• Creating a path of extremely high electrical impedance, thus inhibiting anode-cathode reactions
• Actively passivating the metal surface with the anticorrosion inhibitor contained in the coating
• Providing an alternative anode for the dissolution process

Normally a complete coating system comprises the primer, the intermediate coat and the top coat. The primer is considered the most important layer of the coating system as it directly adheres to the substrate. This requires the primer to be strongly bonded to both the substrate and the intermediate coat (if there is any) or the topcoat, and provide most of the corrosion protection.

For better adhesion and corrosion prevention performance, the metallic substrate normally is treated to form a conversion coating before applying the primer. The term “conversion coatings” is used to describe coatings in which the substrate metal provides ions that become part of the protective coating [8]. A Conversion coating is composed of corrosion resistant inorganic compounds produced by phosphating, chromating, oxidizing or anodizing. The functions of the conversion coatings include:

• To improve the adhesion between the substrate and the organic coating
• To obtain electrically insulting barrier lays
• To provide a uniform grease-free surface for the organic coating
• To provide active corrosion inhibition by reducing the rate of the oxygen reduction reaction, or by passivating the metallic substrate.

1.2.2 Organic coatings

All organic coatings are formulated with binder, pigment, addictives and carrier. The performance
of the coating varies dramatically with the selection of components.

**Binder**  The binder is normally carried by solvents and when the solvents evaporates binder forms the matrix of the coating. The performance and properties of the coating including anticorrosion, adhesion, chemical resistance, UV-resistance, flexibility, hardness, and water and oxygen transport are all determined to some extent by the binder used. The common binders used in the organic coatings are alkyds, epoxies, acrylics, polyurethane, polyesters, chlorinated rubber, or epoxy esters [7, 8].

Each type of binder has its own advantages and disadvantages. Binders are chosen based on what physical and chemical properties are desired for the specific application. Even for a particular type of binder, e.g. epoxies, there are a large number of them commercially available, varying in the molecular weights, functional groups, starting monomers, carrier, additive and other characteristics. Combinations of monomers and polymers are used as binder in some situations, even if the coating belongs to one generic polymer class. Two components coatings, which contain two kinds of binders belonging to different generic polymer class, are also widely used in order to get balanced properties [9].

**Pigment**  Pigments are added into coatings to provide color or to improve corrosion protection properties. This work mainly deals with corrosion inhibitive pigments. The introduction of pigments is elaborated in section 1.4.

**Additives**  The binder and pigment determines the anticorrosion and other major performances of the coatings. Additives are incorporated for film formation, manufacture, easy handling and application, and curing of a coating. Common additives added into modern coatings include flow and dispersion controllers, thixotropic agents, surfactants, dispersing agents, reactive reagents,
contra-environmental chemicals (such as antioxidants, light stabilizers, biocides, and antifouling agents), and special effect inducers (e.g. surface conditioners and olfactory controllers) [7].

**Carrier** The carrier is the vehicle in the uncured paint that carries the binder, the pigments, and the additive. In a conventional solvent-borne coating, the carrier, solvent, reduces the viscosity of the binder and other components so as to enable their homogeneous mixing and thin film formation. Before application the carrier helps to form a stable dispersion or emulsion of binder, pigments and additives in the solvent. This requires that solvents and components be fully compatible and repulsive forces exist between components to avoid clustering [9]. After application, partial solvent evaporates from the wet coating, and components attract each other and form a continuous film. Water is the carrier in the waterborne coatings. It will be elaborated in section 1.5.

### 1.2.3 Current aerospace coating and environmental issues

As shown in Fig. 1.4, a typical coating system currently used on aircraft aluminum alloys consists of conversion coating, primer coating and topcoat. Both primer and topcoat used on aerospace alloys are organic coatings consisting of binder, pigment, additives and carrier, but they are formulated differently to serve a different purpose. Primers accommodate pigments to provide active corrosion inhibition, help increase the water resistance and adhesion. Topcoats act as a barrier layer providing durability to the coating system by imparting improved abrasion resistance, hardness, and protection against sunlight, humidity, radiation or other environmental factors. Specifically, the conversion coating on military aircrafts generally is produced by Alodine™ 1200S or equivalent. The primer used is solvent-borne epoxy-polyamide primer compliant to primer MIL-PRF-23377 or MIL-PRF-85582 specifications. Alodine™ 1200S contains 30-60 wt.% chromic acid, and the primers contains around 20 wt.% strontium chromate and 340 g/l Volatile Organic Compounds (VOCs).
Cr(VI) is known as a strong carcinogen. It has been regulated directly or indirectly, under the broad objective of protecting human health and the environment, through a multitude of regulations controlling the release of chromium into air, land, and water [10].

VOCs can cause health effect including immediate symptoms such as normal eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans [11].

There are increasing urges to eliminate chromate and reduce VOCs from the coating system due to the increasing environmental awareness. This requires: 1) chromate pretreatment to be replaced with an environment-friendly process or chromate conversion coating to be eliminated without impair on the performance; 2) chromate inhibitor to be replaced with a less toxic alternative; 3) VOC content to be reduced to zero or a minimal level. The approach in this study is to replace the chromate conversion coating and solvent-borne chromate-containing primer with “superprimer” which is a one-step, low-VOC, chromate free primer. The concept of superprimer is elaborated in section 1.4.

### 1.3 Silane chemistry

Organofunctional silanes are hybrid organic-inorganic compounds having the general formula of $R'(\text{CH}_2)_n\text{Si(OR)}_3$ (where $R'$= organic functionality; and OR = hydrolysable alkoxy group, e.g., methoxy (OCH$_3$) or ethoxy (OC$_2$H$_5$)). Organofunctional silanes have emerged as outstanding, environmentally friendly anti-corrosion treatments for metal substrates and have shown the potential to replace the conventional chromate pretreatment [12].
Based on the number of Si(OR)\textsubscript{3} groups in a molecule, the silanes suitable for corrosion protection can be divided into two major categories, i.e., ‘mono-silanes’ and ‘bis-silanes’. Fig. 1.5 illustrates the structure of a mono-silane and a bis-silane. Examples of mono-silanes are vinyltriethoxysilane (VS, CH\textsubscript{2}CHSi(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}) and γ-ureidopropytriethoxysilane (γ-UPS, H\textsubscript{2}NCONH(CH\textsubscript{2})\textsubscript{3}Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}). Bis-silanes, with the general formula of (OR)\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{n}R’(CH\textsubscript{2})\textsubscript{n}Si(OR)\textsubscript{3}, are mainly used as crosslinkers for silane coupling agents. Examples of bis-silanes are bis-[3-(triethoxysilylpropyl)] ethane (BTSE, (OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{2}Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}), bis-[3-(triethoxysilyl) propyl]tetrasulfide (bis-sulfur silane, (OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{3}S\textsubscript{4}(CH\textsubscript{2})\textsubscript{3}Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3}), bis-[3-(trimethoxysilylpropyl)]amine (bis-amino silane, (OCH\textsubscript{3})\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{3}NH(CH\textsubscript{2})\textsubscript{3}Si(OCH\textsubscript{3})\textsubscript{3}) [12]. It has been observed that the bis-silanes offer a much better corrosion protection as pretreatment agents than the mono-silanes to various metals and alloys [13-17]. It is believed that the stronger interfacial adhesion and denser films of bis-silanes contribute to their much better corrosion performance on metals, as compared to mono-silanes, especially in unpainted state.

In the presence of water, the silane molecule hydrolyzes and forms silanols (SiOH). It is generally assumed that condensation reaction occurs between these silanols (SiOH) and the metal hydroxyls (MeOH) from the metal surface hydroxides (reaction (1)), and between silanols themselves (reaction (2)) [18].

\[
\text{SiOH(solution) + MeOH(metal surface) \rightarrow SiMe(interface) + H}_2\text{O} \quad \text{(1)}
\]
\[
\text{SiOH(solution) + SiOH(solution) \rightarrow SiOSi(silane film) + H}_2\text{O} \quad \text{(2)}
\]

This simplified condensation process is illustrated in Fig. 1.5. Ideally condensated bis-silane (i.e. silanes containing two organofunctional silane groups) that will form a network consisting of MeOSi and SiOSi covalent bonds, as shown in Fig. 1.6 [13].
Based on the hydrolysis and condensation mechanism silanes have been used as adhesion promoters for several years. Van Ooij et al. at the University of Cincinnati developed substrate pretreatment by a variety of silanes for corrosion protection as a greener alternative to the chromate pretreatment [19]. They showed that silanes, especially bis-silanes pretreatments protected a wide range of metal and alloys such as aluminum and steel alloys, against uniform, galvanic, pitting, crevice and stress corrosion.

1.4 Concept of superprimer

The superprimer concept was developed based the advance of application of organofunctional silane in corrosion inhibition by Van Ooij, et al. at the University of Cincinnati.

In the first stage bis-silanes, specifically mixtures were used as passivation treatment or as pre-paint treatment and silane pretreatments were able to provide a comparable corrosion inhibition to chromate pretreatment. It was also demonstrated that certain silane films can be used for intermediate media between a wide range of metal substrate and various polymer, paint, adhesive or rubber for corrosion inhibition or adhesion promotion [12, 20].

In the second stage it was demonstrated that silane pretreatment can be modified by the addition of inhibitors, nanoparticles or colorants for further improvement on corrosion protection, mechanical properties or visual detection [21].

In stage III, which this study is involved with, silane and primer were combined into a novel primer system that possess functions of both silane pretreatment layer and primer layer. Therefore no chromate conversion coating is required in this primer system. Further, in this study low-VOC or zero-VOC waterborne resins replaced conventional solvent-borne resins, and environment-
friendly inhibitors replace chromate pigments leading to a completely “green” primer system. Such coatings were termed ‘superprimers’. An illustration of superprimer coating system is shown in Fig. 1.7. The unique property of silanes, covalent bonding to the substrate, should be maintained but at the same time considerable film build is expected by the addition of the organic resin. Superprimers can thus be used as pretreatments, as primer, or as self-priming coatings.

The challenges for developing such a one-step and green primer system require:

1) Less toxic inhibitors which provides corrosion protection comparable to chromate and are compatible with waterborne resins.

2) Waterborne resin-compatible and properly working silanes. The silanes found most effective in corrosion protection are hydrophobic. In the superprimer system, silane should mix with other waterborne components well and it should form covalent bonds with the substrate. In addition, the silanes should not de-stabilize the resin dispersion.

3) Waterborne resins that can form a coating with curing rate and properties comparable to solvent-borne resins.

1.5 Pigment study

1.5.1 Pigment

Pigments are solid particle of low solubility incorporated in coatings for one or more of the following reasons [22]:

• to provide color and aesthetic effect
• to replace part of the resin and reduce cost
• to modify the application properties of a coating
• to improve the performance of the films.
Most industrial coatings contain corrosion-protective pigment to protect metal from various forms of corrosion. Based on protection mechanism, corrosion-protective pigments can be categorized into three types: inhibitive, sacrificial and barrier. This study mainly involves corrosion-inhibitive pigments which are the type used in aerospace coatings. For instance, zinc chromate and strontium chromate are the two pigments currently often used in aerospace coatings.

Coatings containing inhibitive pigments (which normally have a proper solubility) release soluble species, such as molybdates or chromates, from the pigment into the water that penetrates the coating. These species are carried to the metal surface via the water to protect the metal. Especially when the coating is scratched the exposed metal relies on the “active protection” from the pigment to prevent corrosion from occurring. The reaction or protection mechanism between the metal and pigment varies with the type of pigment. In most cases, the reaction is complicated and remains not understood completely [7]. Solubility and reactivity are critical parameters for inhibitive pigments.

Sacrificial pigments or galvanic pigments are metal particles that are non-noble relative to the metal substrate. On exposure, these particles (zinc dust on steel) corrode preferentially, while at the original metal surface only the cathodic reaction takes place, hereby the noble metal (original metal) is protected. Those sacrificial pigments, such as zinc, require large enough amount of pigment incorporated in the coating to ensure the flow of electric current. When in electrical contact with the steel surface, the zinc film acts as the anode of a large corrosion cell and protects the steel cathode [9]. Both inhibitive and sacrificial pigments are effective only in the layer immediately adjacent to the steel (i.e., the primer).

Barrier coatings are probably the oldest type of coating [23] and the requirements of their pigments are completely different. Barrier pigments are chemically intern and usually in a form
of flake or plate. Barrier coating can be used as topcoat, intermediate coat or even primer in a non-aggressive environment. This is because the barrier coating does not necessarily have to be coated directly onto the metal surface to facilitate the reaction between the pigment and the substrate.

1.5.2 Anodic and cathodic corrosion-inhibitive pigment

Chemically reactive corrosion-inhibitive pigments or inhibitors can be classified as anodic and cathodic according to their inhibition of the anodic or cathodic part of the corrosion reaction.

Anodic (passivating) inhibitors refers to those which can cause anodic shift of the corrosion potential, forcing the metallic surface into the passivation range [24]. Oxidizing anions such as chromate, nitrite and nitrate can passivate the metal to be protected without oxygen involved. Nonoxidizing anions such as phosphate, tungstate and molybdate require oxygen for the passivation process. Anodic inhibitors are the most effective and consequently the most widely used. However, while they reduce the anodic areas available on metal surfaces, they are rarely able to eliminate all potential corrosive regions, and pitting is likely. Because of this anodic inhibitors are called dangerous inhibitors [25].

Cathodic inhibitors can slow the cathodic reaction by chemically suppressing the reaction rate or by increasing the cathodic surface impedance and limit the diffusion of the reducible species, e.g. oxygen, to cathodic sites through selectively deposition on those area [24]. Specifically, cathodic inhibitors can provide inhibition by three different mechanisms: (1) as cathodic poisons, (2) as cathodic precipitates, and (3) as oxygen scavengers. Cathodic poisons, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Cathodic precipitators such as calcium, zinc, or magnesium ions, may be precipitated to
form a protective layer on the metal as the form of oxides. Oxygen scavengers prevent the cathodic depolarization caused by oxygen and hereby inhibit the corrosion.

1.5.3  Anticorrosion pigments

In this section major classes of inorganic inhibitive pigments for coatings will be discussed. The protection mechanisms of those pigments are explained though some of them are not well established.

1.5.3.1  Lead based paint

Lead is the oldest pigment used in the coatings. The protection mechanism of the red lead used in the lead-based paint is complex. Lead does not react with metal therefore it is not considered as a direct inhibitive pigment. Lead is able to react with certain type of resins and the by-product of the reaction is corrosion inhibitive [26].

The most prevailing explanation of the protection mechanism of lead based paint was proposed by Appleby and Mayne [27, 28]. When used in linseed oil-based paint, lead reacts with the components of the oil. in the presence of water and oxygen, these soaps degrade to, among other things, salts of a variety of mono- and di-basic aliphatic acids [29, 30]. Mayne and van Rooyen also showed that the lead salts of azelaic, suberic, and pelargonic acid were corrosion inhibitors for iron. The lead salts of azelaic, suberic, and pelargonic acid act as corrosion inhibitors; lead azelate is of particular importance in lead-based paint. These acids may inhibit corrosion by bringing about the formation of insoluble ferric salts, which reinforce the metal’s oxide film until it becomes impermeable to ferrous ions, thus suppressing the corrosion mechanism.

1.5.3.2  Chromates
Chromate pigment is the most effective and versatile inhibitor known. It is widely used as inhibitor of Fe, Al, Cu, and Zn corrosion. Chromate protects the metal from corrosion by stimulating the formation of passive layers on metal surfaces [31]. Svoboda described the protection mechanism of chromates as “a process which begins with physical adsorption which is transformed to chemisorption and leads to the formation of compounds which also contain trivalent chromium” [32]. \( \text{CrO}_4^{2-} \) is a typical oxidant passivator of the anodic and cathodic type, and passivates independent of dissolved oxygen [33]. In acidic environment, \( \text{Cr}_2\text{O}_7^{2-} \) is a strong oxidant with high standard potential, according to

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O},
\]

\( e^0 = 1.33\text{V at pH} \approx 2, e^0 \text{ standard potential (V)} \)

In the typical acidic/anodic medium, the redox reaction of \( \text{Cr}_2\text{O}_7^{2-} \) can occur in several different forms. For example the direct interaction with metal normally is

\[
6n\text{M}^0 + \text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ \rightarrow 6n\text{M}^{n+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

where \( \text{M}^0 \) can be Al, Fe, Zn, or, in the significant case of steel and near neutral pH conditions, further oxidation of previously formed oxide/hydroxide layers adherent to metal substrates [34]:

\[
6\text{FeO} + 2\text{CrO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 3\text{Fe}_2\text{O}_3 + 4\text{OH}^-
\]

In near neutral medium the redox reaction takes another form, producing protons, according to [35]:

\[
3\text{Fe}^{2+} + \text{HCrO}_4^{2-} + 8\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{Cr(OH)}_12 + 5\text{H}^+
\]

Whereas in alkaline medium, \( \text{CrO}_4^{2-} \) is significantly weaker with a lower standard potential:

\[
\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^-,
\]

\( e^0 = -0.13\text{V, } e^0 \text{ standard potential (V)} \)
In anodic environments metal cationic ions produced by corrosion processes further hydrolyze and forms hydroxides. Meanwhile in the chromate-inhibited corroding system hydrolysis of Cr\(^{3+}\) also occurs according to:

\[
\text{Cr}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 + 3\text{H}^+ \rightarrow \text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}
\]

and as a result, a layer of protective dense film which is composed of oxides and hydroxides forms on the surface of the substrate. The general composition of the film can be \(\text{M}_2\text{O}_3x/\text{Cr}_2\text{O}_3y\) or \(\text{M(OH)}_3x/\text{Cr(OH)}_3y\), where \(\text{M}^0 = \text{Fe, Al and x, y are variable}\). Hydrolysis processes produces \(\text{H}^+\), which are consumed, however, by redox reactions. It will also be apparent that Cr\(^{3+}\) species produced by several possible redox reactions, and the adherent character and the enhanced resistance to dissolution in diverse conditions of the resulting complex oxide films, are the distinctly unique features of \(\text{CrO}_4^{2-}\)-inhibitive mechanism [36].

Largin and Rosenfeld have proposed that chromates do not merely form a mixed oxide film at the metal surface; instead, they cause a change in the structure of the existing oxide film, accompanied by a considerable increase in the bond energy between the iron and oxygen atoms. This leads to an increase in the protective properties of the film [37].

The common chromate-based pigments are basic zinc potassium chromate (also known as \textit{zinc yellow} or \textit{zinc chrome}), strontium chromate, and zinc tetroxychromate, barium chromate and barium potassium chromate. The anticorrosion effectiveness of chromate pigment depends on its ability to dissolve and release chromate ions. The solubility of chromate pigment is controlled by selection of the cation.

Even though chromate is the most effective and economic pigment, chromate is disappearing due to the toxicity of hexavalent chromium [10].

\textbf{1.5.3.3 Molybdates}
Molybdates have long been used as corrosion pigment for Fe and Al. Molybdates are oxygen-dependent anodic type inhibitor [38]. MoO$_4^{2-}$ and CrO$_4^{2-}$ are isoelectronic and Mo and Cr have equal valence, therefore similar chemical behavior and protection mechanism are intuitively expected. However, the inhibition of MoO$_4^{2-}$ requires presence of oxygen and works effectively exclusively in moderately alkaline medium, where it is stable but practically redox inactive. This is because molybdates cannot promote spontaneous passivation of Fe due to lack of strong oxidizing ability. In a molybdate-inhibiting corrosion system, a primary passivator or oxidant, e.g. dissolved oxygen, must be present for the inhibitor to work [39]. It is generally accepted that in the molybdates-inhibited Fe system the formation of hydrated oxide films of modified compositions mainly contributes to the inhibition. In the presence of dissolved O$_2$, FeMoO$_4$ forms in MoO$_4^{2-}$ inhibited systems, which, incorporated into the outer layers of hydrated Fe$_2$O$_3$ films developed over actively corroding anodic sites, enhance the stability of the Fe$_2$O$_3$ film [25, 33, 34, 40].

It is also reported that MoO$_4^{2-}$ species adsorb on to the oxide film by ion-exchange mechanism, which make the oxide films cation-selective or practically impermeable to Fe$^{2+}$ and Cl$^{-}$ transport. As the result, the corrosion process is inhibited by a barrier effect [41].

MoO$_4^{2-}$ is not an effective corrosion inhibitor in weak acidic medium though in acidic condition it is redox active [42]. MoO$_2$, the reduced product of MoO$_4^{2-}$, does not form adherent protective film on the metal substrate. It also found that MoO$_4^{2-}$ is unstable in acidic conditions and forms iso-polymolybdic acid species according to:

$$7\text{MoO}_4^{2-} + 8\text{H}^+ \rightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$$

which are (and consequently MoO$_4^{2-}$ is) accredited with inhibitive activity of pitting corrosion [43]. As a consequence of the inhibition mechanism, molybdates are much less effective inhibitor than chromates are. However, molybdates are nontoxic and the cost is relatively low.
1.5.3.4 Phosphates

Phosphates are typical anodic type, oxygen-dependent inhibitors widely used on various metals. Due to hydrolysis, the action mechanism of orthophosphates is pH-dependent and only when $[\text{HPO}_4^{2-}] < [\text{PO}_4^{3-}]$ do ionic forms display inhibitive activity in alkaline conditions [44].

Zinc phosphate is the most important phosphate pigment. It can be used in a wide variety of binders due to its low solubility and reactivity. Zinc phosphate suits well in those in those where non-toxic basic pigments show limited stability, e.g. in alkyd binders with a high acid value, and in acid catalyzed systems or in waterborne binders [45]. The mechanism of zinc phosphate as pigment in coating for steel corrosion inhibition has been extensively studied but yet not well established. Several action mechanisms were proposed and some of them are controversial.

1) Phosphate ion donation

It is intuitive that zinc phosphate donates phosphate and forms insoluble salts with Fe. Fortunately, unlike molybdates, the precipitate of Fe and phosphate seems to adhere to the metal [46, 47]. As water penetrates through the coating, zinc phosphate dissolves in the water and at the same time slight hydrolysis occurs, resulting in some secondary phosphate ions. These phosphate ions may react with Fe and form a protective passive layer that, when sufficiently thick, prevents anodic corrosion. The approximate formula for the phosphatized metallic compound is $\text{Zn}_2\text{Fe(PO}_4\text{)}_2\cdot4\text{H}_2\text{O}$. Phosphate ion donation mechanism can be used for ferrous metals only [23].

2) Zinc phosphate re-deposition

Another simple explanation of the protection mechanism is the re-deposition of zinc phosphate. Zinc phosphate as the pigment dissolves when water permeates the coating and exists as the form of ions. When the solution reaches the metallic substrate $\text{Zn}^{2+}$ and $\text{PO}_4^{3-}$ ions slowly re-form as
phosphate on the metallic surface. It is thus proposed that an additional passivation of the surface takes place [23].

3) Formation of inhibitive metallic soap

The anticorrosive behavior of metallic soap has been related to the reaction between zinc phosphate and some acid resins [48, 49]. This reaction produces a metallic soap that acts as an anodic inhibitor. Similarly, Kaminski and others suggested [50] that zinc phosphate or the intermediate compounds formed when the zinc phosphate becomes hydrated and dissociates react with carboxylic and hydroxyl groups of certain oleoresinous binders, resulting in inhibitive complexes, which then react with corrosion products to form a tightly adhering, inhibitive layer on the substrate [51, 52].

4) Protective Film formation on the Anode

Pryor and others [53, 54] suggested this mechanism. Oxygen dissolved in the electrolyte is adsorbed onto Fe and forms a protective film of $\gamma$–Fe$_2$O$_3$ through a heterogeneous reaction. The thickness of the film is 20 nm at equilibrium. The film is able to prevent the outward diffusion of iron, resulting in inhibition of corrosion. Phosphate ions do not appear to directly contribute to the oxide film formation but rather act to complete or maintain it by plugging discontinuities with anion precipitates of Fe (III) ions. Romagnoli has noted that Pryor used soluble phosphates rather than the generally insoluble phosphates used in coatings, so care should be taken in extrapolating these results [55]. Other studies have found both oxyhydroxides and iron phosphates incorporated in the protective film [56].

5) Polarization of the Substrate

Clay and Cox [57] reported the polarization of the cathodic areas by low-solubility basic salts which are formed in presence of zinc phosphate in the electrolyte. The insoluble basic salts are
believed to consists of oxides (γ -Fe2O3), hydroxyoxides (γ -FeOOH, γ -FeOOH) and iron phosphate [58, 59]. The insoluble salt adheres to the metal surface and lowers the diffusion of dissolved oxygen toward the metal surface. A similar inhibition theory was reported by Szklarska-Smialowska and Mankowsky [60].

Some authors [45, 61, 62] are of the opinion that zinc phosphate hardly produces a passive layer due to its low solubility. Particularly in a medium with pH 6.5–8 the solubility of zinc phosphate is extremely weak. Its effect is insignificant, so that some authors [63] even think it acts only as an expensive extender. The mechanism of other phosphate pigments, such as aluminum triphosphate, calcium zinc phosphate, zinc polyphosphate and calcium phosphate, although not quite extensively investigated, is interpreted similarly as that of zinc phosphate [45].

Coatings, mostly solvent-based coatings, pigmented with zinc phosphate have been studied and at the same time compared to other pigments using various corrosion tests. When accelerated tests were used, the estimated inhibition effectiveness of zinc phosphate was lower than when long outdoor exposure tests was employed [45]. According to [64], the discrepancy between long and short tests data or accelerated test and real service life are due to the slow rate at which the zinc phosphate reaction takes place. However, other authors [64-66] attribute the discrepancy to the low solubility of zinc phosphate.

To improve the solubility of zinc phosphate modification was made by compounding zinc oxide and phosphor oxide with other metal oxides such as aluminum oxide. For synergism zinc phosphate may also be compound with other inhibitors, e.g. calcium borate. Those pigments are called the “second-generation” zinc phosphate pigments.

1.5.3.5 Silicates
Silicates are typical oxygen-dependent anodic type inhibitors, which works in two ways: a) by formation of insoluble precipitate with multivalent metal cations, and b) through their alkalinity, in oleoresinous binders, or by forming metal soaps with certain components of the vehicle [7, 33]. The precipitation mechanism of \((\text{SiO}_3^{2-})_n\), \(n>1\), however, is characteristically slow: it requires four weeks to establish protective function [67].

1.5.3.6 Zinc dust

Zinc dust is another traditional pigment that has been used for decades. Those paints containing zinc dust as pigment are called zinc-rich paints (ZRPs) and they have been use on protection for steel construction [68]. The zinc duct can be in flake form or less-expensive granular form. Zinc dust works on Fe via one or more of the following mechanism:

1) Cathodic protection to the steel substrate (the zinc acts as a sacrificial anode). This takes place at the beginning of the coating’s lifetime and naturally disappears with time [69].

2) Barrier action. As a result of the zinc sacrificially corroding, zinc ions are released into the coating. These ions can react with other species in the coating to form insoluble zinc salts. As they precipitate, these salts fill in the pores in the coating, reducing permeability of the film [68].

3) Oxygen reduction. Zinc reacts with the molecular oxygen diffusing through the coating toward the metal and forms a layer of ZnO and Zn(OH)2 [7].

4) Zinc corrodes as sacrificing pigment generating a mild alkaline which inhibits the corrosion of Fe [69].

1.5.3.7 Ferrites

Ferrite pigments have the general formula \(\text{MeO} \cdot \text{Fe}_2\text{O}_3\), where Me can be Mg, Ca, Sr, Ba, Fe, Zn, or Mn. They are synthesized by compounding and calcination of metal oxides at temperatures as high as 1000°C [7]. The principal reaction is:
\[ \text{MeO} + \text{Fe}_2\text{O}_3 \rightarrow \text{MeFe}_2\text{O}_4 \]

Compared to other pigment discussed above, ferrite pigments lack chemical reactivity. The protection mechanisms proposed include 1) creation of an alkaline environment at the metal surface by dissolving and hydrolysis of ferrite in water; 2) formation of metallic soap with certain binders [70, 71]. The protection mechanism of ferrites pigments is similar to that of red lead pigment. Therefore they can be used to overcoat aged lead-based paints.

**1.5.3.8 Calcium-exchanged silica**

Calcium-exchanged silica is prepared by an acid–base reaction between silane groups at silica gel surface and calcium ions in solution. Ca/silica is an alkaline pigment of low specific weight, with relatively high oil absorption when compared with other pigments. This last property allows the use of lower Ca/silica contents in comparison with other pigments to reach a given PVC. Technical bulletins indicate 3–7 wt.% for organic solvent-based paints and 1–4 wt.% for water-based paints as ideal contents [72].

Literature attributes three modes of action to Ca/silica: (i) ion exchange properties which would trap or delay the arrival of aggressive ions (e.g., \( \text{H}^+ \)) to the metal surface, releasing \( \text{Ca}^{2+} \); (ii) Ca/silica would interact with the binder, improving crosslinking; (iii) silica and calcium would become mobile in the coating during permeation process and once reaching the metal surface, they would form a protective film [72, 73].

**1.5.4 Pigment requirement**

Not all corrosion inhibitors are suitable for use in the coatings. One critical requirement for pigment is the solubility in water. If a coating uses a highly soluble pigment, it can act as a semi-permeable membrane under long-term moisture conditions, with water on one side and a
saturated solution of aqueous pigment extract on the other (at the substrate-coating interface). Significant osmotic forces thus lead to blister formation. A solubility in water < 2 g/100 ml is required for pigments. Soluble pigments are therefore not suitable for use in immersion conditions or conditions with long periods of condensation or other moisture exposure.

Other basic requirements for corrosion inhibitor pigments include:

- pH of saturated solution 7–9.5
- Specific gravity 1.5–5
- Particle size distribution average 2–6 µm
- Solubility in organic medium practically insoluble
- Vapor pressure at 20°C <1/10,000 mmHg
- Melting point >100°C

1.6 Waterborne coatings

Waterborne coatings emerged at the 1950’s when latex architectural paints were introduced [74]. The driving forces were initially better performance, easier clean up, and reduced fire hazards and later also the need for lower VOC. Today the use of waterborne coatings is larger than that of the solvent-borne coatings in volume. This trend is expected to continue with the regulation on VOC becoming stricter.

Waterborne coatings can be formulated to offer the best combination of benefits for a particular operation. Besides meeting EPA requirements, they can possess good to excellent properties such as hardness, stain resistance, flexibility and corrosion resistance. Waterborne coatings can have high gloss and excellent solvent and humidity resistance. Another advantage of waterborne coatings is their reduced fire hazard and soap and water clean-up. They are comparatively safe since the levels of flammable, and sometimes toxic, organic solvents are greatly reduced.
Applications where waterborne coatings fit best are where 0.1 to 1.2 mils dry film thickness is adequate. Suitable application techniques include spray, dip, flow or roller coating [75].

Waterborne coatings are not for every application. The cost of waterborne is normally higher than solvent-borne coatings. Because most waterborne coatings have amine in their formulas, they will have a different odor than conventional coatings. Shelf life of waterborne coatings is shorter. Stability is about six months before hydrolization takes place, due to a reaction with water in the formula. When humidity is high, waterborne coatings take longer to dry [75].

Solvent-borne coating can be as simple as a polymer dissolved in solvent system, in which case films forms by evaporation of the solvent. Due to the incompatibility of water and most large-molecule organics, waterborne paints are more complex and more difficult to formulate. Waterborne resins are not formulated simply by replacing the solvent in the solvent-borne resins by water. The whole system is brand new with polymer molecules differing from those in the solvent-borne coatings. However, most waterborne coatings still contain some organic solvent to facilitate resin manufacture, coating production and application, and film formation, though the trend is to eliminate the solvent completely.

As a solvent for the paints, water is different from organic solvents in many aspects that matter. As a consequence, waterborne paints are significantly difference from solvent-borne paints. The following differences between water and organic solvents are most important [7]:

1) Water does not dissolve the polymers that are used as resins in many paints. Therefore, the polymers have to be chemically altered so that they can be used as the backbones of paints. Functional groups, such as amines, sulphonyl groups, and carboxylic groups, are added to the resins to make them soluble or dispersible in water.

2) The latent heat of evaporation of water is much higher than that of organic solvents. As a
result, water evaporates more slowly from the wet coating. Furthermore a wide variety of solvents with different evaporation characteristics make fine-tune evaporation rates from wet solvent-borne coatings possible, while there are no other options with waterborne coatings.

3) The surface tension of water is higher than common organic solvents used in paints. This high surface tension plays an important part in the film formation of latexes. At the same time high surface tension brings paint wettability problem.

Water-reducible coatings and latex coatings are the two largest classes of waterborne coatings used. Smaller amounts of emulsion coatings are also used. Here Water-reducible refers to resins made in solvent and reduced with water to form a dispersion of resin in water. Sometimes they are also called aqueous dispersion resins or water-soluble resins, because the polymers are partially soluble in water. Latexes are the dispersions of solid polymer particles in water, while emulsions refer to dispersions of liquid polymer phase in liquids [22].

1.6.1 Water-reducible coatings

In water-soluble polymers or water-reducible coatings, the polymer molecules, which are naturally hydrophobic, are altered to become partially hydrophilic. This is done by graft of hydrophilic segments, e.g. carboxylic acid groups, sulphonic acid groups, and tertiary amines, onto the polymer chain [7]. Low molecular weight amines are added into the paint to at least partially neutralize the water-soluble polymers containing acid groups.

In water-reducible coatings, the polymer starts out as a solution in an organic solvent that is miscible with water. Water is then added. The hydrophobic polymer separates into colloid particles, and the hydrophilic segments stabilize the colloids [76]. Therefore water-reducible coatings always contain certain amount of organic solvent. Water-soluble polymers are designed
to be directly soluble in water so no organic solvent is needed from the beginning. The drying of the water-soluble polymer then can be as simple as those solvent-borne coating mentioned above in which the drying is the consequence of solvent evaporation.

Waterborne paints neutralized by amines display a characteristic viscosity change when diluted with water. With water being added the viscosity normally experience a rapid drop initially, and then a plateaus, an increases and then finally rapid drop. The solid content of the paint with viscosity in the applicable range are normally lower than the solid content of solvent-borne coatings. Unlike the viscosity of the organic solvent solution of resin which is simply Newtonian, the viscosity of waterborne paint is shear thinning in the region of the peak or plateau. While the viscosity of the organic solvent solution of resin is Newtonian, the viscosity of the water-diluted system is more complex. In the region of the peak or plateau the viscosity is highly shear thinning and when diluted to applicable range it becomes only slightly shear thinning [74].

Most types of resins can be made water-reducible after chemical modification. The most widely available water-reducible resin is acrylics with both carboxylic acid and hydroxy functionality. Water-reducible polyesters are used, but their hydrolytic stability is limited and low molecular weight cyclic oligomers can volatilize in baking ovens. Since polyesters can be synthesized in the absence of solvent, it is possible to make solvent-free dispersions [2]. The resin is cast as a solid, is pulverized, and is stored as a solid until needed, delaying possible hydrolysis. When a coating is to be made, the powdered resin is stirred into a hot aqueous solution of dimethylaminoethanol to make a dispersion. Water-reducible alkyds are fairly popular in Europe, but their use is limited because of the difficulty in achieving adequate saponification resistance for package stability. Water-reducible epoxy esters and uralkyds have better hydrolytic stability. Water-reducible urethanes have superior saponification resistance and a minimum of cyclic oligomers. Solvent-
free and low solvent water-reducible urethanes have also been reported [3]. Urethane resins can give films with excellent properties, but are generally more expensive than acrylic resins.

Water-reducible coatings have their advantage and limitations when compared to other types of coatings [74]. First, since the viscosity at application dilution is almost independent of molecular weight, the high molecular weight can be used in water-reducible coatings. The molecular weight can be as high as that of resins used in conventional solution thermosetting coatings. A disadvantage is that the solid content of the paint with viscosity in application range is low. Typically, the non-volatile matter by volume (NVV) of the paint suitable for application by spraying, roll coating, or curtain coating is around 20 to 30. In order to get the same film thickness, a thicker film is needed with low NVV. However, low NVV can be also an advantage in some situations, such as in automotive metallic coatings, where a thicker wet film results in better orientation of the aluminum pigment flakes in the film.

1.6.2 Latex coatings [7]

Latexes have been used for many years in architectural coatings and are the major type of vehicle for these coatings. For certain household applications, such as flat wall paint, the advantages of latex paints over any solvent-borne paint are so large that solvent-borne paints are seldom marketed. Important advantages of interior latex paints include rapid drying, low solvent odor, absence of odor of oxidation by-products of drying oils and alkyds, easy cleanup, reduced fire hazard, and better long term retention of mechanical properties. For exterior paints, a major advantage is superior exterior durability of high-performance latex paints relative to drying oil or alkyd paints. On wood siding, blistering is reduced, since the latex films are more permeable to water vapor. On the other hand, adhesion of latex paints to chalky surfaces is inferior to that of solvent-borne paints
1.6.3 Emulsion coatings

In an emulsion coating, a liquid polymer is dispersed in water. Many alkyd and epoxy paints are examples of this type of coating. In aqueous dispersion coatings, the polymer is not water-soluble at all. Rather, it exists as a dispersion or latex of very fine (50 to 500 nm diameter) solid particles in water. It should be noted that merely creating solid polymer particles in organic solvent, removing the solvent, and then adding the particles to water does not produce aqueous dispersion coatings. For these coatings, the polymers must be produced in water from the start. Most forms of latex begin as emulsions of the polymer building blocks and then undergo polymerization. Polyurethane dispersions, on the other hand, are produced by polycondensation of aqueous building blocks [3].

Although most waterborne coatings are based on water-reducible or latex binders, emulsion coatings have found some applications and may have potential for wider use.

Two package coatings in which one package is a BPA (or novolac) epoxy resin solution and the second is an amine-terminated cross-linking agent which contains a nonionic surfactant have had significant commercial applications [22–24]. The amine cross-linker package is diluted with water, and the epoxy resin solution package is added with vigorous stirring. The pot life is limited to a few hours, since the epoxy resin can react not only with the amine groups, but also, slowly, with water. Although pot life of solvent-borne epoxy–amine coatings is limited by viscosity increase, emulsion systems show little, if any, change in viscosity with age, since the viscosity is controlled by internal phase concentration, not by molecular weight, and because reaction with water does not lead to cross-linking. Instead, pot life is limited by reduced gloss of applied coatings or by inferior film properties. Such emulsion epoxy paints are used where hard, easily cleaned wall coatings are needed, for example, in hospitals and food processing plants. The residual surfactant reduces the corrosion protective properties for application to metal surfaces.
Emulsion coatings based on aliphatic epoxy resins and aliphatic carboxylic acid-functional resins are reported to give superior pot life and improved properties [25].

### 1.6.4 Acrylic-epoxy coatings

Waterborne two component acrylic-epoxy coatings are gaining popularity due to their attractive handling, application and performance properties, along with their low solvent content and odor, long pot life and short dry times while displaying a range of chemical resistance and physical properties [77].

These are two component coatings, with one component containing a carboxyl-functional acrylic latex, and the other component containing an epoxy emulsion. Upon mixing, cure is believed to proceed via carboxyl-epoxy reaction and / or epoxy homopolymerization. It is interesting that although these reactions usually proceed slowly under ambient conditions, the applied coating has attractive properties. The resulting crosslinked system is responsible for upgraded performance over acrylic latex coatings in properties such as hardness, mar, abrasion resistance, chemical resistance, and water resistance. These coatings also display faster dry and improved exterior durability over many epoxyamine based systems. Other attractive features include low organic solvent content and low odor [78].

Therefore, acrylic-epoxy coatings are finding utility as topcoats in moderate duty industrial as well as high performance architectural applications. Examples of the latter applications are institutional (e.g., schools, locker areas, laboratories, etc.) wall surfaces of metal, masonry, plaster and gypsum wallboard. References 1-5 provide additional information on the history, chemistry and traditional performance of waterborne acrylic-epoxy coatings.
Both liquid epoxy resin emulsions and solid epoxy resin dispersions in water can be used to crosslink these systems. Liquid epoxy resins are lower molecular weight systems emulsified in water with the aid of a surfactant. Because of their relatively low molecular weight and viscosity, these systems exhibit good handling, flow, and coalescence, with little or no coalescing solvent; however, they usually take longer to dry, especially dry hard. Solid epoxy dispersions are dispersed particles of higher molecular weight, solid epoxy resin in water. These systems usually dry faster but they contain 10% co-solvent to aid processing, assist flow, and permit coalescence of the film. From this description, the tradeoffs between liquid epoxy and solid epoxy resins in coating formulations are obvious [77].

1.7 Plasma technique [79]

In this study the plasma technique was used to modify the pigments with higher solubility to prevent blistering occurring. The plasma technique is widely used in materials fabrication. Examples of plasma application include plasma etch, plasma deposition, plasma grafting and plasma spray.

1.7.1 The plasma state

The plasma state is called the fourth state of matter, after solid, liquid and gas. The plasma state exists in nature and the examples are aurora borealis and the polar lights. When a gas is put into an alternating electromagnetic field, molecules trapped within this oscillating field attempt to flip flop in unison with the alternating current. At some point the flip-flopping becomes so great, or excited, that electrons are shed and the molecule is ionized, thereby establishing a plasma. Therefore, a plasma is a partially ionized gas and contains free electrons, cations and excited molecules [29, 80].
The energy required by the creation of a plasma can be from different sources. Alternating current (50 Hz), audio frequency (kHz), radio frequency (MHz) and microwave plasmas (GHz) are the common sources of energy. Plasma can also be generated by a direct current (DC). Those different forms of power generate an electric field, which accelerates the free electrons among the gas molecules. When these free electrons inelastically collide with molecules or atoms, ionization occurs [81]. Inelastic collisions between particle pairs lead to further ionization, thereby causing the initiation of a plasma state. The plasma is characterized by a plasma glow. The molecules that have lost their electrons are unstable or metastable. These unstable and metastable species may attack anything in their environment in an attempt to become whole again. After that they fall back to their base state and emit their excessive energy as photons, resulting in a plasma glow. Each gas has a unique color for specific pressure regimes.

Plasmas are easier to generate and maintain at low pressures (1 Pa to 100 Pa) than at normal atmospheric pressure (100 kPa). At low pressure or high vacuum situation, the charged particles are able to travel longer free mean free paths without collision with other particles, and over longer distances the charged particles can be accelerated and shed with greater energy.

The modern materials engineering techniques which involve plasma include implantation, sputtering, etching, physical and chemical deposition, arc evaporation and e-beam. Their basic mechanism is illustrated in Fig. 9 [82].

1.7.2 Plasma polymerization process and mechanism

In the plasma state, organic monomer forms thin polymer films on surface in contact with the plasma via a polymerization process. This special polymerization process is called plasma polymerization. The deposited thin film is organic in nature. The plasma energy disassociates the monomer molecules into ions, electrons and radicals, which link to each other or to the surface,
finally resulting in larger molecules. The larger molecules constitute thin polymer films at the surface of the substrate.

The unique characteristic of plasma polymerization process is that there is no necessity for a functional group such as a double bond in the monomer to initiate polymerization like conventional polymerization. Most of the reactions in plasma polymerization are reactions between two reactive species. Some other reactions are between an activated species and a molecule, which are essentially the same as the propagation reaction of the conventional addition polymerization. Therefore, plasma-polymerized film usually does not contain repeating units like conventional polymers, as the films are deposited from different entities, created by the fragmentation of the monomer [83]. Also, different from conventional polymer, plasma polymerized polymers are highly crosslinked, as illustrated in Fig. 11.

Several plasma polymerization mechanisms have been proposed and a popular one is by Yasuda [84]. His theory is called rapid step growth polymerization (RSGP), also known as the activation-growth model, which can be described as:

\[
(M^* \_m + M^* \_n \rightarrow M_{m+n}) \times N
\]

Where \(N\) is the number of repetitions of similar reactions and \(M^*\) is the reactive chain carrying species produced in the plasma from monomer \(M\). The subscripts \(m\) and \(n\) indicate the size of the involved species. Figure 1.8 describes the RSGP process in detail, where \(i\), \(j\) and \(k\) merely indicate the difference in the size of species. The overall reaction contains two major routes of rapid step growth. Cycle 1 is via the repeated activation of the reaction products from monofunctional activated species and cycle 2 is via difunctional or multifunctional activated species, designated by \(*M^*\). Both these cycles play important roles in the plasma process.
Reaction (1) and (4) are similar and correspond to propagation by addition. Reaction (2) and (5) correspond to termination by recombination, though the end product of (5) is a bifunctional entity. These functional species may either be ionic or free radicals depending on factors like the plasma parameters and the nature of the gas. If the plasma of the gaseous pre-cursor contains negative ions (e.g. chlorine, oxygen etc.) then ionic species will contribute to the polymerization process. The ionization energies (energy required for breaking bonds and then ionizing the molecules) of organic molecules are very high (> 10 eV) due to which the plasma energy is sufficient enough only to produce free radicals which initiate polymerization reactions.

The advantage of plasma polymerization include [80]:

- Good adhesion can be easily achieved on a wide variety of surface;
- The process eliminates solvents and is environmentally benign;
- The properties of films can be easily tailored by changing the process conditions such as power input, system pressure and treatment duration;
- The plasma film is highly cross-linked there for it has good chemical and corrosion resistance and low permeability;
- Plasma polymerized film can be deposited to any forms of substrate including uneven surface, fibers, flakes and powders.

These advantages, especially its capability of treating various forms of materials make plasma technique more and more popular in material tailoring. Conventionally plasma technique is used to treat fiber or materials with flat surfaces. Van Ooij, et al at the University of Cincinnati has been using the plasma polymerization to tailor the surface of powders to acquire desired properties [80, 85-87]. The treated powders included silica, carbon black and anticorrosion pigments. The powders were used as the filler in rubber or pigment in the coatings.
1.8 Electrodeposition

Electrodeposition was experimented as the application method for the superprimer. Electrodeposition is a popular application method for waterborne coatings which can be a primer or single or two coat systems. Electrodeposition coating, which also called E-coat, electrocoat, electropaint, ED, and ELPO, is high performance coating used on a wide variety of products. Examples of primers by electrodeposition include almost all new cars and many appliances. Aluminum extrusions, drapery fixtures, metal toy trucks, and steel furniture are a few of many examples of single-coat electrodeposition applications [88].

Electrodeposition coating systems can be anionic or cationic, alternatively anodic or cathodic, which corresponds to deposition at the anode or cathode, respectively. In anionic systems, the particles dispersed in water are negatively charged and the object to be coated is the anode of the electrochemical cell. When the voltage is applied to the object particles of coating are electrophoretically attracted to the anode. There the particles precipitate in the presence of hydrogen ions which are the product of electrolysis of water. For cationic coating, the process is similar with charge of the particles and object to be coated changed and particles precipitate in the presence of hydroxide ions [74].

One of the well-developed electrodeposition coating system is E-coat. E-coat solution consists of stabilized emulsion of organic resins in DI water, as well as some solvent and ionic components. In the process of E-coating, electrolysis of water occurs when a DC voltage is applied, which consumes H⁺ and OH⁻ at the anodic and cathodic electrodes, resulting in the pH variations in the solution. The variation of the pH across the anodic and cathodic electrodes is illustrated in Fig. 12; the cathode become alkaline and the anode to become acid. The pH change de-stabilizes the E-coat elulsion of the solution and they coagulate onto the appropriate electrode. Cathodics
electropaints are stable except at high (alkaline) pH and anodics are stable except at low (acid) pH [89]. A typical E-coat system is shown in Fig. 1.13.

An electrodeposition coating bath is normally diluted to 10 to 20% solids with water. This relatively low solids is mainly for the consideration of cost. When the coated object is taken out from the tank after electrodeposition, it must be rinsed to remove the layer of bath liquid adheres to the deposited coating. If the solid content is low, the loss will be lower and also rinsing will be easier. In addition, the electrodeposition tanks for automotive or appliance can be as large as 500,000 L. Lower solid content reduces cost of the bath.

There are two critical requirements for the electrodeposition coatings [74]. First, the coatings must be designed so that all coating components are attracted to the electrode at the same rate. Otherwise, variation of the composition will occurs and the quality of the coating will be compromised. A vehicle in which pigments can be dispersed and cross-linkers dissolved must form a stable, electrically charged dispersion of aggregate particles when diluted with water. The pigment must be preferentially wet by the resin so that it does not migrate out of the resin aggregates. Second, electrodeposition coatings must be able to maintain indefinite stability after dilution. As the electrodeposition bath is being used, coating solids are removed from the aqueous dispersion, and the bath needs to be refilled continually to maintain the same composition in the tank. Other requirements includes resistance to oxidizers, hydrolysis and mechanical agitation as the bath should be able to last for an extended period of time. In addition, the crosslinker must be stable in the diluted coating at a pH over 7 for anionic coatings and under 7 for cationic coatings.

Electrodeposition coatings have their advantages and limitations of electrodeposition compared to conventional application means [74].

1) Electrodeposition is a highly automated process which greatly saves labor compared to
other applications. Also electrodeposition reduces cost by eliminating the paint losses from overspray. The economic advantage of the combination of these factors is large in assembly line operations. However, the capital cost of the automated line is high, limiting applicability of highly automated lines to large production operations.

2) Solvent content of E-coats is relatively low, so VOC emissions are low and fire hazard is reduced. Another environmental advantage over spray applied coatings is that there is no overspray sludge disposal.

3) The flash off time before entering the oven is reduced to 3 to 5 minute because of the solids of E-coat are high, compared to spray applied coatings.

4) Complete coverage is another major advantage of electrodeposition over other application methods, when throw power is ensured. The film thickness may vary in some areas such as recessed areas and edges but the entire surface will be coated, which is difficult to be accomplished by other ways.

5) When heated in the oven, sagging can occur on the electrodeposited coatings, but due to the high solid content/high viscosity nature of the electrodeposited coating, sagging can be less compared to sprayed or dip-coated coatings.

6) Compared to the conventional dip-coating, electrodeposition can relatively reduce the difference in coating thickness between the coating on the top and bottom of the coated object.

7) A possible problem associated with electrodeposited primers is the adhesion of the
topcoat to the surface of the primers. The surface of electrodeposited is relatively glossy and smooth, which makes good adhesion hard to achieve. Adhesion is also affected by the cross-link density of the E-coat and overbaking can result in poor intercoat adhesion.

8) The large volume of the electrodeposition bath makes the formulation changeovers difficult, which is also a problem with all dipping systems.

9) A major limitation associated with the electrodeposition is the requirement that the substrate must be conductive. Electrodeposition is mostly used for metal primers and one-coat metal coatings. Two-coat applications were rarely used and require the first layer of coating to be conductive.

1.9 Thesis objective – summary

The objective of this study is to evaluate the effectiveness of potential corrosion inhibitors on aluminum alloys, find or fabricate less toxic inhibitors to replace chromate, and use those pigments together with organofunctional silane and binders to develop an environment-benign primer for aluminum alloys. The performance of those coatings should be comparable to solvent-based chromate containing coating.

The scope of the work includes:

a) establish an effective testing methodology for corrosion inhibition evaluation and pigment screening
b) Based the result of a), investigate potential inhibitive species and find or fabricate a pigment, compound or mixture as the inhibitor for Al alloys
c) Incorporate the inhibitors into silane-containing waterborne coatings and evaluate the performance of the coating
d) Investigate the functions of inhibitor and silane in the coating

e) Study how the coating protects aluminum alloys, microscopically and macroscopically

f) Study how the corrosion inhibitor actively protects the defect of the coating, e.g., a scribe

g) Explore the possibility of engineering a more organized coating structure based on the protection mechanism of the coating and unique hydrolyzation and precipitation behavior of silane, using the techniques such as electrodeposition.
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Chapter 2 Experimental

2.1 Materials

2.1.1 Metal substrates

AA7075-T6 and AA 2024-T3 aerospace alloys were used in this study. The panels were obtained from Steel Metals and Supply Co., Stillwater, OK, in 15 cm x 10 cm x 0.2 cm size.

2.1.2 Pigments

Potentially corrosion-inhibitive chemicals, magnesium molybdate, dibasic sodium orthophosphate, cerium chloride, cerium acetate, lanthanum acetate, cerium vanadate, sodium vanadate, cerium acetate, zinc sulfate, lanthanum nitrite, sodium metasilicate, cerium metasilicate, benzotriazole and zinc phosphate were acquired from Alfa Aesar, Ward Dill, MA.

*Cortec M381* a water-based corrosion inhibitor was acquired from Cortec Corp. St. Paul, MN

A series of modified phosphate inhibitors, such as CaO·ZnO·MoO₃, CaOZnO·P₂O₅·MoO₃, ZnO·Al₂O₃·MoO₃·P₂O₅, ZnO·Al₂O₃·SrO·P₂O₅·SiO₂, ZnO·Al₂O₃·SrO·P₂O₅·SiO₂, CaO·Al₂O₃·SrO·P₂O₅·SiO₂ and BaO·P₂O₅·SiO₂ were acquired from Heuco Tech Ltd, Fairless Hills, PA.

*Hydrotalcite vanadate* (HTV) was a corrosion inhibitor prepared by Dr. Rudolph G. Buchheit’s group at the Ohio State University through anion-exchange of hydrotalcite-like compounds with vanadates.

*Barium chromate*, which was used as corrosion inhibitor control, was acquired from Fisher
2.1.3 Organofunctional silanes

*Bis-sulfur silane* or bis [3-(triethoxysilyl) propyl] tetrasulfide was obtained from GE Silicones, Wilton, CT; product name: Silquest® A1289. The chemical structure of bis-sulfur silane is shown in Fig. 2.1.

*BTSE* or bis-[triethoxysilyl] ethane, was obtained from GE Silicones, Wilton, CT; product name: Silquest® Y 9805. The chemical structure of BTSE is shown in Fig. 2.2.

2.1.4 Resins for the superprimer formulation

A few waterborne acrylic dispersion and epoxy resins were used for development of the superprimer coatings.

*ECO-CRYL™ 9790*, an acrylic resin dispersion, was acquired from Resolution Performance Products, Houston, TX. ECO-CRYL™ 9790 is a preneutralized, water dispersed acrylic resin, consisting of 42 wt % of anionic dispersion of an acrylate copolymer in water, 3 wt % of triethylamine, 3 wt % of xylene and 7 wt % of propoxy ethanol. This resin was designed for use with liquid epoxy resins in the manufacture of two-package, high performance, ambient cure and thermoset water reducible coatings [1].

*NeoCryl A-6037*, a high solids styrene/acrylic copolymer emulsion was acquired from DSM Neo-Resins, Wilmington, MA. NeoCryl A-6037 consists of 49.8 wt % water, 36 wt % styrene polymer and 12 wt % styrene acrylic copolymer. Other solvents and additives include polyoxyethylene, octylphenol, diethylene glycol monoethyl ether (DGME) and ammonia. A-6037
can be used to formulate clear and pigmented industrial coatings for metal and wood substrates as well as clear overprint varnishes and printing inks for Graphic Arts. Formulations based on NeoCryl A-6037 exhibit high gloss, excellent hardness and block resistance, and good water soak resistance [2].

NeoCryl A-6085, an aqueous, low particle size acrylic copolymer designed for coatings that require outstanding corrosion, water, and humidity resistance at low film thicknesses, was acquired from DSM Neo-Resins, Wilmington, MA. It consists of 39.5 wt % of styrene acrylic copolymer, 60 wt % of water, 0.5 wt % of Ammonia and < 0.2 wt % of styrene. Total solids by weight is 40% and VOC is zero. Coatings formulated with NeoCryl A-6085 generally exhibit high gloss, good chemical, and excellent impact resistance [3].

NeoCryl A-633, an aqueous acrylic copolymer emulsion designed for air dry and forced air coatings for architectural and industrial applications, was acquired from DSM Neo-Resins, Wilmington, MA. It consists of 39.5 wt % of styrene acrylic copolymer, 60 wt % of water, 0.50 wt % of Ammonia and < 0.2 wt % of styrene. Total solids by weight is 42% and VOC was zero. A-633 offers a unique balance of adhesion, chemical resistance and corrosion resistance [4].

NeoCryl A-6115, a water-borne self-crosslinking acrylic copolymer, was acquired from DSM Neo-Resins, Wilmington, MA. It consist of 43.7 wt % of acrylic copolymer, 55 wt % of water, 0.1 wt % of ammonia, < 0.2 wt % of styrene and < 0.001 acrylonitrile. Total solids by weight is 42% and VOC is zero. NeoCryl A-6115 can be formulated into coatings that exhibit an excellent balance of properties. Formulations based on NeoCryl A- 6115 exhibit chemical resistance, hardness and adhesion to a wide variety of plastics [5].
NeoCryl A-6109, a pre-coalesced aqueous acrylic copolymer, was acquired from DSM Neo-Resins, Wilmington, MA. It was especially designed for coatings that require high gloss with excellent corrosion resistance at low film thickness. It consists of 32.1 wt % of styrene acrylic copolymer, 52 wt % of water, 4.6 wt % of modified bisphenol A-epichlorohydrin, 4.1 wt % of dipropylene glycol butoxy ether, 1.6 wt % of dipropylene glycol dibenzoate, 1.6 wt % of calcium alkylaryl sulfonate, 1.6 wt % of propylene glycol butyl ether, 0.8 wt % of 2-propoxyethanol and 0.3 wt % of Ammonia. Total solids by weight is 33% and VOC is 192 g/l. NeoCryl A-6109 exhibits excellent adhesion to different types of metals. Supplied pre-coalesced, NeoCryl A-6109 eliminates the need for further coalescing solvents [6].

NeoCryl A-6099, an aqueous low particle size acrylic copolymer, was acquired from DSM Neo-Resins, Wilmington, MA. It consists of 40 wt % of acrylic copolymer, 59.5 wt % of water, 0.4 wt % of Ammonia and < 0.2 wt % of styrene. Total solids by weight is 40.2 wt % and VOC is zero. NeoCryl A-6099 is the resin of choice for quick hardness development and outstanding water, humidity, and corrosion resistance. NeoCryl A-6099 exhibits outstanding adhesion to different metals and plastics [7].

Rohm and Haas Maincote™ AE-58, an acrylic emulsion crosslinker for general-purpose water-based acrylic/epoxy coatings, was acquired from Rohm and Haas, North Andover, MA. Maincote™ AE-58 can be used on a variety of substrates such as exterior and interior metal and concrete, and enable low VOC, low toxicity, and low odor for coatings. It consists of 42 – 43 wt % of acrylic copolymer, 57 - 58 wt % of water and <=0.1 wt % of aqua ammonia. The advantages of Maincote™ AE-58 include: low VOC, low toxicity, and low odor for coatings; providing the performance profile of conventional solvent-based 2-pack epoxy finishes; Applicable for a wide variety of substrates; long pot-life; low-temperature property response.
Improved durability; and providing the combination of high performance and low hazard application [8].

\textit{Daubond}^{TM} \textit{DC-9010W55}, an aqueous epoxy emulsion, was acquired from Daubert Chemical Company, Chicago, IL. It contains 53-55 wt \% epoxy and 1-2 wt \% ethoxylate. DC-9010W55 is designed for use in water-borne and water-reducible epoxy coatings and adhesives. DC-9010W55 epoxy emulsion offers coating and adhesive formulators the convenience of handling a pre-emulsified epoxy resin that has good viscosity stability and less phase separation during storage. Water-borne industrial coatings containing low levels of co-solvent and industrial adhesives without co-solvents can be formulated with DC-9010W55 and suitable curing agents [9].

\textit{EPI-REZ WD-510}, a liquid, bisphenol A type epoxy resin specifically designed for water dilution, was acquired from Resolution Performance Products, Houston, TX. It contains > 90 wt \% of bisphenol-A-(epichlorhydrin) epoxy resin (number average molecular weight <= 700) and <10 wt \% polymeric dispersant. In combination with epoxy curing agents and dilution with water it forms resin in water emulsions. As a binder it is useful for EPI-REZ WD-510 forms uniform dispersions in water in combination with aliphatic amine curing agents, including adducts, amidoamines, polyamides, and accelerated amines [10].

\subsection{2.1.5 Solvents, surfactant and cleaner}

\textit{De-ionized water} was acquired from the University of Cincinnati lab supplies.

\textit{Butyl cellosolve} (99.9\% pure), also known as ethylene glycol monobutyl ether, ethylene glycol monobutyl ether, EGBE: 2-butoxyethanol, ethylene glycol n-butyl ether, was acquired from Fisher Scientific, Raleigh, NC.
Okemclean® alkaline cleaner was supplied by Chemetall Oakite, Romulus, MI.

Surfynol ® 104H surfactant, which is a mixture of 75 wt % of Tetramethyl-5-decyne-4,7-diol, 2,4,7,9-, and 25 wt % of ethylene glycol, was obtained from Air Products and Chemicals, Inc., Allentown, PA.

2.1.6 Monomer for plasma polymerization
The monomer used for plasma polymerization on the pigments, perfluorohexane (99.7%), was obtained from Alfa Aesar, Ward Dill, MA.

2.1.7 Topcoat and control primers
The following military topcoats and primers, used in the US Navy and Air Force for vehicles and equipments, were used as controls for the superprimer coatings.

CA 7233 High solids epoxy-polyamide military primer containing 25% barium chromate and its activator component CA 7233 B, were procured from PRC DeSoto, Glendale, CA. It conforms to military specification MIL-PRF-23377 H (Type I, class C).

Desothane® HS CA-8214/F36173, solvent-based camouflage gray polyurethane topcoat with a base component and an activator was also procured from PRC DeSoto, Glendale, CA.

Defthane® ELT MIL-PRF 85285 D, a gray military topcoat with a base component and an activator was procured from Deft Chemical Coatings, Irvine, CA.

2.2 Substrate cleaning
The substrates need to be carefully cleaned to remove impurities, grease and oxides to ensure good wetting and adhesion. In this study the aluminum panels were cleaned following the steps below:

a) Wet scrubbing using ScotchBrite® until the metal shines
b) Ultrasonic cleaning in ethanol for 8 minutes at room temperature
c) Alkaline cleaning in Okemclean® alkaline cleaner for 3-5 minutes at 60-65°C
d) Thorough rinsing in DI water until water break-free
e) Blow-air drying

2.3 Superprimer preparation and application

The formulation mixing methodology was different for each type of formulation. It will be explained at various instances in Chapters 3 and 4 wherever it is required.

A high shear blender/mixer manufactured by Ross Mixing Inc., Port St. Lucie, FL was used to mix the superprimer formulation. The micro-mixer/rotor assembly was used at speeds of 1000 rpm to 3000 rpm especially to obtain good dispersion of pigments and homogenization of ingredients.

The superprimers were applied onto the cleaned substrates using either a draw-down bar or spray gun depending on the specific requirement. A draw-down bar is ideal for small-scale laboratory tests. The thickness control is accurate but the substrate must be perfectly flat. On the other hand, spray gun is more versatile, but is more dependent on the painter’s skill.

The draw-down bar used in this study was a #28 one, which gave an average dry-film thickness of 25 μm. The topcoat and control primers were also applied using the same draw-down bar.
The spray gun used in this study was a SoftSpray HVLP Conversion Gun acquired from Wagner Spray Tech Corporation, Minneapolis, MN. This is a typical spray gun used in the paint industry, which is driven by compressed air.

### 2.4 Plasma system and plasma treatment

The plasma reactor used to treat pigment was a radio frequency reactor custom-made for powder treatment, called tumbler reactor. The schematic of the tumbler reactor is illustrated in Fig. 2.3. The reactor consists of a Pyrex cylinder chamber of 40 cm length and 20 cm diameter, motor driven shaft in center, two vanes running in the opposite direction attached to the shaft for refreshing the powder surface exposed to the plasma. The plasma was generated through RF copper coils with 7-8 turns over one module of the chamber and was maintained by RF energy generated by a Kenwood Transceiver 530 CP (power range from 0-200 W) with matching amplifier and capacitors. The reactor was based on horizontally mixing principle and has a capability of treating quantities up to 1 kg depending on the specific density.

The plasma polymerization was carried out after charging about 100 g of pigment into the reactor, evacuating the reactor to 13 Pa and then introducing perfluohexane monomer for the plasma polymerization. The power and treatment time were 60 Watts and 90 minutes.

### 2.5 Performance evaluation tests and characterization

#### 2.5.1 Pigment extraction immersion test

In order to evaluate the inhibition of the pigments and also simulate the working conditions of the pigment in the coatings, aqueous solutions containing 1 wt % of each pigment and 3.5 wt % NaCl were prepared. The solutions were stirred for 12 hours and then were filtered to remove the
undissolved pigment. Cleaned aluminum panels were immersed in the solution at room temperature and the corrosion behavior was observed.

2.5.2 DC polarization test

DC polarization is one of the most important techniques to determine the corrosion rate of the corrosion cell. Fig. 2.4 schematically presents a DC polarization device [11]. An external potential is applied on the working electrode and counting electrode by a potentiostat to facilitate the electron chemical reaction. The polarized metal test electrode dissolves and releases the metal ions toward the counter electrode where the cathodic reaction occurs. The electrons from the testing electrode are removed by the potentiostat and supplied to the cathodic reaction on the countering electrode. The external potential is generally varied from -0.3 volt to 0.3 volt in the experiment, and the current produced is recorded by the ammeter.

Fig. 2.5 shows a typical DC polarization curve that can be obtained from the polarization test [12]. The vertical axis is the external potential applied by the potentiostat and the horizontal axis is the logarithm of absolute current measured by ammeter. The straight lines are the theoretical curves for the anodic and cathodic reactions. The corrosion potential and corrosion current are determined by the cross point of the cathodic and anodic straight lines. The corrosion rate in mm per year can also be calculated with the slopes of the cathodic and anodic straight lines using the equation 2.1 [11].

\[
CR = \frac{I_{corr} KEW}{dA} \quad \text{Equation 2.1}
\]

Where

CR \quad The corrosion rate. Its units are given by the choice of K (see Table 2.1)

I_{corr} \quad The corrosion current in amps
K                A constant that defines the units for the corrosion rate
EW            The equivalent weight in grams/equivalent
d                Density in grams/cm3
A                Sample area in cm2

In this study, the DC polarization test was carried out on those pigments which were identified as effective corrosion inhibitors for aluminum alloys in the bare panel immersion test as described in Section 2.5.1. The electrolytes used in the DC polarization test were prepared in the same way as the solutions used in the bare panel immersion test. Cleaned aluminum panels were immersed in the electrolyte for 20 hours before the test. The DC polarization test was done on Gamry® CMS100 Corrosion Measurement System. The Gamry Echem-Analyst™ software was used to analyze the data.

2.5.3 Electrochemical impedance spectroscopy (EIS) [13]

Electrochemical Impedance Spectroscopy (EIS) is a very useful technique for quantitatively evaluation of coatings, thin films and uncoated metal. The EIS technique is based on a transient response of an equivalent circuit for an electrode/solution interface. The response can be analyzed by transfer functions due to an applied small-amplitude potential excitation at varying signals or sweep rates. In turn, the potential excitation yields current response and vice versa. In impedance methods, a sine-wave perturbation of small amplitude is employed on a corroding system being modeled as an equivalent circuit for determining the corrosion mechanism and the polarization resistance [12].

The electrochemical impedance can be obtained by applying an AC potential to an electrochemical cell and measuring the current through the cell. When a small sinusoidal potential
as shown in Fig 2.6 is applied to the cell, the response is an AC current signal at the same frequency but shifted in phase, in a linear (or pseudo-linear) system.

The sinusoidal excitation signal can be expressed as

\[ E(t) = E_0 \cos(\omega t) \quad \text{--------} \quad \text{Equation 2.2} \]

\( E(t) \) is the potential at time \( t \), \( E_0 \) is the amplitude of the signal, and \( \omega \) is the radial frequency.

In a linear system, the response signal, \( I(t) \), is shifted in phase \( \Phi \) and has a different amplitude compared to \( I_0 \):

\[ I(t) = I_0 \cos(\omega t - \Phi) \quad \text{--------} \quad \text{Equation 2.4} \]

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

\[ Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \Phi)} = \frac{Z_0 \cos(\omega t)}{\cos(\omega t - \Phi)} \quad \text{--------} \quad \text{Equation 2.5} \]

The impedance is therefore expressed in terms of a magnitude, \( Z_0 \), and a phase shift, \( \Phi \). The impedance can also be represented as a complex number [13]:

\[ Z = \frac{E}{I} = Z_0 \exp(j \Phi) = Z_0 (\cos \Phi + j \sin \Phi) \quad \text{--------} \quad \text{Equation 2.6} \]

In Equation 2.6, the expression for \( Z(w) \) is composed of a real and an imaginary part. If the real part is plotted on the X axis and the imaginary part on the Y axis of a chart, this type of plot is called "Nyquist plot", as shown in Fig. 2.7. The Nyquist plot in Fig. 2.7 results from the electrical circuit of Fig. 2.8. Notice that in this plot the y-axis is negative and that each point on the Nyquist plot is the impedance at one frequency.
The major shortcoming of Nyquist plots is the lack of the annotation of the frequency corresponding to each point in the curve. If the impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|Z| = Z_o$) and phase-shift on the y-axis, this type of plot is called Bode plot. The Bode plot corresponding to the circuit of Fig. 2.8 is shown in Fig. 2.9

All the elements such as metal substrates, surface pretreatments, painting system can influence the electrochemical behavior measured by EIS, which is also a function of the environment and the general condition of measuring (temperature, oxygen concentration, etc.). All these factors should be taken into consideration when constructing the equivalent circuit. In addition, there can be a large number of different equivalent electrical circuits that fit the measured impedance curve. In order to use the correct equivalent circuit, all the information obtained about the system, including those results obtained by using non-electrochemical methods, should be taken into consideration as well.

Fig. 2.10 shows an example of the equivalent circuit for a perfect polymer coating on a metal. When corrosion occurs, the model should be changed accordingly. For example, in case of a corroding metal in an electrolyte, a steady-state electrical double layer (EDL) is formed at the metal/electrolyte interface. In this state the metal ions leave the surface of the metal leaving negative charge due to excess electrons behind on the metal. In one of the proposed EDL models, a layer of water molecules adsorbed on the metal surface separates the excess electron layer on the metal surface from the hydrated metal ions present in the vicinity of the metal in the electrolyte. Reduction of electrochemically active species such as hydrogen ions, etc., use up some of the electrons on the metal, creating charge imbalance and thereby releasing more metal ions into the electrolyte in order to achieve charge stabilization and continue corrosion. In any case, this separated opposite charge model of the corroding metal acts as a capacitor.
adsorbed water acts as a dielectric. The electrolyte present has electrical resistance. All those changes must be reflected in the equivalent modeling [14, 15].

In this study EIS measurements were carried out using an SR810 frequency response analyzer connected to a Gamry® CMS100 potentiostat over a frequency range of $10^{-2}$ to $10^5$ Hz. Using Gamry® Framework software, the EIS spectra were collected and the results were analyzed and correlated to the performance characteristics of the superprimer coatings. The EIS measurements were performed using 3.5 wt % NaCl as the electrolyte.

2.5.4 Saltwater immersion test

Saltwater immersion test was used to evaluate the anticorrosion ability of the pigment and the overall quality of the primer. Panels coated with primer (with or without topcoat) were cross-scribed and immersed in 3.5 % NaCl solution at room temperature and their performance was monitored over time. After regular intervals, the panels were inspected for corrosion, blistering, scribe creep or delamination in accordance with the ASTM D714 standard.

2.5.5 Salt spray test

The salt spray (fog) test, ASTM B117 (“Standard Practice for Operating Salt Spray (Fog) Testing Apparatus”), is one of the oldest corrosion tests still in use. In this study, ASTM B117 was used to evaluate the performance of the superprimer coatings. Despite widespread doubt among experts about its accuracy in predicting performance, or even relative ranking, of coatings in most applications, it is still the most frequently specified test for evaluating paints and substrates [16].

In this study the ASTM B117 test was carried out at DACCO SCI, Inc., Columbia, MD. Specimens coated with superprimers and control coating (with or without topcoat) were cross-
scribed and placed at 45° in a certified Singleton salt fog chamber with specifications of 5 wt % NaCl solution (pH 7) sprayed at 35° C. The specimens were removed periodically from the salt fog chamber to check for corrosion in the scribe, formation of blisters and delamination. EIS measurements were also performed as well using a handheld corrosion sensors developed at DACCO SCI, Inc. These sensors allowed the EIS measurements to be taken under ambient conditions unlike the traditional EIS measurements. A geometric mean of the impedance values from the 0.1 to 1 Hz frequency decade was reported along with an image of the exposed coating at regular time intervals. A schematic of a typical salt fog chamber is shown in Fig. 2.11 [17], along with the image of the salt spray chamber at DACCO SCI, that was used for testing the panels in this study (Fig. 2.12).

2.5.6 Outdoor exposure test

Accelerated corrosion testing such as ASTM B117 are used to predict the performance of the coatings and in many occasions those prediction is not consistent with real service performance. On the other hand, outdoor exposure test is able to provide much more accurate evaluation about the coating performance. In this study aluminum specimens coated with superprimer formulations (with or without topcoat) were tested at Q-Lab’s exposure site located south of Miami on the southern tip of Florida. The exposure site is in the only true subtropical region in the continental United States. This site has high-intensity sunlight, high annual UV, high year-round temperatures, abundant rainfall and very high humidity. When combined, these factors create the harsh climate that makes this place the ideal location for testing exterior durability and mildew resistance [18]. The climate profile of the exposure location is listed in Table 2.2. The setup of testing rack is shown in Fig. 2.13.

At regular intervals during the exposure, EIS measurements were taken using the portable corrosion sensors developed by DACCO SCI, Inc.
2.5.7 Tape adhesion test

Aluminum specimens coated with superprimer (with or without topcoat) were subjected to dry and wet tape adhesion tests according to the ASTM D3359-97 standard. A lattice pattern with six cuts in each direction is made in the film, pressure sensitive tape is applied over the lattice and then removed, and adhesion is evaluated in accordance with the following scale [19]:

- 5B: The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
- 4B: Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
- 3B: Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.
- 2B: The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.
- 1B: The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65 % of the lattice.
- 0B: Flaked and detachment worse than grade 1B.

2.5.8 Contact angle measurement

Contact angle measurement (CA) is a simple-to-adopt method for surface analysis related to surface energy and tension.

The contact angle describes the shape of a liquid droplet resting on a solid surface. The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid phase of the droplet, the solid phase of the substrate, and the
gas/vapor phase of the ambient. The geometry of a liquid droplet on a solid surface is regulated by interfacial forces as given by Young’s equation [20]:

\[ \gamma_{SL} = \gamma_S - \gamma_L \cos \theta \] (0\leq \theta < \pi)

Where \( \gamma_{SL} \) = the solid-liquid interfacial energy, \( \gamma_S \) = surface free energy of solid, \( \gamma_L \) = surface free of liquid and \( \theta \) = contact angle. Fig. 2.14 shows a schematic sketch of forces acting on a liquid droplet on a solid surface.

In this study contact angle measurements were performed on a contact angle goniometer VCA2000 manufactured by AST Products, Inc., Billerica, MA. As shown in Fig. 2.15, the goniometer consists of a light source, sample stage, lens and video camera. The contact angle can be assessed directly by measuring the angle formed between the solid and the tangent to the drop surface. A water drop of controlled volume is dispensed on the coated panels from a syringe. The video camera captures digital image of the droplet and the integrated software analyzes the image and calculate the value of contact angle.

2.5.9 Time of flight-SIMS (ToF-SIMS)

In this study ToF-SIMS was used to analyze the interface between metal and superprimer. ToF-SIMS is one of the most surface sensitive techniques providing molecular information of the materials. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) uses a pulsed primary ion beam to desorb and ionize species from a sample surface (as shown in Fig. 2.16). The resulting secondary ions are accelerated into a mass spectrometer, where they are mass analyzed by measuring their time-of-flight from the sample surface to the detector. There are three different modes of analysis in ToF-SIMS; 1) mass spectra are acquired to determine the elemental and molecular species on a surface; 2) images are acquired to visualize the distribution of individual species on the surface; and 3) depth profiles are used to determine the distribution of different chemical species as a function of depth from the surface [21]. ToF-SIMS provides
spectroscopy for characterization of chemical composition, imaging for determining the
distribution of chemical species, and depth profiling for thin film characterization

An Ion-TOF IV from Ion-Tof Inc., Münster, Germany, was used for the ToF-SIMS analysis in this
study. This machine was equipped with a 3-lens $^{69}\text{Ga}^+$ gun, an $\text{Ar}^+$ gun for depth profiling and
flood gun for charge neutralization. The analysis of the interface was carried out by collecting
static spectra of both the polymer and the metal side of a freshly prepared sample.

2.5.10 Scanning electron microscopy/ energy dispersive X-ray spectroscopy

SEM/EDS analysis was used to study the structure of the dry superprimer coating and the
protective mechanism of the pigment and the coating. In scanning electron microscopy, (SEM)
an electron beam is scanned across a sample's surface. When the electrons strike the sample, a
variety of signals are generated. The three signals that of the greatest value in SEM are the
secondary electrons, backscattered electrons, and X-rays. An image of the surface can be obtained
by the detection and analysis of secondary electrons and backscattered electrons. Interaction of
the primary beam with atoms in the sample causes shell transitions which result in the emission of
an X-ray. The emitted X-ray has an energy characteristic of the parent element. Detection and
measurement of the energy permits elemental analysis (Energy Dispersive X-ray Spectroscopy or
EDS). EDS can provide rapid qualitative, or with adequate standards, quantitative analysis of
elemental composition with a sampling depth of 1-2 microns. X-rays may also be used to form
maps or line profiles, showing the elemental distribution in a sample surface [22].

In this study, a Philips XL 30 environmental scanning electron microscope (ESEM) was used.
The elementary compositions of the scribe and cross section were analyzed using energy
dispersive X-ray (EDS) analysis. For EDS analysis small specimens of scribed panels were
sputter-coated with Au-Pd film and analyzed. The cross-sectional samples were prepared in polished epoxy molds. The operating voltage used in SEM analysis was 25 kV.

2.5.11 Inductively coupled plasma mass spectrometry

Inductively Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for trace (ppb-ppm) and ultra-trace (ppq-ppb) elemental analysis.

An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer [23]. Fig. 2.17 shows a schematic representation of an ICP source in an ICP-MS. Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma.

In this study an Agilent 7500 ICP-MS, Santa Clara, CA, was used to analyze the leaching rate of the pigment from the primer coating.
Reference:
Chapter 3 Environmentally Benign Pigments for Aluminum Alloy

3.1 Introduction

This chapter focuses on the identification and evaluation of potential corrosion inhibitors for aluminum alloys. Aluminum alloys have moderate inherent corrosion resistance because of the naturally occurring oxide layer. Aluminum alloys used in common atmospheric or even aqueous do not require strong corrosion protection. Only in the very demanding applications such as aerospace engineering, strong corrosion inhibition becomes necessary. In such applications, chromate naturally became the choice of anticorrosion pigment historically. Only in recent years when the regulations on the use of chromate became stringent, the research aimed at finding chromate replacement for chromate as the corrosion inhibitor is given more attention and such investigations began to be reported.

A lot of the researches on the environmentally benign inorganic inhibitors are focused on rare-earth compound such as cerium, lanthanum and vanadium. Markley et al [1] studied corrosion protection of AA2024-T3 using rare earth diphenyl phosphates. Their results show that cerium diphenyl phosphate (Ce(dpp)_3) acts as a cathodic inhibitor, decreasing cathodic current density and Ecorr by passivating cathodic intermetallic particles on the alloy surface. Mischmetal diphenyl phosphate (Mm(dpp)_3) acts a mixed inhibitor, shifting Ecorr to more noble values, decreasing cathodic current density, increasing the breakdown potential and suppressing pitting.
Iannuzzi et al [2] studied the mechanisms of corrosion inhibition of AA2024-T3 by vanadates using chronoamperometry, polarization curves and adsorption isotherms. They found that metavanadates reduced the kinetics of oxygen reduction to an extent similar to chromates.

Corrosion inhibition of AA2024-T3 by metavanadates might be due to the formation of an adsorbed layer on the surface of the substrate, which likely blocked reactive sites on intermetallic particles, discouraging the oxygen reduction reaction (ORR). Adsorption of the inhibitor on the Al matrix could also displace Cl\textsuperscript{-} ions, increasing the stability of the passive film and reducing the breakdown of S-phase particles. In contrast, decavanadates were not found to be so effective in term of corrosion inhibition on Al.

Yasakau et al [3] investigated the mechanism of corrosion inhibition of AA2024 by cerium and lanthanum inhibitors in chloride media. They proposed that the formation of hydroxide deposits on S-phase inclusions accounts for the inhibition of Ce\textsuperscript{3+} and La\textsuperscript{3+}. The hydroxide deposits buffer the local increase of pH, which otherwise accelerates of the intermetallics dealloying. The hydroxide precipitates can also act as a diffusion barrier hindering the corrosion processes in active zones. Cerium nitrate exhibits relatively higher inhibition efficiency compared to lanthanum nitrate, which can be due to the lower solubility of the respective hydroxide.

There are also a few works focused on the organic corrosion inhibitors. Lamaka et al [4] studied the corrosion inhibition of salicylaldoxime, 8-hydroxyquinoline and quinaldic acid. Their results show that the quinaldic acid, salicylaldoxime and 8-hydroxyquinoline can form a thin organic layer of insoluble complexes on the surface of the alloy, which suppresses of dissolution of Mg,
Al and Cu from the corrosion active intermetallic zones. Triazole and thiazole derivatives are another class of organic corrosion inhibitors for AA2024 aluminum alloy that has been investigated [5, 6]. Triazole and thiazole derivatives also provide corrosion protection to the AA2024 alloy by forming a thin organic layer on the substrate surface. These inhibitors decrease the rate of both the anodic and cathodic processes.

However, no systematic corrosion inhibitor investigation which covers the conventional and newer pigments has been reported. In this work, a comprehensive corrosion inhibitor screening for aluminum alloys was carried out to find a replacement for chromate pigments and the screening would also facilitate the synthesis of new pigments.

The screening covered all categories of possible inorganic inhibitors. The inhibitors were initially evaluated by salt water immersion test in which bare aluminum panels were immersed in the inhibitor solution containing 3.5 wt % NaCl and the corrosion behavior was monitored. The inhibitors determined effective then were further investigated with DC polarization tests. Next the inhibitors were incorporated into coatings and the performance of the coatings was compared with coatings pigmented with a chromate. Furthermore, mixtures of the effective corrosion inhibitors for Al were evaluated to find out if synergism of different inhibitive species exists.

There were other pigments which are effective for corrosion prevention for Al but their solubility was too high to be used in coatings. Such pigments can be treated with plasma surface modification. Plasma-polymerized film capsulates the pigment and make the pigment slow-releasing so that the pigment will not cause coating blistering when exposed to water. A
combination of plasma treated-cerium acetate, benzotriazole (BTA) and sodium vanadate were found by Lin [7] and Manian [8] to be effective on AA2024-T3.

3.2 Pigment screening

The study began with a systematic pigment screening process since no such study on pigments for aerospace alloy had been reported. The reason is that chromate was naturally chosen and has been used ever since. A comprehensive pigment screening would also facilitate the later synthesis of new pigments. The screening study covered the following types of pigments:

- Vanadates
- Zinc salts
- Benzotriazole
- Phosphates
- Cerium salts
- Hydrotalcite-vanadate
- Molybdates
- Lanthanum salts
- Pigment mixtures
- Silicates
- Calcium salts
- Multi-anion or multi-cation compound
- Carbonates
- Praseodymium salts

First, the screening involved the inhibition evaluation method. It is well known that discrepancy exists between different corrosion rate testing methods. Also the larger number of inhibitor candidates to be evaluated required the testing method to be efficient.

A Bare panel immersion test was adopted in this study for pigment evaluation, in which bare aluminum panels were immersed in low-concentration pigment solution which also contained 3.5 wt % NaCl. The corrosion behavior of the panels was monitored. The reason to choose this
method is based on the fact that bare panels exposed to electrolyte with both pigment and Cl− ions present is similar to the real corrosion scenario when coated panels with defects in the coating are exposed to electrolyte.

In the bare panel immersion test excess amounts of chemicals (1 wt %) were added to 3.5 wt % NaCl solution to ensure that saturation or a critical concentration was reached. Some of the chemicals, e.g., CeCl₃, were quite soluble and 1 wt % of it dissolved completely in water, while some of the chemicals, however, had much lower solubility than 1 wt %. Too soluble chemicals are normally considered unsuitable for use in the coatings. The purpose of including them in the test was to find out the inhibition of this class of inhibitors on AA7075. The difference in the solubility of different pigments led to the variation in the actual concentrations of the solutions of 1 wt% different pigments. The actual concentration and pH of the solutions of different pigments was not adjusted to equality in order to simulate the real working condition of the pigment as in the primer.

Among the more than 100 chemicals tested, some categories of corrosion inhibitors were found to be effective on AA7075. Table 3.1 listed the performance of the typical inhibitors of their categories in the bare panel immersion test in a period of 12 days. Without any inhibitor present, AA7075 immersed in NaCl solution showed visible corrosion after 1~2 hours. With chromate present in the electrolyte, AA7075 was protected from visible corrosion for more than 12 days. Some non-chromate inhibitors such as zinc phosphate and modified zinc phosphate also were able to prevent visible corrosion in 12 days. Other inhibitors, like molybdates, phosphate, silicate, vanadate, zinc, lanthanum, magnesium and cerium salts provided different level of corrosion
3.3 Selected pigments and performance

3.3.1 DC polarization (DCP)

The pigments which were found to be corrosion inhibitive in the screening were further tested by DCP which quantitatively measured the corrosion potential and rate and also provided information about the protection mechanism of the pigment.

DC Polarization results of some of the typical inhibitors such as zinc sulfate, lanthanum nitrate, cerium chloride, dibasic sodium phosphate, cerium vanadium oxide, sodium metasilicate, zinc phosphate, calcium zinc phosphomolybdate (CZPM) are shown in Fig. 3.2. The black curve is the blank control, and the red curve is the positive control (barium chromate). Polarization curves demonstrated that those pigments are able to decrease the corrosion rate and change the corrosion potential of AA7075 in NaCl solution. For example, the cathodic curves of AA7075 in ZP and CZPM solution were depressed compared with AA7075 in the blank solution, indicating a suppression of the cathodic reduction of oxygen to OH\(^-\). And both anodic and cathodic curves in ZP and CZPM were shifted to the left, i.e., toward the smaller current density, compared to the blank. The shift resulted in a much lower \(I_{corr}\), considering the x-direction, the current density, is a logarithmic scale. Changes were also observed in the \(E_{corr}\) values, with the shift observed in all inhibitor solution towards cathodic values.
Another group of modified zinc phosphates obtained from Heuco Bach, which is the so-called second and third generations of pigments were included in the DC polarization test. The pigments tested were ZAM (zinc aluminum molybdenum orthophosphate hydrate), ZCP (zinc calcium strontium aluminum orthophosphate silicate hydrate), SACP (strontium aluminum polyphosphate hydrate) and ZAPP (zinc aluminum polyphosphate hydrate). Among those pigments ZAM and ZAPP were found to be effective pigments for aluminum. The polarization curve of aluminum alloy in 3.5 wt % NaCl with ZAM and ZAPP present is shown in Fig. 3.3.

The corrosion inhibition of pigments under different pH environments is of interest because in real service life inhibitors may be used in basic or acidic conditions. Cerium vanadate, a new pigment invented by Van Ooij, et al [7] was investigated on AA7075 for its inhibition in different pH conditions. The curves of AA7075 in 3.5% NaCl solution under pH 2, 4, 6, 8, and 10 are shown in Fig. 3.4. From the polarization curve it can be seen that AA7075 is actually relatively insensitive to minor pH changes from neutral. This can be attributed to its oxide film which is resistant to mild alkaline or acid. AA7075 is most stable at pH=6. The corrosion rate of AA7075 dramatically increases at pH above 10 or below 2.

The polarization curves of AA7075 in 3.5% NaCl solution containing saturated CeVO₄ are shown in Fig. 3.5. curves demonstrated that CeVO₄ works best in neutral to acidic environment. At pH=2, CeVO₄ suppress the corrosion rate from about 100 µA to about 10 µA.

3.3.2 Polarization resistance
Polarization resistance (PR) is an effective electrochemical method of measuring corrosion. PR is most effective in aqueous solutions, and has proven to be a rapid response technique. Polarization resistance $R_p$ can be related (for reactions under activation control) to the corrosion current by the Stern-Geary equation.

$$I_{corr} = \frac{1}{R_p} \cdot \frac{\beta_a \cdot \beta_b}{(2.303 (\beta_a + \beta_b)}$$  \hspace{1cm} \text{Equation 3.1}

In this study PR was employed to measure the inhibition of pigments for AA7075. The PR of inhibitors including BTA, Ce(OOCCH$_3$)$_3$, CeVO$_4$, BaCrO$_4$ and NaVO$_3$ was measured. Beta values were determined from polarization test in the previous section. The calculated corrosion rate of AA7075 in 3.5 wt% NaCl solution containing these pigments listed in Table 3.2. The corrosion rate of AA7075 in 3.5% NaCl measured from PR was 38.62 mpy. With pigments such as chromate the corrosion rate were reduced to less than 10 mpy.

### 3.3.3 Performance of inhibitors in coatings

Pigments which demonstrated corrosion inhibition in bare panel immersion test and DCP were then incorporated into waterborne primer coatings and tested in ASTM D 714 salt water immersion test. The coating used in the test was an early version of the epoxy-acrylic superprimer containing bis-sulfur silane. The formulation of the primer is shown in Table 3.3. 1-10 wt % of pigments was loaded in to the superprimer and the coating was applied on to AA7075 using a #32 drawdown bar. AA7075 panels was cleaned but received no pretreatment before coating. The coating was scratched with an X pattern after curing at room temperature for 14 days. The scratched panels were tested in salt water immersion test in accordance with the ASTM D714
standard. Only the edges of panels were taped and the back of the panels was not. In this way scribe corroded faster and the evaluation could be done sooner. When the back of the panels was not taped, the scratched area became anodic compared to the bulk area on the back of the panel, just like the situation in a pitting or crevice corrosion. And the area ratio between cathodic site and anodic site was high, which led to a fast corrosion rate.

The scratched panels subjected to salt water immersion test are shown in Fig. 3.6 (a) – (d). Consistent with the bare panel immersion test and DC polarization test results, ZnSO₄, Na₂HPO₄, MgMoO₄, Zn₃(PO₄)₂ and Cortec M381 (silicate-based pigment) all showed protective effect on AA7075. Among the pigments, Zn₃(PO₄)₂ and silicate-based Cortec M381 demonstrated corrosion inhibition comparable to that of chromate. Also the load level of pigment in the coatings showed difference in performance. Generally it was found that in the 1 ~ 10 wt % pigment load range a higher load level resulted in better anticorrosion performance. Silicate-based M381 was an exception. That was attributed to its high pH which had a negative effect on the performance of the coating.

3.4 CZPM and zinc phosphate

DC polarization and bare panel immersion tests demonstrated that zinc phosphate and calcium zinc phosphomolybdate are strong inhibitors for AA7075. The bare panels subjected to 40 days of immersion in 3.5 wt % with and without the inhibitors are shown in Fig. 3.7. Severe corrosion occurred on AA7075 coupon in NaCl solution without the protection of pigment, while very minor visible corrosion occurred on the ones immersed in NaCl solution containing CZPM or zinc phosphate.
The corrosion rates of AA7075 in 3.5% NaCl solutions with and without CZPM or zinc phosphate were determined from polarization curves shown in Fig. 3.2 and hereby inhibitor efficiencies were calculated using Gamry® Echem Analyst software. The corrosion rate and inhibitor efficiency calculated though equation (3.2) are listed in Table 3.4.

\[
Inhibitor	ext{ Efficiency} \, (\%) = \left( \frac{CR_{\text{uninhibited}} - CR_{\text{inhibited}}}{CR_{\text{uninhibited}}} \right) \cdot 100
\]

\[\text{Equation 3.2}\]

Where:

\[CR_{\text{uninhibited}} = \text{corrosion rate of the uninhibited system}\]

\[CR_{\text{inhibited}} = \text{corrosion rate of the inhibited system}\]

DC polarization tests demonstrate that the efficiencies of CZPM and zinc phosphate are 66% and 71% respectively, which are comparable to that of barium chromate, 77%.

Zinc phosphate and CZPM were tested in a waterborne epoxy-acrylic superprimer, named L2, containing bis-sulfur silane which was developed by Seth, et al [9]. The superprimer formulation is listed in Table 3.5. 30 wt % of pigments was loaded in to the superprimer and the coating was applied to AA7075 using a #32 drawdown bar. The AA7075 panels were cleaned but received no pretreatment before coating. The coatings were scratched with an X pattern after curing at room temperature for 14 days. The scratched panels were tested in salt water immersion test in accordance with the ASTM D714 standard. The edges and back of panels were sealed with tape.
The epoxy-acrylic superprimer L2 loaded with CZPM and zinc phosphate subjected to 40 days of saltwater immersion test are shown in Fig. 3.8. It should be noted that L2 itself is an excellent primer with certain resistance to corrosion due to the incorporation of silane. Only minor undercutting occurred at the scribe of the coating without pigment. CZPM-pigmented or zinc phosphate-pigmented coatings showed almost no corrosion within 40 days in the saltwater immersion test. The addition of CZPM and zinc phosphate prevented corrosion at the scribe, which achieved the same self-healing effect of chromate conversion coatings and pigments.

The level of pigment loading in the coating affects the performance of the coating. The optimal loading level is dependent on the type of pigment and also on the type of the coating. Generally, a higher loading level increases the corrosion inhibition of the coating. However, a high loading level deteriorates the properties of the coating with increased brittleness, less flexibility, less adhesion, and more possibility of defect. The loading level of CZPM and zinc phosphate was experimented with epoxy-acrylic superprimer L2 with result shown in Fig. 3.9. The pigment loading range tested was 10% ~ 30% for CZPM and 10% ~ 40% for zinc phosphate and the evaluation method was salt water immersion test. As the CZPM worked well at the loading level of 20% ~30%; zinc phosphate worked well only at near 30%.

3.5 Conclusion on the inhibition of the pigments

According to the combined results of the different evaluation techniques, the effective pigments can be sequenced based on their inhibition on aluminum alloy approximately as followed.
(Inhibition from strong to weak)

- Barium chromate
- Calcium zinc phosphomolybdate
- Zinc phosphate
- Sodium silicate
- Cerium vanadate
- Zinc sulfate
- \( \text{ZnO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SrO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2 \) and similar
- Lanthanum acetate
- Sodium phosphate monobasic
- Cerium chloride
- Magnesium molybdate

### 3.6 Mixture study

When two different anticorrosion pigments are mixed together, the corrosion inhibition can be improved or compromised, which is called synergism or antagonism, respectively. The wide variety of the commercial modified zinc phosphate pigments are based on the synergism of pigments, though only a small fraction of them demonstrated real synergism on AA7075 as discussed in previous sections.

Combinations of the four pigments, \( \text{MgMoO}_4 \), \( \text{CeVO}_4 \), \( \text{Zn}_3(\text{PO}_4)_2 \) and \( \text{La(OOCCH}_3)_3 \), which were found effective from previous experiments, were tested for their synergism by salt water immersion test. The electrolyte was prepared by adding 1 wt % of each pigment into 3.5% NaCl solution and filtering out the solid after stirring for 24 hours.
From the immersion test with results shown in Fig. 3.10, it can be found that except for the combination of Zn$_3$(PO$_4$)$_2$ and CeVO$_4$, the binary mixtures between MgMoO$_4$, CeVO$_4$, La(OOCCH$_3$)$_3$ and Zn$_3$(PO$_4$)$_2$ are antagonistic. If used alone, any of these pigments can prevent visible corrosion on AA7075 in 3.5% NaCl from occurring for at least 2 days. When used in binary mixture, the visible corrosion-free time was reduced to about or even much less than 1 day in most cases. Slight corrosion occurred after 10 days of immersion for the mixture of Zn$_3$(PO$_4$)$_2$ and CeVO$_4$ and after 26 days the corrosion was still minor.

CZPM demonstrated strong corrosion protection on aluminum. It was of interest to test its combination with zinc phosphate and similar combinations ZP/calcium zinc molybdate (CZM). In salt water immersion test CZM/ZP and CZMP/ZP combination did outperformed CZPM, as shown in Fig. 3.11. However, the improvement in the coating was not found as obvious as in the bare panel immersion test.

### 3.7 Engineered pigments

#### 3.7.1 Cerium metasilicate

In the synergism study, another pigment combination found to be synergistic were cerium acetate and sodium metasilicate. The reaction product of cerium acetate and sodium metasilicate, cerium metasilicate, was found to have corrosion inhibition equivalent to that of the mixture.

#### 3.7.1.1 Synthesis
Cerium metasilicate is not commercially available and was synthesized through the reaction (3.3). 13.7g cerium acetate was first added to 100g water, stirred and heated to 80°C. 100g (excessive) sodium metasilicate solution was slowly added to the cerium acetate solution. After adequate mixing, the precipitate, cerium metasilicate, was filtered out and washed.

\[
2 \text{Ce(C}_2\text{H}_3\text{O}_2)_3 + 3 \text{Na}_2\text{SiO}_3 \rightarrow \text{Ce}_2(\text{SiO}_3)_3 \downarrow + 6 \text{NaC}_2\text{H}_3\text{O}_2
\]  

(3.3)

3.7.1.2 Evaluation of corrosion inhibition of cerium metasilicate

The techniques used to evaluate the corrosion inhibition of cerium metasilicate for aluminum alloys included DC polarization test, bare panel immersion test, and salt water immersion test. The electrolyte for bare panel immersion test and DC polarization was prepared by adding excess cerium metasilicate into 3.5% NaCl solution and filtering out the solid after stirring for 24 hours. The bare panel immersion test result is shown in Fig. 3.12. For AA 7075 panels, visible corrosion occurred after 1~3 hours on the coupons immersed in blank 3.5% NaCl solution and developed to heavy corrosion after 30 days, while corrosion did not occur within the first 30 days with cerium metasilicate present. For AA2024 panels, corrosion was visible after 1 day in the black 3.5% NaCl, while no corrosion was observed after 30 days in the electrolyte containing cerium metasilicate. The addition of cerium metasilicate significantly suppressed the corrosion on AA2024 and AA7075.
Sanded and alkaline cleaned AA7075 and AA2024 panels were immersed in saturated cerium metasilicate 3.5% NaCl solutions for 20 hours. Then DC polarization tests were done on Gamry® CMS100 Corrosion Measurement System. DC polarization tests were also done in blank 3.5% NaCl solution as control. Polarization curves obtained from the DC polarization test are shown in Fig. 3.13. The polarization curve showed that the addition of cerium metasilicate suppressed the corrosion rate by at least a decade.

Cerium metasilicate was tested in waterborne acrylic-epoxy superprimer to evaluate its performance in coatings. Fig. 3.13 shows the salt immersion result of AA7075 and AA2024 coated with superprimer L2 loaded with 30% cerium metasilicate. After 100 days of immersion, the coating without pigment exhibited undercutting and blistering. Cerium metasilicate-loaded samples only exhibited discoloration of the scribe, which could be due to the compound formed by the cerium metasilicate released from the coating. Fig 3.14 shows the result of salt fog test result of superprimer L2 loaded with 30 wt % of cerium metasilicate. In this test, cerium metasilicate demonstrated strong corrosion inhibition on both AA7075 and AA2024 as well.

3.7.2 Plasma modified pigments

As discussed in previous sections, some chemicals demonstrated strong corrosion inhibition but their solubility is too high to be used in coating. In order to be useable in coatings the solubility of inhibitor in water is limited to 2g/100ml. A novel approach developed by Van Ooij, et al [6] is to modify the surface of the pigment by depositing a thin plasma-polymerized film. The plasma-polymerized film encapsulates the pigment and makes the pigment slow-releasing in aqueous environment. The plasma polymerization technique and the experiment details used to modify pigments were discussed in Sections 1.7 and 2.4.
A pigment combination of benzotriazole (BTA), sodium vanadate and cerium acetate was found by Manian, et al [8] to be very effective for AA2024 when used in a BTSE-based epoxy-acylate coating. Cerium is a new cathodic inhibitor for aluminum alloy that is recently being intensively investigated. Vanadate is known as an anodic inhibitor for aluminum alloys. BTA is a known organic corrosion inhibitor for copper. This combination of pigments is theoretically strong by design. However, the solubility of sodium vanadate and BTA is high, causing blistering when used in the coating.

In this study cerium acetate and BTA were treated using the plasma reactor mentioned in Section 1.7. The pressure before and after introducing the monomer was 10.7 Pa and 26.7 Pa, respectively. The monomer used for polymerization was perfluohexane and the plasma treatment time was 30 minutes.

Together with cerium acetate, plasma-treated BTA and sodium vanadate were tested in the bis-sulfur-based acrylic-epoxy superprimer L2. This combination of pigments was found to be a very efficient inhibitor system which requires very low loading level in the coating. Superprimer L2 loaded with 1 wt% of each pigment was tested in salt water immersion test with the result shown in Fig. 3.15. Compared to the superprimer coating without pigment, it can be concluded the plasma-treated pigment combination improved the anticorrosion property of the bis-sulfur-based acrylic-epoxy coating. Furthermore, coatings loaded with plasma-treated pigments with high solubility did not causing blistering in the coating, which demonstrated that plasma treatment is an applicable method to control the dissolving behavior of pigment in aqueous environment.
3.8 Summary

As the first step for develop a replacement for current primer coating, evaluation and selection of proper pigment is critical for the performance of the coating. This chapter has discussed the research work carried out to find the chromate-replacing pigment, which include:

1) Different types of chemicals were evaluated for their corrosion inhibition for aluminum alloys through salt water immersion and electrochemical techniques.

2) Zinc phosphate and calcium zinc phosphomolybdate were found to be the best inhibitor for aluminum alloys. The inhibitor efficiency of phosphate and calcium zinc phosphomolybdate was measured.

3) Mixtures of different inhibitors were studied. Synergism of cerium acetate and sodium metasilicate was found. Based on this synergism, cerium metasilicate was synthesized and proven to be an effective inhibitor for aluminum alloy.

4) Plasma treatment of pigments is an applicable method to control the dissolving behavior of pigment in aqueous environment. A combination of plasma-treated BTA, plasma-treated-sodium vanadate and cerium acetate prove to be a strong inhibitor system for aluminum alloy.
References:

Chapter 4 Superprimer Coating

4.1 Introduction

In this chapter the development and testing of the superprimer formulation and investigation of the function of the silane in the coating are reported.

Acrylic-epoxy was used as the binder for the coating. The characteristics of acrylic-epoxy coatings were discussed in Section 1.6.4. Different epoxy and acrylic resins were tested. Bis-silanes including bis-sulfur silane and BTSE were evaluated with these resins. A complete coating formulation containing pigment, defoamer, flash rust inhibitor, and co-solvent was developed after optimization of the level of the components.

The acrylic-epoxy superprimer coating that was developed was evaluated in various standard tests including:

i. Electrochemical impedance spectroscopy

ii. ASTM B 117 salt spray test

iii. ASTM D 714 0.6 M NaCl salt solution immersion test

iv. ASTM D 3359 tape adhesion test

v. Florida outdoor exposure test

The function of the silane in the coating was especially studied in terms of anticorrosion performance, hydrophobicity of the coating, adhesion of the coating to the substrate and electrochemical impedance.
4.2 Formulation: silane, binder and additives

The waterborne acrylic resins tested included a few NeoCryl resins from DSM and Maincote from Rohm and Hass. They are NeoCryl A6069, A6099, A6109, A6115, A6085, A6037, A633, XK 110 and Maincote AE58, which were either acrylic polymers or copolymers. The properties of those resins were reported in Section 2.1.4. Unemulsified bisphenol A type epoxy resin, EPI-REZ WD-510, and pre-emulsified bisphenol A type epoxy resin, Daubond DC-9010W55, were used to crosslink the acrylic resin. Among those acrylic resins, NeoCryl A6099, A6109, A6115, A6085, A633 and XK 110 were found to be chemically incompatible with WD510, NeoCryl A6099 and XK 110 were found to be incompatible with DC-9010W55. The incompatibility is normally caused by certain additives in the resins, e.g. an amine, which breaks the dispersion stability in the other resin, resulting in polymer particle precipitation.

The acrylic-epoxy combinations tested are listed in Table 4.1, with compatible combination checked with √. Together with other ingredients, the acrylic and epoxy resin were made into coatings according to the prototype formulation listed in Table 4.2. In the formulation the ratio between acrylic and epoxy resins was 5:1 and zinc phosphate was used as the pigment. Bis-sulfur silane was used and it was compatible with all the resins. This acrylic-epoxy primer was applied onto AA7075 and AA2024 substrates and tested in the salt spray test and salt water immersion test. Fig 4.1 (a) – (e) shows the coatings subjected to 2000 hours of salt spray test. The acrylic-epoxy combinations that performed well are WD510 - A6037, DC9010w55 - A6115, DC9010w55 - A633 and DC9010w55 - AE58. The superprimer coating based on DC9010w55 and AE58 demonstrated the following attractive properties as the binder:

- Easy to handle and completely compatible with the pigment and silane
- Smooth coating surface
- Long pot life (up to 24 hours)
• Short dry time (Set-to-touch in 60 minutes)
• Good chemical resistance
• Fairly good hardness (Pencil hardness HB)

Together with bis-sulfur silane or BTSE silane, DC9010w55 and AE58 in a varied ratio were formulated into coatings for further optimization. The coatings tested are listed in Table 4.3 (a) – (b). The ratio of DC9010:AE58 was varied from 10% to 100% and zinc phosphate was added as pigment. The coatings were evaluated in the salt water immersion test.

Figure 4.2 shows salt water immersion result of the formulations listed Table 4.3 (a) – (b) as coated on AA7075. Basically BTSE-containing acrylic epoxy superprimer and bis-sulfur containing superprimer demonstrated similar corrosion inhibition on AA7075. However, in the formulation process bis-sulfur was found to be more compatible with other components, resulting in longer pot life and smoother coatings. For bis-sulfur-containing coatings the ratio between acrylic and epoxy resin was critical for the performance of the coating. When DC9010 and AE58 were added in a ratio of 1:10, the coating demonstrated good corrosion prevention both in scribed area and unscratched area. When the ratio of DC9010: AE58 was at the level higher than 1:10, the coatings showed black spots after 70 days of salt water immersion, indicating a drop in the barrier property. For BTSE-added coatings, the ratio of DC9010: AE58 did not show a critical effect. However, it was noticed that lower DC9010: AE58 ratio produced better film-forming ability.

Based on the above study, a ratio of DC9010: AE58 at around 1:10 with the bis-sulfur silane was chosen for this binder combination. In addition, Surfynol 104H, a surfactants based on acetylenic diol was added as the surfactant. It serves several purposes in the coating including surface tension reduction, foam control and viscosity stabilization, leading to a better substrate-wetting
paint, better pigment dispersion and fewer defects resulted from bubbles. Butyl cellusolve was added as the coalescing solvent for faster curing and better film form property. 15% sodium nitrite solution was added as flash rust inhibitor in case flash rust poses a problem on some substrates such as CRS. DI water was added as the viscosity modifier. A viscosity of Zahn cup #2 50-55 seconds was found to be a good sprayable range for this particular primer.

Optimization of the acrylic-epoxy superprimer formulation was carried out by further adjustment of the acrylic and epoxy ratio and also optimization of the level of silane and coalescing solvent. The starting formulation of the bis-sulfur-containing acrylic-epoxy superprimer used for optimization is given in Table 4.4. A few variations of the starting formulation were tested including:

- Epoxy: 5.2g, acrylic: 0.8g;
- Epoxy: 5.4g, acrylic: 0.6g;
- 0.9g bis-sulfur silane;
- 0.5g butyl cellusolve;
- 0.375g ~0.8g water

(In any of the variations, the level of other components was kept unchanged)

The formulation variations was applied on AA2024 and tested in the salt spray test for 3500 hours, with the results shown in Fig 4.3. It was observed that:

1) A ratio of 5:1 in epoxy vs. acrylic was better than 5.2:0.8 or 5.4:0.6. Higher acrylic/epoxy level in the coating seemed to induce blistering when the coating was subjected to the salt fog.

2) The silane/resins (epoxy + acrylic) level should be controlled at about 7.5% rather than 15%.
3) The coalescing solvent, butyl cellusolve, should be controlled at a level about 4% (compared to the total amount of the resins) rather than 8%.

The formulation with 0.25g butyl cellusolve and 0.8g water added to the starting formulation demonstrated good film-forming property and strong corrosion protection. After 3500 hours of exposure to salt spray test, both scribe and unscratched coating area appeared to be clean and corrosion-free. Electrochemical measurements, as shown in Fig 4.4 (a) - (c), also indicated that the coating retained its property during 3500 hours of salt fog exposure. Phase angle, low-frequency impedance and EIS all suggested little change in the coating properties after the salt fog exposure. The final developed acrylic-epoxy superprimer formulation is given in Table 4.5.

The value of using accelerated laboratory corrosion tests including the salt spray test to predict real service life has long been controversial. The complexity of the real service condition including UV radiation, water and moisture, temperature and ions (salts such as sodium chloride and calcium chloride) and chemicals makes the simulation in the laboratory difficult. Therefore, outdoor exposure test is necessary for accurate coating performance evaluation. In this study the acrylic-epoxy superprimer was coated on AA2024 and topcoated by Defthane® ELT MIL-PRF 85285 D topcoat. As the control, MIL-PRF-23377G was applied on AA2024 which was pretreated with Alodine®1200, a chromating agent, and the primer was topcoated by Defthane® ELT MIL-PRF 85285 D. The coated AA2024 coupons were sent to Florida Q-Panels outdoor exposure site for testing. The condition of the test has been reported in Section 2.5.6. At regular intervals during the exposure, EIS measurements were performed using the portable corrosion sensors developed by DACCO SCI, Inc.

Epoxy-acrylate superprimer and the control were tested in Florida outdoor exposure site for 317 days. The panels subjected to test are shown in Fig. 4.5. No corrosion or blistering was found at
the scribe and intact area on both panels by visual inspection. Impedance data and phase angles measured at intervals are shown in Fig 4.6. After 202 days of exposure, the impedances and phase angles showed slight increase instead of decreasing. This can be attributed to the continued curing of the coating in the outdoor exposure test. The panels coated with superprimer and topcoated by Defthane performed on par with the panels coated with the chromate-containing primer and Defthane topcoat.

4.3 The functions of silane and pigment in the coating

The silane-containing waterborne acrylic-epoxy superprimer showed great potential as a chromate-replacing environmentally benign primer. Distinguished from other primer coatings, the superprimer contains bis-sulfur silane and zinc phosphate which is not favored in conventional solvent-borne coatings.

To understand how silane and pigment contribute to the performance of the coating, the following coatings were made and compared in a series of tests including adhesion, anticorrosion, contact angle and electrochemical impedance.

- Epoxy and acrylate
- Epoxy, acrylate and silane
- Epoxy, acrylate and ZP
- Epoxy, acrylate, silane and ZP

The salt water immersion test can reveal different aspects of information about coating, such as:

- barrier property of coatings against electrolyte
- effectiveness of the pigment
- adhesion of the coating to the substrate
The coatings subjected to 30 days of salt water immersion test are shown in Fig. 4.7. The coating formed from epoxy and acrylic resins only displayed good film-forming property. The coating formed was smooth and cured at a reasonable rate. When exposed to NaCl solution for extended time, corrosion occurred along the scribe and obvious undercutting occurred. However, no corrosion or blistering occurred on other coated areas. The coating formed from epoxy and acrylic resins with silane showed much less undercutting at the scribe. The acrylic-epoxy coating with zinc phosphate added reduced undercutting to some degree; however, blistering occurred on intact coating and along the scribe blistering and corrosion occurred. On the other hand, the acrylic-epoxy coating with zinc phosphate and pigment added showed good resistance to Cl- containing electrolyte. The following observations can be made from the experiment:

- Zinc phosphate reduces undercutting and protects the scribe. Addition of pigment, however, on the other hand may impair other properties of the coating such as adhesion, permeability of the coating;
- Silane also helps in corrosion prevention which may be attained by enhancing the bonding of the coating to the substrate. When pigment is present, addition of silane also prevents blistering in occurring;
- Both silane and zinc phosphate are critical for a complete protection in a superprimer. A coating with both silane and pigment added, i.e. a superprimer, showed strong protection against aggressive media.

To investigate if silane enhances the bonding of coating to the substrate, the above coatings were tested in the tape adhesion test in wet and dry conditions, as shown in Fig. 4.8. The coating formed from acrylic and acrylic resins only demonstrated good adhesion in dry condition. After exposure to water the film could be easily detached from the substrate. With pigment added, the
acrylic-epoxy coating exhibited even worse adhesion onto substrate. Silane-added coatings exhibited good adhesion in dry and wet conditions. This result is consistent with the previous water immersion result, which is, silane did improve adhesion of the coating to the metal.

In the salt water immersion test it was found that addition of silane improved the barrier property of the coating against electrolyte. The hydrophobicity of the coating was evaluated by measuring the contact angle of a water droplet on the surface. The contact angles of the four coatings mentioned above, plus the same coating with barium chromate added as pigment, are shown in Fig. 4.9. The contact angles of the silane-added coatings are about 20 degrees higher than those of coatings containing no silane. In other words, the addition of the silane increased the hydrophobicity of the coating. It is also found that the addition of pigments, zinc phosphate or chromate, did not change the hydrophobicity of the superprimer coating.

Another technique used to investigate the effect of silane in the acrylic-epoxy coatings was EIS. The electrochemical impedance change of the four coatings mentioned above when exposed to 0.6M NaCl solution were measured by the Gamry potentiostat over a period of 34 days, as shown in Fig. 4.10.

The modulus of the coating formed from acrylic and acrylic resins was about 10M Ohms at low frequencies when the exposure began and the low-frequency modulus dropped to 1 M Ohms in a short time, which was a sign of drop of the performance of barrier properites. At the same time the modulus at all frequencies began to drop with exposure time, which demonstrated that the system began to fail and local pockets of water began to form under the coating. With pigment added, the acrylic-epoxy coating exhibited similar behavior in impedance change and the drop of impedance at all frequencies seems faster. This can be attributed to the reduced bonding of coating to the substrate when the pigment was added, as observed in the adhesion test. The
coatings with silane added demonstrated much higher impedance at low frequencies (500 M ohms compared to 10 M ohms of coating containing no silane). The conclusion from the EIS study corresponds to the results of other tests: addition of silane makes the coating more resistant to electrolyte and for extended exposure time this effect is more prominent.

4.4 Optimal time window for recoating/topcoating

In the finishing process of the airplanes, primer is not allowed to fully cure before the application of topcoat in order to improve the efficiency. However this time cannot be too short so as to impair the performance of the coating, as the solvent contained in the topcoat may dissolve the primer, resulting in the mixing of the primer and topcoat. For epoxy-polyamide primers compliant to Mil-PRF-23377G, the primer coatings shall be air-dried for 5 hours before the application of polyurethane coating conforming to MIL-PRF-85285. Investigating the optimal time to recoat/topcoat is an essential part of the development of a primer coating. The time window for recoating/topcoating may vary with the type of topcoat to be applied over the primer.

When used together with MIL-PRF-85285 polyurethane topcoat, the acrylic-epoxy primer coating followed by a topcoat after a drying interval of 1 day, 2 days and 5 days at ambient temperature was compared in the salt spray test. From the result as shown in Fig. 4.11, the optimal time for topcoating is after 1 day of drying under ambient temperature.

4.5 Summary

The development process of the acrylic-epoxy superprimer coating, which includes the selection of the resins, selection of silanes and optimization of formulation and performance evaluation, was reported in this chapter. The acrylic-epoxy superprimer formulated from Doubond DC9010W55, Maincote AE58, zinc phosphate and bis-sulfur silane demonstrated good corrosion
protection on aluminum panels. The superprimer coating passed 3000+ hours of salt spray test without topcoat and 300+ days of outdoor exposure test in Florida.

The effect of silane and zinc phosphate in the coating was investigated. It was concluded that:

• Both the anticorrosion pigment and silane benefit the anticorrosion performance of the coating.

• The silane improves the barrier property of the coating and improves the adhesion of the coating to the substrate
Chapter 5 Mechanism of Superprimer Coating

5.1 Introduction

In previous chapters, the performance of the acrylic-epoxy superprimer was discussed and the functions of silane and pigment in the coating were investigated. The superprimer exhibited excellent protection on aluminum alloys. Zinc phosphate, which is not considered as a strong inhibitor in solvent-based coatings, worked well in the waterborne superprimer coating. This chapter reports the study performed to understand the protective mechanism of the coating and the anticorrosion pigment.

The cross section of the superprimer coating was examined using SEM and EDAX. A unique stratified structure was revealed. It was found that the upper layer is mainly epoxy and the layer closer to the substrate mainly acrylic. Abundance of silane was observed at the interface between the coating and metallic substrate. Such self-assembled structure is believed to account for the high performance of the superprimer coating. ToF-SIMS further confirmed that the silane existing at the coating-metal interface interacted with the metal surface, which explained the improved metal/coating bonding by addition of silane. Further study of the scribe subjected to corrosion test, leaching of the pigment from the coating and reaction of zinc phosphate with aluminum with time in different conditions revealed the corrosion inhibition mechanism of zinc phosphate. Furthermore, the result was compared to the studies reported in the literature.

5.2 Curing chemistry of the coating
When the carboxyl-functional acrylic latex and epoxy emulsion are mixed into the superprimer coating, cure proceed via carboxyl-epoxy reaction and/or epoxy homopolymerization. In addition, FTIR analysis, liquid-state $^{29}$Si and $^{13}$C NMR studies Seth [1] revealed that in the acrylic-dominated layer hydrogen bonding occurs due to the interaction of the acrylic acid groups with the silanol groups formed due to hydrolysis of the silane. Hydrolysis of silane and crosslinking of silane in the epoxy phase via the C-OH group was also detected.

5.3 Microstructure of superprimer coating

The virginal cured epoxy-acrylic superprimer coating applied on AA7075 not subjected to any test was analyzed using SEM and EDAX. Fig. 5.1 shows the SEM images of the cross-section of the primer coating. It can be seen that two distinct layers exists. These layers are seamlessly bonded. Zinc phosphate particles, the pigment, are dispersed in the bottom layer. The top (far from the substrate) layer contains no pigment. Adjacent to the substrate, there seems to be another thin layer with morphology different from that of the above two.

The composition of these different layers and the surface of the substrate was analyzed using EDAX, as shown in Fig 5.2a - d. The different layers were numbered with A, B, C, and D as shown in the figure.

**Layer A:** Fig 5.2a shows a typical composition of Layer A. EDX analysis revealed that this layer is primarily made up of C, O, and traces of Cl. Since the coating has not been exposed to any salt water, the source of chlorine must be the residual epichlorohydrin, which was used as a precursor for manufacturing bis-phenol A type epoxy. This layer is more hydrophobic than the layer adjacent to the substrate as observed in contact angle measurements. Also no substantial Si or S was detected in this layer, indicating that silane does not substantially exist in this layer. Fig 5.3
shows the SEM image and EDAX data of the cross-section of an identical coating but subjected to 30 days of immersion in 3.5% NaCl solution. In this epoxy-dominated layer, no increase in the content of Cl was observed, as compared to the results in the Fig. 2a. This result suggests that the epoxy-dominated layer, which is located in the upper part of the superprimer coating, is impervious to electrolyte.

**Layer B:** Fig 5.2b shows the typical composition of Layer B. Zn, P, Si and S were detected in this layer. Zinc phosphate is the source of Zn and P. Si and S come from the bis-sulfur silane. As shown in Fig. 5.4, EDAX confirmed the white particle in the coating was the zinc phosphate.

**Layer C:** In the vicinity of the coating-metal interface the morphology of the coating appeared to be different from Layer A or B. EDAX analysis (Fig. 5.2c), revealed that the level of silane was higher than that in layer A or B.

**Layer D** (metal/coating interface): Si and S, as from silane, were detected at the interface between metal substrate and the superprimer coating (Fig. 5.2d). C and Al were also detected as expected. A further study of the interface using ToF-SIMS as reported in the sections following will give more information on the silane reaction at the metal surface.

**Line scans across the cross-section:** Figure 5.5 shows the results of the line scan of EDAX analysis conducted across the cross-section of acrylic-epoxy superprimer coated on AA 7075-T6 for elements C, N, O, Na, Al, Si, P, S, Cl, Fe and Zn. The line scan was conducted across the black line in the central of the cross-section. This result is consistent with the analysis of individual points in the different layers. Si and S, as from silane, mostly distributed in the part of the superprimer coating that was closer to the substrate. Al was detected in the coating in the immediate vicinity to the metal surface, whereas C was not detected on the metallic substrate side.
The surface was carefully cleaned after polishing. C is absent on the metallic substrate side. It is speculated that Al was able to react with the components of the superprimer such as the acrylic and silane. The reaction of Al with silane will be elaborated later. Such reactions are believed to improve the bonding between the superprimer and the metal.

**Elemental mapping across the cross-section:** Elemental mapping was conducted on the cross-section of the cross-section of the acrylic-epoxy superprimer coated on AA7075-T6 for Al, C, Cl, Si, P, O, Zn, Na, S and N using EDAX, as shown in Fig 5.6. The result is consistent with the results obtained from the point scan and line scan.

### 5.4 Scribe subjected to salt water

An AA7075 panel coated with acrylic-epoxy superprimer containing zinc phosphate was scribed and then immersed in 3.5 wt % NaCl solution for 30 days. The scribe appeared to remain clean, showing clean aluminum. This was also confirmed by the examination of the scribe using SEM (the image is shown in Fig. 5.7). The scribe remained smooth and corrosion-free but fine white particles were visible in the scribe. EDAX analysis of the smooth area in the scribe is shown in Fig 5.8. The energy of the electron beam is 20 keV. The composition of the clean scribe surface is mainly aluminum. Other elements detected included Mg, Na, C and Zn. The 3 wt % Zn is believed to be from AA7075-T6 itself, not from the pigment, as P was not detected. The EDAX analysis of white particles with result shown in Fig. 5.9 revealed that the particles were fine zinc phosphate crystals. The sample was rinsed well before the SEM/EDAX analysis and the particles seemed well adhered. The particles could not be the debris from the scratching before immersion test. It is more likely the particles were the zinc phosphate leached out from the coating and redeposited in the scribe either during the immersion or drying when taken out of the immersion
electrolyte. This leaching phenomenon was confirmed in further study, which is reported in the following sections.

5.5 Coating-metal interface

In the previous chapters it was observed that addition of silane improved the adhesion of the coating to the metallic substrate and also reduced corrosion. The mechanism for the adhesion promotion and corrosion inhibition of silane is believed to due to the reaction of silane on the surface of metal as described in Section 1.3. However, the direct evidence for this assumption, adhesion promotion by the formation of Si-O-M bonding, has proved elusive. Researchers have been trying to use various techniques including XPS and SIMS to find the experimental evidence for the assumption [1-5]. Most of these studies used pure silane as the reagent on the metal surface. In this study the level of silane was less than 10 wt% in the wet coating, which made it even more challenging for the investigation.

Time-of-flight SIMS, a highly surface sensitive technique, was used to study the interface and to determine if silane played a role in metal-coating bonding. Bis-sulfur silane-containing superprimer was detached from AA2024 substrate after 7 days of curing. The superprimer coating was not fully cured so the primer coating could be detached completely, which was proven by the fact that no carbon was detected on the metal side. Both metal side and coating side were analyzed as-is using ToF-SIMS without sputtering. The result was compared to that of AA2024 coated with acrylic-epoxy superprimer that did not contain silane. Polished pristine AA2024 was used as control.
Fig. 5.10 shows the ToF-SIMS spectra of polished pristine AA2024. Peaks with mass corresponding to Al and other alloying elements, such as Mg, Mn and Fe, were observed as expected.

Fig. 5.11 shows the ToF-SIMS spectra in as-is condition of the metal-side of delaminated AA 2024-T3 coated with bis-sulfur-containing superprimer. Peaks corresponding to Si and S were observed, which demonstrated that the presence of silane on the metal surface even after the polymer coating had completely been removed. No presence of Zn or P was found. Compared to the pristine AA2024, the intensity of Al was reduced from $2.7 \times 10^5$ to $1.2 \times 10^5$. It is believed the presence of silane could have resulted in this as silane hydrolyzes and forms a siloxane network. On the coating side, as shown in Fig. 5.12, no Zn or P was found either. A low-intensity of Al was observed. This result corresponds to the result of the SEM/EDAX, in which aluminum was found in vicinity of the interface on the coating side. No significant peaks corresponding to Zn or P were observed. Peaks of Si and S with high intensity were observed, which also confirmed the abundant presence of silane at the interface as the SEM/EDAX did. Peaks at 45 m/z in the positive spectra were observed both on the detached metal surface and the coating surface. The peak was identified to be $\text{SiOH}^+$, which was the hydrolysis product of the silane.

Fig 5.13 and 5.14 show the ToF-SIMS spectra of the interface (metal side and coating side) of AA2024 coated with superprimer with silane removed from the formulation. The intensity of Al was much higher than that in the spectra of silane-added superprimer-metal interface, i.e. $2.2 \times 10^5$ vs. $1.2 \times 10^5$. No peaks corresponding to Zn or P were observed, which was also the case in a silane-added superprimer-metal interface. A peak at 96 m/z was seen, which was identified as $\text{SO}_4\text{.}$ $\text{SO}_4\text{.}$ could be the residue from the cleaning process of the metal substrate. The observed Si and S with very low intensity were also believed to be the residue from the cleaning. On the surface of the detached coating, the presence of S was found and Si was missing. The presence of
Zn was observed and P was missing. Therefore no silane or zinc phosphate existed on the surface of the detached coating.

In conclusion, abundant silane was present on both sides of the interface between the silane-containing superprimer and the metal. The hydrolysis of the silane was confirmed. The presence of silane on the surface of the substrate reduced the intensity of aluminum detected. The pigment, zinc phosphate was not found at the interface.

### 5.6 Leaching rate of pigment

In section 5.3, the leaching of the pigment from the coating to the defect of the coating in aqueous environment was observed. To further confirm this phenomenon and measure the leaching rate, an experiment shown in Fig. 5.15 was performed. A cylinder filled with DI water was placed vertically on a free-standing coating with acrylic-dominated layer exposed to DI water. The concentration changes of Zn$^{2+}$ and PO$_4^{3-}$ with time were measured using inductively coupled plasma mass spectrometry (ICP-MS).

The leaching rate measurement by ICP-MS confirmed that zinc phosphate leached out from the acrylic layer. The leaching rates measured are shown in Fig. 5.16. The leached PO$_4^{3-}$ per cm$^2$ reached about 1 µg in a few hours and then maintained at this level. Zn$^{2+}$ was continuously released from the coating and reached 30 µg/cm$^2$ in 30 days. At 30 days the concentration of Zn$^{2+}$ and PO$_4^{3-}$ were 587.4 ng/ml and 22.5 ng/ml, respectively.

Salt immersion test is used to evaluate the corrosion protection of the coatings. However, salt water immersion has limitation. In a realistic working environment, the electrolyte that the coating is exposed to is normally not static. Therefore using a static immersion to evaluate the
performance and predict the service life of a coating can be inaccurate. To address this issue, a testing apparatus was designed to examine the relation between the corrosion rate and the turbulence of the environmental electrolyte. The setup of the circulating salt water corrosion test is shown in Fig. 5.17. The testing apparatus consisted of an electrolyte reservoir, an electric plastic pump to drive the flow of the electrolyte, manual valves to control the flow rate of the electrolyte, a plastic container that holds the sample panels. The container was transparent for easy inspection of the samples. The valve controlled the flow rate of the electrolyte that passed the sample holder.

Samples were prepared in the same way as the ones for ASTM B117 test. In the experiment, the samples were placed in the sample holder horizontally with the scribe facing up. The electrolyte used was 3.5 wt % NaCl. The acrylic-epoxy superprimers with either zinc phosphate or barium chromate pigment were tested for a period of 7 days. The flow rate of the salt water was controlled at 10, 5, 2.5 and 0 cm/s. The results (Fig. 5.18) revealed that the corrosion rate of scribe on pigmented superprimer coating increased with flow rate, which demonstrates the effect of pigment leaching on the scribe. Both the corrosion protection performance of the coatings containing zinc phosphate and chromate were affected by the flow rate, i.e., level of disturbance, of the electrolyte. Zinc phosphate seemed to be more susceptible to the flow rate than barium chromate.

There can be multiple factors affecting the performance of a pigment in this test:

a) The leaching rate of the pigment from the coating

b) The solubility of the pigment in the electrolyte

c) The critical concentration of the pigment, i.e., the minimum concentration needed for the pigment to be effective

d) The protection reaction rate of the pigment
All these factors can determine whether a pigment is suitable for a specific application. Therefore, this testing can be useful for evaluation of pigment in non-stagnant environment. In addition, this method provides a quick evaluation of the coating. Such a testing methodology can be further developed into a standard for pigment efficiency and coatings evaluation.

5.7 Proposed superprimer protection mechanism

The protective mechanism of acrylic-epoxy superprimer as illustrated in Fig.5.19 (a) - (e) is proposed based on the above results. The self-assembled double-layer structure of the acrylic-epoxy superprimer is characterized by a less-penetrable hydrophobic layer (epoxy-dominated) on the top and a hydrophilic layer (acrylic-dominated) accommodating the inhibitors underneath. The top layer functions as the physical barrier against electrolyte ingress, while the layer beneath functions as a fast leaching vehicle for the inhibitor. When the coating is scratched and the scratch is exposed to electrolyte, electrolyte diffuses into the layers of the coating selectively, as shown in Fig 5.19 (d). The acrylic-dominated lower layer is more hydrophilic therefore electrolyte penetrates more easily into this layer. The pigment, zinc phosphate in this case, dissolves in the electrolyte that has penetrated into the hydrophilic layer and moves to the scribe. Hereby the exposed bare metal can be actively protected by the pigment. The presence of silane also improves the adhesion and anti-corrosion performance of the primer.

The selective distribution of zinc phosphate particles in the acrylic-dominated layer can be a consequence of multiple factors. The possible causes are tentatively discussed here:

a) Zinc phosphate dihydrate particles thermodynamically prefer the encapsulation by the hydrophilic acrylic than the hydrophobic epoxy, which would lead to less interface surface area and eventually reduce the free energy.
b) The settlement of the pigment to the bottom under the influence of gravity during the curing process before the solidification of the coating can occur. It could partially account for the selective distribution as the settling of the pigment may promote the process of the stratification since the pigment sitting in an acrylic environment is thermodynamically favored.

It is worthwhile to point out that even though zinc phosphate has very low solubility and the low solubility was demonstrated to inhibit corrosion sufficiently on aluminum alloys, high loading (20-30 wt %) of pigments in the coating is required for stringent applications such as aerospace engineering or corrosive environments. Cost and performance are the main reasons behind the pigment loading level.

The cost of the resins is normally higher than the pigments. Conventionally pigments, especially fillers, are added in to the coatings to reduce the volume of the polymer to be used. Hence the concept of the critical pigment volume concentration (CPVC) was introduced, which describe the pigment loading level where the polymer matrix is just able to wet and fill the voids between the individual particles [6]. CPVC is a transition point and many properties of the paint undergo a marked change above the CPVC [7]. The formation of a smooth, continuous coating with minimal voids requires the PVC to be lower than the CPVC, thus the coating is a composite consisting of pigment particles randomly embedded in a continuously connected matrix of polymer [8].

The properties and performance of the coating are greatly affected by the level of PVC. Bierwagen and Hay concluded the properties of the coating that will be affected by the PVC [9, 10].
(1) Thermal and mechanical properties including: glass transition temperature (Tg), scrub resistance, cold crack resistance, flexibility, tensile strength, and block resistance.

(2) Transport related properties and performance including permeability, corrosion resistance, blistering, stain removal, and electrical resistance.

(3) Optical properties including gloss, opacity, and tint acceptance.

For a primer, the anticorrosion performance is one of the most important factors to be considered when the PVC is to be determined. The optimal PVC normally needs to be determined experimentally and it varies with substrate, binder type and application. In this study the anticorrosion performance of the acrylic-epoxy superprimer coating increases with the PVC initially and reaches the peak at 25 – 30 wt %. When the PVC is above 30 wt %, the performance of the coating drops. Similar results were reported by other researchers [11, 12].

The best anticorrosion performance of the superprimer coating (and many other coatings as well) occurs at higher PVCs. This can be attributed to two reasons:

a) High PVC ensures pigment particles to be distributed throughout the coating. Thus the entire substrate can be protected.

b) High PVC assures that pigment dissolves into the electrolyte at multiple sites, which facilitates adequate pigment release in a timely manner.

Researchers also noticed that the PVC can influence curing of the coatings [13]. Such a phenomenon was also observed in the present study. Addition of certain pigments, such as cerium and calcium zinc phosphomolybdate expedites the curing of the acrylic-epoxy superprimer. The metal ions can act as the catalyst for the polymer reactions during curing. Chromate, however, has no significant effect on curing. Though being a strong oxidizer, chromate is believed not to react with common binders at room temperature. Chromate pigments have been successfully used with
a variety of binders. The primer coating currently used on aircraft is epoxy-polyamide coating loaded with 20 wt % strontium chromate.

### 5.8 Corrosion inhibition mechanism of zinc phosphate

The superprimer coating acts as a vehicle for fast leaching, which makes zinc phosphate a more effective pigment compared to solvent-borne coating. Zinc phosphate leaches out and protects the scribe when the coating is damaged. This active protection relies on the reaction of zinc phosphate with the exposed bare metal. However, the mechanism by which primers pigmented with zinc phosphate protects is not well established. Reported studies are all based on steel substrates, as elaborated in the introduction. In summary, the proposed mechanisms suggest [14, 15]:

a) a greater tendency of physical barrier effect rather than electrochemical mechanism, i.e. phosphatization of the iron surface;

b) blocking of both anodic and cathodic reactions on steel;

c) a passive layer forms in the presence of zinc phosphate consisting of oxides (γ-Fe₂O₃), hydroxyoxides (α-FeOOH, γ-FeOOH) and iron phosphate. The result is a polarization of the cathodic regions due to the formation of limited-solubility basic salts, adhering to the substrate

d) inhibition of the anodic acidification reaction

e) formation of compounds with carboxyl and hydroxyl groups of the binder agent, which react with the products of corrosion resulting in a layer closely adhering to the metallic substrate [16-19]

Other authors [20] are of the opinion that the solubility of zinc phosphate is too low to produce a passive layer. In a medium with pH 6.5–8 the solubility of zinc phosphate is extremely low, so that some authors even think it acts only as an expensive extender[21].
Since no reported study has been done on aluminum and even the conclusions on steel substrates are still controversial, investigation of the inhibition mechanism of zinc phosphate on aluminum was carried out. The following experiments were performed:

1) Comparison study of bare AA2024 coupons immersed in Cl⁻-containing solution with and without zinc phosphate

2) Analysis of the scribe on superprimer-coated aluminum subjected to short-term and long-term exposures to Cl⁻-containing electrolyte

3) Investigation of the interface between the zinc phosphate-pigmented coating and substrate

5.9 Bare AA2024 panels subjected to immersion in Cl⁻-containing zinc phosphate solution

AA2024 mainly contains Al-Cu-Mg and Al-Cu-Fe-Mn intermetallics. The intermetallics are especially susceptible to pitting corrosion. Fig 5.20 - Fig 5.23 shows the SEM images and EDAX analysis of pristine AA2024 matrix, Al-Cu-Mg and Al-Cu-Fe-Mn intermetallics.

Bare AA2024 coupons were immersed in blank 600 ppm NaCl solution and 600 ppm NaCl solution containing saturated zinc phosphate for 2 hours. The Mg, Cu-rich intermetallics, Cu, Fe, Mn-rich intermetallics and the matrix were examined using SEM. Pitting corrosion occurred at some of the Mg, Cu-rich intermetallics, while the Al matrix and Cu, Fe, Mn-rich intermetallics remained unchanged. Fig. 5.23 and Fig. 5.24 show the pitting corrosion at the Mg, Cu-rich intermetallics in the absence of zinc phosphate. Compared to the pristine AA2024, the Mg content decreased 3.0 -4.0 % from a normal level of over 4.0 % and the relative content of Cu naturally increased. Mg is a more active metal than Al, Fe, Cu and Mn. Dissolution of Mg obviously occurred first and fast.
On the coupons immersed in 600 ppm NaCl solution containing saturated zinc phosphate, no pitting corrosion was observed after 2 hours of immersion. Fig 5.25 shows SEM image and EDAX analysis of Al$_2$CuMg intermetallics subjected to the immersion.

However, no zinc or phosphor on matrix or intermetallics of the immersed panel was detected using EDAX with a 20 keV electron beam. The same sample was analyzed using ToF-SIMS, which is a more surface-sensitive technique than EDAX. Fig. 5.26 shows the ToF-SIMS spectra in the mass range 43-84 m/z. Peaks with high intensities corresponding to Zn and P were observed.

5.9.1 The scribe on superprimer-coated aluminum subjected to short-term and long-term exposure to Cl$^-$-containing electrolyte

AA2024 immersed in zinc phosphate-containing NaCl solution for 2 hours did not show any obvious pigment-involved reaction product or precipitated film, as discussed in previous section. Also as shown in Fig. 5.7, the scribe exposed to 30 days of salt water immersion showed a clean scribe but still the scribe did not exhibit any reaction between the pigment and metal.

Fig. 5.27 shows the picture and an SEM image of the scribe on the acrylic-epoxy superprimer coated on AA2024. After exposure to 90 days of exposure to salt spray test (5% NaCl solution). The scribe appeared to be clean with original shiny metal color after exposure. In the SEM image amorphous solids and cracks were seen in the scribe. Fig. 5.28-5.32 shows the composition obtained from EDAX of different areas in the scribe including the amorphous solids, clean area and cracks.
Fig. 2.28 shows the EDAX analysis of the “smooth” area in the scribe (area 1 in Fig. 2.27) where no crack or clusters was absent. Substantial amount of Al, O, Na and Zn, and small amount of Si, Mg were found. These elements constitute the majority of film formed on surface of the scribe.

Fig. 2.29 shows the EDAX analysis of the particles formed in the scribe (area 2 in Fig. 2.27). The particles appeared to be rooted to the scribe instead of being a freestanding particle. Al, Na, O and Zn were found to be in substantial presence. Small amount of P, Mg and Si were found. Except for the level of P, the particles did not demonstrate a substantial difference in the composition compared to the general film (area 1) in the scribe.

Cracks were found in the scribe of dried samples subjected to long-term salt spray test as shown in Fig. 2.27 (area 3). The composition as analyzed using EDAX is shown in Fig. 2.30. Substantial amount of Al, O and Zn, and small amount of P were found to be present in the crack.

Fig. 2.31 shows the EDAX analysis of area 4 in the scribe (shown in Fig. 2.27). The composition of area 4 was found to be Al, O, Zn, Si and P. Al, O and Zn were in substantial presence and Si and P were much less.

There were some clusters formed close to the coating edge. The clusters could be mistakenly identified as the coating. However, EDAX analysis, as shown in Fig 2.32, demonstrated that these clusters were compound of Al, Zn, Si and O, instead of being polymer.

Cl was not found in all the areas in the scribe, which confirmed that no corrosion occurred in the scribe. Zn, O and Al were present in all the areas. It is worthwhile to mention that AA2024 alloy itself contains Zn, however, the concentration is generally lower than 0.3 wt %. The level of zinc
found in the scribe was much higher than 0.3 wt%. P was found in some areas of the scribe, including particles, crack and clean area. Si and Mg were also detected in some areas in the scribe.

5.9.2 Zinc phosphate in the coating

As discussed in previous sections, zinc or phosphate was not found at the interface (either coating side or metal side) through ToF-SIMS and EDAX, which indicates that zinc phosphate did not form a protective film on aluminum in advance. The analysis on the scribe also did not find metallic soap product between zinc phosphate and acrylic or other binders as claimed by other authors as an preventative inhibition mechanism on ferrous substrates [14]. It is worthwhile to point out that when the coating is exposed to electrolyte, it might be possible that zinc phosphate forms a film on the substrate, just like it does when there is a scratch in the coating.

5.9.3 Conclusion on the corrosion inhibition mechanism of zinc phosphate

Through this experiment and also results from the previous sections, the following conclusions about how zinc phosphate protects aluminum alloys in an aqueous environment can be made:

a) Zinc phosphate reforms on aluminum surface in short terms as demonstrated in the ToFSIMS study. The film or deposition is very thin and can be only detected by SIMS. At this time, the anodic protection effect is predominant, as demonstrated in the DC polarization test after 20 hours of exposure and SEM/EDAX analysis. Later when dissolution of Al at cathodic sites begins, OH\(^-\) and Al\(^{3+}\) are generated and Zn ions become involved and provide more noticeable cathodic protection. The intermetallics are anodic and ready to corrode compared to Al matrix, which can account for the more noticeable anodic protection at the early stage.

b) In the long run zinc can form a relatively thick protective film on scribe, as shown in the samples after 90 days of exposure to salt spray. At this time the protection is mostly
barrier effect. The major constituents of the film are Al, Zn, O, Si, P and Mg may also be present in the film. In the case of steel substrate, the formation of oxides (γ-Fe2O3), hydroxyoxides (α-FeOOH, γ-FeOOH), zinc hydroxide, basic zinc salts and iron phosphate were reported. In the case of Al substrate, aluminum hydroxide can form at cathodic sites where OH⁻ is generated. Aluminum hydroxide, as in the form of aluminate, can react with Zn²⁺ and/or other metal ions like Mg²⁺. Spinels like MgAl₂O₄ and ZnAl₂O₄ adhering to the aluminum surface are corrosion-resistant. Oxides, such as MgO and ZnO, may also form as part of the coating and prevent corrosion. At the anodic sites, the phosphate ions can easily react with metal ions and precipitates as in the form of insoluble salts.

c) Large particles or clusters formed on intermetallics containing Mg. Mg becomes the component of the protective clusters.

d) Zinc seems to play a greater role in the protection of the scribe than phosphate does, as zinc is more often seen in the protective film formed. Such phenomenon can be due to the low leaching-out of phosphate in water as demonstrated in leaching rate measurements. As discussed in Chapter 3, both zinc (as in ZnSO₄) and phosphate (as in Na₂HPO₄) are corrosion inhibitive on aluminum alloys, but neither of them alone can provide a performance comparable to zinc phosphate.

e) The protective film formed on the scribe, which consists of Al, Zn, O and other elements can be a hydrate when water is present. The cracks can form during the dehydration process.
f) The low solubility of zinc phosphate is not an issue for corrosion inhibition performance as long as zinc phosphate can leach from the coating. It has been demonstrated in the immersion test of bare panel in NaCl solution containing zinc phosphate that the low saturated concentration of zinc phosphate can reach is sufficient for corrosion protection on Al alloys. This assumption is also confirmed in the case of acrylic-epoxy superprimer with zinc phosphate as inhibitor, in which zinc phosphate was supplied with a channel for fast leaching from the coating.

The whole protection process of the zinc phosphate leached from the coating to the scribe is illustrated in Fig. 3.33 (a) - (c). The growth of the film, the clusters and the particles on the film surface can be continuous as long as such an aqueous environment exists and there is supply of the zinc and phosphate ions leached from the coating. The clusters and particles can also be finally become part of the film when the film grows. The composition of these solids formed on the metal surface can depend on the local composition of the metal surface.

As discussed in Section 5.7, the corrosion protection mechanism of zinc phosphate still remains controversial. Though the substrate is different, it would be of interest to compare the result of this study to the mechanism reported for steel substrates.

a) Some researchers proposed that zinc phosphate inhibits corrosion based on the physical barrier effect. This assumption seems to be valid in the case of aluminum substrates as well. In this study zinc phosphate was found to reforms on the surface of aluminum alloys and forms a film adhering to the alloy surface.

b) In the literature zinc phosphate is considered an inhibitor that can suppress corrosion at both anodic and cathodic sites. Zinc phosphate is dissociated in aqueous solution and becomes Zn\(^{2+}\) and PO\(_4^{3-}\). Zn\(^{2+}\) can react with the OH\(^{-}\) formed at the cathodic sites of the
corrosion, forming zinc hydroxide or basic zinc salts (e.g. basic zinc carbonate). When zinc phosphate is used on steel substrate, the formation of oxides (γ-Fe₂O₃), hydroxyoxides (α-FeOOH, γ-FeOOH) and iron phosphate were reported. The formation of these basic salts of low solubility resulted in a polarization of the cathodic regions. In the case of aluminum alloys, the film formed appear to different and has a more complicate composition due to the alloying elements and impurities in the alloy. The presence of great amount of Zn, Al and O all over the scribe surface exposed to salt spray test as detected in EDAX study provides the evidence for the formation of spinel. The cathodic sites, which accounts for the majority of the aluminum surface, is protected by the formation of the film formed. At the anodic sites, the presence of phosphate was found and insoluble aluminum or magnesium phosphate may precipitate to protect the substrate surface.

c) Zinc phosphate is claimed to inhibit anodic acidification reaction on steel substrate. This is also valid in the case of aluminum alloy. SEM/EDAX studies found a protective film formed unselectively on both anodic and cathodic sites. DC polarization curve demonstrated that the corrosion was surpassed on both anodic and cathodic sides. The addition of zinc phosphate lowered the slope of cathodic curve and shifted the anodic curve to the left in the potential-current density coordinate.

d) The evidence of the corrosion protection by the metallic soap formed from carboxyl and hydroxyl groups from the binder agent [22] with zinc phosphate was not found in this study. However, this type of reaction can vary with the specific resins being used and may take extended time to occur.
e) As to the questioning of the inhibition of zinc phosphate based on its low solubility, it was demonstrated in this study that the low solubility does not necessarily pose a problem for corrosion prevention, given that the pigment can be release promptly from the coating. The so-called second generation inhibitor, i.e., zinc phosphate modified by addition of other anions for increased solubility (e.g., calcium zinc phosphate), however, do not necessarily provide stronger corrosion inhibition, just as demonstrated in the pigment screening experiments.

5.10 Electrodeposition for ideally engineered coating structure

As discussed in Section 1.8, electrodeposition coating systems can be anionic or cationic, corresponding to deposition at the anode or cathode, respectively. In the case of superprimer, cationic deposition could be favored due to the characteristics of the silane. The presence of silane at the interface between coating and substrate was demonstrated to improve adhesion and passive corrosion inhibition. The cationic electrodeposition of superprimer was explored based on the following theories [1, 23, 24]:

a) When DC is applied, electrolysis of water produces OH⁻ at cathode, increasing the local pH. The reaction is:

\[ 4e^- + 4H_2O \rightarrow 4OH^- + 2H_2 \]

b) Silane hydrolyzes fast in alkaline (OH⁻ abundant) environment.

c) The hydrolyzed silane (cationic) will deposit on the cathode by the alkali-catalyzed condensation reaction.

d) Resins deposit quickly on the cathode when pH is high. With electroosmotic effect, water can be driven toward anode and a high density film can be achieved.

e) Electrodeposition tends to give good control over film uniformity and thickness.
Direct electrodeposition was used to deposit the superprimer on metal substrate. The setup for electrodeposition comprises of an electrolytic cell with metal coupon and inert graphite used as electrodes, as shown Fig.5.34. Electrodeposition voltage was 5V and electrodeposition duration was 30 minutes. The thickness of cured deposited superprimer was around 40 microns. Electrodeposited HDG panels were cured at 80ºC for 4.5 hours. Electrodeposited superprimer and dip-coated superprimer were compared on HDG. Fig 5.35 shows the electrodeposited and dip-coated superprimer coating on HDG subjected to 340 hours of salt spray test. No corrosion occurred on either sample, but watermarks showed on the dip-coated sample, indicating water penetrated underneath the coating via the scribe. This result suggests a better adhesion and a water penetration-resistant interface between the HDG substrate and superprimer. Fig 5.36 and 5.37 shows the electrochemical impedance spectra measured during ASTM B117 test. The electrodeposited superprimer coating exhibited higher impedances at low frequencies, suggesting a better barrier property.

The cross-sections of the two coatings were analyzed using SEM/EDAX. The SEM image and EDAX line scan across the cross-section of the coatings are shown in Fig. 5.38 and 5.39. Comparing the elemental line scan obtained from EDAX, the electrodeposited coating seems to have a more uniform distribution of silane. Especially at the interface, the silane concentration in the electrodeposited coating seems to be higher than that of dip-coated coating.

5.11 Conclusions
First the microstructure of the superprimer coating was studied using SEM/EDAX. It was revealed that the acrylic-epoxy superprimer has a self-assembled double-layer structure, which consists of an epoxy-dominated, more hydrophobic layer on the top and an acrylic-dominated, more hydrophilic layer underneath. The top layer provides a good barrier, while the
underneath layer acts as an ideal media for fast pigment leaching. SEM/EDAX on the scribe subjected to salt water immersion test demonstrated that zinc phosphate leaches out from the coating to the area with coating damaged and metal exposed to electrolyte. The leaching phenomenon was further confirmed by the ICP-MS measurements and the leaching rate was determined. Zinc was found to leaches faster and reaches a higher concentration in the electrolyte than phosphor does. The study of the coating-metal interface using ToF-SIMS proved the presence of silane at the interface and the evidence of the hydrolysis of the silane was found. The abundant presence of silane is believed to improve the adhesion and also facilitate the corrosion prevention.

The corrosion inhibition mechanism of zinc phosphate was explored and compared to mechanisms reported in the literature, through the study on a) comparison study of bare AA2024 coupons immersed in Cl-Containing solution with and without zinc phosphate present, b) analysis of the scribe on superprimer-coated aluminum subjected to short-term and long-term exposures to Cl-containing electrolyte and c) investigation of the interface between the zinc phosphate-pigmented coating and substrate. In the short term, zinc phosphate reforms on aluminum surface, which blocks both anodic and cathodic sites and prevent corrosion occurring. In the long run zinc phosphate can form relatively thick protective film on scribe. The protective film has a complex composition and can vary from site to site.

Finally the electrodeposition of superprimer was explored. Electrodeposited acrylic-epoxy superprimer was found to have better corrosion and water permeation resistance than those of dip-coated coating. SEM/EDAX revealed that electrodeposited superprimer has an even distribution of silane and the level of silane at the interface was relatively high.
Reference:
22. A. Burkil, J. Oil Colour Chem. Assoc. 81 274.
Chapter 6 Conclusions and Scope for Further Research

This study has demonstrated that it is practical to find an alternative for chromate-based coating technology used on current aircraft. The approach of this study is to utilize a combination of organofunctional silanes and a compatible inhibitor integrated into high-performance waterborne resins. The developed superprimer based on acrylic-epoxy resins and containing bis-sulfur silane and zinc phosphate demonstrated good corrosion inhibition on aluminum substrates. In the study the following have been performed:

1) Established of an effective testing methodology for corrosion inhibition evaluation and pigment screening and finished evaluation of over 100 chemicals which covered most potential corrosion inhibitive species. Zinc phosphate and calcium zinc phosphomolybdate were found to have the best overall performance on Al alloys. New pigments such as cerium metasilicate were synthesized based on the discovered synergism of different corrosion inhibitive species. Plasma polymerization was utilized to modify the surface property and dissolving behavior of some pigments with high solubility to ensure the pigment could be used in the coating.

2) Developed low-VOC, chromate-free primer (superprimer) using the above pigments with silane and acrylic-epoxy resins. This involved a series of experiments including the selection of silane, the selection of waterborne acrylic and epoxy resins and the optimization of the formulation. The finally developed formulation is based on Doubond DC9010W55 and Maincote AE58, with bis-sulfur silane and zinc phosphate added. The superprimer does not
require a chromate pretreatment on the substrate and it provides 3500 hours of protection for AA 2024 panels in the ASTM B117 test (2000 hours is considered a qualifying requirement for primer coating for aircrafts). The superprimer coating also performed well in other accelerated corrosion tests including Florida outdoor exposure tests.

3) Investigated the functions of inhibitor and silane in the coating. Silane was found to improve the adhesion of the coating to the substrate and also facilitate corrosion prevention. Addition of zinc phosphate to the coating improved the resistance of a scratched area against corrosion. However, addition of pigment generally increases the defects in the coating and impairs the barrier property of the coating. This effect can be alleviated by the presence of silane in the coating as silane greatly increases the hydrophobicity and electrochemical impedance of the coating. In other words, both silane and pigment, i.e., zinc phosphate, were found to be critical for the performance of the superprimer.

4) Studied the microstructure of the epoxy-acrylate superprimer coating. SEM/EDAX revealed that the superprimer has a self-assembled stratified double-layer structure which accounts for the strong anti-corrosion performance of the zinc phosphate pigment.

5) Measured the leaching rate of pigment, and studied the coating-metal interface and the scribe of coated panels subjected to corrosion test. Zinc was found to leach out faster and reach a higher concentration in the electrolyte than phosphor does. ToF-SIMS studies confirmed the presence of silane at the interface and the hydrolysis of the silane. The abundant presence of silane was believed to improve the adhesion and also facilitate the corrosion prevention.

6) Proposed the protection mechanism of the acrylic-epoxy superprimer. The self-assembled double-layer structure of the acrylic-epoxy superprimer consist of a less-penetrable
hydrophobic layer (epoxy-dominated) on the top and a hydrophilic layer (acrylic-dominated) accommodating the inhibitors underneath. The top layer functions as the physical barrier against electrolyte ingress, while the underneath layer functions as a fast leaching-out vehicle for the inhibitor when scribed. When the coating is mechanically damaged, the pigment leaches out and actively protects the uncoated area. The presence of silane also improves the adhesion and anti-corrosion performance of the primer.

7) Studied how corrosion inhibitor actively protects the defect of the coating, e.g., a scribe. The inhibition mechanism of zinc phosphate was explored and compared to those which have been reported. In short term, zinc phosphate reforms on aluminum surface in short terms which blocks both anodic and cathodic sites and prevent corrosion occurring. In the long run zinc can form relatively thick protective film in the scribe. The protective film has a complex composition and can vary from site to site.

8) Explored the possibility of engineering a more organized coating structure based on the protection mechanism of the coating and unique hydrolyzation and precipitation behavior of silane. Based on the protection mechanism of the superprimer, electrodeposition was explored in order to achieve a more organized coating with a better engineered metal/coating interface. The electrodeposited coatings were found to have higher barrier property and anticorrosion performance.

The current research has resulted in a promising alternate to the currently used chromate-based system. Further studies can be carried out in the following directions.

1) Faster curing system: the superprimer developed in this study was found to be a good coating for aluminum alloys. It cures at room temperature and requires 14 days of curing before putting into use. This superprimer was also found to be effective anticorrosion
coating for various substrates including CRS, HDG and Galvalume. However, on these substrates, a faster curing at elevated temperature is normally required. The acrylic-epoxy superprimer can be modified to suit those applications by adding additional curing agent such as blocked isocyanates.

2) The electrodeposition of the superprimer was explored with initial success. However, a more controllable and commercializable electrodeposition requires a better dispersion of superprimer droplets in the emulsion. This should be accomplished by adding compatible surfactant into the superprimer formulation.

3) More versatile and high-performance pigment systems. Zinc phosphate, as demonstrated, works well on certain substrates and provides corrosion inhibition comparable to that of chromates when used in the superprimers. Stronger pigment systems that can work on various substrates need to be developed. Instead of being a single pigment, such pigment systems are more likely to be combinations of synergistic pigments, or even mixtures of inorganic and organic pigments.

4) Superprimers based on other type of resins. The superprimers based on acrylic-epoxy resins were demonstrated in this study. Epoxy-acrylic coatings have their limitations and work best in certain applications. In its short history, polymer coatings have evolved into so many different types with each of which has their unique advantages and limitation. For most of these coatings, a proper surface treatment such as phosphating, chromating is required. Among the large quantity of applications of polymer coatings, the idea of superprimer can certainly find its use, especially in the applications where the pretreatment cannot be easily accommodated.
5) Stand-alone coatings. A complete coating system generally consists of conversion coating, primer and topcoat, with each of them fulfilling certain functions. When evaluated for certain applications, such as protection of cooling tower parts against corrosion, the superprimers worked well as a stand-alone coating without any pretreatment or topcoat. When the epoxy-acrylic superprimer coating which contained 20 wt % zinc phosphate as inhibitor and 5 wt % silica as filler was tested in the Florida outdoor exposure test, the superprimer coating without topcoat exhibited strong protection on aluminum alloys. Fig. 6.1 shows the coatings on AA2024 subjected to 317 days of Florida exposure test. The epoxy-acrylic superprimer containing 30 wt % zinc phosphate turned yellowish after exposure while no severe corrosion was observed. The superprimer coating with filler (silica) added remained its original appearance after exposure, which indicated that silica might be a good candidate of filler for this superprimer. Other fillers can further be added at a higher level for better protection of the coating against UV lights. In summary, the superprimers could be further developed into stand-alone coatings which can have a larger thickness and contain considerable amount of filler for better mechanical properties and UV resistance.

6) Improvement on mechanical properties and chemical resistance. Though having experienced fast and substantive improvement, waterborne coatings still cannot compete with solvent-borne coatings in terms of hardness, flexibility, wear resistance and chemical resistance. The development of high performance waterborne coatings relies on the breakthrough in the waterborne resins.

7) Other applications than aerospace. The superprimers developed in this study were designed for use on aircrafts (aluminum alloys). However, the superprimer coatings were
found to produce promising results in various applications including as the base coating for automobile, anticorrosion coating for cooling tower parts and protective coating for building materials. Upon further refinement, the superprimer coatings could be used to replace the more environmentally hazardous coatings which are being used in these applications.
<table>
<thead>
<tr>
<th>Corrosion Rate Units</th>
<th>K</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm/year (mmpy)</td>
<td>3272</td>
<td>mm/(amp-cm-year)</td>
</tr>
<tr>
<td>millinches/year (mpy)</td>
<td>1.288x10³</td>
<td>milliinches(amp-cm-year)</td>
</tr>
</tbody>
</table>
Table 2.2 The climate profile of the exposure location

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25° 33’ North</td>
<td>80° 24’ West</td>
<td>12 feet (3.6 meters)</td>
</tr>
</tbody>
</table>

**Typical Annual Solar Energy**

<table>
<thead>
<tr>
<th>Direct, 25° South (latitude angle):</th>
<th>TUV</th>
<th>Total Sun</th>
</tr>
</thead>
<tbody>
<tr>
<td>280 MJ/m²</td>
<td>6,588 MJ/m²</td>
<td>69%</td>
</tr>
</tbody>
</table>

**Temperature (Air)**

<table>
<thead>
<tr>
<th>Average Summer Maximum:</th>
<th>32°C</th>
<th>90°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Average Maximum:</td>
<td>28°C</td>
<td>82°F</td>
</tr>
<tr>
<td>Annual Average Minimum:</td>
<td>21°C</td>
<td>70°F</td>
</tr>
<tr>
<td>Average:</td>
<td>24°C</td>
<td>76°F</td>
</tr>
</tbody>
</table>

**Average Humidity**

<table>
<thead>
<tr>
<th>Rainfall</th>
<th>mm</th>
<th>inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summ Max</td>
<td>93% RH</td>
<td>Monthly Max</td>
</tr>
<tr>
<td>Maximum</td>
<td>80% RH</td>
<td>Monthly Min</td>
</tr>
<tr>
<td>Minimum</td>
<td>61% RH</td>
<td>Monthly Avg</td>
</tr>
<tr>
<td>Annual</td>
<td>70% RH</td>
<td>Total/Year</td>
</tr>
<tr>
<td>Rain Days/Year</td>
<td>111 days</td>
<td></td>
</tr>
</tbody>
</table>

- 134 -
Table 3.1 Immersion test of bare AA7075 in water extractions of typical pigments

<table>
<thead>
<tr>
<th>Pigment</th>
<th>pH</th>
<th>Corrosion initiation</th>
<th>Degree of corrosion after 12 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6.5</td>
<td>1-2 hrs</td>
<td>very severe</td>
</tr>
<tr>
<td>HTV</td>
<td>7.0</td>
<td>20 hrs</td>
<td>medium</td>
</tr>
<tr>
<td>MgMoO₄</td>
<td>7.0</td>
<td>1 day</td>
<td>medium</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>6.5</td>
<td>2 days</td>
<td>medium</td>
</tr>
<tr>
<td>CeCl₃</td>
<td>5.0</td>
<td>2 days</td>
<td>medium</td>
</tr>
<tr>
<td>La(OOCCH₃)₃</td>
<td>6.5</td>
<td>2 hrs</td>
<td>slight</td>
</tr>
<tr>
<td>CeVO₄</td>
<td>6.5</td>
<td>2 days</td>
<td>slight</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>5.0</td>
<td>4 days</td>
<td>slight</td>
</tr>
<tr>
<td>La(NO₃)₃</td>
<td>5.0</td>
<td>4 days</td>
<td>slight</td>
</tr>
<tr>
<td>Cortec M381</td>
<td>9.0</td>
<td>10 days</td>
<td>very slight</td>
</tr>
<tr>
<td>NaSiO₃</td>
<td>9.0</td>
<td>none to very slight within 12 days</td>
<td>very slight</td>
</tr>
<tr>
<td>BaCrO₄</td>
<td>6.5</td>
<td>none within 12 days</td>
<td>none</td>
</tr>
<tr>
<td>Zn₃(PO₄)₂</td>
<td>6.0</td>
<td>none within 12 days</td>
<td>None</td>
</tr>
<tr>
<td>CaO·ZnO·MoO₃</td>
<td>7.5</td>
<td>2 days</td>
<td>medium</td>
</tr>
<tr>
<td>CaO·ZnO·P₂O₅·MoO₃</td>
<td>7.5</td>
<td>2 days</td>
<td>medium</td>
</tr>
<tr>
<td>ZnO·Al₂O₃·MoO₃·P₂O₅</td>
<td>6.5</td>
<td>none</td>
<td>slight</td>
</tr>
<tr>
<td>ZnO·Al₂O₃·SrO·P₂O₅·SiO₂</td>
<td>7.0</td>
<td>none</td>
<td>very slight</td>
</tr>
<tr>
<td>ZnO·CaO·Al₂O₃·SrO·P₂O₅·SiO₂</td>
<td>7.5</td>
<td>none</td>
<td>medium</td>
</tr>
<tr>
<td>BaO·P₂O₅·SiO₂</td>
<td>8.0</td>
<td>none</td>
<td>slight</td>
</tr>
</tbody>
</table>
Table 3.2 Polarization resistance and corrosion rate of AA7075 in 3.5% NaCl with saturated inhibitor

<table>
<thead>
<tr>
<th>Item</th>
<th>Control</th>
<th>BTA</th>
<th>Ce(OOCCH$_3$)$_3$</th>
<th>BaCrO$_4$</th>
<th>CeVO$_4$</th>
<th>NaVO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta A (V/decade)</td>
<td>0.35</td>
<td>0.05</td>
<td>0.06</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Beta C (V/decade)</td>
<td>0.30</td>
<td>0.55</td>
<td>0.42</td>
<td>0.32</td>
<td>0.42</td>
<td>0.47</td>
</tr>
<tr>
<td>Icorr (µA)</td>
<td>84.51</td>
<td>3.29</td>
<td>7.14</td>
<td>2.24</td>
<td>9.10</td>
<td>5.88</td>
</tr>
<tr>
<td>Ecorr (A)</td>
<td>-790.80</td>
<td>-834.10</td>
<td>-799.00</td>
<td>-795.85</td>
<td>-799.35</td>
<td>-788.55</td>
</tr>
<tr>
<td>Rp (ohms)</td>
<td>266.85</td>
<td>7.50</td>
<td>3.36</td>
<td>4.59</td>
<td>2.36</td>
<td>2.95</td>
</tr>
<tr>
<td>Corrosion Rate (mpy)</td>
<td>38.62</td>
<td>1.50</td>
<td>3.26</td>
<td>1.02</td>
<td>4.16</td>
<td>2.68</td>
</tr>
</tbody>
</table>
Table 3.3 Formulation of the primer used for evaluation of the pigments

<table>
<thead>
<tr>
<th>Component</th>
<th>Identity</th>
<th>Parts in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silquest® A1289</td>
<td>Bis-sulfur silane</td>
<td>1.5</td>
</tr>
<tr>
<td>ECO-CRYL™ 9790</td>
<td>Acrylic resin</td>
<td>7</td>
</tr>
<tr>
<td>EPI-REZ™ WD - 510,</td>
<td>Epoxy resin</td>
<td>3</td>
</tr>
<tr>
<td>Alink™ - 25</td>
<td>Crosslinker</td>
<td>0.25</td>
</tr>
<tr>
<td>DI water</td>
<td>Viscosity modifier</td>
<td>1~2</td>
</tr>
</tbody>
</table>
Table 3.4  Corrosion rates and inhibitor efficiencies of CZPM, zinc phosphate and barium chromate determined from polarization curves.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Corrosion rate(µA)</th>
<th>Inhibitor efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>CZPM</td>
<td>12</td>
<td>66%</td>
</tr>
<tr>
<td>Zinc phosphate</td>
<td>10</td>
<td>71%</td>
</tr>
<tr>
<td>Barium chromate</td>
<td>8</td>
<td>77%</td>
</tr>
</tbody>
</table>
**Table 3.5** Formulation of the primer used for evaluation of the pigments

<table>
<thead>
<tr>
<th>Component</th>
<th>Identity</th>
<th>Parts in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silquest® A1289</td>
<td>Bis-sulfur silane</td>
<td>21.5</td>
</tr>
<tr>
<td>ECO-CRYL™ 9790</td>
<td>Acrylic resin</td>
<td>100</td>
</tr>
<tr>
<td>EPI-REZ™ WD - 510,</td>
<td>Epoxy resin</td>
<td>42.9</td>
</tr>
<tr>
<td>Alink™ - 25</td>
<td>Crosslinker</td>
<td>4.11</td>
</tr>
<tr>
<td>DI water</td>
<td>Viscosity modifier</td>
<td>15~20</td>
</tr>
</tbody>
</table>
Table 4.1 The combination of acrylic and epoxy resins evaluated. The combinations in which the acrylic and epoxy resins are compatible are marked with √.

<table>
<thead>
<tr>
<th>No</th>
<th>Acrylic</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NeoCryl</td>
<td>WD510</td>
</tr>
<tr>
<td>A</td>
<td>A6069</td>
<td>√</td>
</tr>
<tr>
<td>B</td>
<td>A6099</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>A6109</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>A6115</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>A6085</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>A6037</td>
<td>√</td>
</tr>
<tr>
<td>G</td>
<td>A633</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>XK 110</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>AE58</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.2 The prototype formulation used to evaluate different combination of acrylic and epoxy resins

<table>
<thead>
<tr>
<th>Component</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NeoCryl</td>
<td>5.00</td>
</tr>
<tr>
<td>Epoxy</td>
<td>1.00</td>
</tr>
<tr>
<td>Bis-sulfur silane A1289</td>
<td>0.90</td>
</tr>
<tr>
<td>Alink 25</td>
<td>0.15</td>
</tr>
<tr>
<td>Butyl cellusolve</td>
<td>0.15</td>
</tr>
<tr>
<td>Zinc phosphate pigment</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Table 4.3 Superprimer formulations based on DC9010 and AE58 with ratio varied.
(a) with bis-sulfur silane added

<table>
<thead>
<tr>
<th>No.</th>
<th>Ratio: DC9010/AE58</th>
<th>AE58</th>
<th>DC9010</th>
<th>A1289</th>
<th>Alink25</th>
<th>ZP</th>
</tr>
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<tbody>
<tr>
<td>A1</td>
<td>10%</td>
<td>2.73</td>
<td>0.27</td>
<td>0.44</td>
<td>0.07</td>
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</tr>
<tr>
<td>A2</td>
<td>20%</td>
<td>2.50</td>
<td>0.50</td>
<td>0.44</td>
<td>0.07</td>
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<tr>
<td>A3</td>
<td>30%</td>
<td>2.31</td>
<td>0.69</td>
<td>0.44</td>
<td>0.07</td>
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</tr>
<tr>
<td>A4</td>
<td>40%</td>
<td>2.14</td>
<td>0.86</td>
<td>0.44</td>
<td>0.07</td>
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<tr>
<td>A5</td>
<td>50%</td>
<td>2.00</td>
<td>1.00</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>A6</td>
<td>60%</td>
<td>1.88</td>
<td>1.13</td>
<td>0.44</td>
<td>0.07</td>
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<tr>
<td>A7</td>
<td>70%</td>
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<td>1.24</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>A8</td>
<td>80%</td>
<td>1.67</td>
<td>1.33</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>A9</td>
<td>90%</td>
<td>1.58</td>
<td>1.42</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>A10</td>
<td>100%</td>
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<td>1.50</td>
<td>0.44</td>
<td>0.07</td>
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Table 4.3 Superprimer formulations based on DC9010 and AE58 with ratio varied.
(b) with BTSE silane added

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<th>No.</th>
<th>Ratio: DC9010/AE58</th>
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<th>DC9010</th>
<th>BTSE</th>
<th>Alink25</th>
<th>ZP</th>
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<td>0.27</td>
<td>0.44</td>
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<tr>
<td>B2</td>
<td>20%</td>
<td>2.50</td>
<td>0.50</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>B3</td>
<td>30%</td>
<td>2.31</td>
<td>0.69</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>B4</td>
<td>40%</td>
<td>2.14</td>
<td>0.86</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>B5</td>
<td>50%</td>
<td>2.00</td>
<td>1.00</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>B6</td>
<td>60%</td>
<td>1.88</td>
<td>1.13</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>B7</td>
<td>70%</td>
<td>1.76</td>
<td>1.24</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>B8</td>
<td>80%</td>
<td>1.67</td>
<td>1.33</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>B9</td>
<td>90%</td>
<td>1.58</td>
<td>1.42</td>
<td>0.44</td>
<td>0.07</td>
<td>2</td>
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<tr>
<td>B10</td>
<td>100%</td>
<td>1.50</td>
<td>1.50</td>
<td>0.44</td>
<td>0.07</td>
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Table 4.4 The start formulation of bis-sulfur-containing acrylic-epoxy superprimer used for optimization

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<td>Epoxy</td>
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<tr>
<td>Bis-sulfur silane A1289</td>
<td>0.90</td>
</tr>
<tr>
<td>Surfynol 104H</td>
<td>0.125</td>
</tr>
<tr>
<td>Butyl cellusolve</td>
<td>0.25</td>
</tr>
<tr>
<td>Zinc phosphate pigment</td>
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<tr>
<td>Water</td>
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**Table 4.5** The final acrylic-epoxy superprimer formulation

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<tr>
<td>Silquest A-1289</td>
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</tr>
<tr>
<td>Maincote AE-58</td>
<td>52.30</td>
</tr>
<tr>
<td>Surfynol 104H</td>
<td>1.20</td>
</tr>
<tr>
<td>Daubond DC9010W55</td>
<td>5.75</td>
</tr>
<tr>
<td>Butyl cellusolve</td>
<td>5.15</td>
</tr>
<tr>
<td>15% sodium nitrite solution</td>
<td>1.15</td>
</tr>
<tr>
<td>DI water</td>
<td>1.70</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
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Fig. 1.1 SEM image of intermetallics in AA7075-T6
Fig. 1.2 Schematic of passivation breakdown mechanisms [6]. (a): Penetration mechanism
Fig. 1.2 Schematic of passivation breakdown mechanisms [6]. (b): Film breaking mechanism
Fig. 1.2 Schematic of passivation breakdown mechanisms [6]. (c): Adsorption mechanism
Fig. 1.3 a) Localized corrosion on 2195 Al-Li alloy after a potentiodynamic polarization run in 3.5% NaCl. SEM photomicrograph taken at a magnification of 2,000x. b) Pitting mechanism
Fig. 1.4 The coating system currently used on aerospace alloy
Fig. 1.5 Illustration of the structure of a mono-silane and a bis-silane
Fig. 1.6 Condensation process of silane film [13]
Fig. 1.7 Ideally condensed bis-silane film [13]
Fig. 1.8 Illustration of superprimer coating system
- Fig. 1.9 Processes that can occur in a plasma [82] -
Fig. 1.10 Schematic representation of rapid step growth polymerization (RSGP) mechanism of plasma polymerization [84]
Fig. 1.11 Illustration of the structure of the plasma-polymerized polymer and conventional polymer
Electrolysis of Water

Fig. 1.12 The pH variation across the anodic and cathodic electrodes during the electrolysis of water [89]
Fig. 1.13 Schematic diagram of electrodeposition process [89]
Fig. 2.1 The chemical structure of bis-sulfur silane
Fig. 2.2 The chemical structure of BTSE
Fig. 2.3 Schematic view of RF tumbler plasma reactor
Fig. 2.4 Schematic of a DC polarization testing cell [11]
Fig. 2.5 Schematic polarization curve showing Tafel extrapolation [12]
Fig. 2.6 Sinusoidal Current Response in a Linear System [13]
Fig. 2.7 Nyquist Plot with Impedance Vector [13], equivalent circuit shown in Fig 2.8
Fig. 2.8 Simple Equivalent Circuit with One Time Constant [13]
Fig. 2.9 Bode Plot with One Time Constant, resulted from the circuit as shown in Fig. 2.8 [13]
Fig. 2.10 Example of the equivalent circuit for a perfect polymer coating on metal
Fig. 2.11 A schematic of a salt-spray test chamber [17]
Fig. 2.12 The salt spray chamber set-up at DACCO SCI, INC.
Fig. 2.13 Florida outdoor exposure test setup [18]
Fig. 2.14 Interfacial forces acting on a liquid droplet on a solid surface [20]
Fig. 2.15 The contact angle goniometer, VCA Optima 2000
Fig. 2.16 Schematic diagram of the SIMS process [21]
Fig. 2.17 Schematic of ICP-MS main processes [24]
<table>
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<tr>
<th>Control</th>
<th>MgMoO₄</th>
<th>Na₂HPO₄</th>
<th>Zn₃(PO₄)₂</th>
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<tbody>
<tr>
<td>ZnSO₄</td>
<td>Cortec M381</td>
<td>CeCl₃</td>
<td>La(NO₃)₃</td>
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</table>

Fig. 3.1 (a) Bare AA7075 panels after 12 days immersion in various potential corrosion inhibitor solution containing 3.5 wt % NaCl
Fig. 3.1 (b) Bare AA7075 panels after 12 days immersion in various potential corrosion inhibitor solution containing 3.5 wt % NaCl
Fig. 3.1 (c) Bare AA7075 panels after 12 days immersion in various potential corrosion inhibitor solution containing 3.5 wt % NaCl
Fig. 3.1 (d) Bare AA7075 panels after 12 days immersion in various potential corrosion inhibitor solution containing 3.5 wt % NaCl
Fig. 3.2 Polarization curves of bare AA7075 panels immersed in pigment extraction containing 3.5 wt % NaCl.
Fig. 3.3 Polarization curve of aluminum alloy in 3.5 wt % NaCl with modified phosphate pigment present
Fig. 3.4 Polarization curves of AA7075 in 3.5 wt % NaCl solution under different pH measured in DC polarization test
Fig. 3.5 Polarization curves of AA7075 in 3.5 wt % NaCl solution containing saturated CeVO₄ under different pH measured in DC polarization test.
Fig. 3.6 (a) AA7075 panels coated with superprimer (the formulation listed in Table 3.2) loaded with different corrosion inhibitor subjected to 7 days immersion in 3.5 wt % NaCl. The back of the panels were not taped.

* PP: plasma polymerization treated
Fig. 3.6 (b) AA7075 panels coated with superprimer (the formulation listed in Table 3.2) loaded with different corrosion inhibitor subjected to 7 days immersion in 3.5 wt % NaCl. The back of the panels were not taped.
Fig. 3.6 (c) AA7075 panels coated with superprimer (the formulation listed in Table 3.2) loaded with different corrosion inhibitor subjected to 7 days immersion in 3.5 wt % NaCl. The back of the panels were not taped.
Fig. 3.6 (d) AA7075 panels coated with superprimer (the formulation listed in Table 3.2) loaded with different corrosion inhibitor subjected to 7 days immersion in 3.5 wt % NaCl. The back of the panels were not taped.
Fig. 3.7 Bare AA7075 panels immersed in 3.5 wt % NaCl solution containing inhibitor for 40 days: (a) Blank, (b) CZPM, (c) ZP
Fig. 3.8 AA7075 panels coated with bis-sulfur based superprimer (the formulation listed in Table 3.2) subjected to 40 days of salt water immersion test. Coatings from left to right are unpigmented, CZPM-pigmented and zinc phosphate-pigmented.
**Fig. 3.9** Bis-sulfur silane-based superprimer L2 (the formulation listed in Table 3.2) loaded with different level of CZPM and zinc phosphate. Coating on AA7075 subjected to 40 day of salt water immersion test.
Visible corrosion start time/total immersion time
**AC: acetate

Fig. 3.10 Bare AA7075 panels subjected to immersion test in 3.5% NaCl solution containing pigment combinations
Fig. 3.11 AA7075 tested in 3.5% NaCl solution with pigment present for 40 days.
Fig. 3.12 Bare AA7075 and AA2024 panels immersed in 3.5% NaCl saturated with cerium metasilicate (left) and blank (right) for 28 days.

- **a**: AA7075 panel immersed in 3.5% NaCl containing Ce$_2$(SiO$_3$)$_3$
- **b**: AA7075 panel immersed in blank 3.5% NaCl
- **c**: A2024 panel immersed in 3.5% NaCl containing Ce$_2$(SiO$_3$)$_3$
- **d**: A2024 panels immersed in blank 3.5% NaCl
Fig. 3.13 Polarization curves obtained from DC polarization tests. Substrate: AA7075 and AA2024 panels. Electrolyte: saturated cerium metasilicate solution containing 3.5% NaCl and blank 3.5% NaCl.
Fig. 3.13 AA2024 and AA7075 panels coated with acrylic-epoxy superprimer L2 containing cerium metasilicate immersed for 100 days in 3.5% NaCl.

a: AA2024 panel coated with unpigmented superprimer L2
b: AA7075 panel coated with unpigmented superprimer L2
c: AA2024 panel coated with superprimer L2 loaded with 30% cerium metasilicate
d: AA7075 panel coated with superprimer L2 loaded with 30% cerium metasilicate
Fig. 3.14 AA2024 panels coated with acrylic-epoxy superprimer containing 30 wt % cerium metasilicate subjected to 1750 hrs of salt spray test
Fig. 3.14 AA7075 panels coated with acrylic-epoxy superprimer L2 containing plasma-treated pigments compared to blank L2 coating. Panels subjected to 30 days of water immersion test.
Fig. 4.1 (a) Acrylic-epoxy primer formulated with various binders coated on AA7075 and AA2024. Coatings subjected to 2000 hours of salt spray test.
Fig. 4.1 (b) Acrylic-epoxy primer formulated with various binders coated on AA7075 and AA2024. Coatings subjected to 2000 hours of salt spray test.
Fig. 4.1 (c) Acrylic-epoxy primer formulated with various binders coated on AA7075 and AA2024. Coatings subjected to 2000 hours of salt spray test.
Fig. 4.1 (d) Acrylic-epoxy primer formulated with various binders coated on AA7075 and AA2024. Coatings subjected to 2000 hours of salt spray test.
Fig. 4.1 (c) Acrylic-epoxy primer formulated with various binders coated on AA7075 and AA2024. Coatings subjected to 2000 hours of salt spray test.
Fig. 4.2 Acrylic-epoxy primer based on DC9010 and AE58 with ratio of them varied subjected to 70 days of salt water immersion test. A1-A10: Bis-sulfur silane added; B1-B10: BTSE silane added. Substrate: AA7075. Formulation details are listed in Table 4.3.
Fig. 4.3 Variations of the epoxy-acrylic start formulation (details given in Table 4.4, variation indicated on specific panels) coated on AA2024. Panels subjected to 3500 hrs of salt spray test.
Fig 4.4 (a) Electrochemical impedance of the optimized acrylic-epoxy coating on AA2024 over a period of 87 days
Fig 4.4 (b) Low-frequency impedance of the optimized acrylic-epoxy coating measured in EIS on AA2024 over a period of 87 days
Fig 4.4 (c) Phase angle of the optimized acrylic-epoxy coating measured in EIS on AA2024 over a period of 87 days
Fig. 4.5 AA2024 panels coated with acrylic-epoxy superprimer system and control coating system subjected to 317 days of Florida outdoor exposure test. Left: Epoxy-acrylate superprimer; right: chromate pretreatment and MIL-PRF-23377G primer. Both topcoated with Defthane 85285D.
(a) Epoxy-acrylate Superprimer, topcoated with Defthane 85285 D

(b) Chromate pretreatment, MIL-PRF-23377G primer, topcoated with Defthane 85285 D

Fig. 4.6 The impedance and phase angle measured on AA2024 panels coated with acrylic-epoxy superprimer system and control coating system in the Florida outdoor exposure test.
Fig. 4.7 Acrylic-epoxy primer containing zinc phosphate and silane compared to acrylic-epoxy primers containing no zinc phosphate or silane in salt water immersion test. Substrate: AA2024. Panels immersed in 3.5% NaCl for 30 days.
Fig. 4.8 Acrylic-epoxy primer containing zinc phosphate and silane compared to acrylic-epoxy primers containing no zinc phosphate or silane in adhesion test. Substrate: AA2024.
Fig. 4.9  Acrylic-epoxy primer containing pigment and silane compared to acrylic-epoxy primers containing no zinc phosphate or silane on surface hydrophobicity.
Fig. 4.10 Acrylic-epoxy primer containing pigment and silane compared to acrylic-epoxy primers containing no zinc phosphate or silane on electrochemical impedance over a period of 34 days. Electrolyte: 0.6 M NaCl solution. Substrate: AA2024.
Fig. 4.11 Acrylic-epoxy superprimer followed by MIL-PRF-85285 polyurethane topcoat after drying at ambient temperature for 1 day, 2 days and 5 days. The coatings were cured at room temperature for 14 days and then exposed in the salt spray test. Substrate: AA2024-T. Exposure time: 2000 hours.
Fig. 5.1 SEM image of the cross-section of acrylic-epoxy superprimer coating on AA7075-T6.
Fig. 5.2 a Composition of different areas in the cross-section of superprimer coating obtained from EDAX.

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<th>At%</th>
</tr>
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<tr>
<td>O K</td>
<td>12.90</td>
<td>16.23</td>
</tr>
<tr>
<td>CI K</td>
<td>0.32</td>
<td>0.89</td>
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</table>
**Fig. 5.2 b** Composition of different areas in the cross-section of superprimer coating obtained from EDAX.
**Fig. 5.2 c** Composition of different areas in the cross-section of superprimer coating obtained from EDAX.

<table>
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<td>Al K</td>
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<td>Si K</td>
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**Fig. 5.2 d** Composition of different areas in the cross-section of superprimer coating obtained from EDAX.

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<td><strong>Cl K</strong></td>
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Fig. 5.3 SEM image and EDAX data of the cross-section of acrylic-epoxy coating subjected to 30 days of immersion in 3.5% NaCl solution.

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Fig 5.4 SEM image and EDAX data of the cross-section of acrylic-epoxy coating. EDAX analysis conducted on the white particle in the coating.

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<tr>
<td>Cl K</td>
<td>00.23</td>
<td>00.11</td>
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Fig. 5.5 SEM image of cross-section of acrylic-epoxy superprimer coated on AA 7075-T6 showing results of line scans of EDX analysis for elements C, N, O, Na, Al, Si, P, S, Cl, Fe and Zn along the black line in the central of the cross-section.
Fig. 5.6 Elemental mapping of the cross-section of the acrylic-epoxy superprimer coated on AA7075-T6 for Al, C, Cl, Si, P, O, Zn, Na, S and N using EDAX
Fig. 5.7 SEM image of the scribe in the acrylic-epoxy superprimer coated on AA7075-T6. The sample subjected to 30 days of immersion in 3.5% NaCl (b) EDAX analysis of clean area (1) and particles (2) in the scribe
Fig. 5.8 EDAX analysis of clean area (1) in the scribe in the acrylic-epoxy superprimer coated on AA7075 as shown in Fig. 5.7

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<tr>
<td>Al K</td>
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<td>Na K</td>
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<tr>
<td>Mg K</td>
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<td>1.72</td>
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</table>
Fig. 5.9 EDAX analysis of particles (2) in the scribe in the acrylic-epoxy superprimer coated on AA7075 as shown in Fig. 5.7

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<td>Na K</td>
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<td>23.13</td>
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<tr>
<td>Mg K</td>
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<td>0.13</td>
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<tr>
<td>P K</td>
<td>6.96</td>
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Positive Spectra:

Negative Spectra:

Fig. 5.10 TOFSIMS spectra in as-is condition of polished AA 2024-T3 in the mass range 0-84m/z
Positive Spectra:

![Positive Spectra Diagram]

Fig. 5.11 TOFSIMS spectra in as-is condition of metal-side of delaminated AA 2024-T3 coated with acrylic-epoxy in the mass range 0-84m/z

Negative Spectra:

![Negative Spectra Diagram]
Positive Spectra:

Negative Spectra:

Fig. 5.12 TOFSIMS spectra in as-is condition of coating-side of delaminated AA 2024-T3 coated with acrylic-epoxy in the mass range 0-84m/z
Positive Spectra:

![Positive Spectra Diagram]

Negative Spectra:

![Negative Spectra Diagram]

**Fig. 5.13** TOFSIMS spectra in as-is condition of metal-side of delaminated AA 2024-T3 coated with acrylic-epoxy superprimer with silane removed in the mass range 0-84m/z
Fig. 5.14 TOFSIMS spectra in as-is condition of coating-side of delaminated AA 2024-T3 coated with acrylic-epoxy superprimer with silane removed in the mass range 0-84m/z
**Fig. 5.15** The experiment setup of measurement of leaching rate of the pigment from the acrylic-epoxy superprimer.
Fig. 5.16 The leaching rate of zinc phosphate from the acrylic-epoxy superprimer measured by ICP-MS.
Fig. 5.17 The schematic of the circulating salt water corrosion test device
Fig. 5.18 Acrylic-epoxy superprimer with zinc phosphate and barium chromate as pigment subjected to 7 days immersion in the circulating salt water corrosion test. The flow rate of the salt water is 10, 5, 2.5 and 0 cm/s.

**SP + 30% ZP**

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<tr>
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<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td>2.5 cm/s</td>
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</tr>
<tr>
<td>0 cm/s</td>
<td><img src="image4.png" alt="Image" /></td>
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**SP + 30% barium chromate**

Substrate: AA7075-T6, temperature: 35 °C, exposure time 7 days
Epoxy-acrylic superprimer on Al substrate

Fig. 5.19 Schematic of the proposed protective mechanism of the acrylic-epoxy superprimer coating. (a) Epoxy-acrylic superprimer on Al substrate
Fig. 5.19 Schematic of the proposed protective mechanism of the acrylic-epoxy superprimer coating. (b) Epoxy-acrylic superprimer is scratched
Scribe exposed to electrolyte

Fig. 5.19 Schematic of the proposed protective mechanism of the acrylic-epoxy superprimer coating. (c) Scribe is exposed to electrolyte
Electrolyte diffuses selectively into the coating

Fig. 5.19 Schematic of the proposed protective mechanism of the acrylic-epoxy superprimer coating. (d) Electrolyte diffuses selectively into the coating
ZP dissolves in the electrolyte

Leached-out ZP protects the scribe

**Fig. 5.19** Schematic of the proposed protective mechanism of the acrylic-epoxy superprimer coating. (e) ZP dissolves in the electrolyte
Fig. 5.20 SEM image and EDAX analysis of the matrix (in contrast to the intermetallics) in the pristine AA2024.

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<tr>
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<tr>
<td>Al K</td>
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Fig. 5.21 SEM image and EDAX analysis of the Fe, Mn, Cu-rich intermetallics in the pristine AA2024.
**Fig. 5.22** SEM image and EDAX analysis of the Mg,Cu-rich intermetallics in the pristine AA2024.
Fig. 5.23 SEM image and EDAX analysis of Al$_2$CuMg intermetallics in AA2024 with pitting after 2 hours of exposure to 600ppm NaCl.
Fig. 5.24 SEM image and EDAX analysis of Al$_2$CuMg intermetallics in AA2024 with pitting after 2 hours of exposure to 600ppm NaCl.
Fig. 5.25 SEM image and EDAX analysis of Al$_2$CuMg intermetallics in AA2024 after 2 hours of exposure to 600ppm NaCl solution containing saturated zinc phosphate.
Fig. 5.26 ToF-SIMS spectra in the mass range of 43-84 m/z of bare AA2024 coupon subjected to 2 hours of immersion in 600 ppm NaCl solution containing saturated zinc phosphate
Fig. 5.27 Picture and SEM image of the scribe of the acrylic-epoxy superprimer coated on AA2024. The sample subjected to 90 days of salt spray test. Left: picture; right: SEM image
Fig. 5.28 EDAX analysis of area 1 in the scribe of the acrylic-epoxy superprimer coated on AA2024 (shown in Fig. 5.27). The sample subjected to 90 days of salt spray test.
**Fig. 5.29** EDAX analysis of area 2 in the scribe of the acrylic-epoxy superprimer coated on AA2024 (shown in Fig. 5.27). The sample subjected to 90 days of salt spray test.
Fig. 5.30 EDAX analysis of area 3 in the scribe of the acrylic-epoxy superprimer coated on AA2024 (shown in Fig. 5.27). The sample subjected to 90 days of salt spray test.

<table>
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<td>P K</td>
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<td>Zn K</td>
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Fig. 5.31 EDAX analysis of area 4 in the scribe of the acrylic-epoxy superprimer coated on AA2024 (shown in Fig. 5.27). The sample subjected to 90 days of salt spray test.

<table>
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<td>Zn K</td>
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Fig. 5.32 EDAX analysis of area 5 in the scribe of the acrylic-epoxy superprimer coated on AA2024 (shown in Fig. 5.27). The sample subjected to 90 days of salt spray test.
Fig. 5.33 Metal in the Scribe exposed to electrolyte which contains NaCl and ZP leached from the coating. (a) \( \text{PO}_4^{3-} \) and \( \text{Zn}^{2+} \) attach to and reform on metal surface.
Film and amorphous particles grow on the metal surface

**Fig. 5.33** Metal in the Scribe exposed to electrolyte which contains NaCl and ZP leached from the coating. (b) Film and amorphous particles form on the metal surface
Cracks, amorphous clusters, particles and film form on the dried metal surface in the scribe

**Fig. 5.33** Metal in the Scribe exposed to electrolyte which contains NaCl and ZP leached from the coating. (c) Cracks, amorphous clusters, particles and film formed on the dried metal surface in the scribe
Fig. 5.34 Schematic of the electrodeposition of the superprimer
Fig. 5.35 Electrodeposited HDG panels and (b) dip-coated HDG panels subjected to 340 hours of ASTM B117 test.
Fig. 5.36 Electrochemical impedance and phase angle measured of dip-coated acrylic-epoxy superprimer on HDG during salt spray test from day 0 to day 42.
**Fig. 5.37** Electrochemical impedance and phase angle measured of electrodeposited acrylic-epoxy superprimer on HDG during salt spray test from day 0 to day 42.
Fig. 5.38 SEM image and EDAX line scan across the cross-section of dip-coated acrylic-epoxy superprimer coating
Fig. 5.39 SEM image and EDAX line scan across the cross-section of electrodeposited acrylic-epoxy superprimer coating
Fig. 6.1 Epoxy-acrylic superprimer coated on AA2024 (no topcoat) subjected to 317 days of Florida outdoor exposure test. Left: epoxy-acrylic superprimer containing 30 wt % zinc phosphate; right: epoxy-acrylic superprimer containing 20 wt % zinc phosphate as inhibitor and 5 wt % SiO₂ as filler.