

It has been claimed, usually by individuals and organizations that have a vested interest in the subject matter, that zinc rich paints and epoxies have the same characteristics as that of hot dip galvanizing.

As the Hot Dip Galvanizing Association Southern Africa, we also have a vested interest in this matter. However, as representatives of our segment of the corrosion control industry, our interest extends beyond the pure commercial aspects of the subject and relates rather to that of informed technical knowhow.

In order to examine the fundamentals of the subject matter of this article, one needs to return to the basic requirements of what constitutes a corrosion cell involving different metals. Such corrosion cells are also referred to as Bi-metallic couples or galvanic corrosion.

In order for such a corrosion cell to exist, four conditions must exist. These four conditions are listed below and illustrated in the simplistic diagram below;

- 1. Anode, from which electrons flow,
- 2. Cathode into which electrons flow,
- 3. An electrolyte, which will represent the corrosive environment in which the cell exists, and
- 4. A return external electrical circuit.

Remove any one of these four components and we can effectively stop corrosion. This of course is easier said than done.

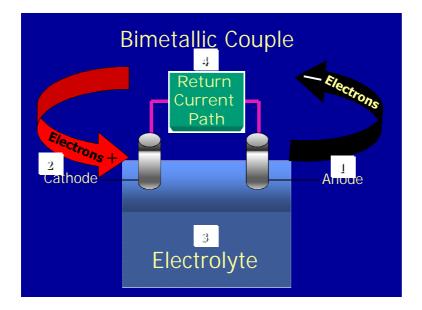


Fig 1: This diagram is designed to illustrate the four requirements of a corrosion cell or bi-metallic couple or galvanic corrosion.

It does not represent the more scientific model, which would normally include the chemical reactions.

Having briefly discussed what constitutes a corrosion cell, we can now introduce the two "different" metals that comprise a specific corrosion cell, viz. zinc and carbon steel. As a result of the relative positions of zinc and carbon steel within the galvanic series of metals, the zinc will always constitute the anode (electro-negative to carbon steel) and carbon steel will be the cathode (electro-positive to zinc). Using these two different metals within a corrosive environment (electrolyte) and providing an electrical connection, we have complied with the requirements of our corrosion cell.

It is for this reason that we define a corrosion cell as an electro-chemical reaction within its environment.



Figure 2 illustrates the point.

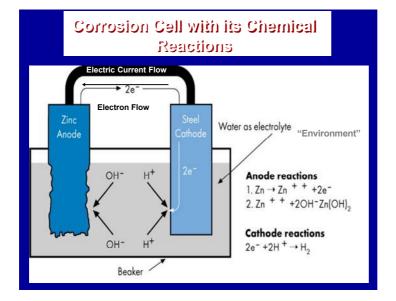


Fig 2: Note how the electronegative zinc anode will sacrifice itself to protect the electropositive carbon steel cathode.

From this physical characteristic of these two materials we can say zinc will provide cathodic protection to the carbon steel.

All forms of corrosion protective coatings applied to carbon steel provide one or other form of "Barrier Protection", separating the corrosive elements within the environment (electrolyte), from making electrical contact with the carbon steel. By fully coating and electrically insulating the carbon steel from the corrosive elements in the environment, we achieve a form of corrosion control.

Having established the basics of a corrosion cell, as applied to two identified metals (zinc and carbon steel) and introducing the primary means of corrosion control, (being that of a barrier protection), we can now examine "How Zinc Protects" carbon steel.

How does Zinc (Zn) Protect?

Introducing a "new and clean" zinc sample to the atmosphere, it will oxidise to form unstable water soluble zinc oxides (ZnO), zinc hydroxides (Zn(OH)₂), which depends on the atmospheric moisture content, and finally an insoluble dense zinc carbonate (ZnCO₃) patina.

The first two products of corrosion, $(ZnO \& Zn(OH)_2)$ are unstable and easily removed and provide no barrier protection. The $ZnCO_3$ layer, by contrast, is stable, not easily removed; matt grey in colour. It is this stable patina that forms the "Barrier Protection" for corrosion control of carbon steel. The following diagram is a simplified illustration of this corrosion process.

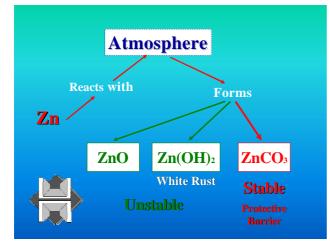


Fig 3: Pure "new zinc" reacts with the atmosphere (Oxygen, Moisture and Carbon Dioxide) and forms three products of corrosion. These corrosion products are zinc oxide, zinc hydroxide and zinc carbonate.



We often refer to zinc as a "wasting" material, due to the fact that it will sacrifice itself to provide corrosion control of carbon steel. It therefore follows that the more zinc (thick coatings) available, the longer the service life performance.

From the above we can now understand how zinc reacts to form its barrier protection, i.e. the $ZnCO_3$ patina. We can refer to this as zinc's 1st line of defence against the corrosion elements within a given environment.

Unlike other coating systems, zinc has a second line of defence. Zinc (anode) being electronegative to carbon steel (cathode), will provide cathodic protection of the carbon steel. This is also referred to as zinc being sacrificial to carbon steel. As an aside, this process is also referred to as a galvanic reaction and from which the term "galvanic corrosion" is derived.

Zinc Rich Paint versus Hot Dip Galvanizing

It has been claimed that zinc rich paint is equivalent to hot dip galvanizing. This claim is based on the fact that paint, being organic or inorganic, contains zinc metallic dust particles.

(Ref 1) "In order for a galvanic process to occur on steel painted with a zinc-rich coating, three conditions must be satisfied:

- 1. The zinc particles in the coating must be in electrical contact with each other.
- 2. The zinc particles must be in electrical contact with the steel.
- 3. A continuous electrolyte must exist between the zinc particles and the steel.

The first two conditions are met by zinc-rich coatings containing sufficiently high zinc content. The third condition is fulfilled when a steel panel bearing a zinc-rich coating is wetted by a film of electrolyte such as a salt solution.

There are two stages in the protective action of zinc-rich coatings. The first stage is a relatively short period in which galvanic protection of the steel by zinc particles is in effect. After this period, the galvanic action between the steel and zinc gradually disappears. The second stage is a long-term barrier protection that is attributed to a greater resistance of the coating to the permeation of aggressive species such as water, oxygen, and salts because the pores in the coating are blocked by the zinc corrosion products. The galvanic action generally decreases with time. The loss of galvanic protection is due to (1) the loss of electrical contact between zinc and steel as a result of corrosion of zinc particles and the formation of nonconductive corrosion products at the interface; (2) the loss of electrical contact between zinc particles as a result of the formation of corrosion products on the surface of the zinc particles; or (3) blockage of the coating surface by zinc corrosion products."

From the above referenced extract, all three conditions are required to be simultaneously applied for cathodic protection to be activated. Consider the following comments in terms of these three requirements.

- 1. The zinc particles in the coating must be in electrical contact with each other. This condition is most unlikely to occur as the majority of the zinc particles are separated by the paint matrix in order to maintain the "Barrier Protection" cohesion of the coating.
- 2. The zinc particles must be in electrical contact with the steel. As with condition 1, the paint matrix will tend to electrically insolate the majority of zinc particles from the steel substrate.
- **3.** A continuous electrolyte must exist between the zinc particles and the steel. This condition is self defeating, in that should the electrolyte be allowed to penetrate to the steel substrate the steel will corrode due to the lack of "Barrier Protection".



We would suggest that the degree of cathodic protection, with a sufficient quantity of zinc dust in the paint, can only be assumed to be, at best, limited. Further, within a short period of time, if cathodic protection was to be active, the individual zinc particles would corrode and thus insulate themselves and cathodic protection would cease all together. The value of the zinc rich paint is not so much that of cathodic protection, but rather that the zinc particles at the outer surfaces of the paint coating, will form corrosion products (ZnO & ZnCO₃) and thus assist to maintain and provide "barrier protection".

Turning to the characteristics of hot dip galvanizing, the coating consists of zinc and zinc / iron alloys that are metallurgically bonded to the steel. The electrical contact to the steel is guaranteed at the same time the zinc is exposed to the environment. It follows that with hot dip galvanizing, cathodic protection only becomes available and is activated should the steel be exposed by some small chip, scratch in the coating or a cut edge. This characteristic is generally referred to as zinc's second line of defence.

The first line of defence is not cathodic protection, but rather that of a barrier protection. A hot dip galvanized coating is impervious from the day it is produced. As described above, the "clean new" zinc will react with its environment to form three basic products of corrosion. Zinc must react or "corrode" and develop the stable ZnCO₃ layer. This layer constitutes the barrier protection or first line of defence against corrosion of carbon steel. One can conclude by saying hot dip galvanizing guarantees both barrier protection as well as long term cathodic protection as long as metallic zinc and zinc iron alloys remains available.

In order to illustrate the fundamental differences between the two forms of corrosion protection systems, we use the micrographic examples of the two coatings.

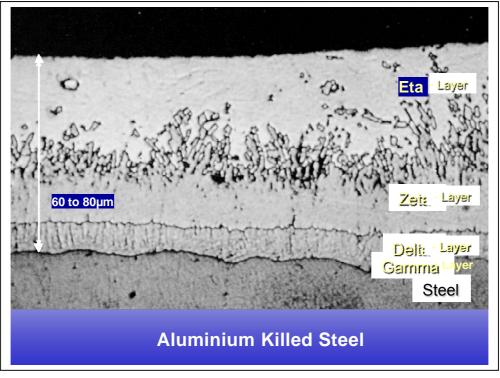


Fig 4: Micrograph of a typical hot dip galvanized coating.

Coatings range from 60 to 120 microns plus.

The metallurgical process of hot dip galvanizing follows the fundamental laws of physics, "If the steel is not perfectly cleaned, it will not galvanize".



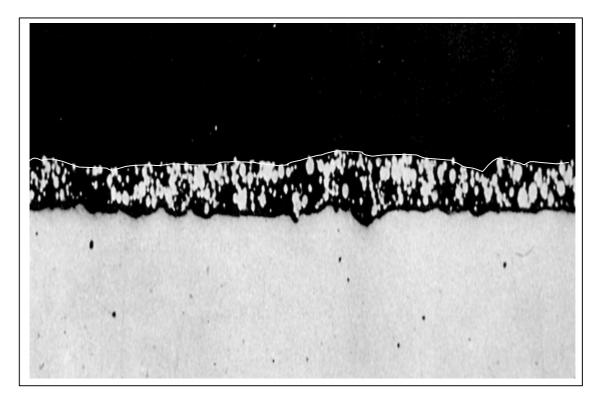


Fig 5: Micrograph of a typical zinc rich paint coating, applied by a skilled or semi-skilled operator.

Coatings can range from 20 to 70 microns, but usually require multiple applications in order to build a suitable coating thickness, which again is dependent on the type of paint.



Conclusions

The differences in the two forms of corrosion control of carbon steel can be summarised as follows.

Characteristic	Zinc Rich Paint	Hot Dip Galvanized
Barrier Protection	Yes, but a function of quality and thickness of coating. Zinc corrosion products assist to maintain the barrier protection.	Yes, follows metallurgical laws, forms a $ZnCO_3$ patina as the barrier protection. (1 st line of defence)
Cathodic Protection	Limited to 80 days or less and a function of the zinc particles within the DFT of the coating.	Yes, always available as long as zinc remains present. Only applicable if steel is exposed. (2 nd Line of defence)
Impervious Coating	Yes, but dependent on painter skills, specification and coating thickness.	The metallurgical process ensures an impervious barrier independent of operator skills.
Coating Thicknesses	± 20µm per application, up to 75µm with multiple applications. Dependent on the skill of the applicator.	The process produces a coating that ranges from $60\mu m$ to > $120\mu m$ dependent on steel thickness and chemistry. Achieved through a single dipping into molten zinc at 450° C.
Adhesion to the Steel	Mechanical bonding, which is a function of preparation in order to "key" the coating to the steel surface. Applying an inorganic coating when the RH is below 50%, without sufficient subsequent curing, can result in poor inter-coat adhesion of the topcoat.	Follows metallurgical laws (no curing) and is independent of operator skills. If the surface is not clean it will not galvanize. Easy to inspect.
Estimated Service Life in a C4 environment based on ISO 9223	8 to 10 years to 1 st maintenance, but dependent on the specification and quality of application.	20 to 40 years with an average of 30 years service life to 1 st maintenance.
Quality Control of the application	Numerous hold points and interim inspections for quality control.	2 hold points, one before galvanizing and one after galvanizing.
Application and process controls	A number of controls and environmental conditions must be in place before a coating application can be carried out.	Factory applied, independent of environmental conditions, but limited to process bath sizes.
Limitations	Not limited to size or site location, but limited by access to all steel surfaces	Limited by component size, factory applied, but all surfaces are accessible.
Continuity and Uniformity	Dependent on the skill of the operator and generally thin at corners and sharp edges	If the steel is not clean, such areas will show up as uncoated spots immediately after removal from the molten zinc.

Hot dip galvanized coatings were first used approximately 170 years ago. In this time, the basic technology has shown little or no significant changes. Hot dip galvanized steel over 100 years ago is fundamentally similar to hot dip galvanized steel today. The same metallurgical laws that applied then are the same laws that apply today. The international reputation of hot dip galvanizing has stood the test of time and has proven its natural ability to provide corrosion control in the majority of environmental conditions encountered in the modern world.



Zinc rich paints on the other hand, have been subjected to numerous changes aimed at improved performances. There is no question that a suitably specified and applied zinc rich paint or epoxy coatings will provide excellent corrosion control performance. However, as is the case with most paint coatings, the quality of the application is a significant factor in the determination of long term performance and service life of a particular system.

Zinc rich paint specifications usually publish the quantity of metallic zinc dust in the dry film thickness as a percentage of zinc by weight. Zinc is approximately seven times as dense as the paint binder material and therefore the actual volume of metallic zinc in the coating is in fact a lot less. When zinc is employed for corrosion control, the concept of "more zinc one has the longer the service life" is applicable.

When we compare hot dip galvanizing to any form of zinc rich paint or epoxy, the characteristics of the two systems are certainly not equivalent in terms of corrosion control and specifically in terms of cathodic protection.

Reference 1: Xiaoge Gregory Zhang: Corrosion and Electrochemistry of Zinc – page 340