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Integral Epoxy Resin-Silane Primer System for Hot-dip Galvanized Steel

A thesis submitted to the Division of Research and Advanced Studies at the University of Cincinnati in partial fulfillment of the requirements for the degree of

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ABSTRACT

This work deals with the development of a non-chromate, one-step finishing system for corrosion protection of hot-dip galvanized steel. Environmental regulations demand that chromate pretreatments and chromate pigments used in primers be replaced. Previously the Silane Research Group has reported on the effectiveness of silane pretreatments and suggested silane formulations for replacing chromate pretreatments. In this project a pretreatment-free, chromate-free one-step finishing system was needed for hot-dip galvanized steel used in automotive coils in cars. Pretreatments act as adhesion-promoters and bind coatings to metals and since silanes, especially systems using bis-amino silane and bis-sulfur silane, have been shown as excellent adhesion-promoters by this lab, the idea of incorporating silanes in primers for obtaining adhesion to metals emerged. Whether this also meant increased corrosion protection was investigated.

The coating formulation exhibiting the best corrosion resistance is a mixture of hydrolyzed and non-hydrolyzed silanes incorporated into a commercial epoxy resin-curing agent system. Salt spray analysis indicated that the coating exhibits good corrosion resistance. Impedance values were significantly higher for the integral resin-silane coating, as compared to the commercial resin. Impedance values of the integral primer coatings increased with time, as secondary curing reactions imparted by the presence of the non-hydrolyzed silane proceed. Due to the presence of the hydrolyzed silanes, the investigated coatings exhibited good adhesion to both the hot-dipped galvanized steel substrate and a polyester coating.

Coating characterization was carried out using liquid and solid-state NMR and infra-red spectroscopy. It was found that bis-sulfur silane did not react during curing, it

was seen unaffected in the cured film of the coating. Hydrolysis of the silane took place after curing. It was concluded that the coating consisted of two interpenetrating networks containing polyurethane and siloxane groups.

It was clear from the performance results and characterization experiments that silanes perform positively, in terms of enhanced corrosion protection of the metal substrate and adhesion, when the silane's reacting functionalities are prevented from chemical reaction during curing of the coating system. This is because the silane functionalities are needed for hydrolysis and condensation and form chemical bonds with topcoat and metal which increases corrosion-protection and adhesion. For the silane functionalities to remain intact during the curing process it was important to choose appropriate curing agent and resin. The system of blocked polyisocyanate and epoxy resin was very reactive and did not interfere with the silane system. The polyurethane network resulted from the curing agent-resin reaction.

A chromate-free, one-step finishing system without need for pretreatment and exhibiting enhanced corrosion protection and adhesion to metal was developed.

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1. Introduction

This thesis focuses on the development and study of a primer system that provides corrosion protection and adhesion to a hot-dip galvanized surface. The introduction chapter discusses the galvanized steel, corrosion on the zinc surface, corrosion protection offered by organic coatings, pretreatments and primer systems that are used, and finally the aim of this thesis.

1.1 Galvanized steel - Duplex system

Galvanized steel is produced for applications where corrosion resistance is an important service requirement. These applications include automotive parts such as body panels and structural members; building panels, equipment and machinery, guide rails, heating equipment, furnace parts, prefabricated buildings, freezers, and wall panels. In all of these applications, the galvanized coating is specified because it provides enhanced corrosion resistance, and thus, lengthens the useful life of the manufactured products. Zinc is a reactive material and will corrode and erode slowly. For this reason, the protection offered by a galvanized coating is proportional to its thickness and to the corrosion rate. It is therefore important to understand zinc's corrosion mechanism and what factors affect the rate. This will be discussed further in this chapter

For many years, protecting steel from corrosion typically involved either the use of hot-dip galvanizing or some type of paint system such as chromate conversion coatings or paints with chromate inhibitors; chromates in paints are effective¹ but not

needed these days due to legislation. However, powder coating of steel that has been hot-dip galvanized after fabrication is practiced in industries now.

Batch Galvanization: The combination of a paint system with a hot-dip galvanized coating is often referred to as a “duplex system”². According to a recent report from the American Galvanizers Association, the galvanized coating prevents under-film development of iron oxide while the paint gives barrier protection to the galvanized steel. The paint slows the rate at which the zinc is consumed thereby greatly extending the life of the galvanized steel. When paint and galvanized steel are used together, the corrosion protection is superior to either protection system used alone³.

Many types of paint and paint systems have been successfully used with galvanized steel. However some type of paints will not adhere adequately to galvanized steel. It is important to find a suitable paint system with a first coat that is fully compatible with a zinc surface. The first coat serves as a “tie coat” or interface between the galvanized steel and the topcoat⁴. This thesis aims to study such a “tie coat”.

1.2 Corrosion

Corrosion is the destructive result of chemical reaction between a metal or metal alloy and its environment^{5,6}. Corrosion is electrochemical in nature because the corrosive chemical reactions involve a transfer of charge. The metal ions go into solution causing the metal to become negatively charged with respect to the electrolyte. The difference in the charge causes a potential to develop and produces a voltage between the electrolyte and the metal. The two conditions typically required for a metal to undergo general corrosion are: 1) metal and water in the same environment, and 2) a chemical

reaction between the metal and water that forms an oxide. For accelerated corrosion, the presence of electrochemically active species such as oxygen, ions from salts etc is needed.

1.2.1 Cathodic Protection

Cathodic protection from corrosion occurs when a metal to be protected is forced to be the cathode of the corrosion cell by coupling it to a metal more easily oxidized than it. Metal fences and sheets made of iron can be protected by galvanizing them, which consists of coating them with zinc. The galvanized metal will not corrode until after the zinc coating does, since zinc corrodes more readily than does iron. Protection of an oil pipeline with a magnesium sacrificial anode also works this way. The anode will corrode but the pipeline will not. Hot-dip galvanizing of metals for automotive applications is done for the purpose of cathodic protection of steel by the sacrificial zinc. However, this zinc also needs corrosion protection and organic coatings are extensively used to protect the HDG steel used in automotive coils.

1.2.2 Corrosion Mechanisms

Hot-dip galvanizing is the most important galvanizing process. It is the process in which cleaned steel is immersed in molten zinc or zinc alloy, and reaction takes place to form a metallurgically bonded coating. Zn-coated steel behaves similarly to zinc, hence the corrosion mechanism of zinc is considered. A useful booklet on the mechanism of corrosion of a galvanized coating has been produced by Daesen (1975). Consideration of the corrosion of zinc is primarily related to the slow general dissolution from the surface.

Zinc is attacked only slightly by pure air, even if its moisture content is considerable. Below about 200°C, the film grows very slowly and exhibits good adhesion⁷.

Freshly exposed galvanized steel reacts with the surrounding atmosphere to form a series of zinc corrosion products. In air, newly exposed zinc reacts with oxygen to form a very thin zinc oxide layer. When moisture is present, zinc reacts with water, resulting in the formation of zinc hydroxide. The final corrosion product is zinc carbonate, which forms from zinc hydroxide reacting with carbon dioxide in the air. Zinc carbonate is a thin, tenacious, and stable (insoluble in water) layer that provides protection to the underlying zinc, and is the primary reason for its low corrosion rate in most environments⁸. The series of chemical reactions described above are:

In most applications, the passive surface film that forms on zinc, while tenacious, is not totally protective, and continued corrosion does occur over time. In automotive steel coils there is often a formation of white rust which is zinc hydroxide and not zinc carbonate. Zinc carbonate forms a passive film as mentioned above, but in storage conditions galvanized steel coils do not come in contact with carbon dioxide and hence zinc hydroxide remains as white rust and does not passivate. When white rust does occur, there is an actual loss of zinc coating, and some of the zinc that is intended to protect the coated steel product while in service is lost. This is why painting over hot-dip galvanized is done, the duplex system of paint over galvanized surface offers very effective

corrosion protection as the combined corrosion resistance of zinc and paint provides a synergistic effect.

1.3 Corrosion protection by organic coatings

Corrosion protection of metallic substrates has been one of the important roles performed by organic coatings. Such coatings remain cost-effective for many users who would like to have substrates coated just once and assume appearance and function will be maintained. Organic coatings are often used as a protective layer over the metal substrate to prevent the substrate from oxidizing in a manner deleterious to the function and appearance of an object. They do so in several ways⁹. First, they act as a barrier limiting the passage of current necessary to connect the areas of anodic and cathodic activity on the substrate. This occurs especially if the coating wets the substrate surface very well and has good adhesion in the presence of water and electrolyte. Coatings do not really stop oxygen sufficiently to make concentrations at the surface rate limiting and they do not completely stop water ingress into coatings. However, a good barrier coating slows water and electrolyte penetrations and is not displaced by water at the substrate/coating interface¹⁰.

The major areas where protective organic coatings are used are automotive coatings systems, appliance systems, metal coil coatings; powder coatings for heavy-duty use, especially pipeline coatings; farm and construction equipment coatings; and general use for objects used in exterior exposure. These are major Original Equipment Manufacturing areas where corrosion protection is critical. Industrial, architectural,

aircraft and marine equipments are other areas where coatings are important for the protection they offer against corrosion.

Organic coatings are applied often as multi-layer systems called broadly as finishing system¹¹. A full finishing system will require a metal pretreatment or conversion coating which is a special formulation of inorganic chemicals which react with the metal to produce a strongly adherent, corrosion-inhibiting conversion coating, such as a phosphate or chromate, on the metal surface. This coating often provides a better surface than the original metal oxide layer for obtaining good adhesion of the paint layers. Continuing on the requirements of a full finishing system, the next level of coating coated over a pretreatment is the primer system whose role is to enhance corrosion protection and provide adequate adhesion. A primer system also is a reservoir for pigments and inhibitors such as chromates and phosphates which leach out to protect cracks that develop when a coating undergoes weathering and damage¹². Epoxy resins, polyurethanes, alkyds, polysiloxanes, acrylates are some of the resins that are used as primers. On top of the primer system come the undercoat and the final finish systems. These are typically UV resistant paints such as polyesters, a final finish is provided to provide aesthetic appeal. All of these layers may not be used in a finishing system, the use or non-use of certain layers is dependent on factors such as size and shape of article, protection required, severity of exposure, cost of production etc. Fig 1.1 shows typical coating system.

1.3.1 Pretreatments used for metals

Pretreatment processes often cause toxic waste, are expensive and does not lend to a marketing argument by providing appearance to the product. It is often a cumbersome method to provide treatment to metallic sheets in a production line. However, chemical pretreatments are necessary as they provide for a clean surface devoid of oils and greases which the sheets pick up during manufacturing process. It also provides for good paint adhesion and gives good wetting properties^{13,14,15,16}. Chromate pretreatments provide exhibit excellent adhesion and corrosion protection, however research had begun more than a decade ago to replace chromate pretreatments as they are carcinogenic and have been banned in several places such as in the defense arena and in Europe. Several alternatives to chromates have been investigated, some of them are molybdates², rare earth metals such as Ce¹⁷, acids of Ti and Zr¹⁸, silanes^{19, 20, 21} and polymer based film forming treatments⁷. Organofunctional silanes pretreatments have performed equivalently compared to chromates and are seen as replacement to chromating²¹.

1.3.2 Silanes

Silanes have been used as an adhesive agent in several applications²². Silanes can be used to bind organic materials to inorganic substrates such as metals and glasses, silanes are used in a wide range of applications, performing a variety of functions including adhesion promotion and crosslinking. They are used in paints, adhesives, inks, polishers, dyes, sealant primers etc. Silanes tend to improve the electrochemical and mechanical properties of the films they form²³.

Silanes are monomeric silicon compounds with four substituent groups attached to the silicon atom. These substituent groups can be nearly any combination of nonreactive, inorganically reactive, or organically reactive groups. They are represented generically in the following way –

The general formula for a silane coupling agent typically shows the two classes of functionality. X is a hydrolyzable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Alkali metal oxides and carbonates do not form stable bonds with Si-O-. The R group is a nonhydrolyzable organic radical that may possess a functionality that imparts desired characteristics²⁴. Based on this mechanism silanes have been used as adhesion promoters for several years. This mechanism was studied in a metal pretreatment application. Silanes were first studied as corrosion protection agents by Van Ooij et al.^{25, 26, 27}. They showed silane pretreatments protected metals, especially aluminum and steel, against uniform, galvanic, pitting, crevice and stress corrosion. They also proved that silane pretreatments performed equal to chromates in terms of corrosion protection and paint adhesion. It was found by Van Ooij et al. that bis-type organofunctional silanes, such as bis-(3-triethoxysilylpropyl) tetrasulfide, which have two silicon atoms in its molecule, provided better corrosion inhibition performance on a wide range of metals and alloys as

compared with mono-silanes. The improved corrosion inhibition performance was attributed to the fact that the bis-silanes formed denser films. The bis-silanes, especially bis-sulfur silane, provide excellent adhesion of coatings to metal substrates and better corrosion protection under severe corrosive conditions such as seawater immersion tests and the corrosion behavior was found to be comparable to chromates^{25, 26, 27}. The hydrolysis of silanes is an important step in the pretreatment of metals. The figure below shows the mechanism by which silane hydrolyses and condenses to form covalent bond with the substrate.

B. Arslan, CHEMTECH, 7, 766, 1977

The hydrolyzed silane containing silanol groups is deposited by simply dipping the metal in a silanol bath or by electrodeposition²⁸. Upon drying two key condensation

reactions take place in the metal/silane interfacial region. SiOH groups from silane and MeOH groups from the metal covalent metallo-siloxane bonds (SiOMe).

The excess silanol groups would condense among themselves to form siloxane groups.

1.3.3 Priming of metals

A primer is a paint formulated to be applied to a substrate before any other paint is applied. Sometimes only primer is the only layer applied on the substrate, but often another layer – top coat – is applied over the primer. The major function of primers is to provide lasting adhesion of subsequent paint layers. Primers also protect the substrate from weathering and corrosion²⁹. The primer is designed to strongly adhere to the substrate and to provide a surface to which the top coat will adhere well. Usually primers need not be resistant to UV; however, if the top coat does not give complete hiding, UV can penetrate to the primer/top coat interface and may lead to degradation and loss of intercoat adhesion. Incorporation of UV absorber can minimize the problem. Primers also carry inhibitors, pigments and nanoparticles to strengthen self-healing, mechanical and adhesive properties^{30, 31, 32}. In designing primers for steel, saponification resistance is an important criterion; in the case of galvanized steel it is critical³¹. If the metal is not phosphate treated shortly before coatings, the binder in the primer must be very resistant to saponification. Thus choice of binders becomes important. There are several binders

used and their use is dictated by cost and needs. The binders in a large fraction of all primers used on metal substrates are bis-phenol A type (BPA) epoxy resins and their derivatives. Experience has shown that BPA epoxy resin-based coatings exhibit superior adhesion (31). For applications where moderate resistance properties are adequate, alkyd resins are used because of their lower cost. Polyesters, acrylics, urethanes, silicones and fluorinated resins are some examples of binders that are frequently used in primer coatings. Primers are dissolved in either organic solvents or water; water-based primer coatings are more popular because they are environment-friendly. Alternatively, high-solids low-VOC coatings are also used. However in certain applications solvent-borne primers are still used. In this thesis, a solvent-borne, BPA epoxy resin-based, high temperature cured primer system is studied.

1.3.4 BPA Epoxy resin

The most common epoxy resins are glycidyl ethers of alcohols or phenolics. Liquid epoxy resin is the diglycidyl ether of bisphenol A (DGEBA) and represents greater than 75% of the resin used in industrial applications. They find applications in protective coatings, adhesives, electrical laminates, reinforced plastics and commercial flooring systems bearing testimony to the versatility and high performance characteristics of these materials³³. Epoxy resins are the reaction products that result when epichlorohydrin is reacted with bisphenol-A. For the coating to form a cured, useful film, the epoxy resin must be further reacted with another resin.

The figure below shows the idealized chemical structure of a typical DGEBA epoxy resin monomer –

A typical DGEBA epoxy resin polymer is shown below –

The unique features of an epoxy resin are due to epoxy groups in the molecule as well as reactive (OH) groups³⁴. The curing of an epoxy resin system normally takes place in stages. The first of these is the combining of the two reactive materials - the epoxy resin and the curing agent. Normally, these two components are kept apart until reaction is desired. The resin is normally a viscous liquid and the curing agent may be a liquid or a low-melting solid. When combined and a catalyst and heat are added, the resin and curing agent react with a release of additional heat. Reactive epoxy systems always release heat when curing, thus, they are classified as exothermic reactions. The exothermic heat acts to increase the speed of reaction. This second stage of reaction results in formation of linear chains of combined epoxy resin and curing agent. As the linear chains form, the material is still in a liquid form but viscosity is increasing rapidly. Heat and catalyst promote further reaction. The linear polymer chains are combined through chemical

reactions in a cross-linking process to form a polymerized system approaching an extremely high molecular weight. During this third stage of reaction, the material changes from a viscous liquid to a solid gel³⁵. Epoxide ring opening reactions are widely used in the coatings industry. Ring opening reactions lead to coatings with low shrinkage, which is especially important when the polymerization reaction is the final curing step in the coating process. Overall coating performance will depend on formulation and cure variables such as epoxide/OH mole ratio, catalyst level, cure time/temperature, polyol and epoxide functionality³⁶.

1.3.5 Epoxy Curing Agents

The chemical chosen to react with the epoxides is referred to as the curing agent (or hardener), and it typically has active hydrogen attached to nitrogen, oxygen, or sulfur. The selection of the curing agent depends on many parameters and will determine, to a large extent, the performance of the final epoxy thermoset. Amine curing agents are the most common and can be primary or secondary, aliphatic or aromatic, or cycloaliphatic. The amines typically have three reactive sites per molecule that facilitate the formation of a three-dimensional polymer network when mixed with the epoxy resin. Traditional aliphatic polyamines such as diethylenetriamine, triethylenetetramine and other aliphatic hydrocarbon-based amines have been used for ambient-cure temperature epoxy resin systems in applications such as civil engineering, adhesives and architectural and maintenance coatings^{37,38}. Unmodified polyamines tend to absorb moisture and carbon dioxide from the air, resulting in reduced coating performance. Cycloaliphatic diamines such as isophoronediamine, bis-p-aminocyclohexylmethane and 1,2-diaminocyclohexane are used as epoxy resin curing agents for both ambient and heat-cure epoxy resin

systems. While they have advantages as epoxy resin hardeners (light colors and good chemical resistance), they have the disadvantage of slow cure at low temperatures. Aromatic diamines such as diaminodiphenylmethane (MDA) have been used as heat or ambient-curing hardeners after chemical modification.

In addition to the above types of curing agents there are also non-amine based curing agents. Either aromatic or aliphatic isocyanates may also be used as curing agents for epoxy resins. The isocyanates react through the hydroxyl groups of the epoxy resin and provide very good low temperature curing, good flexibility, good impact and abrasion resistance as well as good adhesion³⁹. Epoxy resins contain secondary hydroxyl groups as reactive groups only or secondary hydroxyl plus amine. The isocyanate diffuses into the epoxy resin forming an interphase with a thickness of some micrometers. Depending on the functional groups available in the epoxy resin, urethane and urea groups are formed in the interphase⁴⁰.

1.3.6 Epoxy resin and silane mixture

The outstanding properties of epoxy resins- toughness, rigidity, elevated temperature performance, chemical resistance and adhesive properties have enabled their acceptance in a wide range of critical electronic, optical and aerospace applications. Silicon-based materials play key roles in extending the range of physical properties of conventional epoxy resin systems enabling acceptance in applications with challenging requirements²⁴. Generally, amino silanes and epoxy resins react in systems such as glass/polymer²². However, in certain cases in an interphase between epoxy resin and silane, there is little or no reaction as the silane molecules are entrapped due to their

adsorption⁴¹. Epoxy absorbs moisture easily, and the diffusion of absorbed water into the epoxy–steel interface weakens the interfacial adhesion strength between epoxy and steel, particularly in wet conditions⁴². To overcome this problem, silane coupling agents have been used in combination with epoxy resin⁴³. Silanes reduce epoxy primer shrinkage and also provide enhanced adhesion to the substrate as it has hydrolysable groups. So far only Jang et al. have used silanes and epoxy resins together in a primer system. They were mono-silanes which were non-hydrolyzed. In their system the reaction between epoxy resin and silane used the reacting groups of silane and left no functionalities in the silanes. This will not help in improving the adhesion of the primer as the silane will not be able to hydrolyze and condense.

In order for an epoxy primer system to be enhanced, in terms of adhesion and corrosion protection, silanes can be incorporated. Adding silanes in an epoxy primer system will be effective only when the epoxy resin does not react and use up all of the hydrolyzable functionalities in the silane. If this objective is achieved a primer system consisting of a mixture of epoxy and silane will yield good performance results. This thesis details such a study.

1.4 Objective of thesis

This thesis details the development and study of a primer system which will incorporate properties of silanes and epoxy resins in one layer and whose adhesion is good even without a pretreatment applied and whose corrosion protection is comparable to commercial primers. The primer system consists of epoxy resin, an isocyanate curing agent and silanes and applied to hot-dip galvanized steel. Hot-dip galvanized steel is

chosen as this coating has to ultimately be used in automotive coils made of HDG in automobiles. The thesis aims to show that the incorporation of silanes in an epoxy primer system is unique in terms of the form of silanes used. Organofunctional bis-silanes are used, both in hydrolyzed and non-hydrolyzed forms. The combination of hydrolyzed and non-hydrolyzed silanes is shown to be unique and effective in terms of performance.

The goal of this thesis project is to obtain a primer system that –

- Is devoid of toxic chemicals such as chromates
- Uses minimal amount of silanes
- Uses silanes in a way that the hydrolysable groups are shown to hydrolyze and condense rather than react with the epoxy resin groups
- Exhibits excellent adhesion and corrosion protection
- Does not need pretreatment of metal

The thesis also attempts to determine the mechanism of the primer system.

2. Experimental

The primary objective of the experiments was to establish that a single coating system applied directly to metal, without pretreatment and without use of carcinogenic chemicals such as chromates, performed optimally in terms of corrosion-protection and adhesion to metal. The following write-up describes materials used for the coating system, the surface preparation methods, testing methods used to evaluate performance and finally characterization techniques used for mechanistic studies.

2.1 Materials

2.1.1 Resin and curing agent

The coating system is an integral primer which comprises a mixture of diglycidyl ether of bisphenol A (DGEBA) resin, a polyisocyanate-blocked curing agent, a tin catalyst, a hydrolyzed bis-amino silane and optionally a hydrophobic silane such as bis-sulfur silane.

The resin is an epoxy resin of the following generic structure –

The epoxy resin was obtained from the sponsor of the project. The polyisocyanate-blocked hexamethylene diisocyanate curing agent used was a commercially available as DESMODUR VP LS 2253 made by Bayer AG. Since it is blocked in room temperature, the curing agent does not react, the resin and curing agent need to be cured at elevated temperature for the crosslinking to take place. Both the epoxy resin and curing agent are

solvent-based, the solvent predominantly used to dissolve the resin and curing agent was n-butoxy ethanol.

2.1.2 Silanes

Silanes represented by the following formulae were used – $\text{Si}(\text{OX})_4$, $\text{Y-Si}(\text{OX})_3$ wherein X and Y represent alkyl groups. Bis-functional silanes of the following formula were used: $(\text{R}^1\text{O})_3\text{Si}(\text{R}^2)_n\text{Y}(\text{R}^3)_n\text{Si}(\text{OR}^4)_3$ wherein each R^1 , R^2 , R^3 , and R^4 , independently or simultaneously, may be a linear or branched alkyl radical or alkenyl radical and Y can be a functional group such as amine or sulfur. Specifically, the following two silanes were used –

1. Bis-amino silane: $(\text{H}_3\text{CO})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ trade name – A1170
2. Bis-sulfur silane: $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{S}_4(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ trade name – A1289

Bis-amino silane was used in a hydrolyzed form and bis-sulfur silane was used hydrolyzed and non-hydrolyzed forms. Since bis-amino is very hydrophilic it formed Si-OH which was needed for adhesion. Bis-sulfur silane was used without hydrolysis as it was hydrophobic and was allowed to hydrolyze in the film coated on metal, in some cases bis-sulfur silane was also hydrolyzed. Both bis-amino silane and bis-sulfur silane were obtained from GE Silicones.

2.1.3 Metal

Hot dip galvanized (HDG) steel was used as this is the metal used in automotive applications. The ultimate application of the coating developed from this project was

galvanized steel automotive coils used in automobiles. The panels were obtained from Metaspec, San Antonio, TX.

2.1.4 Catalyst

Any catalyst that catalyzes the reaction between curing agent and resin is suitable, in particular tin organic catalysts. Di-butyl tin dilaurate (DBTDL) having the formula $C_{32}H_{64}O_4Sn$ was used. This tin catalyst is commercially available from Sigma-Aldrich Inc. This is used very sparingly, about 0.5 weight percent or less of the coating system.

2.2 Metal surface preparation

Metal surface preparation is a very important step as the coating prepared has to wet the metal completely. Improper wetting will lead to delamination of the coating; wetting can be achieved by ridding the metal surface of dust and oil that are deposited during the metals' manufacture.

All metals were ultrasonically cleaned with acetone and ethanol, sequentially for 5 minutes each. After solvent cleaning, alkaline cleaning was done using an alkaline cleaner from Henkel. Alkaline cleaner is a 7% vol. KOH or NaOH in water. The temperature of the alkaline cleaner bath was maintained between 65°-70°C and the metal substrate was dipped in the cleaner for 4-5 minutes. Immediately after that, the metal was cleaned in a stream of de-ionized water to remove the residues of the alkaline cleaner, followed by drying the metal with blown air. The metal was tested for a "water break-free" surface using the DI water stream, if the water wetted the metal surface completely without breaks appearing in the surface, then the surface was considered clean.

2.3 Integral Primer Preparation and Surface Treatment

The integral silane-primer was prepared in three steps. First, the primer was prepared by mixing the epoxy resin (81.9 wt. %), curing agent (17.5 wt. %), catalyst (0.6 wt. %) (Composition A). Second, the silanes were prepared. The bis-amino silane was hydrolyzed by mixing 6.8 ml BIS-AMINO SILANE, 84.3 ml ethanol, 1.9 ml acetic acid and 6.8 ml H₂O. The bis sulfur silane was used either neat or in a hydrolyzed form. The hydrolyzed bis sulfur silane was prepared by mixing 6.8 ml BIS-SULFUR SILANE, 84.3 ml ethanol, 1.96 ml acetic acid, and 6.8 ml H₂O. Third, the primer and silanes were mixed to obtain a homogeneous solvent-based mixture, the integral primer, as shown in Table 2.1. The integral primer was immediately applied on the cleaned metal surface using a draw-down bar to obtain a uniform coating. The fresh coating was cured in an oven at 140 °C for 20 min.

As a control, a test panel was made comprising a silane-based pretreatment and an epoxy primer. The pretreatment solution was prepared by first mixing neat BIS-AMINO SILANE and neat vinyl triacetoxysilane(VTAS) in the weight ratio of 5:1. This mixture was hydrolyzed by mixing 5 ml of the 5:1 BIS-AMINO SILANE/VTAS solution, 95 ml water and 0.5 ml of acetic acid. This mixture was allowed to hydrolyze for a minimum of two hours. A cleaned hot-dipped galvanized steel panel was dipped in to the pretreatment bath (immersion time) and cured at 100 °C for 5 mins.

2.4 Characterization

2.4.1 Nuclear Magnetic Resonance Spectroscopy

The NMR phenomenon is based on the fact that nuclei of atoms have magnetic properties that can be utilized to yield chemical information. Quantum mechanically subatomic particles (protons, neutrons and electrons) have spin. In some atoms (eg ^{12}C , ^{16}O , ^{32}S) these spins are paired and cancel each other out so that the nucleus of the atom has no overall spin. However, in many atoms (^1H , ^{13}C , ^{31}P , ^{15}N , ^{19}F etc) the nucleus does possess an overall spin. If the number of neutrons and the number of protons are both even, the nucleus has no spin. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. $1/2$, $3/2$, $5/2$). 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). In a magnetic field, spinning nuclei have lower energy when aligned with the field than when opposed to it because they behave like magnets. This energy difference corresponds to radio frequencies hence the nuclei are able to absorb and reemit radio waves.

The precise resonant frequency is dependent on the effective magnetic field at the nucleus that is affected by electron shielding which is in turn dependent on the chemical environment. This frequency dependence is called as chemical shift. In general, the more electropositive the nucleus, the larger its chemical shift. Chemical shift is proportional to the magnetic field strength so it is measured as a ratio of frequencies, usually in parts per million (ppm). The effective magnetic field is also affected by the orientation of neighboring nuclei. This effect is known as spin-spin coupling which can cause splitting of the signal for each type of nucleus into two or more lines. The size of the splitting is

independent of the magnetic field and is therefore measured as an absolute frequency (usually Hertz). The number of splitting indicates the number of chemically bonded nuclei in the vicinity of the observed nucleus. Basically NMR spectrometer consists of the following components:

- An intense, homogeneous and stable magnetic field.
- A “probe” which enables the coils used to excite and detect the signal to be placed close to the sample.
- A high-power RF transmitter capable of delivering short pulses.
- A sensitive receiver to amplify the NMR signals.
- A digitizer to convert the NMR signals into a form which can be stored in computer memory.
- A “pulse programmer” to produce precisely times pulses and delays.
- A computer to control everything and to process the data.

A detailed description of this technique is beyond the scope of this thesis.

NMR equipments in Chemistry Department, Oklahoma State University were used. ^{29}Si NMR spectra were recorded on a Varian Inova 600 MHz spectrometer using a Varian broadband probe. Spectra were collected with a one pulse experiment using a 9 ms pulse width with a 30 seconds pulse delay and 472 scans. All chemical shifts were referenced to TMS. In order to observe the silane hydrolysis reaction as a function of

time, spectra were collected with a 2 hour delay between data acquisition. ^{13}C NMR was also used for analysis. The film was scrapped from the metal using a sharp knife and crushed to fine powder. This powder was dissolved in deuterated chloroform. Silanes in pure and hydrolyzed forms were also analyzed. For ^1H -NMR experiments, Bruker AMX 400 instrument in Chemistry Department, University of Cincinnati was used for the analysis and the number of scans for each sample was 8.

2.4.2 Infra-red Spectroscopy

Principle of Infrared Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with a chemical substance. The nature of the interaction depends upon the properties of the substance. When radiation passes through a sample (solid, liquid or gas), certain frequencies of the radiation are absorbed by the molecules of the substance leading to the molecular vibrations. The frequencies of absorbed radiation are unique for each molecule which provide the characteristics of a substance. The electromagnetic spectrum covers an immense range of wavelengths. Fig. 2.1a shows schematic of interaction of radiation with matter. The infrared regions are classified as follows:

- Near Infrared 12500 to 4000 cm^{-1} (0.8 to 2.5 μm)
- Mid Infrared 4000 to 200 cm^{-1} (2.5 to 50 μm)
- Far Infrared 200 to 12.5 cm^{-1} (50 to 800 μm)

Instrumentation

The basic components of an infrared spectrometer are shown in block diagram form on Fig. 2.1b. The system consists of an interferometer, a computer, a data station, and a

printer and/or plotter for data output. With an infrared data station, the computer acquires, processes, stores and retrieves spectral data. Many commercial software packages including spectral enhancement, quantitation and searching are available for infrared spectroscopy.

The pure and hydrolyzed silanes and epoxy resin were analyzed using Biorad FTS-40 equipment in the transmission mode (resolution 8cm^{-1}). The samples were prepared using potassium bromide pellets. The spectra of epoxy resin, curing agent and silanes were taken individually and also in mixtures to observe the changes in chemistry. The pellet was also used to prepare samples obtained from dry films in powder form.

The dry film of the silane-primer was formed on a cleaned Hot-Dip Galvanized steel substrate and analyzed with the reflection IR (RAIR) set-up of the Biorad equipment. The number of scans for all cases was 100. Attenuated Total Reflection Infrared (ATR-IR) spectroscopy was also used for the dry films as it is suitable for characterization of materials which are either too thick or too strong absorbing to be analyzed by transmission spectroscopy. For the bulk material or thick film, no sample preparation is required for ATR analysis.

2.4.3 Electrochemical Impedance Spectroscopy

EIS has been successfully applied to the study of corrosion systems for thirty years and been proven to be a powerful and accurate method for measuring corrosion rates. An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal, usually a voltage

between 5 to 50 mV, is applied to a specimen over a range of frequencies of 0.001 Hz to 100,000 Hz. The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system.

Electrochemical impedance theory is a well-developed branch of ac theory that describes the response of a circuit to an alternating current or voltage as a function of frequency. The mathematics of the theory is beyond the scope of this discussion, but we will present the basic theory here. In dc theory (a special case of ac theory where the frequency equals 0 Hz) resistance is defined by Ohm's Law: $E = I R$ (1). Using Ohm's law, you can apply a dc *potential* (E) to a circuit, measure the resulting current (I), and compute the *resistance* (R) - or determine any term of the equation if the other two are known. Potential values are measured in *volts* (V), current in *amperes or amps* (A), and resistance in *ohms* (Ω). A *resistor* is the only element that impedes the flow of electrons in a dc circuit. In ac theory, where the frequency is non-zero, the analogous equation is: $E = I Z$ (2). As in Equation 1, E and I are here defined as *potential* and *current*, respectively. Z is defined as impedance, the ac equivalent of resistance. Impedance values are also measured in *ohms* (Ω). In addition to resistors, *capacitors and inductors* impede the flow of electrons in ac circuits. In an electrochemical cell, slow electrode kinetics, slow preceding chemical reactions, and diffusion can all impede electron flow, and can be considered analogous to the resistors, capacitors, and inductors that impede the flow of electrons in an ac circuit. Fig. 2.2a shows a typical plot of a voltage sine wave (E) applied across a given circuit and the resultant ac current waveform (I). Note that the two traces are different not only in amplitude, but are also shifted in time. with respect to each other - that is, they are out of phase. In the case of a purely resistive network, the

two waveforms would not be shifted. They would be exactly in phase, differing only in amplitude. The current sine wave can be described by the equation: $i(t) = A \sin(\omega t + 0)$ (3) where $i(t)$ = instantaneous current A = maximum amplitude ω = frequency in radians per second $= 2\pi f$ (where f = frequency in Hertz) t = time ϕ = phase shift in radians.

Figure 2.2b shows a Bode Plot. The Bode plot format lets one examine the absolute impedance, $|Z|$ and the phase shift of the impedance, each as a function of frequency. Since frequency appears as one of the axes, it is easy to understand from the plot how the impedance depends on the frequency. The plot uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The Bode plot also shows the magnitude ($|Z|$) on a log axis so that one can easily plot wide impedance ranges on the same set of axes. This can be an advantage when the impedance depends strongly on the frequency, as is the case with a capacitor. In general, the Bode plot provides a clear description of the electrochemical system's frequency-dependent behavior.

In this project, EIS curves were measured by software which collects signals from an apparatus containing a cell made of calomel and graphite electrodes, salt solution as electrolyte and the coating as dielectric and a potentiostat. The set-up is shown in Fig. 2.3. EIS measurements were carried out using a frequency response analyzer connected to a Gamry potentiostat. The measured frequency range was from 10^{-2} to 10^5 Hz, with AC excitation amplitude of 10 mV. A saturated calomel electrode was used as the reference electrode; a graphite rod was used as the counter electrode. The distance between the electrodes and the tested area was around 6 cm.

2.4.4 Contact Angle Measurements

One way to quantify a liquid's surface wetting characteristics on a coating surface is to measure the contact angle of a drop of liquid placed on the coating surface. The contact angle is the angle formed by the coating/liquid interface and the liquid/vapor interface measured from the side of the liquid. Wetting ability of a liquid is a function of the surface energies of the solid-gas interface, the liquid-gas interface, and the solid-liquid interface. The surface energy across an interface or the surface tension at the interface is a measure of the energy required to form a unit area of new surface at the interface. The intermolecular bonds or cohesive forces between the molecules of a liquid cause surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material (or the desire to create adhesive bonds) will tend to spread over the second material. Liquids with strong cohesive bonds and weaker adhesive forces will tend to bead-up or form a droplet when in contact with the second material.

To determine the hydrophobic or hydrophilic nature of the coated surface deionized water droplet coming out of a syringe was used to wet the coating surface. The contact angle obtained was used in comparative analysis and the coating surface was thus characterized. Higher contact angles indicate higher hydrophobicity of the coating.

Contact angle measurements were performed on a contact angle analyzer VCA2000 manufactured by AST Products, Inc Billerica, MA. Water was used on coated

panels. Contact angle measurements were obtained from the software given by the manufacturer.

2.5 Mechanical Tests

2.5.1 Salt Immersion

This is a simple laboratory test. Coated panels are scribed and taped at the edges and immersed in 3.5wt-% sodium chloride solution in glass jars and periodically pumped for ensure oxygen supply, this is done for three to four weeks and corrosion performance of the coating is checked.

2.5.2 Salt Spray Test

This test (ASTM B117) was used to evaluate bare corrosion protection of metal panels coated with primers and 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°C in the chamber, exposing the panel to salt fog for a certain length of time.

2.5.3 Adhesion Test

Crosscut adhesion tape test (ASTM D3359) was used to assess the adhesion of coated films to metallic substrates. A cutting tool device such as SiC tip having a cutting edge angle between 15° and 30° was chosen. 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 2.5cm 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. In the wet adhesion test, the scribes were immersed in deionized water for 48 hours and then thoroughly dried and then the tape was stuck on the scribes and ripped off. The number of squares in the scribe where the paint has been scrapped off determines the classification mentioned in the ASTM test. Figure 2.4 shows the amount of flaking for each classification.

3. Results and Discussion

3.1 Coating Systems Investigated

The corrosion resistance properties of four coating systems were investigated. Coating A, used as a control, comprised a commercially-available DGEBA epoxy resin coating used in conjunction with a silane-based pretreatment. Coating B was prepared by adding hydrolyzed bis-amino silane to coating A. Coating C was prepared by adding hydrolyzed bis-amino silane and hydrolyzed bis-sulfur silane to coating A. Coating D, was prepared by adding hydrolyzed bis-amino silane and non-hydrolyzed bis-sulfur silane to coating A. Coatings B, C, and D incorporate the silane directly into the epoxy resin system; this preparation method is in contrast with coating A, which uses the silane as a pretreatment.

3.2 Corrosion Resistance and Adhesion results

Figure 3.1 shows the results of 336 hour salt spray testing for the investigated coatings. The control coating A exhibited moderate corrosion resistance and adhesion, as evidenced by localized pitting on the face of the test coupon and corrosion product in the scribe. The addition of hydrolyzed bis-amino silane produced an increase in corrosion resistance, as evidenced by a slight reduction in the amount of pitting observed on the test panel. A further enhancement in corrosion resistance was observed upon incorporation of both hydrolyzed bis-amino silane and hydrolyzed BIS-SULFUR SILANE. The addition of hydrolyzed BIS-AMINO SILANE and non-hydrolyzed BIS-SULFUR SILANE produced the coating exhibiting the best corrosion resistance properties of those

investigated. Very little pitting or corrosion was observed on the face of the test panel and no corrosion product was observed in the scribe.

Electrochemical impedance (EIS) results as a function of time for the investigated coatings are shown in Figure 3.2. Pore resistance values for the coatings as a function of time are shown in Figure 3.4. For the control panel A, the pore resistance was found to decrease with time. Initially, the coating exhibited one resistance plateau, indicating a homogeneous coating. With time, the pore resistance of the coating decreased and a tail at very low frequency was observed, indicating a second resistance plateau out of the applied frequency range. The pore resistance was found to decrease from approximately 17 k Ω to 4 Ω as the immersion time increased from 2 to 10 days. These results clearly show the degradation of the protective properties of the control coating with time.

Figure 3.3 shows EIS results for the silane-modified coatings as a function of time. The impedance of each of the three silane-modified coatings was not found to significantly decrease during the exposure period. Coating B, containing hydrolyzed BIS-AMINO SILANE, showed pore resistance values on the order of those for the control coating, though the coating did not show significant degradation during the exposure period. Specifically, pore resistance values of approximately 26 and 36 k Ω were observed after 2 days and 3 weeks, respectively. The properties of this coating have not deteriorated significantly, indicating an enhancement in corrosion resistance properties afforded by introduction of the hydrolyzed BIS-AMINO SILANE. Similar results were obtained for coating C, though the magnitude of the pore resistance for this coating was higher, 42 k Ω , than for coating B. For coatings containing the hydrolyzed

silane, the pore resistance values remained relatively constant or slightly increased with immersion time, in contrast to the behavior of the control coating.

The addition of non-hydrolyzed BIS-SULFUR SILANE, coating D, produced a significant increase in pore resistance of the coating as compared to the control or the coating modified with hydrolyzed BIS-AMINO SILANE only or the hydrolyzed BIS-AMINO SILANE/hydrolyzed BIS-SULFUR SILANE combination. This effect is presumably due to the hydrophobicity of the BIS-SULFUR SILANE silane concentration in the coating, as coatings Band D exhibited contact angles of 61 and 85 respectively. After 2 days, a pore resistance value of 154 k Ω was observed for coating D, as compared with 26 k Ω for coating B. In contrast to the control coating, the pore resistance of coating D increased during the exposure period; after 3 weeks immersion, the pore resistance of the coating was approximately 217 k Ω .

The adhesion properties of the integral primers with the hot-dipped galvanized steel substrates were analyzed using a 2 hour deionized (DI) boiling water adhesion test. For this test, a polyester topcoat was applied to the integral coatings B, C, and D. The test coupons were scribed and immersed in boiling water for 2 hours. Subsequently, adhesion properties were analyzed using the tape test in accordance with ASTM D3359 specifications. Integral coatings B, C, and D all exhibited a classification of 5, indicating that the addition of silane enhanced adhesion properties, as compared to the topcoat used without an integral primer coating, which delaminated during the boiling water immersion.

In order to investigate the compatibility and performance of the integral primer coatings with a commercial topcoat, a 2000 hour salt spray test was performed. For this

test, a polyester topcoat was applied to a commercial primer or coatings B, C, and D. Results are shown in Figure 3.5. For each of the coatings investigated, good compatibility between the integral primer and the polyester coating was observed, as evidenced by the absence of blistering or delamination of the topcoat. Small amounts of corrosion product were observed in the scribe, though this is expected as the coatings investigated did not contain active corrosion inhibitors.

In this study, a commercially-available epoxy resin coating system was modified using (a) hydrolyzed silanes or (b) a combination of hydrolyzed and non-hydrolyzed silanes. The corrosion resistance properties of the investigated coatings increased coating A (control) < coatings B (hydrolyzed BIS-AMINO SILANE) < coating C (hydrolyzed BIS-AMINO SILANE/hydrolyzed BIS-SULFUR SILANE) < coating D (hydrolyzed BIS-AMINO SILANE/non-hydrolyzed BIS-SULFUR SILANE). While both classes of additives were found to produce an enhancement in corrosion resistance of the hot-dipped galvanized steel substrate, the combination of hydrolyzed and non-hydrolyzed silanes produced the most significant improvement in corrosion resistance.

Addition of hydrolyzed silanes to the resin system was shown to increase coating adhesion and is expected to increase coating density. The rapid hydrolysis and condensation of the silanes forms a dense, polysiloxane network, and thereby increasing coating density. The presence of reactive silanol groups are expected to increase coating adhesion, through promotion of condensation reactions between the silane and the underlying zinc substrate.

In addition to increasing coating density and adhesion, the addition of non-hydrolyzed BIS-SULFUR SILANE was found to increase coating hydrophobicity, as

evidenced by the increase in contact angle from approximately 61 to 85 °. The BIS-SULFUR SILANE is slow to hydrolyze in the absence of a catalyst, as compared to BIS-AMINO SILANE, providing an additional curing mechanism. As the coating containing the non-hydrolyzed BIS-SULFUR SILANE is exposed to atmospheric moisture, the BIS-SULFUR SILANE is capable of further hydrolysis and condensation reactions, leading to the formation of a secondary polysiloxane network. The silanol groups formed by the hydrolysis of the BIS-SULFUR SILANE are then able to react with either silanol groups from the BIS-AMINO SILANE or C-OH groups from the epoxy resin, thereby removing defects or areas of hydrophilicity in the base coating. These reactions, presumably, lead to the increase in pore resistance with time during the EIS analysis.

3.3 Summary of Performance Results: A typical coating system on hot-dipped galvanized steel consists of metal/pretreatment/primer/topcoat. Integral primers, using the best characteristics of silanes and the epoxy primer, have been shown to exhibit enhanced corrosion protection and adhesion to both metals and topcoat. The use of rapidly hydrolyzed and non-hydrolyzed silanes in combination with a commercial epoxy resin system has been found to produce a coating system with unique corrosion protection properties. The hydrolyzed silane addition was found to increase coating density and adhesion, eliminating the need for the use of a surface pretreatment or tie coat on hot-dipped galvanized steel. The non-hydrolyzed silane addition was found to enhance the hydrophobicity of the coating and provide a secondary curing mechanism, as evidenced by an increase in the impedance of the coating with time. The use of silanes

provides for improving the coatings' adhesion and corrosion performance improvement *without altering* the epoxy network's properties of chemical resistance, toughness etc.

3.4 Mechanism Study

3.4.1 ^{13}C and ^{29}Si NMR results

The coating system components were studied using carbon and silicon NMR techniques. The purpose of these experiments is to determine the mechanism by which the integral primer coatings functions. The goal is to determine if resin reacts with curing agent and/or silane. Four experiments were performed -

- NMR spectra of the pure resin and silanes
- NMR spectrum of the initial solution
- NMR of the solution after a period of time
- NMR of the cured film after it was heated at 140°C

The solution and cured film are that of coating type D. Table 3.1 shows individual components of coating D.

Pure Resin: Fig. 3.6 shows C-NMR spectrum of the DGEBA epoxy resin dissolved in n-butoxy ethanol that was used in the formulation of coating D. A representative structure is shown here.

With the exception of peaks at 158.6, 84, 50-60, and 22-24 ppm the spectrum appears to contain resonances due to DGEBA resin and butoxyethanol. It is notable, however, that the epoxide peaks at 50 and 44 ppm is absent. The unassigned peaks are assigned to an additive in the resin. DEPT spectra of the resin were collected to confirm peak assignments. The assignment of all peaks is shown in Table 3.2.

Coating D as a function of Stir Time (Figs. 3.7, 3.8): The solution of freshly prepared coating D was used for obtaining the initial spectrum in Fig. 3.7. After 43h another spectrum of the same solution was obtained (Fig. 3.8). The initial spectrum contains peaks due to the resin, the solvents, and the silanes. These peaks did not change during the reaction time. A small peak at 49.3 ppm due to methanol was observed, indicating partial hydrolysis of BIS-AMINO SILANE was taking place. This peak did not increase in intensity with time, indicating further hydrolysis reactions were not occurring. The

peaks at 58.7 and 18.5 ppm due to the ethoxy functionality on BIS-SULFUR SILANE were prominent in the initial spectrum and did not change significantly with time. The 68 ppm internal C-OH peak did not change significantly with time. *These observations indicate that the resin is not reactive with either the curing agent or the silanes even after stirring at room temperature for 43 hours.*

Solid State NMR Analysis of Powdered Cured Films: The coatings were cured at 140 °C, scraped off the panel and ground for analysis. Fig. 3.9 shows C-NMR of powdered cured film of coating D. Table 3.3 contains C-13 NMR peak assignments of powdered cured film. From Sankar et al ⁴⁴ it is determined that the peaks at 150.0 and 62.7 ppm are due to the urethane linkage.

Anticipated resin - polyisocyanate (curing agent) product

Immersion of Coating in water for 2 weeks: The ²⁹Si (Figs. 3.10 and 3.11) and ¹³C NMR (Fig. 3.12) spectra were recorded for coatings that had been immersed in water for 2 weeks. The immersion period is expected to promote hydrolysis reactions. A small decrease in the intensity of the 58.9 ppm peak was observed indicating additional hydrolysis takes place. Other spectral features remained constant.

Peak percentages for the ^{29}Si NMR spectra changed as follows:

Peak Position	Initial	Immersed
T^0	12.4	4.2
T^1	22.1	13.0
T^2	35.1	30.4
T^3	30.2	52.1

These results may account for the small changes observed in the ^{13}C NMR spectra and also indicate that the coating is susceptible to hydrolysis after curing.

3.4.2 ^1H -NMR Results

^1H -NMR experiments were carried out to determine the reaction mechanism of the epoxy resin. Protons attached to epoxy resin are seen in H-NMR spectrum and changes in the peak values of such protons are indicative of the chemical reaction taking place in the coating. The coating systems investigated was cured film powder of standard resin coating A (epoxy resin and curing agent), coating B (additionally containing hydrolyzed bis-amino silane) and coating D.

Fig. 3.13 shows the ^1H -NMR spectrum of the coating B containing epoxy resin, curing agent (polyisocyanate) and hydrolyzed bis-amino silane. The spectrum shows the same pattern of products as in the ^1H -NMR of Fig. 3.14 (epoxy and curing agent). However, here, hydrolyzed silane has been added. From the spectrum it is clear that the epoxy did react with the curing agent and not with the silane. The silane addition has not altered the reaction mechanism between epoxy resin and curing agent.

Fig. 3.15 shows the ^1H -NMR spectrum of coating D. The spectrum shows the characteristic peaks of coating B. The aromatic protons are present on either side of 7 ppm and the $-\text{CH}_2\text{O}-$ peak is shown at 3.7 ppm. The height ratio between these peaks

also remains the same. Therefore, since the protons of coating B were retained in this coating, the bis-sulfur silane has not really interfered with the reaction mechanism seen in the coating B. The new peaks at 3.8 ppm and 1.2 ppm show the protons belonging to $-\text{OCH}_2-$ and $-(\text{OCH}_2)\text{CH}_3$, respectively. Thus, the reacting group in bis-sulfur silane: $(\text{OC}_2\text{H}_5)_3\text{Si}-$ has not been affected while was still fresh (i.e. not immersed in water). Therefore, the silane was free to hydrolyze and condense resulting ultimately in enhanced corrosion protection due to the bis-sulfur silane.

3.4.3 Infra-red Spectroscopy

Fig. 3.16 shows the IR spectrum of the non-hydrolyzed bis-sulfur silane: $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{S}_4-(\text{CH}_2)_3-\text{Si}(\text{OC}_2\text{H}_5)_3$. The likely reacting group are the end groups $(\text{C}_2\text{H}_5\text{O})_3\text{Si}$. These can hydrolyze and form silanols ($\text{Si}-\text{OH}$) and further condense to form an $-\text{Si}-\text{O}-\text{Si}-$ network. However, there is no water in the coating for this reaction to occur. The other way for this reaction to occur is to absorb moisture from air, or absorb water when immersed in salt water. Another reaction possibility is the reaction between epoxy resin and bis-sulfur silane. The peak at 960 cm^{-1} is critical, it belongs to $\text{Si}-\text{O}$ asymmetric stretching of SiOC in $\text{Si}(\text{OC}_2\text{H}_5)_3$.

Fig. 3.17 shows the IR spectrum of coating D. All peaks characteristic of epoxy resin and bis-sulfur silane are seen. Therefore when the silane-incorporated primer had not yet been made in to a film on metal, there seemed to be no reaction of epoxy resin with either the curing agent or bis-sulfur silane.

Fig. 3.18 shows the IR spectrum of the coating D cured film on metal. Since the $\text{C}-\text{H}$ at 2973 cm^{-1} seen in the bis-sulfur IR was unaffected and more importantly because

of the presence of Si-O asymmetric stretching of SiOC in $\text{Si}(\text{OC}_2\text{H}_5)_3$ at 956cm^{-1} it was clear that bis-sulfur silane had not reacted. Accordingly, curing agent and epoxy resin formed a network and silane in the system formed another network.

3.5 Summary of characterization results: Initially the BIS-SULFUR SILANE does not react with the resin. The hydrolysis reaction appears to be facilitated by moisture after (or by humid air, etc during) curing. The BIS-AMINO SILANE does not appear to react with the resin either. The primary curing mechanism is through the isocyanate at elevated temperatures. Thus the coating film consists of two reaction products in interpenetrating networks – one, the polyol turned epoxy resin and polyisocyanate reaction product yielding polyurethane and two, silane hydrolysis and condensation yielding siloxanes. Fig. 3.19 shows the reactions taking place in the coating system. The epoxy resin becomes a polyol. This polyol reacts with isocyanate group to yield urethane. The ethoxy groups in bis-sulfur silane hydrolyse to form silanols which further condenses to form siloxane network.

The epoxy resin, curing agent and silane do not react at room temperature. However, prolonged aging leads to gelling which is attributed to crosslinking between sulfur in bis-sulfur silane and carbons in epoxy resin. At elevated temperatures the curing agent gets unblocked and reacts with the epoxy resin (which has OH groups). The OH groups in the epoxy resin and NCO groups in polyisocyanate react to form urethane product. This is formed as a network chain; the reaction is catalyzed by tin laurate. The silanes in the coating system starts to hydrolyze and forms silanols and further condenses to form –Si-O-Si- interpenetrating network and this bond is formed at the top surface and

also at the interface, the silanol and siloxane groups are responsible for the enhanced adhesion of the coating.

Thus it is clear that for enhanced corrosion protection of hot-dip galvanized steel and for good adhesion of the coating, the silane functionalities, which are used for hydrolysis and condensation after the primer is cured, should not react with the resin during preparation and application of the coating. Therefore, the curing agent and resin chosen were appropriate as polyisocyanate and epoxy resin react to form polyurethane network without interfering in the bis-sulfur silane hydrolysis and condensation even after the curing of the coating. This helps in the adhesion of the integral of the primer to the metal and topcoat as siloxanes forms covalent bonds with the oxides of the metal and alcohols of the topcoat.

4. Conclusions and scope for further research

A mixture of non-hydrolyzed bis-sulfur silane and hydrolyzed bis-amino silane incorporated in an epoxy resin-polyisocyanate primer system yielded enhanced performance on hot-dip galvanized steel. Based on EIS and adhesion tests it was observed that the silanes increased the impedance and hydrophobicity of the coating system. The standard resin coating without silanes showed a decreasing impedance trend over a period. It also showed poor adhesion results as the coating peeled off in the salt spray test. However, the silane-incorporated primer systems showed increasing impedance trends over a period. It also displayed good corrosion protection in salt spray testing. The adhesion of the silane-incorporated primer to the metal and to the topcoat was comparable to adhesion levels of commercial primers.

The liquid state NMR analysis showed that the epoxy resin-blocked polyisocyanate in n-butoxy ethanol does not react with the silanes incorporated. The solid state ^{13}C and ^{29}Si solid state analysis showed that the silanes undergo hydrolysis and condensation after curing of the coating. ^1H -NMR and IR analysis showed that bis-sulfur silane remained unaffected in the cured film. This is the reason the coating shows enhanced corrosion protection and adhesion as the silane functionalities start reacting to moisture after the cure of the coating.

In summary, based on the results presented, the following conclusions can be drawn:

- a) The use of silanes increases corrosion protection and adhesive properties of the epoxy primer. Silane-based coatings lasted one week more than coatings with no silane in salt spray tests.
- b) A mixture on hydrolyzed and non-hydrolyzed silanes was found to provide the coating with the best adhesion and corrosion protective properties (as compared to coating systems made of a) epoxy primer with no silane, b) hydrolyzed silane and epoxy primer and c) non-hydrolyzed silane and epoxy primer). The coating containing mixture of hydrolyzed and non-hydrolyzed silanes lasted full two weeks in salt spray tests and had absolutely no peel-off in adhesion tests.
- c) The use of silane in the epoxy primer eliminates the need for adhesion-promoting pretreatments.
- d) The coating system developed eliminates the need for chromate corrosion inhibitors.
- e) Use of hydrolyzed silanes is cost-effective as their use is 95% by volume lesser in coating systems compared to non-hydrolyzed silanes.
- f) The silanes in the coating system are shown to hydrolyze and condense rather than react with the epoxy resin groups.

There is scope for further research in mechanistic study of the interface between substrate and coating system. ToFSIMS could be used to determine the exact nature of covalent bonds that are formed and determine the chemistry of the metal-silane interface. Water-based coating systems based on the principle of preserving silane functionalities during curing process should also be investigated. Phase separations in organic coatings

occur when mixture of polymers is used and the mechanisms involving them are worthy of further research initiatives.

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Table 2.1: Preparation of integral primers.

Composition	n-butoxy ethanol (wt %)	Standard Primer (wt.%)	Hydrolyzed BIS-AMINO SILANE (wt.%)	Neat BIS- SULFUR SILANE (wt%)	Hydrolyzed BIS- SULFUR SILANE (wt%)
A	50.0	50.0	---	---	---
B	53.4	36.1	10.5	---	---
C	48.0	32.5	9.5	---	10
D	48.0	32.5	9.5	10	---

Table 3.1: Components comprising coating D used in NMR analysis

Component	Purpose	Comment
DGEBA epoxy resin	Resin	Butoxyethanol solvent
Polyisocyanate	Curing Agent	Blocked
Dibutyltindilaurate	catalyst	---
BIS-SULFUR SILANE	Silane	Non-hydrolyzed
BIS-AMINO SILANE	Silane	Hydrolyzed
Ethanol	Solvent	---
H ₂ O	Hydrolysis	---

Table 3.2: C-13 NMR peak assignments of standard resin

Peak Position	Component	DEPT	Assignment
158.6	Additive	---	---
157.0	Resin	Not observed	Quaternary phenyl ring C
143.3	Resin	Not observed	Quaternary phenyl ring C
127.9	Resin	C-H	Phenyl ring C
114.3	Resin	C-H	Phenyl ring C
84.0	Additive	---	---
72.3	Butoxyethanol	CH ₂	C-O-C Butoxyethanol
71.0	Butoxyethanol	CH ₂	C-O-C Butoxyethanol
69.5	Resin C-O-C	CH ₂	Internal C-O-C
68	Resin C-OH	CH	Internal C-OH
61.5	Butoxyethanol	CH ₂	CH ₂ OH Butoxyethanol
50-60	Additive	---	---
41.8	Resin	41.8	Quaternary resin carbon
32.3	Butoxyethanol	CH ₂	CH ₂ Butoxyethanol
31.3	Resin	CH ₃	(CH ₃) ₂
22-24	Additive	---	---
19.5	Butoxyethanol	CH ₂	Butoxyethanol
14.1	Butoxyethanol	CH ₃	Butoxyethanol

Table 3.3: C-13 NMR peak assignments of powdered cured film

Peak	Component	Assignment
159.3	Resin	Phenyl C
150.0	Urethane Linkage	C-N
145.4	Resin	Phenyl C
128.5	Resin	Phenyl C
116.2	Resin	Phenyl C
71.0	Resin	Internal C-O-C
62.7	Urethane Linkage	C-OH
58.9	BIS-SULFUR SILANE	OCH ₂ CH ₃
41.6	Resin	Quaternary carbon
31.1	Resin	(CH ₃) ₂
23	BIS-SULFUR SILANE	SCH ₂ CH ₂ CH ₂ Si(OR) ₃
19.3	BIS-SULFUR SILANE	OCH ₂ CH ₃
14.5	BIS-SULFUR SILANE	SCH ₂ CH ₂ CH ₂ Si(OR) ₃

→ For aesthetic purposes
→ UV resistant

→ Reservoir of pigments and inhibitors
→ Provides corrosion protection and adhesion

→ Adhesion promoter

1.1 Typical Organic Coating System

2.1a Interaction of radiation with matter **Figure 2.1b** Basic components of IR spectrometer

Figure 2.2a AC Waveforms for an Applied Potential and a Resulting Current

Figure 2.2b Bode Plot for a Simple Electrochemical System

Figure 2.3 EIS set-up **Figure 2.4** Adhesion tape test classification

Surface of cross-cut area from which flaking has occurred. (Example for 6 parallel cuts)	None					Greater than 65%
Classification	5	4	3	2	1	0

Figure 3.1: Results of 168 hour salt spray testing for (a) coating A (control), (b) coating B (hydrolyzed BIS-AMINO SILANE), (c) coating C (hydrolyzed BIS-AMINO SILANE/ hydrolyzed BIS-SULFUR SILANE), and (d) coating D (hydrolyzed BIS-AMINO SILANE/ neat BIS-SULFUR SILANE).

Figure 3.2: EIS measurements for the control P/Si coating.

Figure 3.3: EIS spectra for (A) coating B, (B) coating C, and (C) coating D.

Figure 3.4: Pore resistance as a function of immersion time for (I) control coating A, and (II) coatings B, C, and D.

Figure 3.5: Results of 2000 hour salt spray test for (a) commercial epoxy primer/polyester topcoat, (b) coating B, (c) coating C, and (d) coating D.

Figure 3.6. ^{13}C NMR - DGEBA epoxy resin + n-butoxy ethanol (standard resin)

Figure 3.7. ^{13}C NMR – Freshly prepared coating solution D

Figure 3.8. ^{13}C NMR – Coating solution D aged for 43h

Figure 3.9. solid state ^{13}C -NMR – powdered cured film of coating D

Figure 3.10. solid state ^{29}Si -NMR – Powdered cured film of coating D

Figure 3.11. solid state ^{29}Si -NMR – Powdered cured film of coating D after immersion of coating in water for 2weeks

Figure 3.12. solid state ^{13}C -NMR – powdered cured film of coating D after immersion of the coating in water for 2weeks

Figure 3.13. ^1H -NMR of powdered cured film of coating B

Figure 3.14. ^1H -NMR of DGEBA epoxy resin + curing agent

Figure 3.15. ^1H -NMR of powdered cured film of coating D

Figure 3.16. Infra-red Spectrum of non-hydrolyzed bis-sulfur silane – $(\text{C}_2\text{H}_5\text{O})_3\text{Si} - (\text{CH}_2)_3 - \text{S}_4 - (\text{CH}_2)_3 - \text{Si}(\text{OC}_2\text{H}_5)_3$

Figure 3.17. Infra-red spectrum of coating solution D

Figure 3.18. Infra-red spectrum cured film of Coating D on metal

Figure 3.19 Reactions taking place in the coating system

Epoxide bond breaks to yield reactive OH groups

Hydrolysis of ethoxy groups in bis-sulfur silane. Condensation of silanols yields siloxane network.