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P151508 Major Project Corrosion

Testing 2019

by Christopher Jones

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Corrosion Test Benchmark for the Saftey Letterbox Company

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RENZ

**THE SAFETY
LETTERBOX
COMPANY LTD**



This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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Date:

Abstract

Corrosion protection is a consistent occurrence in many materials. Exposure of certain metals and alloys to the environment leads to oxidation in which the material loses its electrons to the oxygen in the atmosphere which in turn forms corrosion products in the form of positive metal ions that are shed from the material. This occurs as a result of the atmosphere around the material acting as an electrolytic substance allowing for a medium through which the oxidation reaction is driven. There are various ways to mitigate the effects of corrosion which are outlined in this report. One method of protection of steel from corrosion is by coating the steel with a zinc substrate also known as galvanised steel. The tests performed in this report observe the nature of cut edge corrosion, whereby the protective substrate (Zn) is severed during the cutting process of the sheet metal during the manufacture of products. As well as describing the process of corrosion and the various protection methods used in industry, the report also explores the possibility of self-healing mechanisms that can be mixed into primer coatings and applied to the materials.

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1 Aims and objectives of the project

Oxidation is the process by which an atom/compound loss an electron to an oxidising agent. Oxygen is usually the main cause of the oxidation process due to its abundance and its high electronegativity and this is why it is referred to as oxidation, fluorine is the only element in the periodic table to have a higher level of electronegativity but is less available in the atmosphere when compared to oxygen. Reduction is the process by which an atom/compound gains an electron from a reducing agent.

Changes in chemical properties associated with the redox reaction are frequently linked to diminishing the integrity and functioning of structures and components due to degradation of the materials that are used in the manufacturing process. This can decrease the life span of a product and increase maintenance costs.

1.1 The aim of the project

To provide the company safety letter box (SLB) with valuable insight into how their products react in an external environment and to test a specific product material that will be exposed to varying pre-treatment processes. These processes have been obtained from SLB in order to determine the cause of corrosion and to utilise the research methods to facilitate the analysis of the tests in order to suggests possible improvements that can be introduced into the manufacturing process.

Phase 1: Benchmark

In order to provide a benchmark for SLB, corrosion tests will be performed on samples obtained from SLB.

Testing method

Simulating an atmospheric condition that the product is likely to experience by placing the test samples into a salt spray chamber that will be provided be the UWTSD and observing the rate of corrosion that the product undergoes.

Test Chamber

Cyclic Corrosion Test Chamber

Models:

CC1000ip

Phase 2: Improvement

Research and implement possible improvements that can be introduced into the manufacturing process.

2 Timing Plan

11/09/18: Meet with safety letterbox to establish the problem

19/09/18: Meeting: With SLB to review the manufacturing process

26/09/18: Meeting: with SLB to identify the testing method necessary, ISO 9227

07/11/18: Meeting with A thorn to discuss samples and testing method.

08/11/18: Meeting with R Alexander to discuss points of consideration for the dissertation

19/11/18: Meeting with R Alexander to discuss the sample range and colour of samples

12/12/18: *Interim oral examinations*

04/12/19: Test chamber set up and calibrated

01/02/19: Meeting with Mark Hacker to discuss sample size and set a date delivery of samples.

04/02/19: Calibration of dip troughs at SLB

06/02/19: Samples ready for collection

11/02/19: Start of testing

14/02/19: Chamber malfunction

06/03/19: Start of testing (2) Separate chamber

15/04/18: Test specimens out of chamber ready of analysis

16/04/19: Analysis of results

30/04/19: *Final Dissertation report due*

01/05/19: *End Final Viva*

3 Research

3.1 Cost of corrosion

As products and manufacturing products become larger and more complex it is important increase attention on the corrosion in general. This is because the penalties that come with failure from corrosion whether they be, safety hazards, financial, or interruptions in plant operations, have generally increased. The costs of corrosion can either be in the form of direct costs to the owners and operators, and indirect costs to the users. Most studies are based on direct costs as indirect cost are more difficult to calculate. An example of indirect costs are things like traffic delays due to bridge repairs or higher costs to the public for equipment maintenance etc.

[1]

Table 1: Global cost of corrosion by Region/Sector (Billion USD)

Economic Regions	Agriculture CoC USD billion	Industry CoC USD billion	Services CoC USD billion	Total CoC USD billion	Total GDP USD billion	CoC % GDP
United States	2.0	303.2	146.0	451.3	16,720	2.7%
India	17.7	20.3	32.3	70.3	1,670	4.2%
European Region	3.5	401	297	701.5	18,331	3.8%
Arab World	13.3	34.2	92.6	140.1	2,789	5.0%
China	56.2	192.5	146.2	394.9	9,330	4.2%
Russia	5.4	37.2	41.9	84.5	2,113	4.0%
Japan	0.6	45.9	5.1	51.6	5,002	1.0%
Four Asian Tigers + Macau	1.5	29.9	27.3	58.6	2,302	2.5%
Rest of the World	52.4	382.5	117.6	552.5	16,057	3.4%
Global	152.7	1446.7	906.0	2505.4	74,314	3.4%

[2]

The table shown above is an example of the global cost of corrosion using past studies, it is therefore not a reflection of new data and is limited by the number of studies available and the content of each study.

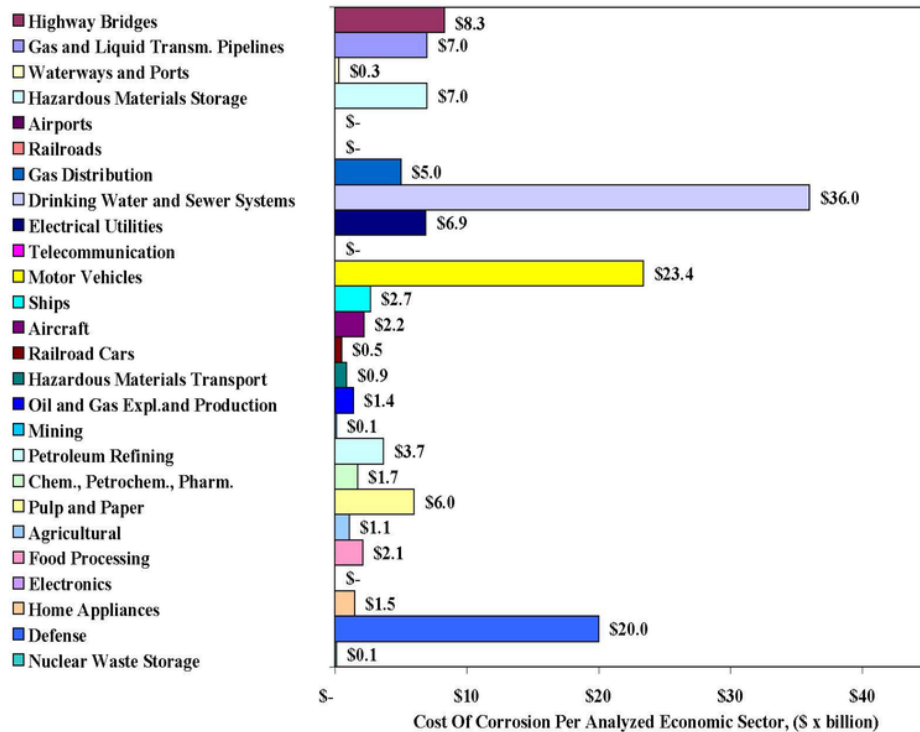


Figure 1: US study of costs due to corrosion by sector

The information above is provided by the NACE International Corrosion Society and outlines the cost by economic sector in the US. It provides an example of the areas most affected by the problem of degradation by corrosion and the costs involved. It should be noted that all costs are direct corrosion costs and it does not include:

- Costs of labor attributed to corrosion management activities
- Cost of the equipment required because of corrosion-related activities
- Loss of revenue due to disruption in supply of product
- Cost of loss of reliability

[3]

A recent study estimated the total annual cost of corrosion in China at over 310 billion US dollars, representing 3.34% of the country's GDP. If the same percentage is applied to global economy, the total cost of corrosion worldwide amounts to ~2.5 trillion US dollars per year.

[4]

3.2 What is corrosion?

3.2.1 Galvanic Corrosion

Corrosion is the result of a chemical reaction in which the metal being corroded is losing electrons to another element, which is usually, in the case of atmospheric corrosion, oxygen. An observation of this can be made with a simple device known as a Daniel cell which simulates how two dissimilar metals react through an electrolyte to get a spontaneous redox reaction.

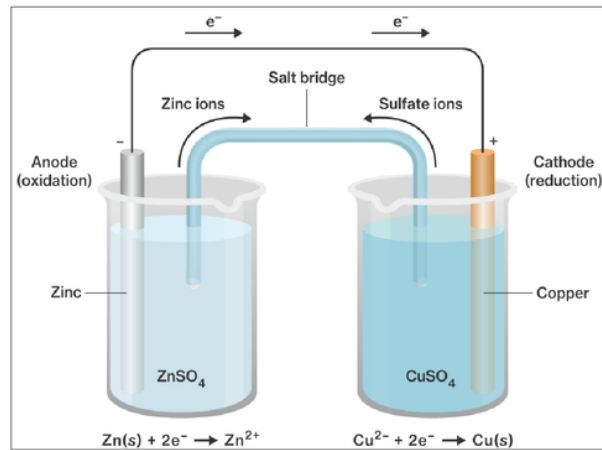
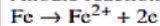


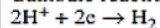
Figure 2: Imaged sourced from [39]

The diagram above shows how the zinc (Zn) anode reacts with the zinc sulphate (ZnSO_4) solution. The reaction between the Zn and the ZnSO_4 is due to oxidation. Zn ions form and diffuse into the solution to react with the negatively charged ZnSO_4 while the electrons are maintained within the anode. The electrons are then conducted through a wire into the more electro positive copper (Cu) cathode and begins and begins to increase the negative charge on the Cu cathode which in turn leads the positive Cu ions in the CuSO_4 solution to bond with the negatively charged Cu anode. The salt bridge allows for the exchange of ions in the solution in order to balance the charge and essentially maintain the conduction of the electrons in the wire. This combination of metals and electrolyte solution shows how the more reactive Zn gets oxidised and loses its electrons to the copper, shedding its positive metal ions, meanwhile, the copper is being reduced by gaining the electrons and the positive Cu ions in the electrolyte leaving a more negative SO_4 solution balancing out the positive charge from the Zn ions

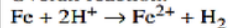
Anodic reaction:



Cathodic reaction:

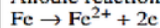


Overall reaction:

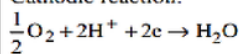


and the reaction due to dissolved oxygen is:

Anodic reaction:



Cathodic reaction:



Overall reaction:

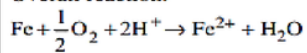


Figure 3: Chemical reaction of iron and hydrogen [30]

3.2.2 Electrochemical Series, Galvanic Series

Anode

- The electrode of an electrochemical cell at which oxidation occurs: such as
- The positive terminal of an electrolytic cell
- The negative terminal of a galvanic cell

Cathode

- The electrode of an electrochemical cell at which reduction occurs:
- The negative terminal of an electrolytic cell
- The positive terminal of a galvanic cell Anode

[5]

Table 1
GALVANIC SERIES
In Flowing Seawater

<i>Alloy</i>	<i>Voltage Range of Alloy vs. Reference Electrode*</i>	
Magnesium	Anodic or	-1.60 to -1.63
Zinc	Active End	-0.98 to -1.03
Aluminum Alloys		-0.70 to -0.90
Cadmium		-0.70 to -0.76
Cast Irons		-0.60 to -0.72
Steel		-0.60 to -0.70
Aluminum Bronze		-0.30 to -0.40
Red Brass, Yellow Brass, Naval Brass		-0.30 to -0.40
Copper		-0.28 to -0.36
Lead-Tin Solder (50/50)		-0.26 to -0.35
Admiralty Brass		-0.25 to -0.34
Manganese Bronze		-0.25 to -0.33
Silicon Bronze		-0.24 to -0.27
400 Series Stainless Steels**		-0.20 to -0.35
90-10 Copper-Nickel		-0.21 to -0.28
Lead		-0.19 to -0.25
70-30 Copper-Nickel		-0.13 to -0.22
17-4 PH Stainless Steel †		-0.10 to -0.20
Silver		-0.09 to -0.14
Monel		-0.04 to -0.14
300 Series Stainless Steels ** †		-0.00 to -0.15
Titanium and Titanium Alloys †		+0.06 to -0.05
Inconel 625 †		+0.10 to -0.04
Hastelloy C-276 †		+0.10 to -0.04
Platinum †	Cathodic or	+0.25 to +0.18
Graphite	Noble End	+0.30 to +0.20

* These numbers refer to a Saturated Calomel Electrode.

** In low-velocity or poorly aerated water, or inside crevices, these alloys may start to corrode and exhibit potentials near -0.5 V.

† When covered with slime films of marine bacteria, these alloys may exhibit potentials from +0.3 to +0.4 V.

Figure 4: Galvanic series [6]

Galvanic series

The energy that gets released when a metal corrodes can be considered to have a voltage potential and the potentials are different for different metals in varying environments. These differences can be observed by measuring the direction of the current that is generated by the metals in a specific environment. Dissimilar metals placed in seawater is a method used quite frequently as a first approximation of the probable direction of the galvanic effects in other environments.

Taking any two metals in a galvanic series and placing them in an electrolytic environment results corrosion of the metal higher in the list being accelerated while corrosion of the metal lower in the list, reduced. Metals with more positive corrosion potentials are called noble or referred to as active or anodic. A factor that affects the values of potentials is changing the type of electrolytic solution that the metals are immersed in, other factors such as temperature, aeration, and velocity of movement.

As an example, zinc is normally very negative or anodic to steel at ambient temperatures, as indicated in the galvanic series. However, the potential difference decreases with an increase in temperature until the potential difference may be zero or actually be reversed at 60°C.

[6]

3.3 Mechanisms of oxidation

If the material is exposed to a marine environment, it is highly probable that the surrounding atmosphere will contain oxygen as other elements such as sodium, sulphur and chlorides that can act as the electrolyte for the reaction. As the material is exposed to the atmosphere oxygen will bind to the surface of the active material which in this case would be the steel, or with the protective coating the zinc. Oxygen naturally forms a diatomic molecule however, when it binds to the active surface it dissociates into oxygen atoms otherwise known as free radicles which highly unstable and so will form a much stronger bond to the active surface material.

Initially, the adsorbate will consist of oxygen molecules that are weakly bound to the surface. This is called physical adsorption or physisorption. On most metals, the oxygen molecules rapidly dissociate into oxygen atoms, and the resulting layer of atoms is more strongly bound to the metal surface. This stage is called chemical adsorption or chemisorption. The oxidation begins by the diffusion of oxygen atoms into surface layers of the metal. These do not form recognised oxides but a dilute solid solution that exists only in the surface regions. Nucleation of chemically recognisable oxides then occurs. At high temperatures and low partial pressures of oxygen, this takes place at random. This is an idealised picture and individual metals vary in their response to oxygen attack. Moreover, the overall reaction path is sometimes dependant on the temperature.

[7]

3.4 The basic aspects of corrosion

3.4.1 Forms of corrosion

Table 2: Corrosion product groupings

Group I	Group II	Group III
• Uniform corrosion • Pitting • Crevice corrosion • Galvanic corrosion	• Erosion • Cavitation • Fretting • Intergranular • Exfoliation • De-alloying	• Stress corrosion cracking • Corrosion fatigue • Scaling • Internal attack

Forms of corrosion can be categorised into groups, here is a brief explanation of the groups:

Group I: Corrosion problems readily identifiable by visual examination.

1. *Uniform corrosion is characterised by an even. Regular loss of metal from the corroding surface.*
2. *Localised corrosion during which all or most of the metal loss occurs at discrete areas. In this scheme crevice corrosion is said to be a particular to form of pitting usually due to localised differences in the environment. (pitting, crevice)*
3. *Galvanic occasioned by electrical contact between dissimilar conductors in an electrolyte.*

Group II: Corrosion damage that may require supplementary means of examination for identification.

1. *Velocity effects include erosion-corrosion, a form of attack caused by high velocity flow; cavitation caused at even higher flow by the collapse of bubbles formed at areas of low pressure in a flowing stream; and fretting that is caused by vibratory relative motion of two surfaces in close contact under load. (Erosion-corrosion, cavitation, fretting)*
2. *Intergranular corrosion at the grain boundaries in the metal structure. (intergranular, exfoliation)*
3. *Dealloying corrosion due to the selective dissolution of one component of an alloy.*

Group III: Corrosion specimens for these types should usually be verified by microscopy of one kind or another.

1. *Cracking phenomena includes corrosion fatigue, a mechanical phenomenon enhance by nonspecific corrosive environments, and environmental cracking, in which a brittle failure is induced in an otherwise ductile material under tensile stress in an environment specific for the alloy system (stress corrosion cracking, fatigue)*
2. *High-temperature corrosion (scaling, internal attack)*
3. *Microbial effects caused by certain types of bacteria or microbes when their metabolism produces corrosive species in otherwise innocuous environment, or when they produce deposits which can lead to corrosion attack.*

[1]

3.5 Uniform corrosion

This form of corrosion has the greatest metal weight loss and is quite common in structures that have been abandoned and left for long periods of time. This particular type of corrosion is not a major issue due to the fact that it is relatively detectable and has effects that can quite easily be predicted. The major concern with this type of corrosion arises if the material being corroded is hidden from site. Buried or submerged components, hard to reach components and internal corrosion of pipes is an example of when this type of corrosion can become a problem due to the difficulty experienced with monitoring.

One way of dealing with this is to design components with a certain allowance for corrosion to occur based on material thickness.

Another way of monitoring this form of corrosion is through ultrasonic inspection which employs a device that measure the time take for a wave of a known velocity to travel through material. Many ultrasonic inspection devices only operate for single-point thickness measurements however there are improvements being made so that tens of thousands of points can be measured over an area as small as 0.1m^2 , this data can then be converted into mass loss and pitting corrosion rates.

3.6 Pitting

Considered possibly the most common type of localised corrosion. Pitting corrosion can occur on a metal surface in a stagnant or slow-moving surface. It may be the first stage of crevice corrosion. It is observed as small volumes of metal removed from specific areas to create craters or pits. Although pitting corrosion happens on a smaller scale in terms of area when compared to uniform corrosion is can be considered more dangerous because it is more difficult to detect and therefore design against. If left un-monitored, pitting corrosion can perforations in pipes and vessels and affect whole systems. Even if the initial amount of corrosion is small, perforations can prove to be costly issues to repair for expensive equipment. One characteristic of pitting corrosion is that cavities may fill with corrosion products to form caps creating nodules. Factors that are known to contribute to initiation and propagation of pitting corrosion are as follows:

- *Localised chemical or mechanical damage to a protective oxide film.*
- *Water chemistry factors that can cause breakdown of a passive film such as acidity, low dissolved oxygen film less stable and high chloride concentrations.*
- *Localised damage to or poor application of a protective coating.*
- *The presence of non-uniformities in the metal structure of the component, for example, non-metallic inclusions.*

[1]

Pitting corrosion depends on the thickness of the metal and on the rate of penetration. Generally, if the rate of penetration decreases then the number of pits increases. This is because other pits that form within the area have to share the available cathodic area which controls the corrosion current that can flow.

3.7 Crevice corrosion

In order to gain a better understanding of crevice corrosion, it is important to take into consideration the affect that the surface area will have on the anodes rate of corrosion.

3.7.1 Surface area effect

An important factor in crevice corrosion is the area effect or the ratio of cathodic to anodic area. If, in comparison to the anode, the cathodic surface area is much larger, oxygen reduction at the cathodic site increases and as a result, induces a greater galvanic current. Having a very large cathode connected to a small anode increases the occurrence of corrosion at the anode due a large flow of electrons into the larger surface area of the cathode this restores the electrical balance of the system.

$$I_{anodic} = I_a * S_a = I_{cathodic} = I_c * S_c$$

$$I_a = I_c \frac{S_c}{S_a} \quad (1)$$

A large surface area ratio is a significant aggravating factor

Anodic current that is concentrated on a small surface area will be much greater than the effect of the same amount is dissipated over a much larger area. When the ratio $\gg 1$ it is an amplifying factor and a stifling factor when $\ll 1$ e.g. Steel rivets and large copper plates. I_c of large copper plates will be low and cathodic polarisation will be slight. At the same time I_a on the anodic steel rivets will be high and the corrosion quite severe. If the situation is reversed the galvanic effects of the large steel plates will be less noticeable.

[1]

3.7.2 How crevice corrosion is formed

Takes place in cracks or crevices formed where metal surfaces meet and usually takes the form of pitting or etched patches. It can also occur under scale and surface deposits and under loose fitting washers and gaskets that do not prevent the entry of liquid between them and the metal surface. Crevices may proceed inward from a surface exposed to air or may exist in an immersed structure.



Figure 5: Pitting Corrosion on Flange

Dissolved oxygen in the electrolyte which is deep in the crevice reacts with the metal, in crevice corrosion, what is known as a differential aeration cell occurs. This is caused by an imbalance that is created due to the inability of the cathodic oxygen reduction reaction to be sustained in the crevice area and this makes the area inside the crevice anodic (S_a), and the large surface which, due to it being more accessible to oxygen in the air becomes cathodic (S_s). The ratio (S_c/S_a) that forms in these conditions is a definitive aggravating factor of the corrosion reaction. This may lead to the creation of highly corrosive micro environmental conditions in the crevice and also cause pH changes at each of the sites which encourages an increase in corrosion. To summarise:

- Metal ions produced by the anodic corrosion reaction readily hydrolysed giving off protons (acid) and forming corrosion products. The pH in a crevice can reach very acidic values. For example, a pH of zero may develop in crevices involving noble alloys exposed to a neutral environment.
- The acidification of the local environment can produce a serious increase in the corrosion rate of most metals.
- The corrosion products seal even further the crevice environment
- The accumulation of positive charge in the crevice becomes a strong attractor to negative ions in the environment, such as chlorides and sulphates that can be corrosive in their own right.

[1]

3.8 Testing

In order to test the resilience of a given material to corrosion it is necessary to run tests on the material. This can be achieved by simulating a natural environment that would be conducive to corrosion and analysing the severity of the corrosion experienced by the material. This can be achieved either by placing the materials outside in an environment considered to have a high salt content such as a marine or coastal environment in order to induce corrosion. Another approach is to use a closed system and subject the material to a series of conditions designed to emulate a naturally occurring environment. There are many factors to consider when thinking about what the parameters should be for the simulated environment as well as taking into consideration how the material is to be used and what it is likely to be exposed to. This method is also conducive to testing protective coatings and substrates.

Many coatings available today are capable of withstanding quite severe environments. How well the material performs in any given environment is primarily due to the adhesion of a primer to the base metal. ASTM B117 Salt Spray, humidity and sulphur dioxide tests will tend to influence the development of coatings although there are still products that can reach the market that fail in practice. These accelerated tests consequently bear little or no resemblance to natural weathering. Formemost among these tests is the hot salt spray for example. This test method has been and is still widely used and accepted as the definitive accelerated test to assess reliability. It is, in reality, toatally unrealistic, as the majority of the products are not exposed to the conditions of this test in their working environment. After application to a substrate, coatings are subjected to many if not all elements of natural weathering and experiences these elements combination rather than individualistically. An alternative was sought for this test as, even though it was initially developed throughout the 1910-1920 and standardised in 1939, it was still widely used in industry during the 1970's.

[8]

Initially, salt spray tests were a method of simply creating an environment that would induce corrosion. Understanding that an electrolyte is needed for the transfer of electrons, and this can be achieved by either immersion in an electrolytic substance or by saturating the samples in a vaporised form of the electrolyte, a solution containing a specific amount of sodium chloride for example, can be used to encourage corrosion to take place and even increase the rate of corrosion. Repeating this test with varying material and structural dynamics, we observe how different rates of corrosion occur for each test performed.

F.D Timmins began to question this test and the various parameters of it, for instance, it was understood that a sodium chloride solution should be 5% to simulate a marine environment, but why a set temperature of 35 °C why use a continuous spray? What type of conditions are these parameters analogous to? [9]

Marine environments naturally carry through the atmosphere due to close proximity to seawater in which the mineral content (salinity) is known to be 35 parts per thousand on average. [10] This means that the atmospheric conditions of marine environments tend to be more conducive to corrosion in certain materials.

The environment that the material is exposed to in order for it to corroded is generally thought to have, not only the possibly of different concentrations of minerals in the atmosphere but other variables such as temperature, local weather conditions, pH levels, and UV interaction. A salt spray test will determine what will happen when a material is subjected to a certain temperature and salinity in the atmosphere but there are more parameters to consider. There may be other elements in the atmosphere that will affect the rate of corrosion, as well as the daylight cycle that results in temperature change and possibly even exposure to UV waves if the material is positioned in direct sunlight.

Around 1962 it was noted by Dr.J.B.Harrison and T.C.K Tickle that the behaviour of zinc phosphate primers were generally excellent outdoors in an industrial environment, their performance during accelerated salt spray testing was poor. Harrison developed a mixture of commonly occurring atmospheric salts by weight: 3.25% ammonium sulphate and 0.25% sodium chloride. [11]

In order to simulate an environment similar to the atmospheric conditions that the material will be placed in, it is important to consider both the concentration of the solution used in the test and the temperature of the test. Another test that can be performed, otherwise known as a cyclic corrosion test, can be utilised to cycle through the different atmospheric conditions in order to achieve testing conditions that resemble the natural weathering cycles that the material is exposed to.

Timmins however, decided to produce a weaker solution of the mixture developed by Harrison consisting of 0.40% ammonium sulphate and 0.05% sodium chloride and also decided that the temperature of the spray should resemble that of ambient temperature in order to correspond to natural weathering. [8]

3.8.1 Prevention of corrosion of iron and steel

As previously discussed, given that it is highly likely that metal will corrode in specific environments due to the reactivity of the material and the surrounding environment. There are various measures that can be taken in order to reduce or prevent corrosion, allowing the operational life span of the material to be extended and reducing the cost of maintenance.

- **Corrosion resistant alloys**

Alloys such as stainless steels, nickel-based alloys and titanium alloys are used when environments become severe such as oil production and refinery, chemical process industries, high heat, and similar environments conducive to severe corrosion conditions. Titanium alloys are also used within aerospace and military industry where there is a need for a high strength to weight ratio and resistance to high temperatures.

- **Corrosion inhibitors**

A substance that is added to an environment to reduce the rate of corrosion the material in that environment experiences. Corrosion inhibitors are implemented into carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys. It can be implemented or changed in situ without disrupting a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product additive industries.

- **Engineering plastics and Polymers**

Can be a good way of combatting the costs of corrosion and although plastics and polymers are used primarily for various other reasons, it has its uses as polyvinyl chloride (PVC) piping and polyethylene piping.

- **Cathodic and Anodic Protection**

The largest share of the cathodic protection market is taken up by sacrificial anodes of which magnesium has the greatest market share. Major markets for sacrificial anodes are the water heater market and the underground storage tank market.

- **Protective coatings**

Organic and metallic coatings can be used to protect metallic substrates (usually carbon steel) and increase service life. A metallic coating most widely used for this purpose is zinc. Applying a zinc coating to a metallic substrate is known as galvanising. The most common process of galvanising is known as hot-dip galvanising which consists of emerging any metallic substrate into a bath molten zinc.

[12]

In the case of the Renz product testing for the safety letterbox company outlined in this report, the main focus for protection against corrosion is galvanising the steel used in the product. This allows the zinc substrate to act as a sacrificial material that oxidises instead of the steel. When the steel is cut, the zinc coating is severed, and the protective coating loses its integrity at the location of the cuts. This can also lead the paint coating on the product to crack, bubble, and disintegrate in a process known as delamination.

Paint delamination from cut edges of model coil coated hot dip galvanized materials exposed at a marine test site for 5 years increased with steel thickness and decreased with zinc coating thickness. To gain a deeper understand of how zinc coated metals react to atmospheric weathering and how organic paint delamination progresses.

[13]

Paint delamination can also carry quite a significant financial cost in industry. If paints and coatings undergo failure during operation, then it can be difficult to resolve the issue without large scale rigs and equipment to gain access to the affected area and even ceasing the day to day operations of any plant or machinery for maintenance. Some of the main reasons for paint delamination range from the wrong coating being selected or the substrate surface not being correctly prepared to improper application of the coating and poor handling of the product leading to mechanical damage.

- **Improper surface preparation** – the substrate surface is not adequately prepared for the coating that is to be applied. This may include cleaning, chemical pre-treatment or surface roughening.
- **Improper coating selection** – either the paint or coating selected is not suitable for the intended service environment, or it is not compatible with the substrate surface.
- **Improper application** – this can be a problem with either shop-applied or field applied coatings and occurs when the required specifications or parameters for the application are not met.
- **Improper drying, curing and over coating times** – again, this problem relates to a lack of conformance to the required specifications or parameters.
- **Lack of protection against water and aqueous systems** – this is a particularly serious problem with aqueous systems containing corrosive compounds such as chlorides.
- **Mechanical damage** – which results from improper handling of the painted or coated substrate, resulting in a breach in the paint or coating.

[14]

In the case of paint delamination for the Renz product samples, it is highly probable that the delamination of the paint occurs as a result of being both affected by the corrosion products of the steel and also the interaction between the atmosphere inside the test chamber and the paint layer. However, if the problem is only assigned to the latter and assumed that it is the coating and how it is applied that is the problem, it still leaves the problem that is caused by the corrosion products produced by the steel corroding underneath the coating. Below are some issues that are considered in regard to paint delamination from cut edge corrosion.

Increase of steel area to be protected in time:

As the dissolution of the zinc coating decreases with time, the area of steel to be protected increases and this in turn increases the dissolution of the zinc coating and paint delamination.

Inhibition of oxygen reduction on steel by deposited zinc corrosion products.

As the reduction of the zinc coating increases, zinc (Zn^{2+}) ions begin to diffuse and migrate toward the steel and form a deposit of low-soluble corrosion products and reduce the rate of the oxygen reduction reaction.

Changing electric resistance of the film of surface electrolyte and corrosion products affecting the action of galvanic protection.

The thickness of the electrolyte layer varies as a function of climatic conditions. Ionic conductivity of the surface film is affected by its thickness, composition, phase structure and compactness. If there are cut edges of thick steel substrates or largely degraded cut edges after long exposure, the ionic conductivity can be insufficient for zinc to protect the steel defect completely and permanently. Any further increase in the cut edge area leads to more intense red rust formation.

Formation of red rust boosting the cathodic activity.

As red rust increases, the efficiency of the cathodic reaction on the steel increases and so increases the demand for zinc dissolution.

[13]

As the reaction between the anodic (zinc) and cathodic (steel) continues, the zinc acts as the sacrificial material and sheds its positive metal ions as it loses its electrons to the oxygen in the atmosphere. The fact that zinc is less noble in comparison to steel helps this method of protection not only by being oxidised by the atmosphere instead of the steel but also by providing a small amount of cathodic protection current.

[Sir Humphry] Davy was able to consider the use of two techniques of cathodic protection, namely sacrificial anodes and impressed current, and two types of sacrificial anode, namely zinc and cast iron. [15]

Two categories that can be considered when approaching the process of corrosion protection are active and passive. In active corrosion protection, the aim is to either intervene in the process or avoid it altogether by planning or suitable material selection. The second is passive corrosion protection which is primarily concerned with keeping the corrosive substances away from the surface in need of protection.

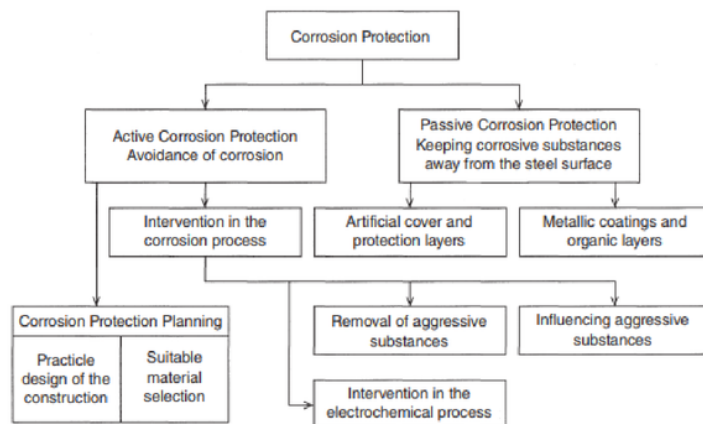


Figure 6: Methods, measures, and procedures of corrosion protection (Oeteren, 1990)

As well as the method of cathodic corrosion protection previously mentioned, there are several approaches to corrosion protection.

Zinc electroplating or electrolytic galvanising

Protection through the application of a zinc coating by means of electrodeposited metal coating

Thermal spraying with zinc

Protection by molten coating metal sprayed onto the surface that needs the protection. Different are combustion wire spraying, combustion powder flame spraying, electric arc wire spraying and plasma spraying (DIN EN 22063).

Metallic Coatings with zinc powder

Protection using zinc powder to achieve zinc coatings, or an alloy of iron and zinc layers applied on to the material for protection (DIN EN ISO 12683).

Hot dip Galvanising

Batch galvanising: Parts are individually galvanised by immersion in molten zinc (DIN EN ISO 1461)

Continuous galvanising: Method of hot-dip galvanised sheet metal or steel strips of mild steel for cold forming (DIN EN 10142) for constructional steels (DIN EN 101471) and wire (DIN EN ISO 10244-2), continuous method process in automatic plants.

[16]

The primary focus of the Safety Letterbox Company is passive corrosion protection and keeping the core steel structure of the product from reacting with the environment by means of coating it with protective layers. A number of methods that can be employed for this task are outlined below.

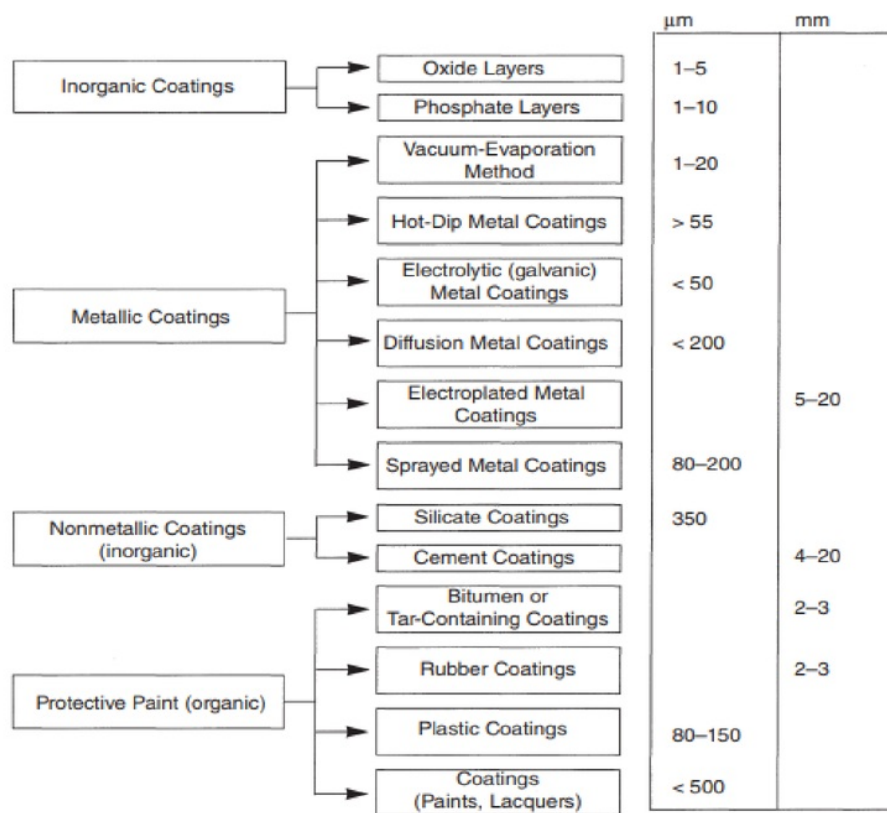


Figure 7: Overview of passive corrosion-protection [38]

Galvanised coatings generally have a high coating thickness, superior corrosion resistance and excellent sacrificial protection capability. However, the rising cost of zinc and demand for better and more durable coatings have led to the developments of more versatile metal coatings which are chiefly based on Zn–Al alloys.

[17]

The manufacturing process utilised by the Safety Letterbox Company involves using three of the methods shown above, namely; Inorganic coatings (Gardobond A4931 phosphate layer), metallic coating (Zn), and Organic Electrostatic paint coating.

In solving the problem of cut edge corrosion on this particular occasion, it may be useful to consider other methods of providing corrosion resistance given that the price of zinc is expected to rise.

Zinc prices traded at USD 2.724 per metric ton in March, 0.8% higher than on the same day in the previous month and was up 8.1% on a year-to-date basis. Zinc stocks registered with the London Metal Exchange are currently at their lowest since 2007, while inventories at the Shanghai Futures Exchange remain at historically low levels. Depleted stocks in large part reflect reduced production of refined zinc in China amid stricter environmental regulations faced by smelters. Significant quantities of the base metal have flowed into China with imports of refined zinc hitting a record-high last year and remaining elevated in January compensated for decline in output draining availability in the global market.

A report by the International Lead and Zinc Study Group revealed a marked deficit for the third year running in 2018, exerting upward pressure on prices.

[18]



Figure 8: High Grade Zinc, prices in USD per metric ton.

The overall cost of mitigating the effects of corrosion across all areas of industry is quite significant. Conventional methods of corrosion and maintenance are steadily improving as research into this field continues to grow. However, if the cost of the materials involved in corrosion protection continue to rise then it is imperative that more efficient methods and procedures are implemented in the manufacturing process.

A recent study estimated the total annual cost of corrosion in China at over 310 billion US dollars, representing 3.34% of the country's GDP. If the same percentage is applied to global economy, the total cost of corrosion worldwide amounts to ~2.5 trillion US dollars per year. Among the corrosion mitigation measures, organic protective coatings are the most widely used, and their costs add up to two-thirds of all anti-corrosion expenditures.

[4]

Self-healing mechanisms embedding into protective coatings and primers may be able to reduce the overall cost of corrosion mitigation quite significantly. More information has been provided in the recommended further work section.

4 Work carried out

4.1 Company details

Managing Director: Alison Orrells

Site Manager: Mark Hacker

Initial information

Part of the RENZ Group – Based in Heubach, South Germany. Recognised as leading manufacturer in the punching and binding industry. In combination with SLB to be considered one of Europe's largest mailbox and parcel box groups enabling distribution of product range worldwide.

The Safety Letterbox Company - Based in South Wales UK

Designing, manufacturing and supplying secure mailboxes and parcel boxes that can be utilised in a range of environments i.e. Security mail/parcel boxes that can be situated inside or outside (with additional weather shielding).

Employs a bespoke production method that allows for products that can be made to fit any site profile and budget with total flexibility in price, finish, size and application.

A horizontal mailbox designed and manufactured to offer a high quality finish combined with an affordable pricing

- Mailbox Dimensions (mm): 276W x 125H x 360D
- Aperture Dimensions (mm): 235W x 30H
- Manufactured using zintec steel and finished with polyester powder coating to a choice of colours from our standard RAL colour range.
- For interior application as standard or exterior placement with additional weather shielding
- Lateral variation of the mailbox available (contains larger width and reduced depth)
- Can be manufactured as a single item or in a bank of multiple mailboxes to suit any configuration
- Can be wall mounted, wall recessed or freestanding to suit project requirements

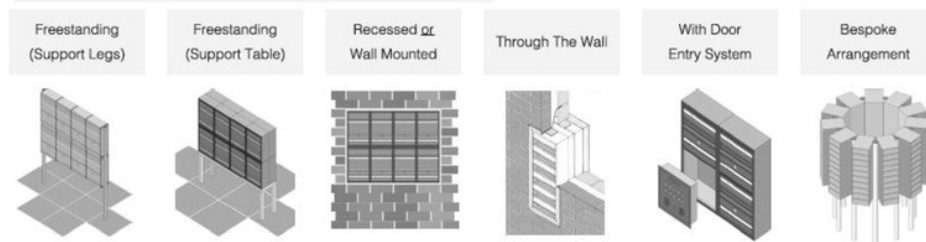


Figure 9: Steel 2 product details

Structure of unit production

1. Substrate material: Zintec (Zinc plated steel) 1 x 1 (M)
2. Cut: *Drawing and punching, CNC sheet metal work*
3. Welding
4. Pre-treatment (1st stage)

Gardobond A4931 (De-greaser and phosphate coating)

Chemetall Ltd Recommendation	SLB Confirmed Process
pH: 4.0-5.0	pH: Not tested at this time
Bath temperature: 45-75 °C	Bath temperature: 45 °C
Immersion time: 2-5 minutes	Immersion time: 2 minutes

5. Water bath (2nd stage: This is the final pre-treatment stage for the Steel 2 product)
6. Post-treatment (Al)
7. Oven dried (Temperature: 180-200 °C, Time: 20 minutes)
8. Paint: *Powder coating*

AkzoNobel

Physical and chemical properties

<i>Physical state:</i>	<i>Solid [Powder]</i>
<i>Upper/Lower flammability or explosive limits:</i>	<i>20-70 g/m³</i>
<i>Relative density:</i>	<i>1.2 – 1.9 [ISO 8130-2/-3]</i>
<i>Solubility (Insoluble in the following):</i>	<i>Cold/Hot water</i>
<i>Auto-ignition temperature:</i>	<i>450-600 °C</i>
<i>Minimum ignition energy (mJ):</i>	<i>5 - 20</i>

9. Oven cured (Temperature: 180-200 °C, Time: 20 minutes)
10. Engraving
11. Assembly and packing

Main focus areas

1. Substrate material: Zintec (Zinc plated steel) 1 x 1 (M)
2. Pre-treatment (1st stage)
Gardobond A4931 (De-greaser and phosphate coating)
3. Paint: **Powder coating**
AkzoNobel (Electrostatic powder coating)

4.2 Establish the problem

Cut edge corrosion

There are several protection mechanisms that are implemented in the manufacture of the safety letter box, yet there is still a problem of corrosion.

The methods employed to protect against corrosion are as follows:

Galvanised steel (zinc substrate)

Phosphate undercoat

Phosphates are usually classified as non-oxidising anodic inhibitors, effective only in the presence of oxygen, although they have also been claimed to act as cathodic inhibitors under certain conditions.

[19]

Porous paint layer (electrostatic powder)

After consideration of how the environment reacts with each successive layer of protection and the state of the finished product, an observation was made with regards to the cutting phase of the manufacturing process.

The first stage of the manufacturing process (after delivery of the galvanised steel sheets), various cuts are made, and the flat steel is mechanically shaped into a container of dimensions that are dependent on the products design brief. As these cuts are made, the protective zinc coating is compromised, and the underlying steel is exposed to the environment.

Although the zinc coating will continue to be oxidised, the steel is now also susceptible to oxidation and results in

the steel undergoing the process of corrosion. As the metal ions from the corroded steel begin to fall away, previously un-oxidised parts of the steel now also become susceptible to corrosion.

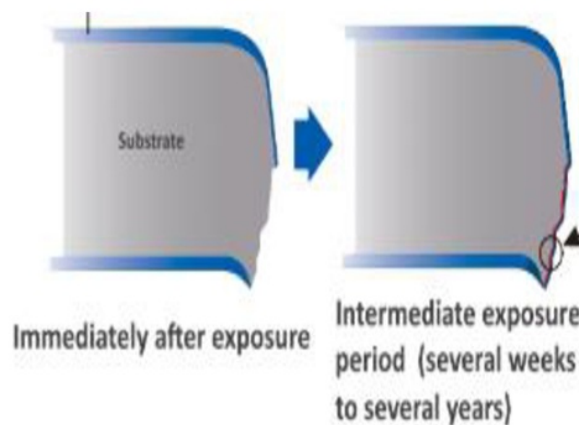


Figure 10: Diagram of cut edge corrosion

4.3 Corrosion test

Test for corrosion: Salt spray test

ISO 9227: The Safety Letterbox Company have performed salt spray tests, the parameters of which are outlined in the ISO 9227 specification report. However, a cyclic corrosion test was chosen to simulate the fluctuating conditions of natural weathering.

4.3.1 ISO 9227: Primary specifications

Neutral salt spray (NSS)

- Neutral 5% sodium chloride solution atomised under a controlled environment

Acetic acid salt spray (AASS)

- Acidified 5% sodium chloride solution with addition of glacial acid under a controlled environment

Copper accelerated salt spray (CASS)

- Acidified 5% sodium chloride solution with addition of copper chloride and glacial acid under a controlled environment

Test solutions

- Dissolve sodium chloride in distilled or deionised water with a conductivity not higher than $20 \mu\text{S/cm}$ at 25°C to produce a concentration of $50\text{g/l} \pm 5\text{g/l}$.
- Specific gravity range for a $50\text{g/l} \pm 5\text{g/l}$ solution is **1,029 to 1,036** at 25°C

Specific gravity = (Ratio of the density of a substance to the density of a reference substance)

- Must not contain mass fraction of heavy metals in total more than 0.005%
- Must not contain mass fraction of sodium iodide in total more than 0.1%
- Must not contain mass fraction of total impurities more than 0.5% calculated for dry salt

pH adjustments

- Adjust pH of salt solution so that sprayed solution is **(6.5 to 7.2)** at $25^\circ\text{C} \pm 2^\circ\text{C}$

pH to be checked using electrometric measurement using electrodes suitable for measuring in weakly buffered sodium chloride solutions in deionised water. Corrections can be made with the addition of hydrochloric acid, sodium hydroxide or sodium bicarbonate solution.

Possible changes in pH can result from loss of carbon dioxide in the solution when it is sprayed. Such changes can be avoided by reducing the carbon dioxide content of the solution by heating it to a temperature of above 35°C before it is placed in the apparatus, or by making the solution using freshly boiled water.

Spraying device

The compressed air supplied to the atomisers shall be passed through a filter to remove all traces of oil or solid matter, and the atomising pressure shall be at an overpressure of **70 kPa to 170 kPa**. Typically, **$98\text{kPa} \pm 10\text{kPa}$** depending on the type of cabinet and atomiser used.

$1\text{kPa} = 1\text{kN/m}^2 = 0.001\text{atm} = 0.01\text{bar} = 0.145\text{psi}$

4.4 Cyclic corrosion testing

The idea behind Cyclic corrosion testing is to be a more realistic way to perform test for corrosion because the transient nature of a corrosive environment. Both wet and dry conditions exist in the exposure environments and the cyclic corrosion test can simulate this more accurately than standard salt spray tests.

Research indicates that, with cyclic corrosion tests, the relative corrosion rates, structure and morphology are more similar to those seen outdoors. Simple exposures like Prohesion may consist of cycling between salt fog and dry conditions. More sophisticated automotive methods call for multi-step cycles that may incorporate immersion, humidity and condensation, along with salt fog and dry-off.

Prohesion Test: developed in England for industrial maintenance coatings applications. The Prohesion electrolyte solution is much more dilute than traditional salt fog. In addition, the spray atomizing air is not saturated with water.

Corrosion/Weathering Cycle: For industrial maintenance coatings, the addition of UV. UV damage to a coating can make it more vulnerable to corrosion.

Japanese Automotive Cyclic Corrosion Tests: The Japanese have developed a number of cyclic corrosion tests. Most are primarily for automotive applications, including CCT-1, CCT-4 and Acid Rain Test.

[20]

Cyclic corrosion testing generally uses a more dilute salt solution during the testing cycle and also introduces chemicals that are used to lower the pH of the solution.

The fog electrolyte solution used in this practice is only 0.5% in sodium chloride vs. 5% for the standard salt spray test. However, it also contains 0.35% of ammonium sulphate used to lower the pH's solution range of 5 to 5.4 instead of 6.6 to 7 for salt spray testing. The ASTM D5894 test can also be modified to better simulate your specific applications. For instance, there are different corrosive electrolyte formulations that can be used in ASTM G85.

[21]

There are several tests that have been developed for cyclic corrosion research, the test cycle chosen for this project is one of a number of tests developed in Japan for automotive assemblies and components. This test was preferred due to the accelerated time scales and cyclical nature. It was also considered adequate due to its implementation in the automotive industry which require vigorous testing methods to ensure the safety and integrity of the components set to be marketed.

4.5 CCT-4

This is an accelerated laboratory corrosion test method that can be used to determine the corrosion resistance of automotive assemblies and components. It is cyclic in nature, i.e.; test specimens are exposed to changing climates over time.

Test specimens are placed in an enclosed chamber and exposed to a changing climate that comprises of a relatively short period of salt spray, followed by exposure to hot/humid and hot/dry atmospheres. The entire test cycle comprises of a main cycle and a sub-cycle. 1 entire test cycle takes 24 hours to execute. The number of entire cycle repeats and therefore the test duration is variable.

The main test cycle begins with 10 minutes exposure to a continuous indirect spray of salt water solution, in a chamber temperature of +35C. This is followed by 155 minutes of air drying at +60C. This is followed by 75 minutes exposure to a high humidity climate of 95%RH at +60C.

This is then followed by a repetitive sub-cycle comprising of 160 minutes of exposure to an air drying at +60C, followed by 80 minutes exposure to a humid climate of 95%RH at +60C. This sub-cycle is repeated 5 times in total, before the main test cycle starts again.

[22]

4.6 Acquired test samples

Samples were required for testing, below is the initial list considered for testing;

Type	Pre-treatment/Painted	Pre-treatment only	Painted only
SLB	1	1	1
RENZ	1	1	1
RENZ/SLB	1	1	1

Figure 11: First sample range

Originally three units but in order to get more data and for repeatability purposes, samples were, the list of possible samples are as follows:

Product: SLB			Product: RENZ UK			Product: RENZ Substrate w SLB treatment		
Colour Scheme	Phosphate pre-treatment	Un-treated	Colour Scheme	Phosphate pre-treatment	Un-treated	Colour Scheme	Phosphate pre-treatment	Un-treated
Carmin Red	1	1	Carmin Red	1	1	Carmin Red	1	1
Melon Yellow	1	1	Melon Yellow	1	1	Melon Yellow	1	1
Dark Sapphire blue	1	1	Dark Sapphire blue	1	1	Dark Sapphire blue	1	1
Light Blue	1	1	Light Blue	1	1	Light Blue	1	1
Moss Green	1	1	Moss Green	1	1	Moss Green	1	1
Agate Grey	1	1	Agate Grey	1	1	Agate Grey	1	1
Chocolate Brown	1	1	Chocolate Brown	1	1	Chocolate Brown	1	1
Satin silver	1	1	Satin silver	1	1	Satin silver	1	1
Special request			Special request			Special request		
Metallic with Lacquer	1	1	Metallic with Lacquer	1	1	Metallic with Lacquer	1	1
Satin Gold	1	1	Satin Gold	1	1	Satin Gold	1	1
Bronze	1	1	Bronze	1	1	Bronze	1	1
Total samples per substrate			16 Total samples x3			48		
Total Samples w/Sr			22 Total samples x3			66		

Figure 12: Revised sample range

This led to a new set of samples being considered as follows:

Product: SLB		
Colour Scheme	Phosphate pre-treatment	Un-treated
Dark sapphire blue	5	5
Light Ivory	5	5
Pure white	5	5
No paint	5	5

Figure 13: Finalised sample range

4.7 Test Cycle

The following test is the test that was chosen for this project.

CCT-4 Japanese Automotive Cyclic Corrosion Testing

CCT-4 is specified by some Japanese automotive manufacturers. In the SAE and AISI research projects, CCT-4 was shown to be one of the exposures that best correlated with actual vehicle corrosion results.

The exposure conditions include:

Electrolyte Solution 1.5% sodium chloride by weight

Solution Acidity not specified

Typical Duration 50 cycles (1,200 hours)

The CCT-4 exposure cycle is:

10 minutes Salt fog application at 35°C

155 minutes Dry Off at 60°C

75 minutes Humidity at 60°C, 95% RH

160 minutes Dry Off at 60°C

80 minutes Humidity at 60°C, 95% RH

10 minutes Salt fog application at 35°C

155 minutes Dry Off at 60°C

75 minutes Humidity at 60°C, 95% RH

160 minutes Dry Off at 60°C

80 minutes Humidity at 60°C, 95% RH

10 minutes Salt fog application at 35°C

155 minutes Dry Off at 60°C

75 minutes Humidity at 60°C, 95% RH

160 minutes Dry Off at 60°C

80 minutes Humidity at 60°C, 95% RH

[21]

RH is considered to be the percentage of moisture in the atmosphere of the chamber, a brief explanation of the relative humidity factor is as follows:

Relative humidity (RH): Modern RH sensors, technically referred to as hygrometers use electrical resistance and capacitance techniques to measure moisture in the air. There is usually a trade-off between accuracy and resistance to condensation. Corrosive solutions decrease the accuracy of the measurements and cause premature failure of these sometimes-costly sensors.

[23]

The instrumentation for measuring the relative humidity for this project is known as the wet and dry bulb hygrometer. Which is made up of two thermometers, one is dry, and one is wrapped in a cloth like wick that is saturated with water. The wet bulb cools as the water from the wick evaporates and difference in temperature allows for the RH to be calculated.

Wet and dry bulb hygrometer

When water evaporates it requires heat from an external source and the rate of evaporation is dependent on the amount of moisture in the atmosphere. The wet and dry bulb hygrometer takes this into account and uses two thermometers, one that has a wick wrapped around the bulb at the bottom that is saturated and also dipped into water, the other is a dry thermometer. When the water evaporates from the wick of the wet bulb it will begin to cool relative to the dry thermometer. The two are situated next to each other in order to see the difference in temperature which is dependent on the amount of humidity in the air.

[24]



Figure 14: Hygrometer used in test chamber

5 Results

Due to the occurrence of cut edge corrosion being of primary concern, the samples were not etched. It was determined that this would better simulate what is being experienced by the material of the product itself. The samples were not sealed in anyway, in order to observe how the material corrodes and where the initial points of corrosion begin. A small hole roughly 4mm in diameter used for treatment and painting procedures during the manufacture of the samples was also left un-sealed in order to monitor any cut edge corrosion that may form as a result of the hole.

In order to gain an effective comparison, the samples were split into two main categories. The main difference between the two categories is the phosphate coating that is employed before the final coat of paint is applied. The phosphate coating is applied as an additional layer of protection from corrosion of the final product. Each category then has three different colour schemes applied ranging

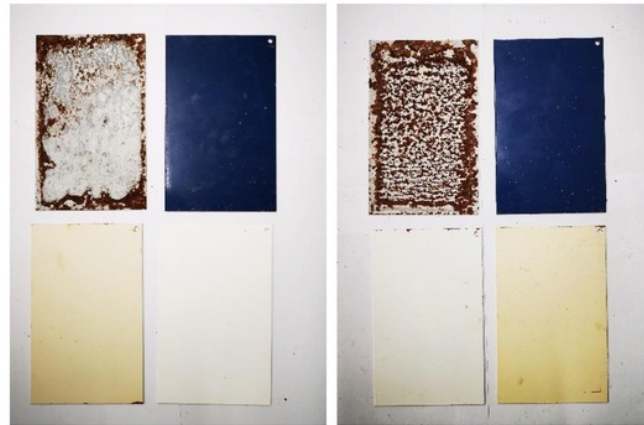


Figure 15: Treated (left) Un-Treated (right) Comparison of sample range

from dark to light with one sample left unpainted. This sampling method was chosen to observe any variance that may occur due to the pigmentation paint coating the sample.

Initial observation of the test samples shown in (figure 15) indicates that the un-painted samples have undergone quite a significant amount corrosion, with the treated sample experiencing a larger amount of corrosion. The painted samples do not show the same level of corrosion however, corrosion can be observed at the edges of the sample plates which indicates that this may have been caused by the cutting process involved in making the sample.

After the test the samples were cleaned and dried before being weighed. Comparing the weight of the highly corroded un-painted samples with the control samples that did not undergo any testing and accounting for the weight of the phosphate coating reveals that the treated samples loose roughly a 0.1g of mass compared to the reduction 0.2g for the un-treated product material. The average weight for the painted samples didn't not change, although it is necessary to assume that the painted samples also experienced a very small reduction in mass.

A closer examination of the painted samples in (figure 16) reveals that corrosion is primarily exhibited along the edge of the sample.

A small amount of corrosion is shown to be at the top corner of the sample located around the hole of the treated sample. The untreated sample shows that more corrosion has taken place located in the same area as the untreated sample.

With the 'light ivory' and 'pure white' test samples, there appears to be a more significant amount of corrosion along the edge of the sample and as expected, less corrosion occurring on the treated sample.



Figure 16: Comparison of treated (left) and un-treated (right) of paint free samples

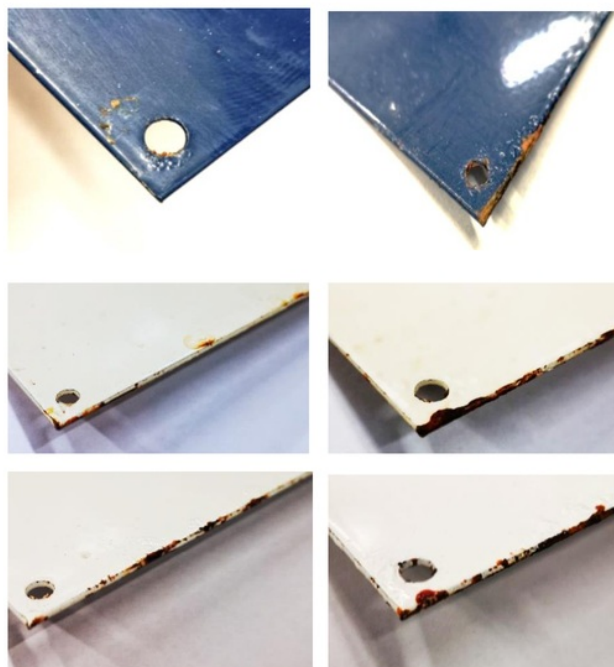


Figure 17: Comparison of painted samples, treated (left) un-treated (right)

Taking the whole sample range (Figure 18) the majority of the corrosion is shown to be along the edge of the sample. This is indicative of the cut edge corrosion seen on the actual product.

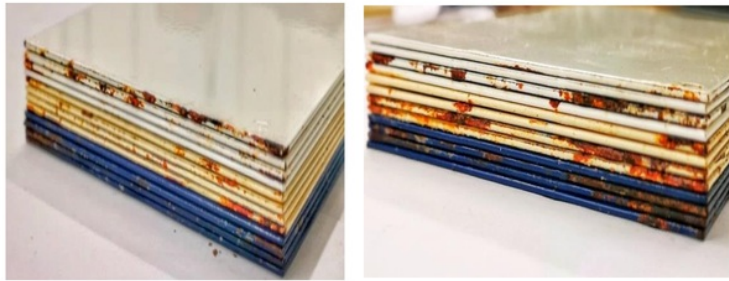


Figure 18: Over all comparison of edge corrosion, treated (left) un-treated (right)

This is due to the zinc coating on the plate being severed along the length of edge revealing the steel underneath. The corrosion takes place due to the electrostatic paint coating being porous at the microscopic level, allowing for the solution to seep through and act as electrolyte, oxidising the steel.

Once the steel has been oxidised, it begins to discolour and the metal ions that form begin to flake off allowing for the surface underneath to continue the reaction.

As well as the corrosion products that occur as a result of the steel being oxidised, each sample is observed to have undergone a process of delamination. (Figure 19) shows that the delamination experienced by the samples is minimal and located at the site of corrosion for each sample, indicating that the cut edge corrosion observed in the samples and ultimately in the product will experience an ongoing process of delamination with time if it is placed in an environment conducive to corrosion, such as a marine environment.

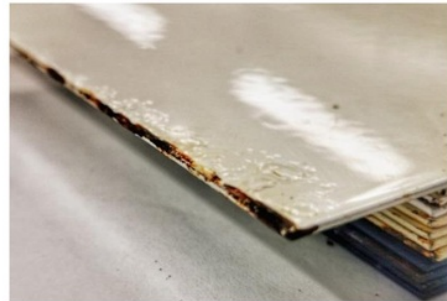


Figure 19: Delamination of paint

A report is provided in the appendix.

6 Discussions and conclusions

6.1 Discussions

Several factors of the testing performed for this project need to be taken into consideration.

Timescale: The test chamber that was initially considered for the project had recently been transported from a previous site, this resulted in a delay in testing due to the chamber acquiring installation and calibration. This limited the amount of time that the samples were able to undergo testing. An increase in timescale can either prolong the exposure of samples or even facilitate a series of tests.

Chamber malfunction: During the first weeks cycle a component of the chamber malfunctioned which affected the draining of the chamber and rendered the equipment inoperable for a short period of time. Given that the repair was expected to take anywhere between several days to more than a week, an alternative chamber was used. Chamber capacity was reduced as a result and the positioning and placement of the samples were in very close proximity and in contact with the surface of the chamber. However, the same test cycle was able to be implemented.

UV testing: Introduction of UV light was not considered for this test. A list of specifications provided as a recommendation for further work offer parameters for the implementation of UV into the test method. Performing the same test with the introduction of UV light into the test cycle may offer a more accurate representation of how the product will corrode in natural weather conditions.

Solution: The solution used for the testing was, by weight, a 1.5% sodium chloride solution. No other salts were utilised in the testing of the products. With regards to further testing, it may be permissible to introduce other chemicals such as acetic acid or copper chloride in order to observe how a change in the pH of the solution would affect the overall result.



Figure 20: Alternative chamber

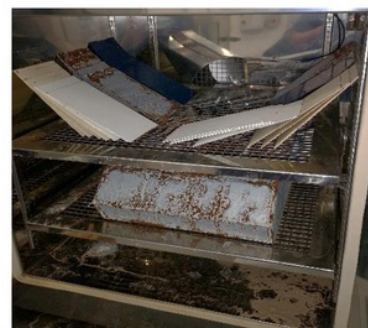


Figure 21: Positioning of samples

6.2 Conclusions

This report shows how cut edge corrosion can form underneath a layer of protective coating under specific conditions outlined in the report. The non-painted samples experienced a larger amount of corrosion with a more concentration amount of corrosion occurring at the periphery of the sample. This was expected as, even though the paint coating is porous, it is likely to interfere with the oxidation reaction experienced by the sample. The painted samples do exhibit a small amount of corrosion and delamination at the edges of the sample. There appears to be little difference in the amount of corrosion experienced by samples of different colour pigmentation although treated samples, as expected, seem to experience a reduction in noticeable corrosion products that accumulated at the cut edges. A small amount of delamination occurring at the edges of the sample that had undergone oxidation, the amount delamination was minute and appeared consistent across the whole sample range. An increased amount of exposure time may reveal a considerable comparison of delamination based on colour and whether the sample has been treated or un-treated.

7 Recommended further work

For future testing, a list of the following summarised specifications can be used to construct a more accurate test. For instance, ASTM D5894 pertains to a method of testing painted metal samples by alternating the exposure of the samples between fog/dry cabinets and UV/condensation cabinets

Used to simulate outdoor corrosion on painted metal it simulates many environmental factors at once, such as corrosive environment, rain, alternating wet/dry conditions, temperature variations and outdoor UV light (340nm). ASTM D5894 is also known as Cyclic Salt Fog/UV Exposure of Painted Metal test. Micom-Laboratories offers testing to ASTM D5894 test as part of our Coating testing services. The underlying principle of this test is to expose samples to alternating exposures in a fog/dry cabinet and a UV/condensation cabinet. This practice is to be used on painted metal samples. It uses alternating one-week periods of cyclic corrosion with a wet/dry cycle based on ASTM G85 test, Annex V, and a fluorescent UV exposure based on ASTM G154 test.

ASTM D5894 has been found useful for air-dry industrial maintenance paints on steel and zinc primers used for cathodic protection.

[21]

ASTM Standards

ASTM D5894

Test is a cyclic salt fog / UV exposure of painted metal test. This test consists of exposing samples to alternating exposures in a fog/dry cabinet and a UV/condensation cabinet.

ASTM G85

Test is a standard practice for modified salt spray (fog) testing. Although ASTM G85 is based on ASTM B117, it offers more aggressive test conditions such as using a test solution with a lower pH, alternating between corrosive and neutral atmosphere or by using an aggressive electrolyte mix.

ASTM G44

Test is a standard practice for exposure of metals and alloys by alternate immersion in neutral 3.5 % sodium chloride solution. This test is mainly used for aluminium and ferrous alloys as well as any other alloy susceptible to chloride ions.

ASTM D2247

Tests for water resistance of coating in 100% relative humidity.

ASTM D4585

Tests for rain and condensing humidity.

ASTM D610

Practice for Evaluating Degree of Rusting on Painted Steel Surfaces

ASTM D714

Test Method for Evaluating Degree of Blistering of Paints

ASTM D1654

Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments

ASTM D4587

Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings

[25]

Self-healing mechanisms in smart protective coatings

The implementation of self-healing mechanisms into the coating and the primer of a given product means that any damage that can occur to the material during its lifespan can be quickly remedied at the source of the damage. This, in turn, will increase the life-span of any components exposed to natural weathering reducing the cost associated with corrosion mitigation such as, maintenance, access to affected areas (cease of operation of production plants and machinery), materials, and replacement components.

A particular method currently being researched by the Advanced Innovation Centre for Materials Genome Engineering at the University of Science and Technology in Beijing, are self-healing mechanisms that are embedded into the coating itself. These autonomous healing mechanisms can consist of polymerizable healing agents or corrosion inhibitors in the matrix of the coating.

Self-healing based on defect-filling effect

By reacting with either catalysts co-existing in the coating or with moisture or oxygen in the environment, these materials can polymerize into a film with a certain strength and thickness to fill the coating defect and restore the barrier properties of the coating. To effectively seal the defect, the microcapsules should be ideally mixed in the primer and placed near the metal substrate. However, the incorporation of microcapsules could reduce the adhesion of the primer to the metals and it has been recommended to place the microcapsules in a separate layer on top of the primer

Self-healing based on corrosion inhibitors

Realized by embedding corrosion inhibitors in coatings. Coatings primarily consist of phosphates, nitrites, molybdates, tungstates, vanadates, borates and rare earth salts and the organic corrosion inhibitors employed include benzotriazole (BTA), mercaptobenzothiazole (MBT), imidazoline, 8-hydroxyquinoline (8-HQ) and aliphatic amines. The inhibition of anodic dissolution can be achieved by inhibitors that can increase the passivity of the oxide layer on the exposed metals, while cathodic reactions are often retarded by inhibitors which induce the precipitation of oxide and hydroxide at the cathodic sites. Inhibitor-based coatings account for a majority of all reported self-healing coatings for corrosion protection. More adhesive when directly mixed with coating materials.

[4]

As can be seen above, there are many combinations of salts and chemicals that can be incorporated into the development of self-healing mechanisms. Although chromate has been utilised for its highly protective qualities, other methods are being researched due to health concerns.

A common inhibitor incorporated into the primer is chromate, which is extremely effective for corrosion protection [26]. However, environmental and health concerns are driving the search for replacements to chromate in coating formulations [1, 7-14]. Alternative inhibitor systems are therefore a very important aspect of the design of self-healing coatings.

[27]

As well as mixing the corrosion inhibitors into the primer, Nano-containers can also be used as a delivery method.

Basically, nanocontainers can release encapsulated corrosion inhibitors in a controlled manner and be used to develop a new group of rapid self-repairing coatings which possess passive functionality and active response to changes in the local environment.

[28]

8 Bibliography

- [1] P. R. Roberge, Corrosion Engineering (Principles and Practice), 2008.
- [2] D. GL, "Assessment of Global Cost of Corrosion," 2015.
- [3] N. G. T. M. P. B. J. H. P. Gerhardus H. Koch, "The United States Cost of Corrosion Study," 2014.
- [4] P. J. M. P. D. Z. Y. H. G. L. X. L. Fan Zhanga, "Self-healing mechanisms in smart protective coatings: A review," *Elsevier*, 2018.
- [5] M. Webster, Merriam-Webster Inc, 2019.
- [6] S. Dexter, "Galvanic Corrosion," Sea Grant, 1958.
- [7] R. Tilley, Understanding Solids, John Wiley and Sons Ltd, 2004.
- [8] N. Cremer, "Prohesion Compared to Salt Spray and Outdoors Cyclic Methods Of Accelerated Corrosion Testing," 1989.
- [9] F. Timmins, "The history of Prohesion," in *Oil Color Chemists*, 1979, p. 131.
- [10] N. C. f. E. I. NOAA, "Salinity Data, National Oceanographic Data Center NODC," 2018.
- [11] T. T. Dr.J.B.Harrison, "Oil Color Chemists," in *Oil Color Chemists*, 1962, p. 571.
- [12] C. Technologies, "Corrosion Costs and Preventive Strategies in the US," 2002.
- [13] A. N. H. X. S. L. D. T. T. Proseka, "Role of steel and zinc coating thickness in cut edge corrosion of coil coated materials in atmospheric weathering conditions; Part 1: and 2," *Elsevier*, 2016.
- [14] M. Z. George T. Bayer, "Failure Analysis of Paints and Coatings," Matco Associates, Inc, Pittsburgh, Pennsylvania, 2004.
- [15] V. Ashworth, Principles of Cathodic Protection, Third ed., Elsevier B.V, 2010.
- [16] P. Maaß, Handbook of Hot-dip Galvanization, WILEY-VCH Verlag GmbH & Co, 2011.
- [17] R. K. Rajiv P. Edavan, "Corrosion resistance of painted zinc alloy coated steels," *Elsevier*, 2009.
- [18] Focus Economics, "Zinc Price Outlook," 2018.
- [19] J. T. R. P. J. F. A.M. Simões, "Corrosion inhibition at galvanized steel cut edges by phosphate pigments," Elsevier Ltd, 2009.
- [20] Products Finishing, "An Introduction to Cyclic Corrosion Testing a more realistic way to perform salt spray tests," 2012.
- [21] Micom Labs, "CCT-4 Japanese Automotive Cyclic Corrosion Testing," 2019.
- [22] Ascott Analytical Equipment Ltd, "CCT-4 Corrosion test method for Automotive Materials," 2019.
- [23] Q.-L. Corporation, "An introduction to Cyclic Corrosion testing," 2012.
- [24] T. Al-Shemmeri, Energy Audits 'A workbook for Energy Managment in Buildings', Wiley-Blackwell, 2011.
- [25] ASTM International, "ASTM D5894-16, Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal, (Alternating Exposures in a Fog/Dry Cabinet and a UV/Condensation Cabinet)," 2016.

- [26] A. H. R.G. Buchheit, "Chromate and chromate-free coatings," in *Corrosion: Fundamentals, Testing and Protection*, American Society for Materials, 2003, pp. 720-736.
- [27] A. Hughes, "SELF-HEALING COATING SYSTEMS FOR CORROSION PROTECTION," 2007.
- [28] C. Arunchandran, "Self-Healing Corrosion Resistive Coatings Based on InhibitorLoaded TiO₂Nanocontainer," The Electrochemical Society, 2012.
- [29] S. Lyon, "Pitting and crevice corrosion," in *Chapter 1: Overview of Corrosion Science*, 2012.
- [30] A. International, "Fundamentals of Electrochemical Corrosion," ASM International, 2000.
- [31] H.A.Tyler, "Explanation of Oxidation and Reduction," in *Science and Materials*, p. 131.
- [32] H.A.Tyler, "Information on Corrosion," in *Science and Materials* , pp. 170 - 179.
- [33] X. Zhang, "Corrosion Ratios of Steel to Zinc in natural Corrosion environments," *NACE International* , 1999.
- [34] H. K. Yasuda, C. M. Reddy, C. E. Moffitt, D. M. Wieliczka and J. E. Deffeyes, ""Barrier-adhesion" Principle for corrosion protection," Aug 2001.
- [35] S. Fowlwer, Considerations for Relative Humidity and Temperature Control in Atmospheric Corrosion Test Standards.
- [36] LibreTexts, "The Cell Potential," 2016. [Online]. Available: [https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_\(Analytical_Chemistry\)/Electrochemistry/Voltaic_Cells/The_Cell_Potential](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Voltaic_Cells/The_Cell_Potential).
- [37] D. D. Ebbing, General Chemistry: Standard Electrode Potentials in Aqueous Solution at 25°C, Houghton Mifflin, 1990.
- [38] K.-A. v. Oeteren, Corrosion protection of steel structures by coatings on steel and hot-dip galvanized steel, DIN 55928 ed., 1990.
- [39] Course Hero, "What Is a Galvanic Cell?," Course Hero, Inc., 2019..
- [40] I. S. B. S. Alicja Stankiewicz, "Self-healing coatings in anti-corrosion applications," 2013.

9 Appendix

Report

Date of testing: 06/03/19 – 15/04/19

Specification used and the test performed:

ISO 9227 method was utilised initially as a reference

ASTM parameters were utilised such as cyclic temperature and humidity although no specific ASTM specification was used.

Testing cycle based on CCT-4 Japanese Automotive Cyclic Corrosion Testing

Exposure conditions include:

Electrolyte Solution 1.5% sodium chloride

Typical Duration 40 cycles (984 hours)

Type/purity of salt and water used:

1.5% sodium chloride solution by weight

Description of the material or product tested:

Galvanised steel (zinc substrate)

Phosphate undercoat

Porous paint layer (electrostatic powder)

Preparation of the test specimen, nature and area of the surface tested:

Small hook hole (4mm) diameter drilled and utilised to simulate a small cut edge. Samples were also painted and treated.

Dimensions of the test sample were 160mm x 70mm x 2mm

Known characteristics of any coating, with an indication of the surface area:

Gardobond A 4931 phosphate coating

Electrostatic paint coating

Number of test specimens subjected to the test representing each material or product:

Dark sapphire blue = 4 treated, 4 un-treated, 1 control

Light Ivory = 4 treated, 4 un-treated, 1 control

Pure white = 4 treated, 4 un-treated, 1 control

No paint = 5 treated, 5 un-treated, 1 control

Method used to clean test specimens after the test with, where appropriate, an indication of the loss in mass resulting from the cleaning operation:

Treated samples loose roughly a 0.1g of mass compared to the reduction 0.2g for the un-treated product material.

Angle at which the tested surfaces were inclined:

Samples were not inclined due to chamber inefficiencies

Start and end date, duration of the test and the results of any intermediate inspections:

Wednesday 6th March – Monday 15th April (948 hours total)

Properties of any reference specimens placed in the cabinet to check the stability of the operating conditions:

Un-painted treated/un-treated samples

Test temperature:

30 minutes at 35 degrees per cycle

470 minutes at 60 degrees per cycle

Any abnormality or incident occurring during the entire test procedure:

Main test chamber out of operation due to component failure, different test chamber used.