

Fundamentals of Corrosion and Its Relevance to Prepainted Metal

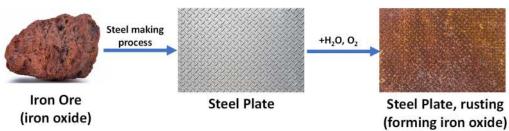
#### Introduction

This document introduces the fundamentals of corrosion and its relevance to coil-coated metal. The intent is to provide general background information on the subject that may be useful to both technical and non-technical personnel who will encounter corrosion during their career. The tool kit is not intended to be an exhaustive dissertation on the subject of corrosion chemistry.

#### The Nature of Metals

Metals ordinarily exist naturally as oxides (*e.g.*, iron oxide, aluminum oxide; any metal that has reacted with oxygen and water) because oxides represent their lowest energy state (*i.e.*, iron would rather exist as an oxide, not a metal; the same with aluminum and most other metals). We may think of iron, steel and aluminum as stable materials, but we know that steel oxidizes (rusts), which is nothing more than iron attempting to change back to its preferred state—iron oxide.





Aluminum is considered to be an inherently corrosion-resistant metal, but aluminum oxidizes almost instantaneously to form a very thin aluminum oxide layer, and this impervious layer prevents further oxidation. Like iron, aluminum too is driven to its preferred oxide state.

#### **Electrochemical Aspects of Corrosion**

Corrosion is an electrochemical process (*i.e.*, a chemical reaction in which electrons are generated in one part of the reaction and consumed in another part). These reactions are also called oxidation-reduction reactions (often abbreviated "redox"). There is a copious amount of literature if one wishes to take a deep dive into corrosion chemistry. This chemistry is not trivial, and many accelerating factors (*e.g.*, salt, acidic pollution, caustic environments) further complicate the chemistry. For this tool kit, therefore, we will only address the practical aspects of corrosion and the means to minimize this tendency. However, a bit of chemistry at this point is important. When iron (*e.g.*, the steel plate shown above) rusts, it happens in a number of steps, the first being:

**Fe** (metal)  $\longrightarrow$  **Fe**<sup>2+</sup> (iron ions in an aqueous solution) + 2e<sup>-</sup> (electrons)

The iron ions and electrons will then react with water and the oxygen in the air to form red rust. The important observation here is that electrons are produced in one reaction and

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educational aids developed by the

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consumed by water and oxygen in second reaction (not shown here for the sake of simplicity). The involvement of electrons in these reactions is the "electrochemical" aspect of corrosion chemistry.

## **Preventing Corrosion of Metals**

In a practical sense, there are just two ways to prevent corrosion:

1.) Barrier protection—This is what aluminum does when it forms a very thin, impervious oxide layer, eliminating or drastically minimizing the metal's exposure to water, oxygen, salt, etc. Aluminum does this on its own, but iron and steel are another matter. Very thick coatings are needed for an application utilizing steel, of which there are many. A bridge or water tank—both comprised of steel components—may have 15 mils of coating applied to the structure, which provides an excellent barrier, keeping the steel protected from the elements. In other words, if you can keep water and oxygen away from steel, the chemical reaction shown above will not take place.



 $Source: http://resource.npl.co.uk/docs/science_technology/materials/life_management_of_materials/publications/online_guides/pdf/protection_of_steel_bridges.pdf$ 

We deal with substantially thinner films in coil coatings, so barrier protection in most cases is not a useful option. Also, prepainted coils are processed (*e.g.*, cut, punched, notched, etc.), creating "cut edges," making an effective barrier at this edge a substantial challenge.

2.) Galvanic protection—This is the preferred method used to protect steel substrates and will be discussed in detail below.

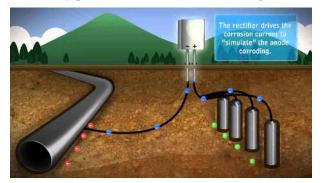
## **Galvanic Protection of Steel**

For massive steel objects, such as oil and gas pipelines, where even a pinhole perforation can lead to a catastrophic event, a direct current power supply pumps electrons into the steel pipe, which prevents the iron (steel) pipe from losing electrons, which is what happens as steel corrodes. The process is called cathodic protection. This requires complex engineering and is an expensive way to prevent corrosion, but it is justified with considering critical infrastructure. Although the term "cathodic" has not yet been discussed, there is a way to better understand how this mechanism actually prevents corrosion. Referring to the aforementioned electrochemical reaction, chemists like to talk about the right-side and the left-side of a reaction (*i.e.*, the right-side of the arrow and the left-side of the arrow). In the case of cathodic protection, electrons

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are pumped into the steel pipeline, which is akin to flooding the right-side of the chemical equation, which effectively prevents iron (Fe) from forming  $Fe^{+2} + 2e^{-}$ .



Source: GSG Systems

The other approach to controlling the corrosion of steel is to connect a material to the steel substrate that is more reactive—will corrode more readily—than steel. In this fashion, this material is "sacrificed" to preserve the steel. Some Navy vessels, for example, attach large zinc plates to the steel hulls.



In the coil coating industry, we do much the same thing with the various metallic-coated steel products (hot-dipped galvanized steel; zinc-aluminum products such as Galvalume® and Galfan®; and magnesium-modified zinc-aluminum coatings). These three metals—zinc, aluminum, and magnesium—are more reactive than steel, and they will, as a result, preferentially corrode, protecting the steel substrate in the process. This sacrificial process of protecting steel is yet another electrochemical process.

Although this tool kit is avoiding a deep discussion about corrosion electrochemistry, a modicum of information at this point is needed. The description of how zinc protects steel in our industry is best described by the GalvInfo Center, in their GalvInfo Note  $3.6.^1$ 

Corrosion reactions require four components: an anode, a cathode, an electrical circuit and an electrolyte. Galvanic corrosion is the corrosion that results when two dissimilar metals with different potentials are placed in electrical contact in an electrolyte. The difference in electrical potential that exists between the different metals serves as the driving force for electrical current flow through the electrolyte. This current results in corrosion of one of the metals. The larger the potential difference, the greater the probability of galvanic corrosion. Galvanic corrosion only causes deterioration of one of the metals. The

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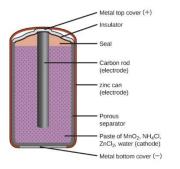
<sup>&</sup>lt;sup>1</sup> https://www.galvinfo.com/wp-content/uploads/sites/8/2017/05/GalvInfoNote-3-6.pdf

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less resistant, active metal becomes the anodic corrosion site. The stronger, more noble metal is cathodic and is protected. The electrolyte is almost always an aqueous medium that conducts electricity. It can be any moisture that is in contact with both metals, including condensate, dew, rain, bulk water (flood, etc.), damp debris that contacts both metals, moisture in soil, etc. When zinc and steel are in contact in the presence of an electrolyte, a current will flow from the steel to the zinc, so that the zinc becomes an anodic electronproducing region while the steel is cathodic and consumes electrons, preventing it from combining with oxygen and forming rust. This property of zinc is used in many applications as a galvanic protector of steel. The zinc coating also acts as a barrier, further protecting the steel.

The highlighted sentence above explains the fundamental corrosion chemistry associated with typical metallic-coated steel. If the above discussion of anodes, cathodes, and an electrical circuit sounds like how one might describe a battery, that observation is apropos. Consider a D cell alkaline battery. If you were to dissect it, you would find a graphite rod (the cathode), a zinc casing, which is the wall of the D cell battery, and a paste-like material, the electrolyte.



Source: BCampus OpenED, Creative Commons

When one connects the battery to a circuit to activate a motor or to light a bulb, the zinc casing undergoes an electrochemical reaction with the electrolyte and releases electrons. The zinc casing is the anode of the battery. These electrons flow through the copper wires of the electrical circuit, and return to the battery's cathode, the carbon rod in this example. To produce the electrons, the zinc must react, and, at some point, all the zinc metal is consumed, and the battery no longer works. The electrochemical, oxidation-reduction reaction in battery is fundamentally the same kind of reactions that occurs as metals corrode. As you might imagine, there is a great deal more going on that allows a battery to function as well as it does. The point being made, however, stands: Certain chemical reactions cause electrons to become available that have an effect to either illuminate a light bulb (via a battery) or cause corrosion, which is the topic being discussed here.

Keeping the terminology straight and understanding what is producing electrons and which material is receiving them is admittedly a topic best left to those *researching* various ways to eliminate corrosion. For

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the vast bulk of people, this level of understanding has only limited practical value. The following scale, however, will simplify and clarify some issues.

Galvanic Series of Metals and Alloys					
	Corroded End (anodic, or increasingly ive)				
	Magnesium and Magnesium alloys Zinc				
	Aluminum 1100 Cadmium Aluminum 2024-T4 Iron and Steel				
	Lead Tin Nickel (active) Inconel nickel-chromium alloy (active) Hastelloy Alloy C (active)				
	Brasses (Cu-Zn alloys) Copper Bronzes (Cu-Sn alloys) Copper-nickel alloys Monel (70Ni-30Cu)				
	Nickel (passive) Inconel (80Ni-13Cr-7Fe)				
	304 Stainless Steel (passive) 316 Stainless Steel (passive) Hastelloy Alloy C (passive)				
	Silver Titanium Graphite Gold Platinum				
	Platinum rotected End (cathodic or reasingly inert)				

Source: Fastenal

The Galvanic Scale describes an order of reactivity of metals. Toward the top of the list lie metals that are more reactive (*e.g.*, zinc, aluminum, steel/iron), compared to metals that fall toward the bottom of the list that are not prone to corrosion reactions (*e.g.*, gold, silver, platinum). To protect steel, it needs to be coated with other metals that lie *above* steel and iron on the Galvanic Scale. Commonly-used metals are zinc, aluminum and magnesium. These metals are more anodic than steel and therefore will preferentially corrode. Coating steel with zinc (or the various zinc-aluminum-magnesium combinations) makes the metallic layer the anode—the part of the "battery" that corrodes during an electrochemical reaction.

## **Corrosion of Prepainted Metal**

In a typical coil coating process, metallic-coated steel and aluminum is cleaned and pretreated, before painting. We have already mentioned that the coils as received have built-in corrosion resistance: Aluminum has its natural barrier coatings (that thin aluminum oxide coating), and metallic-coated steel has a sacrificial

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coating provided by the mills. Cleaning the coils removes oxides and mill oils, which is required for the pretreatment to successfully wet the substrate and react with it. A properly pretreated substrate will maximize the adhesion between subsequent organic coatings (primer, topcoat). Both the pretreatment and primer play a role in corrosion protection, but most of the protection is associated with the substrate. Aluminum is inherently corrosion-resistant, but metallic-coated steel is more of a challenge.

When corrosion occurs, it occurs within the metallic substrate. As corrosion occurs beneath the primer layer, alkaline (caustic) species may be formed, and most organic binders are sensitive to aggressive, caustic conditions. Epoxy and phenolic resins are often the go-to binders for industrial maintenance applications (water tanks, oil platforms, refineries), because of their excellent chemical resistance. Epoxy and phenolic resins, however, are not very flexible, which limits their use in coil coatings.

Adhesion of the organic primer to the pretreated metal is an underappreciated phenomenon. If a primer has excellent adhesion to the substrate, and if a small spot of corrosion take place (*e.g.*, from a scratch), the corrosion *might* remain localized. If, however, the adhesion to the substrate is poor, it is easy to imagine that corrosion would more readily creep under the primer and progresses along the substrate.

Considering the cleaned, pretreated, and painted metal substrate as a system, and recognizing the prepainted metal products in the building and construction industry will have cut edges, there are important factors to consider when designing a product with sufficient corrosion resistance.

As mentioned earlier in this tool kit, the mechanisms that describe corrosion are complex. The *result* of corrosion taking place, however, is far easier to discuss, since there are a number of failures that one will encounter, each of which are easily observed:

- 1. Galvanic corrosion (dissimilar, or mixed-metal, corrosion)
- 2. Cut-edge corrosion
- 3. Blistering
- 4. Filiform corrosion

## **Galvanic Corrosion**

When considering the Galvanic Scale, the further apart two metals are on the scale the greater the electrochemical reaction will be, which leads into two important and practical considerations, both of which are part of the overall problem of galvanic corrosion:

1. **Dissimilar metals**: A copper gutter, which is a beautiful architectural feature, presents a real problem for galvanized steel and aluminum prepainted metal. Copper falls far below both in the Galvanic Series. Once moisture is introduced into the steel-copper, zinc-copper or aluminum-copper "battery," massive corrosion of the substrate will occur. Copper is more noble the steel, zinc and aluminum, and these beautiful gutters drive the corrosion mechanism of galvanized steel and aluminum. A similar corrosion problem will occur when the wrong fastener is chosen. For example, it may seem sensible to use a stainless steel screw to affix a hot-dipped galvanized roofing panel to a wooden frame. By referencing the Galvanic Series (above), it will be seen that stainless steel falls

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far below zinc and steel. As a result, galvanic (mixed-metal) corrosion will occur. The set of suggestions below will give the reader myriad variables to consider to avoid galvanic corrosion.

	Fastener Material									
Metal Roof or Wall Cladding Material	Zinc Plated Steel Screws <sup>2</sup>	Organic Coated Steel Screws <sup>2</sup>	Hot-Dip Galvanized Steel Nails <sup>3</sup> and Screws	Zinc-Alloy Head Steel Screws	Stainless Capped Head Steel Screws	Aluminum	Copper and Copper Alloys	300 Series Stainless Steel	400 Series Stainless Steel	
Unpainted Galvanized Steel	Yes <sup>4</sup>	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	
Painted Galvanized Steel	Yes⁴	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	
Unpainted Galvalume Steel	No	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	
Painted Galvalume Steel	Yes⁴	Yes	Yes	Yes	Yes	Yes	No	Yes*	Yes <sup>4</sup>	
Aluminum	No	No	No	No	No	Yes	No	Yes	No	
Copper & Copper Alloys	No	No	No	No	No	No	Yes	Yes <sup>4</sup>	Yes <sup>4</sup>	
Stainless Steel	No	No	No	Yes	Yes	No	No	Yes	Yes	
Zinc alloy	No	No	No	No	No	No	No	Yes	Yes	

Note 1: Cautionary Guideline: This table serves as a guideline for the selection of fasteners used with metal roofing. The performance of compatible fasteners shown in this table matches the expected life of the metal roof or wall cladding materials. However, in highly corrosive environments such as heavy industrial, coastal marine, high airborne pollutants or salt spray, preservative treated lumber or fire-retardant lumber, the compatibility of certain fasteners with metal roofing or wall cladding materials may be affected. In those types of applications, the manufacturers of the fastener and metal panel will have specific and unique recommendations.

In addition, in the event that certain coating barriers are damaged or scratched through to the substrate there is increased potential for premature corrosion. Care should be taken during installation and during routine maintenance of the panels in order to protect the integrity of the coatings used for metal panels.

Note 2: Screws should be plated/coated per ASTM F1941

Note 3: Nails should be galvanized per ASTM A153

Note 4: Not recommended for coastal and heavy industrial environments

Note 5: Commercial availability of threaded aluminum fasteners is very limited due to their lower torsional, tensile, and shear properties.

Source: Metal Construction Association

In the pictures below, the photo to the left shows under-film blistering, resulting from using a stainless steel fastener with a Galvalume®/Zincalume® prepainted panel. Once the blistered paint is scraped away, corrosion is seen on the metal substrate, *but not the fastener*. In this case, the

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substrate is being sacrificed, while the fastener remains uncorroded. The importance of choosing the proper fastener for the prepainted metal being used cannot be overstated.



Source: Steelscape

There are other examples of dissimilar-metal corrosion, but the key takeaway remains: The further apart metals lie on the galvanic series, the more aggressive the corrosion will be.

2. **Graphite**: The second observation is to note where graphite lies in the Galvanic Series. It is one of the most noble metals, which is why using a pencil to mark a building panel is not recommended. As innocuous as it may seem, there are many examples of graphite-prepainted metal corrosion problems that have been observed. Here is an example of what may happen:



Source: U.S. Steel Corporation

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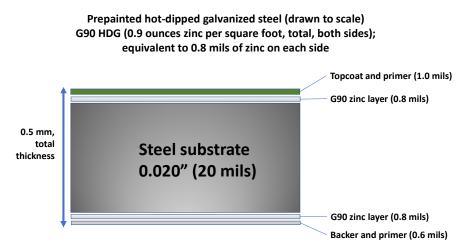
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Graphite is about a far away from zinc, aluminum, magnesium and steel as a material can get, which explains why a using a pencil to mark a panel can lead to an area that corrodes badly...and also explains why a D cell battery has a graphic rod as a cathode.

## **Cut-edge Corrosion**

Mentioned earlier, nearly all prepainted metal is processed, and this processing produces a fresh crosssection of metal. Whether steel or aluminum, corrosion at the exposed surface is very likely to occur. For aluminum, this fresh metallic surface will oxidize quickly, and an effective aluminum oxide barrier will form, curtailing additional corrosion. Steel is a different scenario.

The following is example of a typical prepainted metal cross-section of a metal building product, where 0.020-inch G90 hot-dipped galvanized steel is pretreated and painted.



Source: National Coil Coating Association

It is well known that a thicker galvanized zinc layer offers greater protection than thinner layers. A standard zinc layer thickness is G90. But, relative to the thickness of a typical gauge thickness used in the industry—0.020 inch, in this example—the zinc thickness is thin relative to the thickness of the steel substrate; yet G90 HDG is a substrate with a 50+ year lifetime. This very thin layer of zinc provides amazing benefits.

Corrosion is most likely to form where the steel substrate has been completely exposed during processing (*e.g.*, from a cut edge), or from a scratch that penetrates the paint system, the pretreatment, and the metallic coating (HDG in above example). It is easy to visualize red rust corrosion occurring at the cut edge of a prepainted metal roof panel (also described as the drip edge of the roof panel). If you are viewing this edge head-on, however, the thickness of this panel is only 0.5 mm. So long as the cut edge corrosion is confined to this exposed face of the panel, the inconsequential cosmetic red rust may not be apparent and is not usually of much concern. Problem occurs, however, when the corrosion at the cut edge begins to migrate *up* the roofing panel, and where you might see, for example, one inch (25 mm) of corrosion activity. Even if this corrosion remains cosmetic (*i.e.*, not creating a mechanical problem), a noticeably rusted area may result in a complaint. This is where a G90 layer of zinc provides the necessary corrosion

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resistance. Recall that it is sacrificing itself—corroding—to prevent the steel substrate from corroding. The thicker the layer of zinc, the longer it can sacrifice itself to protect the steel substrate, especially in aggressive environments. In the "acid rain era"—now to a large degree abated—it was shown that G60 HDG failed at a much greater rate than G90.

Although cut edge corrosion is a theoretical weakness to using prepainted metal, studies have shown that this edge, if designed properly (*i.e.*, choosing the proper substrate, pretreatment, primer, topcoat and backer), does not present a problem, and may provide better edge performance than a similar part that has had a paint system *post*-applied (*i.e.*, spray painted, or powder coated).

During installation, prepainted metal panels may be scratched in a wide variety of ways. Although a scratch down to the steel substrate should be avoided, this kind of scratch may only be 1 mm wide and 10 mm long (10 mm<sup>2</sup>), and it is surrounded by a vast area of zinc metal, all of which is available to minimize corrosion and limit the damage to just the scratched area.

The severity of corrosion at cut edges and scratches is dependent upon the environmental conditions. Long wet times, high chloride levels, acidic and caustic conditions will exacerbate corrosion.

## Blistering

Blistering always involves moisture permeation through the organic coating. It might have *nothing* to do with corrosion. Blistering may occur simply because moisture permeates the coating, but cannot effectively diffuse out of the coating. If there is sufficient pressure exerted by the moisture in the film, a small bubble (*i.e.*, a blister) will form. Of course, the same defect—blistering—may occur from moisture permeating the coating and becoming involved in an electrochemical reaction with the surface of the substrate. Poor inherent adhesion of the primer to the substrate will exacerbate a blistering tendency. Formation of corrosion products occurs, and eventually the corrosion products become voluminous enough to lift the paint film and give an unsightly appearance. When discussing a corrosion condition with others, you may encounter the terms "cathodic delamination" or "anodic delamination." Although these terms may accurately describe the chemistry of corroding metal, they are often inaccurately used and of little value when considering the root cause of problem, or when attempting to develop technology that reduces *any* kind of corrosion chemistry. It is important, however, to know for a fact whether corrosion is causing the blister to form, or whether it is any of a number of other non-corrosion causes of corrosion.

#### **Filiform Corrosion**

Filiform corrosion is a special type of corrosion. It is an unusual type of attack, since it does not weaken or destroy metallic components, but only affects surface appearance. The attack appears as a network of

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corrosion product trails. The filaments consist of an active head and a corrosion product tail. The filaments are 2 mm or less wide, and corrosion occurs only in the filament head.



Source: https://commons.wikimedia.org/wiki/File:Filiform corrosion on painted aluminum.jpg

Filiform corrosion only occurs between 65% and 90% relative humidity. The most common instance of filiform corrosion of coil-coated metal is prepainted aluminum or steel used or stored in humid environments (e.g., washing machines, building components such as eaves or gutters/downspouts). There is no completely satisfactory way to prevent filiform corrosion. Two approaches to minimize it are to store and use painted metal in low humidity environments, and to use paint coatings of very low moisture permeability.

## Conclusion

Corrosion science is very complex. The chemistry of the environment dramatically effects the type of corrosion chemistry that takes place. Because of the variety of environments into which prepainted metal is placed, there can be no one accelerated test to determine how a product will perform in these various environments. Unlike sunlight weathering in Southern Florida—a universally-accepted standard weathering location—corrosion has no such standard weathering site. Industry does real-time, near-shore ocean testing, but this only assesses long wet time, high chloride conditions. One learns almost nothing about the performance of prepainted metal that will be installed in environments that are caustic or acidic. Fortunately, at our current level of understanding, the coil coating industry routinely produces prepainted metal with an extensive service life, and work continues to drive the understanding of corrosion chemistry and to develop ways to further improve the performance of products.

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