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“SUPERPRIMER”: Chromate-Free Coating System For DoD Applications

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MASTER OF SCIENCE
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By

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ABSTRACT

The idea of this research topic was to develop a novel, environmentally benign coating system for metal alloy structural components in DoD systems. The coating was chromate-free and contained little or no volatile organic compounds (VOC’s). The integrated organosilane system replaced the chromate system entirely including all chromate pretreatment and all corrosion-inhibiting chromate pigments. The complete system and also most or all of its components were water-borne. The term used to denote this particular primer is “superprimer.” This primer was based on organofunctional silanes that possess an extraordinary ability to protect metals against corrosion.

The proposed work integrated organosilanes into a full water-borne coating system. The objective was to replace the current system (metal pretreatment, primer and topcoat) with no sacrifice of corrosion performance.

Chapter 1 gives a brief overview on important concepts including corrosion and its control, significance of chromium in corrosion control and its use, silane technology, idea of the superprimer and the objective of this thesis.

Chapter 2 gives information about the materials used for preparation of the superprimer. Procedures used for the testing and preparation of the superprimer are discussed.
Chapter 3 gives detailed information about the superprimer. In the beginning it gives information about the choice of selecting the components that constitute the primer followed by initial formulation and their results. The developments that led to the final formulation are discussed in detail. Test results including EIS and salt spray results are provided whenever necessary.

The silane plus resin combinations can lead to coating formulations but in order to make it perform on par with chromate primers further additions need to be made. Detailed explanation of the idea, purpose and expectations of these additives in the primer are already given in Chapter 1. In Chapter 4, details about the mixing procedure of the additions, different kind of additives tried and their test results are given. There are primarily two important kinds of additives, nanoparticles and corrosion inhibitors. Many commercially available particles and inhibitors were tried and tested for corrosion performance. Test results by EIS and salt spray are provided.

Zinc-rich primers are as the name suggests primers with heavy loads of zinc metal dust in it. The zinc dust/powder is used as filler and is held in the coating by using a binder. Paints with zinc pigments contain about 80% by weight pigment of which 20% is oxide. Zinc-rich coatings contain 85-95% metallic zinc, by weight, in the dry coating with little or no oxide. Depending the type of binder used the primer can be organic or inorganic. Organic binders can be epoxy, polyurethane, acrylate etc. In inorganic zinc-rich primers the binders are usually silicates. Chapter 5 starts with a
brief explanation on the uses, application, and mechanism of action and the idea of zinc-rich primers. It also includes the idea of the zinc-rich superprimer, the formulations, test results etc.

Chapter 6 discusses the characterization work that was done in the final stages of this thesis work. The NMR characterization technique was used in the trials to investigate the chemical structural characteristics and changes in the superprimer formulations. For this NMR instruments at Oklahoma State University in Stillwater, OK were used. Both carbon and silicon NMR analysis were applied.

Chapter 7 summarizes the conclusions of this thesis.

Chapter 8 discusses the recommendations for future work.
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CHAPTER 1: INTRODUCTION

This chapter gives a brief overview of important concepts including corrosion and its control, significance of chromium in corrosion control and its use, silane technology, idea of the superprimer and the objective of this thesis.

1.1 Corrosion

1.1.1 Definition

Corrosion is an electrochemical reaction process which leads to continuous loss of metal or metal alloys. Energy is needed to extract metals from their mineral state to the pure state. The same amount of energy is emitted during the formation of its chemical compounds or in other words during the process of corrosion. [1] Corrosion returns the metal to its combined state in chemical compounds that are similar or even identical to the minerals from which the metals were extracted. Thus corrosion has been called extractive metallurgy in reverse [2-4]. An attempt has been made in the next few paragraphs to explain the science behind the corrosion process in simple terms.

1.1.2 Theory

It is a natural law for materials to exist in the lowest energy state possible. This law applies to metal atoms also, which is the reason why they exist in mineral or chemically compounded state
instead of their pure metal state. Every metal surface (except in the case of noble metals such as gold) has a layer of its own oxide on top with pure metal alloy underlying this oxide surface. The formation of an oxide on a pure metal or metal alloy surface is instantaneous. So even in the case of scratches and damages, a metal surface metal oxide will be formed almost instantaneously from the underlying metal upon exposure to atmosphere. This formation of oxide is due to a normal chemical reaction.

Every chemical reaction requires a driving force or in technical terms, energy in some form. The energy required for a certain reaction to proceed forward is called its potential. Consider the following common reaction between a metal and an acid as an example,

\[ M + nH^+ \rightarrow M^{n+} + \frac{n}{2}H_2 \quad [eq \, 1] \]

Each reactant in the above reaction is reacting with the other to form another more stable form of its own, in the exposed conditions. Metal is reacting to form a metal salt as a product which is more stable than metal itself when exposed to this particular acid. Similarly hydrogen, which was at first in an acid, reacts to form hydrogen and liberate itself into a more stable form of hydrogen gas. These reactions/stabilizations of materials in any conditions happen/occur by transfer of their electrons. Since transfer of electrons involves transfer of charge and transfer of charge is termed
as current, the potential/driving force which makes the reaction happen is given an electrical term of Electrochemical Potential.

Every material bears a certain amount of charge on it. Increase in the amount of this charge by transfer of electrons from it is called the oxidation/anodic reaction. Acceptance of electrons from other materials is called the reduction/cathodic reaction. In every reaction one reactant passes through oxidation and the other through reduction. So each of the reactions has some potential attached to it. The above reaction can be divided into 2 reactions. A schematic is shown in Figure 1.1:

\[
M \rightarrow M^{n+} + ne^- \quad \text{Anodic Reaction} \quad e_a \quad \text{[eq 2]}
\]

\[
nH^+ + ne^- \rightarrow \frac{n}{2} H_2 \quad \text{Cathodic Reaction} \quad e_c \quad \text{[eq 3]}
\]

The \(e_c\) and \(e_a\) mentioned above are the potential of each of these half reactions. The reactions are called as half-cell reactions and the potentials are half-cell electrode potentials or redox potentials. The potential required for the complete reaction to happen will be the sum of the half-cell electrode potentials. This information is very useful in detecting the reaction mechanisms when two or more reactants are involved.

\[E = e_a + e_c\]
This electrochemical potential can be related to the most basic free energy change using the equation:

\[ \Delta G = -FE \]  \[\text{eq 4}\]

At standard state or when reactants react in standard amount at a standard known temperature the above relation would be,

\[ \Delta G_0 = -F E_0 \]  \[\text{eq 5}\]

Where \( E_0 \) and \( G_0 \) are standard values for any reaction/reactant, \( n \) is the number of electrons or equivalents involved in the reaction and \( F \) is Faraday’s constant, 96,500 coulombs per equivalent.

Thus we have a fundamental relationship, in which a charge, \( nF \), taken reversibly at equilibrium through a potential \( E_0 \), corresponds to an energy change \( \Delta G_0 \).

When reactants react at conditions different from the standard conditions the potential or the driving of the reaction to proceed will change. This change can be monitored using the following reaction,

\[ E = E^0 + (2.303RT/nF) \times \log (A) \]  \[\text{eq 6}\]

Where \( E \) = the total potential (in mV) developed between the sensing and reference electrodes.
E⁰ = is a constant which is characteristic of the particular ISE/reference pair (It is the sum of all the liquid junction potentials in the electrochemical cell)

2.303 = the conversion factor from natural to base10 logarithm.

\( R = \) the Universal Gas Constant (8.314 joules/K/mole).

\( T = \) the Absolute Temperature.

n = the charge on the ion (with sign).

\( F = \) the Faraday Constant (96,500 coulombs).

\( \log (A) = \) the logarithm of the activity of the measured ion

In the right half of the above reaction the terms T and A denote the dependence of a reaction potential on temperature (T) and concentration (A).

Corrosion involves similar chemical reactions. Availability of reactants at cathode, anode and an electrolyte to allow the movement of electrons will drive the chemical reaction forward and repeat itself. This combination is the reason behind the continuous deterioration of corroding metal. For this particular reason corrosion is termed as an electrochemical reaction instead of just a chemical reaction.
1.1.3 Corrosion Control and its Significance

Nature’s simple low energy law is acting as a starting point for corrosion. Corrosion is involved in many aspects of life and has both direct and indirect effects on most of them. From a common stain in a kitchen sink to a major aircraft accident can be caused by corrosion. CC technologies and NACE international study shows that the cost of corrosion in US alone is 280 billion dollars per year. The major industry getting affected by this is the Department of Defense which includes Army, Navy and Air force. Plans for control or prevention of this corrosion are no doubt a matter of greatest concern.

It was mentioned in the previous section that as long as reactants and oxidation species are available, the corrosion of any metal is going to continue until its complete deterioration. Controlling the environment by removing/decreasing the corrosion causing species in it can be one method. Limiting and prevention of metal exposure to the corrosion causing species are other options. Corrosion protection by organic/inorganic coatings has been in use for several decades and has been proven to be a very effective option.

Organic coatings have been extensively used as barrier coatings which prevent the entry of water and ions and inhibit the cathodic reduction reaction from taking place [5]. These coatings form a cross-linked net-like sheet structure over the substrate and this coating adheres to the metal substrate. The efficiency of the coatings depends on the ability of the coatings to prevent the
corrosion causing species like water and oxygen from seeping through the coatings to the metal underneath. Thus it depends mainly on the cross-linking density if the coating itself and also its adhesion to the metal. Bolger and Michaels [6] showed that a good interfacial adhesion at the metal coating interface is very important for good corrosion performance. Coating delamination failures are mainly due to formation of corrosion causing formation of hydroxyl at the metal-coating interface. These hydroxyl ions initiate the cathodic reactions and hence drive the corrosion reactions forward. This phenomenon was demonstrated by Dickie and Floyd [7].

So, it is first necessary that the coating prevents the passage of these species to the metal. If for a reason the coating fails to prevent the passage, the interface or the metal surface should be passive for these species to react. This condition of the passivity on any metal surface depends on conditions like pH and the stability of the surface. The metal oxide itself can be passive but it again depends on the pH of the environment. The metal oxide can be turned to a more passive layer by making it react with other compounds. These compounds are called inhibitors and they can be organic or inorganic. Organic inhibitors were extensively studied by several authors [5-7]. Most of the organic inhibitors are in the form of weak acids and their derivatives from insoluble salts at the metal surface [5]. This insoluble passive insulating layer prevents the electrochemical reactions to take place and inhibit corrosion. Inorganic corrosion inhibitors such as chromates, phosphates and recently, cerium salts have been widely used for corrosion control of various
metals and alloys. These corrosion inhibitors work in the same way by the formation of passivating hydroxide/oxide films and suppressing the cathodic reaction by limiting the diffusion of the electrolyte, oxygen and water to the substrate. It will also limit the transfer of electrons to the metal interface. Inorganic inhibitors are active corrosion inhibitors that undergo reduction at active corrosion sites (pits, precipitates or inclusions) to form insoluble oxides.

There are many methods like the above which are used and there are many other options that are still under development and have a huge prospect. This corrosion problem and the cure for it as a whole give a very large scope for an extensive research and study.

1.2 Corrosion in the Department of Defense

The Department of Defense (DoD) acquires, operates and maintains a vast array of physical assets, ranging from vehicles, aircraft, ships, and other material to wharves, buildings and other stationary structures that are subject to corrosion. It maintains equipment and infrastructure worth billions of dollars in many environments where corrosion is causing military assets to deteriorate, shortening their useful service lives. A typical heavy corrosion environment is shown in Figure 1.2. The resulting increase in required repairs and replacements drives up costs and takes critical systems out of action, reducing mission readiness. In 2001, a government-sponsored study estimated the costs of corrosion for military systems and infrastructure at about $20 billion
annually and found corrosion to be one of the largest components of life-cycle costs for weapon systems. Typical examples of corrosion are shown in Figures 1.3 – 1.5

The metals used by DoD include Cold Rolled Steel, Hot Rolled Steel, electro-galvanized steel, Hot Dip Galvanized, titanium zinc sheets, galvalume sheet, galvannealed sheet, aluminum alloys, 1XXX, 2XXX, 3XXX, 5XXX, 6XXX, 7XXX, copper, brass, nickel and magnesium alloys. But primarily aluminum alloy AA 2024 T3 finds its use in the aircraft industry and carbon steel is still found to have a major usage in the construction side. This thesis primarily concentrated the testing and trials on these two substrates. In the next few paragraphs of this section an understanding of the corrosion of these two metals is given.

Aluminum and aluminum alloys have been used as aerospace materials especially in commercial airplanes due to their high strength/stiffness to weight ratio, mechanical properties and corrosion resistance. The aluminum oxide formed on the surface is very stable in ordinary conditions. The conditions where the oxide is stable and unstable can be easily derived using a Pourbaix diagram. According to it the oxide layer is stable in the pH ranges of 3.9 and 8.6. At conditions lower than this pH range aluminum oxidizes to aqueous cations following the reaction

\[ \text{Al} \rightleftharpoons \text{Al}^{3+} + 3\text{e}^- \]  \[\text{eq 6}\]
When the pH is in between the range 3.9 – 8.6 aluminum converts to aluminum oxide in the presence of cathodic reaction-deoxidizer.

\[ 2\text{Al} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad \text{[eq 7]} \]

When the pH is above this range the aluminum changes to soluble anions

\[ \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{AlO}_2^- + 2\text{H}^+ \quad \text{[eq 8]} \]

According to the above information the aluminum metal is not susceptible to corrosion (passive to corrosion) as long the conditions are in oxide forming stage. When the conditions shift to either of the sides the aluminum metal/oxide layer is susceptible to corrosion. Factors like pH and concentration play a major role in determining the conditions. Their dependence is already explained in the previous sections.

The passive oxide film is susceptible to localized breakdown leading to loss of the underlying aluminum metal. If the localized attack occurs at an open surface it is called pitting corrosion. These corrosion forms can lead to structural breakdown by acting as sites of crack initiation. The following review helps in understanding pitting corrosion as it is the main form of corrosion in aircraft aluminum alloys [3].
Pitting corrosion has been studied in great depth by several authors [8-9]. Frankel [10] suggested various stages of pitting to explain localized corrosion initiation and growth. He reported that any of these stages is important involving passive film breakdown, growth of metastable pits and growth of larger stable pits. The second and the final stages are associated with the understanding of pit initiation, growth and repassivation of the metal surface. It was suggested that localized corrosion is controlled by factors relating to stabilization and growth of pits rather than the influence of the passive film which is secondary in nature [10].

The most widely used aircraft aluminum alloy is the AA2024-T3 alloy. Many researchers [8-10, 11] have done extensive work in order to understand the corrosion mechanism of AA2024-T3 alloy. The AA2024-T3 alloy is made up of Al, 3.8-4.9 Cu, 1.2-1.5 Mg, 0.3-0.9 Mn, 0.5 Si, 0.5 Fe, 0.1 Cr, Zn and Ti. The heterogeneous distribution of the copper-aluminum phases in the alloy is the cause of the low resistance of the alloy. These second phase particles give added mechanical strength to the aluminum matrix but they are undesirable for corrosion resistance of the alloy. Pitting is the major form of corrosion but corrosion forms such as intergranular and stress corrosion also occur.

According to Buchheit et al., there are many second-phase particles that are formed in AA2024-T3 alloy [12]. He suggested that the concentration of copper in second phase particles and the local depletion of copper in certain micro-structural areas establish a local galvanic cell that
results in localized attacks [12]. They are called S phases as they are characterized by spherical shape. Literature suggests two major types of second phase particles: Al-Cu-Mg which is called the S phase characterized by high copper content and Al-Cu-Fe-Mn second phase particles. The formation and the distribution of these second phase particles lead to the poor corrosion resistance properties of the AA2024-T3 alloy [12].

Iron can exist in the oxidation states of +2 and +3, which complicate the Pourbaix diagram. At above neutral conditions the iron forms a protective layer which makes the iron passive. In the lower and neutral conditions it corrodes because the oxide is not formed. For better understanding and more information about the reaction of iron at different conditions the reader is referred to [1].

1.2.1 Coating Technology in DoD

Defense equipment and infrastructure are exposed to the harshest environments and are highly prone to be corroded easily and also quickly. Most of the defense equipment is very expensive and the need to maintain them in their best shape is imperative. Corrosion of the equipment could in fact be the main reason for their deterioration and poor performance. So the department uses an efficient state-of-the-art-three-layer coating technology for most of their equipment. Figure 1.6 shows a schematic of this technology and Figure 1.7 shows an example of a typical corrosion repair in DoD.
Painting and coating operations fall into three primary categories. These categories are:

- Surface preparation/Conversion coating
- Priming
- Painting (including cleaning and maintenance);

Surfaces must be treated before painting for corrosion control and to ensure proper paint adhesion. Most services also employ some type of Chemical Agent Resistant Coating (CARC) to protect equipment from chemical attack and exposure. Surface preparation typically involves cleaning and preparing the surface, treating the surface and changing its characteristics, and rinsing and cleaning the treated surface. The current pre-treatment technique used is primarily chromate conversion coating. The thickness of this coating layer ranges from 0.06 µm to 2 µm. This layer is of prime importance to the corrosion protection and adhesion of the next coating layer, i.e., primer above it. The method and mechanism is discussed in more detail in the next section. But this chromate conversion can lead to wastewater treatment requirement and hazardous waste disposal issues because it is a known fact that chromium is declared a prominent carcinogenic and its use is facing extension.

The primer, which is the second layer, is usually comprised of a pigmented organic resin matrix. The thickness of this layer can vary from 5-20 µm. The pigmented formulation may be formulated
with chromates or not in the resin matrix. The main purpose of this layer is to improve corrosion performance and also act as an intermediate between the organic top-coat and the inorganic pretreatment. This particular organic layer acts as a bridge between the two end layers. The use of chromium is also frequent in this layer. Some DoD primers contain about 20 – 25 % by weight of chromate as pigments in them. These pigments leach out from the primer layer and form a passivating layer on the metal in place of scratches and damages. Besides the use of chromium the primers have other issues like air quality issues. Some of the current coatings contain high concentrations of Volatile Organic Compounds (VOC’s) and Hazardous Air Pollutants (HAPs).

The final layer is a topcoat which is supposed to be flexible, have a matte finish and be chemically resistant with maximum exterior durability. The topcoat also provides the aircraft with decoration and camouflage. A typical topcoat is made of polyurethane resin and the thickness varies between 50 and 200 µm.

Painting operations can vary greatly depending on the facility and the end-use of the item to be painted, but most opportunities for painting, deal with the lowering of VOC emissions during paint application and paint equipment cleaning. Examples of opportunities in the area of painting include low-VOC paints, waterborne paint systems, powder coat paint systems, automatic and non-solvent gun cleaning equipment, as well as equipment and methods to improve the application of paint.
1.2.2 Chromium: Use, Mechanism, Advantages and Disadvantages

1.2.2.1 Use and Methods

The following information can be obtained from multiple websites A.1, A.2, A.3 listed in the appendix, and from literature ref [23-24]. Chromate films are chemical conversion coatings, in the process of which the substrate metal participates in the coating reaction and becomes a component of the coating; and it has a profound influence on the properties of the coating [13-14].

Among the metals commercially chromated are zinc and cadmium electroplates; zinc die castings; hot-dipped galvanized steel; aluminum (in almost every conceivable form); and sometimes copper and silver alloys. Chromate coatings improve corrosion resistance and appearance of metals and adhesion of organic topcoats [14].

The chromating process involves a chemical reaction between the metal surface and an aqueous solution containing chromates and some activator ions. The activators can be sulfates, chlorides, fluorides, phosphates and complex cyanides. Usually chromating process can be substrate specific but some solutions can be used on different kinds.

The solutions for chromating are acidic. A simplified reaction proceeds along the following lines. Metal at the interface is dissolved by the acid and enters the solution as metal ions. There is a
local rise in pH (lowering acid content) in the immediate vicinity of the interface. Basis metal ions combine with chromate ions to form a compound that is insoluble at the local (higher) pH. This compound precipitates on the metal surface as an adherent coating. Reaction by-products enter the main solution.

Coatings formed by the reaction are of necessity built up from the inside out. Since coatings can only be produced by the interaction of the solution with the metal, the solution must diffuse through prior layers of coating and reaction products must diffuse outward [13-14].

This inward-outward diffusion of solution can have a detrimental effect on thicker coatings. They may be powdery and loosely adherent. And solution trapped in the coating interstices can lower final corrosion resistance [13].

Because the chromating process involves a continuous chemical reaction, the depletion of the solution content is obvious. It is necessary to maintain solution concentration steady so that uniform coating properties can be maintained over the entire working life of a chromating bath. In the next following paragraphs a few types of chromating processes have been discussed. Figure 1.8 shows an example of commercially available chromating types.

**Zinc and Cadmium Electroplate**

A typical cycle used to chromate electroplated work follows these steps:
1. Electroplate.

2. Rinse (multiple rinses may be employed).

3. Optional dip in 0.25-0.50 pct nitric acid.


5. Cold rinse.

6. Leach (if required).

7. Cold rinse.

8. Warm-air dry off.

Plated parts are to be chromated are placed on racks or in stainless steel baskets convenient for the dipping step. Corrosion resistance depends on the particular chromate selected. Appearance also is a consideration. Plated parts are to be chromated with a minimum thickness of 0.006 mm. An average of 0.0012 mm is consumed by the chromating process, leaving 0.0048 mm, which is required for satisfactory corrosion resistance.

**Clear Bright.**

This is one of the earliest types of chromating process in which the solution was a concentrated (100 g/liter chromic acid) solution that did a certain amount of chemical polishing. The solution consists of chromates, sulfates and buffers such as borates or acetates, and, it deposits a gold
film which can be removed by a subsequent immersion in dilute alkali (leaching, sometimes called bleaching). This coating was once very popular for wire goods such as refrigerator racks since the polishing of the chromate produces an appearance similar to that of chromium.

To use this process on zinc plate, the process was modified. The two-step process has been largely replaced by more dilute, single-dip processes. This greatly reduces the cost of maintaining a highly concentrated solution and the cost of waste-treating the spent chromate. The double-dip process, i.e., chromate plus alkali leach, is still often used on cadmium plate.

**Blue Bright**

Single-dip solutions for passivating zinc plate and providing a degree of stain resistance are used in both rack and barrel plating. Plated fasteners, steel stampings and wire goods are now commonly chromated in these solutions. The baths consist of chromates, fluorides and large amounts of nitric acid. The concentrated proprietary products are available in liquid form (which contains nitric acid) or as a granular powder (to which the user adds nitric acid).

Working solutions will contain only about one g/liter of chromic acid (or even less), about one percent of the amount in the former baths. Naturally, the cost of preparing these and of subsequent waste treatment is considerably lower.
Chromate films from this type of bath can be dyed a variety of colors with organic dyes. This can serve as identification, especially for screws, nuts and small parts. These solutions are specific for zinc electroplate and will not work on cadmium or other types of zinc.

**Gold Films**

Gold chromate films are produced by solutions containing chromates with sulfate or chloride activators produce gold colors. These films contain considerably higher amount of hexavalent chromium than clear films, and the gold color can be due to this reason. Corrosion resistance is better. Baths of this type can be used for zinc, cadmium and some zinc die castings.

**Olive Drab**

The olive drab in chromate films is achieved by inclusion of organic acid modifier. The higher corrosion resistance of these coatings can be due to the same reason. These are applied to zinc and cadmium electroplates from baths similar to those used for gold coatings. The color is not especially pleasing, however, and coatings of this type are functional rather than decorative.

**Black**

The black color in chromate films can be achieved by the incorporation of a soluble silver salt into a gold chromate solution which produces a deposit of black silver chromate. This coating has excellent corrosion resistance and a jet black matte appearance, with good light absorbance. These products should find some applications in coating parts for solar collectors. The use of a
silver salt tends to make the process expensive and sensitive to chloride contamination. The sensitivity to chlorides can be an issue when the chloride baths are used in the chromating process.

**Zinc Die Castings**

Zinc-die-castings are extensively used in decorative and functional automotive applications. Parts such as carburetors and fuel pumps are highly susceptible to the ravages of water-gasoline corrosion, which is a particularly aggressive combination. Without chromate protection, a gelatinous precipitate of zinc hydroxide quickly fouls small orifices and ventures. A gold chromate deposit prevents this problem.

A typical cycle for chromating Zamak die castings is as follows:

1. Deburr (mechanical or thermal).
2. Alkali clean.
3. Cold rinse.
4. Acid activation (dilute sulfuric or phosphoric acid, often with included fluorides).
5. Cold rinse.
6. Warm rinse.
7. Warm-air dry.
Hot-Dipped Galvanized Steel

Hot-dipped galvanized steel coils can be susceptible to the formation of white zinc corrosion products during their storage. To prevent this they might need to be chromated at the mill. Or they can be chromated on high-speed coil-coating lines as a pre-paint treatment, to provide corrosion resistance and excellent paint adhesion. Unfortunately the first process is no substitute for the second. The mill process is intended only for passivation and is an inferior adhesive coat for paint. It is also extremely difficult to remove, so that galvanized steel that is ultimately to be painted should be specified without mill chromate passivation (it should be oiled instead).

Mill Chromate

Typically, two types of mill chromating are used. One has a fluoride activator, while the other is based on reduced (trivalent) chromium. The process involves flooding of the solutions over the coil after it comes from the galvanizing pot (after water quench). The chromate solution is dilute (1 g/liter) and is not rinsed, but squeegeed off. A thin film remains, it reacts with the zinc and the coating is dried in place. Coatings are clear, colorless and intended to provide protection until sheet is fabricated, often under outdoor storage conditions at construction work sites.

Paint-Base Chromate

Applied on high-speed coil-coating lines, these are chromate solutions of moderate concentration (10 g/liter) with complex fluoride activators. New coil-coating lines can handle widths of metal up
to 152 cms wide and run at 1.5 m/sec. Coil is painted in-line by reverse-roll-coat methods and subsequently fabricated into residential siding and architectural building panels.

**Gold Chromate**

Gold chromates of this type used for zinc plate and Zamak are sometimes used on galvanized steel stampings and hardware.

**Aluminum**

Chromates for aluminum fall into two categories: chrome-phosphates, primarily those used on architectural aluminum extrusions to provide a paint-bonding coat, and chrome oxides applied to almost every type of aluminum, i.e., sheet, coil, stampings and castings. Purposes: paint bonding and corrosion resistance.

**Chrome Phosphate**

Baths for applying chrome phosphate consist of chromate ions, phosphates and fluorides.

Although the solution contains chromium in the hexavalent form (Cr (vi)) chemical reduction takes place on the metal at the point of application, so that the chromium in the coating is essentially all trivalent chromium (III) phosphate. Most lines for applying this type of chromate spray it on cleaned aluminum extrusions, but some dip lines are in operation. Since the chromate coating itself contains no hexavalent chromium, it is common practice to use a passivating hexavalent chromium rinse as the final step in the treatment. A typical cycle would be:
1. Alkali clean

2. Rinse

3. Chromium-phosphate

4. Rinse

5. Hexavalent chromium rinse (seal)

Paint is customarily applied in-line by electrostatic spray and then baked producing a finished extrusion ready for assembly into window casings and such. This process produces remarkable adhesion. Corrosion resistance is also excellent if the final seal and paint are properly selected. The coating has an almost colorless to pale green appearance, making it very suitable for the application of white and pastel colors (no bleed through).

Chrome Oxide

Chrome oxide treatments deposit a chromate film ranging in color from nearly colorless through gold to brown. Baths contain chromates, fluorides, nitrates and an accelerator, which may be ferricyanide or a metal from group 7 or 8 of the periodic table. Ferri-cyanide-accelerated baths are fastest, developing the most coating for a given time. They are also quite easily controlled and rejuvenated. The main objection to ferricyanide baths is the complex cyanide radical in the subsequent rinse water, which is difficult to remove or destroy, and decomposes to cyanide in the presence of ultraviolet light.
Gold chromate films are used both with and without paint. Unpainted, they give corrosion protection on aluminum stampings, tubular products, extrusions, die castings and aluminum heat exchangers. As a base for paint, the gold chromates afford both adhesion and corrosion resistance to coil-coated sheet used for residential siding and building panels. Unlike the chrome-phosphate, chrome oxide coatings are rich in hexavalent chromium and need no additional seal to develop their maximum corrosion resistance.

**Process Parameters**

In general, the operation and control of a chromate processing solution are simplicity itself.

Treatment times, whether by spray or dip, are relatively short, ranging from a few seconds (for a bright dip on zinc plate) to a maximum of five minutes (for the heaviest coatings on aluminum). Temperature requirements are also moderate: most solutions operate at or near room temperature and few require temperatures above 54°C.

The solutions are aggressive, especially those that contain fluorides. Satisfactory acid-resistant materials are stainless steel (316 ELC), polyethylene, polypropylene, PVC and rubber.

The usual chemical control of a chromating solution consists of a titration to determine hexavalent chromium, and pH measurements to regulate acidity. Titration of total acid is sometimes used, but the build-up of reaction products makes pH a more reliable choice.
Chromate films should not be dried at elevated temperature, since they rupture (mud cracking) and lose protective value. For films on zinc, drying temperature should be below 54°C, while aluminum can tolerate temperatures to about 82°C with no adverse effects.

**Testing**

All chromates are intended to increase the service life of the finished article and this implies improved corrosion resistance. Accelerated tests have been developed in an attempt to predict service life and to compare various treatments. The most common of these is exposure to salt fog (ASTM B-117).

When evaluating results, comparing results between different test sites or recording results, give particular attention to the following:

1. Use of good quality sodium chloride in the test solution, and pH adjust.
2. Measure atomization rate (amount of salt solution sprayed).
3. Specify what constitutes a significant surface. A significant surface is customarily exposed at an angle of 15° from vertical. This may be particularly difficult in the case of odd-shaped parts or small screws. In these cases, the angle or position of exposure must be agreed upon, since it is of paramount importance and results are otherwise not
comparable. Companies or trade associations may specify how parts are to be positioned.

4. Specify what constitutes corrosion, e.g., a white pinpoint, heavy white corrosion products or red rust. If possible, have photographs or examples to illustrate degrees of corrosion.

5. Specify if parts are to be observed at periodic intervals (e.g., 24 hours) and tested until failure, or exposed for a certain time (e.g., 168 hours), then evaluated and rated after completion.

These points are directed to the salt spray test but are valid for other corrosion tests as well.

All corrosion tests are subject to interpretation. Outdoor exposure tests are among the most reliable, but even these really measure only what happens under a very specific set of conditions in a single environment; they should not be interpreted as "real world performance".

**EPA**

Chromium, whether in hexavalent or trivalent form, is classified as hazardous waste by EPA. Chromate-containing effluents are also regulated on the federal, state and local level. Rinse waters and spent solutions must be treated to remove chromium before discharge.

Most commonly, hexavalent chromium is reduced to the trivalent form with sodium metabisulfite. The trivalent chromium is then precipitated by pH adjustment with alkali such as liquid caustic or
lime. The precipitated solids containing the chromium are mechanically separated from the liquid by settling or filtration. They can then be removed (by a certified waste hauler) to an approved landfill.

1.2.2.2 Mechanism

The CCC formation involves destabilization of the passive oxide film by fluoride, followed by reduction of chromate by the exposed aluminum. Figure 1.9 shows a schematic of the mechanism of chromium coatings.

$$2 \text{Al} + \text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ \rightarrow 2\text{Cr} (\text{OH})_3 + \text{H}_2\text{O} + 2 \text{Al}^{3+} \quad [\text{eq} \ 9]$$

Exposure to chromate-containing CCC solution results in the reduction of the hexavalent chromium to trivalent chromium which is retained in the chromate conversion coating. In summary the mechanism of chromate inhibition of aluminum (AA2024-T3) is that chromate is a very soluble, high-valence oxidizing ion with a lower-valence which is insoluble and creates an extremely protective oxide/hydroxide film. The formation of an insoluble trivalent chromium oxide/hydroxide film stops the localized corrosion in AA2024-T3 alloy.

Chromate conversion coatings in addition to their excellent corrosion properties, adhesion and paintability are noted for their ability to self-heal if damaged by mechanical or chemical action provided they are not severe. This behavior was observed by several researchers [13-14] when
the coating was subjected to an aqueous environment. Self-heal or active protection involves release of soluble chromate ions from the coating, transport through the solution and subsequent action at the site of damage, namely the pits. This active corrosion protection is different from passive or barrier corrosion protection which is a thickened oxide/hydroxide film at the metal surface. This property allows the structure or component to withstand minor mechanical or chemical damage on the coating sustained during service without having maintenance.

According to researchers in the Fontana Corrosion Research Center at Ohio State University [8-10] there is direct and indirect evidence supporting the idea that a leached-out chromate ion results in the dynamic repair by interacting with the defects or pits in the coating. On the basis of their experimentation Buchheit et al., were able to establish testable criteria and place a set of guidelines for the self-healing ability of chromates. A schematic of this explanation of chromate mechanism is shown in Figure 1.9.

They are:

1) The coating must contain a reservoir of inhibiting compound which can be released when needed.

2) The inhibitor must be water-soluble and be released into the contact solution.
3) The leached-out inhibitor must be able to diffuse out of the coating and be transported through the solution.

4) The transported inhibitor must act on damaged or exposed areas and inhibit further corrosion.

Given these distinct characteristics chromate conversion coatings have been and still are the most widely used surface pretreatment process in the aircraft industry.

1.2.2.3 Advantages of chromate conversion coatings

1) CCC gives excellent corrosion protection to the metal substrate (passes 336 hours of standard salt spray test- ASTM B117)

2) They improve adhesion between many paint and metals

3) They exhibit active corrosion protection, i.e., the self healing effect

4) They are visible to the naked eye so they are used in decorative coating industries

5) Chromate coatings are easy to apply and are economically viable

6) They are completely water-based surface treatments without any organic solvent
1.2.2.4 Disadvantages of chromate coatings

The major disadvantage associated with the chromates is not its performance or properties but its toxic carcinogenic effects. Chromate and chromate-containing compounds have been limited since 1982 by the Environmental Protection Agency through several acts. In Europe, for example, a directive was issued by their environmental board to eradicate the use of chromium by 2003, but it has now been delayed to 2007. Because of this a green corrosion inhibitors revolution has taken shape in the last decade to replace chromates [15]. The EPA states that the hexavalent chromium Cr6+ whose properties make it an excellent corrosion inhibitor is environmentally unsafe. It is believed that the strong oxidation properties of chromates have brought much scrutiny concerning its use. The Cr6+ undergoes reduction which eventually damages the DNA cells. Chromate exposure through inhalation, ingestion and skin contact is the most common ailment resulting in lung cancer. The environmental burden of using chromate has greatly affected the aerospace industry due to its dependence on using aluminum alloys. Thus it becomes imperative that chromates be replaced by environmentally benign coatings that offer the same performance levels of the chromates. The next section discusses one of the promising environmentally acceptable treatments.
1.3 SUPERPRIMER

1.3.1 Definition

The silane research group of Dr. William van Ooij defines this coating system to be, ‘a chromate free, low or no VOC, no HAP, completely water-reducible universal coating system which is a direct onto metal coating and does not require an extra conversion coating. It will eliminate the use of chromium in the form of both conversion coating and in the form of pigments in the current coating practice. Their use will be replaced by an integrated organosilane system in combination with a compatible polymer. Further additions of particles and corrosion inhibiting pigments including color will be made to give the coating system a shape of a complete ready to commercial primer. Van Ooij’s research gave it the generic name ‘SUPERPRIMER’.

1.3.2 Background and Origin

1.3.2.1 Silane Pretreatments: Performance and Promise

Silanes, technically called as organofunctional trialkoxy silanes have been known and used as adhesion promoters for decades in various industries [16-23]. They are very efficient in binding two unlike materials like organic and inorganic materials together; hence the name coupling agent is given to it. This property of silanes allows them to be efficient in many areas like reinforced plastics, fiber reinforced thermoplastics, electric cables of cross-linked polyethylene, adhesion
promoters in resins and coatings, sealant primers, shell molds, brake linings, polishers, adhesives, printing oils, etc [24-36].

This ability of silanes is due to their unique chemical structure. The ability of silanes to act as adhesion promoters is attributed to their unique chemical structure. Organofunctional silanes have a general formula $X_3–Si–(CH_2)_n–Y$ where $Y$ represents an organofunctional reactive group and $X$ is a hydrolyzable ester group which is capable of reacting with inorganic materials. The functional groups can be a vinyl, sulfur or an amine group and many others which can interact with organic materials such as polymers. A schematic of silane mechanism is shown in Figure 1.10.

Plueddemann et al. [16] studied in great depth the ability of silanes to improve properties of glass/polymer composites. He was able to demonstrate that the mechanical properties of the glass/polymer composites can be enhanced with the application of silane coupling agents like vinyl, amine or methacrylate silanes. Plueddemann proposed various theories to explain the silane solution chemistry and its bonding mechanisms to the inorganic material. According to him the alkoxy ester groups need to be hydrolyzed with water to form silanol groups (Si-OH). These silanol groups are expected to form strong covalent bonds with a hydrated inorganic material. The silanol groups undergo condensation reactions on contact with an inorganic/metal surface leading to the formation of siloxane chains and metallo-siloxane bonds at the interface. The presence of
more active silanol groups in the hydrolyzed silane mixture is important in order to get good reactivity at the surface and subsequently more metallo-siloxane bonds are formed. The bonding of reactive groups to polymers has also been studied in great depth [37-38]. The good adhesion of the silane to the polymer is attributed to the chemical reactions that occur between the functional group in the silane and the reactive functional group in the polymer.

In order to understand the theory and application of this silane coupling agents many researchers conducted various analytical and characterization techniques and studied film properties like structure, morphology and interaction with metals and polymers. They also varied process parameters like pH, rate of hydrolysis, method of application, curing and choice of solvent [37-39]. The application of silanes towards corrosion protection of metals was not studied in detail until Van Ooij et al. [40-45], who initiated research in this area. Initially corrosion performance of mono-silanes was investigated. Petrunin studied the corrosion protective properties of silanes coupling agents such as γ-GPS and γ-APS on aluminum surfaces. Duquensay [46] treated aluminum alloys with silanes such as γ GPS. All authors were convinced of the formation of a covalent bond that forms at the interface.

Van Ooij and his coworkers concentrated on the corrosion inhibiting property of silanes to establish a suitable environmentally acceptable surface treatment. They were able to prove that silanes can protect metals especially aluminum and steel from all forms of corrosion, such as
uniform, galvanic, pitting, crevice corrosion and stress corrosion cracking to name a few. Recent research activities of this group are focused on inhibiting microbiologically induced corrosion and corrosion fatigue cracking by silanes. During the initial stages of research on silanes, Subramanian and Van Ooij [45] measured corrosion properties of mono-silanes and bis-silanes films deposited on steel and aluminum. They found that the bis-type silanes gave better corrosion performance as compared with the mono-silanes. They used potentiodynamic direct current polarization tests to confirm this behavior. Later Electrochemical Impedance Spectroscopy (EIS) was used to characterize and explain the corrosion behavior of these bis-silane films [45].

Zhu and Van Ooij further developed a number of silane systems for bare metal corrosion and surface pretreatment. An electrochemical study of silane mixtures of bis-sulfur and bis-amino silane showed better corrosion resistance than an individual silane system [11]. Further, the effect of hydrolysis time, and curing temperature was investigated to explain the corrosion mechanism of the silane films. They suggested that the corrosion inhibiting properties of the silane film were due to the high hydrophobicity of the fully cross-linked film. They also developed completely water-based silane systems without the use of solvent to further the potential of using silanes as effective corrosion-inhibiting systems.

Palanivel and Van Ooij further developed modified silane systems for improved corrosion protection for aluminum alloys [3]. They showed that additions of particles to silane films at an
optimum level increase the performance. They also showed that self-healing ability of chromate films can be imitated in silanes by addition of corrosion inhibitors.

The above research took the silane research group’s study further into areas of primer development and to the idea of a primer with the unique abilities. The next section discusses the origination of this idea. An attempt is made to develop a primer whose single coating would perform equally well when compared to the two layer conversion coating plus primer system.

1.3.2.2 Superprimer Idea and the Objective of this Thesis

When used as a corrosion protection treatment without paint, a silane film has limitations in that its film thickness cannot be greater than about 0.3 µm. Silane films are brittle when deposited at greater thickness. Although such thin films provide a remarkable level of protection against various forms of corrosion, they are easily damaged. Therefore a necessity to develop a coating with a greatly enhanced film build came up. The increased film build will be the result of the incorporation of nanoparticles, which will interact strongly with the silane molecules. Brittleness of the films will be controlled by incorporating one or more polymer resins to improve film toughness. Success in this task will generate metal treatment systems that are more robust and can be used as self-priming coatings, superprimers, or as metal pretreatments.

The proposed coating will comprise the following components.
A: One or more of an organofunctional silane preferably selected from the class of bis-silanes which Van Ooij and co-workers found to be considerably more effective than mono-silanes [8-10, 28]. They have also discovered that mixtures of two silanes are often markedly more effective than either silane alone. Examples of bis-silanes that they have used successfully in a variety of corrosion and bonding applications are (X = CH₃ or C₂H₅ (methoxy or ethoxy) :

- bis-[triethoxysilyl]ethane: (XO)₃-Si-CH₂CH₂-Si-(OX)₃
- bis-[triethoxysilylpropyl]amine: (XO)₃-Si-(CH₂)₃-NH-(CH₂)₃-Si-(OX)₃
- bis-[triethoxysilylpropyl] ethylenediamine: (XO)₃-Si-(CH₂)₃-NH-CH₂CH₂-NH-(CH₂)₃-Si-(OX)₃
- bis-[triethoxysilylpropyl] urea: (XO)₃-Si-(CH₂)₃-NH-CO-NH-(CH₂)₃-Si-(OX)₃.

B: A low-molecular weight water-soluble polymer or copolymer selected from the generic class of epoxy, polyester, polyurethane or acrylate.

C: A reinforcing filler material, preferably of nanoparticle size, of the metal oxide type that adsorbs silanes. Examples are zinc oxide, aluminum oxide, iron oxide, magnesium oxide and silica. The particle size is of the order of 50-100 nm. The pigment will be dispersed into the coating by solgel methods or by high-shear blending.
D: A water-soluble inhibitor for corrosion protection of metals. This component is variable in that it is selected on the basis of the substrate. A range of inhibitors is available for metals such as steels, aluminum alloys, zinc, and brass. The inhibitor will be leachable from the coating at a controlled rate.

C: Additional components such as emulsifiers, surfactants, film builders, UV absorbers, or thickeners. These agents are present in low concentrations, e.g., of the order of 0.5% solids. The UV absorber can be a pigment such as ZnO or TiO₂.

The functional group R in the silane will be selected so that it reacts with functional groups in the polymer backbone. Attempts to exploit the linkage between soft and hard phases to generate tough films by nano-phase reinforcement [48-49] will be made. The novelty of the design of this primer is that we add enough silane so that, in addition to crosslinking with the polymer, the silanes will also crosslink with itself and form a three-dimensional siloxane network, interpenetrated with the cross-linked polymer. The result will be a polymer-toughened siloxane film. The mechanical strength is further improved by incorporation of the nanoparticle reinforcing filler. These particles are bonded to themselves and to the polymer by the silane.

The nanoparticles will improve the scratch resistance of the coating and lower its permeability to electrolyte. Nanoparticles can also accelerate the cure of the coating by catalytic effects, as
Palanivel and Van Ooij in their recent experiments have shown [3]. The bis-silane is clearly playing multiple roles, which presumably account for the effectiveness of these films. Linkage to the polymer (through the R-group) provides toughening. Crosslinking of the bis-silane with itself leads to a hydrophobic network with extremely low water permeability. Finally, the silane anchors the film to the metal substrate by formation of the interfacial conversion product.

Van Ooij and co-workers in their prior research have identified the hydrophobicity of the film as critical to performance. Other factors, such as porosity, oxide bonding, and corrosion inhibition are present as well, but hydrophobicity is the key. [50, 13-15, 51] Hydrolyzed silanes are very hydrophilic due to the silanol groups. As a result, they readily adsorb on hydrophilic surfaces, such as metals, glass or metal oxide powders. After adsorption and curing they become hydrophobic, as they lose water and crosslink to Si-O-Si units, which are hydrophobic. The transition from hydrophilic to hydrophobic is what makes silanes so unique. No other surface treatment or coupling agent shows this behavior.

Because of the dominant influence of hydrophobicity, any coating system must completely encapsulate (or dissolve) any hydrophilic resin molecules, which are necessarily somewhat hydrophilic to assure dispersion in the carrier fluid. After curing, a transition must take place that renders the entire film highly hydrophobic. In other words, it is crucial that phase separation between the siloxane and the resin be avoided or at least restricted to nanometer dimensions. An
attempt to specifically study the phase behavior of various silane-resin combinations will be made.

The proposed technology is compatible with conventional corrosion inhibition strategies. The function of a conventional inhibitor is to provide corrosion protection in nicks and scratches in the coating. The initial primer film is densely cross-linked, an addition of a water-soluble inhibitor to the coating that will leach out very slowly due to the extreme hydrophobicity of the film. This approach gives great flexibility in selecting the inhibitor. Optimizing the inhibitor based on the target substrate can be made. The inhibitor replaces the defect-healing capabilities of chromates used in conventional metal primers. Palanivel and Van Ooij already have published results that confirm the validity of this concept [3]. Of the other additives; the UV absorber is built-in if we use zinc oxide (a UV absorber) as the nanoparticles. Silanes are known to adsorb on zinc oxide. TiO2 (a UV scatterer) can also be used. Nanoparticles of various types (SiO2, Fe2O3, and CuO) can be generated by \textit{in-situ} sol-gel methods from alkoxy compounds. These particles can play a number of roles such as reinforcement, pigmentation and UV protection. Figures 1.11 and 1.12 give a schematic of superprimer adsorption on a metal and its crosslinking in the film.

In summary, this primer will provide outstanding corrosion protection for most metals, by itself or with an overcoat. It can function as a self-priming coating if used at the maximum coating weight, which we estimate to be about 20-30 µm. Since the film can be tailored to specific substrates, it
can be used as stand alone coating on aircraft, ships, missiles, munitions and support equipment.

It will be water-based, environmentally compliant and simple enough to be applied by semiskilled workers. Coating maintenance will be straightforward as the film can be overcoated and cured.

Overall, the coating system that will be developed here will meet the following requirements:

- The coating is devoid of chromates or other toxic components
- The coating protects various metals against all common forms of corrosion, including localized attack such as pitting, stress corrosion cracking (SCC) and corrosion fatigue cracking (CFC)
- The coating adheres very well to the metal and is paintable by all common paint systems such as epoxies, polyesters, acrylates, and polyurethanes
- The chemicals used in the coating mixture are all water-soluble (low VOC)
- The film thickness is variable and ranges from 1 to 20 µm
- The coating cures thermally at or near room temperature
- The coating can withstand mechanical deformation such as deep drawing, i.e., the coating is flexible
- The coating is UV resistant without over-coating
- The coating can be applied by dipping, wiping, spraying or brushing
- The coating is translucent allowing direct inspection of both the film and substrate
• The coating is thermally stable to at least 250°C for one hour

• The coating is very hydrophobic (surface energy typically that of silanes, i.e., ~25 mJ/m²)
CHAPTER 2: MATERIALS AND TESTING PROCEDURES

The following chapter gives information about the materials used for preparation of the superprimer. Procedures used for the testing and preparation of the superprimer are discussed.

A. Materials

A.2.1 Silanes

Table 2.1 shows the list of silanes which were experimented with, along with their trade names and chemical formulas.

All the above silanes, except for VTAS, were obtained from GE Silicones. VTAS was obtained from Gelest Inc. (Tullytown, PA). The silanes were used without further purification. Some silanes were used in hydrolyzed state and the others in non-hydrolyzed state. A detailed explanation about the preparation of silane solutions is given in later chapters while introducing superprimer formulations.

Bis-amino (A-1170) and VTAS silanes are mixed in their pure state. The reaction is exothermic. The reaction mixture is allowed to stay on the shelf for at least 24 hours. This gives sufficient time for the reaction between the two silanes to go to completion. This mixture is water-soluble. But the order of mixing of water and silane does matter in this case. Addition of DI water at ordinary pH can result in immediate condensation of the amine content of the mixture resulting in threads.
of polymerized particles in the solution. To avoid this, the pH of the appropriate amount of DI water taken needs to be adjusted first around 3 to 4 using acetic acid. After this pH is adjusted, the required amount of the silane-reaction-mixture needs to be added slowly while stirring to DI water. Dilution of silane mixture by this method gives uniform clear silane solutions. This particular method of mixing is not uncommon in industries and pretreatment companies. So to 90 parts of DI water the pH of which is adjusted to about 3 to 4, 10 parts of A-1170:VTAS (5:1) mixture is added slowly while stirring. After the clear solution is obtained, the solution is allowed about 4 hours of hydrolysis time. After these four hours the solution is good for coating or for use in coating formulations.

A.2.2 Resins

The following Table 2.2 is a list of resins which were used for formulation of superprimer. All of the resins were obtained from Resolution Performance Products (Houston, Texas). All the resins mentioned here are epoxy resins. Although other types of resins can be used for formulation of superprimers this thesis concentrates on the formulations based on water-based epoxy primers.

EPON 828 Resin-X-75 is a 95% DGEBPA type epoxy resin solids in 5% xylene. It is a completely solvent-based resin whereas the rest of the resins in the table are completely water-based epoxy resins. EPI-REZ Resin 3510-W-60 is a waterborne dispersion of a low-molecular weight liquid Bisphenol A epoxy resin EPON Resin 828-type. It has 60% solids in water and has no co-solvent.
EPI-REZ Resin 3515-W-60 is a waterborne dispersion of a semi-solid Bisphenol A epoxy resin. It has 63% percent solids in water and has no co-solvent. EPI-REZ Resin 3540-WY-55 is a waterborne dispersion of a solid Bisphenol A epoxy resin (EPON 1007-type) with an organic co-solvent 2-propoxyethanol. It has 55% solids in water and 11% co-solvent. All the resins were used in the obtained state without further dilution or modifications. Information about any other commercial resins or topcoats used for experiments in this thesis is given at the time of their mentioning.

A.2.3 Particles

The following Table 2.3 shows a list of particles of nano-size which were included in the superprimer formulations. The particles were chosen on basis of their affinity towards silanes and the resins that were used in the superprimer formulations. All of the particles were used in the obtained state without further purification or dilution. They were added to the final superprimer formulation. Detailed explanations of mixing procedure are given in later chapters.

A.2.4 Inhibitors

A variety of corrosion-inhibiting pigments was tried in the superprimer formulations. The idea and the mechanism in which they work are discussed in the later chapters. Commercial inhibitors from many companies were obtained and tried. They were first tested for compatibility with the
contents of the superprimers and then they were used in the final formulations with the recommended percentages. The following Table 2.4 shows the list of inhibitors which were compatible and were tried in the final formulations. All the inhibitors were used in the obtained state without further purification or dilution.

A.2.5 Metals/Alloys

AA2024-T3 and cold-rolled steel panels with dimensions of 10 cm * 15 cm * 0.06 cm were purchased from Stillwater Steel Supply (Stillwater, OK). The sheets were cleaned with an uninhibited alkaline cleaner (AC 1055®, Brent America., Lake Bluff, IL). The metal substrates were first solvent scrubbed with red scotch brite pads dipped in ethanol. Then they were cleaned and rinsed thoroughly with DI water to remove all the grit and dust caused by the scrubbing. Then the panels were ultrasonically cleaned with ethanol in an ultrasonic bath for 10 minutes each. The cleaned panels were further alkaline cleaned with 7.5 vol % of the AC 1055 aqueous solution at 60-70°C for 3-5 minutes. The cleaned panels were then rinsed in DI water. The panels were blow-dried with compressed air. The cleaned metal panels were checked for water-break-free surface. This water-break-free surface confirms that the surface was sufficiently clean for coatings to be applied.
B. Testing Procedures

B.2.1 Electrochemical Impedance Spectroscopy

*Electrochemical Impedance Spectroscopy measurements (EIS)* were employed to evaluate the corrosion performance and film properties of the coatings on metal panels in a 0.6 M NaCl solution (pH 6.5). The EIS measurements were carried out using an SR810 frequency response analyzer connected to a Gamry PC-3 potentiostat. The measured frequency range was from $10^{-2}$ to $10^5$ Hz, with AC excitation amplitude of 10 mV. SCE was used as the reference electrode and coupled with a graphite counter electrode. The surface area exposed to the electrolyte was 5.16 cm$^2$.

B.2.2 Salt Spray Test (ASTM B 117)

*ASTM B117 (Salt spray (fog) test, SST)* this test was employed to evaluate bare corrosion protection of silane-treated metals without topcoats. According to the specifications, 5% salt solution (NaCl) is atomized in a salt spray chamber at 35°C with the solution pH around 7. The tested panels were placed at an angle of 45° in the chamber, exposing the panel to salt fog for a certain length of time.
B.2.3 NMR Spectroscopy

*NMR Spectroscopy* was done on superprimer formulations both in liquid and dry forms. For testing in dry form, fine powder was obtained by scraping the coatings from the metal panels after coating and curing. These scrapings from the coatings were made into a very fine powder by grounding it manually using a mortar and pestle. Liquid formulations were also tested directly without further modifications. NMR spectroscopy was done at Oklahoma State University, Stillwater, OK. The following brief explanation is given with the help of the information published in A.4.

NMR spectroscopy is an efficient analytical technique which can be used for characterization of different kinds of solid and liquid materials. Within a sample specific NMR active nuclei can be observed, which provides a unique level of selectivity for NMR spectroscopy technique. Solid-state and liquid-state NMR spectroscopes can be used to discriminate between the reactant components and final superprimer mixture. Liquid-state NMR spectroscopy can be an efficient method to determine molecular structure and conformation. It can be used for both qualitative and quantitative analysis of specific components in a mixture, and, it also provides a sensitive method to quantify impurities, reaction products, or residual solvents including water. In most of the cases this type of spectroscopy the sample size can be only a few milligrams of material while solid-state NMR experiments may require approximately 50 mg of material.
Subatomic particles, electrons, protons and neutrons can be imagined as spinning on their axes.

The spins of these particles in most of the atoms like $^{12}\text{C}$, are paired against each other, such that the nucleus of the atom results in no overall spin. However, in some atoms (such as $^1\text{H}$ and $^{13}\text{C}$) the nucleus does possess an overall spin. The net spin can be determined by the number of neutrons and the number of protons; when they are both even, the nucleus has no spin. In the other case when the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$) the final case would be if the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e., 1, 2, 3).

Much of the quantum mechanics depends on the overall spin $I$. A nucleus with spin $I$ will have $2I + 1$ possible orientations whereas a nucleus with spin $1/2$ will have 2 possible orientations. When an external magnetic field is not applied the energy levels have equal energy, but in the presence of the magnetic field the energy levels split and each level is given a magnetic quantum number $m$.

Sometimes the nuclei of isotopes contain an odd number of electrons and/or an odd number of neutrons, in which case the mechanical spin phenomena exhibited by them is associated with angular momentum which is characterized by a nuclear spin quantum number $I$ such that,

$$I = \frac{1}{2}n,$$

where $n$ is an integer $0, 1, 2, 3, \ldots$ etc.
Some nuclei like that of $^{12}\text{C}$ and $^{16}\text{O}$, fall into the category in which the $I$ value is equal to 0. In this case there is no angular momentum or the mechanical spin phenomena. Nuclei for which $I = \frac{1}{2}$ include $^1\text{H}$, $^{19}\text{F}$, $^{13}\text{C}$, $^{31}\text{P}$ and $^{15}\text{N}$, while $^2\text{H}$ and $^{14}\text{N}$ have $I = 1$.

When atomic nuclei associated with a charge spin on their axes they generate a small electric current and a certain amount of magnetic field is associated with it. This magnetic dipole moment varies with each element. When a finite amount of external magnetic field is applied, a certain amount of torque is experienced by the nuclear magnet which tries to align itself with the external magnetic field. For example, a nucleus with $\frac{1}{2}$ spin has two possible orientations, one in the direction of the applied field with low energy and one against the field with high energy. The orientation with low energy will be more populated than the higher energy one.

**Energy levels for a nucleus with spin quantum number $1/2$**

![Energy Levels Diagram]

On application of electromagnetic radiation with enough frequency, the oriented nuclei of the lower energy state spin-flip to the higher energy state after the absorption of a definite amount of
energy/radiation. During the process of this transition the nuclei is said to be in resonance with the applied radiation. Hence the procedure is named as nuclear magnetic resonance.

The spin-flip transition of every nucleus does not occur at the same frequency even if the magnetic dipole moment is the same. It depends on the number of rotating electrons which determines the amount of shielding experienced by a certain nuclei. So the greater the number of electrons in an environment the greater the shielding will be on a nuclei. So the number of electrons will play a part in the magnetic field of the nuclei making each nucleus nuclear magnetic resonance signal unique.
The resulting shift in the NMR signal for a given nuclei is called as the Chemical Shift. The protons or carbons adjacent to electronegative atoms will be de-shielded and moved to a higher chemical shift. The chemical shift is defined by the equation shown below:

Chemical Shift (\(\Delta\)) = (shift observed/oscillator frequency) x 10^6 ppm

The factor of 10^6 is introduced into the equation to give a simple whole number scale for convenience.

For both \(^1\)H and \(^{13}\)C NMR, the NMR absorption of the molecule tetra methyl silane ((\(\text{CH}_3\))\(^4\)Si) is set to be zero. When compared with other organic molecules the carbons and protons of this molecule are more shielded. The length of the scale for \(^1\)H NMR is 0-12 ppm and for \(^{13}\)C nuclei it is 0-220 ppm.

The nucleus of \(^{29}\)Si NMR has very low sensitivity so the spectrum gives rise to sharp lines. Its wide chemical shift range helps to determine the chemical environment in silicon compounds. At -90 ppm a background signal due to the glass tube and the probe is observed.

One further feature of proton NMR is the fact that the intensity of the absorbance of a given class of nuclei (with a certain chemical shift) is proportional to the number of protons giving rise to the signal; that is, the area under a given peak (the integration) is directly proportional to the number of that type of protons in the molecule. Integrations are typically given as simplest whole-number
ratios, hence, acetic acid, CH₃COOH, will have two peaks in the proton NMR, one at ∆= 2, area = 3, and a second at ∆=12, area = 1. Methyl acetate, CH₃COOCH₃, will also have two peaks in the proton NMR, one at ∆= 2, area = 1, and a second at ∆= 4, area = 1 (the relative areas of both peaks are the same, but each one represents three hydrogens).

### B.2.4 Infrared Spectroscopy

RAIR characterization was used to study the chemical structures of the deposited silane films. The reflection-absorption infrared spectroscopy spectra was obtained using a BIO-RAD FTS-40 FT-IR spectrometer equipped with a BIO-RAD variable angular 32 reflectance attachment at an angle of 75°. The spectra were acquired for 256 scans using 4cm⁻¹ resolution. These tests were performed at the Chemistry Department, University of Cincinnati, Cincinnati, Ohio.

Coates in [52] gave the best explanation for IR spectroscopy by stating that the vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an “unknown” with previously recorded reference spectra. This is the basis of computer-based spectral searching. In the absence of a suitable reference database, it is possible to effect a basic interpretation of the spectrum from first principles, leading to characterization, and possibly even identification of an unknown sample. [52]
All types of matter absorb energy when exposed to electromagnetic radiation. Energy in light or electromagnetic radiation exists in form of photons. The amount to energy depends on the frequency of the radiation. The radiation is divided into Microwave, Infrared, Visible and Ultraviolet regions. On the high-energy side of the complete spectrum lies the ultraviolet and on the low-energy side is the infrared. The portion of the infrared region is most useful for analysis of organic compounds.

The energy possessed by any molecule can be distributed into rotational, vibrational, electronic and translational energies. The sum of these energies gives the total energy. The translational energy relates to the displacement of molecules in space as a function of normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which the result of absorption of energy in the microwave region. The electronic component of the energy is linked to the energy transitions of electrons as they are distributed throughout the molecule and this energy is observed only when the radiation is in visible or ultraviolet portions. The vibrational energy component corresponds to the energy associated with the molecule when the component atoms vibrate about their mean center of their chemical bonds.
The following explanation is from the information published on A.5.

Photon energies associated with this part of the infrared are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent.

The energy of a photon of light is given by the Planck-Einstein equation:

\[ E = h\nu \quad [\text{eq 10}] \]

Where:

- \( h \) = Planck’s constant \((4 \times 10^{-13} \text{ kJ / mol})\)
- \( \nu \) = frequency of light \((\text{s}^{-1})\)

The relationship between frequency and wavelength of light is:

\[ \nu = \frac{c}{\lambda} \quad [\text{eq 11}] \]

Where:

- \( c \) = speed of light \((3 \times 10^{10} \text{ cm/s})\)
- \( \lambda \) = wavelength of light \((\text{cm})\)
A molecule will not absorb all incoming light, but only that light which has energy equal to a quantized transition within the molecule. Depending upon the energy of the incident light, several electronic (or nuclear) transitions are allowed as described below.

- exciting a molecule from one rotational level to another - microwaves
- exciting a molecule from one vibrational level to another - infrared
- exciting a molecule from one electronic level to another - UV/Vis

The larger the energy gap between levels, the higher the frequency $(n)$ and the smaller the wavelength $(l)$ must be for the incoming radiation.

The infrared radiation excites the component atoms in a molecule to a vibration state. This excitation causes the bond in between the component atoms to stretch and bend. The frequency of the radiation at which a bond bends or stretches is unique and can be found from simple formulas. From a simple statement of Hooke’s Law we can express the fundamental vibrational frequency of a molecular ensemble according to equation:

\[
v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad [\text{eq 12}]
\]
Where \( n \) = fundamental vibration frequency, \( k \) = force constant, and \( m \) = reduced mass. The reduced mass, \( m = m_1 m_2 / (m_1 + m_2) \), where \( m_1 \) and \( m_2 \) are the component masses for the chemical bond under consideration. This simple equation provides a link between the strength (or springiness) of the covalent bond between two atoms (or molecular fragments), the mass of the interacting atoms (molecular fragments) and the frequency of vibration. Although simple in concept, there is a reasonably good fit between the bond stretching vibrations predicted and the values observed for the fundamentals. [52]

Infrared spectroscopy involves the absorption of infrared light causing chemical bonds to bend and stretch. Infrared light has wavelengths (\( \lambda \)) between 2.5 and 25 mm and wave numbers (\( N^0 \)) between 4000 and 400 cm\(^{-1} \)

\[
N^0 \text{ (cm}^{-1}\text{)} = 1 / \lambda \text{ (cm)} \quad \text{[eq 13]}
\]

The wave number is directly proportional to the energy so it increases with the wave number. Determining stretching frequencies for bonds, Hooke’s Law can be used to estimate the wave number of light that will be absorbed by different types of chemical bonds.

\[
N^0 = 4.12 \times (K \div m)^{1/2} \quad \text{[eq 14]}
\]

Where:

\( K \) = force constant (in N / cm)
• for single bond: $K = 5 \text{ N/cm}$

• for double bond: $K = 10 \text{ N/cm}$

• for triple bond: $K = 15 \text{ N/cm}$

$m = \frac{M_1M_2}{M_1 + M_2}$ (M₁ and M₂ are molar masses of atoms involved in bond) [52].

**B.2.5 Scanning Electron Microscopy (SEM/EDX)**

*Scanning Electron Microscopy (SEM/EDX)* was used for micro structural characterization and analysis of the precipitates and compounds such as cerium in panels and along scribes of panels. The Scanning Electron Microscope is an incredible tool for observing objects of interest at a micro-level. It is very different from the conventional light microscopes which use a series of glass lenses to bend light waves and create a magnified image. The magnified images given by the SEM are created by the use of electrons instead of light waves. The SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope. The images created without light waves are shown in black and white. Extreme care has to be taken during the sample preparation because the samples have to withstand the vacuum inside the microscope. Biological specimens are dried in a special way that prevents them from shriveling. Because the SEM illuminates them with electrons, they also have to be made to conduct electricity. The sample is placed inside the microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun emits a beam of high energy
electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample. EDX was used to characterize the presence of compounds and elements in corroded AA2024-T3 at an accelerating voltage of 20 kV. A Hitachi S-3200 N SEM machine was used for the analysis.

**B.2.6 Film Hardness Test**

ASTM D 3363 Pencil Hardness testing method was used to observe the hardness values of the primer films. This test uses lead pencils with a broad range of hardness values. The softest to hardest is in the order of 2B - B - HB - F - H - 2H - 3H - 4H - 5H - 6H. The scratch resistance is equal to the hardness value of the pencil which makes a scratch and a gauge hardness value of the primer films is equal to the hardness value of the pencil which removes the film. In previous research on silanes [3] fifteen indentation experiments were performed on bis-sulfur silane-treated samples using MTS Nanoindenter XP and the patented Continuous Stiffness
Measurement (CSM) technique, the details of which are best discussed in reference [53]. Those techniques were not used for testing primer films here.

Similarly, Ellipsometry experiments were performed over a wide range of wavelengths of 300-800 nm with angle of incidence at 60, 65, 70, 75 degrees respectively. The Psi and the delta values were calculated and a computer was used for data acquisition. Further information about ellipsometry can be referred to [54]. Those techniques will not be useful for use on primer films.

B.2.7 Tape Adhesion Test

*Crosscut adhesion tape test (ASTM D3359)* was used to assess the adhesion of coating films to metallic substrates by applying and removing pressure. A cutting tool device having a cutting edge angle between 15 and 30° was chosen, that will make several cuts simultaneously. Cuts were made on the coating in one steady motion with sufficient pressure on the cutting tool. After making two such cuts at 90° the grid area was brushed and a 2.5 cm wide semi-transparent pressure-sensitive tape was placed over the grid. The tape was rubbed with an eraser on the end of a pencil. After 30 s of application, the tape was removed rapidly and the grid inspected according to the ASTM standards. The amount of coated area retained under the tape corresponds to the adhesion efficiency of the primer. The more coated material removed by the tape, the poorer the adhesion of the coating to the substrate.
B.2.8 Solvent Resistance Test

The ASTM D 4752 test for evaluating the solvent resistance of the primer films was performed.

This test method is used to determine the degree of cure of a baked film by the paint film resistance to a specified solvent. The Solvent Rub Test is usually performed using methyl ethyl ketone (MEK) as the solvent. The MEK resistance applies to paints, topcoats and primers.

This test involves rubbing the surface of a baked film with cheesecloth soaked with MEK until failure or breakthrough of the film occurs. The type of cheesecloth, the stroke distance, the stroke rate, and approximate applied pressure of the rub are specified. The rubs are counted as a double rub (one rub forward and one rub backward constitutes a double rub). The test is used widely in the paint industry because it provides a quick relative estimation of degree of cure without having to wait for long-term exposure results.
CHAPTER 3: SUPERPRIMER: FORMULATION, PREPARATION AND TEST RESULTS

This chapter gives detailed information about the superprimer. In the beginning it gives information about the choice of picking of the components that go into the primer followed by initial formulation and their results. The developments that lead to the final formulation are discussed in detail. Test results including EIS and salt spray results are provided whenever necessary.

3.1 Choice of the components

Following the background information provided in Chapter 1 about the superprimer, the choice of components that has to be made primarily targets on the kind of resin and the silanes/silane mixtures that are compatible with the particular resin chosen. The choice of resin can be any water-borne commercially available resin primarily an epoxy, polyurethane or acrylic-based. Even the choice of mixtures of two different resins is also a matter under current research. After the resin is chosen then a list of all the silanes which in theory would be compatible with the resin is made. Table 3.1 shows the resin class and the compatible silane class.

These silanes were checked for their compatibility with the resins by observing their mixture solution stabilities, viscosity changes, gel times, flow abilities etc. Since the basic aim was to formulate a primer which can be coated over a metal substrate, the requirements of a solution for
it to pass for a primer are taken into consideration. These requirements include pot lives, solution viscosity, dilution ability, proper wetting characteristics and film forming capability. This thesis is mainly aimed at producing a superprimer using an epoxy-based resin. A detailed explanation of the formulations and the procedure for their preparation is given in the later sections.

3.1.1 Chemistry

The basic idea of the superprimer as mentioned in Chapter 1 is to from a primer out of a resin and a silane combination. Other additions to it are to enhance the performance characteristics of this primer. This primer would not require any additional pretreatment application and can used as a direct on to metal coating.

When an epoxy-based resin is chosen, silanes or silane mixtures that contain amino groups are preferred. The amino groups in silanes such as bis-amino may react and open the epoxy ring in the resin and lead to cross-linking. Self cross-liking of both the silane and resin to themselves is also expected to occur although it was not demonstrated here. This cross-linking is enhanced while the curing/drying of the films over the substrate. The following list shows the chemical reactions that occur in an epoxy resin and amino silane combination.

Figures 3.1.1 and 3.1.2 show model reactions between an epoxy group and a tertiary aliphatic amine and primary amines, respectively.
The OH groups on the metal oxide surface may undergo a condensation reaction with the OH groups of the resin and thus lead to adhesive bonds between the resin and the surface. OH groups follow a condensation reaction to also allow cross-linking in the coatings.

3.2 Initial Formulations and Results

3.2.1 Formulations

This section discusses about the gradual improvements towards final superprimer formulations.

The experimental results of the initial failed formulations were only provided as a comparison with final superprimer formulations.

To check if addition of an amine-functional silane would actually be able to cross-link/react with epoxy resin, a simple mixing trial was adopted. Bis-amino silane was mixed with EPON 828, a high solid DGEBA epoxy resin. A 2:1 ratio of amine silane and epoxy resin was mixed at slightly elevated temperature and at constant stirring. The so obtained clear liquid was used for coating on alkaline-cleaned AA 2020 T3 panels. The solution gave rise to clear and tough films after an hour cure at 100°C. The mixed solution had a potlife of only an hour. This observation proved that silane alone can be used as a curing agent for a resin and coatings can be obtained from it.

Although the above mixture showed some excellent corrosion resistant characteristics like high modulus in EIS plot and good salt immersion results, the mixture was not water-reducible. The
idea was to obtain a water-reducible primer so the work was shifted towards water-based epoxy resins. EPI-REZ Resin 3510-W-60, a waterborne dispersion of a low molecular weight liquid bisphenol A epoxy resin EPON Resin 828-type, was obtained. Mixtures of it with amine-functional silanes like bis-amino were tried but observed to have poor film characteristics such as improper curing ability and poor adhesion. Even after 3-week curing at room temperature the films were still found to be tacky and wet.

EPI-REZ 3510-W-60 resin is a completely water-based resin with water as the only solvent and also the mixtures of it with amine silane contain only water as a solvent. The coatings formed from these resin-silane mixtures do require a lot of energy to drive the water from the film and give a dry film. This is the basic observed difference between the solvent-based and water-based coatings. Solvents usually require far less energy than water to evaporate, thus solvent-based coatings have far better curing and film characteristics than water-based coatings.

Following the above factor, EPI-REZ 3540-WY-55, water-based epoxy resin but with a co-solvent was chosen for trials. This resin contains 11% of 2-propoxyethanol as a co-solvent besides water. The formulations showed a promising way towards a complete coating.
3.2.2 Results

EIS results were used to evaluate the film characteristics of the coatings. The impedance values in Bode plots gives information about the resistance of the film and water penetration through the film with time.

The thicknesses of silane pretreatment films are usually in the nano-meter scale. The thickness usually increases with concentration of the silane mixtures. But as the thickness increases the films become brittle. The idea of superprimer actually began with the thought to make thick silane films flexible enough so as not to break at higher thicknesses. Addition of a compatible polymer to silane solutions which would react with the silane to give flexible, tough and highly cross-linked film was tried.

Bayer PU 410, water-based polyurethane resin was found to be compatible with AMME silane. The effect of increasing the resin content with silane on film properties was observed using EIS. Figure 3.2.1 shows a Bode plot of a few of the initial formulations and their comparison with silane pretreatments. An increase in modulus value is observed with the increase in resin content of silane + resin mixtures.

This observation gave us an idea for mixing of formulations. In the next result we show an EIS result of a resin + silane mixture of an epoxy + amino silane and comparison of the film properties
with silane pretreatment alone. The EIS result of the silane + resin mixture showed high film modulus and an equally good performance in a salt immersion test. The salt immersion results of these panels are not discussed here.

The above two results and similar others led us to believe that thicker pretreatment films can in fact be achieved and primer films which do not require a conversion coating can be obtained from silane + resin combinations.

### 3.3 Superprimer Formulations

As mentioned in the previous sections those initial water-based superprimer formulations with EPI-REZ 3510 showed some poor film characteristics. Formulations with EPI-REZ 3540-WY-55 showed some promising characteristics of a primer. So this particular resin was chosen to serve the purpose of a polymer in the superprimer definition.

Bis-amino silane was chosen for the formulations. Although other mono-silanes could be compatible and be used for formulations, bis-silanes proved in previous occasions to work better than mono-silanes [11]. Although bis-amino silane alone mixed well with the resin, the formulations showed low pot lives and gave brittle films. Bis-amino is a very basic silane so it is subjected to immediate condensation in a higher pH environment of the resin. Even hydrolyzed
solutions of bis-amino silanes require acetic acid to adjust the pH of the water solution. Their solutions in water are very unstable and gel up in a very short period of time.

For the purpose of obtaining solutions with comfortable shelf life before mixing, the idea of using silane mixtures was tried. Silane mixtures of bis-amino and vinyltriacetoxy silane have proven to give water soluble silane solutions with indefinite shelf life [11].

**Parts and Preparation of Superprimer**

Part A: EPI-REZ 3540-wy-55 epoxy resin was used as obtained without further dilution.

Part B: 10% diluted solution of AV5 at pH 5. AV5 is mixture of A-1170 and VTAS mixed in the ratio of 5:1 by weight in pure state.

**Preparation of Part B:** A-1170 and VTAS silanes were mixed in their pure state. The reaction is exothermic. The reaction mixture was allowed to stay on the shelf for at least 24 hours. This gives sufficient time for the reaction between the two silanes to go to completion. This mixture is water soluble. But the order of mixing of water and silane does matter in this case. Addition of DI water at ordinary pH can result in immediate condensation of the amine content of the mixture resulting in threads of polymerized particles in the solution. To avoid this, the pH of the DI water taken needs to be adjusted to around 3 to 4 using acetic acid. After this was adjusted, the required amount of the silane reaction mixture needs to be added slowly while stirring the DI water.
Dilution of silane mixture by this method gives uniform clear silane solutions. This particular method of mixing is not uncommon in industries and pretreatment companies. So to 90 parts of DI water the pH of which was adjusted to about 3 to 4, 10 parts of A-1170: VTAS (5:1) mixture was added slowly while stirring. After the clear solution was obtained, the solution was allowed about 4 hours of hydrolysis time. After these four hours the solution is good for coating or for use in coating formulations.

Part C: Tetraethoxysilane, a common cross-linking silane with four hydrolyzable alkoxy groups.

*Weight Percentages:* 80% of Part A + 19% of Part B + 1% of TEOS

*High Shear Mixing:* A laboratory High Shear Mixer from Charles Ross Mixers and Blenders Company (Model LC 10) was purchased and used especially for mixing primer formulations. All the components mentioned above were mixed in the above weight ratio and high-shear mixed for 10 minutes at a speed of 2000 rpm.

*Cleaning, Coating and Curing Method:* After the formulations were mixed an incubation time of 30 minutes is allowed before coating. This would give enough time for the reaction between amine and epoxy groups to take place. The formulations can be coated using a drawdown bar, brushed or sprayed on. Formulations can be diluted to sprayable viscosity.
Aluminum alloy AA 2024-T3 panels were ultrasonically cleaned in ethanol for 5 minutes followed by alkaline cleaning at 65°C for 3 minutes in a 7% by volume Brent uninhibited alkaline cleaner solution in DI water. After alkaline cleaning the panels are thoroughly rinsed in DI water and then blow dried. The panels were tested for water-break-free films indicating a clean surface.

Carbon steel panels were first solvent-scrubbed using ethanol as solvent and scotch-brite pads to remove the dirt, corrosion products and expose clean, shiny metal-oxide surface. After the scrubbing, the panels were cleaned with water spray and then followed by ultrasonic cleaning in ethanol for 5 minutes. The final stages of cleaning included alkaline cleaning similar to the one followed for aluminum but at lower temperature of 55°C and for only 1 or 2 minutes. CRS is a very sensitive substrate so care was taken not to spoil the metal-oxide surface before coating with superprimer.

After coating the panels were either cured for 1 hour at 100°C or for one week at room temperature.

3.4 Test Results

Table 3.4.1 summarizes the test results of Superprimer formulation named ‘F’. The results are compared with a control primer. The control was a chromium containing primer from the Navy named PRC Desoto MIL-PRF, containing about 25% wt of chromate.
Salt Spray: Figure 3.4.1 shows result of control and formulation F after 2 weeks. After 2 weeks the control did not show any corrosion in the scribe but superprimer F did. The corrosion resistance performance in other areas of the panel looked comparable. The corrosion of the scribe in formulation F coated panels was expected because the superprimer formulations do not have the so called self-healing effect of chromate-containing primers.

EIS Results: Figures 3.4.2 and 3.4.3 show the EIS Bode plots of formulation F and the control. The plots show considerable difference in the film’s resistance and water penetrability of the coatings. The decrease in impedance values with due time indicates the decrease in resistance due to water penetration.

EIS plot of formulation F shows that the modulus values decrease with time. The figure also shows appearance of a second time constant which indicates appearance of a second conducting layer in due time. These two factors prove the hydrophilic nature of the formulation. Due to this nature the coating seems to attract water molecules through its pores. The second conducting layer might be due to the complex molecular film formed by these and other hydrophilic groups in between the coating and the metal substrate. The EIS plot of the control did not show any signs of second time constant even though the modulus values decrease in due time.
3.5 Improved Formulations

Although we were able to formulate successful coating formulations from silane resin combinations, the performance of superprimer formulation F was not up to par with the chromium-containing controls. The coatings showed considerable hydrophilic nature. In an effort to improve the hydrophobicity of the film an addition of a known silane with extreme hydrophobic nature was sought. Bis-sulfur silane has been proven to be an efficient silane for use against corrosion protection in previous work [11]. A new formulation F-6 was formulated and tested in this effort.

The following gives the information about the formulation.

**Formulation F-6**

The components and mixing procedure of Formulation F-6 are:

- **Part A**: EPI-REZ 3540-WY-55 Epoxy resin
- **Part B**: AV5 10% in water at pH 6
- **Part C**: TEOS
- **Part D**: Bis-sulfur was used in pure as obtained state without further hydrolysis.

By weight:

Part A (80%) + Part B (9%) + Part C (1%) + Part D (10%)

High-shear blended for 10 minutes at 2000 rpm. Bis-sulfur silane is not water soluble. But solutions which were uniform to the visible eye were obtained after high shear mixing of
the components. Even the coatings which were obtained from these coatings did not show any signs of immiscibility. The formulations did not separate into different layers in due time either.

After allowing 20 minutes of incubation time cleaned aluminum panels were either brushed or coated using a drawdown bar.

Panels cured at 100˚C for 1 hour.

3.6 Test Results of Formulation F-6

The addition of hydrophobic sulfur silane improved the hydrophobic nature of the superprimer coating. Figure 3.6.1 shows an EIS Bode plot comparing the modulus values of F-6, F and the control. The plot shows no drop in the F-6 curve even after 1 week of immersion. Whereas the EIS curves of formulation F were observed to drop with time.

Figure 3.6.2 shows an aluminum panel coated with F-6 and salt spray tested for 2 weeks. The picture shows no pitting in the unscribed area and also no considerable corrosion in the scribe.

Table 3.6.1 summarizes all the test results of F-6, F and control. Results of test such as hardness and tape adhesion showed considerable improvement in superprimer formulation F-6 in comparison to F.
3.7 Conclusions

Silanes or silane solutions at high concentrations can be used for coating purposes by modifying silanes with resins. Primer formulations were obtained by silane plus resin combinations, called by a generic term ‘superprimers’. Formulations were developed and tested from low concentrations of resin followed by increased percentages of resin. A completely water-soluble superprimer formulation was developed using a waterborne resin and water-soluble silane solutions. Hydrophobicity and anti-corrosion performance of the superprimer were improved by inclusion of hydrophobic silane into the formulation. Test results including EIS and salt spray exposure showed that improved superprimer formulation had very good anti-corrosion performance. In the next chapter additions to superprimer will be discussed. Additions like nano-size particles and corrosion inhibiting pigments added to give specific qualities will be discussed in detail along with the formulations and test results.
CHAPTER 4: ADDITIVES TO PRIMER

The silane plus resin combinations can lead to coating formulations but to make it perform on par with chromate primers further additions need to be made. Detailed explanation of the idea, purpose and expectations of these additives in the primer were already given in Chapter 1. In this chapter details about the mixing procedure of the additions, different kind of additives were tried and their test results are given. There are primarily two important kinds of additives, nano-particles and corrosion inhibitors. Many commercially available particles and inhibitors were tried and tested for corrosion performance. Test results by EIS and salt spray exposure are provided.

4.1 Pigments/Particles

Particles and pigments are usually added to the paint to impart special characteristics or improve the film properties to the primer/paint coating. When in use for coloring of paint, ink, plastic, fabric and other material, a pigment is a dry colorant, usually an insoluble powder. There are both natural and synthetic pigments, both organic and inorganic ones. Pigments work by selectively absorbing some parts of the visible spectrum (see light) whilst reflecting others. Most of the nano-particles have a catalytic effect on the chemical reactions occurring in the paint/primer systems. The particles for inclusion in the superprimer were also selected on the basis of their effect on the chemical reactions and curing of the primer. Previous studies indicated that inclusion of silica particles improved the anti-corrosion performance of silane films [3]. It was proposed that silane
films formed from the 5 ppm silica-containing silane solution behaves as a cathodic barrier like cerium compounds [55-56]. This type of activity is done with paint systems where the mechanical properties are improved by adding particles such as fillers, pigments and extenders in paint systems [57]. The following particles were tried and tested in superprimer formulations:

- Silica
- Alumina
- Carbon Black
- Zinc Dust
- Corrosion Inhibitors

A separate chapter is devoted for formulation and testing results of zinc dust inclusion. The others are discussed in this Chapter.

### 4.1.1 Silica, Alumina and Carbon Black

The mixing procedure of superprimer with particles is not different from the procedure of silane and resin mixture. The particles are included along with other components and mixed using the high-shear mixer. The curing conditions were also not changed. The metal panels were cleaned in the same manner as mentioned before in chapter 3.
Table 4.1.1 gives a detailed description of the components, their weight percentages in the mixtures and their corresponding formulation number. In some formulations there are no particle additions. Silanes such as A-link 25 and A-link 15 were tested to increase the cross-linking density of the films. Formulations numbered F 10 to F 12 are with alumina particles in increased weight percentages. F13 to F15 are with calcium zinc molybdate, a corrosion inhibitor from Molywhite Corporation. Similar information about the additions in other formulations is clearly given in the table.

4.2 Results and Discussion

Previous work over modified silane films [3] showed that increase in the percentage values of silica in the silane solutions actually decreased the performance against corrosion. Figure 4.2.1 shows an EIS plot showing the effect of various amounts of silica in silane films. A probable theory for the mechanism of how the silica particles are acting towards the improvement of anti-corrosion performance was also given.

Figure 4.2.1 combined with other test results proved that an optimized amount of silica is required for the best performance of the silane films. A similar observation is observed in case of superprimer formulations also. Formulations F 10, F 11 and F 12 have alumina nano-particles in increased weight percentages of 2.5, 5.0 and 10.0. A simple salt immersion test of AA 2024-T3 panels coated with the above three formulations showed that increased weight percentages of
alumina in fact decreased the anti-corrosion performance. Figure 4.2.2 shows salt immersion results after 7 days in 3.5% wt in DI water.

EIS impedance values of the above coatings F10, F11 and F12 conformed to the above observation. Formulation F10 with 2.5 % alumina showed better impedance values with time. Figure 4.2.3 shows EIS impedance values of salt fog-tested coatings with time. Impedance values of F10 were higher than F11 and F12 in most cases.

Figure 4.2.4 shows a similar plot with the same coatings but now with a topcoat over them. The topcoat used was a polyurethane based topcoat manufactured by DEFT. The impedance values of F10T and F11T, coating formulations of F10 and F11 with same topcoat showed similar performance.

Figures 4.2.5, 4.2.6 and 4.2.7 shows Bode plots of the coatings with and without topcoats tested over for a period of time. The numbers in the legend of the figures denote the number of days the panels has been exposed to the salt solution. Bode plots of coatings without topcoat show gradual decrease in the impedance values with time. All the three formulations behaved in the same way. This decrease in impedance values can be attributed to water penetration into the film with time. Bode plots of coatings with topcoat showed varying results with time. The change in impedance values was not consistent with or linear with time. But the impedance values in all
three cases were high, which showed an obvious fact that the water resistance of the coatings with topcoat is greater than the coatings without topcoat.

The salt spray test results conformed to the observations made using EIS test. Figure 4.2.8 shows salt spray results of F10, F11 and F12 formulations with and without topcoat after 3 weeks of testing.

The EIS Bode plots of the individual formulations containing alumina showed an appearance of a second time constant for longer immersion times. The 7 day curve of F10 was a rather flat when compared to curves of F11 and F12. The change in slope of the curves which indicates the appearance of a second time constant was more prominent in F11 and F12 than in F10. This second time constant mentioned before indicates the appearance of a second hydrophilic layer beneath the topmost layer and above the metal oxide surface. This might indicate that water penetration through the films is less in case of F10 when compared to F11 and F12 for a short period of time. After 2 weeks all the 3 curves showed similar behavior in Figures 4.2.5, 4.2.6, and 4.2.7.

This particular observation leads us to an explanation that can be given to behavior of the particles in the primer. According to researchers [58] there is a critical amount of pigment that can be added to an organic coating system, beyond which the coating becomes more permeable or
porous. Nano-particles are known to have a catalytic action on the chemical reactions in the primers [59-60]. This observation was evident in case of formulations containing alumina, i.e., F10, F11 and F12. The pot life of a primer is defined as the amount of time the primer stays at coat-able viscosity before gelling up after all the components are mixed. The pot lives are usually high for water-based primers when compared to solvent-based primers. In case of superprimer formulation F-6, it is close to a week. The pot-life changed with the kind of addition that is made to the primer. The weight of alumina in the formulations had an inverse linear relation with the pot-life. The pot-life of the formulations decreased with increasing percentage of alumina. Similar behavior was found even in the case of inhibitor addition mentioned in the later part of the chapter.

The factor that can influence the performance is that the particles being hydrophilic in nature obviously attract water into the films. This is evident in the poor performance of the formulation with higher percentages of alumina. A similar explanation is given as a mechanism for silica in silane films [3].

**Carbon Black**

Carbon black is one of the oldest fillers used in the paint industry. It was used 27000 years ago for cave paintings, and in 2500 before Christ by the Egyptians in inks. It was also used for the printing process during the middle Ages.
The rubber industry is the biggest user of carbon blacks by a large margin, in comparison. The paint industry is only a modest user. The printing inks industry also uses significant quantities.

Finer particle blacks are used for high-quality finishes such as in automotive paints on account of their higher jet-ness. Medium size blacks are used for intermediate quality paints, whereas the coarser pigments are used for decorative paints. For tinting purposes coarser grades are usually used as their lower strength meaning they are easier to control.

Carbon-black pigments are very fine particulates of sub-crystalline carbon fused into larger aggregates. It is a mixture of partially burned hydrocarbons. Carbon black is produced by partial combustion of natural gas. It is used as a black pigment for inks and paints, and is used in large amounts by the tire industry in the production of vulcanized rubber. Lampblack resembles carbon black, but is produced by burning liquid hydrocarbons, e.g., kerosene; it is often somewhat oily, is duller than carbon black, and may have a bluish undertone. It is sometimes used in making contact brushes for electrical apparatus. Any of various finely divided forms of carbon derived from the incomplete combustion of natural gas or petroleum oil and used to reinforce rubber and as an ingredient in inks, paints, crayons, and polishes.

Carbon blacks can be difficult to disperse as they have very small particles with a correspondingly large surface area. Improved dispersions can be attained by oxidizing the surface of the pigment.
or by adding small quantities of organic groups such as carboxylic acids. Such groups decrease the pH of the aqueous extract and aid the wetting of the particles.

The viscosity of the paint is affected by the inclusion of carbon particles. Particles of carbon form clusters which are often compared to a cluster of grapes, held together by forces ranging from weak physical attraction to chemical bonds. This structure affects the dispersibility, the jet-ness, gloss, and, above all, the viscosity of the paint.

One of the problems with carbon black can be due to the absorption character of it. The light dusty form of carbon blacks allows them to be converted to an easy-to-disperse pellet form by the dry pelleting process. Over a period of time carbon blacks absorb active ingredients in a paint formulation, such as the metal soaps used as driers in air-drying alkyds. This absorption can lead to problems; however, doubling the dosage of drier content is a common way of compensating for this issue.

**In the Superprimer**

Carbon black was tested as a pigment addition in the superprimer formulation. F28 is the formulation number corresponding to this formulation. 3% by weight of carbon black was introduced into the resin plus silane mixtures. The mixture was prepared using a high-shear blender similar to the other methods. The formulation was coated on AA 2024-T3 panels and was
cured at 100°C for 1 hour. The coating resulted had an appearance of a glossy black paint.

Performance tests like EIS and Salt Fog exposure were used to evaluate the coating.

Figure 4.2.9 shows the salt fog performance of the F 28 panel after 28 days. It can be observed from the figure that the performance showed no decrease for the first 7 days of exposure but gradually decreased after 28 days.

The observation in the salt fog conformed to the impedance change in Figure 4.2.10. This figure shows an increase in the impedance values in the initial days of exposure. After 7 days the impedance showed a gradual decrease and the impedance values stabilized after 1 month exposure. The modulus value of the coating initially showed increase. This means that the resistance of the coating is increasing and the penetration of the corrosion causing species is difficult or slow. In due time the modulus values showed a decrease in their values and stabilized after 30 days. This shows that the coating’s conductive nature improved with time or in other words the resistance of the coating decreased. This behavior can be explained by the penetration of water, oxygen and other corrosion causing species after long exposure times. After long exposure times the conducting species such as water penetrate through the coating and make the film more conductive. Initially the silane hydrolyzes thus increasing the resistance but after long periods of time the resistance drops due to passage of ions to the substrate.
The same observation and deduction can be made from Figure 4.2.11 which shows the individual impedance curves not clear.

### 4.3 Corrosion Inhibitors

The idea of including a corrosion inhibitor is used to achieve what is called a ‘self-healing’ effect in superprimers. A few promising chromate replacements inhibitors have been derived from cerium and molybdenum salts. These are believed to inhibit corrosion by controlling the cathodic reaction by precipitating hydroxide/oxide layers at local regions of high pH [61-62]. Chromium-containing primers have this property and it is this character which makes them so efficient. The detailed explanation of this effect was given earlier in Chapter 1. This effect can also be seen in the left side panel of Figure 3.4.1. Corrosion inhibitors were loaded and tested in silane films before [3]. Some water-soluble silane mixtures showed excellent corrosion behavior comparable to that of chromates [63]. However, it was observed that alcohol-based silanes offer a higher corrosion resistance to the water-based silane systems [64]. Vignesh et al [3] showed that one of the ways to increase the corrosion performance of these silanes is to add corrosion inhibitors to the films which can leach out slowly. The results that are reported here for various organic and inorganic inhibitors were studied for the corrosion inhibition of AA2024-T3 alloys in 0.5 M NaCl solution. Examples are benzotriazole [65-66], tolyltriazole [67] and rare earth metal salts, e.g., cerium nitrate [67-69].
Many inhibitors were selected and tried by including them in the formulations. Formulations numbered F13, F14 and F15 in formulation table have calcium zinc molybdate in increasing weight percentages. Formulations F20 to F29 except for F26 and F28 are primers containing different kinds of corrosion inhibitors from different companies. Only those inhibitors which are recommended for their use in waterborne primer formulations were tested and tested. Chemical information of these inhibitors was provided in Chapter 2.

4.3.1 Results and Discussion

Figure 4.3.1 shows the change in impedance values with time of the formulations F13, F 14 and F15. The curve of F15 which has the highest amount of calcium zinc molybdate (CZM) showed marginally higher values of impedance values than the formulations with lower weight percentages.

Figure 4.3.2 shows the salt spray results of the formulations with and without topcoat in Figure 4.3.5. The results show that formulations with higher percentages of CZM performed better. This observation conformed to the EIS impedance plot above. The individual EIS Bode plots show that impedance value decrease at high magnitude for the first few days and then the modulus curves change at a very low magnitude. This observation might indicate that coating formulations
containing corrosion inhibitors form insoluble corrosion products in due time which form or make
the coating less accessible to water and other corrosion causing species.

The individual EIS plots of the above formulations with topcoat did not show much change in the
impedance values with due time. But the performance results of formulations with and without
topcoat showed similar behavior i.e., formulations with higher percentages of CZM performed
better. Figure 4.3.5 shows the test results of formulations with topcoat after 6 weeks of testing.

Other corrosion inhibitors from companies like Cortec and Fluka were also tried. Figure 4.3.6 and
Figure 4.3.7 show the EIS and salt spray results of the formulations F20, F21, F22, F24 and F 25.

Figure 4.3.6 shows that the impedance values of almost all the inhibitors formulations without
topcoat are close by and decrease with time. This decrease in modulus values stabilize after
some time. This stabilization of the impedance values may be attributed to the fact that these
inhibitors form insoluble corrosion products by reacting with corrosion causing elements. The
mechanism by which these corrosion inhibitors work follows next.

Metal oxide or corrosion product over metal substrates like aluminum and steel delaminates
easily from the surface to expose fresh metal, thus allowing for continued corrosion. Under
normal atmospheric conditions (without inhibitors present), the corrosion products does not form
an adherent or so-called `passive´ layer on the metal surface. It is also well established that most
organic coating films are not sufficiently impermeable to water and oxygen to prevent corrosion based on barrier properties alone. Effective corrosion inhibition by coatings therefore requires other protection mechanisms. When a coating film containing corrosion inhibitors becomes exposed to moisture, component ions of the inhibitors for example molybdate ions in case of Calcium Zinc Molybdate will pass into solution and migrate to the metal surface due to the controlled solubility characteristics of these pigments. The ability of these ions like molybdate ions to stabilize a thin, adherent and protective layer on iron and other metals is the key to the effectiveness of corrosion inhibitors. The oxide layer effectively insulates (i.e. passivates) the metal from attack and halts the corrosion process. The passivating properties of molybdates, zinc compounds, vanadium compounds etc are well recognized and documented in the field of corrosion science [70].

The main aim of using the corrosion inhibitors was to imitate the self-healing characteristic of chromates. This particular character of chromates like it is explained in chapter 1 allows the chromates to leach out of the coating and form insoluble chromium corrosion products over the scribes, scratches or any other kind of mechanical damages and protect them from further damage. The same kind of behavior was tried to achieve in the superprimer by addition of corrosion inhibitors. Though the performance of the coatings improved in un-scribed areas most of the cases but none of the corrosion inhibitors tried gave the superprimer a self-healing
capability. None of the coating formulations with corrosion inhibitors showed nil-corrosion in the scribe. Visible corrosion was observed in all the cases. This means that the inhibitors so far tried were not able to imitate the chromates in this aspect. It is one of the areas research still needs to be continued. Trials to find the right inhibitor still need to be done extensively.

4.4 Conclusions

Particles and corrosion inhibitors were added to silane plus resin mixtures to provide superprimer with better film properties and anti-corrosion performance. Alumina, carbon black and zinc were tried as particle inclusions along with commercially available corrosion inhibitors. EIS and salt spray standard tests were used to monitor the film properties and anti-corrosion performance simultaneously.

Test results showed that alumina addition to superprimer enhances the anti-corrosion performance. Increasing levels of alumina leads to decrease in the corrosion performance. Increase in porosity and hydrophylicity with increase in the amount of particles is considered to be the likely explanation behind this observation.

Carbon black was loaded as a pigment in the superprimer formulations. EIS and salt fog tests conformed to a single observation that the coatings resistance increased initially and the conductive nature of the coating increased with the exposure time. The performance of the
coating decreased with the increased in the conductive nature of the coating. A probable explanation of formation of hydrophilic hydroxyl complexes of the coatings components is given for the observation.

Corrosion inhibitors were tried to provide enhanced corrosion protection to the superprimer. This idea was put to trial so as to imitate the self-healing characteristic of the chromate primers. Test results showed that the corrosion performance did increase and primer coated surfaces showed less pitting and general corrosion in un-scribed areas. But the inhibition could not protect the scribed areas. Visible corrosion was found in most of the formulations. Quest for the right inhibitor still needs to be continued and this particular area gives scope for further research.
CHAPTER 5: ZINC-RICH SUPERPRIMER

Zinc-rich primers are as the name suggests primers with heavy loads of zinc metal dust in it. The zinc dust/powder is used as filler and is held in the coating by using a binder. Paints with zinc pigments contain about 80% by weight pigment of which 20% is oxide. Zinc-rich coatings contain 85-95% metallic zinc, by weight, in the dry coating with little or no oxide. Depending the type of binder used the primer can be organic or inorganic. Organic binder can be epoxy, polyurethane, acrylate etc. In inorganic zinc-rich primers the binders are usually silicates. In the next few sections a brief explanation on the uses, application, mechanism of action and the idea of zinc-rich primer is described.

5.1 Uses and Applications

The amount of zinc in zinc pigments is not sufficient to permit galvanic protection by zinc. However, the zinc/zinc-oxide combination serves as an inhibitor for atmospheric, in both primer and finish coats [1]. The zinc-pigmented coatings show excellent adhesion, coverage and are very effective coatings for rural and mild industrial atmospheres but zinc-rich coatings are used and preferred for more aggressive atmospheres.

The use of metallic zinc in primer formulations to achieve sacrificial protection of steel structures has been well-established in the protective coating industry. The outstanding protective properties
of metallic zinc-based primers are based on the sacrificial properties of these primers in combination with their barrier properties and physical characteristics.

The majority of the zinc-based primers are formulated with either the inorganic silicate binders or with epoxy resin systems. In the United States the zinc silicates are predominantly used as primers for new buildings, such as for offshore structures and bridges. The only time zinc epoxy primers are used in service is for touch-up of coatings applied during fabrication, where severe damage to bare metal has occurred. Conversely, in Europe zinc epoxies are prevailingly used, particularly in the North Sea offshore industry based in U.K. and Norway [71].

Zinc primers are found to be useful in many areas of an industry. Zinc primers are strongly suggested for use in the conditions where there is frequent wetting by salt water, condensation, splashing, spray or frequent immersion and in the areas where there is chemical exposure with pH range 5 to 10 [1]. DoD also is a major consumer of zinc-rich primers. Some of the zinc primers used by DoD are A-9-73, MIL-P-21035, MIL-P-24441, MIL-P-26915B, TT-P-641, TT-P-645A, TT-P-645B, TT-P-1046A and TT-P-1757.

A-9-73, MIL-P-21035, MIL-P26915B are zinc-dust primers used for ferrous metals, marine use, severe atmospheric exposures (when topcoated), regalvanizing welds, bridges, steel pipes, chemical plants (when properly topcoated) or architectural equipment.
MIL-P-24441 is a polyamide epoxy zinc Primer for use where excellent adhesion is needed on solvent-cleaned steel or for a marine environment protective coating.

TT-P-641 Type II is a zinc dust primer for steel or galvanized metal surfaces.

TT-P-645A is a zinc chromate primer for metal surfaces.

TT-P-645B is a zinc alkyd primer for steel or aluminum.

TT-P-1046A is a zinc rich primer for bare ferrous metals, marine use, bridges, steel pipes, chemical plants (when top-coated), and where there are severe atmospheric exposures (when top-coated).

In the case of application, zinc-pigmented coatings differ from zinc-rich coatings. Zinc-pigmented coatings can be applied using brush, roller, or spraying and they do not have stringent substrate cleaning requirements. In some formulations they can be even applied over rusted surfaces unlike for zinc-rich coatings where the substrate surface needs to be very clean before coating.

Application conditions and requirements for zinc-rich coatings such as those mentioned needs to be more clean and precise. The metal surface for zinc-rich coatings before application needs to be extremely clean. Any traces of organics, dust, grease, etc., which prevent the contact between the iron and zinc need to be removed from the surface in order to maintain electrical contact
between the two metal surfaces. The importance of the contact in performance will be clearer after the explanation in the mechanism section.

In the next section we will discuss two main types of primers.

According to the Steel Structures Painting Council Zinc (SSPC), zinc-rich primers employed in coating films at loadings that insure the film conductivity, will form an efficient anode of a galvanic couple with steel, sacrificially corroding itself, and overriding local cell activity on the steel which becomes entirely cathodic and protected.

The concept is easily adaptable to practical coating systems, and such primers are the most efficient of all. Zinc-rich primers based on both organic and inorganic vehicles are widely and successfully employed. They are discussed in the following

A. ORGANIC ZINC-RICH PRIMERS

Organic zinc-rich primers are used where resistance under coating damages is necessary, for which reason they are used under exterior topcoats and finishes and where decorative colors and finishes are provided by topcoats. For applications requiring resistance to water immersion, salt, high humidity and mild chemical fumes zinc-rich coatings are used as an efficient option. These applications include highway bridges, chemical process plant equipment, sewage and water treatment plants, marine structures, ship hulls, ballast tanks, ship structures and many others.
However they are not suitable for environments of pH<5 or >10, where the zinc is more readily dissolved.

The pigment volume concentration (P.V.C) of the organic zinc-rich primers is usually high. This allows it to maintain zinc particle to zinc particle contact within its continuum and contact between pigment and substrate to ensure electrical conductivity within the film end across the interface. Because of these requirements the paints are formulated at a pigment volume concentration slightly above the critical pigment volume concentration (C.P.V.C). The coatings made from these primers should also display sufficient adhesion at these loadings. Usually chlorinated rubber, epoxy/polyamides, high molecular weight linear epoxies and epoxy ester systems are used as binders. The coatings will display properties which vary and depend on the vehicle type.

When the P.V.C is adjusted to values just higher than the C.P.V.C the primer will achieve the tightest particle to particle concentration and zinc encapsulation with the binder is reduced. When different particles sizes are used at optimized values it may also assist here to provide more uniform packing, resulting in better particle contact and ultimate galvanic protection. Too high of pigment volume concentration might effect the coating’s adhesion to the substrate. If zinc were the only pigment used the fixation for P.V.C would be very simple, but usually the formulations are very complicated and they include anti-gassing agents, thixotropes, anti-settling agents, extenders, etc. Sometimes even small amounts of oil-absorbent materials decrease the C.P.V.C
value but not the P.V.C value due to which the coating might become very porous. But optimized amounts might help maintain a P.V.C:C.P.V.C, ratio by reducing the amount of zinc required, thus obtaining a strong film. This provides enough film and film/substrate conductivity for good protection.

Application of organic zinc-rich primers needs to be done with care. Proper mixing and agitation is a must to ensure homogenous film to be formed. Sometimes even with the use of the best thixotropes settlement of zinc is possible. Due to this zinc encapsulation might be possible which might result in nullification of cathodic protection.

B. INORGANIC ZINC-RICH PRIMERS

Post-cured organic zinc-rich paints, though comparably are difficult to apply and require very precise surface preparation, they are more resistant. Some water-based zinc-rich coatings are initially applied as suspension of zinc dust in a sodium silicate solution and then after the water has evaporated the coating is washed with an acid phosphate solution which will convert the zinc to insoluble silicates and phosphates [1]. But self-cured zinc-rich coatings are formulated in such a way that the carbonic acid that is formed by dissolving of carbon-dioxide from air will cure the coatings by the same chemistry as for the post-cured coatings. Before application of topcoats on organic zinc-rich primers, they need to be washed to remove the excess acid, but rinsing and washing are usually not necessary for self-cured coatings [1].
Silicates which are used as binders in inorganic zinc-rich paints react with zinc to form primary bonded zinc silicate matrices. In organic zinc rich primers the particles do not react but are held within a polymer matrix. Vehicles may generally be classified as either alkaline silicates (water solutions of sodium, potassium, lithium, or quaternary ammonium silicates) or alkyl silicates which may be ethyl silicate (the most common) or higher alkyl or alkoxy homologues.

INORGANIC VS ORGANIC

For inorganic zinc-rich primers the zinc levels can be lower than that required for organic zinc-rich primers without sacrificing the performance. Zinc levels of 70% by weight can be enough to give good performance. Whereas for organic primers, the percentage levels of the zinc should be considerably high to ensure good performance.

Inorganic zinc-rich primers are better than organic rich primers as far as performance is concerned. They are strong, hard, and resistant to impact and abrasion. They are quite resistant to heat. The performance of inorganic primer films does not deteriorate with age but organic zinc-rich primers do. Weathering may actually improve their physical properties.

Inorganic types are better than the organic adhesion-wise also. It is also suspected that it might be due to the formation of primary valency linkages with the substrate as well as the zinc. The mechanism of adhesion at this point is unknown. But the surface preparation requirements of
inorganic zinc-rich primers are exceptionally higher than the organic primers (particularly with the alkaline silicate systems). A commercial blast is the very minimum acceptable, and a white or near white blast with a typical surface profile of 1 to 2 mils being more usual and often mandatory. Alkyl silicates are rather more tolerant of poorly blasted substrates than the water-based type, probably reflecting their higher organic content and lower surface energies.

The inorganic zinc-rich coatings can be considered as better and safer coatings than organic type even though they are incompatible with poorly prepared surfaces. Sometimes the organics may mislead the applicator by adhering to poorly prepared substrates but in fact in the areas where there is no proper contact with the pure surface a good performance cannot be expected. Inorganics require such contact (through good surface preparation) not only for protection, which may be initially difficult to determine, but also for good initial adhesion, which is easy to determine. If an inorganic sticks, it should protect. If an organic sticks, protection is still an open question.

**Secondary Mechanisms**

If cathodic protection were the sole mechanism of zinc-rich primers, they would rapidly break down as zinc was consumed. In practice, this is not the case. As zinc corrodes, its corrosion products (depending upon the environment) tend to polarize the reaction, coating the zinc and bridging the voids within the film, thereby packing them so that the primer is sealed from the
environment. The film is slowly transformed from a zinc-rich primer to a barrier primer, and, in this state, it is maintained until the zinc is again exposed by some abuse. The zinc will then corrode again and be healed with corrosion product (providing that the agents of physical or chemical abuse have been removed). These phenomena are primarily responsible for long term zinc-rich protection.

Zinc-rich primers are normally applied at approximately 25 µm. Some compositions form good films at thicknesses up to 150 µm, while others may severely mud-crack at these high builds.

The porosity of zinc-rich films (particularly the inorganic ones) can lead to problems because of air occlusion during top coating. The resultant bubbling and pin-holing of applied top-coats may necessitate the use of mist coats, thinned finish coats or tie coats before finish coat application. Careful formulation of solvent system and pigmentation of the finish coat can mitigate this problem, and many manufacturers carefully tailor finish coats for bubble-free application over the zinc-rich primers.

CHROMIUM USE IN ZINC PRIMERS

The use of chromium in zinc-rich primers is not uncommon. Zinc chromate pigments can be added to primers made of several different resin types, such as epoxy, polyurethane, alkyd and others. Some of the primers used by DoD contain chromate in them. Chromium proves its
efficiency in corrosion protection in these primers too. Zinc salts added to chromates form
$\text{ZnCrO}_4$, a cathodic inhibitor, which is more effective than the simple summation of the individual

cathodic effects of $\text{Zn}^{2+}$ and $\text{CrO}_4^{2-}$ taken alone [1].

Zinc chromate is simply a corrosion-resistant pigment that is added to certain coatings. In the
case of a wash primer, the phosphoric acid actually reacts with the metal, whereas in the case of
zinc chromate this is not the case. In dry, low-humidity weather the zinc chromate does not do
anything other than remain in the coating. On the other hand, when the humidity in the air
increases or on rainy day moisture from the air penetrates the primer coating and slightly
dissolves the zinc chromate. The dissolved zinc chromate solution now does react with the
underlying metal surface and forms a passive layer (like a blanket) that prevents corrosion. As
soon as the weather becomes dry again the zinc chromate no longer plays a role at least until the
next time it rains, when the process is repeated. If there are frequent cycles of high and low
humidly the zinc chromate will eventually be depleted and soon after one might start to see
corrosion of the metal. However the use of chromium is avoided in these primers, too, because of
their ill effect on life.

5.2 MECHANISM OF CORROSION PROTECTION OF ZINC-RICH PAINTS

From the early 1800’s cathodic protection has developed rapidly and its use has become
widespread. New materials such as sacrificial alloys of magnesium and aluminum and superior
impressed current anodes together with developments in electrical and electronic engineering have allowed great advances in the techniques. Cathodic protection is now established as an essential engineering service with a sound and comprehensive scientific background. The mechanism of zinc cathodic protection comes into this category.

The basic principle of corrosion protection is simple. A metal dissolution is reduced through the application of a cathodic current. Cathodic protection is often applied to coated structures, with the coating providing the primary form of corrosion protection. The CP current requirements tend to be excessive for uncoated systems. Cathodic protection has probably become the most widely used method for preventing the corrosion deterioration of metallic structures in contact with any forms of electrolytically conducting environments, i.e. environments containing enough ions to conduct electricity such as soils, seawater and basically all natural waters. Cathodic protection basically reduces the corrosion rate of a metallic structure by reducing its corrosion potential, bringing the metal closer to an immune state. The two main methods of achieving this goal are by either using sacrificial anodes with a corrosion potential lower than the metal to be protected using an impressed current provided by an external current source. Zinc-rich primers mechanism of corrosion protection comes into the sacrificial anode category.
As the basic reason of zinc is lower than iron in the electrochemical series zinc acts as a sacrificial anode in the galvanic couple of iron and zinc. In a common galvanic couple between iron and zinc the following will be the anodic reaction:

\[
Zn \rightarrow Zn^{2+} + 2e^- \quad [eq \ 15]
\]

Zinc in the above reaction oxidizes to zinc ions. Whereas at the cathode the following reaction happens:

\[
2e^- + H_2O + \frac{1}{2} O_2 \rightarrow 2(OH)^- \quad [eq \ 16]
\]

The idea of cathodic protection is to artificially shift the potential of a metal so that it becomes either immune or passive. In natural soils and waters it is normal to shift the potential of steel to the immune region whereas for steel in concrete it is preferable to re-establish passivity.

In sacrificial anode cathodic protection, a galvanic cell is set up by connecting the steel to a more reactive metal, usually zinc. The zinc then undergoes the anodic reaction and corrodes whilst the steel is rendered entirely unreactive because the whole surface undergoes the cathodic reaction mentioned above and the iron no longer dissolves. This may also be thought of as the anodic sites on the steel being shifted to the zinc.
Conventional primers contain a polymer network which prevents the electrolyte penetration and thus corrosion. Zn-rich primers have loads of zinc dust in them and a binder which keeps all this zinc metal dust in tact, thus providing a way to coat the zinc metal over steel and protect it from corroding.

The corrosion products of zinc are usually zinc hydroxides formed at the anodic sites. These corrosion salts of zinc which are insoluble by nature form near or in the pores and thereby shielding the underlying surface from the atmosphere. These deposits prevent the penetration of moisture and other corrosive species from reaching the substrate. This prevents the underlying steel from getting corroded.

### 5.3 ZINC–RICH SUPERPRIMER

The idea of zinc-rich primer started with the trials to test the superprimer’s performance with particles in it. Zinc was used in it to formulate a zinc-rich superprimer. Zinc rich SUPERPRIMER is nothing but a zinc paint which uses the superprimer as a binder and it would not include the pigments, color and nanoparticles. It is chromate-free, completely waterborne and has very low VOC in it. After several trials it was evident from the results that the waterborne superprimer formulation mentioned in the previous chapters had to be modified for best performance in the zinc-rich primers. The results and observation are discussed in the following chapters.
5.3.1 FORMULATION, MIXING AND COATING

The formulation of the zinc-rich primer is different from the usual superprimer with particles in it.

The following shows information about the components and their mixing procedure:

- Part A: Superfine (grade 5) zinc dust at 70 % (by weight in the total formulation)

- Part B: WSP-1 (30% by weight in the total formulation) which contains 80% EPI REZ-3540 resin + 19% (A1170: VTAS [5:1] ; 10% solutions in water) + 1% TEOS + defoamer [if needed]

- Part B is shear-blended for 10 minutes at 2100 rpm. Then Part A is added in small batches and blended for 20 minutes at 3000 rpm

The cleaning requirements for zinc-rich coatings are equally stringent as in conventional primers. Measures have to be taken to make sure that proper electrical contact is maintained in between the zinc in the coating and the steel substrate. Cleaning procedure is similar to the one in the previous chapters. Zinc-rich coatings can be applied using brush, drawdown or by a spraying method.

The zinc-rich superprimer coatings were cured at 100°C for 30 minutes and then letting the coating set at room temperature for 1 week. Zinc-rich primers work better performance-wise if the
coatings were allowed to retain some moisture inside them for some time. This moisture retention will help form the zinc corrosion products and seal the pores of the coating. So for zinc-rich coatings a slight under-curing is preferred.

5.3.2 RESULTS AND DISCUSSION

In this section the test results using EIS, Salt Spray and SEM techniques are discussed.

*Percentage of Zinc Dust*

The percentage of zinc dust in the zinc-rich primers is critical and it determines the performance. It needs to be high enough for the primers to perform their function efficiently. Since these primers work on the basis of cathodic protection, it is necessary that the zinc metal particles maintain electrical contact not only with the steel substrate but also with each other. So for the particles to be tight and intact in the coating over the substrate the percentage of zinc in dry zinc rich coating needs to be high.

Carbon steel panels were first solvent-scrubbed using ethanol as solvent and scotch-brite pads to remove the dirt, corrosion products and expose clean, shiny metal-oxide surface. After the scrubbing, the panels were cleaned with water spray and then followed by ultrasonic cleaning in ethanol for 5 minutes. The final stages of cleaning included alkaline cleaning similar to the one followed for aluminum but at lower temperature of 55°C and for only 1 or 2 minutes. CRS is a
very sensitive substrate so care was taken not to spoil the metal-oxide surface before coating with superprimer.

EIS and salt spray tests were used to analyze this effect. Figure 5.3 shows EIS curves of a formulation containing 40% zinc 60% superprimer mixture for 0 to 42 days. Figure 5.4 shows a similar result of formulation with 70% zinc and 30% superprimer.

Figure 5.5 shows the salt spray result after 3 weeks of both 40% and 80% zinc formulations. The performance of 80% formulation was better than the one with 40%. It was not that evident from the comparison between both of their EIS curves. The significance of increasing modulus is explained here.

Figure 5.6 shows a comparison of the 6-week EIS result of a commercial chromate containing primer from Carbozinc and zinc-rich superprimer. All the EIS impedance curves show an increase in the impedance values with due time. Because of the conductive metal zinc in zinc-rich coatings it has less resistance in the beginning. When the immersion time increases the zinc is corroded and forms its insoluble corrosion products. These corrosion products seal the pores and make the coating less permeable to water. In other words, this means an increase in the resistance. This behavior of the zinc rich coatings can be accounted for their increasing impedance behavior.
Salt fog results showed an equally good or better performance of the zinc-rich superprimer when compared to the commercial primer. Figure 5.7 shows the comparison. However, the zinc-rich superprimer has the following advantages than most of the commercial primers:

- Completely water-reducible
- Easy clean-up
- Excellent adhesion to topcoat
- Low VOC
- Equal or better performance when compared to solvent-borne commercial paints
- Chromate-free
- Low solvent odor
- Pot life of close to 24 hours

Both primers performed equally well in terms of corrosion performance. No visible red corrosion products of steel were observed on the steel panels. In Figure 5.7 white corrosion products of zinc were observed in the scribe. These white deposits of zinc hydroxide are highly insoluble to water and other species. The formation of these deposits is, in fact, an indication of good performance by the zinc-rich coatings. However, similar white corrosion products were not observed in the scribe of panels with both zinc rich coating and a polymer topcoat over it. Figure 5.8 shows the 200 hour salt fog result of zinc rich primers with topcoat.
The noticeable difference between Figure 5.7 and 5.8 is the formation of red corrosion product of steel in the scribes of the panels with topcoat. Formation of zinc corrosion products at the scribe were not observed when the panels are coated with a topcoat. Thus the scribes of the panels were not protected. The reason for the zinc-rich primers to be not as efficient under the topcoat can be attributed to the fact that application of a topcoat over a zinc rich primer will actually decrease/cut-off the electrical contact between the zinc, iron and the environment (which acts as an electrolyte). As explained in the previous sections, a contact between the three is necessary for the corrosion protection action of the zinc.

At the areas of a defect or a scribe only a small portion of zinc is exposed to the environment which can sacrifice itself and protect the steel. In the non-top coated panels a larger portion of the zinc surface is exposed and sacrificed, which will in turn help the steel underneath from getting corroded.

**SEM Results**

An attempt was made to observe the corrosion protection of zinc using the EDS technique. The idea was to observe the formation of zinc corrosion products in the scribe with time.

A 1 cm by 1 cm portion of a steel panel coated with zinc-rich superprimer was cut and scribed in the center. Analysis was done on two areas, one at the coating surface and one area in the
scribe. First analysis was done in both the areas immediately after curing and another after 48 hours of immersion in 5% NaCl solution. The aim was to observe any traces of zinc that leached out from the coating to the scribe with time by forming zinc hydroxides.

Analysis of the coated areas before the immersion revealed the presence of only Si compounds. This Si is from the silane content in the zinc-rich coating. Analysis on the coated area after the immersion revealed the presence of zinc and traces of iron. To rectify this difference or strange observation further tests and studies need to be conducted.

Analysis of scribed areas revealed some useful information. Before the immersion the only species detected were iron compounds. This is obvious because after a fresh scribe, formation of a shiny iron oxide layer is obvious. After the immersion, traces of zinc compounds were detected. This observation can be made using Figures 5.9 to 5.12.

5.4 CONCLUSIONS

Zinc-rich Superprimer can be a promising replacement for solvent-based chromate containing zinc-rich primers. A successful formulation was optimized after running trials with different percentages of the components. EIS and salt spray results were used to test the formulations. It was proven that a higher percentage of zinc is needed for better corrosion performance. Higher percentage of zinc ensures proper electrical contact in between the zinc particles and the steel
substrate. This electrical contact is needed because zinc performs according to sacrificial anode mechanism.

EIS and salt spray results proved that zinc-rich superprimer formulations performs equally well or better than a commercial chromate containing zinc-rich primer. However the superprimer has the advantage of being completely water-based with very low VOC and additionally it is chromate-free. It is very comfortable to work with and because it is water-soluble the effort in cleaning issues is reduced.

The superprimer showed excellent adhesion to a topcoat and had no adhesion issues. However it was observed both in the cases of the superprimer and a commercial primer that the scribes are not protected when used with topcoat. This observation was attributed to the fact that using a topcoat actually reduces the amount of exposed zinc on a substrate. The amount of zinc exposed is critical in the performance wise for a zinc-rich coating. So for the zinc-rich coatings to perform efficiently they need to be used without a topcoat.
CHAPTER 6: CHARACTERIZATION

This chapter discusses the characterization work that was done in the final stages of this thesis work. $^{13}$C NMR and IR characterization techniques were used to investigate the chemical structural characteristics and changes in the superprimer formulations. NMR equipment in Chemistry Department at Oklahoma State University was used. $^{29}$Si NMR spectra were recorded on a Varian Inova 600 MHz spectrometer using a Varian broadband probe. Spectra were collected with a 1-pulse experiment using a 9 ms pulse width with a 30 seconds pulse delay and 472 scans. All chemical shifts were referenced to Tetra Methoxy Silane. Both carbon and silicon NMR analysis were tried. The RAIR spectra were obtained by using a Spectrum One FTIR spectrometer from Perkin Elmer, Wellesley, MA. A variable angle diffuse reflectance accessory was used with the incidence angle being fixed at 80°. The scanning range was from 4000 cm$^{-1}$ to 450 cm$^{-1}$ of and 64 scans of each film were taken.

Characterization was aimed at observing the possible or expected chemical reactions in the coating system. They are:

Secondary amine NH and Epoxy reaction
Silane condensation reactions

\[ \text{SiOH} + \text{SiOH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O} \quad [\text{eq 18}] \]

\[ \text{SiOH} + \text{HO-C(epoxy)} \rightarrow \text{Si-O-C} + \text{H}_2\text{O} \quad [\text{eq 19}] \]
6.1 NMR Characterization

6.1.1 Objective and Sample Preparation

It was our intention to gather information on the chemical reactions in the superprimer coating by using the NMR technique both before and after coating. In this view, samples were tested using the carbon NMR technique both in liquid and solid form. Individual components of the superprimer including the silanes and the resins were tested in as-obtained liquid form for reference and then the final superprimer solution prepared in the following way was tested. Cured coatings of superprimer were scraped from metal surfaces, powdered and tested for solid-state NMR.

The following is the primer formulation under focus:

*Formulation F-6*

The components and mixing procedure of Formulation F-6 are:

Part A: EPI REZ 3540-WY-55 Epoxy resin
Part B: AV5 10% in water at pH 6. Bis-amino and vinyltriacetoxysilane mixed in 5:1 volume ratio and then diluted with water.

Part C: TEOS

Part D: Bis-sulfur silane

By weight:

Part A (80%) + Part B (9%) + Part C (1%) + Part D (10%)

High-shear blended for 10 min. at 2000 rpm

After allowing 20 minutes of incubation time, cleaned aluminum panels were either brushed or coated using a drawdown bar

Panels cured at 100˚C for 1 hour

$^{13}$C NMR spectra were taken of the primary components and the final formulation. Analysis was done by comparing the spectra for the appearance of new peaks which might show the progress of the chemical reactions that could happen in the final formulation. Liquid $^{13}$C NMR was done on AV5, bis-sulfur, 3540 resin and the F6 formulation.
Solid $^{13}$C NMR was done on a cured coating of the completed formulation. Cured coatings made on the aluminum in the above fashion were scraped using an ordinary blade and then the scrapings were ground to a powder form using mortar and pestle. An NMR spectrum was taken of solid powders. Si$^{29}$ NMR was done on liquid samples only.

6.1.2 Observations

_Epirez wy 55 3540 Resin_

The chemical structure of the typical DGEBA resin is shown in Figure 6.1. This is a water-based epoxy resin with 2-propoxyethanol as a co-solvent. The peaks observed and their assigned bonds are mentioned in Table 6.1. Figure 6.2 shows the spectrum.

The superprimer was prepared by the usual mixing procedure mentioned in the previous chapters. No additions of particles or inhibitors were made to it. The mixture was analyzed initially, after 16 hours and after 8 days after mixing. The NMR peaks taken with time are shown in Figure 6.5 and Table 6.2. This was done to monitor the hydrolysis of the silanes in it.

The initial spectrum of the superprimer mixture contains resonances due to the component resin, solvent, and silanes. A small peak at 49.3 ppm due to MeOH is present initially and increases in intensity with time, indicating that hydrolysis of the bis-amino silane continues with time.
The relative intensities of the ethanol peaks at 57.5 and 17.7 ppm, initially decrease and then increase with time as compared with the intensities of the ethoxy peaks at 58.4 and 18.5 ppm, indicating that hydrolysis of the bis-sulfur silane continues with time. Initially the decrease in peak sizes might be caused because of the evaporation of ethanol that is present as solvent in the coatings. With time the intensities increase which might be due to formation of ethanol by the hydrolysis of bis-sulfur silane.

The intensity of the 69 ppm C-OH peak decreases with time, though a clear reaction product is not observed. The intensities of the epoxide peaks do not appear to change with time.

_Cured Superprimer Coating_

Solid state NMR spectra of the cured coating were collected and the peak assignments observed are shown in Table 6.3 and the spectrums shown in Figure 6.6.

The spectrum showed peaks due to the resin and unreacted bis-sulfur. The unreacted bis-sulfur was also observed in the $^{29}$Si NMR spectra of the coating, as $T^0$ (non-hydrolyzed), $T^1$, $T^2$, and $T^3$ peaks accounted for approx. 35.5, 9.1, 12.2, and 43.0 % of the total peak area. $^{29}$Si NMR spectrum of the cured coating is shown in Figure 6.7.

Only two successful conclusions about hydrolysis of bis-amino and bis-sulfur silanes could be drawn from the NMR tests so far. Peaks at around 70 ppm could not be positively assigned to
either Si-O-C or C-O-C because they were observed in both resin and the final formulation. This makes it uncertain to relate the observation to the cross-linking of the epoxy groups. However further tests using the IR technique are conducted to determine this observation.

6.2 IR Characterization

6.1.1 Equipment and Sample Preparation

The chemical structures of the superprimer coatings and the component silanes and resins on aluminum AA 2024 T3 were studied by reflection-absorption infrared (RAIR) spectroscopy. The RAIR spectra were obtained by using a Spectrum One FTIR spectrometer from PerkinElmer, Wellesley, MA. A variable angle diffuse reflectance accessory was used with the incidence angle being fixed at 80°. The scanning range was from 4000 cm⁻¹ to 450 cm⁻¹ of and 64 scans of each film were taken.

Coatings of the superprimer and also its component resin and silanes were made on aluminum panels. The IR absorbance spectra were taken on coatings at different cure conditions. The conditions are specified whenever necessary in the next section. Coatings were made from water-diluted 10% silane mixture of bis-amino and VTAS (5:1) and pure bis-sulfur silane. Spectra were also taken of coatings made from only resin and complete superprimer formulation F6. Peak assignments were made in detail for each spectrum in the following section.
6.2.2 IR Spectra

AV5 Coatings

Bis-amino and vinyltriacetoxy silanes are mixed in 5:1 volume ratio. A 10% diluted solution was prepared in water at pH 6. Cleaned aluminum 2024 T3 panels were dip-coated and cured at 100°C for 1 hour. The IR spectrum taken over such a sample is shown in Figure 6.8. Important peak assignments are shown in the figure and also mentioned in Table 6.4. Important peaks for Si-O-Si, Si-O-Me and secondary amines which are peculiar for the silane mixture are found and noted. Peaks for OH groups are also found which can be from silane hydrolysis and formation of alcohol.

Bis-sulfur Coatings

Pure bis-sulfur silane coatings were dip-coated on aluminum panels and cured at 100°C for 1 hour. The IR spectrum with peak assignments taken of such a sample is shown in Figure 6.9. Peaks for Si-O-Si and Si-O-Si can also be seen here. Any peaks showing the presence of sulfur bonds are not prominent because unlike oxygen containing bonds, C-S and C-S-H vibrations tend to give weak absorptions in the infrared spectrum. The higher mass of sulfur, compared with oxygen, results in the characteristic group frequencies occurring at noticeably lower frequencies than the oxygen-containing analogs [33].

Resin and Superprimer Coatings
The commercial EPIREZ 3540 wy-55 resin used in the superprimer formulation (F6) was coated using a drawdown bar on a cleaned aluminum panel. The superprimer formulation F6 which contains 80% resin, 10.5% bis-sulfur silane, 9% AV5 (105 diluted) and 0.5% tetraethoxysilane was prepared and coated using a drawdown bar. The resin coating was cured at 100°C for 1 hour. Superprimer coatings were cured both at 100°C for different timings and also at RT for a number of days. The time and conditions are mentioned whenever necessary while discussing the spectra. The IR spectrum with peak assignments of the resin coating is shown in Figure 6.10. The IR spectra of the F6 formulation at different curing conditions are shown in Figures 6.11 and 6.12.

EPIREZ 3540 is a water-based DGEBA resin showed characteristic epoxy peaks at ~1259 cm⁻¹ and at ~ 890 cm⁻¹. A combination of peaks at ~1600 and 1500 cm⁻¹ shows the aromatic nature of the resin. A broad peak in the range of 3600 cm⁻¹ – 3200 cm⁻¹ shows the hydrogen bonding in the resin. Peaks in the same range are observed also in Figures 6.10 and 6.11 of the superprimer spectra cured at different conditions. Superprimer is a multi-component mixture hence the spectra showed a few peaks which are related to other bonds present in the primer. Peaks observed in the range of 1130 cm⁻¹ – 1000 cm⁻¹ prove the presence of siloxane linkages (Si-O-Si) obtained from condensation of both the silanes. Siloxane linkages to metal (Si-O-Me) which improve the
adhesion are also observed in the range 1000 cm\(^{-1}\) – 900 cm\(^{-1}\). Some peaks in the range of 1150-1050 cm\(^{-1}\) might also be due to an alkyl substituted C-O-C stretch which results from the crosslinking of epoxy groups. Some peaks around 950 cm\(^{-1}\) might also be due to condensation reactions between silanol SiOH and C-OH groups which lead to Si-O-C linkage.

To observe the cure trend IR spectrum was taken over F6 coated sample at different cure occasions. In Figure 6.12 spectra of F6 coatings cured at 100°C for 1, 2 and 3 hours and at room temperature for 1 hour and 5 days are shown. A marginal increase in the intensity of peaks in the range for Si-O-Si and Si-O-Me linkages are observed in between the spectrum cured at RT for 1 hour and at RT for 5 days. This shows that silanes in the superprimer hydrolyze and condense and thus crosslink better with time than in the fast cure conditions. This can be explained by the fact that a reasonable amount of sulfur silane in the coating is present in its pure unhydrolyzed state at the time of coating. This silane hydrolyzes with the moisture in air while curing at room temperature. Condensation reactions happen with due time and thus increase the cross-linking of the films. Increase in the intensity of the peaks which show the Si-O-Me linkages in the range 1000 cm\(^{-1}\) – 900 cm\(^{-1}\) is also observed.
CHAPTER 7: CONCLUSIONS

Silanes or silane solutions at high concentrations can be used for coating purposes by modifying silanes with resins. Primer formulations were obtained by silane plus resin combination, called 'superprimer'. Formulations were developed and tested from low concentrations of resin followed by increased percentages of resin. A completely water-soluble superprimer formulation was developed using a waterborne resin and water-soluble silane solutions. The hydrophobicity and anti-corrosion performance of the superprimer were improved by inclusion of hydrophobic silane into the formulation. Test results over the coatings formed by base formulation including EIS and salt spray exposure showed that the improved superprimer formulation has very good anti-corrosion performance. The coatings passed 2 weeks of ASTM B117 salt spray. Outdoor exposure testing was also done at a testing center in Hawaii. Coatings from the base formulations with topcoat over steel panels were exposed. Figure 7.1 and Figure 7.2 show the tested panels both before and after exposure. The coatings over carbon steel showed filiform corrosion in the scribed areas, whereas the coatings over aluminum panels showed no signs of visible corrosion as of yet. Figure 7.3 shows the aerial view of the exposure sight in Florida. And figure 7.4 shows how the panels are exposed at the sight. Figure 7.5 shows the position of the panels at the exposure center. Additions such as nano-size particles and corrosion inhibiting pigments added to give specific qualities were discussed in detail along with the formulations and test results.
Particles and corrosion inhibitors were added to silane plus resin mixtures to provide superprimer with better film properties and anti-corrosion performance. Alumina, carbon black and zinc were tried as particle inclusions along with commercially available corrosion inhibitors. EIS and salt spray standard tests were used to monitor the film properties and anti-corrosion performance simultaneously. Coatings from formulations F10 which contains about 2.5 % by weight of alumina, showed good anti corrosion performance. These coatings without any topcoat passed 500 hours in salt spray testing, and passed 1000 hours in salt spray when tested with topcoat. Similarly, coatings from inhibitor formulations namely calcium zinc molybdate (F-15 with 10% by weight), passed 500 hours in salt spray testing without a topcoat, and 1000 hours with topcoat. These two formulations can be recommended as suitable primer formulations for aluminum.

Also, test results over different formulations showed that alumina addition to superprimer enhances the anti-corrosion performance. However, increasing level of alumina leads to decrease in the corrosion performance. Increase in porosity resulted by the increase in the amount of particles can be considered as a possible explanation behind this observation. But, the loaded percentages are far below the CPVC value of the alumina in a coating. Alumina used here was a water-based paste and by nature alumina is considered to be very hydrophilic. So, the increase in its weight percentage can actually increase the hydrophylicity of the coatings and
hence decrease the performance. And this was quite evident from the performance test results of F10, F11 and F12 coatings both with and without topcoat.

Carbon black was loaded as a pigment in the superprimer formulations. EIS and salt fog tests conformed to a single observation that the coatings resistance increased initially and then decreased with time. The conductive nature also of the coating increased with the exposure time. The performance of the coating decreased with the increased in the conductive nature of the coating. A possible explanation of formation of hydrophilic hydroxyl ions migrating to the substrate through the coatings is given for the observation.

Corrosion inhibitors were tried to provide enhanced corrosion protection to the superprimer. This idea was put to trial so as to imitate the self-healing characteristic of the chromate primers [3]. Test results showed that the corrosion performance did increase and primer-coated surfaces showed less pitting and general corrosion in un-scribed areas. But the inhibition could not protect the scribed areas. Visible corrosion was found in most of the formulations. The search for the right inhibitor which can provide the scribe protection still needs to be continued and this particular area gives scope for further research.

A zinc-rich superprimer can be a promising replacement for solvent-based chromate-containing zinc-rich primers. A successful formulation was optimized after running several trials with different
percentages of the components. EIS and salt spray test results were used to analyze the formulations. It was proven that higher percentage of zinc is needed for better corrosion performance. Higher percentage of zinc ensures proper electrical contact in between the zinc particles and the steel substrate. This electrical contact is needed because zinc performs according to a sacrificial anode mechanism. A chromate-free, completely water-based, very low VOC zinc rich superprimer formulation was obtained which performed equally better with a commercially available zinc-rich primer. Salt spray results proved this observation. The developed zinc rich superprimer has better ease to work with, easy to clean and has comfortable potlife. These factors coupled with its good performance can be an excellent promise as coatings for steel.

EIS and salt spray results proved that zinc-rich superprimer formulations performs equally or better than a commercial chromate containing zinc-rich primer. However the superprimer has the advantaged of being completely water-based with very low VOC (~50 g/l) and additionally it is chromate-free. It is very comfortable to work with and being water-soluble reduces the effort and cost in cleaning issues.

The superprimer showed excellent adhesion to topcoats. However it was observed both in the cases of superprimer and commercial primer that the scribes were not protected when used with topcoat. The reason was attributed to the fact that using a topcoat actually reduces the amount of
exposed zinc on a substrate. The amount of zinc exposed is critical for the performance of a zinc-rich coating. So for the zinc-rich coatings to perform efficiently they need to be used without a topcoat.

Characterization using IR and NMR techniques proved that hydrolysis of the component silanes takes place with time. A two-step cure starting with a room temperature then force curing it at a certain higher temperature might be show promise towards increased adhesion to the substrate. This is due to the observed fact that the component silane which exists in its pure state undiluted state hydrolysis in due time and its cross-linking within the coating and adhesion to the substrate increase gradually with time.

Si-O-Si chemical linkages from silanol-silanol condensation, Si-O-Me from silanol-hydroxy condensation and Si-O-C from silanol-epoxy condensation were expected to occur in the coating system. The peaks with reasonable intensity for the first two linkages were observed. A possible overlap of the peaks in IR range 1000 cm\(^{-1}\) – 900 cm\(^{-1}\) made it hard prove the possible reactions of epoxy-silanol crosslinking which occurs at around 950 cm\(^{-1}\).
CHAPTER 8: RECOMMENDATIONS FOR FUTURE WORK

This thesis work is one of the three initial works on the superprimer idea. Other works include solvent-borne superprimer idea. This thesis concentrated its work primarily on trying to find the aimed coating system with an epoxy resin as a base. The work was started from scratch just by simple mixing of solutions. Many important things were realized during the course of this work. Much more can be achieved and researched with further work. Here are a few recommendations which might help the future work in this area.

It is suggested to use the equivalent weight method to determine the required ratio between the resin and its curing agent (reactive agent like silane in the system) for its complete reaction. This simple method requires one to find the weight per epoxide chain of the resin that is being used and to mix it with an equivalent amount of the curing agent that will react with the whole epoxide. This sort of method might decrease the cumbersome trial and error methods commonly used. Many factors like pot life of the material, viscosity, etc., can be controlled once the ratio for complete reaction is known, i.e., for example less curing agent can be used to increase the pot life and flexibility of the coating. This method is commonly used for high-solids coatings in automotive industries and it is worth trying here too.
Further increasing the amount of solvent in the superprimer system for better curing ability of the system can be a valuable trial. This can be simply tried by using hydrolyzed bis-sulfur system in ethanol rather than using pure silane alone. NMR results revealed that there is a lot of unreacted sulfur silane left in the superprimer coatings.

It is also suggested to use a high epoxide containing resin, which are available commercially. High molecular weight epoxies might have better effect on the performance of the coatings.

Similar trials can be made for zinc-rich superprimer work also. Addition of solvent based bis-sulfur silane into the binder of the superprimer can be a valuable trial. This way of inclusion of solvent in the system will increase the curing ability and hence the performance of the zinc-rich coatings.

Care should be taken not to include too much of silane as it is expected that too much of silane can encapsulate the zinc particles and decrease its performance in the coatings.

Further optimization of the percentage of zinc can be a trial worth doing.
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Patent 6,328,878, December 11, 2001


APPENDIX

A.1 http://www.techsolve.org/p2iris/metalfinish/1058-s.htm

A.2 http://www.pfonline.com/articles/pfd0020.html

A.3


A.4 http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/nmr1.htm

A.5 http://www.chemistry.ccsu.edu/glagovich/teaching/472/ir/em.html

A.6

Table 2.1: List of Silanes used with trade names and chemical formulas

<table>
<thead>
<tr>
<th>TRADE NAME</th>
<th>CHEMICAL NAME</th>
<th>CHEMICAL FORMULA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1170</td>
<td>Bis(trimethoxysilylpropyl)amine</td>
<td>(OCH3)3Si(CH2)3NH(CH2)3Si(OCH3)3</td>
</tr>
<tr>
<td>A-1289</td>
<td>Bis(triethoxysilylpropyl)tetrasulfide</td>
<td>(OC2H5)3Si(CH2)3S4(CH2)3Si(OC2H5)3</td>
</tr>
<tr>
<td>Y-9805</td>
<td>Bis(triethoxysilylpropyl)ethane</td>
<td>(OC2H5)3Si(CH2)2Si(OC2H5)3</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
<td>Si(OC2H5)4</td>
</tr>
<tr>
<td>A-Link 15</td>
<td>Nethyl-3-trimethoxysilylethylpropanamine</td>
<td>CH3CH2NHCH2CH(CH3)CH2Si(OCH3)</td>
</tr>
<tr>
<td>A-Link 25</td>
<td>Gamma-Isocyanatopropyltriethoxysilane</td>
<td>NCO(CH2)3Si(OC2H5)3</td>
</tr>
<tr>
<td>VTAS</td>
<td>Vinyltriacetoxyisilane</td>
<td>CH2=CH(CH)2Si(OCOCH3)3</td>
</tr>
</tbody>
</table>
### Table 2.2 Resins used in superprimer formulations

<table>
<thead>
<tr>
<th>Resin Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPON 828 Resin-X-95</td>
</tr>
<tr>
<td>EPIREZ Resin 3510-W-60</td>
</tr>
<tr>
<td>EPIREZ Resin 3515-W-60</td>
</tr>
<tr>
<td>EPIREZ Resin 3540-WY-55</td>
</tr>
</tbody>
</table>

### Table 2.3 Particles used in superprimer formulations

<table>
<thead>
<tr>
<th>NAME</th>
<th>TYPE</th>
<th>MANUFACTURER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal Silica</td>
<td>Silica nano-particles(suspension in water)</td>
<td>Cabot Corporation, Tuscola, IL</td>
</tr>
<tr>
<td>Aluminasol</td>
<td>Alumina nano-particles 10% by weight(suspension in water)</td>
<td>Nissan Chemical, Houston, TX</td>
</tr>
<tr>
<td>Carbosil</td>
<td>Carbon nanoparticles(Dry)</td>
<td></td>
</tr>
<tr>
<td>Zinc Dust</td>
<td>Zinc nanoparticles(Dry)</td>
<td>U.S.Zinc, Houston, TX</td>
</tr>
</tbody>
</table>
### Table 2.4: Corrosion Inhibitors used in the superprimer formulations

<table>
<thead>
<tr>
<th>NAME</th>
<th>COMPANY</th>
<th>TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZM</td>
<td>Molywhite, Cleveland, OH</td>
<td>Calcium Zinc Molybdate</td>
</tr>
<tr>
<td>M-119 LV</td>
<td>Cortec Corporation, St. Paul, MN</td>
<td>Trade Secret of the company</td>
</tr>
<tr>
<td>M-5120</td>
<td>Cortec Corporation, St. Paul, MN</td>
<td>Trade Secret of the company</td>
</tr>
<tr>
<td>M-118</td>
<td>Cortec Corporation, St. Paul, MN</td>
<td>Trade Secret of the company</td>
</tr>
<tr>
<td>Fluka-Sodium Vanadate</td>
<td>Sigma Aldrich</td>
<td>Sodium Meta Vanadate</td>
</tr>
<tr>
<td>SZP-391</td>
<td>Halox Pigments, Hammond, IN</td>
<td>Strontium Zinc Phosphate</td>
</tr>
<tr>
<td>Corrostain 228</td>
<td>Wayne Pigment Corp, Milwaukee, WI</td>
<td>Trade Secret of the company</td>
</tr>
<tr>
<td>UC-Pigment</td>
<td>University of Cincinnati</td>
<td>Plasma Polymerized Pigment</td>
</tr>
</tbody>
</table>
Table 3.1: Resins and compatible silanes

<table>
<thead>
<tr>
<th>RESIN</th>
<th>SILANE CLASS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>Amine, Epoxy, Choloroalkyl, Mercapto</td>
</tr>
<tr>
<td>Polyester</td>
<td>Amine, Methacrylate, Styryl, Vinyl</td>
</tr>
<tr>
<td>Urethane</td>
<td>Amine, Alkaloamine, Epoxy, Isocyanate</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Acrylic, Styryl, Epoxy</td>
</tr>
</tbody>
</table>
Table 3.4.1: Comparison of performance of test results between control PRC Desoto MIL PRF and Superprimer Formulation F

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Control Description</th>
<th>Formulation F Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt spray</td>
<td>No corrosion in the scribe after 2 weeks</td>
<td>Corrosion in the scribe after 2 weeks</td>
</tr>
<tr>
<td>Salt immersion</td>
<td>Sustained for 1 month</td>
<td>Sustained for 1 month</td>
</tr>
<tr>
<td>Contact angle</td>
<td>69.5°</td>
<td>65.5°</td>
</tr>
<tr>
<td>EIS</td>
<td>6 ohm for 1 week</td>
<td>3 ohm for 2 days</td>
</tr>
<tr>
<td>Hardness</td>
<td>F</td>
<td>HB</td>
</tr>
<tr>
<td>Adhesion to Substrate</td>
<td>5B</td>
<td>4B</td>
</tr>
<tr>
<td>Paint Adhesion</td>
<td>5B</td>
<td>5B</td>
</tr>
</tbody>
</table>
Table 3.6.1: Summary of test results of the control, F-6 and F

<table>
<thead>
<tr>
<th></th>
<th>CONTROL</th>
<th>FORMULATION F</th>
<th>FORMULATION F-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt spray</td>
<td>No corrosion in the scribe after 2 weeks</td>
<td>Corrosion in the scribe after 1 week</td>
<td>Corrosion in scribe after 2 weeks</td>
</tr>
<tr>
<td>Salt immersion</td>
<td>Sustained for 1 month</td>
<td>Sustained for 1 month</td>
<td>Sustained for 2 months</td>
</tr>
<tr>
<td>Contact angle</td>
<td>69.5˚</td>
<td>65.5˚</td>
<td>78.4˚</td>
</tr>
<tr>
<td>EIS</td>
<td>1 Mohm for 1 week</td>
<td>100 kohm for 2 days</td>
<td>1 Gohm for 1 week</td>
</tr>
<tr>
<td>Hardness</td>
<td>F</td>
<td>HB</td>
<td>F</td>
</tr>
<tr>
<td>Adhesion to substrate</td>
<td>5B</td>
<td>4B</td>
<td>5B</td>
</tr>
<tr>
<td>Paint Adhesion</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
</tbody>
</table>
Table 4.1.1: Formulation chart of modified superprimers with particles/inhibitors

<table>
<thead>
<tr>
<th>FORMULATION (BY WEIGHT)</th>
<th>RESIN</th>
<th>AV5 (10%)</th>
<th>SULFUR SILANE</th>
<th>TEOS</th>
<th>ADDITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6</td>
<td>80</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>nil</td>
</tr>
<tr>
<td>F10</td>
<td>77.5</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(Alumina) 2.5</td>
</tr>
<tr>
<td>F11</td>
<td>75</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(Alumina) 5.0</td>
</tr>
<tr>
<td>F12</td>
<td>70</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(Alumina) 10.0</td>
</tr>
<tr>
<td>F13</td>
<td>77.5</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(CZM) 2.5</td>
</tr>
<tr>
<td>F14</td>
<td>75</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(CZM) 5.0</td>
</tr>
<tr>
<td>F15</td>
<td>70</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(CZM) 10.0</td>
</tr>
<tr>
<td>F16</td>
<td>80</td>
<td>9</td>
<td>10</td>
<td>nil</td>
<td>A-LINK-15</td>
</tr>
<tr>
<td>F17</td>
<td>80</td>
<td>9</td>
<td>10.9</td>
<td>nil</td>
<td>(A-link 25) 0.1</td>
</tr>
<tr>
<td>F18</td>
<td>80</td>
<td>9</td>
<td>10.9</td>
<td>nil</td>
<td>A-LINK-15 0.1</td>
</tr>
<tr>
<td>F19</td>
<td>80</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>BTSE (10%)</td>
</tr>
<tr>
<td>F20</td>
<td>78.8</td>
<td>9</td>
<td>10</td>
<td>1</td>
<td>(Cortec M119 LV)1</td>
</tr>
<tr>
<td>F21</td>
<td>78</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>Cortec M-5120(1%) + A-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>F22</td>
<td>78</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>Cortec M-118(2%) + A-LINK-15(0.5)</td>
</tr>
<tr>
<td>F23</td>
<td>78</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>Sodium Vanadate 2% + A-LINK-15(0.5)</td>
</tr>
<tr>
<td>F24</td>
<td>75</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>Sodium Vanadate 5000 ppm + A-LINK-15(0.5)</td>
</tr>
<tr>
<td>F25</td>
<td>77</td>
<td>9</td>
<td>10</td>
<td>0.5</td>
<td>Halox SZP-391 Strontium Zinc Phosphosilicate 3% + A-LINK-15(0.5)</td>
</tr>
<tr>
<td>F26</td>
<td>80</td>
<td>9</td>
<td>10.5</td>
<td>0.5</td>
<td>nil</td>
</tr>
<tr>
<td>F27</td>
<td>77</td>
<td>9</td>
<td>10.5</td>
<td>0.5</td>
<td>Wayne Pigment Corp., Corrostain 3%</td>
</tr>
<tr>
<td>F28</td>
<td>77</td>
<td>9</td>
<td>10.5</td>
<td>0.5</td>
<td>Carbon Black 3%</td>
</tr>
<tr>
<td>F29</td>
<td>77</td>
<td>9</td>
<td>10.5</td>
<td>0.5</td>
<td>UC Pigment 3%</td>
</tr>
</tbody>
</table>
Table 6.1: Peak assignments in the carbon spectrum of commercial resin;

Spectra for the component silanes AV5 and bis-sulfur are shown in Figures 6.3 and 6.4. Refer to Figure 6.1

<table>
<thead>
<tr>
<th>PEAK POSITION</th>
<th>COMPONENT</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>156.8</td>
<td>Resin</td>
<td>Phenyl</td>
</tr>
<tr>
<td>143.4</td>
<td>Resin</td>
<td>Phenyl</td>
</tr>
<tr>
<td>127.9</td>
<td>Resin</td>
<td>Phenyl</td>
</tr>
<tr>
<td>114.3</td>
<td>Resin</td>
<td>Phenyl</td>
</tr>
<tr>
<td>72.9</td>
<td>Propoxyethanol</td>
<td></td>
</tr>
<tr>
<td>72.1</td>
<td>Propoxyethanol</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>Resin</td>
<td>Internal C-O-C</td>
</tr>
<tr>
<td>69.1</td>
<td>Resin</td>
<td>Internal C-OH</td>
</tr>
<tr>
<td>61.2</td>
<td>Propoxyethanol</td>
<td></td>
</tr>
<tr>
<td>50.4</td>
<td>Resin</td>
<td>Epoxide</td>
</tr>
<tr>
<td>44.3</td>
<td>Resin</td>
<td>Epoxide</td>
</tr>
<tr>
<td>41.6</td>
<td>Resin</td>
<td>Quaternary C</td>
</tr>
</tbody>
</table>
Table 6.2: Table showing the change in intensities at certain peak of Figure 6.5 varies with time.

Time is shown in the Y-axis of the table and the peak values in the X-axis of the table.

<table>
<thead>
<tr>
<th>ppm</th>
<th>49.3</th>
<th>17.9</th>
<th>57.5</th>
<th>18.6</th>
<th>58.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.4</td>
<td>35.9</td>
<td>32.1</td>
<td>170.7</td>
<td>119.8</td>
</tr>
<tr>
<td>16 hours at RT conditions</td>
<td>11.8</td>
<td>11.8</td>
<td>11.3</td>
<td>118.3</td>
<td>103.8</td>
</tr>
<tr>
<td>8 Days at RT conditions</td>
<td>12.38</td>
<td>37.34</td>
<td>46.6</td>
<td>105</td>
<td>89.1</td>
</tr>
</tbody>
</table>
Table 6.3: Solid State NMR spectrum of cured superprimer coating shown in Figure 6.6

<table>
<thead>
<tr>
<th>PEAK</th>
<th>COMPONENT</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>158.5</td>
<td>Resin (phenyl)</td>
<td>Phenyl</td>
</tr>
<tr>
<td>145.4</td>
<td>Resin (phenyl)</td>
<td>Phenyl</td>
</tr>
<tr>
<td>129.3</td>
<td>Resin (phenyl)</td>
<td>Phenyl</td>
</tr>
<tr>
<td>116.3</td>
<td>Resin (phenyl)</td>
<td>Phenyl</td>
</tr>
<tr>
<td>70.7</td>
<td>Resin (internal C-O-C)</td>
<td>Internal C-O-C</td>
</tr>
<tr>
<td>59</td>
<td>Bis-sulfur silane (OCH2CH3)</td>
<td>OCH2CH3</td>
</tr>
<tr>
<td>42.7</td>
<td>Resin (possible bis-sulfur overlap?)</td>
<td>Quaternary carbon</td>
</tr>
<tr>
<td>32.2</td>
<td>Resin (CH32)</td>
<td>(CH3)2</td>
</tr>
<tr>
<td>24.1</td>
<td>Resin (SCH2CH2CH2Si(OR)3)</td>
<td>SCH2CH2CH2Si(OR)3</td>
</tr>
<tr>
<td>18.8</td>
<td>Resin (OCH2CH3)</td>
<td>OCH2CH3</td>
</tr>
<tr>
<td>11.1</td>
<td>Resin (SCH2CH2CH2Si(OR)3)</td>
<td>SCH2CH2CH2Si(OR)3</td>
</tr>
</tbody>
</table>
Table 6.4: Peak assignments for bands in IR spectra

<table>
<thead>
<tr>
<th>FUNCTIONAL GROUP</th>
<th>MOLECULAR MOTION</th>
<th>WAVENUMBER (CM⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-H stretch</td>
<td>2950-2800</td>
</tr>
<tr>
<td></td>
<td>CH₂ bend</td>
<td>~1465</td>
</tr>
<tr>
<td>alkanes</td>
<td>CH₃ bend</td>
<td>~1375</td>
</tr>
<tr>
<td></td>
<td>CH₂ bend (4 or more)</td>
<td>~720</td>
</tr>
<tr>
<td></td>
<td>=CH stretch</td>
<td>3100-3010</td>
</tr>
<tr>
<td></td>
<td>C=C stretch (isolated)</td>
<td>1690-1630</td>
</tr>
<tr>
<td></td>
<td>C=C stretch (conjugated)</td>
<td>1640-1610</td>
</tr>
<tr>
<td></td>
<td>C-H in-plane bend</td>
<td>1430-1290</td>
</tr>
<tr>
<td></td>
<td>C-H bend (monosubstituted)</td>
<td>~990 &amp; ~910</td>
</tr>
<tr>
<td></td>
<td>C-H bend (disubstituted - E)</td>
<td>~970</td>
</tr>
<tr>
<td></td>
<td>C-H bend (disubstituted - 1,1)</td>
<td>~890</td>
</tr>
<tr>
<td></td>
<td>C-H bend (disubstituted - Z)</td>
<td>~700</td>
</tr>
<tr>
<td></td>
<td>C-H bend (tri-substituted)</td>
<td>~815</td>
</tr>
<tr>
<td></td>
<td>acetylenic C-H stretch</td>
<td>~3300</td>
</tr>
<tr>
<td>alkynes</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

163
<table>
<thead>
<tr>
<th>Category</th>
<th>Example</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aromatics</td>
<td>C,C triple bond stretch</td>
<td>~2150</td>
</tr>
<tr>
<td></td>
<td>acetylenic C-H bend</td>
<td>650-600</td>
</tr>
<tr>
<td></td>
<td>C-H stretch</td>
<td>3020-3000</td>
</tr>
<tr>
<td></td>
<td>C=C stretch</td>
<td>~1600 &amp; ~1475</td>
</tr>
<tr>
<td></td>
<td>C-H bend (mono)</td>
<td>770-730 &amp; 715-685</td>
</tr>
<tr>
<td></td>
<td>C-H bend (ortho)</td>
<td>770-735</td>
</tr>
<tr>
<td></td>
<td>C-H bend (meta)</td>
<td>~880 &amp; ~780 &amp;</td>
</tr>
<tr>
<td></td>
<td>C-H bend (para)</td>
<td>~690</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850-800</td>
</tr>
<tr>
<td>alcohols</td>
<td>O-H stretch</td>
<td>~3650 or 3400-</td>
</tr>
<tr>
<td></td>
<td>C-O stretch</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1260-1000</td>
</tr>
<tr>
<td>ethers</td>
<td>C-O-C stretch (dialkyl)</td>
<td>1300-1000</td>
</tr>
<tr>
<td></td>
<td>C-O-C stretch (diaryl)</td>
<td>~1250 &amp; ~1120</td>
</tr>
<tr>
<td>aldehydes</td>
<td>C-H aldehyde stretch</td>
<td>~2850 &amp; ~2750</td>
</tr>
<tr>
<td>ketones</td>
<td>C=O stretch</td>
<td>~1725</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~1715</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
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Figure 1.2: Heavy Corrosion Environment [A.6]
Figure 1.3: Corroded C-141 aircraft. [A.6]
Figure 1.4: Corroded aircraft part. [A.6]
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The use of Chromium Pigments
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Step 1:

\[
\text{R.N: } \rightarrow C \quad \overset{O}{\text{C}} \quad C \quad C \quad O \quad R
\]

Step 2:

\[
\text{R}_3\text{N}^+ \quad C \quad C \quad C \quad O \quad R
\]
Step 3: Further polymerization
Step 4:

Figure 3.1: Schematic showing the probable reactions between epoxy-epoxy and epoxy-tertiary amine.
Figure 3.1.2: Reaction between primary amine and an epoxy group
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EIS Bode plots for 6 weeks of immersion of F 14
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Individual impedance plots of formulations F 13 with topcoat

Individual impedance plots of formulations F 14 with topcoat
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Without topcoat (after 21 days of salt spray)

With topcoat (after 42 days of salt spray)

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Zinc-rich superprimer + Polyamide Topcoat          Commercial zinc-rich primer + Polyamide Topcoat

Figure 5.8: 200 hours salt fog result of zinc-rich primers with Polyamide topcoat
Figure 5.9: Zone 1 area in the scribe before immersion.

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Figure 5.10: Zone 2 coated area before immersion

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Figure 5.11: Analysis over zone 2 with coated surface after immersion.

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Figure 5.12: Zone 1 in the scribe after immersion

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