

# USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY TO EVALUATE CORROSION BEHAVIOR OF PAINTED GALVANIZED STEEL IN ATMOSPHERIC AND SOIL EXPOSURE

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## ABSTRACT

A review of galvanized steel and painted galvanized steel processes is provided, as well as the fundamentals and requirements for painted galvanized steel products. The corrosion processes found with both galvanized steel and painted galvanized steels are discussed. In the evaluation of painted galvanized steels, various laboratory techniques have proven most useful, with electrochemical impedance spectroscopy (EIS) as a sensitive quantitative technique for measuring coating degradation and corrosion protection. A detailed overview of the EIS technique is provided. Two case studies are provided for the laboratory evaluation of replacement and repair coatings for painted galvanized structures, featuring EIS and other laboratory techniques.

## INTRODUCTION AND GALVANIZED STEEL PRODUCTION PROCESSES

Galvanizing is an attractive and economical means of corrosion protection for a wide variety of commercial and industrial steel articles. Typical examples are galvanized roofing, siding roofing nails and other fasteners, sidings, beams, box sections, utility poles, fencing and general industrial and agricultural components.

Commercial use of zinc-coated iron and painted galvanized steel dates back to the mid 19th century. Hot-dipped galvanized corrugated sheet, used as a roofing material, found its way from British mills to California during the gold rush of 1849. In the original hot-dip process, individual sheets of steel were dipped by hand into a molten zinc bath after a sulfuric acid cleaning and ammonium chloride fluxing. Galvanized structural steel first became an important material of construction in the 1950's.

The development of techniques for continuous galvanizing of strip allowed for mass production of the zinc-coated steel product. The Sendzimir coating process was the first to fulfill the basic coating requirements in a continuous galvanizing operation. A coating line was installed by the Armco Steel Corporation at Butler, Pennsylvania in 1936 and proved the soundness of the process. The key factor in its success was in suppressing the formation of the brittle iron-zinc alloy layers at the steel/zinc interface by the addition of aluminum to the bath. By the early 1980's, batch-galvanized was supplanted by continuous-galvanized steel as the primary type used in production of sheet material such as that used in cooling towers.

The role of aluminum as an essential bath component is discussed further below in the sections on continuous-coating and on the microstructure of the coated products.

## **Production of Galvanized Steel**

Batch or Hot-Dip Galvanizing. For many years galvanizing was done by passing single sheets of steel through a coating pot, the so-called batch or hot-dip method. This process is divided into several stages. The first operation is degreasing to remove any extraneous matter on the surface other than oxide scales and films. Then any scale formed on it by previous heat treatments is removed by passing the steel through an acid pickling bath. Pickling is followed by a thorough rinse. The next stage depends on the galvanizing process.

Batch galvanizing involves prefluxing by immersion in an aqueous solution of zinc ammonium chloride, followed by drying. Drying is essential when the molten bath contains aluminum; otherwise, the aluminum will vaporize as aluminum chloride, throwing off the aluminum concentration in the bath. This is followed by passage through fused flux. The fused flux attacks the steel surface, activating it and promoting wetting of the steel by the molten zinc. The steel then passes through the zinc bath. Immersion time in the bath ranges from several minutes up to half an hour for large structural steel components. Bath temperature control is vital since if the bath is only slightly too hot it will actually consume the pot walls.

Continuous galvanizing. In the modern continuous strip process, the steel strip is heated in an oxidizing atmosphere to burn off rolling oil. It is then reduced in an atmosphere of cracked ammonia and annealed in-line. After cooling, the strip enters a pot of molten zinc through a chute which dips below the surface of the zinc, thereby avoiding contact of the strip with air and consequent oxidation. After passing under a sinker roll in the pot, the strip moves vertically upwards through the zinc as it leaves the bath. The zinc coating-thickness is controlled by air knives as the strip exits the pot resulting in the desired coating thickness and a very smooth surface. The strip then passes through a chemical treatment section where it may be oiled or chemically treated, depending on the intended use. Finally, the strip is roller-leveled.

## **Microstructures of Galvanized Products**

Microstructures of batch produced materials. The steel substrate and the molten zinc begin to interact immediately on contact, progressively producing several distinct iron-zinc intermetallic alloy layers, each richer in zinc and poorer in iron than the last as they progress away from the steel surface. The thin layer next to the steel is called the gamma layer, with about 25% iron concentration. Above this is a somewhat thicker delta layer typically with about 10% iron concentration. Above this is the zeta layer, with about 5-6% Fe, usually comprised of more or less coarse columnar intermetallic crystals of iron and zinc. The outer layer is known as “Free Zinc” even though it usually also contains a surface coating of aluminum oxide and other impurities or segregants. The picture below illustrates these features. . Total thickness usually ranges from 1.6 to 4 mils (40 to 100 micrometers), depending on the substrate. The aluminum content of the galvanizing bath has a great influence on thickness, appearance, and white rust formation.

The formation of the alloy layers is a diffusion-controlled process, with iron diffusing out through the layers in the solid state. The development process depends upon time, temperature, the composition of the steel substrate, and the composition of the galvanizing bath.

The outer surface of a galvanized coating is made up of zinc crystals, sometimes quite large, known as “spangles,” the well-known zinc bloom pattern. These spangles are often quite bright. This ductile zinc surface layer commonly comprises at least 40% and as much as 80-90% of the total coating thickness.

Galvanizing some steels produces zinc-iron layers that grow right through to the surface, producing a matte gray rather than bright finish. Both of these coatings are equivalent in protective value.

Silicon, in silicon-killed steels or any steel containing more than about 0.04 to 0.1% Si, accelerates the reaction between Fe and Zn, resulting in a coating that can consist completely of Fe-Zn intermetallic layers. Higher Si concentrations can also result in coatings that are thicker overall than coating specifications require. Galvanized coatings on Si-containing steels are usually more brittle than typical zinc coatings and can have poor adhesion. Thick coatings on the order of 11 mils or more are especially brittle and will crack and peel off under mechanical stress or even powder if severely bent

Microstructure of continuously-produced “strip” materials. The bath for continuous-coating contains a higher concentration of Al than in batch-production, promoting the formation of a very thin intermetallic aluminum-bearing gamma layer which almost blocks the diffusion of Fe into the zinc and prevents the formation of the thicker multi-phase intermetallics typical of bath-produced materials. Thus the structure of these materials is largely the substrate, overlain by the thin three-component intermetallic layer overlain by a thicker layer of relatively flexible Free Zinc, able to be formed without breaking.

## **CORROSION PROCESSES ON GALVANIZED SURFACES**

Zinc is a highly reactive metal. It exhibits a low corrosion rate only if a continuous passive film forms on the surface. A key requirement of corrosion control with zinc is that the surface needs to remain largely dry and in contact with the air in order to develop and maintain this passive film. Storage stain (white rust) is simply the chemical compounds, zinc hydroxide/zinc carbonate, which forms when zinc is kept in contact with moisture during storage or transportation.

Zinc corrosion products are typically white, but under certain conditions may also take the form of a gray or black deposit on the metal surface. White rust can occur when galvanized surfaces are held for extended periods in wet conditions. The surfaces may become wet either by rain fall, or by condensation of atmospheric humidity. The corrosion products form after zinc reacts with moisture. Corrosive elements such as chlorides from marine atmospheres accelerate the formation of white rust.

The extent of the white rust is primarily dependent on:

- a) Duration of the exposure to moisture.
- b) Temperature that is experienced during storage or transportation.
- c) Presence of accelerating corrosive agents, such as chloride-containing salts.
- d) Position of galvanized component (vertical or horizontal).
- e) Metallurgical structure of galvanized layer and surface composition.

The surface of the galvanized coating in the area that experiences extensive white rust formation will be “etched” and no longer will have the bright, reflective appearance of as-produced galvanized sheet. In this case removing the white rust will not eliminate the etched appearance. This is why, for applications where appearance is critical, galvanized surface should be treated by conversion coatings. The conversion coating (chromate or non-chromate treatment) that preserves brightness also inhibits this formation of storage stain during storage and transportation.

### **White Rust Formation Mechanism**

White rust, storage stain and “tiger striping” develop on freshly-coated galvanized products if they are stored in environments that allow drops or thin layers of water to remain on the surface of the zinc before it has developed a protective zinc carbonate coating. The most common cause of storage stain formation is moisture entrapped in a tightly coiled strip. “tiger striping” develops when moisture condenses or falls on the top of horizontally-stored freshly coated galvanized pipes or cylinders such as light standards. The corrosion process begins on the top wet surface and as more water accumulates and runs down around the cylinders, the corrosion process continues, forming circumferential white stripes of corrosion product. The presence of moisture either as condensed droplets or thin layers of water on freshly prepared galvanized steel is a necessary condition for the formation of white rust.

The effect of pH can be explained by experiments performed by the authors concerning the type and form of corrosion products that may be present on the surface. In near-neutral solutions, insoluble corrosion products form and retard corrosion. Conversely, in more acidic or alkaline water, soluble corrosion products are formed, destroying protective films and permitting corrosion to proceed. Water drops standing on the fresh zinc surface allow the solution of the zinc metal, increasing the pH within the drops and promoting further accelerated dissolution of zinc and the formation of unsightly corrosion products of zinc. Localized pH in the droplets increases from normal neutral as the freshly prepared galvanized coating dissolves in the droplet. If, however, protective basic carbonate forms before the coating becomes wet, the increase in pH does not take place and no white rust forms. In the presence of passive basic zinc carbonate, the corrosion resistance of a galvanized layer is increased because the protective basic carbonate extends the region of passivation toward neutral pH values). In this case the droplet of water or the thin layer of water can no longer cause white rust. The key question for prevention of white rust or tiger striping, then, is: How to create the basic protective carbonate film prior to storage and transportation of galvanized articles?

## **Role of Aluminum and Lead in the Formation of White Rust**

Aluminum in the zinc galvanizing bath has a significant beneficial role in preventing the formation of white rust. Other non-zinc constituents of the galvanized coating such as lead and antimony also play important roles. Deposits of these species are found unevenly distributed over hot-dipped galvanized surfaces.

By contrast, aluminum (and magnesium when present) is uniformly distributed over the entire surface as an oxide. There is very little zinc in the outermost layer of the coating. In fact, zinc is found on less than 10% of the surface. The segregation of aluminum and magnesium to the coating surface results not only from the phase segregation phenomenon discussed below, but also from the much greater tendency of aluminum to oxidize than has zinc, providing a chemical potential driving aluminum towards the oxygen-rich surface environment.

When the liquid zinc bath begins to solidify on the metal surface, the dissolved impurities such as lead, antimony, aluminum and magnesium are concentrated in the remaining liquid immediately at the solid-metal interface. This is the phenomenon of rejection of an element relatively insoluble in the solid phase during solidification of molten alloy. In a hot-dipped galvanized coating, spangle growth begins at the steel substrate surface, that is, the zinc coating solidifies from the steel substrate outward. As the solidification front progresses from the zinc-steel interface to the final coating surface, those elements less soluble in the solid phase remain in the liquid phase and are finally left at the surface of the zinc coating. Faster cooling allows less opportunity for these elements to be rejected toward the surface and instead they became trapped between the fast growing dendrites.

The most prevalent surface problems in continuously-coated galvanized strip created by the processes discussed above include:

- a.) very thick aluminum oxide films, and
- b.) high concentrations of lead, magnesium or antimony at the galvanized surface.

These conditions could delay or prevent the formation of the protective zinc-containing films, permitting the formation of undesired zinc corrosion products or, in the alternative, permitting an aluminum oxide film with lead impurities to remain, covering a virgin zinc surface. This means that a new structure, at installation, could have a galvanically active, unpassivated surface at the metal/water interface.

## **PAINTED GALVANIZED STEEL**

In general, galvanizing is the deposition of zinc onto a metal surface, usually steel, which creates a sacrificial layer designed to inhibit corrosion of the metal being coated. Zinc is a highly reactive metal which reacts readily into hydroxides and carbonates on its surface. This reaction occurs on the galvanized surface before the corrosion of steel substrate takes place.

Painted galvanized steel has been in commercial use since early 20<sup>th</sup> century. The main attributes that makes it so desirable in architectural applications are:

- 1) Corrosion resistance and galvanic protection
- 2) Color retention
- 3) Formability
- 4) Cost

The painted galvanized steel is used as architectural panels in roofing and siding, utility poles and lattices in electric transmission lines and when e-coated as automobile body panels and various components. The painted galvanized steel finds its way to numerous applications that require galvanic protection due to mechanical damage. The latter makes it the most desirable coated material in atmospheric and some soil water immersion applications.

### **SURFACE PREPARATION OF GALVANIZED STEEL PRIOR TO PAINTING**

Knowledge of the condition of the galvanized surface layer before paint application is critical to producing an effective coating system. There are three general conditions experienced on the galvanized surface layer.

- Freshly galvanized – this condition usually is seen only within the first 48 hours after galvanizing. In the freshly galvanized condition, there are little or no zinc hydroxides or carbonates on the surface.
- Partially weathered – this condition is usually seen from between 48 hours to 2 years of outdoor exposure of the galvanized surface. The surface possesses a thin layer of zinc hydroxides and/or carbonates (patina) on the surface which is not well adhered to the substrate.
- Fully weathered – this condition is typically seen after 2 years of exposure of the galvanized surface, and possesses a thick adherent patina layer on the surface.

To obtain good adhesion of a paint coating, the galvanized surface should be rather flat with no protrusions and slightly roughened and profiled to provide a larger surface area of adhesion. Care must be taken not to damage or remove the galvanized coating.

One of the ways to increase the surface area is with sweep blasting. Sweep blasting creates a surface profile for the coating to create tighter adhesion of the coating to the galvanizing, and is suitable for both freshly galvanized and partially weathered galvanizing. However, for partially weather galvanizing, it may be advisable to provide chemical surface treatments to remove any possible contaminants and improve the adhesion of the coating

In sweep blasting, care must be taken not to remove too much of the zinc coating. The particle size of the blasting medium should range between 200 and 500 microns. The types of blasting mediums used successfully have been aluminum/magnesium silicate and organic materials such as corn cobs, walnut shells, limestone, and mineral sands with a hardness of 5 or less. The blast pressure should be 40 psi maximum with a blasting angle of 45 degrees at a distance from 300-400 mm. Finally, the nozzle type should be a minimum 10 mm venturi.

All these parameters will cause minimum damage to the galvanized coating and will remove no more than 10 microns of zinc from the surface. It is also important to ensure that the air used in the blasting is dried air and not saturated with water. Moisture added to the zinc patina will form carbon dioxide and affect the adhesive ability of the substrate.

Fully weathered galvanizing does not require a sweep or brush blast because the tightly adherent zinc patina has an excellent surface profile and is tightly adhered to the substrate. However, a high pressure power wash is required to remove contaminants.

Sometimes during handling or installation, the galvanized steel may get damaged. These areas should be repaired by zinc-rich coatings first before coating the structure.

The sweep blast procedure is the most difficult part of the process of coating galvanized steels, as it is prone to several potential operator errors. These errors include the following.

- Removal of too much zinc, wasting zinc from the galvanized layer.
- No profile, leaving residual contaminants and lack of adhesion of the paint coating.
- Cracking of the galvanized layer, leading to blistering and peeling of paint coating later or in the service conditions

There are three primary causes of failures of coated galvanized steels that result from improper surface preparation of the galvanized surface prior to coating. These are over-blasting, under-blasting, and residual surface contamination.

Over-blasting involves the removal of too much zinc during the blast procedure. This results in areas of little or no zinc remaining on the surface, and cracks the zinc layer and results in its delamination. Under-blasting is the removal of too little of the zinc patina during the blast procedure. This leaves contaminants on the surface, which leads to premature coating failure. Residual surface contamination, which may be picked up even after a successful blasting operation, is also responsible for poor coating adhesion and premature coating failure.

Various chemical treatments may be employed prior to paint and organic coating application to the galvanized surface. Zinc phosphate treatment provides a good surface for the coating to adhere to. However, zinc phosphate is not recommended if a zinc-rich primer is to be applied in cases where galvanic protection is required. So-called wash primers are used to neutralize hydroxides and carbonates on the galvanized surface, and they promote coating adherence.

Finally, after all the necessary steps have been taken for good surface preparation, the coating itself should be compatible with the galvanized coating to create a successful synergistic effect. Usually a two coat system is used. The first coat is fully compatible with the zinc surface and is considered a “tie coat”. The second coat is the top coat to protect the “tie coat”

When coatings are applied to new structures or where the previous coating has been completely removed, the following coating systems with adequate thickness are acceptable in highly corrosive environments. Note that the best top coat is aliphatic polyurethane. However, these types of coatings would cost too much. Using a thin layer of aliphatic polyurethane with the proper primer and intermediate coat would be sufficient if the cosmetic appearance of the final product is not an issue.

| System | Primer                            | Intermediate Coat                 | Top Coat                |
|--------|-----------------------------------|-----------------------------------|-------------------------|
| 1      | Inorganic Zinc Rich               | Epoxy                             | Aliphatic polyurethane  |
| 2      | Waterbased inorganic zinc rich    | Waterbased Acrylic                | Waterbased Acrylic      |
| 3      | Polyurethane organic zinc rich    | Polyurethane                      | Aliphatic polyurethane  |
| 4      | Epoxy organic zinc rich           | Epoxy                             | Aliphatic polyurethane  |
| 5      | Polyurethane Micaceous Iron Oxide | Polyurethane Micaceous Iron Oxide | Aliphatic polyurethane  |
| 6      | Polyurethane organic zinc rich    |                                   | High build polyurethane |
| 7      | Epoxy organic zinc rich           | Waterbased Acrylic                | Waterbased Acrylic      |
| 8      | Thermally sprayed zinc            | ---                               | Waterbased Acrylic      |
| 9      | Thermally sprayed zinc            | ---                               | ---                     |

When the coatings are involved in spot repairs and/or overcoatings, the following coatings are suggested over the previous polyurethane layer in a highly corrosive environment:

| System | Primer              | Intermediate Coat   | Top Coat               |
|--------|---------------------|---------------------|------------------------|
| 1      | Epoxy               | Epoxy               | Aliphatic Polyurethane |
| 2      | Polyurethane        | Polyurethane        | Aliphatic Polyurethane |
| 3      | Epoxy Mastic        | Epoxy Mastic        | Aliphatic Polyurethane |
| 4      | Water based Acrylic | Water based Acrylic | Water based Acrylic    |

Using a coating over galvanized steel is called duplex coating. A zinc-rich layer and coating in a synergistic combination produce a corrosion protection approximately 2 times the sum of the corrosion protection that each alone would provide. Additionally, duplex coatings are easy to repaint, are considered excellent safety marking systems, and have good color-coding. Painting over galvanized steel that has been in service for many years also extends the life of the zinc coating.

## **Types of Paints/Coatings That Have Worked With Galvanized Steels**

Factory applied coatings include baked on powder paint, sprayed on chemically cured epoxy resins, electrostatically applied fusion bond epoxy and sprayed on coal tar or petroleum based enamel. Field applied coatings are usually brush applied enamels, mastics, polyurethane, reinforced plastics or epoxies.

Zinc-rich paints. Zinc-rich paints have been known for their excellent paint adherence to both new and weathered galvanized surfaces. They have been used in US for more than 75 years due to their barrier and cathodic protection. In many studies, zinc-rich paints outperformed all other classes of paint. One of the main reasons for its success is that it has the same characteristics as the galvanized zinc coating. These paints synergistically combine with the desired properties of the metallic zinc coating. In addition, zinc-rich paints are widely used for repairing damaged galvanized coatings. These types of paints are often used alone but for a more attractive finish, a top coat is used.

Aliphatic polyurethanes. This is a two component system, generally applied over a polyamide epoxy primer. Aliphatic polyurethanes have superior weathering and chemical resistance with good adhesion and an enamel-like finish. This type of coating requires stringent application procedures. The cost per gallon precludes the development and use of aliphatic polyurethanes for protective coating applications. However, in urethane films, excessive intra-film bubbling may occur due to carbon dioxide formation or air entrapment during fast curing.

Epoxy-polyamide cured. This type of epoxy would have excellent adhesion to any type of galvanized surface. However, since they are aromatic, they are not resistant to sunlight. Many times epoxy-polyamide cured coatings are used as the 'tie coat' and then an aliphatic polyurethane top coat is used. This type of system is considered to be a superior combination for barrier protection coating.

Latex-acrylics. Latex acrylics are fast drying, water-based materials that have excellent adhesion, durability, and weathering characteristics. Usually this type of coating is used as a top coat. Not only is this type of coating suitable for new and weathered galvanized steels, it is environmentally friendly.

## **Types of Paints/Coatings That Have Not Worked with Galvanized Coatings**

Alkyds. Alkyds are not commonly used over galvanized coatings. It is widely known that in wet areas zinc will produce an alkaline surface. If alkyds are used, the alkaline surface with moisture would cause saponification to occur which would result in premature peeling and flaking.

Asphalts. Asphalts, a petroleum based product are also not recommended for use with galvanized steel.

## **CORROSION RESISTANCE OF PAINTED GALVANIZED STEEL**

The corrosion resistance depends on corrosivity of the environment and the type of exposure. In general, corrosion resistance depends on the following four factors:

- 1) Atmospheric exposures/UV.
- 2) Underground soil water table exposure.
- 3) Coating adhesion
- 4) Presence of thinly coated or uncoated spots.

Atmospheric exposures do not require thick coatings. However, the underground soil and water exposures demand much more thickness. In general low pH and acidic chloride environments will require pin hole free corrosion resistant coatings with no mechanical damage.

## **LABORATORY TECHNIQUES FOR EVALUATION OF COATINGS ON GALVANIZED STEELS**

There is a wide variety of testing methods currently available for evaluation of paints and coatings on galvanized steel. Sophisticated and highly calibrated laboratory equipment can detect the slightest imperfections on a specimen, and accurately identify the inherent characteristics.

### **Laboratory Techniques**

A macroscopic examination of the surface of the selected specimen begins this stage of analysis, followed by a microscopic examination. A close examination using a stereo microscope at magnification of 50x or less may reveal that one of the layers is brittle and full of cracks, or perhaps that an entire layer of paint is missing. An examination of failed and non-failed samples may reveal that all of the failed samples are of improper thickness. Optical and electron microscopy at magnifications ranging from 50x to 1000x magnification can be used to examine the cross section of coated galvanized samples for voids or inclusion, as well as observation of underlying corrosion products on galvanized substrates.

Physical testing provides important characteristics in the evaluation of a coated galvanized specimen which may reveal primary causes for degradation and failure. Important physical tests include thickness testing, pin hole testing, adhesion testing, determination of the plane of delamination, hardness testing, and surface roughness (profile) testing. Pin holes are caused by poor application technique, solvent evolution from the film, corrosion due to trapped materials, and the presence of sharp globules on the surface which are difficult to completely coat initially and easy to abrade subsequently. Poor adhesion is caused by improper surface preparation procedure, as well as incompatibility of coating layers or of the primer with the substrate. The determination of the plane of delamination of a failed coating is critical to ascertaining the possibility of coating layer incompatibility or improper surface preparation.

A chemical analysis of the paint or coating, as well as the galvanized substrate and corrosion products is usually the next step. Chemical analysis techniques typically used in the laboratory for paint and coating failure analysis are Fourier transform infrared spectroscopy (FTIR) for organic functional group analysis, gas chromatography – mass spectrometry (GM-MS) for organic compound separation, identification and quantification, differential scanning calorimetry (DSC) for melt range and thermal properties, scanning electron microscopy (SEM) with associated energy dispersive x-ray spectroscopy (EDS) for elemental analysis, and Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) for surface elemental analysis.

Accelerated environmental exposure tests, such as salt spray (fog) tests, humidity tests, and ultraviolet light (QUV) exposure tests can help to confirm the proposed failure mechanism of a painted or coated galvanized sample. Accelerated exposure testing can be complemented with electrochemical impedance spectroscopy (EIS). The organic coating resistance generally degrades with time. The degradation is associated with corrosive ions and water penetration into the coating, transport of ions through the coating, and subsequent corrosion reactions at the polymer–metal interface. Typical standard coating immersion tests can take hundreds or thousands of hours. However the EIS technique can provide reliable data on performance in rather short time.

### Electrochemical Impedance Spectroscopy

The resistance of an organic coating generally degrades with time. The degradation is associated with corrosive ions and water penetration into the coating, transport of ions, through the coating, and subsequent corrosion reactions at the polymer–metal interface. Typical standard coating immersion tests can take hundreds or thousands of hours. However the electrochemical impedance spectroscopy (EIS) technique can provide reliable quantitative data on performance in rather short time.

The electrical impedance of a coating is the most direct measure of a coating's barrier properties and ability to protect against corrosion. All coating properties relevant to corrosion protection can be described in terms of their effect on coating impedance: Embrittlement, cracking, excessive porosity, poor adhesion, and ultraviolet degradation are common coating problems whose ultimate failure mechanism is the creation or enlargement of channels through which water, dissolved oxygen, and soluble ions can reach the substrate. Electrochemical Impedance coupled with exposure to the intended environmental stressors is the most direct method of establishing the quality of corrosion preventative coatings.

Definition of impedance. Electrochemical impedance is measured by applying a small sinusoidal voltage  $V(t) = V_m \sin(\omega t)$  across the coating, and measuring the induced current  $I(t) = I_m \sin(\omega t + \theta)$  through the coating. The ratio of the voltage to the current defines the electrical impedance. The voltage used is small to remain within the linear region of the current-vs voltage curve of the substrate, and to avoid polarizing the coating. The magnitude of the impedance is  $|Z| = V_m/I_m$ , and its phase is  $\theta$ . Typically the impedance is expressed as a complex number, ie.  $Z = (|Z|\cos(\theta) + j|Z|\sin(\theta))$ , which simplifies manipulation and analysis. Due to the presence of capacitance and time-dependent kinetics, the magnitude and the phase of the impedance change with the angular frequency  $\omega$  of the stimulus. It is the spectra of these frequency dependencies that yield diagnostic information about the coating. Typically, one fits a model electrical circuit's spectrum to the observed data and discusses the changing values of the model.

Only in the case of a resistor does the impedance not vary with frequency, and the induced current is in phase ( $\theta = 0$ ) with the applied voltage. Painted metals exhibit varying degrees of capacitance, or the ability to store electric charge on conductors separated by an insulator. Ideal coatings' impedance spectrum is exclusively capacitive, and is modeled by Figure 1. Capacitance causes the induced current from an applied sinusoidal voltage to be phase-shifted as an electric field charges and discharges with each cycle. The impedance of a capacitor  $Z_{cap}$  is  $1/j\omega C$ , where  $C$ =capacitance in Farads,  $\omega$  is the angular frequency =  $2\pi f$  and  $f$  is frequency in hz, and  $j$  is  $\sqrt{-1}$  (It is assumed that the reader is familiar with complex number notation of impedance.) It will be noticed that since  $\omega$  is in the denominator, as  $\omega \rightarrow 0$ ,  $Z_{cap} \rightarrow \infty$ , thus the impedance of a capacitor to steadily

applied voltages (ie.  $\omega=0$ ) is infinite and no current flows. At non-zero frequencies, a capacitor by itself shifts the phase of induced current by  $-90^\circ$  relative to the voltage waveform as well as scaling the magnitude by  $1/C$ . Figure 1 shows the equivalent electric circuit of an ideal coating modeled as a capacitor in series with a highly conductive electrolyte. Figure 2 shows the impedance magnitude vs. frequency for a range of ideal coating capacitances. Usually coatings are not ideal, ie. the impedance magnitude vs. frequency is not the straight line of Figure 2. Instead, they exhibit some finite resistance  $R$  in parallel with the coating capacitance through which current can leak when a steady voltage is applied (Figure 3). The impedance of this system is  $Z = (R^{-1} + j\omega C)^{-1}$ . This resistance is known as the pore resistance or equivalently the coating's resistance to ionic transport. (When performing EIS on good or even mediocre coatings, one need not be overly concerned by the inclusion of the impedance of the electrolyte solution,  $R_{\text{soln}}$ , since even poor coatings have impedances  $> 10^6$  ohms, while the typical 3.5wt% NaCl electrolyte is  $< 10^2$  ohms. Excellent coatings are commonly  $> 10^{10}$  ohms.) By fitting a model so its impedance agrees with the observed spectrum, the two most informative coating properties, coating resistance to ionic transport ( $R$ ) and coating capacitance ( $C$ ) can be determined. Of these, exposure-induced changes in the coating resistance to ionic transport is the most fundamental predictor of corrosion resistance of a coating.

An ideal coating. An ideal coating acts electrically like a perfect capacitor in series with the small resistance of the electrolyte used to wet the coating (Figure 1). The phase of the induced current will be phase shifted  $-90^\circ$ , and as the frequency of the applied voltage approaches zero (DC) the impedance will approach  $\infty$  (ie. no current  $I$  will pass the coating since  $I=V/Z = V/\infty = 0$ ). Most visually salient is the linearity of a plot of  $\log_{10}(|Z|)$  vs.  $\log_{10}(\omega=2\pi f)$ , which has a slope of  $-1$ . The coating capacitance can be read from the impedance vs. frequency plot, since  $|C| = 1/(2\pi fZ)$ .

Changes with exposure. As coatings are exposed to the environment, changes in the electrical impedance indicate the progress of the coating through the stages of hydration, increasing pore conductivity, and active corrosion:

### 1) Hydration

Hydration of the coating results in an increase in the coating's relative electrical permittivity, since the relative permittivity of the water which hydrates the coating is in the range of 10 to 40 times higher than that of the coating or air. This increase in permittivity results in a proportional increase of the coating's capacitance  $C$ , whose quantity is:

$$C = \frac{\epsilon_o \epsilon_r A}{d}$$

Where

$C$  = Capacitance

$\epsilon_o$  = electrical permittivity

$\epsilon_r$  = relative electrical permittivity

$A$  = surface area of coating face

$d$  = coating thickness

As coating capacitance increases, there is a reciprocal decrease in  $Z_{cap}$  ( $Z_{cap} \equiv \frac{1}{j\omega C}$ ). Figure 2 shows the impedance versus frequency for pure capacitances. When impedance curves are observed to translate in this fashion, coating absorption of water can be concluded and estimated using the relative electrical permittivities of the coatings.

## 2) Beginnings of Corrosion

As an electrolyte permeates a coating and makes contact with the underlying metal, the impedance spectrum reveals an increasingly conductive path circumventing the coating, modeled as a decreasing resistance  $R_{pore}$  in parallel with the coating capacitance. The simplest approximation of this circuit is known as a Randles cell, shown below (Figure 3). In contrast to the impedance spectrum of an ideal capacitance which is unbounded at low frequencies, the low frequency impedance of a Randles cell is bounded by the pore resistance (Figure 4).

The pore resistance is particularly informative since once corrosion has begun, it determines the rate of sub-surface corrosion, according to the following formula:

$$Corrosion\_rate = A(I_{corr})$$

$$I_{corr} = \frac{B}{R_p}$$

$$B = \frac{b_a * b_c}{2.3(b_a + b_c)}$$

$A$  is a constant depending on the mass properties of the material;  $B$  is a constant derived as shown from the electrochemical properties of the material, the anodic and cathodic Tafel slopes,  $b_a$  and  $b_c$ . By showing how the polarization resistance  $R_p$  changes over time, we can infer how corrosion rates will change over time.

In general, corrosion activity is not significant if the coating exhibits capacitive dielectric behavior and  $R_p$  does not change as a function of time. On the other hand a decreasing  $R_p$  certainly means there is electrolyte at the interface and corrosion is taking place (dispersed versus water at the interface). An  $R_p$  greater than or equal to  $10^{10}$  ohm-cm indicates that no corrosion is taking place.

### 3) Disbondment

As corrosion progresses, disbondment of the coating from the substrate may occur in the vicinity of ion-conductive pores. In the resulting blister, additional dynamics are introduced by the parallel capacitance and resistance of the metal-liquid boundary, but the impedance of this boundary is in all but the worst coating failures dwarfed by the much larger pore resistance.

The *Percentage of Protection* measure is used to summarize the changing frequency-dependent impedance of a coating. Coupled with an estimate of the low frequency impedance which approximates the pore resistance, these measures form a reliable method of comparative coating evaluation. Percentage of initial Protection is defined as the percentage of initial area under the impedance magnitude plot (on log-log axes).

$$\text{Percent Protection}(t) \equiv 100 \cdot \frac{\int_{f_{low}}^{f_{high}} \text{Log}_{10} |Z(f, T = t)| df_{\log}}{\int_{f_{low}}^{f_{high}} \text{Log}_{10} |Z(f, T = 0)| df_{\log}}$$

$$f_{\log} = \text{Log}_{10}(\text{Frequency})$$

In addition to the impedance magnitude and comparative measures discussed above, Information about the kinetics of ion transport across the coating is contained in the plot of the real vs. the imaginary components of the impedance over the range of frequencies studied, the so called Nyquist Diagram, but for reasons of space this paper is limited to more generally useful information contained in the impedance magnitude plots. For an excellent review of electrochemistry and impedance spectroscopy, the reader is referred to the following references (1, 2).

Careful application of EIS technique in conjunction with other methods of testing can be tremendous aid in quickly selecting good coatings and excluding bad ones. Salt spray testing in accordance to ASTM B 117-03, "Standard Practice for Operating Salt Spray (Fog) Apparatus," (3) or ASTM G 85-02e1, "Standard Practice for Modified Salt Spray (Fog) Testing" (4) is frequently used to measure the corrosion resistance properties of the coating in the presence of corrosive conditions containing chlorides. Although salt spray testing accelerates the corrosion attack experienced on coated panels, it can take 2000-5000 hours for visible signs of degradation to appear. Changes in the impedance spectrum appear well before such macroscopic degradation, as shown in the following case studies.

## CASE STUDIES

The following two case studies are presented illustrating the use of electrochemical impedance spectroscopy in conjunction with other laboratory techniques to determine the suitability of various paint/coating systems as replacement and repair coatings for galvanized structures.

### Case Study 1 – Coatings for Galvanized Structures Used in Both Atmospheric and Soil Environments

In accordance with a client's request, the authors conducted extensive long term exposure testing of seven different types of coating systems. The coating systems were supplied by four different manufacturers. The objective of the exposure testing was to determine which of the coating systems performed the best when exposed to various simulated environmental conditions. The results of the testing were to allow the client to make informed decisions on the next generation of galvanized structures used in both atmospheric and soil environments. The testing included the following:

1. Salt fog exposure, including electrochemical impedance spectroscopy (EIS) and creepage and adhesion evaluation.
2. Acidic chloride exposure, including EIS.
3. UV accelerated weathering testing.
4. Cathodic disbondment testing.
5. Physical testing.

The test sample key below outlines the different sample manufacturers and coating types of each of the samples.

| <i>Sample Name</i>                | <i>Coating Type</i>            |
|-----------------------------------|--------------------------------|
| Control – Client's Current System | Polyurethane                   |
| Manufacturer 1 – A                | Epoxy / Aliphatic Polyurethane |
| Manufacturer 1 – B                | Epoxy                          |
| Manufacturer 2                    | Polyurethane                   |
| Manufacturer 3 – A                | Epoxy                          |
| Manufacturer 3 – B                | Epoxy / Aliphatic Polyurethane |
| Manufacturer 4 – A                | Polyurea without Wash Primer   |
| Manufacturer 4 – B                | Polyurea with Wash Primer      |

Salt spray exposure and EIS. The samples received between 700 and 3500 hours of salt spray exposure per ASTM B 117-03. This amount of exposure showed some definitive evidence of how the coating systems are currently performing in a salt fog environment. EIS testing indicates that the Manufacturer 1 – B epoxy sample

performed the best under salt fog exposure. The Manufacturer 1 - A epoxy with aliphatic polyurethane topcoat also sample performed well. The Manufacturer 4 - B coating system without the wash primer also performed well. However, the Manufacturer 4 - A coating system with the wash primer performed poorly in this environment and was eliminated after 700 hours of exposure. The Manufacturer 3 - A epoxy coating exhibited fair performance in this evaluation. The Manufacturer 3 - B epoxy/aliphatic polyurethane performed the best. Figure 5 presents the successive EIS spectra over time for the Manufacturer 3 – B coating system, which illustrates the best retention of protection over the exposure period.

The table below outlines the EIS results during salt fog exposure:

| Sample             | Duration of Exposure | Final Percent Protection | Ranking |
|--------------------|----------------------|--------------------------|---------|
| Manufacturer 3 – A | 1100 Hours           | 68%                      | 5       |
| Manufacturer 3 – B | 2000 Hours           | 94%                      | 1       |
| Manufacturer 2     | 1100 Hours           | 44%                      | 6       |
| Manufacturer 1 – A | 3500 Hours           | 66%                      | 4       |
| Manufacturer 1 – B | 3500 Hours           | 74%                      | 2       |
| Manufacturer 4 – B | 700 Hours            | 68%                      | 5       |
| Manufacturer 4 – A | 2900 Hours           | 70%                      | 3       |
| Control            | 2000 Hours           | 68%                      | NR      |

Creepage and adhesion after salt spray exposure. To confirm the EIS test results, exposed specimens were also evaluated in accordance with ASTM B 117-03, which measures three visible failure modes: (1) blisters over the exposed panels, (2) corrosion along the scribe line on the panels, and (3) loss of adhesion where the electrolyte has penetrated the interface between the substrate and coating. Creepage is defined as the distance that the corrosion advances from the scribe line and is measured in millimeters or inches. In thin films, the degraded coating may flake off or even peel back. But, with thicker films, the failure may not be obvious. The evaluation included the following procedures.

Samples were removed from the salt spray chamber and then wiped dry. A heavy gage adhesive tape was used to check for loss of adhesion. Many of the samples resisted the adhesive tape pull test, but after cutting deeper along the scribe line and repeating the adhesion test, several of the coatings delaminated or separated from the substrate. The exposed substrate showed signs that the electrolyte had undercut the coating, and white or red iron rust was deposited between the coating and the substrate.

All coated panel specimens were evaluated for creepage and adhesion properties. Test results indicated that Manufacturer 1 - B primer and Manufacturer 1 - A topcoat performed the best in comparison to the other tested specimens. Manufacturer 1 - B primer did not show any signs of blisters and did not experience any adhesion

loss. The coating remained very tough and is difficult to penetrate. However, the Manufacturer 1 – A topcoat experienced some adhesion loss at the intersection of the scribe lines.

The polyurethane control sample (with a coating thickness of 11 mils) exhibited severe adhesion loss and creepage in a relatively short period of time. However, blistering has not been observed.

The samples from Manufacturers 2, 3, and 4 show loss of adhesion and some large areas of creepage, particularly at the intersection of the two scribed lines. Along the scribe lines, these samples had creepage ranging from 1/32" to 1/4". Specific test data are listed in the table below. Manufacturer 3 – B showed the best performance.

| Samples               | Salt Spray (Hrs) | Corrosion                       | Adhesion            | Creepage          | Rank |
|-----------------------|------------------|---------------------------------|---------------------|-------------------|------|
| Manufacturer 3 – A    | 2500             | White Rust                      | Loss, De-lamination | 1/8" – 1/4"       | 4    |
| Manufacturer 3 – B    | 3000             | None                            | Very little         | None              | 1    |
| Manufacturer 2        | 2500             | Red Rust at Scribe Intersection | De-lamination       | Complete Undercut | 6    |
| Manufacturer 4 – B    | 700              | Extensive Rusting below Coating | Loss, De-lamination | Extensive         | 7    |
| Manufacturer 4 – A    | 1900             | Red Rust                        | De-lamination       | 1/32" – 1/4"      | 5    |
| Manufacturer 1 – B    | 2500             | None                            | None                | None              | 2    |
| Manufacturer 1 – A    | 2500             | None                            | Very little         | None              | 3    |
| Control Panel 10-mils | 2000             | White rust                      | De-lamination       | None              | NR   |

Acidic chloride immersion and EIS. The samples were immersed in an acidic chloride solution consisting of 0.1 Molar hydrochloric acid at room temperature. The table below shows the status of the coatings as of up to 3000 hours, based on EIS measurements.

| Sample (No. in Figure 2) | Duration of Exposure | Final Percent Protection | Ranking |
|--------------------------|----------------------|--------------------------|---------|
| Manufacturer 3 – A (#0)  | 2100 Hours           | 64 %                     | 4       |
| Manufacturer 3 – B (#1)  | 3000 Hours           | 100 %                    | 1       |
| Manufacturer 1 – B (#2)  | 2100 Hours           | 54 %                     | 5       |
| Manufacturer 1 – A (#3)  | 3000 Hours           | 93 %                     | 3       |
| Manufacturer 2 (#4)      | 2800 Hours           | 99 %                     | 2       |
| Manufacturer 4 – A (#5)  | 3000 Hours           | 100 %                    | 1       |
| Manufacturer 4 – B (#6)  | 3000 Hours           | 100 %                    | 1       |

As the table shows, the one coat systems do not perform nearly as well as the two coat systems. Since the Manufacturer 4 – A and 4 – B sample panels were coated to over 40 mils, this may explain the superior performance exhibited of the coating during immersion testing. The acidic chloride immersion test samples did not exhibit corrosion attack after up to 3000 hours of immersion. This is probably due to a lower exposure temperature as compared to salt spray testing. Figure 6 presents successive EIS spectra over time for Manufacturer 1 – B (Sample #2), illustrating the continuous degradation of the coating over time.

Cathodic disbondment. Cathodic disbondment is an ASTM G 8-96(2003), “Test Methods for Cathodic Disbondment of Pipeline Coatings,” (5) a test method for evaluating coatings that may be buried beneath the ground without such protection. Breaks or holidays in the coatings make it possible for the migration of moisture into the coating interface and causing corrosion. Normal soil potentials may cause loosening of the coatings beginning at the holidays’ edge. This test provides accelerated conditions for loosening to occur and therefore give a measure of resistance of coating to this type of action. There are four main factors that influence the performance of coatings in this test:

- (a) Temperature (150<sup>0</sup> F).
- (b) Electrolyte (3% sodium chloride solution).
- (c) Time or Duration of test (48 hours).
- (d) Voltage (-1.5 Volts).

Elevated temperature allows electrolyte to penetrate the coatings more readily than room temperature. It is believed that temperature has the most significant effect on short-term results. The heat flow or temperature gradient in this experiment was designed to pass through the coatings into the electrolyte. It was decided that 150<sup>0</sup>F was an appropriate temperature to run this experiment. The temperature was measured on the coated steel.

The electrolyte was warmed to 150° F at the start of the experiment and replaced after each test. The pH was recorded for all tests. The test duration: was determine by running the procedure on the control panels and measure the effect on the coating. The coating was unaffected after 24 hours so the test was extended to 48 hours. This became the benchmark. This is short-term testing. An applied voltage of – 1.5 Volts was used for the test.

A 1/8” holiday was drilled into the coating panels and inspected under microscope to assure that the 2” area was free from unwanted coating breaks and also to inspect the holiday for penetration into the metal. The holiday opening did not penetrate the steel. The panel was then clamped to the glass cylinder cell with the aid of rubber gaskets. The 3% sodium chloride solution was warmed to 150<sup>0</sup> F and used to fill the cell to 5/8” from the top. The opening was closed with a rubber stopper that had openings for a thermometer, the calomel electrode, and platinum electrode. The completed cell was placed on a hot plate so that the metal panel was in direct contact with the hotplate. The coating was removed from a small area on the panel to accommodate the anode connection. All electrical connections were made and the potential was adjusted to – 1.5 V. The duration of the test was run for 48 hours.

At the end of the test period the cell was disconnected and the electrolyte was drained. The coating was cut along the radius from the holiday. After test sample cooled to room temperature, attempts were made to lift the

dis-bonded coating with utility knife /scapula. Measurements were taken from the disbonded coating edge to the center of the holiday. These measurements are reported in millimeter radius.

| <i>Samples</i>     | <i>Coating - Removed</i> | <i>Ranking</i> |
|--------------------|--------------------------|----------------|
| Control            | 4mm radius               | 5              |
| Manufacturer 2     | 2 mm radius              | 4              |
| Manufacturer 1 – B | 1.5mm radius             | 2              |
| Manufacturer 1 – A | 0.7mm radius             | 1              |
| Manufacturer 3 – A | NA                       | Not tested     |
| Manufacturer 3 – B | 1.5mm radius             | 2              |
| Manufacturer 4 – A | NA                       | Not tested     |

The Control lost adhesion on the tested area and was clearly affected by the process. The Manufacturer 1 – A and 1 - B coatings were far better performers in this test. Although the control coatings had thicker coating films, the electrolyte absorbed through the holiday was sufficient to de-bond the coating in the tested area. Some coating outside of the tested area was removed but the metal was not tarnished, this is an indication that the electrolyte did not make contact with the metal in that area.

The Manufacturer 1 - A coating system recovered quickly after it was cooled to room temperature i.e., the coating was very tough and difficult to penetrate. It is important to note that the Control coating was softened by the hot electrolyte and did not recover as quickly as the Manufacturer 1 - A coating.

Summary of test results. Based on test results, it had been determined that epoxy/polyurethane coating systems exhibit the best performance of all tested specimens when exposed to simulated laboratory test environments. The epoxy coating systems tested by were Manufacturer 1 and Manufacturer 3 coating systems. Based on the authors' field and lab investigation of galvanized structures, it has become obvious that the future generation of coatings must be resistant to cathodic delamination, provide an effective barrier to corrosive compounds and moisture, and exhibit superior adhesion properties in corrosive environments. In addition, the selected coating must have UV resistance when exposed to pole storage environments and when exposed to in-service conditions. Although the test results are not resented here, of the coating systems tested and evaluated, it was found that Manufacturer 1 - A coating system, with the UV top coat, exhibited the best overall all performance including UV.

The major cathodic reaction at pin holes, mechanically damaged areas as well as any penetration to the coating/galvanized interface is oxygen reduction or hydrogen evolution reaction (her). This cathodic reaction produces a strong concentration of hydroxide ions, which results in the dissolution of zinc and the formation of white rust. Therefore, a coating that contains alkaline resistant resins will be very effective in inhibiting the corrosion reaction and the loss of paint adhesion. One well known resin that is resistant to alkaline attack is epoxy. The use of an epoxy resin in the coating system will provide protection to the pole structures in corrosive soil environments and at the mechanically damaged areas or at pinholes. Both Manufacturer 1 and Manufacturer 3 coating systems contain epoxy resin.

## Case Study 2 – Repair Coatings for Painted Galvanized Structures

The authors were contracted by a client to perform testing to evaluate two (2) types of repair coatings for repair coating of galvanized structures, designated here as Repair Coating A and Repair Coating B. In order to evaluate these coatings, a series of standardized tests were performed to evaluate specific coating characteristics.

These two coatings have been applied over the client's previous coating system, designated here as Client Coating. The manufacturers of Repair Coatings A and B supplied their coatings over the previous system to see which coating would perform the best as a repair coating. The list below outlines the different tests that have been performed on the coated panels:

1. Physical property evaluation.
2. Cross section microscopy.
3. Environmental exposure with EIS measurements in salt spray, acidic chloride and corrosive soil.
4. QUV exposure.

Physical property evaluation. The following table displays the results of the physical property evaluation: thickness measurements, pencil hardness, solvent resistance, and adhesion tape tests. The film thickness for each coating system was measured using a Posi-tector Model 6000. The pencil hardness measurements are ranked from 5H being the hardest to 6B being the softest; this test evaluates the relative hardness of a coating. The solvent resistance test evaluates how well a coating performs when exposed to a solvent (acetone). The adhesion tape test determines how well the coating is adhered to the substrate; in this test there was only a pass / fail result.

| <i>Samples</i>   | <i>Film Thickness</i> | <i>Pencil Hardness D3363, Method A</i> | <i>Solvent Resistance (Acetone)</i> | <i>Adhesion Tape Test D2259</i> |
|------------------|-----------------------|--|-------------------------------------|---------------------------------|
| Repair Coating A | 44 – 53 mils          | F                                      | 100 double rubs – soften            | Pass                            |
| Repair Coating B | 25 - 28 mils          | B                                      | 100 db rubs – No Affect             | Pass                            |

Cross section microscopy. Representative samples of each coating system were cut and mounted for cross section microscopy. Cross section microscopy revealed adequate adhesion between the base coat and topcoats on both systems. The Repair Coating A system, provided additional urethane basecoat and then an aliphatic topcoat while the Repair Coating B system provided only an aliphatic topcoat system. This difference in coating selection accounts for the difference in the coatings' film thicknesses.

Salt spray testing with EIS measurements. The panels were exposed to ASTM B 117-03 cabinet testing and were evaluated at different time intervals. EIS measurements indicate changes in impedance plots between the

samples before and after salt fog exposure. By comparing the coating integrity (% Protection) of the submitted samples over the test time interval, we will be able to judge which coating is performing the best. The samples have been exposed to 900 hours of salt fog exposure. After this time an EIS evaluation of the coatings integrity was performed. The results of this evaluation are shown in the table below.

| <i>Sample</i>    | <i>Duration of Exposure</i> | <i>Final Percent Protection</i> | <i>Ranking</i> |
|------------------|-----------------------------|---------------------------------|----------------|
| Repair Coating A | 900 Hours                   | 98%                             | 1              |
| Repair Coating B | 900 Hours                   | 98%                             | 1              |

These results show that both coating systems perform well in the salt fog environment.

Acidic chloride exposure with EIS measurements. Another method to determine a coating's durability is to expose the coating to an acidic chloride solution and perform EIS analysis at pre-determined intervals. The coated samples were exposed to 1500 hours of acidic chloride exposure and have not shown a significant degradation as shown in the table below and in Figures 7 and 8. This small degree of change indicates that the coatings have a strong resistance to acidic chloride exposure.

| <i>Sample</i>    | <i>Duration of Exposure</i> | <i>Final Percent Protection</i> | <i>Ranking</i> |
|------------------|-----------------------------|---------------------------------|----------------|
| Repair Coating A | 1500 Hours                  | 97%                             | 1              |
| Repair Coating B | 1500 Hours                  | 98%                             | 1              |

Corrosive soil exposure with EIS measurements. Another method of evaluating the coating integrity of these samples is to use the soil that the coating may contact while in service. In order to set up this experiment, Matco obtained soil samples from on-site investigations. After these soils were analyzed in our laboratory, highly corrosive soils were selected to expose the coated panels to, at periodic times during the exposure the samples were evaluated with EIS techniques. The table below shows that the Repair Coating B system is performing slightly better than the Repair Coating A system in the corrosive soil environment, however a degree of change is not significant enough to determine that the Repair Coating B is better than the Repair Coating A.

| <i>Sample</i>    | <i>Duration of Exposure</i> | <i>Final Percent Protection</i> | <i>Ranking</i> |
|------------------|-----------------------------|---------------------------------|----------------|
| Repair Coating A | 900 Hours                   | 96%                             | 2              |
| Repair Coating B | 900 Hours                   | 99%                             | 1              |

QUV exposure with color and gloss measurements. Repair Coated A and B steel panel sample were exposed to equal light and dark periods of six (6) hours, resulting in twelve (12) hours of QUV exposure and twelve (12) hours of high humidity daily per ASTM G 154-04, "Standard Practice for Operating Fluorescent Light

Apparatus for UV Exposure of Nonmetallic Materials.” (6) Color and gloss measurements were taken before testing, after 500 hours and final after 1000 hours. Color samples were read on CIELAB color scale under illuminants D 65 and observed 10° angles. Photo-spectrometer measures tristimulus values as L\*, a\*, b\*. Delta L, Delta a, Delta b represent the color shift after panels were exposed to QUV. The three tristimulus values are designed so that positive value on the L\*a\*b\* axis describe white (lightness), red (hue), yellow (chromatic) therefore negative value on the L\*a\*b\* axis describe black (darkness), green (hue), blue (chromatic). The samples’ gloss values were measured initially and after 1000 hours of QUV exposure per ASTM D 523-89(1999), “Test Method for Specular Gloss,” (7) by BYK - Gardner gloss meter at 60° angle.

| <i>Samples</i>         | <i>(L*)<br/>Initial /<br/>500h /<br/>1000 h</i> | <i>(a*)<br/>Initial /<br/>500h /<br/>1000h</i> | <i>(b*)<br/>Initial<br/>/500h /<br/>1000h</i> | <i>Δ L*<br/>500 h /<br/>1000 h</i> | <i>Δ a*<br/>500 h /<br/>1000 h</i> | <i>Δ b*<br/>500 h /<br/>1000 h</i> | <i>ΔE 500<br/>h / 1000<br/>h</i> | <i>Gloss<br/>Initial /<br/>1000<br/>Hours</i> | <i>ΔGloss<br/>500 h</i> |
|------------------------|---|--|---|------------------------------------|------------------------------------|------------------------------------|----------------------------------|---|-------------------------|
| Repair<br>Coating<br>A | 58.33 /<br>58.33 /<br>58.39                     | -1.57 / -<br>1.63 / -<br>2.00                  | -0.56 /<br>0.03 /<br>0.80                     | 0 / 0.06                           | -0.05 / -<br>0.42                  | 0.59 /<br>1.36                     | 0.59 /<br>1.43                   | 78.0 /<br>39.6                                | 38.4                    |
| Repair<br>Coating<br>B | 40.69 /<br>40.27 /<br>46.71                     | 46.38 /<br>45.28 /<br>41.25                    | 26.13<br>/25.02 /<br>21.28                    | -0.44 /<br>6.02                    | -1.1 / -<br>5.13                   | -1.1 / -<br>4.85                   | 1.62 /<br>9.28                   | 83.2 /<br>54.5                                | 28.7                    |

Coatings that are applied for decoration must maintain excellent gloss over long periods of time. The coatings for the galvanized poles are mainly functional, i.e., the corrosion resistance properties are more essential than the unchanged gloss with time. However, loss of gloss and color shift may indicate that a coating lacks resistance to UV radiation. This coupled with salt spray or humidity results allow us to rank coatings properties. Both the brown and the red variables Delta E\* values were very high and that indicates lack of lightfastness, but this should not be interpreted as a poor polymer, instead it should be recognized that red pigments, except for iron oxide and DPP red, weather poorly. Brown pigments also weather poorly if they are not made from inorganic pigments. When cost is part of the equation, the choice of pigments is often overlooked because lightfast pigments are very expensive, particular organics. Light fast color like grays can be manufacture at lower pigment cost than reds, blues, greens, and browns.

Some of the other variables were produced with a low gloss and there were no significant change in gloss and as we observed the shift in gray colors will be approximately 1.5 Delta E\*. It was recommended that the client request a low to medium gloss, gray color as the target coating. Black absorbs IR and converts a larger portion of the energy to heat that will lead to polymer degradation. White coatings get dirty and high chroma colors require expensive pigments to limit fading.

## CONCLUSIONS

Paint coatings have an outstanding history in protecting galvanized steel from corrosion in atmospheric and soil/water table environments. Experience has shown that a proper surface treatment program prior to painting is an effective means of preventing corrosion of galvanized steel in corrosive environments. Further research should focus on specific aspects of the corrosion of painted galvanized coatings in various environments and possible non-chromate pretreatments effective in establishing a protective film. Electrochemical impedance spectroscopy (EIS), in conjunction with environmental tests, will provide a sound scientific basis for this comparison and corrosion protection performance that are not readily obtainable with traditional accelerated corrosion tests.

A coatings' corrosion performance can be evaluated from its EIS data. Coatings exhibiting  $10^7 - 10^{10}$  Farads capacitance and above 85% protection in 2000 hours salt spray provide long term protection in chloride-containing environments. Based on these criteria, an epoxy primer with aliphatic polyurethane top coat on galvanized steel provides long term protection in corrosive environments.

EIS data can also provide a minimum thickness for a coating to act as an effective barrier. The capacitance magnitude may be used to determine what type of corrosion process is occurring at the coating – galvanizing interface.

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6. ASTM G 154-04, "Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials," American Society for Testing and Materials (ASTM) International, West Conshohocken, PA, 2004.

7. ASTM D 523-89(1999), "Standard Test Method for Specular Gloss," American Society for Testing and Materials (ASTM) International, West Conshohocken, PA, 1999.

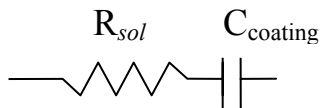


Figure 1: Electrical equivalent of an excellent coating.  $R_{soln}$  is the resistance of the electrolyte used, is not a property of the coating, and is negligible in the context of most coatings (1ppm or less).

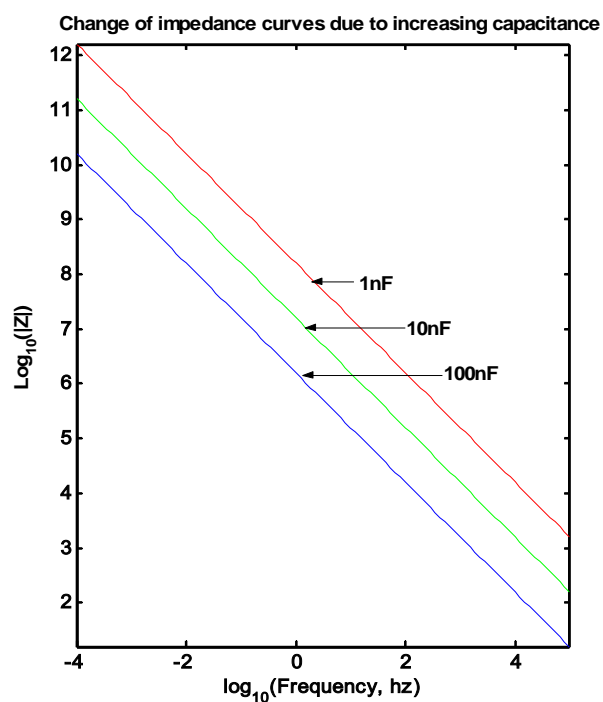


Figure 2: Changes to a modeled coating undergoing hydration and resulting shift in the impedance spectrum.

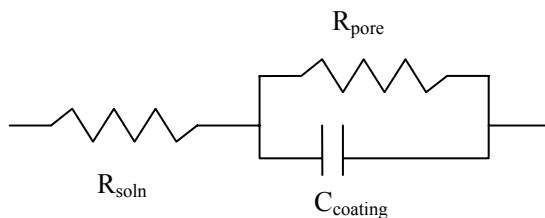


Figure 3: Randles Cell Equivalent circuit model of a non-ideal coating.

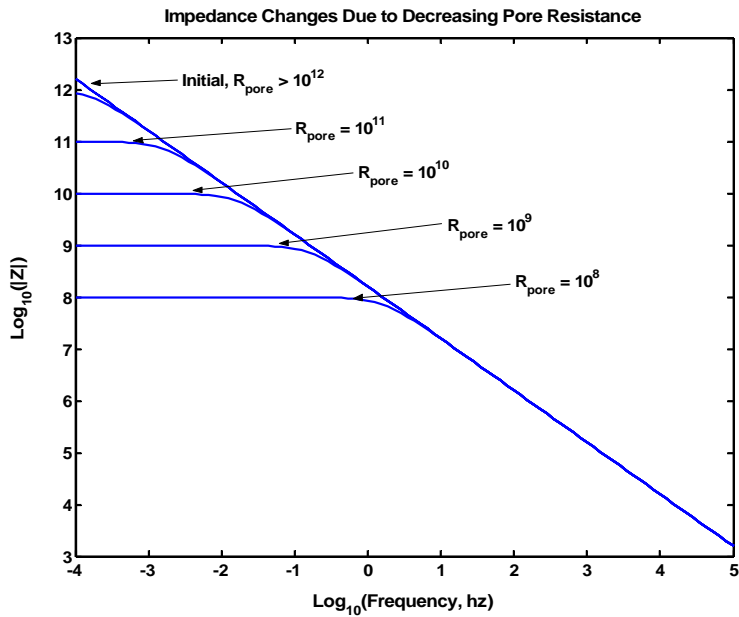


Figure 4: The pore resistance which is in parallel with a coating's capacitance forms an upper limit for the coating's impedance, as shown here in a simulation. The pore resistance can be seen to steadily decrease during aging. The rate at which the pore resistance decreases is an excellent indicator of coating endurance.

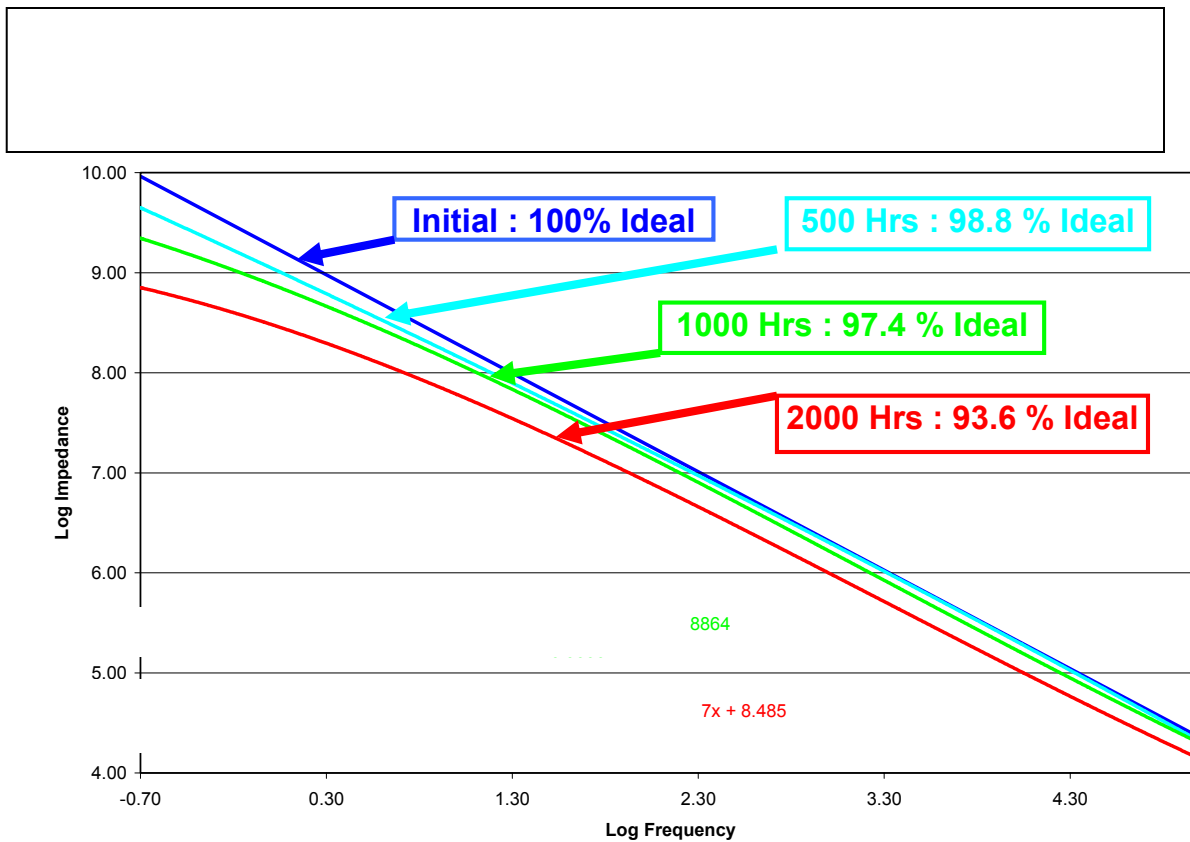


Figure 5. Manufacturer 3-B coating, consisting of Epoxy / Aliphatic Polyurethane, showed the least degradation with 2000 hours of salt spray exposure, and exhibited a moderately decreasing but very high coating resistance of in excess of  $10^9$  ohms\*cm<sup>2</sup> as well as a slight increase of coating capacitance.

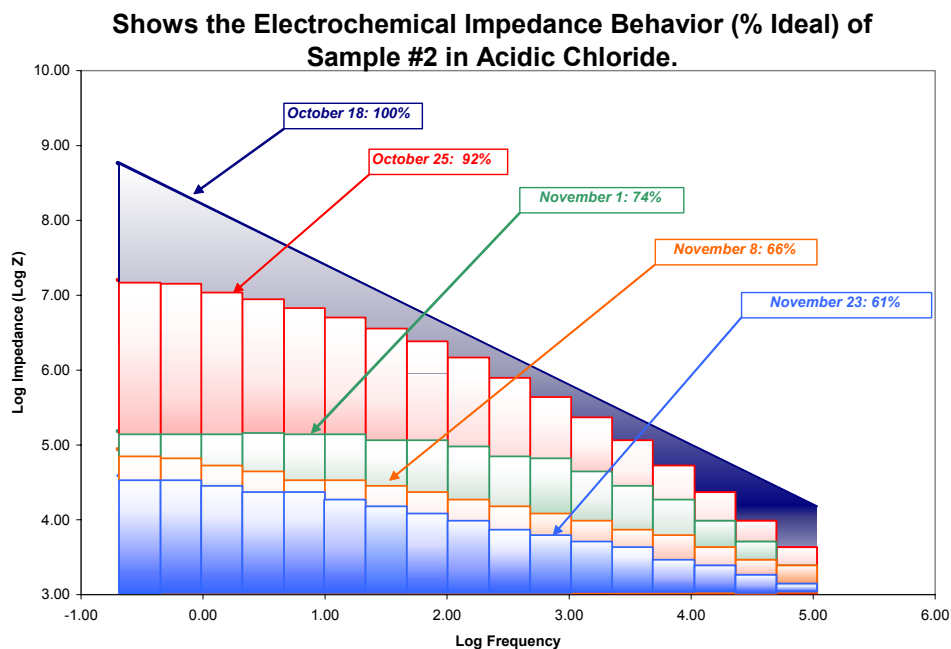


Figure 6: EIS behavior over time, expressed as percentage of initial protection, for sample #2 (Manufacturer 1 – B coating system) in acidic chloride solution.

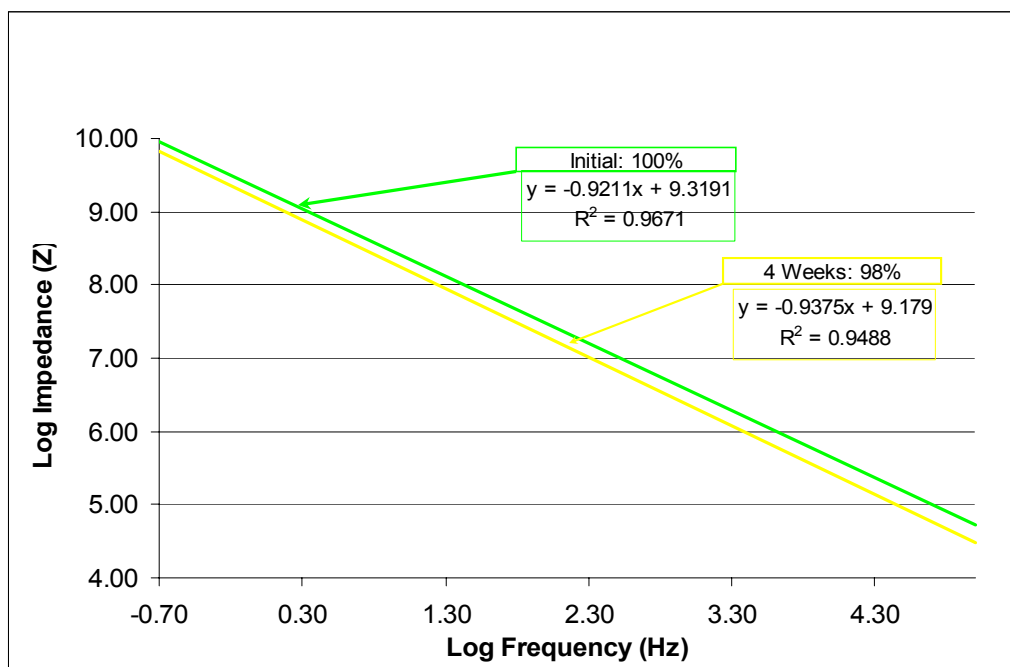


Figure 7: EIS percent protection comparison of the Repair Coating A Sample in acidic chloride solution.

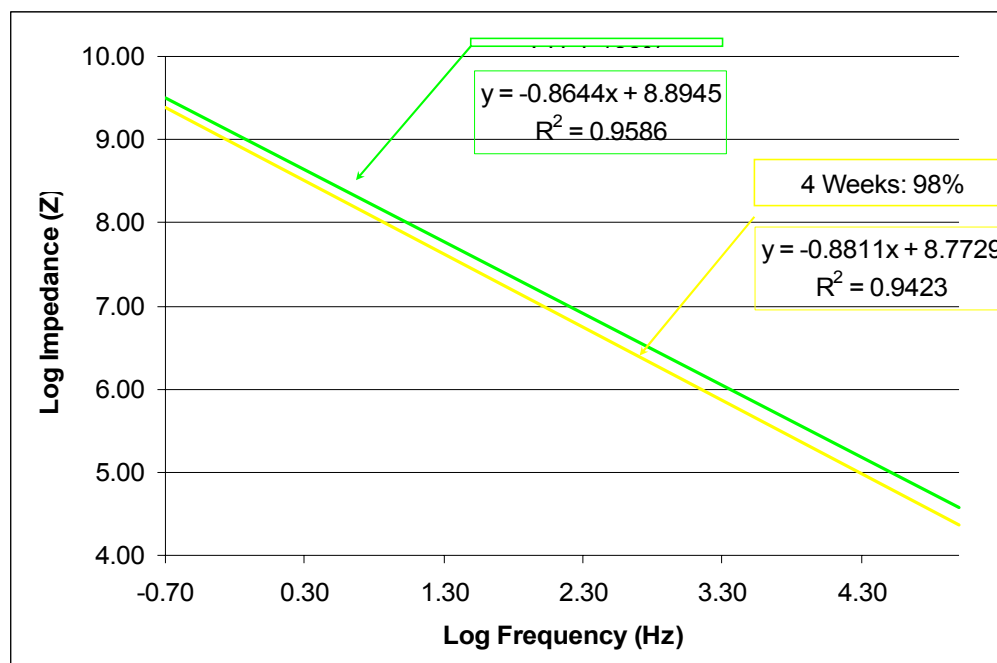


Figure 8: EIS percent protection comparison of the Repair Coating B Sample in acidic chloride solution.