POLITECNICO
MILANO 1863

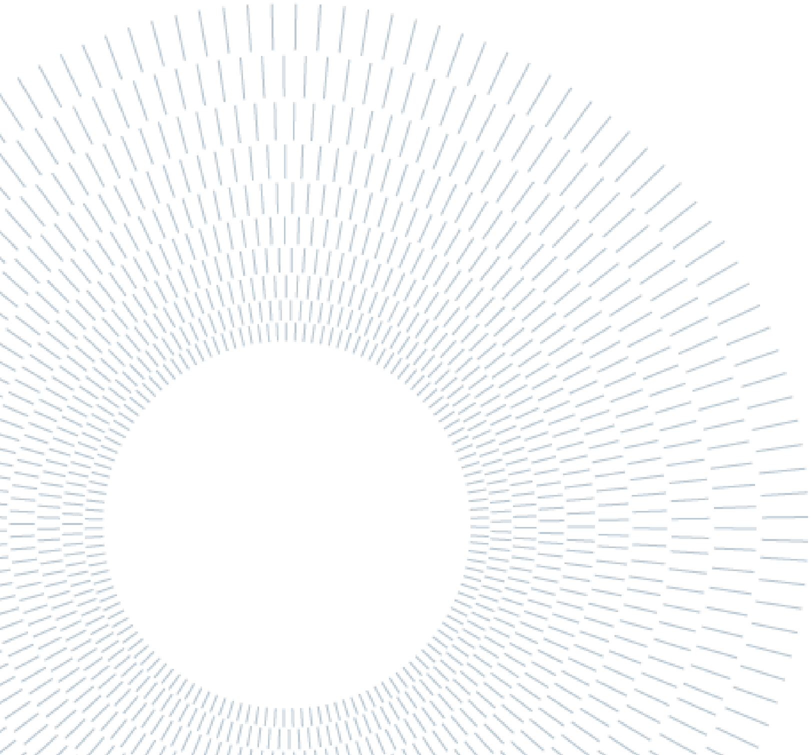
SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

Optimization of Barrel Electroplating Process for Acid Zinc

TESI DI LAUREA MAGISTRALE IN
MATERIALS ENGINEERING AND NANOTECHNOLOGY
INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

Author: **Tomaso de Carli**

Student ID: 946707
Advisor: Luca Magagnin
Academic Year: 2020-21



Abstract

Acid barrel zinc electroplating is a surface treatment, which consists in a deposition of a zinc layer on a substrate. The purposes of this treatment can be different, but the most important are the improved corrosion resistance and the esthetical appearance. Before the electroplating degreasing and pickling pretreatments should be performed to clean the substrate. Instead, after the electroplating a conversion coating and a sealer could be applied to further increase the corrosion resistance or to change the esthetic (only the conversion coating for the last one).

In this thesis work, analyses on a real acid barrel zinc electroplating plant were done, with the aim of improving the quality of the final products. For this purpose, analyses of components concentration of the pretreatments and zinc baths were performed for each final product samples, these analyses are based on titration of the baths; in addition further study on the zinc bath were done through Hull cell tests. Moreover, measurement of the zinc layer thickness with X-ray analyses and corrosion resistance with NSS (neutral salt spray) test were done for each samples. Finally some of the samples were cut to then be analyzed with optical microscopy and SEM (scanning electron microscopy).

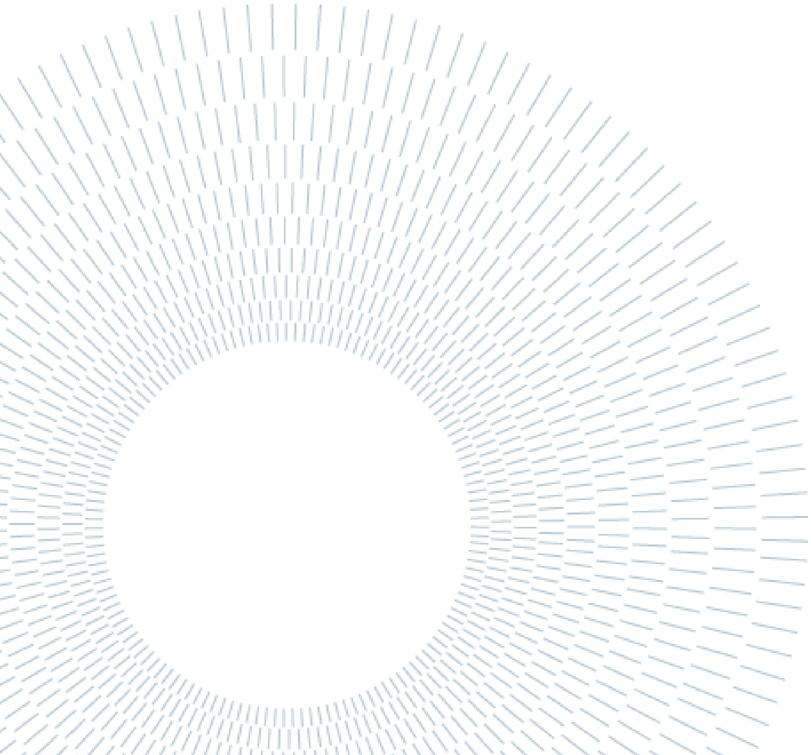
Key-words: Acid Barrel Zinc Electroplating, Surface Treatment, Galvanic Treatment, Corrosion Resistance, Chromium Conversion Coating

Abstract in italiano

La zincatura acida a rotobarile è un trattamento superficiale, che consiste nella deposizione di uno strato di zinco su un substrato. Gli scopi di questo trattamento possono essere diversi, ma i più importanti sono il miglioramento della resistenza alla corrosione e l'aspetto estetico. Prima della zincatura, è necessario eseguire pretrattamenti di sgrassaggio e decapaggio per pulire il substrato. Invece, dopo la zincatura si può essere applicato un rivestimento di conversione e un sigillante per aumentare ulteriormente la resistenza alla corrosione o per modificare l'estetica (solo il rivestimento di conversione per l'ultimo).

In questo lavoro di tesi sono state effettuate analisi su un impianto reale di zincatura elettrolitica acida a rotobarile, con l'obiettivo di migliorare la qualità dei prodotti finali. A tale scopo sono state eseguite analisi di concentrazione dei componenti dei bagni sia dei pretrattamenti che dello zinco per ciascun campione di prodotto finale, tali analisi si basano sulla titolazione dei bagni; in aggiunta sono stati condotti ulteriori studi sul bagno di zinco mediante test con celle di Hull. Inoltre, per ciascun campione sono state effettuate la misura dello spessore dello strato di zinco con analisi ai raggi X e la resistenza alla corrosione con test NSS (nebbia salina neutra). Infine alcuni dei campioni sono stati tagliati per poi essere analizzati con il microscopio ottico e con il SEM (microscopio a scansione elettronica).

Parole chiave: Zincatura Acida a Rotobarile, Trattamento Superficiale, Trattamento Galvanico, Resistenza a Corrosione, Strato di Conversione di Cromo



Contents

1 Introduction

1.1. Zinc Coating

To prevent corrosion and to improve the esthetic of components, now a day, various type of coatings are used, like paint or metallic coating. Zinc coating is one of the most used metallic coating because is one of the cheaper metallic coating on the market, but it is not the only reason.

Another important reason for the diffusion of zinc coating is that his metal nobility is low (Figure 1 and Figure 2) [1].

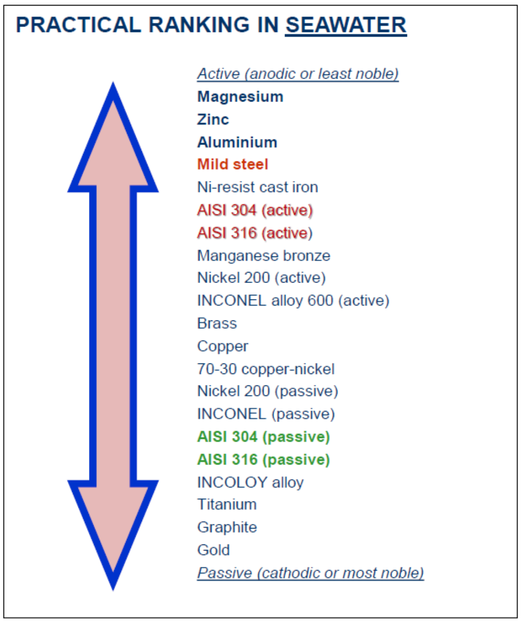


Figure 1 - Metal nobility in seawater [1]

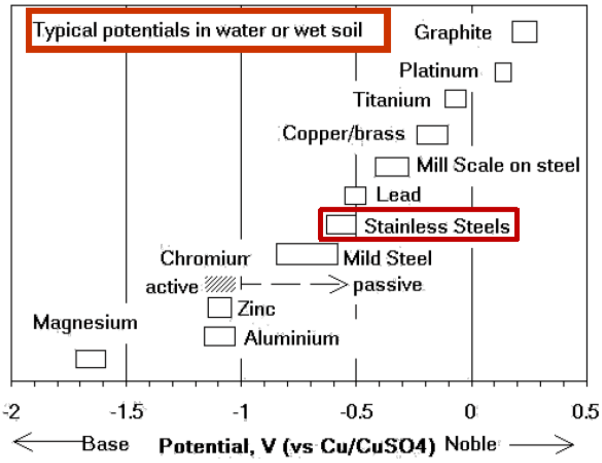


Figure 2 - Metal potential in water or wet soil [1]

Therefore, when the base material is a metal/metal alloy with higher nobility (for example steel) and there are defects on the protection layer, leading to an exposure of the base material, the zinc coating will also guarantee cathodic protection (or active protection) [2] (Figure 3).

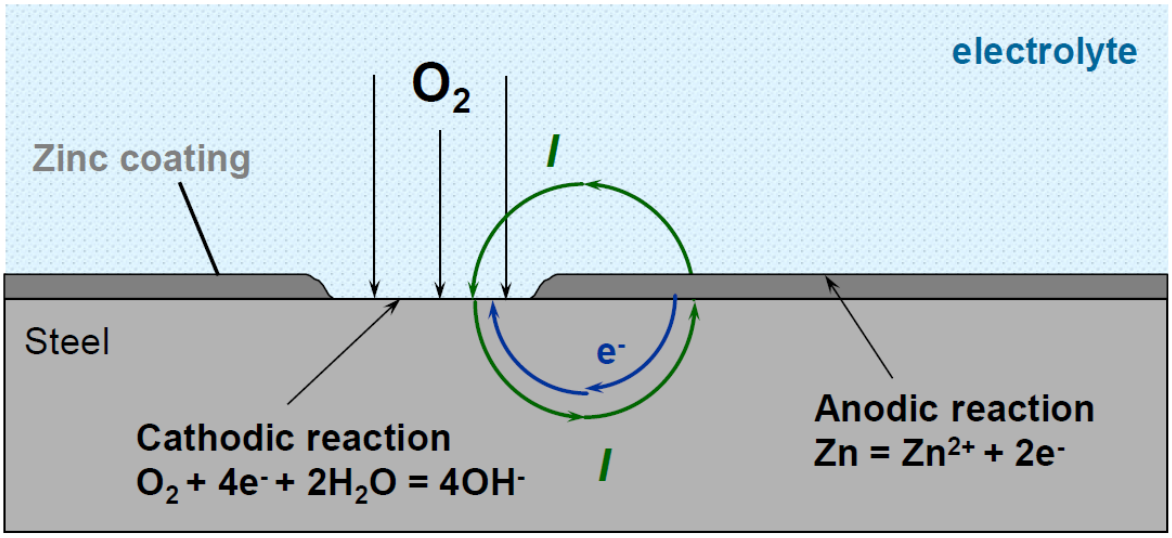


Figure 3 - Zinc cathodic protection mechanism [1]

So the advantages of zinc coating are not only the low price and the corrosion rate that is around 20 times smaller than carbon steel, but also that in case of defects that expose the base material the corrosion will still happen in the zinc layer thanks to the cathodic protection. In case of defects in the zinc coating the increase of corrosion rate of the coating is only of an order of 5% [1], for this reason the requirement on the imperfection on the zinc layer are not so tight.

It is important to note that not all the metal coating offer cathodic protection, for example in case of steel coated with a copper layer we will have a galvanic coupling that increases the corrosion rate of steel (less noble than copper) (Figure 4).

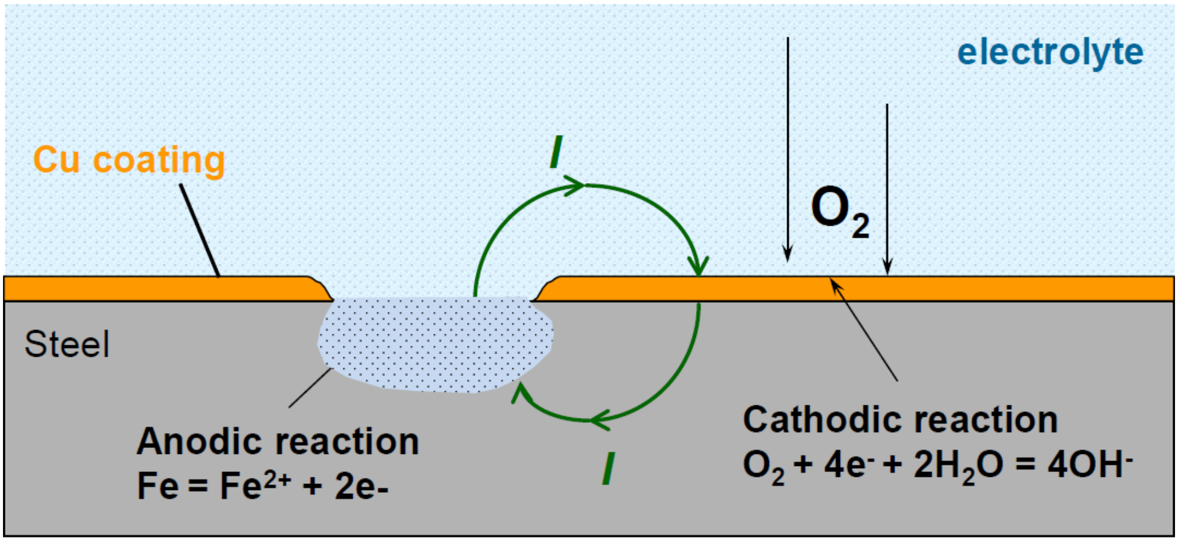


Figure 4 - Copper galvanic coupling mechanism [1]

The metal coating imperfection may be due to various reason, the most common are:

1. Preparation and application of the coating – The metal or the alloy does not deposit, does not deposit well due to the fact the substrate has not been pretreated in a good way or does not stick well.
2. Manufacturing of the product – Cutting, welding and so on.
3. Operating condition – Through not adequate regulation of parameters, as temperature, pressure, voltage and current density for instance, or wear or unexpected events. [3]

A brief and simple scheme of corrosion mechanism is proposed in Figure 5.

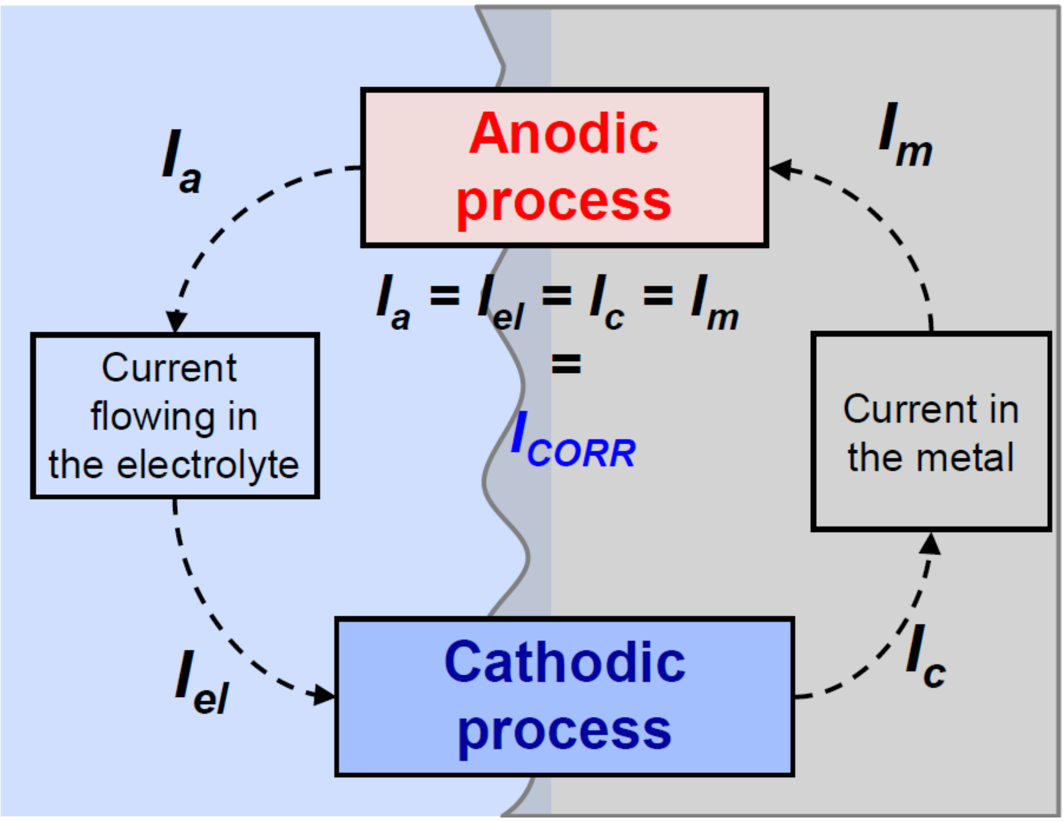


Figure 5 - General corrosion mechanism [1]

In case the metal in Figure 5 is zinc the reaction in the two process will be:

Anodic reaction

$Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e^-$ (1)

$Zn(OH)_2 \rightarrow ZnO + H_2O$ (2)

Cathodic reaction

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (3)

When zinc meets atmospheric moisture, generalized or uniform corrosion takes place and $Zn(OH)_2$ forms, covering the substrate surface in reaction (1). Then, $Zn(OH)_2$ transforms in ZnO in reaction (2), which is compact and protective. ZnO in atmosphere then could react with CO_2, forming $ZnCO_3$ which passivate zinc, improving corrosion resistance. [3]

Zinc alloy protects steel-based parts from corrosion through the following mechanisms:

1. Barrier mechanism: the zinc acts as mechanical insulation of the steel from the corrosive surrounding environment.
2. Galvanic mechanism: in case of defects and vacancies on the zinc coating, the underlying steel is galvanically protected, thanks to the fact that zinc is less noble than steel and so preferentially dissolved ($Zn^{2+} + 2e_{-} \rightarrow Zn$ ($E° = -0.83$) vs $Fe^{2+} + 2e^{-} \rightarrow Fe$ ($E°= -0.44$)).
3. Zinc corrosion products: it can be seen as a combination of the previous two effects: in case of defects and vacancies on the zinc coating, the underlying steel is mechanically protected anyway, thanks to the presence of barrier – layer of zinc corrosion products (ZnO and $ZnCO_3$). [3]

1.2. Zinc deposition

Now a day various techniques exist to coat a base material with zinc, each one with their advantages and disadvantages. The most common techniques are: mechanical deposition, zinc flakes, hot dip galvanizing, sherardizing and electroplating.

1.2.1. Mechanical deposition

The mechanical deposition is performed by inserting inside a rotating reactor (Figure 6) the parts that need to be zinced, zinc flakes and hard balls. When the reactor starts to rotate the hard balls press the zinc flakes onto the parts leading to a mechanical bond and also a metallic bond between parts and zinc. During the process, the zinc flakes go through a ductile deformation.

The obtained coating is homogeneous and of few micrometers of thickness.

In this technique, steel substrate does not necessarily have to be degreased and pickled (but highly recommended) [3], so hydrogen embrittlement phenomena could not appear. If needed after the deposition of zinc is possible to perform posttreatment on the parts.

This technique is only usable for small parts, due to the limits of the rotating reactor [4].

Figure 6 - Rotating reactor for mechanical zinc deposition [4]

1.2.2. Zinc flakes

The zinc flakes coating is a sort of paint made of lots of little flakes, which primarily protect the coated part from corrosion. [4]

The coating generally contain a combination of zinc flakes and aluminium flakes [5], which are fused together by an inorganic matrix (polymer), usually epoxy resin. The aluminium flakes are used primarily to improve the mechanical properties of the coating, instead the zinc ones work as sacrificial anode providing active protection from the environmental influences (active cathodic protection).

The deposition of zinc flakes on components consists in placing both the substrate and the zinc enriched epoxy in an open “cage” and then centrifuging for a certain amount of time. Since steel substrate is previously degreased and pickled, some hydrogen embrittlement phenomena could happen. Posttreatment could be done. [3]

The result of this process is a homogeneous coating with a thickness around 8 to 12 micrometres. Also if in the matrix is possible to add pigment and so is possible to obtain different colours for the final result. [4]

1.2.3. Hot dip galvanizing

Hot dip galvanizing is a simple technique that consist in the immersion of the parts in molten zinc at around 460°C [6]. The coating that is developed during the galvanizing process is metallurgically bonded to the base material (usually steel). This technique is essentially an isothermal solidification process, followed by additional solid state diffusional transformations [7].

During the reaction in the kettle, the zinc interacts with the iron in the steel to form a series of zinc-iron alloy layers (Figure 7). Usually, a hot-dip galvanized coating consists of a series of layers. Starting from the steel surface, each layer is an iron–zinc alloy with increasingly lower iron content. These phases are: Γ (18–31% iron), Γ_1 (19–24% iron), δ (8–13% iron) and ζ (6–7% iron), the outer phase (η) being a zinc-rich solid solution with approximately 0.04% iron [8].

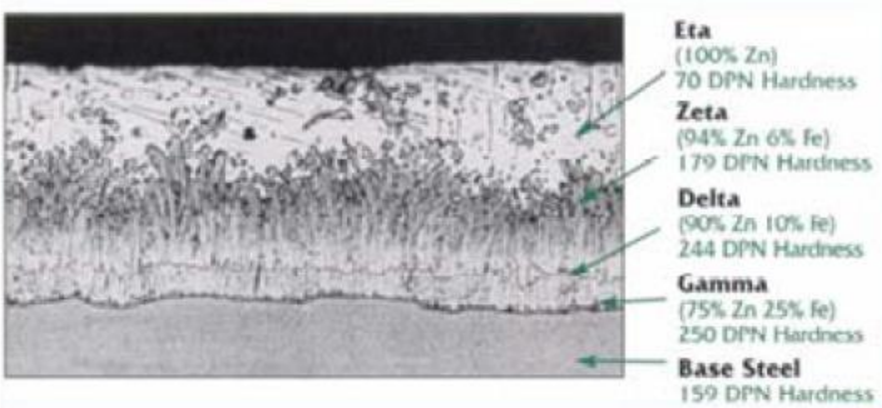


Figure 7 - Metal phase of a hot dip galvanized steel part

This process permit to obtain thick deposit without hydrogen embrittlement and that has a variation in hardness (softer on the outside and harder near the substrate). The thickness of the zinc layer is strictly dependent on the time of dipping and the temperature, the largest thickness is obtained around 480°C [9].

After the hot dip galvanizing is possible to perform posttreatment.

This technique is preferable to be done in big component. [4]

1.2.4. Sherardizing

This technique takes its name from its discoverer (Sherard Osborn Cowper-Coles) [10] and consist in the diffusion of the coating material in the substrate, the process can be divided in two subsequent steps: (I) zinc transfer and deposition, and (II) chemical diffusion (multiphase diffusion) in the solid state [11]. To achieve the diffusion the components to be coated are heated in a revolving drum with powder of the coating material.

The steel articles to be coated need to be pretreated (degreasing and pickling), then they are packed with zinc dust and zinc oxide powder in a steel drum which is provided with electrical heating arrangement, and heated to around 400°C [3]. The high temperature is needed to favour the solid diffusion. It is rotated by means of motor.

The obtained coating is similar to the one of hot dip galvanizing and like in hot dip galvanizing is possible to perform posttreatment on the coated component. [4]

Because sherardizing leads to highly uniform layer thicknesses that allows coating of irregular shapes and threaded parts like bolts, screws, etc. [12]

1.2.5. Electroplating

Zinc electroplating is a technique to deposit, on a component, a thin film of zinc using a redox reaction, which reduces metallic ions to form a metallic deposit using a specific reducing agent. The component can also be glassy or polymeric. The obtained coating is thus very thin, uniform and ideal for a following new finishing treatment like hardening. It has also good adhesion and good ductility: this last point makes it ideal even for bending without the risk of breaking of the coating.

The galvanic process of deposition of zinc or a zinc alloy through the phenomenon of electrolysis in which electric energy developed in the system is converted into chemical energy, giving birth to a set of reactions. The overall reaction is a redox reaction triggered by the electrical current going through the system, as a result of reduction of positive ions Zn^{2+}, thanks to the acquirement of electrons, metallic Zn is deposited. At the same time hydrogen discharge due to oxidation reactions in the aqueous solution. When a controlled electric current is provided, Zn^{2+} positive ions dissolved into the electrolyte go towards the negative pole, where they deposit in the form of a metallic layer of Zn; at the positive pole, instead, release of electrons occurs, which is fundamental for the deposition to go on. The main electrochemical reactions that occur at the two electrodes are written below.

Cathodic processes:

$Me^{z+} + ze^- \rightarrow Me$

$2H^+ + 2e^- \rightarrow H_2$

Anodic processes:

$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

(acid aqueous solution, unsoluble anode)

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

(alkaline aqueous solution, unsoluble anode)

where Me^{z+} is the metallic ion to be deposited and Me is the electrochemically deposited metal, in this case Zn, so $Zn^{2+} + 2e^- \rightarrow Zn$ [3].

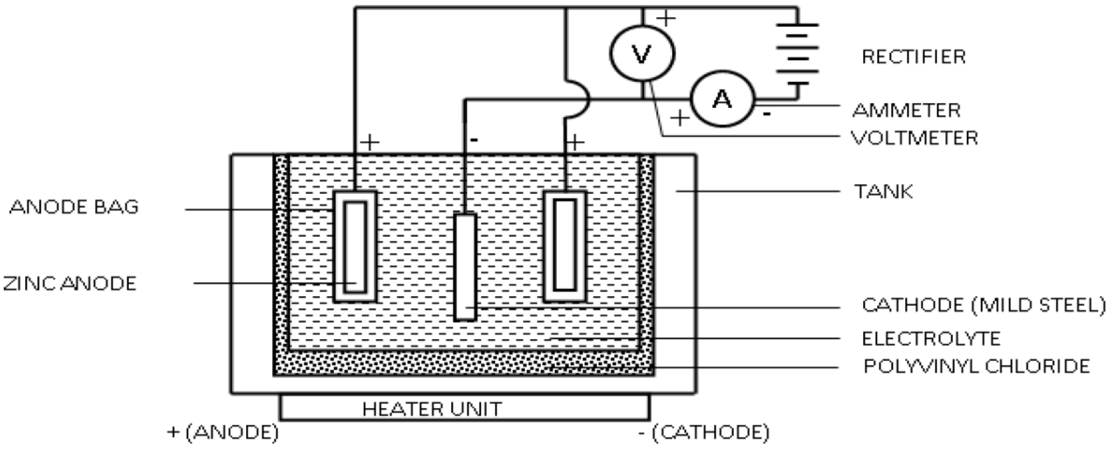


Figure 8 - Zinc electroplating scheme [42]

Zinc is anodic to iron and steel and therefore offers more protection when applied in thin films of 7 to 15 µm (0.3 to 0.5mil) than similar thicknesses of nickel and other cathodic coatings, except in marine environments where it is surpassed by cadmium (which is somewhat less anodic than zinc to iron and steel). When compared to other metals it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities. Zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Electroplated zinc without subsequent treatment becomes dull gray in appearance after exposure to air. Bright zinc that has been subsequently given a chromate conversion coating or a coating of clear lacquer (or both) is sometimes used as a decorative finish. Such a finish, although less durable than heavy nickel chromium, in many instances offers better corrosion protection than thin coatings of nickel chromium, and at much lower cost. [13]

Much recent attention has been focused on the development of techniques for electroplating alloys such as zinc-iron, zinc-nickel, and zinc-cobalt.

Commercial zinc plating is accomplished by a number of distinctively different systems: cyanide baths, alkaline noncyanide baths, and acid chloride baths. In the 1970s, most commercial zinc plating was done in conventional cyanide baths, but the passage of environmental control laws throughout the world has led to the continuing development and widespread use of other processes. Today, bright acid zinc plating (acid chloride bath) is possibly the fastest growing system in the field. [13]

The preplate cleaning and postplate chromate treatments are similar for all zinc processes; however, the baths themselves are radically different.

Zinc-plated steel cannot be used for equipment that is continually immersed in aqueous solutions and it must not be used in contact with foods and beverages because of dangerous health effects. Moreover, although zinc may be used in contact with gases such as carbon dioxide and sulfur dioxide at normal temperatures if moisture is absent, it has poor resistance to most common liquid chemicals and to chemicals of the petroleum and pharmaceutical industries.

1.2.5.1. Cyanide zinc bath

Bright cyanide zinc baths may be divided into four broad classifications based on their cyanide content: regular cyanidezinc baths, mid cyanide or half-strength cyanide baths, low-cyanide baths, and microcyanide zinc baths.

Cyanide baths are prepared from zinc cyanide (or zinc oxide sodium cyanide), and sodium hydroxide.

Standard cyanide zinc baths

Standard cyanide zinc baths have a number of advantages. They have been the mainstay of the bright zinc plating industry since the early 1940s. A vast amount of information regarding standard cyanide bath technology is available, including information on the technology of operation, bath treatments, and troubleshooting.

The standard cyanide bath provides excellent throwing and covering power. The ability of the bath to cover at very low current densities is greater than that of any other zinc plating system. This capability depends on the bath composition, temperature, base metal, and additives used, but it is generally superior to that of the acid chloride systems. This advantage may be critical in plating complex shapes. This bath also tolerates marginal preplate cleaning better than the other systems.

Cyanide zinc formulas are highly flexible, and a wide variety of bath compositions can be prepared to meet diverse plating requirements. Zinc cyanide systems are highly alkaline and pose no corrosive problems to equipment. Steel tanks and anode baskets can be used for the bath.

The cyanide system also has a number of disadvantages, including toxicity. With the possible exception of silver or cadmium cyanide baths, the standard cyanide zinc bath containing 90 g/L (12 oz/gal) of total sodium cyanide is potentially the most toxic bath used in the plating industry. The health hazard posed by the high cyanide content and the cost for treating cyanide wastes have been the primary reasons for the development of the lower-cyanide baths and the switch to alkaline noncyanide and acid baths.

Another disadvantage is the relatively poor bath conductivity. The conductivity of the cyanide bath is substantially inferior to that of the acid bath, so substantial power savings may be achieved by using the latter.

The plating efficiency of the cyanide system varies greatly, depending on such factors as bath temperature, cyanide content, and current density. In barrel installations at current densities up to 2.5 A/dm2 (25 A/ft2), the efficiency can range within 75 to 90%. In rack installations, the efficiency rapidly drops below 50% at current densities above 6 A/dm2 (60 A/ft2).

Although the depth of brilliance obtained from the cyanide zinc bath has increased steadily since 1950, none of the additives shows any degree of the intrinsic leveling found in the acid chloride baths. The ultimate in depth of color and level deposits reached in the newer acid baths cannot be duplicated in the cyanide bath. [13]

Midcyanide Zinc Baths

In an effort to reduce cyanide waste as well as treatment and operating costs, most cyanide zinc baths changed to the so-called midcyanide, half-strength, or dilute cyanide bath concentration. Plating characteristics of midcyanide baths and regular cyanide baths are practically identical. The only drawback of the midcyanide bath, compared with the standard bath, is a somewhat lower tolerance to impurities and poor preplate cleaning. This drawback is seldom encountered in practice in the well-run plant. Greater ease of rinsing, substantially less dragout, and savings in bath preparation, maintenance, and effluent disposal costs are responsible for the prominence of this type of bath. [13]

Low-cyanide zinc baths

Low-cyanide zinc baths are generally defined as those baths operating at approximately 6 to 12 g/L (0.68 to 1.36 oz/gal) sodium cyanide and zinc metal. They are substantially different in plating characteristics from the midcyanide and standard cyanide baths. The plating additives normally used in regular and midstrength cyanide baths do not function well with low metal and cyanide contents. Therefore special low-cyanide brighteners have been developed for these baths.

Low-cyanide zinc baths are more sensitive to extremes of operating temperatures than either the regular or midcyanide bath. The efficiency of the bath may be similar to that of a regular cyanide bath initially, but it tends to drop off more rapidly (especially at higher current densities) as the bath ages. Bright throwing power and covering power are slightly inferior to those of a standard midcyanide bath. However, most work that can be plated in the higher cyanide electrolytes can be plated in the low-cyanide bath. Despite the fact that low-cyanide baths have significantly lower metal and cyanide contents, they are less sensitive to impurity content than the standard or midcyanide bath. Heavy metal impurities are much less soluble at lower cyanide contents. The deposit from a low-cyanide bath is usually brighter than that from a regular or midcyanide system, especially at higher current densities. These baths are used extensively for rack plating of wire goods. Unlike the other cyanide systems, low-cyanide baths are quite sensitive to sulfide treatments to reduce impurities. Regular sulfide additions may reduce the plating brightness and precipitate zinc. [13]

Microcyanide zinc baths

Microcyanide zinc baths are essentially a retrogression from the alkaline noncyanide zinc process discussed in the following section. In the early history of alkaline baths it was often difficult to operate within its somewhat limited parameters; many platers used a minimal amount of cyanide in these baths, 1.0 g/L (0.13 oz/gal), for example. This acted essentially as an additive, increasing the overall bright range of the baths. However, it negated the purpose of the alkaline noncyanide bath, which is to totally eliminate cyanide. [13]

1.2.5.2. Alkaline non cyanide baths

Temperature control is more critical in noncyanide zinc baths than in cyanide baths. The optimum temperature for most baths is approximately 29 °C (84 °F). Low operating temperatures result in no plating or, at most, very thin, milky white deposits. High operating temperatures rapidly narrow the bright plating current range, cause dullness at low current densities, and result in very high brightener consumption. However, because these temperature limitations for noncyanide zinc are within those commonly used in regular cyanide zinc, no additional refrigeration or cooling equipment is required in the plant respect to the cyanide bath.

Normal voltages used in standard cyanide zinc plating are adequate for the noncyanide zinc bath, in both rack and barrel range. Normal voltage will be approximately 3 V with a range of 2 to 20 V, depending on part shape, anode-to-cathode relationship, temperature, barrelhole size, and variables that are unique to each operation.

The maximum allowable cathode current densities of the noncomplexing noncyanide bath closely approximate those of a standard cyanide bath. Current density ranges from 0.1 to more than 20 A/dm2 (1 to 200 A/ft2) can be obtained. This extremely wide plating range permits operation at an average current density of 2 to 4 A/dm2 (20 to 40 A/ft2) in rack plating, which makes a noncyanide system practical for high-production work.

Standard zinc ball or slab anodes in steel containers are used in the noncyanide electrolyte. During the first 2 or 3 weeks of installation of noncyanide zinc baths, the anode area should be watched carefully to determine the appropriate anode area to maintain a stable analysis of zinc in the system. Whenever possible, zinc anodes should be removed during weekend shutdown periods to avoid excessive metal buildup.

Filtration of noncyanide baths is not an absolute necessity. However, the occurrence of roughness in these baths presents a greater potential problem than in regular cyanide baths. This is due to the nature of the deposit, which may become amorphous at very high current densities if the brightener is not maintained at an optimum level, and to anode polarization problems, which result in sloughing off of anode slimes, a more common occurrence in these baths. Carbon filtration may be required to remove organic contamination caused by marginal preplate cleaning practices.

The bright plating range of the alkaline, noncyanide zinc bath is totally dependent on the particular additive used. Without any additive, the deposit from an alkaline, noncyanide bath is totally useless for commercial finishing, with a powdery, black amorphous deposit over the entire normal plating range. Proper maintenance of the addition agent at the recommended level is extremely important in noncyanide alkaline zinc baths. Low brightener content rapidly leads to high- and medium-currentdensity burning, because in the noncyanide bath, as in the low-cyanide bath, burning and brightness are interdependent.

Cathode current efficiency of a noncyanide bath is a very critical function of the metal content (Figure 9). At lower metal concentrations of approximately 4 g/L (0.5 oz/gal), efficiency is less than that of a standard cyanide bath, whereas at a metal content of approximately 9 g/L (1.2 oz/gal), efficiency is somewhat higher than in either regular or low-cyanide baths. Thus, if a plater can maintain metal content close to the 9 g/L (1.2 oz/gal) value, there will be no problem in obtaining deposition rates similar to those obtained with cyanide baths. [13]

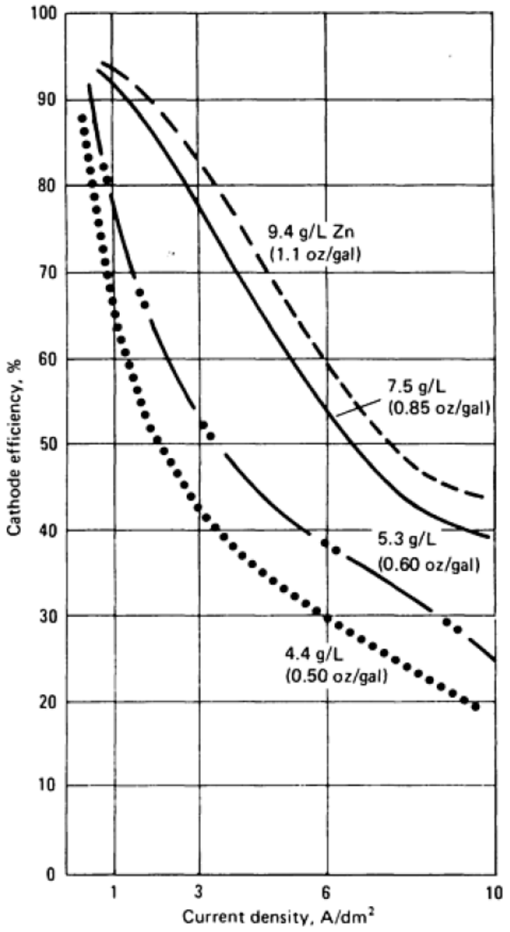


Figure 9 - Cathode current efficiency of alkaline noncyanide zinc baths as related to zinc metal contents. NaOH, 80 g/L (11 oz/gal); Na2CO3, 15 g/L (2 oz/gal) [13]

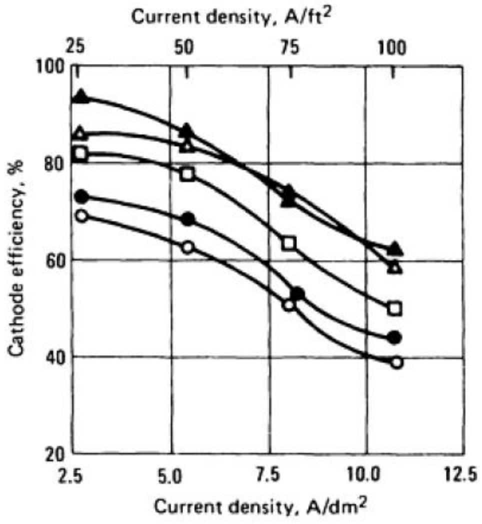


Figure 10 - Effect of zinc and sodium hydroxide concentration on the cathode efficiency of noncyanide zinc solutions. Temperature: 26 °C (77 °F).
◦ : 7.5 g/L (1 oz/gal) Zn, 75 g/L (10 oz/gal) NaOH;
•: 7.5 g/L (1.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH;
□ : 11 g/L (1.5 oz/gal) Zn, 110 g/L (15 oz/gal) NaOH;
▲ : 15 g/L (2.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH;
Δ : 11 g/L (1.5 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH. [13]

1.2.5.3. Acid bath

Acid chloride zinc baths currently in use are principally of two types: those based on ammonium chloride and those based on potassium chloride. The ammonium-based baths, the first to be developed, can be operated at higher current densities than potassium baths. Both systems depend on a rather high concentration of wetting agents, 4 to 6 vol%, to solubilize the primary brighteners. This is more readily accomplished in the ammonia systems, which makes bath control somewhat easier. Ammonium ions, however, act as a complexing agent in waste streams containing nickel and copper effluents, and in many localities they must be disposed of by expensive chlorination. This was the essential reason for the development of the potassium chloride bath.

The latest acid chloride zinc baths to become available to the industry are those based on salt (sodium chloride) rather than the more expensive potassium chloride. In many of these baths, salt is substituted for a portion of either ammonium or potassium chloride, producing a mixed bath. Sodium acid chloride baths at present are generally restricted to barrel operation, because burning occurs much more readily in these baths at higher current densities.

Acid chloride zinc baths are now being explored as the basis of zinc alloy plating incorporating metals such as nickel and cobalt, to improve corrosion for specific applications and possibly eliminate standard chromate treating.

A number of zinc baths based on zinc sulphate and zinc fluoborate have been developed, but these have very limited applications. They are used principally for high-speed, continuous plating of wire and strip and are not commercially used for plating fabricated parts.

Anodes for acid chloride zinc should be special high grade, 99.99% Zn. Most installations use zinc ball or flat top anodes in titanium anode baskets. Baskets should not be used if the applied voltage on an installation exceeds 8 V, because there may be some attack on the baskets. Baskets should be kept filled to the solution level with zinc balls. Slab zinc anodes, drilled and tapped for titanium hooks, may also be used. Any areas of hooks or splines exposed to solution should be protective coated. Anode bags are optional but recommended for most processes, especially for rack plating where they are useful to minimize roughness. Bags may be made of polypropylene, Dynel, or nylon. Before being used they should be leached for 24 h in a 5% hydrochloric acid solution containing 0.1% of the carrier or wetting agent used in the particular plating bath.

Zinc, total chloride, pH, and boric acid, when used, should be controlled and maintained in the recommended ranges by periodic replenishment using chemically pure materials. Excess zinc causes poor low-current-density deposits, and insufficient zinc causes high-current-density burning. Excess chloride may cause separation of brighteners, and insufficient chloride reduces the conductivity of solutions. Excessively high pH values cause the formation of precipitates and anode polarization, and excessively low pH values cause poor plating. Insufficient boric acid reduces the plating range. Brighteners also have to be replenished by periodic additions.

Agitation is recommended in acid chloride baths to achieve practical operating current densities. Solution circulation is recommended in barrel baths to supplement barrel rotation. In rack baths, solution circulation is usually accomplished by locating the intake and discharge of the filter at opposite ends of the plating tank. Cathode rod agitation is suitable for many hand-operated rack lines.

Air agitation is the preferred method for most installations. A low-pressure air blower should be used as a supply source.

Temperature control is more critical in acid zinc baths than in cyanide zinc baths, and auxiliary refrigeration should be provided to maintain the bath at its maximum recommended operating temperature, usually 35 °C (95 °F). Cooling coils in the bath itself should be Teflon or Teflon-coated tubing. Titanium coils may be used if they are isolated from the direct current source.

Operating an acid chloride bath above its maximum recommended temperature causes low overall brightness, usually beginning at low current densities and rapidly progressing over the entire part. High temperatures may also bring the bath above the cloud point of the brightener system. As the acid bath gets hot, additives start coming out of solution, giving the bath a milky or cloudy appearance and causing bath imbalance. Conversely, low temperatures, usually below 21 °C (70 °F), cause many baths to crystallize and cause organic additives to separate out of solution. This produces roughness and, in extreme cases, a sticky globular deposit on the bath and work, which clogs filters and completely curtails operations.

The high cathode current efficiency exhibited by acid chloride zinc baths is one of the most important properties of these baths. As shown in Figure 11, the average cathode current efficiency for these baths is approximately 95 to 98% over the entire range of operable current densities. No other zinc plating system approaches this extremely high efficiency at higher current densities, which can lead to productivity increases of 15 to 50% over those obtainable with cyanide baths. In barrel plating, barrel loads can often be doubled in comparison with those for cyanide baths, and equivalent plating thickness can often be achieved in half the time.

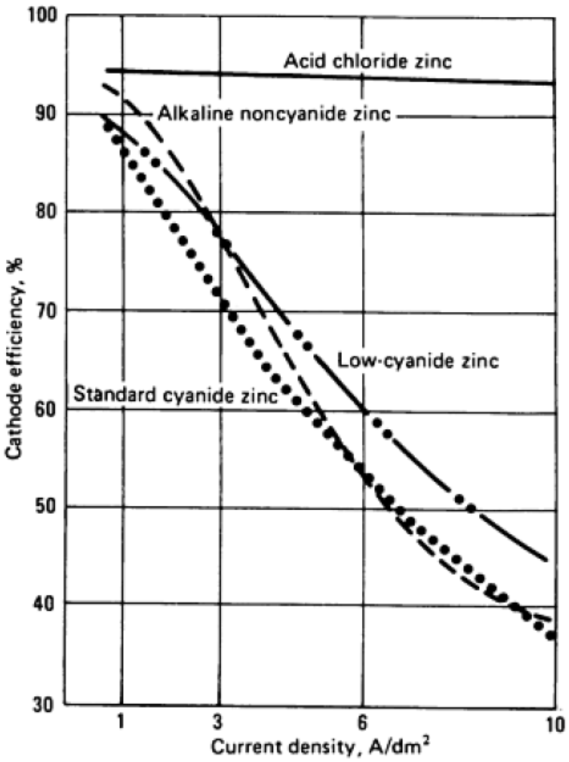


Figure 11 - Comparison of cathode current efficiencies of bright zinc plating electrolytes [13]

pH control of acid zinc baths should usually be monitored on a daily basis. The pH of a bath is lowered with a hydrochloric acid addition; when required, the pH may be raised with a potassium or ammonium hydroxide addition.

Iron contamination is a common problem in all acid chloride zinc baths. Iron is introduced into the bath from parts falling into the tank during operation, from attack by the solution on parts at current densities below the normal range, such as the inside of steel tubular parts, and from contaminated rinse waters used before plating. Iron contamination usually appears as dark deposits at high current densities; in barrel plating it appears as stained dark spots reproducing the perforations of the plating barrel. A high iron content turns the plating solution brown and murky.

Iron can be readily removed from acid chloride baths by oxidizing soluble ferrous iron to insoluble ferric hydroxide. This is accomplished by adding concentrated hydrogen peroxide to the bath. Approximately 10 mL (0.34 fl oz) of 30% hydrogen peroxide should be used for every 100 L (26.4 gal.) of bath. Dissolved potassium permanganate can be used instead of peroxide. The precipitated iron hydroxide should then be filtered from the bath using a 15 µm (0.6 mil) or smaller filter coated with diatomaceous earth or a similar filter aid.

The continuing development of acid zinc plating baths based on zinc chloride has radically altered the technology of zinc plating since the early 1970s. Bright acid zinc baths have a number of intrinsic advantages over the other zinc baths:

- They are the only zinc baths possessing any leveling ability, which, combined with their superb out-of bath brightness, produces the most brilliant zinc deposits available.
- They can readily plate cast iron, malleable iron, and carbonitrided parts, which are difficult or impossible to plate from alkaline baths.
- They have much higher conductivity than alkaline baths, which produces substantial energy savings.
- Current efficiencies are 95 to 98%, normally much higher than in cyanide or alkaline processes, especially at higher current densities, as shown in Figure 11.
- Minimal hydrogen embrittlement is produced than in other zinc baths because of the high current efficiency.

The negative aspects of the acid chloride bath are that:

- The acid chloride electrolyte is corrosive. All equipment in contact with the bath, such as tanks and superstructures, must be coated with corrosion-resistant materials.
- Bleedout of entrapped plating solution occurs to some extent with every plating process. It can become a serious and limiting factor, prohibiting the use of acid chloride baths on some fabricated, stamped, or spot welded parts that entrap solution. Bleedout may occur months after plating, and the corrosive electrolyte can ruin the part. This potential problem should be carefully considered when complex assemblies are plated in acid chloride electrolytes. [13]

1.2.6. Conversion coating

Chromate conversion coating has been widely used for many engineering materials to provide improved corrosion resistance, desirable surface finishes and paint adhesion characteristics. [14]

Because corrosion is rapid in industrial and marine locations, zinc-plated parts that must endure for many years are usually protected by supplementary coatings. Steel with 5 µm (0.2 mil) of electroplated zinc is often painted to obtain a coating system for general outdoor service; a phosphate or chromate post-plating treatment ensures suitable adherence of paint to zinc.

In uncontaminated indoor atmospheres, zinc corrodes very little. A 5 µm (0.2 mil) coating has been known to protect steel framework on indoor cabinets for more than 20 years. Atmospheric contaminants accelerate corrosion of zinc if condensation occurs on cooler parts of structural members inside buildings. In 10 years or less, 12.5 µm (0.5 mil) of zinc may be dissipated. Zinc-plated steel in such locations is usually given a protective coating of paint.

Chromate conversion coatings, coloured or clear, are almost universally applied to zinc-plated parts for both indoor and outdoor use to retard corrosion from intermittent condensation, such as may occur in unheated warehouses. Chromate films minimize staining from fingerprints and provide a more permanent surface appearance than bare zinc. [13]

There are four major type of conversion coating: clear or blue- bright, yellow or iridescent, olive drab and black.

The clear or blue-bright coating is typically used for decorative purpose, giving a bluish cast. The conversion process is obtained by a single-step dip or by two-step dip (less common). This passivation is based on hexavalent chromium compounds, trivalent chromium compounds or trivalent chromium reaction products. All three provide the bluish cast, but corrosion protection does vary, going from the more protective hexavalent chromium to the less protective trivalent chromium. The advantage of the trivalent chromium is that is not toxic and so it has an advantageous waste treatment.

The yellow or iridescent passivation give a yellowish cast and good corrosion protection. Now a day the coating is formed using hexavalent chromium or trivalent chromium whit a single dip process.

The olive drab conversion coating offers the maximum corrosion protection of all the named type of conversion coating. It gives an olive drab colour to the treated parts. The treatment is based on hexavalent chromium and in single-dip process.

The black conversion coating is produced with the use of silver based chromate or with proprietary chromates formulated without silver. It is the most expensive chromate finishes if formulated with silver. As the name suggest it provides a black finish with corrosion protection that can even surpass the olive drab if used the proprietary formulations. [4]

In the recent years the hexavalent chromium is been removed from the conversion process due to its toxicity and the stricter regulation on the matter in many country [15] and it is been replaced principally by the trivalent chromium (non-toxic) [16], but also free chromium passivation have been studied like the molybdate passivation [17]. The corrosion behaviour of zinc coatings submitted to a trivalent chromium based passivation treatment show a worse corrosion behaviour compared with the hexavalent chromium, but if they sustain, after the passivation, a sealing process, they can also surpass the hexavalent chromium conversion coating [18].

The quality of the chromate conversion coating is strictly related in all the case to the dipping time [19]. The longer the passivation time the thicker the conversion coating will be, but the time should remain under certain limit to prevent the formation of extensive crack on the chromate layer [20]. During the drying of process of passivated parts the temperature needed is around 50-60°C and should not be exceeded, because otherwise there is the risk of a too rapid elimination of water which can lead to cracks on the chromate passivating film surface [20].

All the chromate conversion coating can be dyed, but it needs to be done immediately after the rinsing because when the passivation has been dried and aged it cannot be dyed anymore.

In Table 1 is written the corrosion resistance of the various type of chromate conversion coatings.

Table 1 - Chromate conversion coating corrosion resistance [4]

Chromate conversion coating	**Salt spray hours (h)**
Hexavalent chromium – clear	8-24
Trivalent chromium – clear	4-8
Iridescent yellow	96
Olive drab	144-172
Black (with silver)	36-48
Black (without silver)	>200

1.2.7. Pretreatment

Most of the deposition techniques named above need a pretreatment of the substrate before the start of the process to remove the oxide, the corrosion products, the grease and the oil.

In selecting a metal cleaning process, many factors must be considered, including:

- The nature of the soil to be removed
- The substrate to be cleaned (ferrous, nonferrous, etc.)
- The importance of the condition of the surface to the end use of the part
- The degree of cleanliness required
- The existing capabilities of available facilities
- The environmental impact of the cleaning process
- Cost considerations
- The total surface area to be cleaned
- Effects of previous processes
- Rust inhibition requirements
- Materials handling factors
- Surface requirements of subsequent operations, such as phosphate conversion coating, painting, or plating

Very few of these factors can be accurately quantified, which results in subjective analysis. Frequently, several sequences of operations may be chosen which together produce the desired end result.

Because of the variety of cleaning materials available and the process step possibilities, the selection of a cleaning procedure depends greatly on the degree of cleanliness required and subsequent operations to be performed. Abrasive blasting produces the lowest degree of cleanliness, followed by solvent, solvent vapor degrease, emulsion soak, alkaline soak, alkaline electroclean, alkaline plus acid cleaning, and finally ultrasonics for the cleaner surface. In addition to these conventional methods, very exotic and highly technical procedures have been developed in the electronics and space efforts to produce clean surfaces far above the normal requirements for industrial use. [13]

Usually, industries refer to international standards and specifications promoted by recognized organizations, such as the SSPC (Society for Protective Coatings, formerly the Steel Structures Painting Council) in USA, CEN-ISO and the Swedish Standard Association in Europe, which contains also photographic examples as a practical guide. In particular:

1. “Degreasing with solvents and detergents” means cleaning from grease, oil and dust by means of organic solvents, emulsions, biphasic detergents or alkaline detergents. To remove impurities remained stuck on the substrate even after degreasing, a mechanical action is necessary, as produced by impingement made by liquids or gas bubbles in electrochemical treatments or by ultrasounds.
2. “Pickling” consists of immerging the substrate in strong inorganic acids as sulfuric, hydrochloric, phosphoric, nitric, hydrofluoric or a mixture of them at a temperature higher than the ambient one to remove oxides formed during manufacturing at high temperature or by previous corrosion. This surface treatment is quite ideal for the application of coatings. Pickling is followed by rinsing in neutralizing solutions. For common steels sulfuric acid in concentration 1–50% and hydrochloric acid is used.
3. “Sandblasting” is the action of spraying, at a high-speed, abrasive powder onto the substrate. Silica sand, whether natural or obtained by grinding, corundum, cast iron and steel granules are the main alternatives, depending on economical liquidity. It can be performed dry or wet; the former is often preferred due to the shorted working time with respect to the latter in which abrasive particles are dispersed in a water stream so then need to be dry. In current practice, different sandblasting grades are defined.

“ISO 8504, Preparation of steel substrates before application of paints and related products - Surface preparation methods, International Organization for Standardization, CH-1211” is the applicable relevant regulation. In general, every time an intense cleaning of the substrate is required (degreasing, pickling and sandblasting), hydrogen forms and may remain entrapped during production process. The most frequent strategy to free entrapped hydrogen, thus preventing hydrogen embrittlement, is a preheating treatment. A direct consequence of such an increase in temperature is the formation of intermetallic compounds which improve adhesion; these compounds have brittle behavior, so it is important to have a controlled number of them, in order not to decrease the hardness of the final coating. [3]

2 Production plant

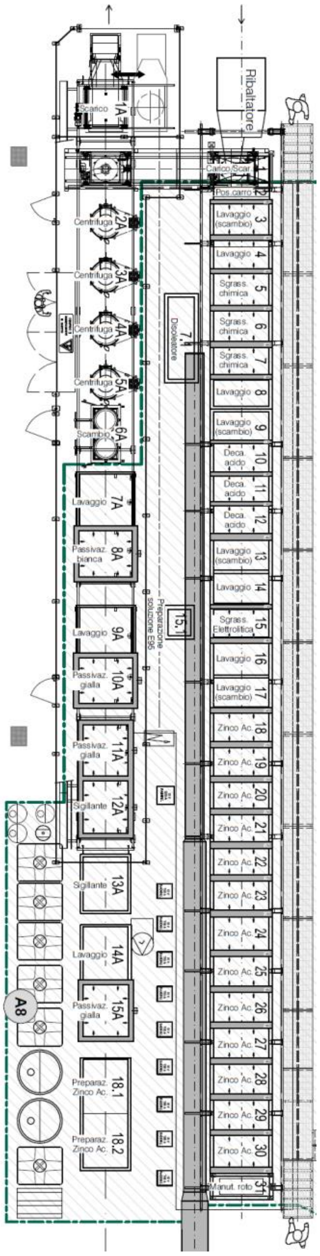


Figure 12 - Plant layout

The production plant can be divided in two parts connected by a cart. The first part of the plant is dedicated to the load of the materials to be zinced, to pretreatment and to zinc electroplating (in Figure 12 position from 1 to 31), instead the second part is dedicated to passivation and sealing process, to drying and to the unload of the finished product (in Figure 12 position from 1A to 15A). The first part has three rail barrel movers, instead the second part of the plant have only two rail barrel movers. All the tanks are made of steel and coated internally with PVC.

The load of the barrel is performed in the first position (Figure 12) by letting the pieces slide inside the open barrel (Figure 13). After the barrel is loaded, it is closed manually by an operator and it is ready to be moved to the next position by a rail barrel mover.

Figure 13 - Loading operation of a barrel

The next position that the barrel takes is in the chemical degreasing (in Figure 12 positions number 5-6-7). The 3 positions of the chemical degreasing (Figure 14) are divided in two tanks, two positions in one tank of 1,7 m^3 capacity and one position in the other tank of 0,85 m^3 capacity, both with the same bath composition thanks to the continuous mixing of the two degreasing bath through the oil separator (Figure 15) next to the tanks. The bath should maintains 40 g/l concentration of sodium hydroxide, 4% concentration of the additive used and a temperature between 50 and 60°C [21]. The additive is formulated to allow the stratification of the emulsified dirt on the surface of the work tank. In this way, using an oil separator is possible to increase the life duration of solution.

Figure 14 - Chemical degreasing position

Figure 15 - Oil separator (on the left) and its recovery tank (on the right)

After the chemical degreasing a rinse in a dedicated position is done. For the sake of simplicity from now on it will not be repeated but also after the other pretreatments, the electroplating and the passivation there are dedicated position for the rinse. It is important to note that each passivations have its own dedicated rinse and that after the sealing (if applied) there will be no rinse, otherwise the sealer will be simply removed during the rinsing.

The pickling is the next pretreatment phase and is performed in a tank with three position (in Figure 12 positions number 10-11-12) (Figure 16). The volume of the tank is 2,9 m^3. For pickling is used a 20-40% hydrochloric acid (HCl 37%) solution.

Figure 16 - Pickling position

As last pretreatment an electrolytic degreasing is done (in Figure 12 positions number 15). There is only one position for this passage (Figure 17) and it is in a tank of 0.85 m^3. The solution for this pretreatment is composed by sodium hydroxide 70-120 g/l and by an additive that should be in the concentration range of 8-10%. This additive allows you to prepare electrolyte solutions with a high sequestering and dispersing power. The solution have the best performance in the temperature range 50-60°C.

Figure 17 - Electrolytic degreasing position

After the pretreatments is the turn of the zinc electroplating, for this 13 position for different barrel are available (in Figure 12 positions number from 18 to 30). The 13 positions (Figure 18) are divided in two tanks, six positions in one tank of 6,1 m^3 capacity and seven position in the other tank of 8 m^3 capacity, both with the same bath composition thanks to the continuous mixing of the two zinc bath through the zinc preparation tanks next to the line. The two zinc preparation tanks pump in from both zinc baths and then pump out again in both the zinc baths. The two zinc preparation tanks are used for adding some components in the bath if needed. The zinc bath solution is so composed:

Table 2 - Composition of zinc bath [22]

Zinc Chloride	65-75 g/l
Potassium Chloride	180-220 g/l
Boric Acid	20-30 g/l
Additive 1	40 ml/l
Additive 2	0,5 ml/l

The chlorides in the bath will dissolve the zinc anodes constantly supplying the bath with zinc, which is needed for the formation of the coating. Salts also imcrease the conductivity of the bath improving the current distribution. Instead, the boric acid act as a buffer in the solution, helping in the maintenance of the pH (pH shuld remain between 4,6 and 5,2). The additive 1 is needed to help the dissolution of the second additive and to increase the effects of salts. The additive 2 improve the brightness and the uniformity of the final coating.

Figure 18 - Zinc bath positions

This formulation facilitates the precipitation and subsequent filtration of the iron by means of small additions of hydrogen peroxide (H_2O_2), keeping the working solution always clear (Figure 19) [22].

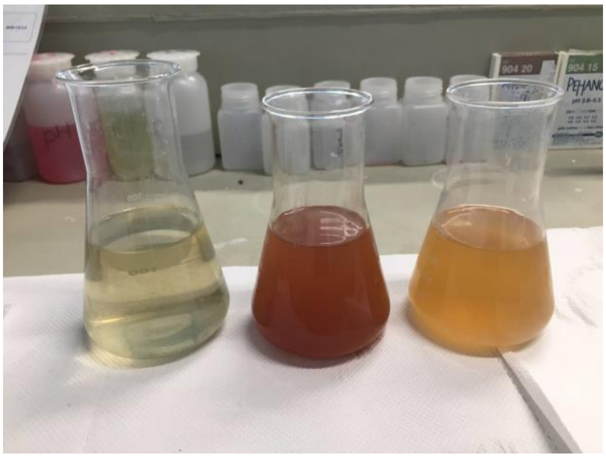


Figure 19 - From left to right: zinc bath, zinc bath + H_2O_2, filtered zinc bath + H_2O_2

Done the electroplating and the following rinse the barrel return to position number 1, so that the zinced pieces could be transferred to another type of barrel (Figure 20) used in the other side of the plant. To transfer the pieces the barrel is opened and turned in a way that the parts can fall in the funnel connected to the other barrel (Figure 21).

Figure 20 - Barrel type used in the second part of the plant

Figure 21 - Funnel used to transfer the parts from one type of barrel to the other

The new barrel is moved to the other part of the plant through a cart (Figure 22) to then proceed with the passivation. Meanwhile the empty barrel get filled again with new pieces and start again the process.

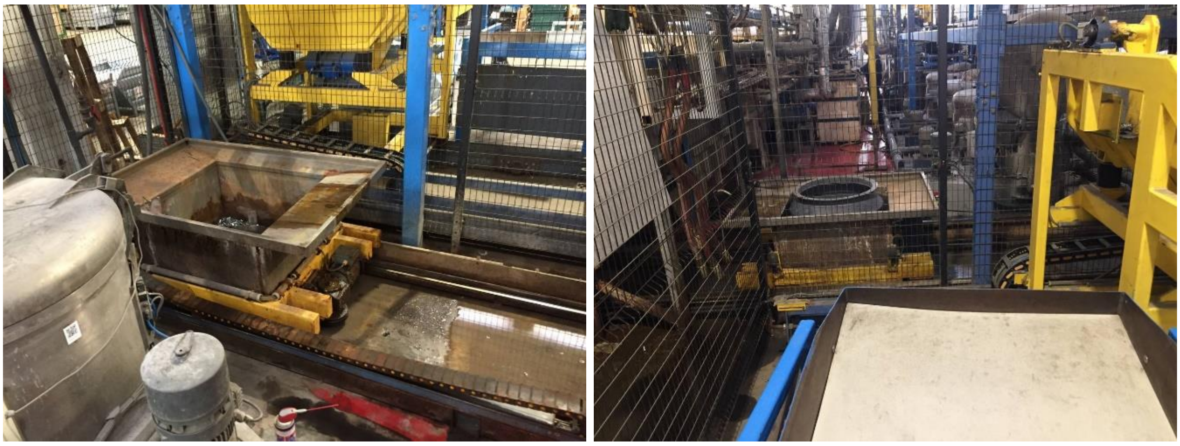


Figure 22 - Cart that transfer the second type of barrel between the two parts of the plant

The next step is the chromate conversion coating. In this plant different type of passivations are used, one blu-bright passivation (in Figure 12 position number 8A) (Figure 23) and three different yellow passivations (in Figure 12 position number 10A-11A-15A), all the passivation are based on trivalent chromium. The chromate conversion coating in position number 10A and 15A should be mantained at pH 1,8-2,0 [23] [24], instead for the other two the working condition are pH 2,0-2,5 [25]

[26]. For all the passivations additions of nitric acid may be required to keep the pH at working values. The temperature should remain for all the passivation baths between 20-30°C [23] [24] [26] [25]. All the tanks containing the zinc chromate conversion coatings have a volume of 1,5 m^3.

Figure 23 - Blue-bright passivation position

Following the passivation the parts could be sealed and in that case there are two different type of sealer used each one with its tank (in Figure 12 position number 12A and 13A) of 1,5 m^3 of volume. The sealer in position 12A working condition are pH 9,5 , temperature between 20-30°C and the following drying should be performed at 80°C. Caustic soda additions may be required to keep the pH in optimal working parameters. It is advisable not to bring the pH value below 8.5, otherwise a lower pH will cause the product to flocculate [27]. Instead the sealer in position 13A working condition are pH 11-12, temperature between 20-50°C and the following drying is suggested to be performed with a temperature between 50 and 120°C. Also in this case caustic soda additions may be required to keep the pH in optimal working parameters [28]. Both the sealers are silicon based.

For drying four spin-dryer (Figure 24) are used (in Figure 12 position from 2A to 5A).

Figure 24 - Spin dryer

As last step the barrel is unloaded in position 1A (Figure 25).

Figure 25 - Unloading position

To maintain the right composition and parameters of the various baths dosing pumps are used. They are used for caustic soda in both the degreasing, for all additive and for the potassium chloride in the zinc baths.

3 Experimental procedure and instruments

3.1. Chemical analysis

In this chapter the reagents and procedures for carrying out the analyses for the zinc bath and of the pretreatments will be explained. It should be added that in the factory's laboratory was not possible to measure the concentration of the additives used in zinc bath, in the two type of degreasing and in the various passivation. For this reason the supplier periodically performs analyse of all the baths in the production plant (pretreatments, zinc bath, passivations and sealers).

3.1.1. Determination of zinc (Zn)

The following analyse is done to measure the concentration of zinc in the zinc bath.

Reagents:

- Concentrated Ammonia (30%) (NH_3)
- Nero Eriocromo T
- E.D.T.A. 0.05M (disodium salt 0,05 mol/l)
- Formaldehyde (8%)

Procedure:

1. Pour 1 ml of bath into a 250 ml conical flask,
2. Add about 50 ml of distilled water (H_2O),
3. Add about 10 ml of Concentrated Ammonia,
4. Put a tip of Nero Eriocromo T as an indicator,
5. Add 5 ml of an 8% Formaldehyde solution,
6. Titrate with EDTA 0,05M until the solution tone to blue [29].

Formulas:

Zn (g/l) = EDTA 0,05M (ml) x 3,25 [29]

$ZnCl_2$ (g/l) = metallic Zn (g/l) : 0,479 [29]

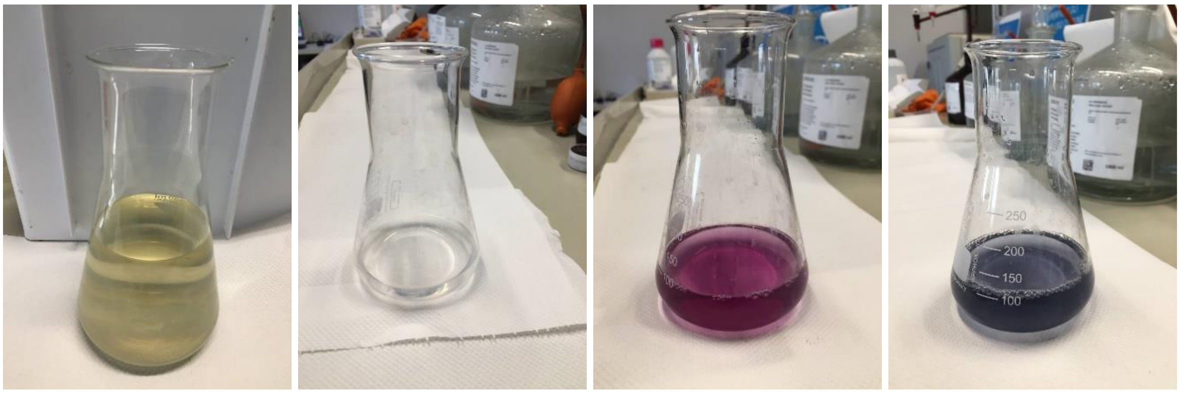


Figure 26 - From left to right: zinc bath, diluited zinc bath, diluited zinc bath + NH_3 + formaldehyde + nero eriocromo, previous solution titrated with E.D.T.A.

3.1.2. Determination of chlorides (Cl^-)

The following analyse is done to measure the concentration of chlorides in the zinc bath, knowing the chlorides and the zinc present in the bath is also possible to calculate the concentration of potassium chloride.

Reagents:

- Potassium Chromate (saturated solution in H_2O)
- Silver Nitrate 0,1N ($AgNO_3$ 0,1 mol/l)

Procedure:

1. Pour 0,5 ml of bath into a 250 ml conical flask,
2. Add about 50 ml of distilled water (H_2O),
3. Add a few drops of Potassium Chromate as an indicator,
4. Titrate with $AgNO_3$ 0,1N until the solution tone to red with white precipitate [29].

Formulas:

Cl^- (g/l) = $AgNO_3$ 0,1N (ml) x 7,092 [29]

KCl (g/l) = [Cl^- (g/l) – ($ZnCL_2$ (g/l) x 0,52)]: 0,475 [29]

Figure 27 - From left to right: diluited zinc bath + potassium chromate, previous solution titrated with $AgNO_3$

3.1.3. Determination of boric acid (H_3BO_3)

The following analyse is done to measure the concentration of boric acid in the zinc bath.

Reagents:

- Bromo Cresol Porpora (Alcoholic solution 1%)
- Sodium Hydroxide 0,1N (NaOH 0,1 mol/l)
- Sorbitol ($C_6H_{14}O_6$)

Procedure:

1. Pour 2 ml of bath into a 250 ml conical flask,
2. Add about 50 ml of distilled water (H_2O),
3. Add a few drops of Bromo Cresol Porpora as an indicator,
4. Add about 20-30 ml of Sorbitol,

5. Titrate with NaOH 0,1N until the solution tone to violet [29].

Formulas:

$$H_3BO_3\ (g/l) = NaOH\ 0{,}1N\ (ml) \times 3{,}091 \quad [29]$$

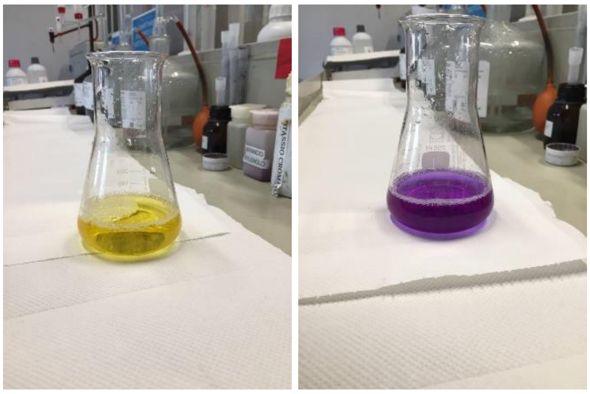


Figure 28 - From left to right: diluited zinc bath + bromo cresol porpora + sorbitol, previous solution titrated with NaOH

3.1.4. Determination of hydrochloric acid (HCl)

The following analyse is done to measure the concentration of hydrochloric acid in the pickling pretreatment.

Reagents:

- Blu di Bromofenolo,
- Sodium hydroxide 0,1N (NaOH 0,1 mol/l)

Procedure:

1. Pour 1 ml of bath into a 250 ml conical flask,
2. Add about 50 ml of distilled water (H_2O),
3. Add a few drops of Blu di Bromofenolo as an indicator,
4. Titrate with NaOH 0,1N until the solution tone from yellow to blue [30].

Formulas:

$$\text{HCl 37\% (g/l)} = (\text{NaOH 0,1N (ml)} \times 3{,}65) / 0{,}37 \qquad [30]$$

Figure 29 - From left to right: pickling bath, diluted pickling bath, diluted pickling bath + blu di bromofenolo, previous solution titrated with NaOH

3.1.5. Determination of sodium hydroxide (NaOH)

The following analyse is done to measure the concentration of sodium hydroxide in both degreasing process.

Reagents:

- Hydrochloric acid 1N (HCl 1 mol/l)
- Phenolphthalein

Procedure:

1. Pour 5 ml of bath into a 250 ml conical flask,
2. Add about 50 ml of distilled water (H_2O),
3. Add a few drops of Phenolphthalein as an indicator,
4. Titrate with HCl 1N until the solution tone from red/pink to colourless [31].

Formulas:

$$\text{NaOH (g/l)} = \text{HCl 1N (ml)} \times 8 \qquad [31]$$

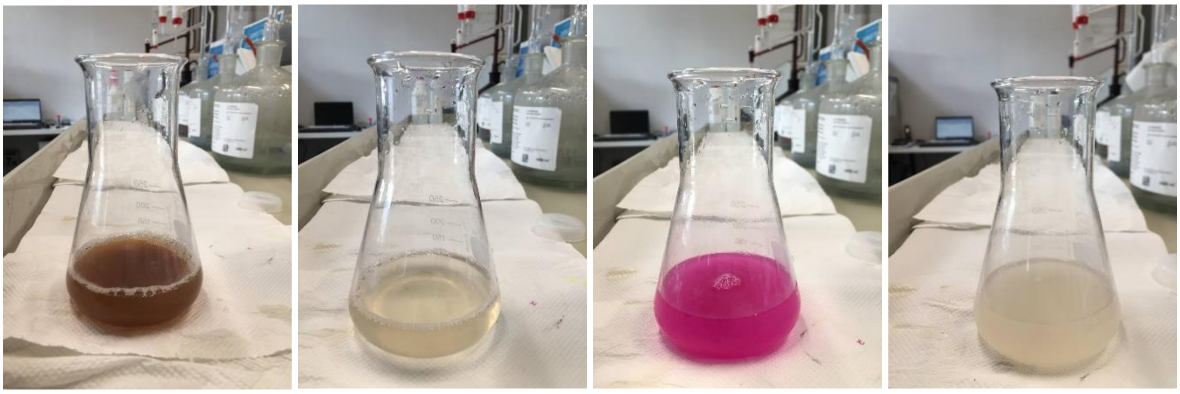


Figure 30 - From left to right: chemical degreasing bath, diluted chemical degreasing bath, diluted chemical degreasing bath + phenolphthalein, previous solution titrated with HCl

Figure 31 - From left to right: electrolytic degreasing bath, diluted electrolytic degreasing bath, diluted electrolytic degreasing bath + phenolphthalein, previous solution titrated with HCl

3.2. Hull cell test

3.2.1. Hull cell test description

This section briefly introduces to the basic knowledge of Hull cell. The Hull cell is a tank for experiments about plating, invented by Dr. R. O. Hull. The Hull cell is an analytical electrochemical cell designed with trapezoidal geometry to incorporate a range of current densities into a single experiment [32] and, in this way, it has become easier to see the relationship between current density and anode-cathode distance. In fact, by creating different distances between the anode and cathode, a deposited coating from different current densities (from high to low) can be observed on a single test sample.

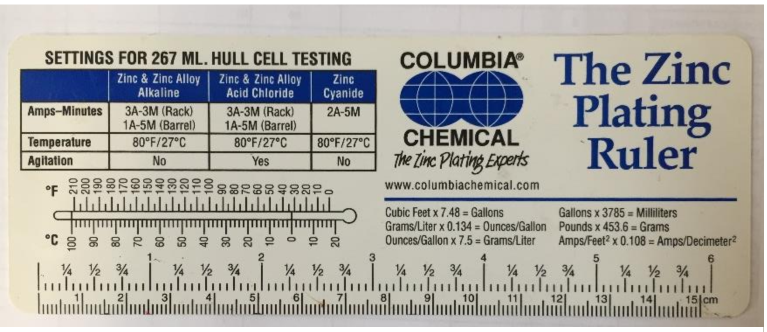
It is important to underline that the Hull cell test's feature is that Hull cell test performs an actual plating. So, the observer can see a real coated sample and thus check, in a first place, its state of uniformity, brightness and presence of imperfections; secondly, the conditions of the bath. To perform the analysis, one needs to fill the cell with the selected electrolyte, insert the anode and the cathode in their prearranged positions and make the necessary electrical connections.

Current density distribution on the sample depends on total current. It can be calculated using the following formula

$C.D. = I \cdot (5,10 - 5,24 \cdot \log(L))$

where C.D. is the current density (A/cm^2) or (A/dm^2), I is the total current (A) and L is the distance from the edge of high current side on the cathode.

However, it is usually observed more simply by using the "Hull cell Scale" reported in Figure 32.



SETTINGS FOR 267 ML. HULL CELL TESTING

	Zinc & Zinc Alloy Alkaline	Zinc & Zinc Alloy Acid Chloride	Zinc Cyanide
Amps–Minutes	3A-3M (Rack) 1A-5M (Barrel)	3A-3M (Rack) 1A-5M (Barrel)	2A-5M
Temperature	80°F/27°C	80°F/27°C	80°F/27°C
Agitation	No	Yes	No

Cubic Feet x 7.48 = Gallons
Grams/Liter x 0.134 = Ounces/Gallon
Ounces/Gallon x 7.5 = Grams/Liter
Gallons x 3785 = Milliliters
Pounds x 453.6 = Grams
Amps/Feet² x 0.108 = Amps/Decimeter²

Figure 32 - Zinc plating ruler

Many kinds of superficial defects can occur: localized defects, which have small extension, more or less regular; extensive defects, which affect the totality or almost the totality of the surface and adhesion-cohesion defects, concerning the connection between the growing deposit and the underlying substrate ("lack of adhesion" when there is a deposit loss immediately after deposition; "lack of cohesion" when deposit loss occurs at a later moment, often following the application of variable degrees of stress).

The most frequent localized defects are:

- Burning spots: small non regular spots, usually localized at the edges of the sample where current density is higher, rarely localized in the inner part of the sample.
- Stains: group of spots, both of smaller and bigger dimensions.
- Pits: sort of microporosities, very similar to the homonymous in corrosion classification, generally spherical.
- Bubbles and vesicles: accumulations of air and gases, generally spherical, which can be embedded during coating growth, leading to bad adhesion.
- Streaking: sort of concentric rings or stripes from high to low current density areas.
- Hazes and cloudiness: areas in which the deposit is translucent and whitish, “cloud-like”.
- Post oxidation dark spots: spots formed immediately after deposition and drying.

Extensive defects one may found are:

- Burnt areas: large portions of the deposit with rough and irregular appearance, with coarse finish.
- Dull deposit: large portions with opaque finish.
- Discoloration: areas with different colors, alternation of lighter and darker areas or iridescent phenomena.
- Low levelling: typical of thick deposits, bad homogeneity such that discontinuities similar to super imposed planes occur.

Finally, adhesion-cohesion defects are:

- Peeling: generation of laminas, the deposit flakes.
- Blistering: generation of a sort of powder, the deposit crumbles. [3]

3.2.2. Hull cell test procedure

The procedure used to perform the hull cell test is the following.

Procedure:

1. Pickle the iron sheet in hydrochloric acid at 20% volume concentration,
2. Rinse the sheet,
3. Degrease with Vienna lime the sheet,
4. Rinse the sheet,
5. Place the sheet in the Hull cell with active stirring,
6. Connect the + terminal to the anode and the - terminal to the sheet,

7. Set the rectifier to 1 Ampere,
8. After 10 minutes remove the sheet,
9. Rinse the sheet,
10. Wash in water and 0.5% nitric acid (pre-passivation) to remove the organic layer on the surface of the sheet,
11. Rinse the sheet,
12. Dry the sheet. [33]

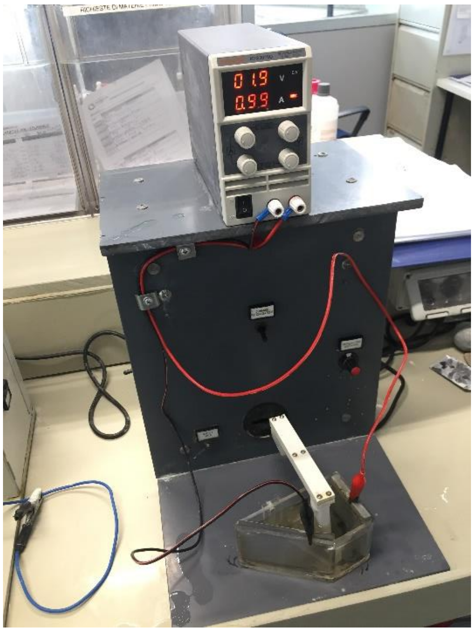


Figure 33 - Hull cell test setup

Figure 34 - Pickling of the metal sheet

3.3. X-ray

Thickness assessment on electroplated Zn coating is normally performed through X-ray Fluorescence spectroscopy (XRF). With this system, precise and non-contact measurements can be obtained. Currently, it is widely used not only in laboratory, but also by industrial companies who want to certify they production.

A Helmut-Fisher type XDL-XYmZ (Figure 35) where used to measure the thickness of the sample.

Figure 35 - Helmut-Fisher type XDL-XYmZ

XRF analysis is the most used method for evaluating thickness and for analyzing composition: it can be used for measuring coatings as well as for the qualitative and quantitative determination of the elemental composition of the considered sample thanks to the study of X ray fluorescence phenomenon. In fact, this radiation is emitted by each atom composing the sample as a consequence of excitation following irradiation by X rays. The most used instrument is the FISCHERSCOPE® XRF.

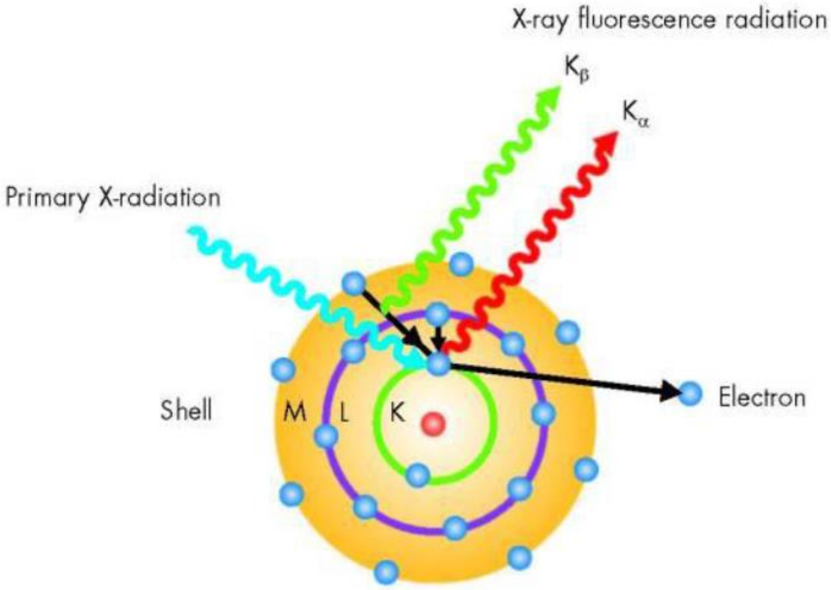


Figure 36 - Physical principle of an XRF analysis [3]

FISCHERSCOPE® XRF instrument has the following advantages:

- Non-destructive: the X-radiation has no lasting influence on the material; it fully retains its quality,
- Fast: the XRF method needs very simple sample preparation and short measurement times in the range of seconds,
- Clean: no chemicals are used,
- Safe**:** method without the use of environmentally hazardous chemicals and X-radiation poses no risk for operator due to the protective instrument design,
- Universally applicable: The XRF method is suitable for material analysis and thickness measurements in a very broad range of applications. [3]

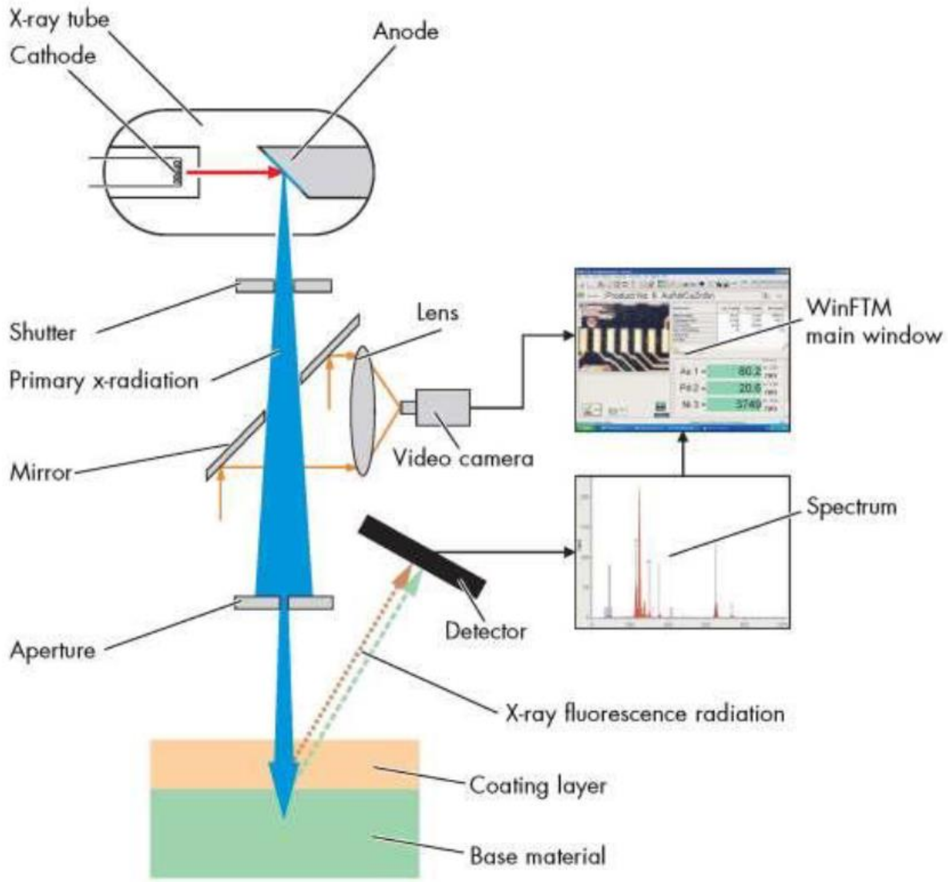


Figure 37 - Functional working principle of a FISCHERSCOPE® X-Ray Fluorescence Spectroscopy (XRF) Instrument [3]

3.4. Salt spray

An Angelantoni DCTC600 (Figure 38) has been used to perform the Salt Spray test of the samples and so to determine their corrosion behaviour.

Figure 38 - Salt spray machine Angelantoni DCTC600

Salt spray test simulates a corrosive attack to coated samples: the appearance of corrosion products is evaluated after a pre-determined period of time. The overall duration depends on the corrosion resistance of the coating; generally, the more resistant the coating is, the longer is the period of testing before the appearance of corrosion products.

It is important to note that the time spent by the pieces in the salt spray chamber before the appearance of corrosion products does not correspond to the time needed to have the appearance of the corrosion products in the real application of the pieces. In fact salt spray tests do not replicate the real world conditions (change in humidity, temperature, pollutions, ecc.), instead the tests are performed in a strictly controlled environment with the various parameters regulated by norms, for example UNI ISO 9227 or ASTM B 117/97. The parameters change depending on the material that is tested.

The corrosion resistance data collected in this work were obtained performing a neutral salt spray test (NSS), commonly used for steel based parts, that consists in a closed chamber where a salty water (5%±1% NaCl [34]) solution is nebulized, through a spray nozzle, using pressurized air. The pH of the solution should be between 6,5 and 7,2 and its conductivity should be less than 20 µS [34] (5 µS for ASTM B 117/97 [35]). The temperature should remain in the range of 35±2°C [34]. This is a kind of severe corrosive environment of dense saltwater fog in which samples are placed. The sample should not be placed in front of nozzle and need to be placed with the major surface to be evaluated at a 20-25° angle [34] (or 15-30° angle [36]).

3.5. Microscopy

To prepare the samples for the microscopy analyses they needed to be cut and then to be embedded in a chemical resin (Figure 39).

Figure 39 - Cut and embedded samples

After the embedding the samples should be lapped, for this purpose a Mekton Forcipol 1V has been used (Figure 40) [37].

Figure 40 - Lapping instrument Mekton Forcipol 1V

3.5.1. Optical microscopy

To obtain the optical image a Everone Enterprises LTD microscopy (Figure 41) has been used.

Figure 41 - Everone Enterprises LTD microscopy

3.5.2. SEM

For SEM (Scanning Electron Microscopy) analyses a Phenom 10250-XL (Figure 42) has been used. The setted parameters for the analyses were 1850x magnification, a voltage of 15 kV and a pressure of 0.1 Pa.

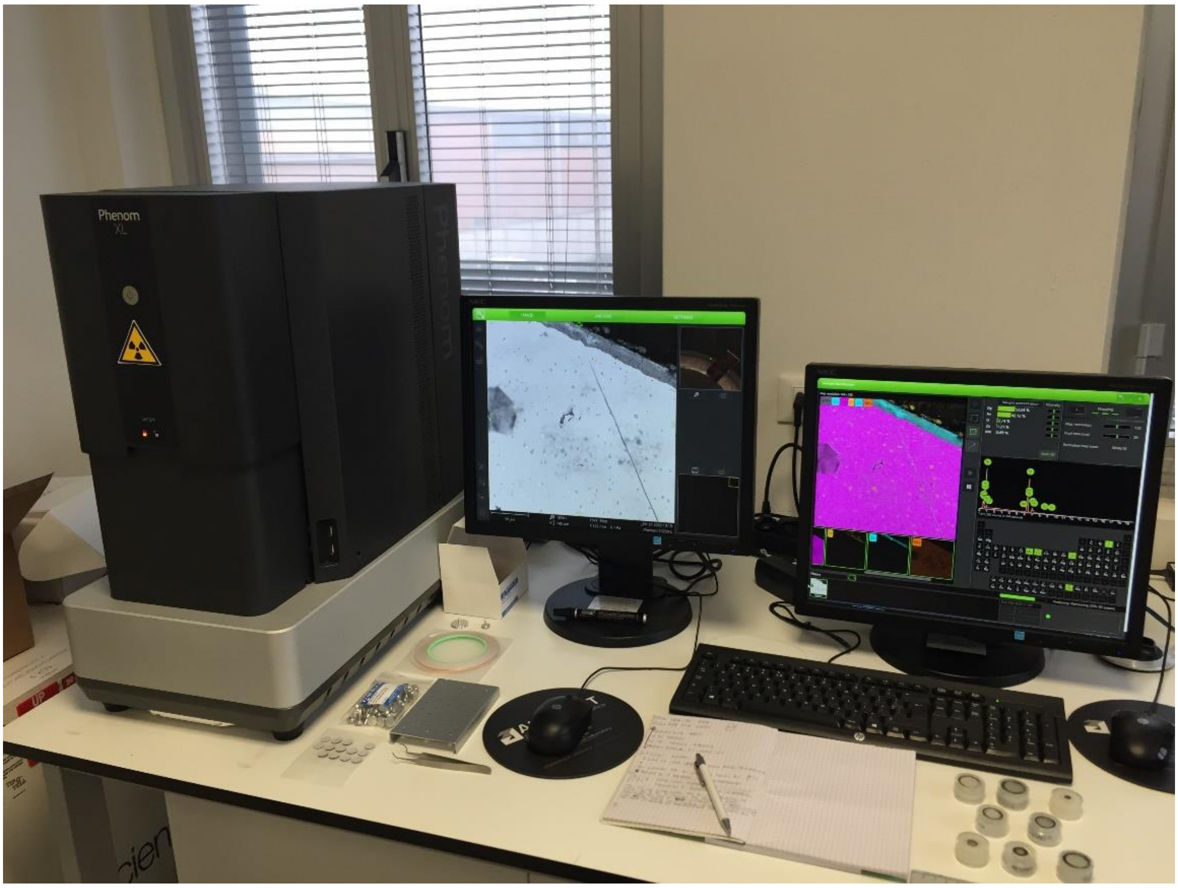


Figure 42 - SEM Phenom 10250-XL

In addition, because the used resin was not conductive a metal base for the samples and a copper scotch tape that connected the samples and the metal base were used (Figure 43). This is done because otherwise the sample, being isolated, will result in distortion of the primary beam and loss of image resolution [38].

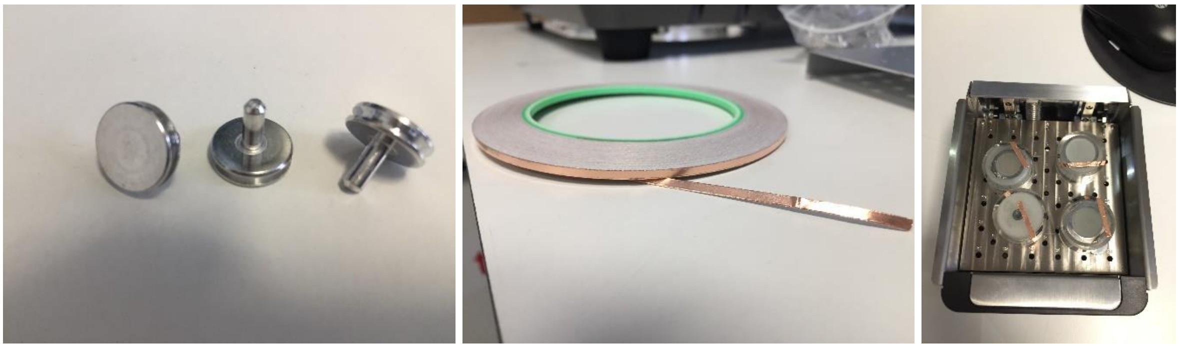


Figure 43 - From left to right: metal base for the embedded samples, copper scotch tape, embedded sample positioned in the SEM shelf

Complex interactions occur when the electron beam in an SEM impinges on the specimen surface and excites various signals for SEM observation. The secondary electrons, BSEs (Back Scattered Electrons), transmitted electrons, or the specimen current might all be collected and displayed [39].

The analysis will be done through applying a beam of electrons (having high-energy) in the range between (100-30,000 electron volts). Usually a thermal source is used for electron emission.

The spot size produced from the gun is too large to generate a sharp image therefore the SEM equipped with the lenses to compress the spot and direct the focused electron on the specimen. The spot size of most SEMs is less than (10 nm) with electrons collected from the final lens interact with the specimen and penetrate to a depth of (1μm) to generate the signals used to produce an image.

The image of the specimen is formed point by point depending on the movement of the scan coils, which cause the electron beam to move to discrete locations in a form of straight lines until a rectangular raster is produced on the surface of the specimen. All the process depends on magnification required. In case when the operator requests a higher magnified image, the scan coils make the beam to deflect a cross a smaller area. It is worth mentioning that the working distance, which is the distance from the last lens to the surface of the specimen, has an effect on the magnification, in which in the modern SEM this is solved by automatic adjustment.

Electron detector is to detect the emitted electrons (signals) from the scanned sample. In the absence of the detectors each signal generated due to the interaction between the electron beam and the surface of the sample can generate an image alone, which is un-understandable. Both secondary electrons (SE) and backscattered electrons (BSE) are used in SEM image production. When a positive voltage is directed to the collector screen, both SE and BSE will be collected. However, only BSE will be collected in case of negative voltage applied on the collector screen.

The signals then are displayed on the viewing screen and the operator will control the brightness and the intensity until a reasonable clear image is obtained. In case where small details are required within the specimen, magnification beyond (10,000x) should be applied [40].

Strengths of the SEM include:

- a wide variety of specimens can be examined,
- relatively easy and quick sample preparation,
- ease of use due to user-friendly and automated equipment,
- rapid imaging, quick results, time-efficient analysis, and fast turnaround time,
- relatively straightforward image interpretation,
- large depth of field (ability to focus large depths of samples at one time and produce 3-D like images),
- microchemical analysis capability from Be to U,
- samples can be dry or wet,
- nondestructive (some beam damage may result) [41].

4 Data and discussion

4.1. Pretreatments

4.1.1. Degreasing

4.1.1.1. Chemical degreasing

Table 3 shows the main parameters of the chemical degreasing for each collected samples.

Table 3 - Chemical degreasing main parameters for each samples

Samples	Date	Sodium Hydroxide (g/l)	Density (°Bé)	Notes
A-1/B-1	22/07/2021	65,6	12	
C-1/D1	26/07/2021	66,4	12	
C-2	29/07/2021	57,6	10	
E-1	03/08/2021	59,2	10	
C-3	04/08/2021	58,4	10	
C-4	17/08/2021	39,2	7	
C-5	23/08/2021	41,6	8	
C-6/C-7	23/09/2021	64,8	11	
C-8	27/09/2021	52,8		
F-1/G-1/J-1/K-1	18/10/2021	54,4	9	morning
H-1/I-1	18/10/2021	52,8	9	afternoon
G-2/L-1	19/10/2021	48,8	9	
M-1/N-1/J-2	20/10/2021	48,8	10	
O-1/P-1	21/10/2021	49,6	10	morning
D-2	21/10/2021	51,2	10	afternoon
O-2/Q-1	22/10/2021	53,6	10	
F-2/D-3	25/10/2021	52,8	10	
O-3/O-4/R-1/R-2/J-3	27/10/2021	48,8	10	

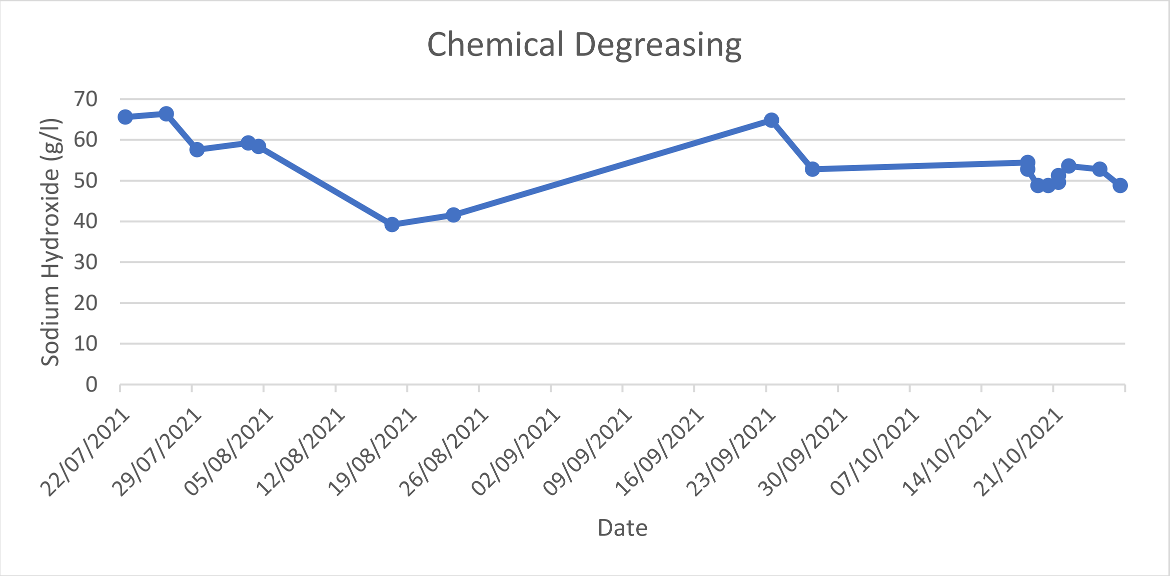


Figure 44 - Trend of sodium hydroxide for chemical degreasing, with analyses done for each collected samples

The graph in Figure 45 represents the general trend of sodium hydroxide in 5 months with analyses done weekly. It is easy to see that the variation of the parameter is significant, going from a minimum of about 40 g/l to a maximum of a little bit less than 80 g/l.

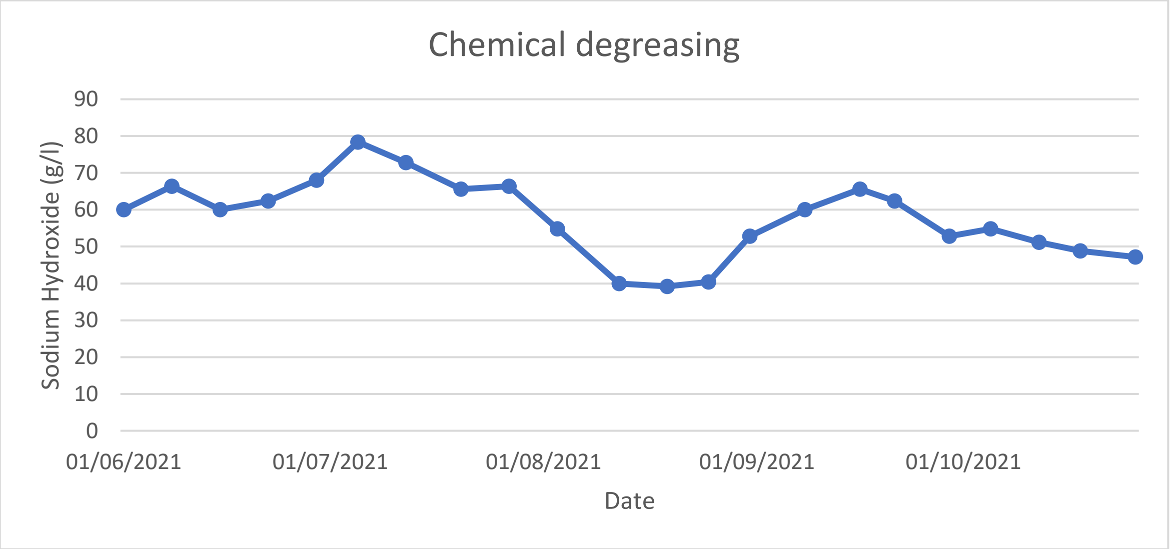


Figure 45 - Trend of sodium hydroxide for chemical degreasing, with analyses done weekly by the supplier

4.1.1.2. Electrolytic degreasing

Table 4 shows the main parameters of the electrolytic degreasing for each collected samples.

Table 4 - Electrolytic degreasing main parameters for each samples

Samples	Date	Sodium Hydroxide (g/l)	Density (°Bé)	Notes
A-1/B-1	22/07/2021	92,8	15	
C-1/D1	26/07/2021	83,2	13	
C-2	29/07/2021	53,6	9	
E-1	03/08/2021	77,6	13	
C-3	04/08/2021	82,4	13	
C-4	17/08/2021	85,6	13	
C-5	23/08/2021	92	14	
C-6/C-7	23/09/2021	88	11	
C-8	27/09/2021	86,4		
F-1/G-1/J-1/K-1	18/10/2021	70,4	10	morning
H-1/I-1	18/10/2021	72	10	afternoon
G-2/L-1	19/10/2021	69,6	10	
M-1/N-1/J-2	20/10/2021	72,8	11	
O-1/P-1	21/10/2021	75,2	11	morning
D-2	21/10/2021	74,4	11	afternoon
O-2/Q-1	22/10/2021	76,8	11	
F-2/D-3	25/10/2021	78,4	12	
O-3/O-4/R-1/R-2/J-3	27/10/2021	71,2	11	

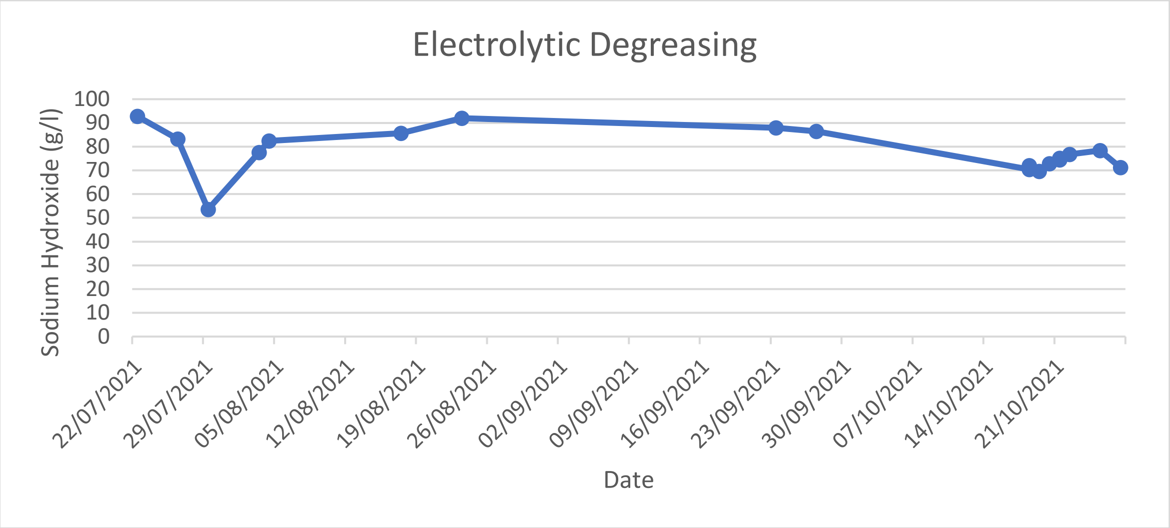


Figure 46 - Trend of sodium hydroxide for electrolytic degreasing, with analyses done for each collected samples

The graph in Figure 47 represents the general trend of sodium hydroxide in 5 months with analyses done weekly. It is easy to see that the variation of the parameter is significant, going from a minimum of about 40 g/l to a maximum around 120 g/l.

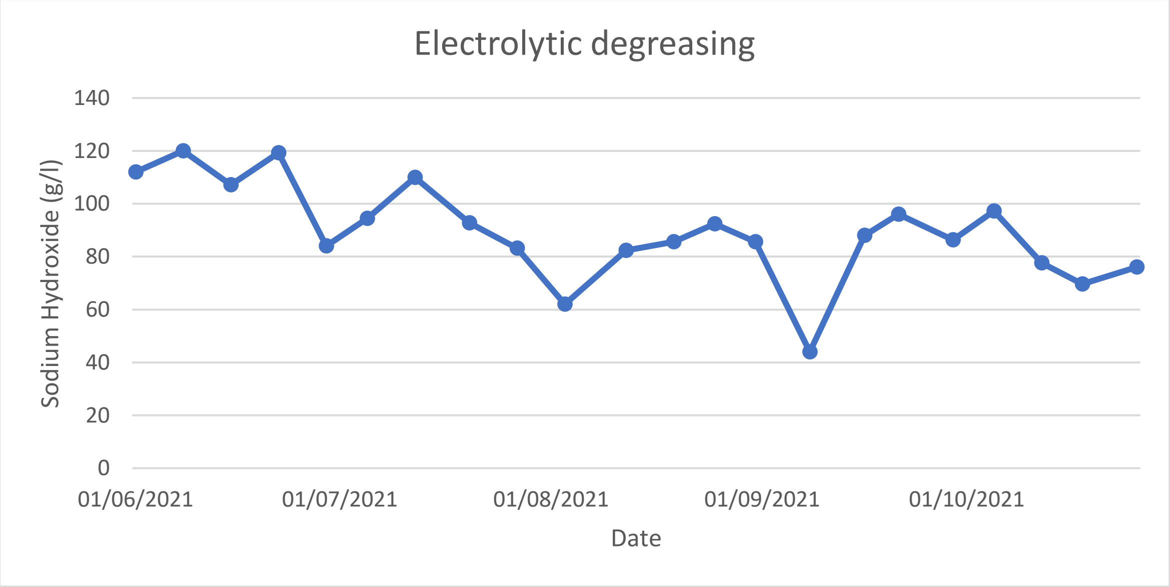


Figure 47 - Trend of sodium hydroxide for electrolytic degreasing, with analyses done weekly by the supplier

4.1.2. Pickling

Table 5 shows the concentration of hydrochloric acid used during pickling pretreatment for each collected samples.

Table 5 - Pickling main parameters for each samples

Samples	Date	HCl 37% (concentration %)	Notes
A-1/B-1	22/07/2021	14,403	
C-1/D1	26/07/2021	14,008	
C-2	29/07/2021	11,838	
E-1	03/08/2021	10,457	
C-3	04/08/2021	9,766	
C-4	17/08/2021	33,047	
C-5	23/08/2021	36,599	
C-6/C-7	23/09/2021	29,595	
C-8	27/09/2021	11,470	
F-1/G-1/J-1/K-1	18/10/2021	31,666	morning
H-1/I-1	18/10/2021	31,864	afternoon
G-2/L-1	19/10/2021	36,500	
M-1/N-1/J-2	20/10/2021	29,496	
O-1/P-1	21/10/2021	25,649	morning
D-2	21/10/2021	26,043	afternoon
O-2/Q-1	22/10/2021	28,509	
F-2/D-3	25/10/2021	32,258	
O-3/O-4/R-1/R-2/J-3	27/10/2021	34,922	

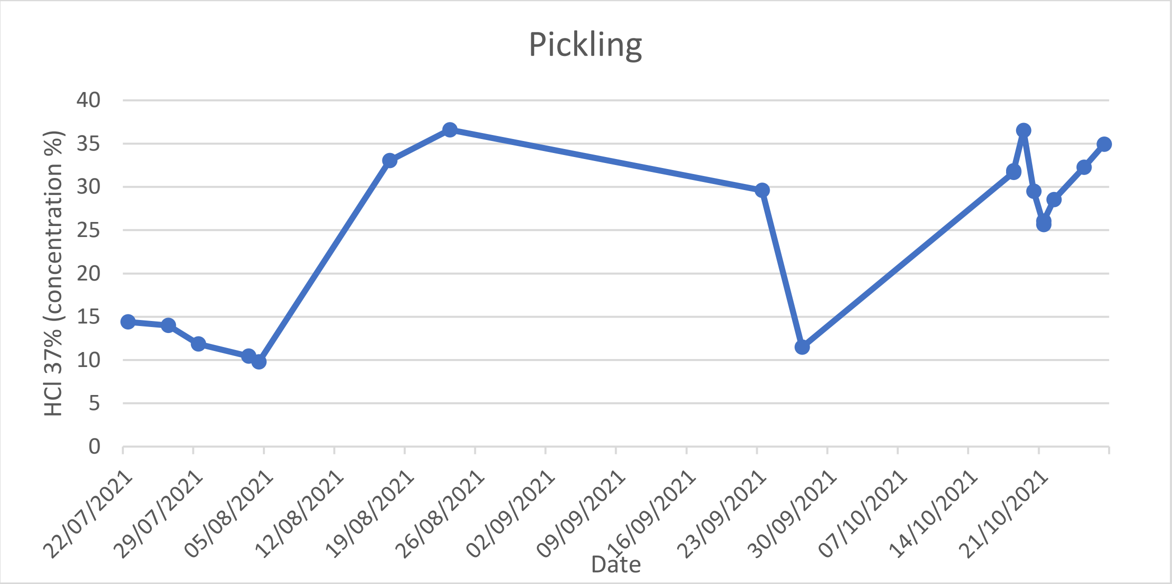


Figure 48 - Trend of hydrochloric acid for pickling, with analyses done for each collected samples

The graph in Figure 49 represents the general trend of hydrochloric acid concentration in 5 months with analyses done weekly. It is easy to see that the variation of the parameter is significant, going from a minimum of about 5% to a maximum above 35%.

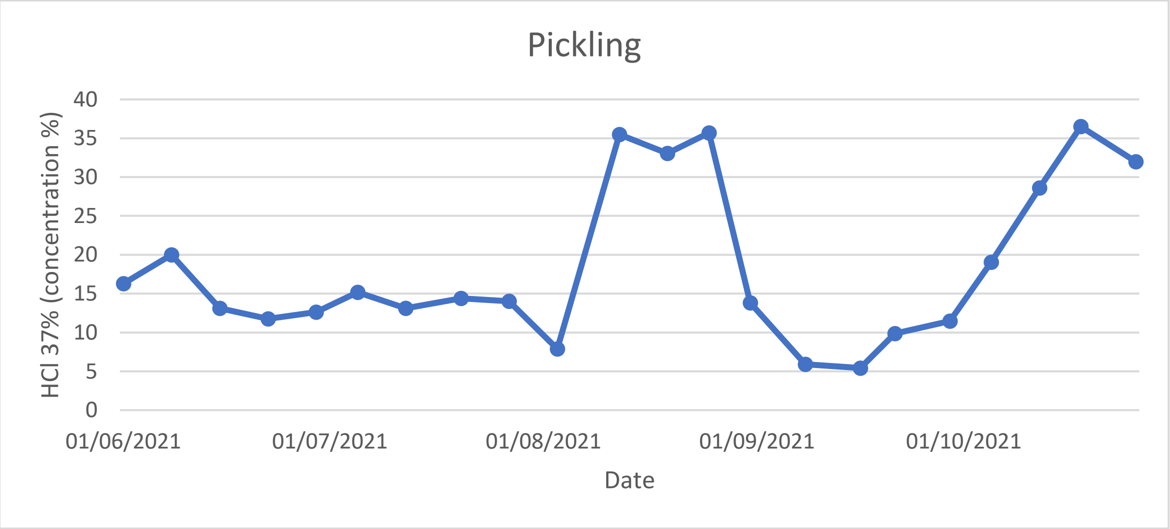


Figure 49 - Trend of hydrochloric acid for pickling, with analyses done weekly by the supplier

The graph in Figure 50 indicate the amount of pollutants inside the hydrochloric acid bath in 5 months with analyses done almost monthly. Iron is considered a problem if it is above 20 g/l, instead zinc is problematic above 30 g/l. So the two pollutants, every time it was conducted the relative analysis, were considered acceptable.

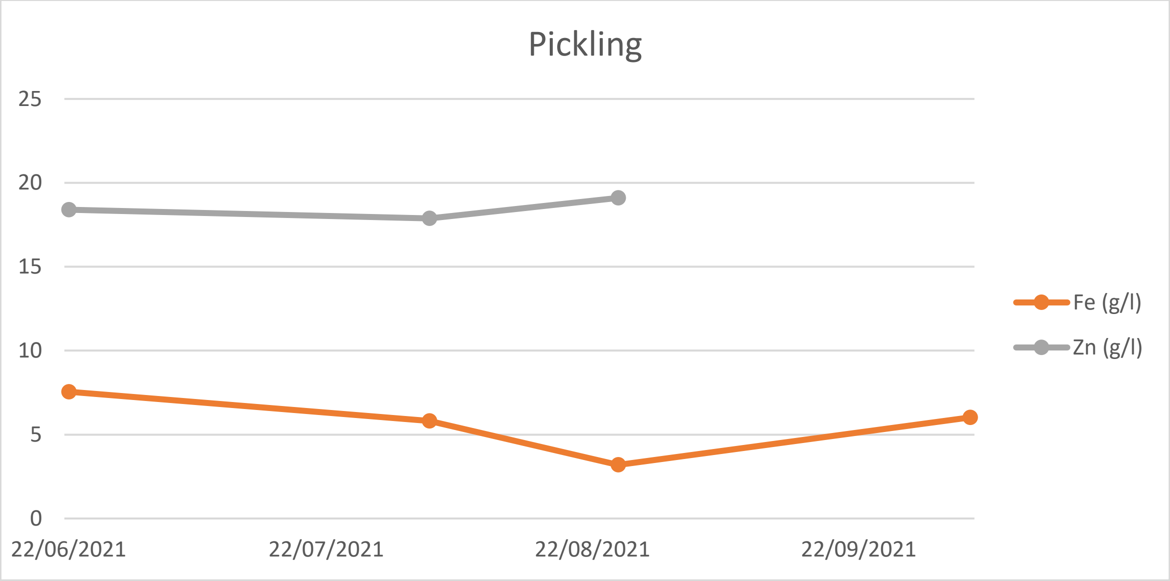


Figure 50 - Pollutants inside the hydrochloric acid bath, with analyses done monthly by the supplier

4.1.3. Pretreatment process time

In the Table 6 are written the processing times and parameters of the pretreatment of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

Most of the parameters in Table 6 are similar, because the pretreatment is done in similar way for every products with some exceptions (like some really dirt products). The main reason for the difference in the process times is the fact that there are only three rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels. Instead, the principal reason for the differences in the current delivered in the electrolytic degreasing is the weight inside a barrel that is directly proportional to the surface of the products.

Table 6 - Pretreatments processing time and processing parameters for each samples

Samples	Date	Barrel Dripping Time (s)	Barrel Rotation (Hz)	Voltage Electrolytic Degreasing (V)	Chemical Degreasing (h:min:s)	Chemical Degreasing (°C)	Rinse (h:min:s)	Pickling (h:min:s)	Rinse (h:min:s)	Electrolytic Degreasing (h:min:s)	Electrolytic Degreasing (A)	Rinse (h:min:s)
A-1	22/07/2021	10	40	8	00:09:41	57	00:00:58	00:09:11	00:00:42	00:03:20	592	00:00:41
B-1	22/07/2021	10	40	8	00:10:11	55,9	00:07:14	00:09:21	00:00:39	00:02:33	489	00:00:41
C-1	26/07/2021	10	40	8	00:09:34	56,8	00:00:49	00:01:08	00:00:47	00:04:47	408	00:00:40
D-1	26/07/2021	20	40	8	00:09:44	58,3	00:00:46	00:08:16	00:00:40	00:02:26	165	00:00:40
C-2	29/07/2021	10	40	8	00:14:26	61,8	00:00:45	00:01:07	00:00:41	00:04:29	0	00:00:40
E-1	03/08/2021	10	40	8	00:08:50	58,2	00:00:46	00:07:46	00:00:47	00:03:57	508	00:00:40
C-3	04/08/2021	10	40	8	00:08:53	57,6	00:00:54	00:01:07	00:00:40	00:03:50	572	00:00:41
C-4	17/08/2021	10	40	8	00:11:23	62,1	00:01:08	00:12:21	00:00:14	00:02:04	335	00:00:13
C-5	23/08/2021	10	40	8	00:11:07	52,9	00:00:45	00:01:58	00:00:08	00:01:57	3	00:00:12
C-6	23/09/2021	10	40	8	00:10:44	56,7	00:00:43	00:02:00	00:00:20	00:01:13	414	00:00:20
C-7	23/09/2021	10	40	8	00:14:38	58,8	00:03:45	00:01:57	00:00:20	00:03:40	485	00:00:16
C-8	27/09/2021	10	40	8	00:11:58	61,1	00:01:45	00:01:58	00:00:13	00:02:11	457	00:00:15
F-1	18/10/2021	10	40	8	00:09:49	60,9	00:02:52	00:01:59	00:00:08	00:01:50	497	00:00:40
G-1	18/10/2021	10	40	8	00:13:55	60,9	00:00:46	00:02:04	00:00:08	00:01:50	429	00:00:41
H-1	18/10/2021	20	40	8	00:11:52	61,5	00:00:43	00:09:38	00:00:08	00:01:27	469	00:00:13
I-1	18/10/2021	10	40	8	00:43:37	61,7	00:03:33	00:21:55	00:00:08	00:04:06	310	00:00:11
J-1	18/10/2021	10	40	8	00:10:36	61	00:00:51	01:09:57	00:02:54	00:02:32	0	00:00:53
K-1	18/10/2021	10	40	8	00:09:49	60,9	00:02:50	00:10:43	00:00:08	00:01:18	464	00:01:30
G-2	19/10/2021	10	40	8	00:08:56	58,6	00:01:46	00:08:57	00:00:08	00:01:50	393	00:00:09
L-1	19/10/2021	10	40	8	00:08:51	58,3	00:01:44	00:08:55	00:00:08	00:01:58	469	00:00:09

M-1	20/10/2021	10	40	8	00:08:49	57,7	00:01:45	00:08:53	00:00:08	00:01:50	457	00:00:09
N-1	20/10/2021	10	40	8	00:09:51	58,2	00:00:43	00:09:40	00:00:08	00:01:16	395	00:00:09
J-2	20/10/2021	10	40	8	00:09:48	59,4	00:00:45	00:09:34	00:00:08	00:01:15	428	00:00:09
O-1	21/10/2021	10	40	8	00:09:51	57,4	00:01:00	00:10:30	00:00:08	00:02:31	444	00:00:40
D-2	21/10/2021	20	40	8	00:09:47	57,9	00:00:43	00:09:34	00:00:08	00:01:35	321	00:00:12
P-1	21/10/2021	10	30	8	00:09:47	58,2	00:00:43	00:09:40	00:00:08	00:01:16	385	00:00:11
O-2	22/10/2021	10	40	8	00:11:15	57,2	00:01:45	00:09:40	00:00:08	00:01:17	459	00:00:11
Q-1	22/10/2021	20	40	8	00:09:46	57	00:00:45	00:09:34	00:00:08	00:02:00	413	00:00:11
F-2	25/10/2021	10	40	8	00:08:47	58,3	00:01:43	00:02:29	00:00:08	00:03:45	333	00:00:09
D-3	25/10/2021	10	40	8	00:08:46	57,9	00:01:41	00:08:48	00:00:08	00:01:52	346	00:00:09
O-3	27/10/2021	10	40	8	00:16:35	58,5	00:00:43	00:05:55	00:00:08	00:05:09	438	00:00:09
O-4	27/10/2021	10	40	8	00:10:51	59,9	00:00:52	00:08:02	00:00:08	00:01:53	505	00:00:10
R-1	27/10/2021	10	40	8	00:09:41	59,9	00:03:01	00:05:21	00:00:08	00:02:53	0	00:00:09
R-2	27/10/2021	10	40	8	00:10:36	60,7	00:01:22	00:09:28	00:00:09	00:02:38	496	00:00:09
J-3	27/10/2021	10	40	8	00:09:32	58,1	00:01:04	00:09:40	00:00:08	00:01:23	418	00:00:09

4.2. Zinc bath

Table 7 shows the main parameters of the zinc bath for each collected samples.

In Table 7 the temperature parameter is to be considered more like an indication than a real value, because between the collection of a sample of the zinc bath and the actual measurement of temperature it will pass some minutes, so the real temperature will be some degree higher.

Table 7 - Main parameters of the zinc bath for each collected samples

Samples	Date	Zinc (g/l)	Zinc Chloride (g/l)	Cl- (g/l)	Potassium Chloride (g/l)	Boric Acid (g/l)	pH	Density (°Bé)	Temperature (°C)	Notes
A-1/B-1	22/07/2021	25	53	116	187	20	4,84	19		
C-1/D1	26/07/2021	24	50	124	207	17	4,74	20	29,4	
C-2	29/07/2021	25	53	126	208	20	4,34	19	31,8	
E-1	03/08/2021	23	49	121	200	20	4,79	19	29,1	
C-3	04/08/2021	23	48	116	192	25	4,2	18	28	
C-4	17/08/2021	26	54	120	194	27	4,72	20	28,1	
C-5	23/08/2021	27	56	88	124	24	4,5		29	
C-6/C-7	23/09/2021	23	49	124	208	23	4,72	19	30,8	
C-8	27/09/2021	22	47	115	190	23	4,6	18		
F-1/G-1/J-1/K-1	18/10/2021	28	59	131	212	23	4,37	20	28,8	morning
H-1/I-1	18/10/2021	29	60	135	220	24	5,1	20	27,4	afternoon
G-2/L-1	19/10/2021	27	57	131	214	22	4,49	20	27,1	
M-1/N-1/J-2	20/10/2021	27	56	137	227	21	4,76	21	28,2	
O-1/P-1	21/10/2021	29	60	135	219	21	4,9	20	29,1	morning
D-2	21/10/2021	27	57	137	226	20	4,94	20	29,3	afternoon
O-2/Q-1	22/10/2021	27	57	135	221	20	4,83	20	26,9	
F-2/D-3	25/10/2021	27	57	137	226	24	4,24	20	27,6	
O-3/O-4/R-1/R-2/J-3	27/10/2021	26	55	137	228	23	4,91	20	29	

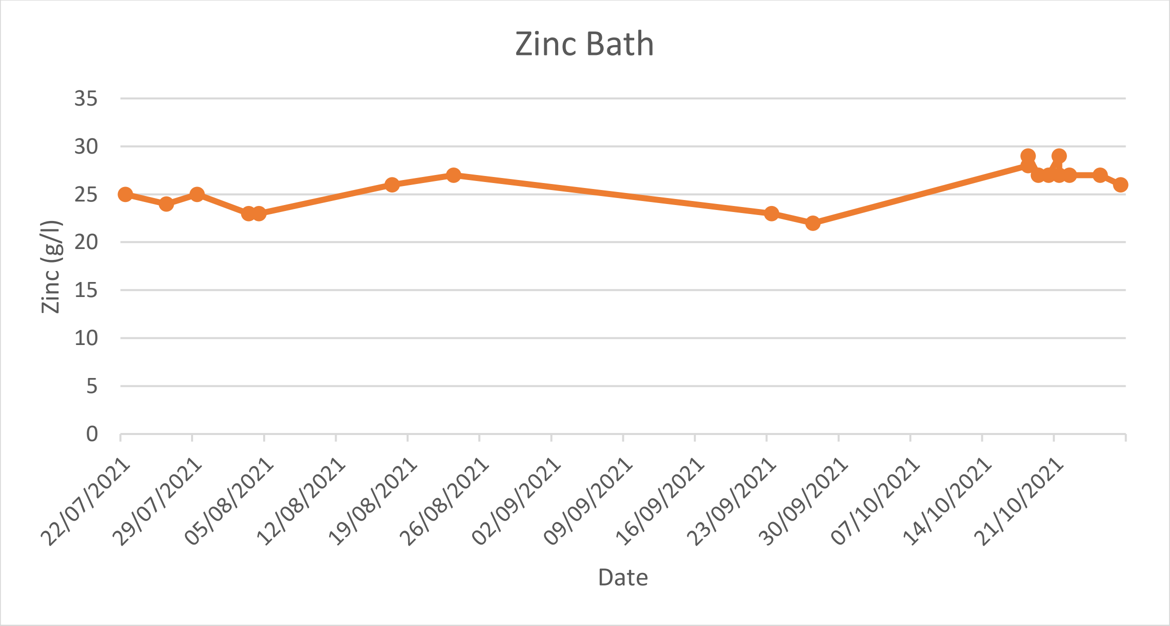


Figure 51 - Trend of zinc inside the zinc bath, with analyses done for each collected samples

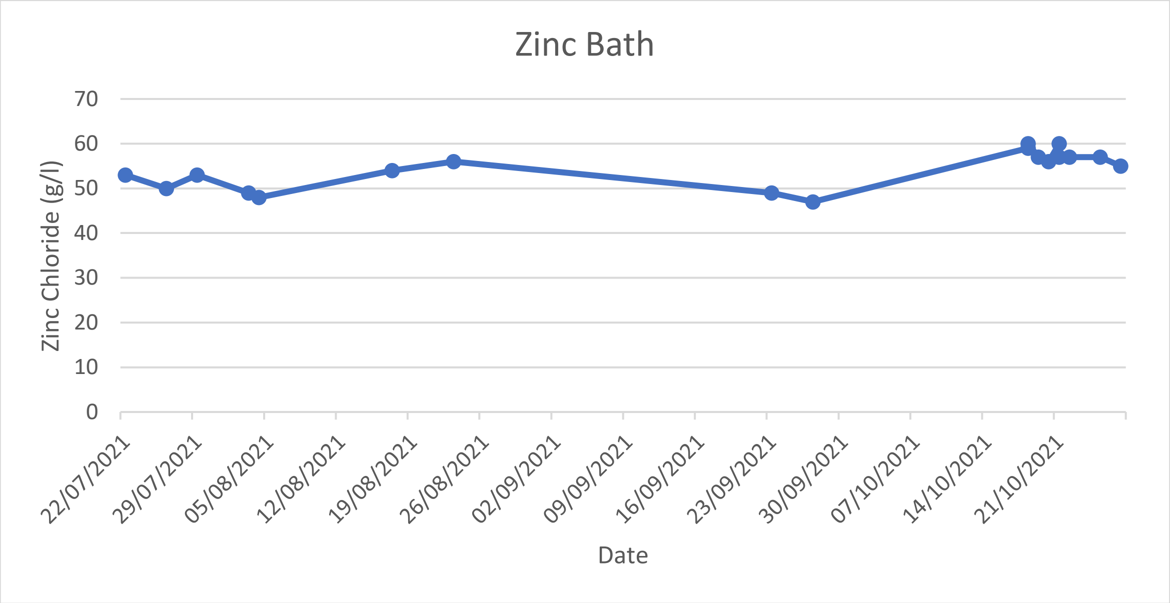


Figure 52 - Trend of zinc chloride inside the zinc bath, with analyses done for each collected samples

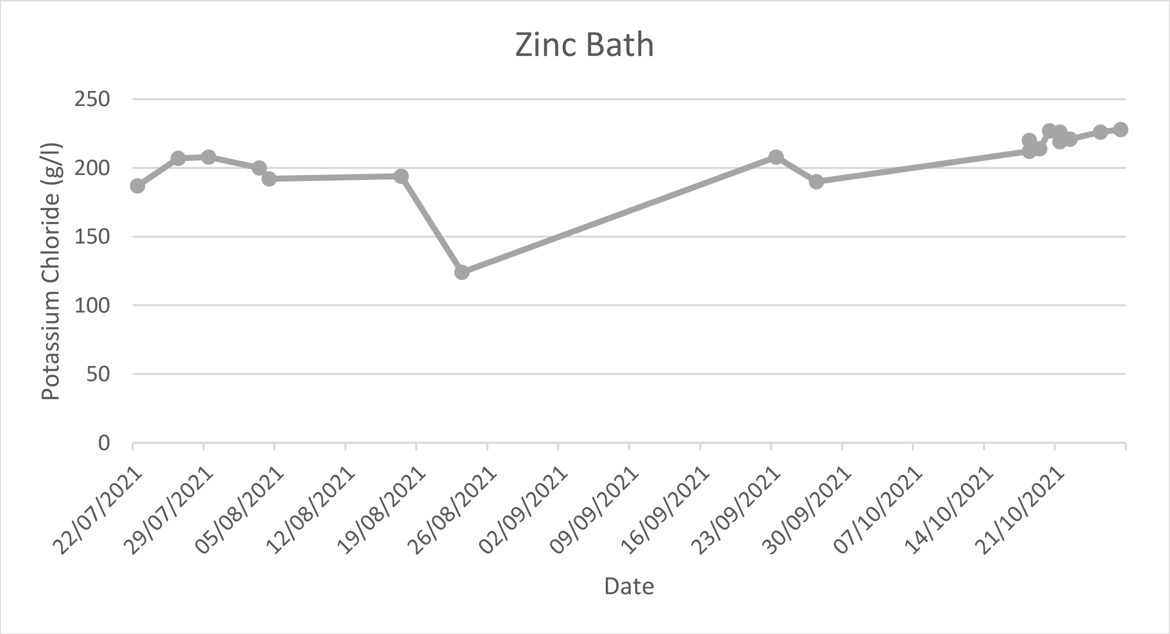


Figure 53 - Trend of potassium chloride inside the zinc bath, with analyses done for each collected samples

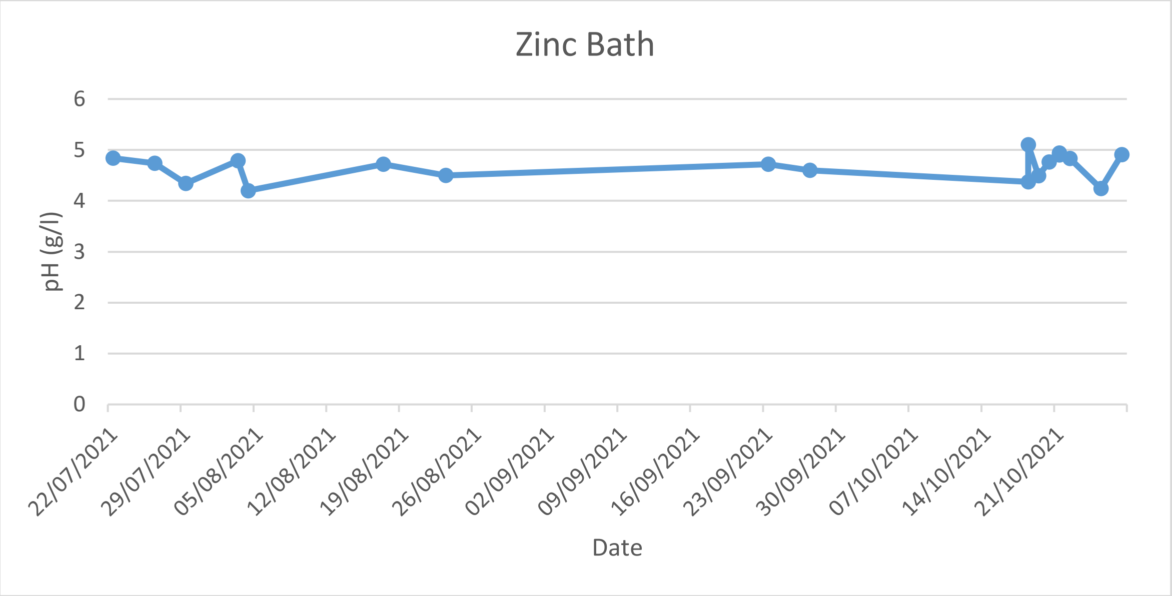


Figure 54 - Trend of the zinc bath pH, with measurements done for each collected samples

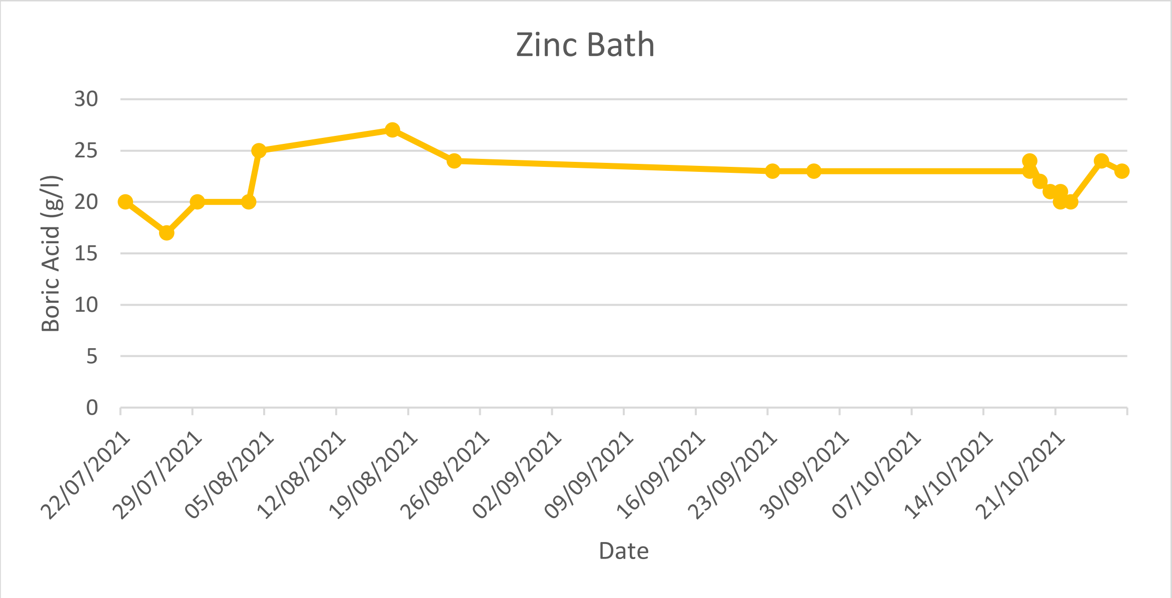


Figure 55 - Trend of boric acid inside the zinc bath, with analyses done for each collected samples

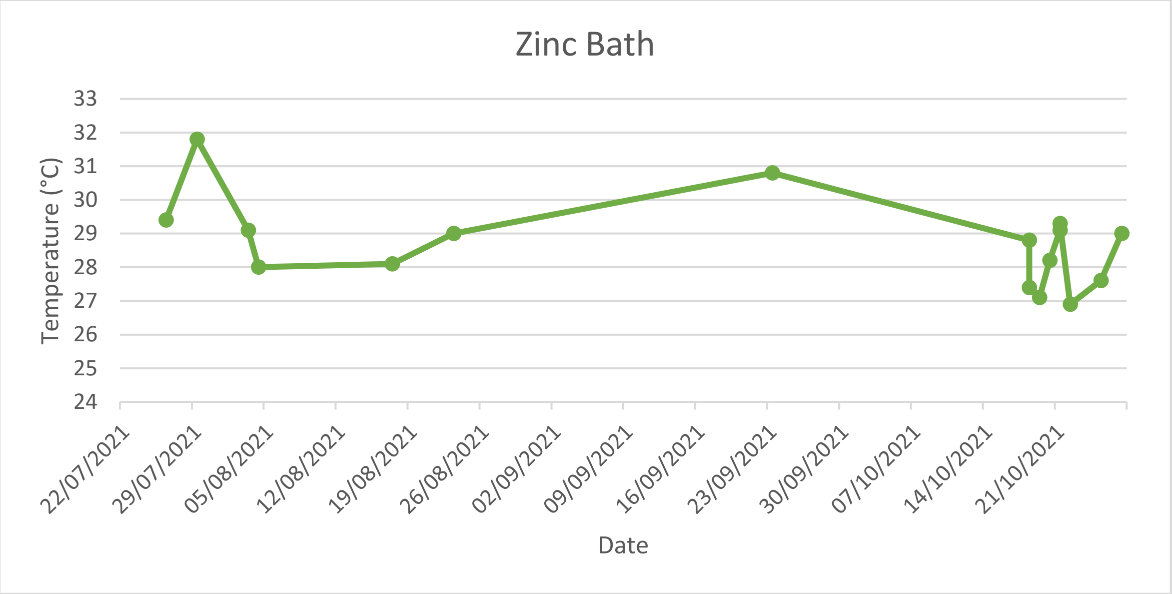


Figure 56 - Trend of the zinc bath temperature, with analyses done for each collected samples

The graphs in Figure 58Figure 57Figure 59Figure 60 represent the general trend of zinc bath in 5 months with analyses done weekly. As one would aspect, these graphs have a trend slightly different from the ones with analyses done only for the days when a sample was collected.

As it possible to observe from Figure 58 and also from Figure 51 the zinc inside the bath remain almost always between 25 and 30 g/l and so it maintain the correct parameter (optimal range 25-40 g/l).

From Figure 52Figure 57 is notable that zinc chloride have a pretty much a constant trend, but a little bit under the optimal parameter (65-75 g/l).

From Figure 53Figure 57, it is possible to see that also potassium chloride remain in the optimal range (180-220 g/l) almost always.

As one would aspect the chloride follow the potassium chloride trend (potassium chloride content is derived from the chloride content) and this is possible to note in Figure 57.

The boric acid curve that is possible to observe in Figure 59 does not have a constant trend on the contrary of what is possible to observe in figure Figure 55, but nonetheless most of the time remain in the optimal range (20-30 g/l).

Zinc bath pH remain always between 4,0 and 5,3, as it it is possible to see in Figure 54Figure 60, but the optimal range is 4,6-5,2.

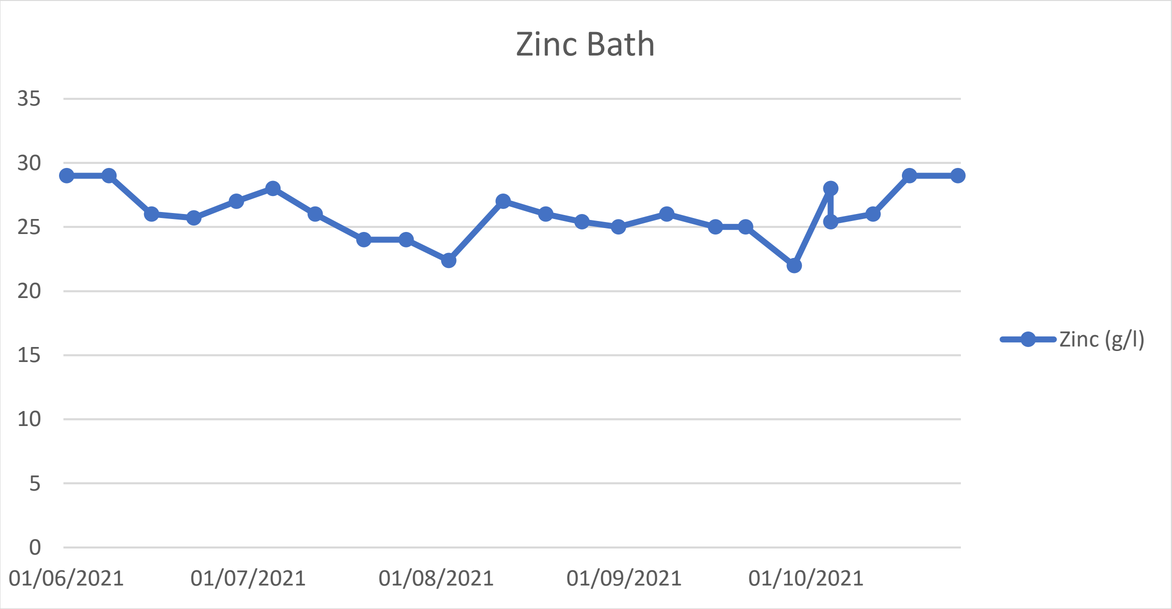


Figure 57 - Trend of zinc inside the zinc bath, with analyses done weekly by the supplier

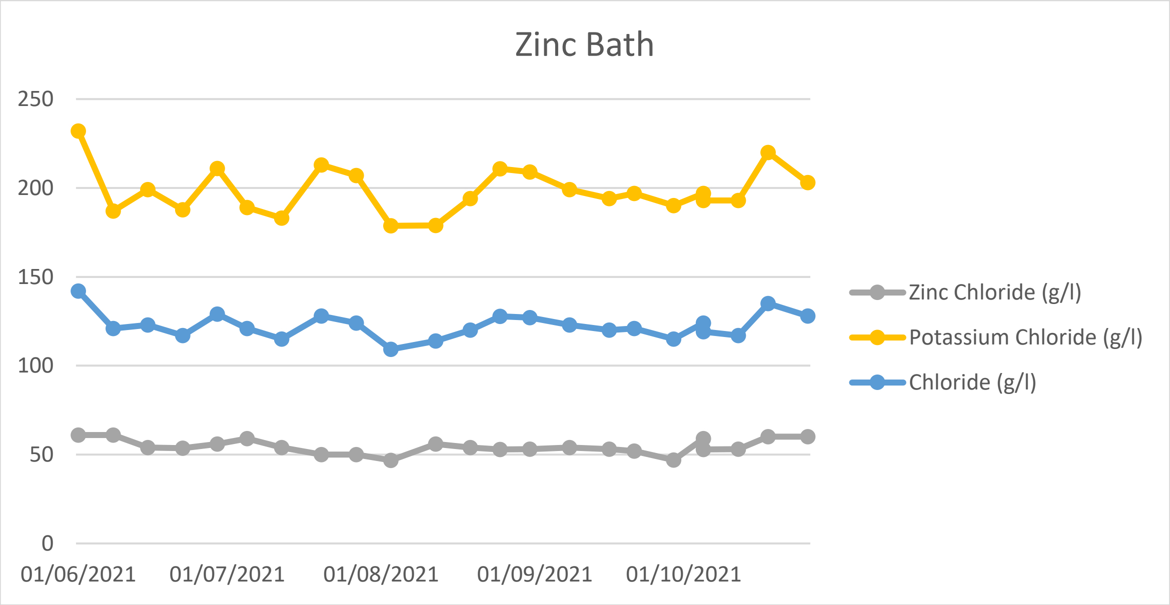


Figure 58 - Trend of zinc chloride, potassium chloride and chloride inside the zinc bath, with analyses done weekly by the supplier

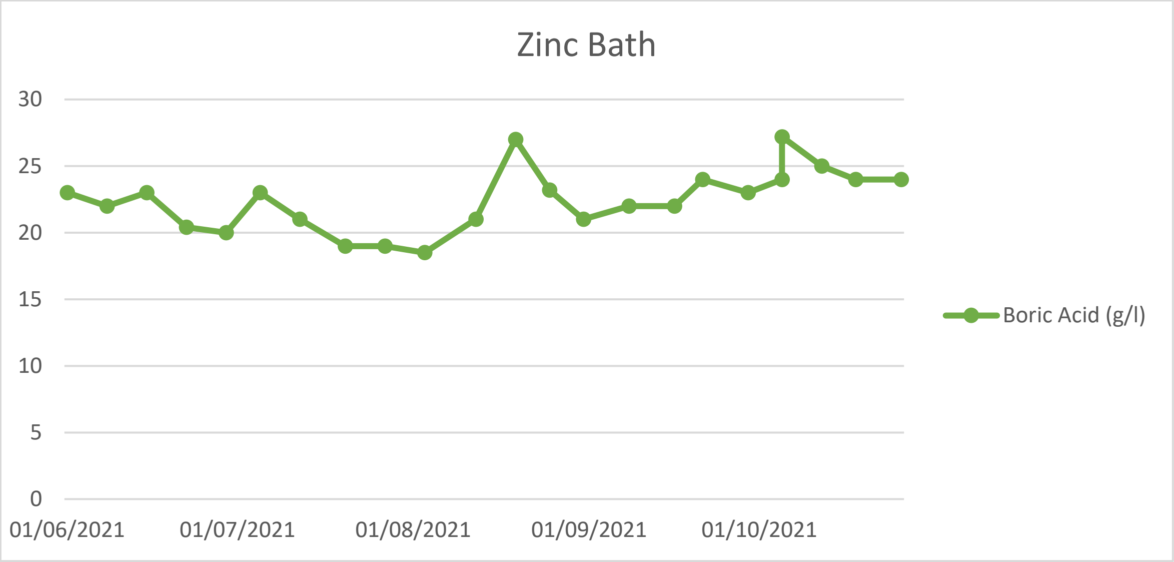


Figure 59 - Trend of boric acid inside the zinc bath, with analyses done weekly by the supplier

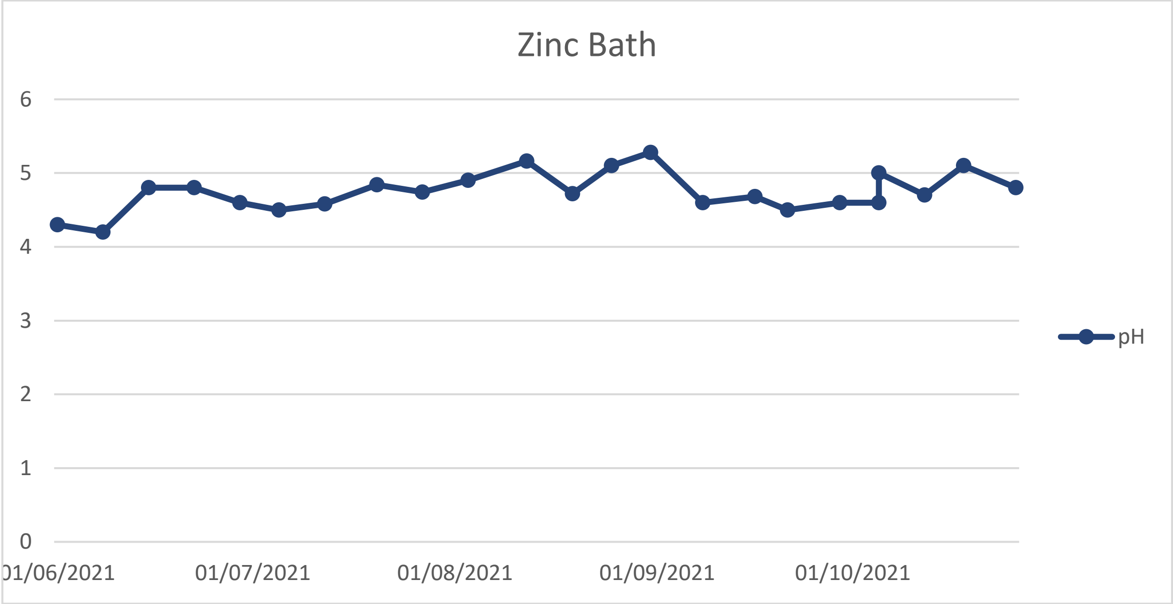


Figure 60 - Trend of the zinc bath pH, with analyses done weekly by the supplier

The graph in Figure 61 indicate the amount of pollutants inside the zinc bath in 5 months with analyses done almost monthly. Iron is considered a problem if it is above 120 g/l. So the pollutant, every time it was conducted the relative analysis, was considered acceptable.

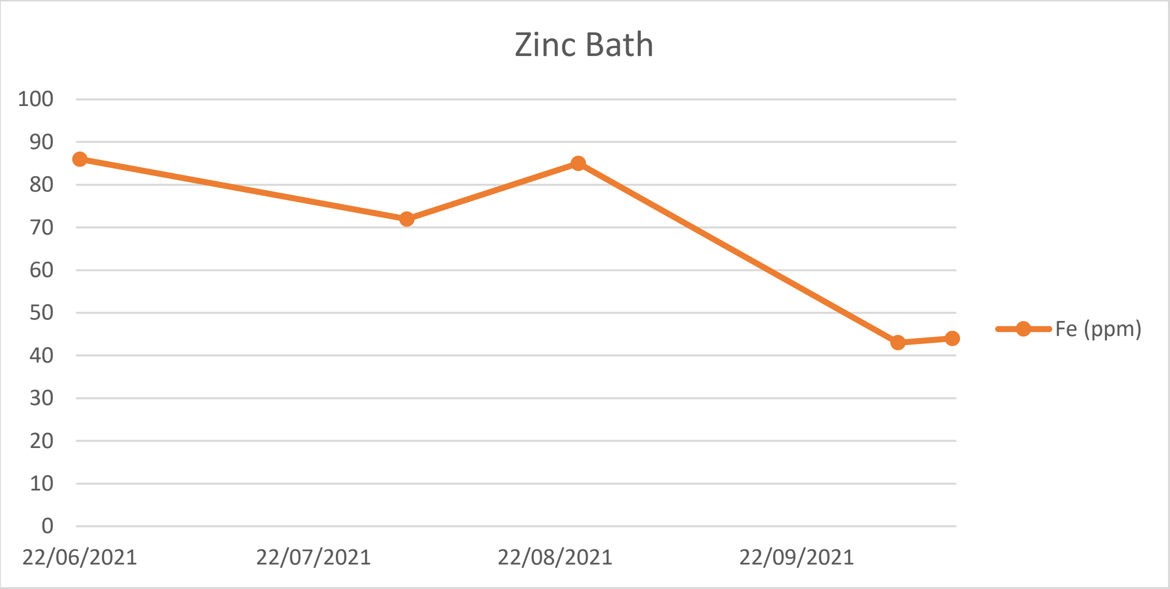


Figure 61 - Trend of iron pollutant inside the zinc bath, with analyses done weekly by the supplier

In the Table 8 are written the processing times and parameters of the zinc plating process of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

The main reason for the difference in the zinc process times and the voltage applied in zinc bath is the thickness of the required zinc layer. Meanwhile, the principal reason for the differences in the current delivered, in the case with the same voltage applied, is the weight inside a barrel that is directly proportional to the surface of the products.

Instead the motif for different rinse time is the fact that there are only three rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels.

Table 8 - Zinc electroplating processing time and processing parameters for each samples

Samples	Date	Voltage Zinc Bath (V)	Barrel Dripping Time (s)	Barrel Rotation (Hz)	Zinc Bath (h:min:s)	Zinc Bath (A)	Rinse (h:min:s)
A-1	22/07/2021	4,5	10	40	01:00:22	259	00:01:56
B-1	22/07/2021	5	10	40	00:49:31	244	00:03:11
C-1	26/07/2021	9	10	40	01:01:26	575	00:01:53
D-1	26/07/2021	5	20	40	00:43:17	255	00:01:59
C-2	29/07/2021	9	10	40	00:48:05	645	00:02:06
E-1	03/08/2021	7	10	40	00:52:23	430	00:02:48
C-3	04/08/2021	9	10	40	00:44:06	369	00:02:20
C-4	17/08/2021	9	10	40	01:02:36	534	00:02:35
C-5	23/08/2021	9	10	40	01:09:29	701	00:01:45
C-6	23/09/2021	9	10	40	01:10:34	568	00:01:56
C-7	23/09/2021	9	10	40	01:03:49	707	00:04:18
C-8	27/09/2021	9	10	40	00:49:43	741	00:02:34
F-1	18/10/2021	7,5	10	40	00:45:39	591	00:01:54
G-1	18/10/2021	5	10	40	00:47:15	298	00:01:49
H-1	18/10/2021	7	20	40	00:54:57	517	00:02:24
I-1	18/10/2021	5	10	40	00:48:10	301	00:02:36
J-1	18/10/2021	5	10	40	00:18:26	286	00:02:19
K-1	18/10/2021	4,5	10	40	01:12:52	294	00:01:52
G-2	19/10/2021	4,5	10	40	00:46:43	257	00:03:58
L-1	19/10/2021	4,5	10	40	00:50:01	274	00:02:48
M-1	20/10/2021	6	10	40	00:46:01	374	00:01:54
N-1	20/10/2021	6	10	40	00:46:08	365	00:02:36
J-2	20/10/2021	5	10	40	00:46:36	282	00:01:54
O-1	21/10/2021	4	10	40	00:47:44	231	00:02:13
D-2	21/10/2021	3	20	40	01:08:05	137	00:02:25
P-1	21/10/2021	4,5	10	30	00:46:41	258	00:02:33
O-2	22/10/2021	5	10	40	00:46:36	297	00:02:28
Q-1	22/10/2021	5	20	40	00:47:48	267	00:02:40
F-2	25/10/2021	4	10	40	00:46:54	198	00:02:35
D-3	25/10/2021	5,5	10	40	00:48:41	277	00:03:01
O-3	27/10/2021	5	10	40	00:48:30	291	00:02:15
O-4	27/10/2021	5	10	40	00:56:05	344	00:01:44
R-1	27/10/2021	5	10	40	00:57:13	345	00:02:12
R-2	27/10/2021	6	10	40	00:49:33	422	00:02:29
J-3	27/10/2021	4	10	40	01:02:39	214	00:02:41

4.3. Conversion coating

All the collected samples have sustained a chromate conversion coating to improve their corrosion resistance. In addition, some of that have been sealed to further increase their corrosion resistance.

The chromate conversion coatings used are all based on trivalent chromium and are:

- a blue conversion coating;
- two iridescent yellow conversion coating;

4.3.1. Blue Conversion Coating (BCC)

Table 9 shows only the pH of the BCC bath for each collected samples, because it is the only parameter that it is possible to obtain in the factory.

Table 9 - BCC pH for each collected samples

Samples	Date	pH
E-1	03/08/2021	1,9
J-1/K-1	18/10/2021	2,5
L-1	19/10/2021	2,3
N-1/N-2	20/10/2021	2,4
J-2	20/10/2021	2,5
J-3	27/10/2021	2,1

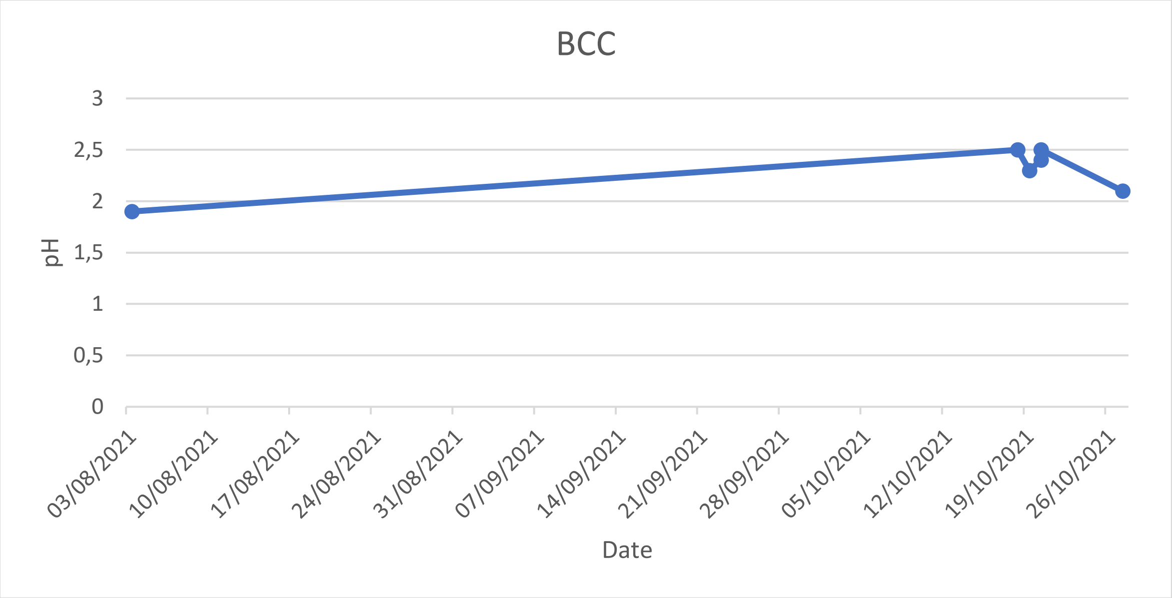


Figure 62 - BCC pH for each collected samples

The supplier of the BCC performs a more complete analysis weekly as it is possible to see in the Figure 63. It appears immediately that the concentration does not have a constant trend and that pH oscillates between 1,5 and 2,5, but the admitted range is 1,8 and 2,0.

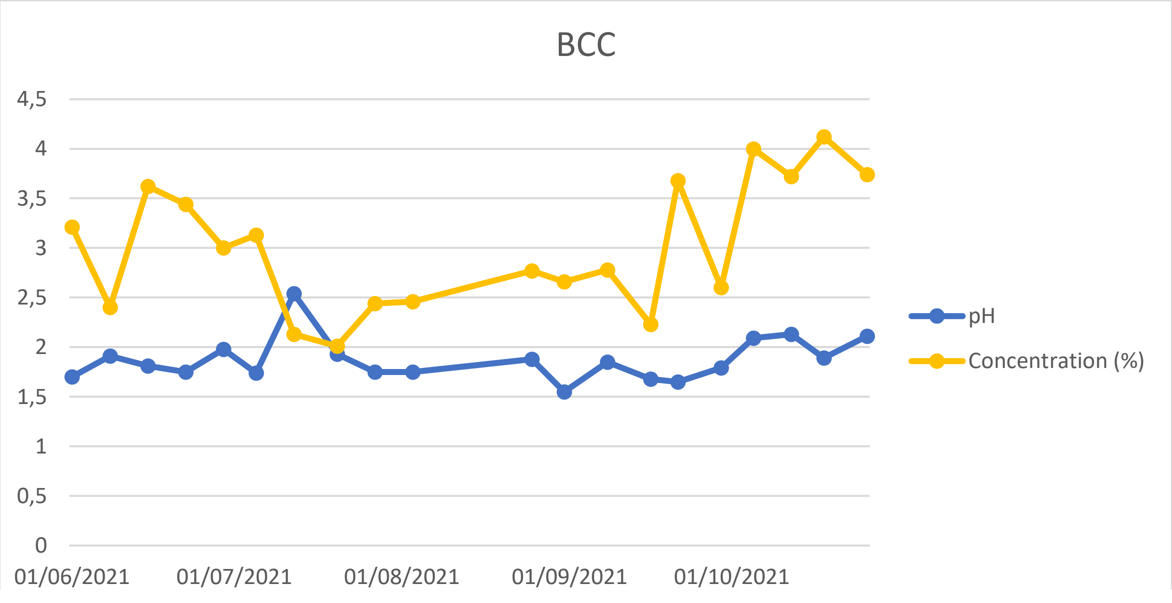


Figure 63 - BCC pH and concentration, analyses done weekly by the supplier

The graph in Figure 64Figure 65 indicate the amount of pollutants inside the BCC bath in 5 months with analyses done weekly. Iron is considered a problem if it is above 250 ppm, instead zinc is considered a problem above 8 g/l. So the pollutant, every time it was conducted the relative analysis, was considered acceptable.

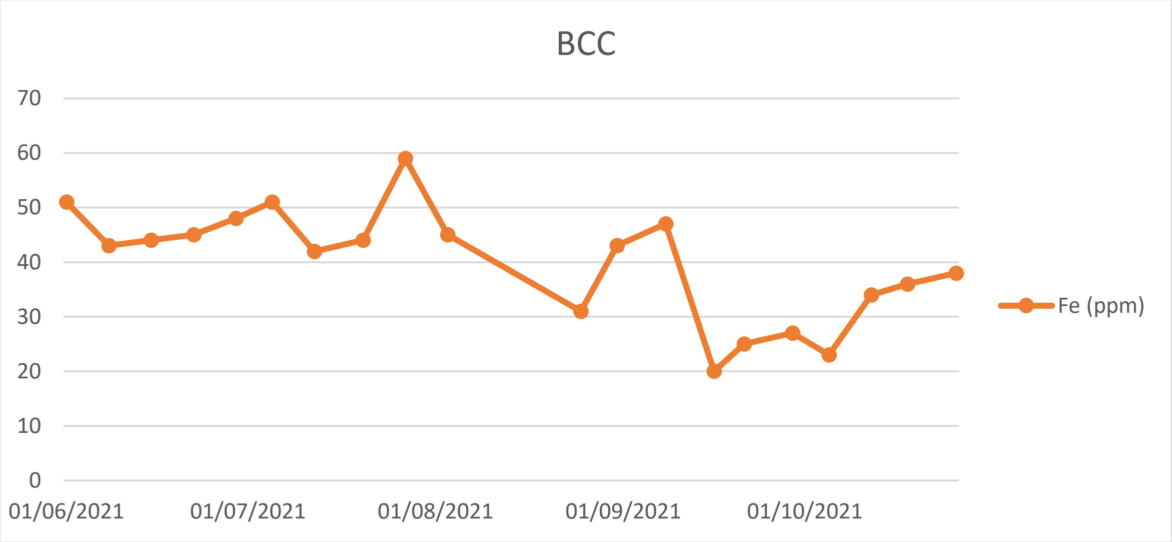


Figure 64 - Trend of iron pollutant inside the BCC, with analyses done weekly by the supplier

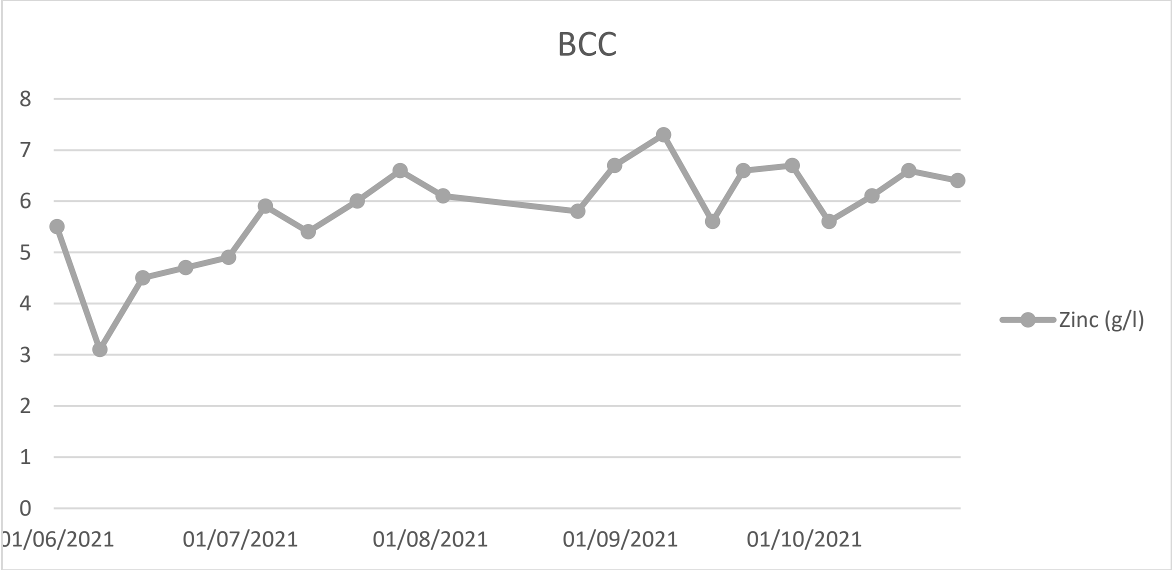


Figure 65 - Trend of zinc pollutant inside the BCC, with analyses done weekly by the supplier

In the Table 10 are written the processing times and parameters of the chromate conversion coating of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

Most of the parameters in Table 10 are similar, because the conversion process is done in the same way for every products. The main reason for the difference in the process times is the fact that there are only few rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels.

Table 10 - Passivation with BCC processing time and processing parameters for each samples

Samples	Date	Centrifuge Velocity (Hz)	Barrel Dripping Time (s)	Barrel rotation (Hz)	BCC (h:min:s)	BCC (°C)	Rinse (h:min:s)	Centrifuge (h:min:s)	Centrifuge (°C)
E-1	03/08/2021	40	10	40	00:00:27	25,2	00:00:17	00:15:51	104,7
J-1	18/10/2021	35	10	40	00:00:22	24,9	00:00:17	00:14:54	107,1
K-1	18/10/2021	40	10	40	00:00:22	25,1	00:00:17	00:22:00	91,2
L-1	19/10/2021	40	10	40	00:00:27	25,4	00:05:27	00:11:24	97,2
N-1	20/10/2021	40	10	40	00:00:27	25,3	00:00:17	00:14:47	105,6
N-2	20/10/2021	40	10	40	00:00:27	24,8	00:00:17	00:13:54	96,3
J-2	20/10/2021	40	10	40	00:00:22	24,8	00:00:17	00:14:54	107,2
J-3	27/10/2021	40	10	40	00:00:22	25,2	00:00:17	00:18:08	107,9

4.3.2. Iridescent yellow conversion coating 1 (IYCC1)

Table 11 shows only the pH of the IYCC1 bath for each collected samples, because it is the only parameter that it is possible to obtain in the factory.

Table 11 - IYCC1 pH for each collected samples

Samples	Date	pH
D-1	26/07/2021	2,3
H-1	18/10/2021	2,6
D-2	21/10/2021	2,4
Q-1	22/10/2021	2,8
D-3	25/10/2021	2,5

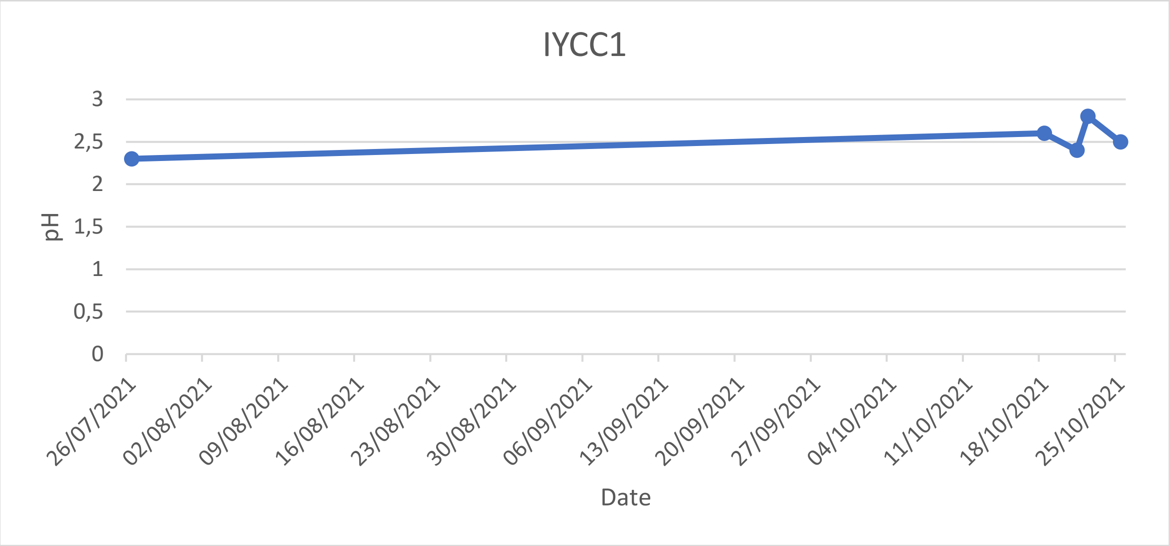


Figure 66 - IYCC1 pH for each collected samples

The supplier of IYCC1 performs a more complete analysis weekly as it is possible to see in the Figure 67Figure 68. It appears immediately that the concentration does not have a constant trend and that pH oscillates between 1,4 and 2,8, but the admitted range is 2,0 and 2,5.

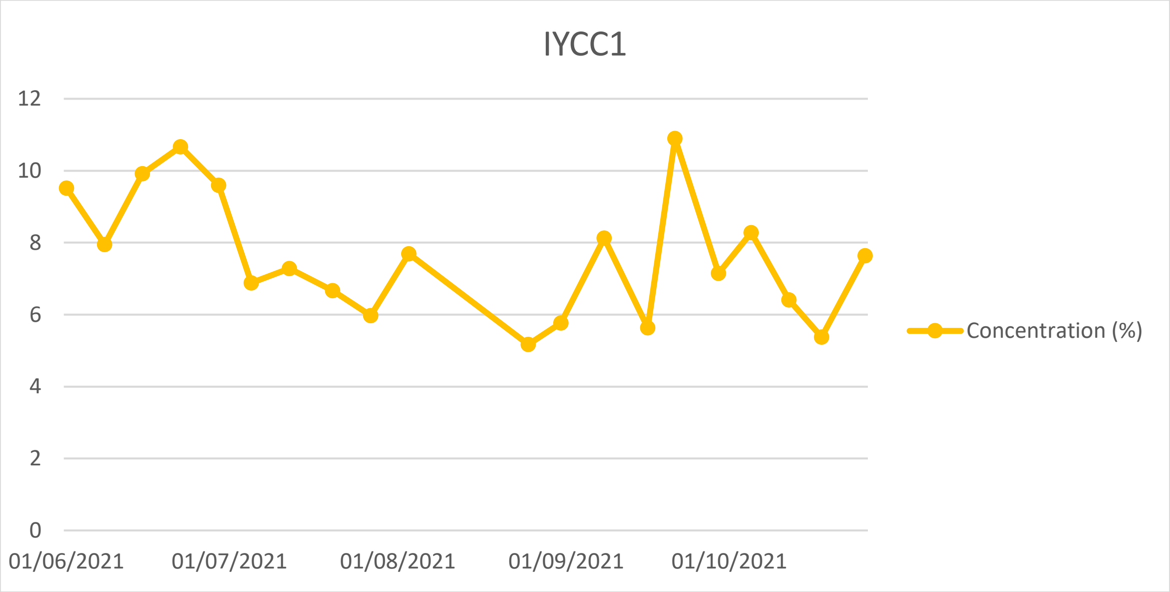


Figure 67 - IYCC1 concentration, analyses done weekly by the supplier

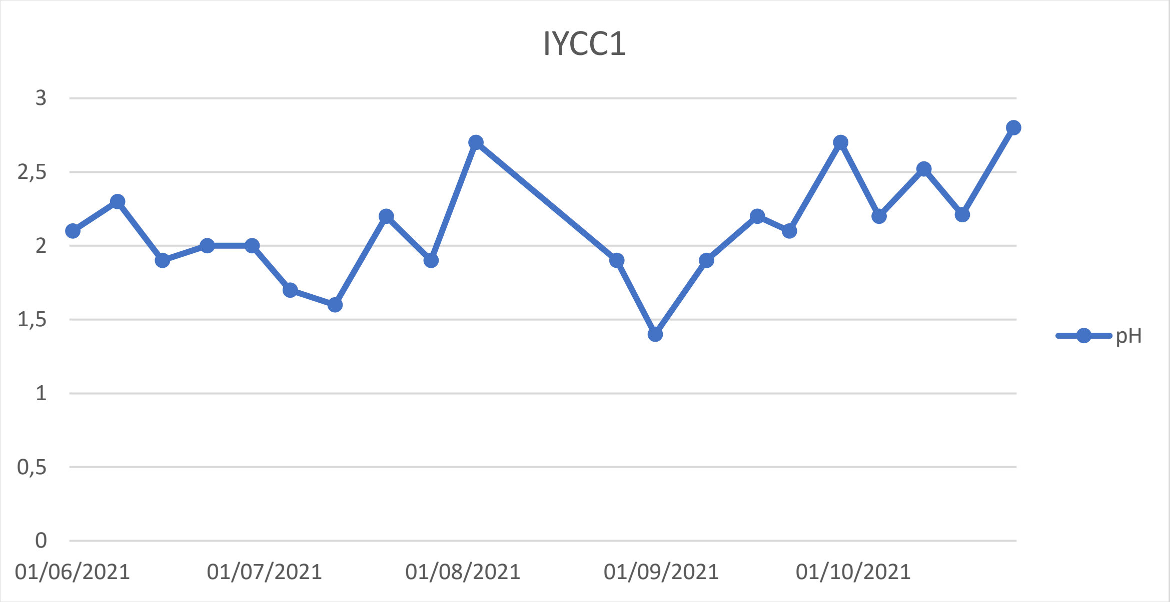


Figure 68 - IYCC1 pH, analyses done weekly by the supplier

The graph in Figure 69Figure 70 indicate the amount of pollutants inside the IYCC1 bath in 5 months with analyses done weekly. Iron is considered a problem if it is above 250 ppm, instead zinc is considered a problem above 12 g/l. So in the case of iron, every time it was conducted the relative analysis, it was considered acceptable. On the contrary, zinc exceeded the acceptable value some time. It is also easy to see that the value the week after the exciding of the limit or getting near the limit of zinc has a drastic drop easily traceable to a partial or total remaking of the IYCC1 bath.

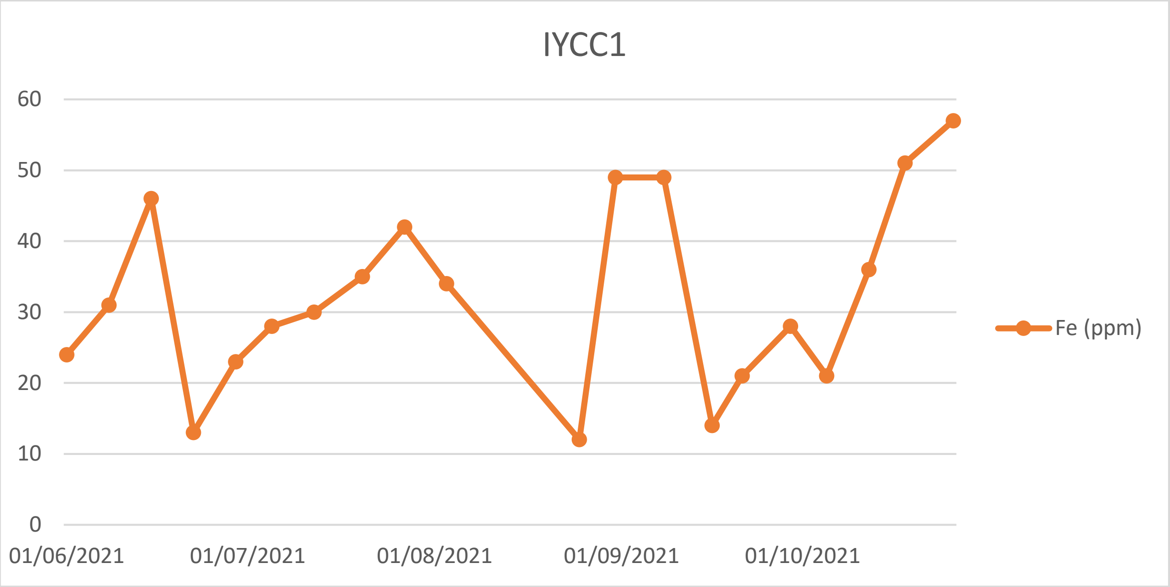


Figure 69 - Trend of iron pollutant inside the IYCC1, with analyses done weekly by the supplier

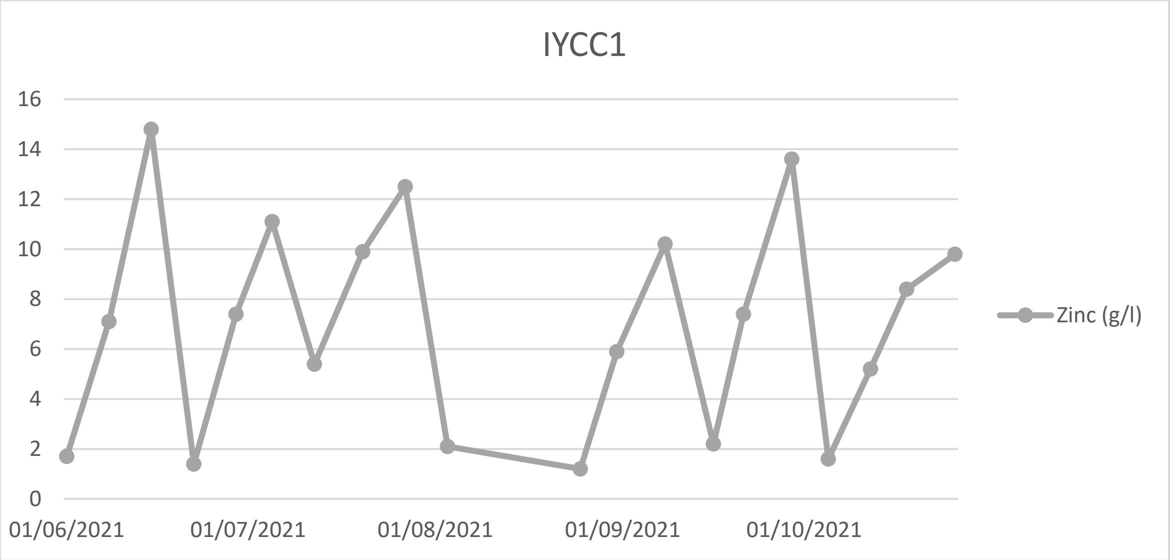


Figure 70 - Trend of zinc pollutant inside the IYCC1, with analyses done weekly by the supplier

In the Table 12 are written the processing times and parameters of the chromate conversion coating of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

Most of the parameters in Table 12 are similar, because the conversion process is done in the same way for every products. The main reason for the difference in the process times is the fact that there are only few rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels.

Table 12 - Passivation with IYCC1 processing time and processing parameters for each samples

Samples	Date	Centrifuge Velocity (Hz)	Barrel Dripping Time (s)	Barrel rotation (Hz)	IYCC1 (h:min:s)	IYCC1 (°C)	Rinse (h:min:s)	Centrifuge (h:min:s)	Centrifuge (°C)
D-1	26/07/2021	40	20	40	00:00:32	28	00:00:17	00:12:26	97,6
H-1	18/10/2021	40	20	40	00:00:32	27,9	00:00:17	00:13:47	96,1
D-2	21/10/2021	40	20	40	00:00:32	27,9	00:00:17	00:14:59	99,6
Q-1	22/10/2021	40	20	40	00:00:32	28	00:00:17	00:13:33	95,8
D-3	25/10/2021	40	10	40	00:00:47	28	00:00:17	00:11:46	105

4.3.3. Iridescent yellow passivation 1 (IYCC1) + Sealer

Table 13 shows only the pH of the IYCC1 bath for each collected samples, because it is the only parameter that it is possible to obtain in the factory.

Table 13 - IYCC1 pH for each collected samples that also got sealed

Samples	Date	pH	Notes
C-1	26/07/2021	2,4	
C-2	29/07/2021	2,6	
C-3	04/08/2021	2,4	
C-4	17/08/2021	2	
C-5	23/08/2021	3,3	
C-6	23/09/2021	2,1	morning
C-7	23/09/2021	2,4	afternoon
C-8	27/09/2021	2,1	
F-1/G-1	18/10/2021	2,8	
G-2	19/10/2021	2,6	
O-1	21/10/2021	2	
O-2	22/10/2021	2,8	
F-2	25/10/2021	2,5	
O-3	27/10/2021	2,5	morning
O-4/R-1/R-2	27/10/2021	2,1	afternoon

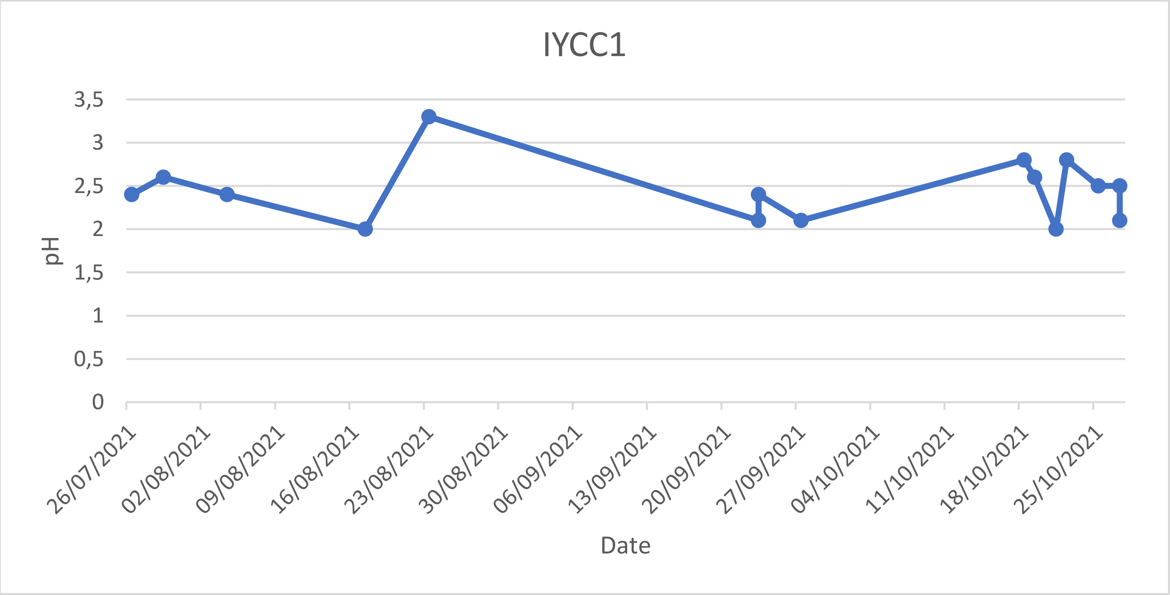


Figure 71 - IYCC1 pH for each collected samples that also got sealed

Is possible to see a more complete analysis of IYCC1 in chapter 4.3.2 Iridescent yellow conversion coating 1 (IYCC1).

The supplier performs a weekly analysis on the sealer bath as it is possible to see in the Figure 72Figure 73. It appears immediately that the concentration does not have a constant trend and that pH oscillates between 7,5 and 1,0, but the pH should not go below 8,5.

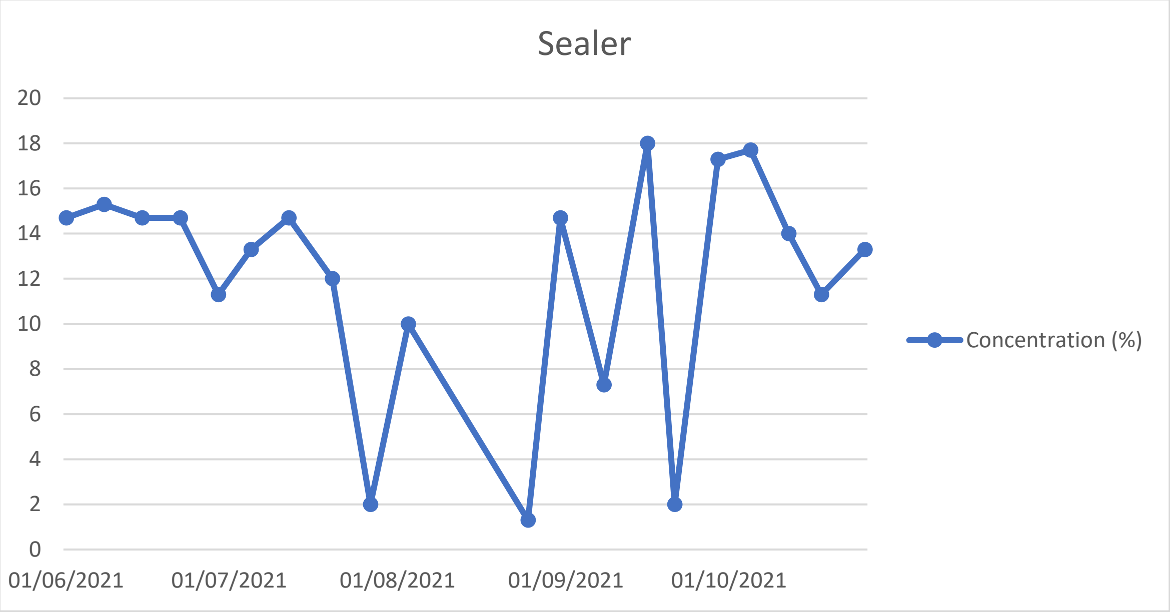


Figure 72 - Sealer concentration, analyses done weekly by the supplier

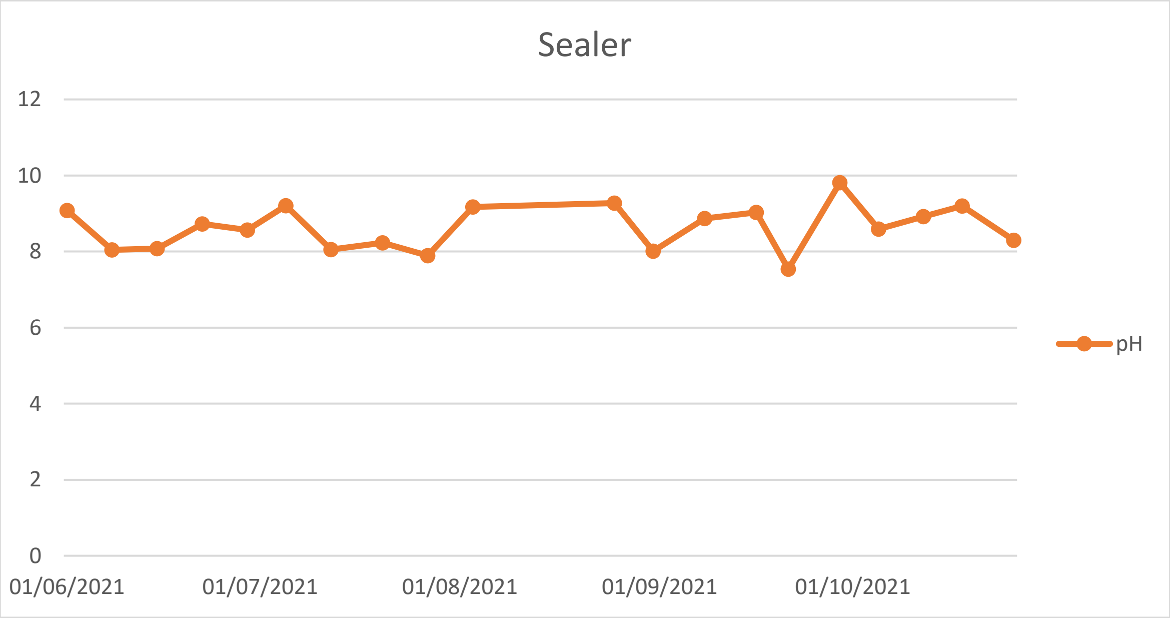


Figure 73 - Sealer pH, analyses done weekly by the supplier

In the Table 14 are written the processing times and parameters of the chromate conversion coating of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

Most of the parameters in Table 14 are similar, because the conversion process is done in the same way for every products. The main reason for the difference in the process times is the fact that there are only few rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels.

Table 14 - Passivation with IYCC1 and sealing with sealer processing time and processing parameters for each samples

Samples	Date	Centrifuge Velocity (Hz)	Barrel Dripping Time (s)	Barrel rotation (Hz)	IYCC1 (h:min:s)	IYCC1 (°C)	Rinse (h:min:s)	Sealer (h:min:s)	Sealer (°C)	Centrifuge (h:min:s)	Centrifuge (°C)
C-1	26/07/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	21,6	00:15:36	102,5
C-2	29/07/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	24,8	00:12:35	95,8
C-3	04/08/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	25,3	00:15:25	57
C-4	17/08/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	22,7	00:15:45	62,5
C-5	23/08/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	27,3	00:20:45	110,1
C-6	23/09/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	22,8	00:12:40	105,7
C-7	23/09/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	23,3	00:19:12	109,5
C-8	27/09/2021	40	10	40	00:00:42	28,4	00:00:17	00:00:27	22,2	00:15:40	101,3
F-1	18/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	22,3	00:12:49	97,5
G-1	18/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	22,4	00:14:22	99,6
G-2	19/10/2021	40	10	40	00:00:42	28	00:00:17	00:00:27	23,5	00:15:15	92,6
O-1	21/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	23,4	00:16:08	96,4
O-2	22/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	23,8	00:14:23	96,9
F-2	25/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	20,4	00:15:28	96,5
O-3	27/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	23,6	00:13:09	96,1
O-4	27/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	22,5	00:15:37	95,8
R-1	27/10/2021	40	10	40	00:00:42	27,9	00:00:17	00:00:27	22,4	00:12:21	64,6
R-2	27/10/2021	40	10	40	00:00:43	27,9	00:00:17	00:00:27	22,2	00:15:31	96,7

4.3.4. Iridescent yellow conversion coating 2 (IYCC2) + Sealer

Table 15 shows only the pH of the IYCC2 bath for each collected samples, because it is the only parameter that it is possible to obtain in the factory.

Table 15 - IYCC2 pH for each collected samples that also got sealed

Samples	Date	pH
A-1/B-1	22/07/2021	2,3
I-1	18/10/2021	2,2
P-1	21/10/2021	2

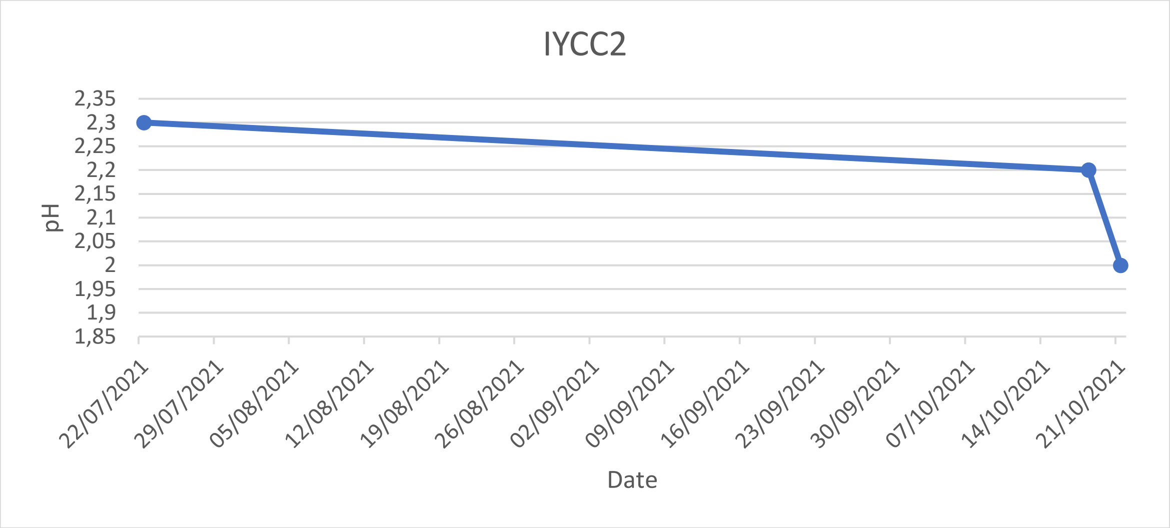


Figure 74 - IYCC2 pH for each collected samples that also got sealed

The supplier of the IYCC performs a more complete analysis weekly as it is possible to see in the Figure 75Figure 76. It appears immediately that the concentration does not have a constant trend and that pH oscillates between 1,5 and 2,8, but the pH should remain between 2,0 and 2,5.

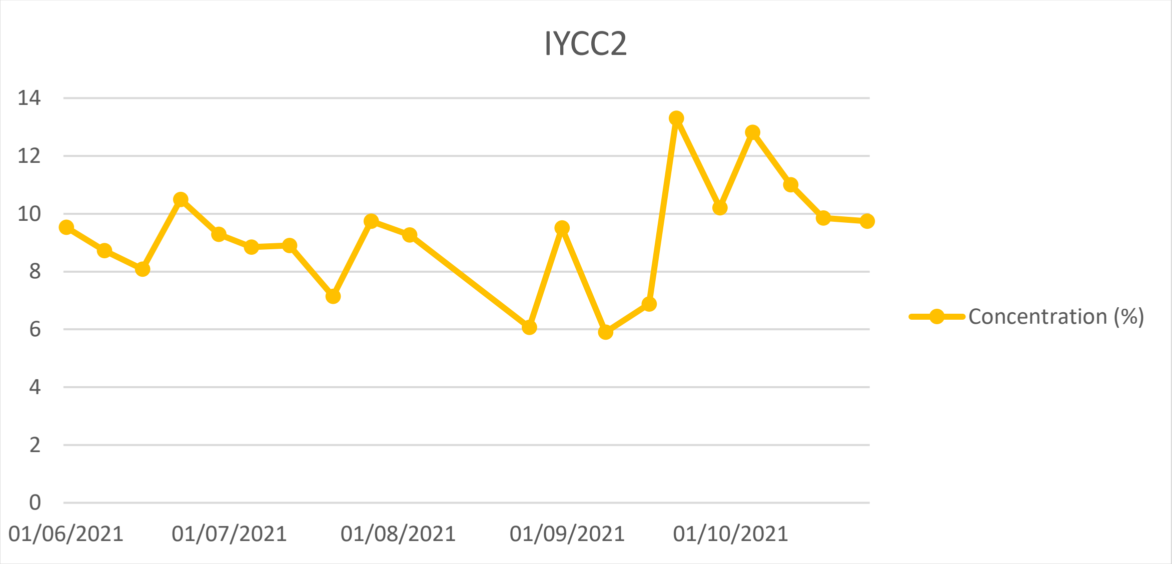


Figure 75 - IYCC2 concentration, analyses done weekly by the supplier

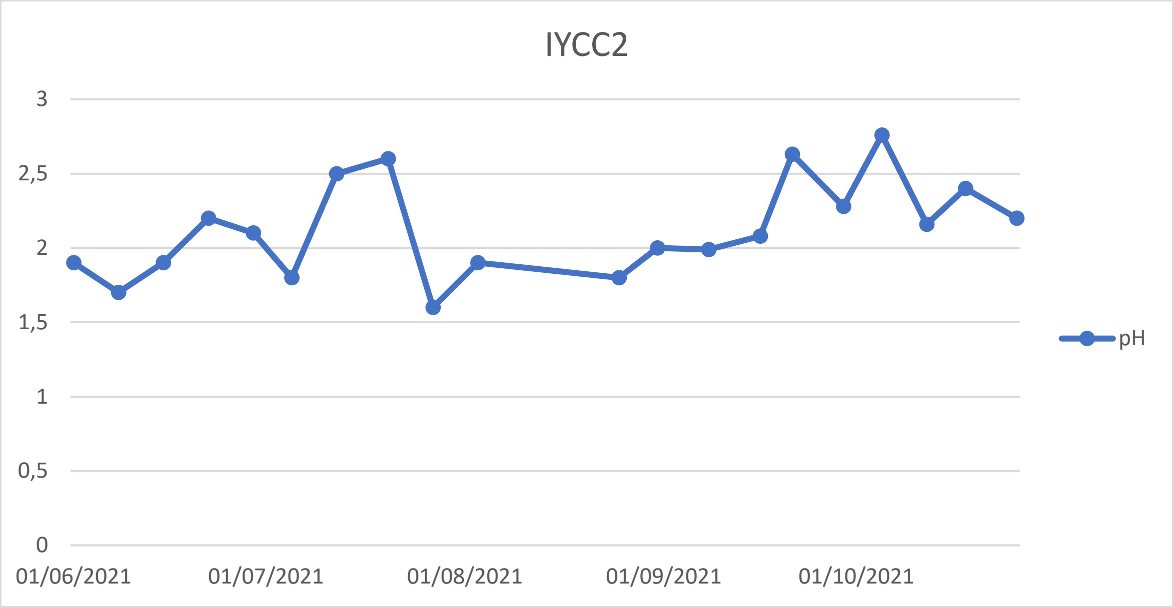


Figure 76 - IYCC2 pH, analyses done weekly by the supplier

The graph in Figure 77Figure 78 indicate the amount of pollutants inside the IYCC2 bath in 5 months with analyses done weekly. Iron is considered a problem if it is above 250 ppm, instead zinc is considered a problem above 12 g/l. So in the case of iron, every time it was conducted the relative analysis, it was considered acceptable. On the contrary, zinc exceeded the acceptable value some time. It is also easy to see that the value the week after the exciding of the limit or getting near the limit of zinc has a drastic drop easily traceable to a partial or total remaking of the IYCC2 bath.

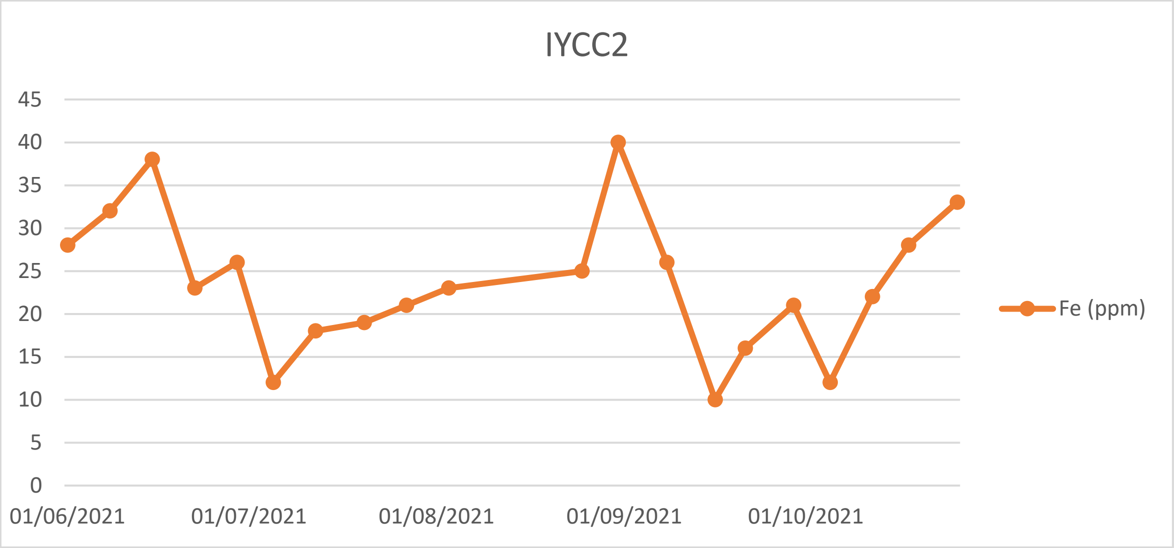


Figure 77 - Trend of iron pollutant inside the IYCC2, with analyses done weekly by the supplier

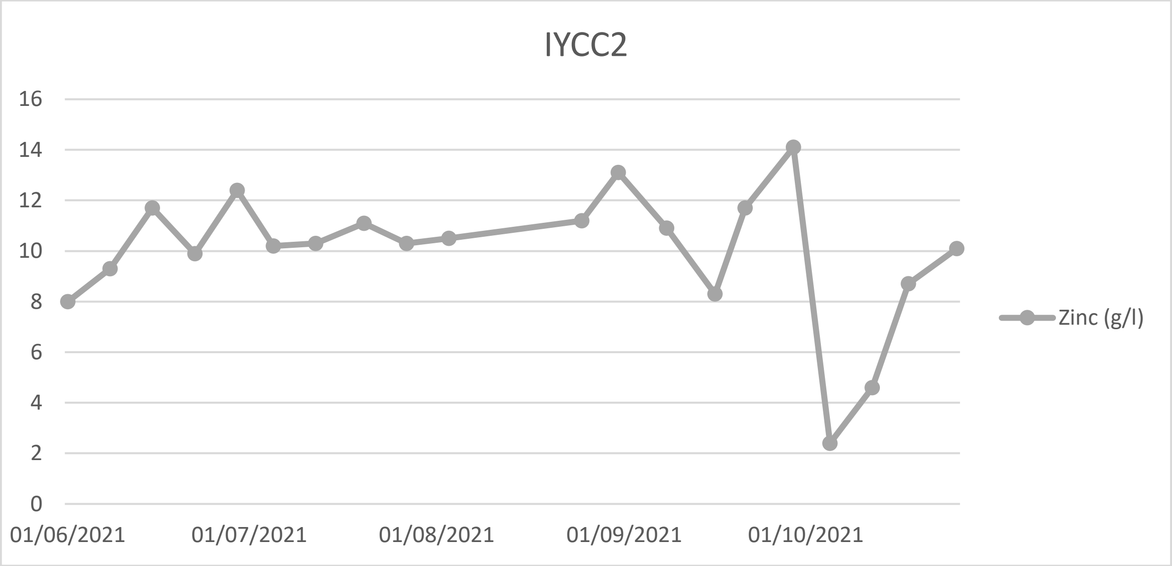


Figure 78- Trend of zinc pollutant inside the IYCC2, with analyses done weekly by the supplier

Is possible to see the analysis of sealer in chapter 4.3.3 Iridescent yellow passivation 1 (IYCC1) + Sealer.

In the Table 16 are written the processing times and parameters of the chromate conversion coating of each samples directly collected during the production and also the barrel parameter (dripping time and rotation frequency).

Most of the parameters in Table 16 are similar, because the conversion process is done in the same way for every products. The main reason for the difference in the process times is the fact that there are only few rail barrel movers and this can lead sometimes to delay or advance in the movement of the barrels.

Table 16 - Passivation with IYCC2 and sealing with sealer processing time and processing parameters for each samples

Samples	Date	Centrifuge Velocity (Hz)	Barrel Dripping Time (s)	Barrel rotation (Hz)	IYCC2 (h:min:s)	IYCC2 (°C)	Rinse (h:min:s)	Sealer (h:min:s)	Sealer (°C)	Centrifuge (h:min:s)	Centrifuge (°C)
A-1	22/07/2021	40	10	40	00:00:47	29,2	00:00:17	00:00:27	23	00:20:00	64,2
B-1	22/07/2021	40	10	40	00:00:47	29,4	00:00:17	00:00:27	22,5	00:14:55	96,5
I-1	18/10/2021	40	10	40	00:00:47	29,1	00:00:17	00:00:27	21,1	00:13:28	103,6
P-1	21/10/2021	30	10	30	00:00:47	29,3	00:00:17	00:00:27	23,8	00:14:02	96,9

4.4. Zinc layer thickness

In the Table 17 are written the value of the zinc layer thickness of all the samples.

Table 17 - Zinc layer thickness of all the samples

Samples	Date	Average (µm)	Minimum Measure (µm)	Maximum Measure (µm)
A-1	22/07/2021	7,27	5,51	9,68
B-1	22/07/2021	9,41	7,45	11,2
C-1	26/07/2021	13,3	12,7	14,1
D-1	26/07/2021	8,74	7,35	9,98
C-2	29/07/2021	10,6	9,17	12,2
E-1	03/08/2021	7,59	6,86	8,17
C-3	04/08/2021	15,1	13,7	16,1
C-4	17/08/2021	14,3	11,9	16,4
C-5	23/08/2021	17,4	15,7	18,5
C-6	23/09/2021	17,3	16,1	18,8
C-7	23/09/2021	11,5	10,8	12,6
C-8	27/09/2021	11,6	10,6	12,8
F-1	18/10/2021	10,5	7,17	16,2
G-1	18/10/2021	5,45	3,61	9,16

H-1	18/10/2021	15,9	14,5	17,2
I-1	18/10/2021	4,5	4,19	5,16
J-1	18/10/2021	11,6	8,85	15,1
K-1	18/10/2021	10,4	7,46	13,4
G-2	19/10/2021	4,81	3,01	8,11
L-1	19/10/2021	8,98	8,21	10
M-1	20/10/2021	7,71	6,65	9,08
N-1	20/10/2021	7,3	5,11	9,74
J-2	20/10/2021	8	5,08	10,9
O-1	21/10/2021	7,33	5,14	11
D-2	21/10/2021	6,09	5,27	7,12
P-1	21/10/2021	7,21	6,22	8,66
O-2	22/10/2021	6,7	4,24	11,4
Q-1	22/10/2021	9,55	7,22	11,5
F-2	25/10/2021	4,79	3,43	7,22
D-3	25/10/2021	8,79	7,39	9,97
O-3	27/10/2021	4,81	2,74	9,45
O-4	27/10/2021	8,58	3,61	15
R-1	27/10/2021	7,56	5,46	11,9
R-2	27/10/2021	8,54	5,66	13,6
J-3	27/10/2021	9,03	5,42	12,1

Looking at the Table 17 is immediately observable that the minimum thickness value of the various sample can be a lot smaller than the maximum value. This is due to the fact that in the smaller part of a piece there is a concentration of the current, during the zinc electroplating, and so a higher amount of zinc deposited.

4.5. Salt spray results

The salt spray machine used to obtain the corrosion value of the varies pieces is the Angelantoni DCTC 600.

In the Table 18Table 19Table 20Table 21 the values of "White Corrosion (h)" indicate the hours that the sample has spended inside the salt spray before the appearance of the corrosion product of zinc (that are white). Therefore, it indicate the corrosion resistance of the conversion layer. Instead, the values of "Red Corrosion (h)" indicate the time before the appearance of the corrosion product of steel, the base material of the sample. Therefore, the value of "Red Corrosion (h)" minus the value of "White Corrosion (h)" indicate the corrosion resistance of the zinc layer.

In the Table 18Table 19Table 20Table 21 are also reported the thickness value of the zinc layer (the same that are written in Table 17).

4.5.1. Blue conversion coating (BCC)

Table 18 - NSS corrosion resistance of all sample that performed the passivation with BCC

Samples	Date	White Corrosion (h)	Red Corrosion (h)	Red Corrosion - White corrosion (h)	Average Thickness (µm)	Minimum Thickness (µm)	Maximum Thickness (µm)
E-1	03/08/2021	48	120	72	7,59	6,86	8,17
J-1	18/10/2021	48	264	216	11,6	8,85	15,1
K-1	18/10/2021	48	216	168	10,4	7,46	13,4
L-1	19/10/2021	48	120	72	8,98	8,21	10
N-1	20/10/2021	48	120	72	7,71	6,65	9,08
N-2	20/10/2021	48	96	48	7,3	5,11	9,74
J-2	20/10/2021	48	120	72	8	5,08	10,9
J-3	27/10/2021	48	336	288	9,03	5,42	12,1

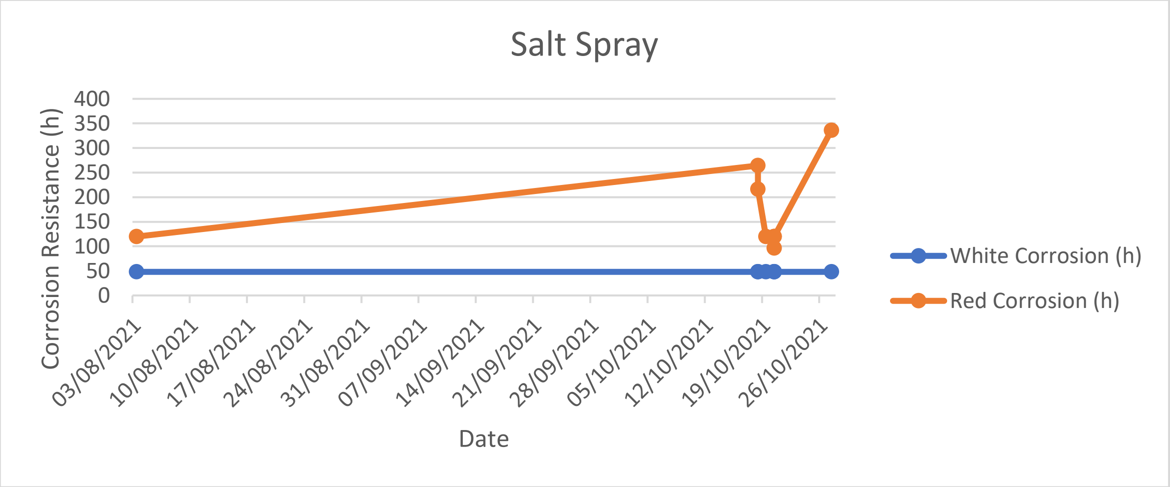


Figure 79 - NSS corrosion resistance of all sample that performed the passivation with BCC

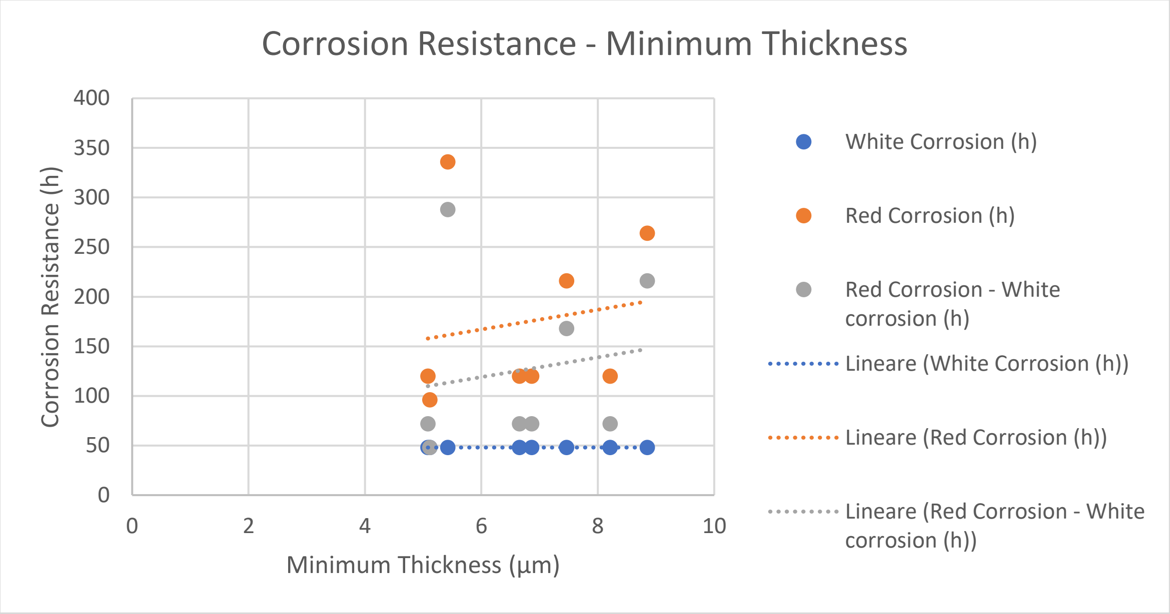


Figure 80 - NSS corrosion resistance vs minimum thickness of all sample that performed the passivation with BCC

The white corrosion resistance remains constant with the increase of the zinc layer thickness (Figure 80). This is what should ideally happen with a conversion coating performed correctly, because as written previously the white corrosion resistance is only related to the conversion coating and so it is to be related only to the quality of the passivation layer. Instead, the red corrosion resistance has the tendency to increase with the increase of the zinc layer thickness (Figure 80). Therefore, the resistance of the zinc layer increases with the layer thickness, and again this is what should ideally happen.

4.5.2. Iridescent yellow conversion coating 1 (IYCC1)

Table 19 - NSS corrosion resistance of all sample that performed the passivation with IYCC1

Samples	Date	White Corrosion (h)	Red Corrosion (h)	Red Corrosion - White corrosion (h)	Average Thickness (µm)	Minimum Thickness (µm)	Maximum Thickness (µm)
D-1	26/07/2021	96	168	72	8,74	7,35	9,98
H-1	18/10/2021	48	216	168	15,9	14,5	17,2
D-2	21/10/2021	48	192	144	6,09	5,27	7,12
Q-1	22/10/2021	72	264	192	9,55	7,22	11,5
D-3	25/10/2021	144	480	336	8,79	7,39	9,97

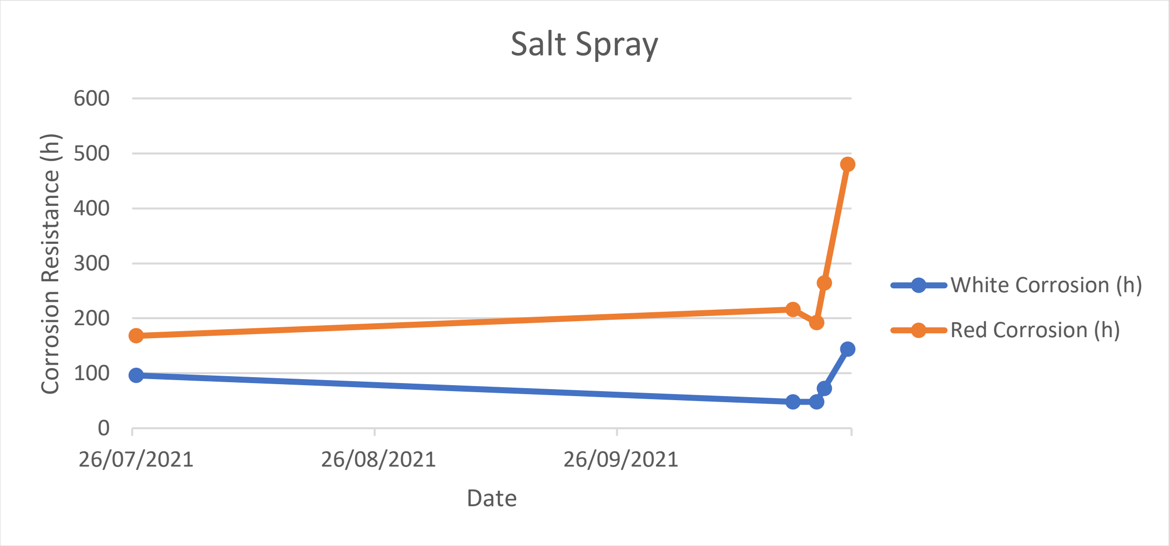


Figure 81 - NSS corrosion resistance of all sample that performed the passivation with IYCC1

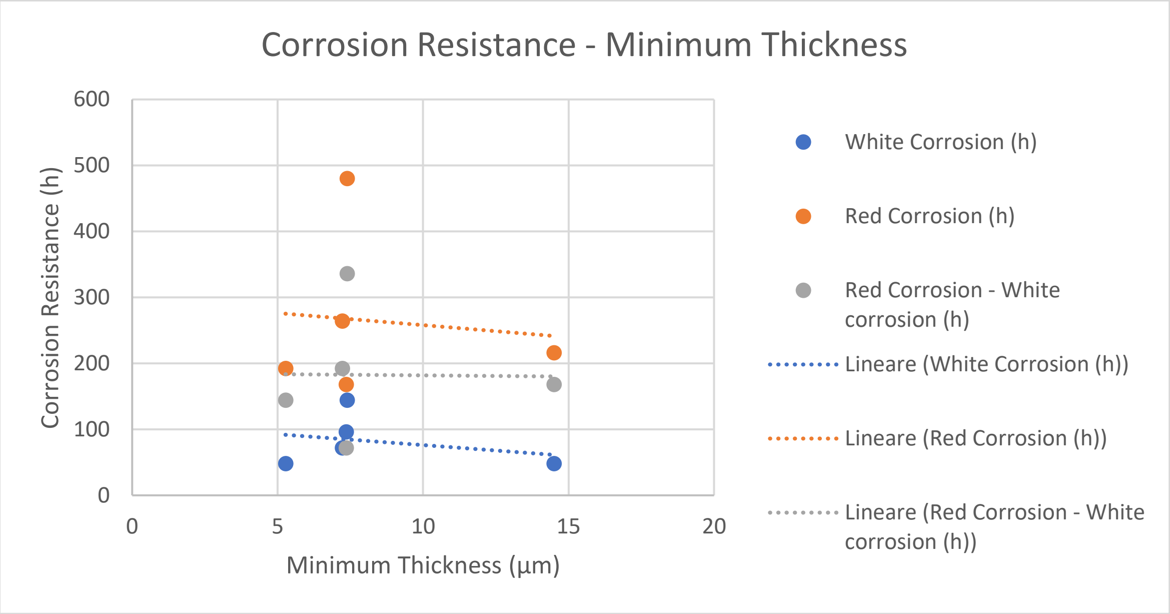


Figure 82 - NSS corrosion resistance vs minimum thickness of all sample that performed the passivation with IYCC1

The tendency to decrease the white corrosion resistance with the increase of the zinc layer thickness (Figure 82) should be considered a coincidence, because as written previously the white corrosion resistance is only related to the conversion coating and so is to be related only to the quality of the passivation layer. Moreover, the red corrosion resistance has the same tendency of the white one, therefore the resistance of the zinc layer doesn’t increase with the layer thickness, probably because of a non-optimal zinc layer in the sample with high zinc layer thickness.

It is important to take in consideration that these observations are done with a small amount of data and that can be wrong for that reason.

4.5.3. Iridescent yellow conversion coating 1 (IYCC1)+ Sealer

Table 20 - NSS corrosion resistance of all sample that performed the passivation with IYCC1+Sealer

Samples	Date	White Corrosion (h)	Red Corrosion (h)	Red Corrosion - White corrosion (h)	Average Thickness (µm)	Minimum Thickness (µm)	Maximum Thickness (µm)
C-1	26/07/2021	96	168	72	13,3	12,7	14,1
C-2	29/07/2021	96	240	144	10,6	9,17	12,2
C-3	04/08/2021	96	240	144	15,1	13,7	16,1
C-4	17/08/2021	168	384	216	14,3	11,9	16,4
C-5	23/08/2021	168	384	216	17,4	15,7	18,5
C-6	23/09/2021	120	432	312	17,3	16,1	18,8
C-7	23/09/2021	120	264	144	11,5	10,8	12,6
C-8	27/09/2021	168	432	264	11,6	10,6	12,8
F-1	18/10/2021	168	240	72	10,5	7,17	16,2
G-1	18/10/2021	72	264	192	5,45	3,61	9,16
G-2	19/10/2021	48	144	96	4,81	3,01	8,11
O-1	21/10/2021	120	264	144	7,33	5,14	11
O-2	22/10/2021	144	336	192	6,7	4,24	11,4
F-2	25/10/2021	144	336	192	4,79	3,43	7,22
O-3	27/10/2021	144	480	336	4,81	2,74	9,45
O-4	27/10/2021	144	336	192	8,58	3,61	15
R-1	27/10/2021	144	336	192	7,56	5,46	11,9
R-2	27/10/2021	144	336	192	8,54	5,66	13,6

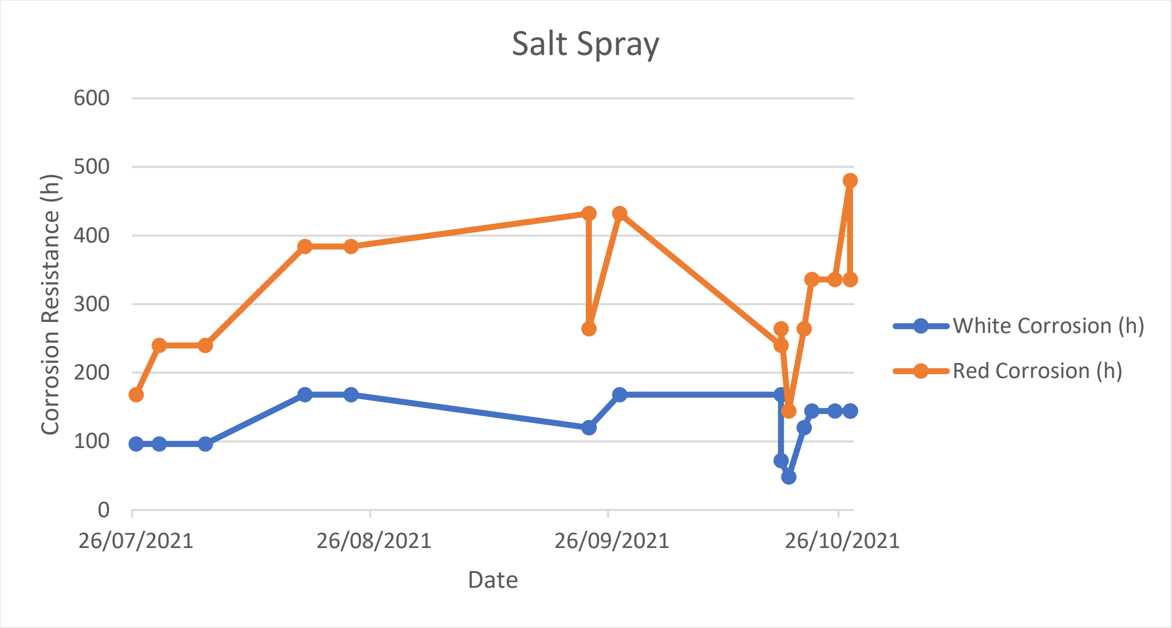


Figure 83 - NSS corrosion resistance of all sample that performed the passivation with IYCC1+ Sealer

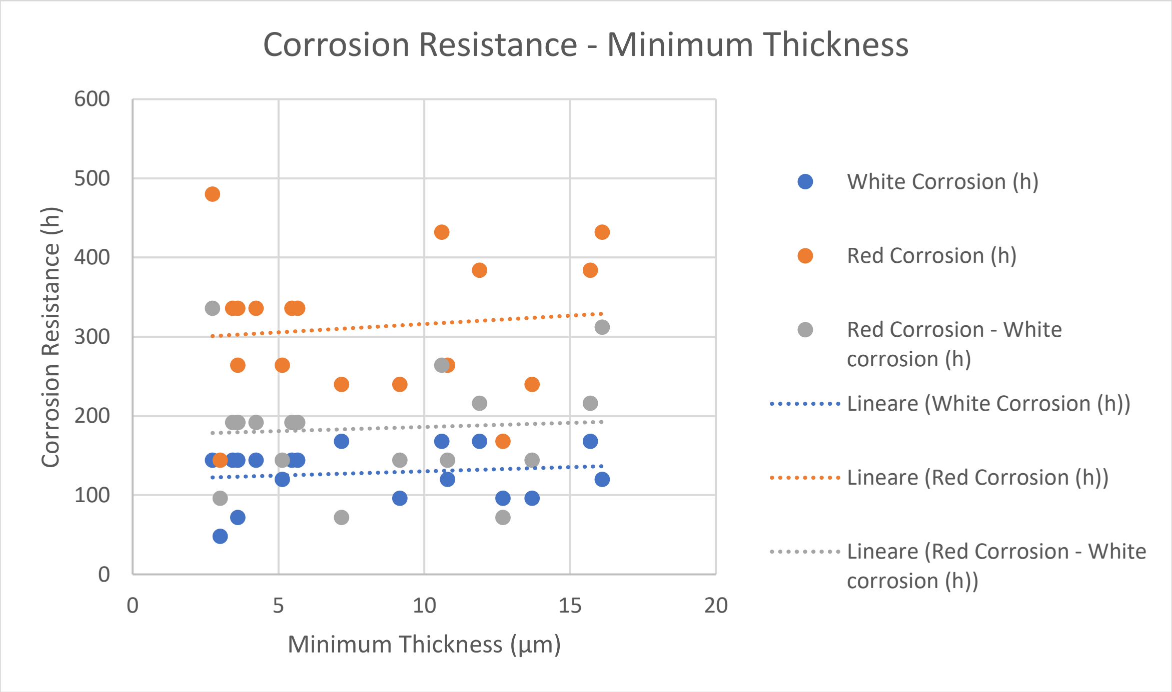


Figure 84 - NSS corrosion resistance vs minimum thickness of all sample that performed the passivation with IYCC1+Sealer

The white corrosion resistance increases with the increase of the zinc layer thickness (Figure 84). This should be considered a coincidence, because as written previously the white corrosion resistance is only related to the conversion coating and so is to be related only to the quality of the passivation layer. Also, the red corrosion resistance has the tendency to increase with the increase of the zinc layer thickness (Figure 84), but with a bigger increase. Therefore, the resistance of the zinc layer increases with the layer thickness, and this is what should ideally happen.

4.5.4. Iridescent yellow conversion coating 2 (IYCC2) + Sealer

Table 21 - NSS corrosion resistance of all sample that performed the passivation with IYCC2+Sealer

Samples	Date	White Corrosion (h)	Red Corrosion (h)	Red Corrosion - White corrosion (h)	Average Thickness (µm)	Minimum Thickness (µm)	Maximum Thickness (µm)
A-1	22/07/2021	168	216	48	7,27	5,51	9,68
B-1	22/07/2021	168	216	48	9,41	7,45	11,2
I-1	18/10/2021	72	144	72	4,5	4,19	5,16
P-1	21/10/2021	120	264	144	7,21	6,22	8,66

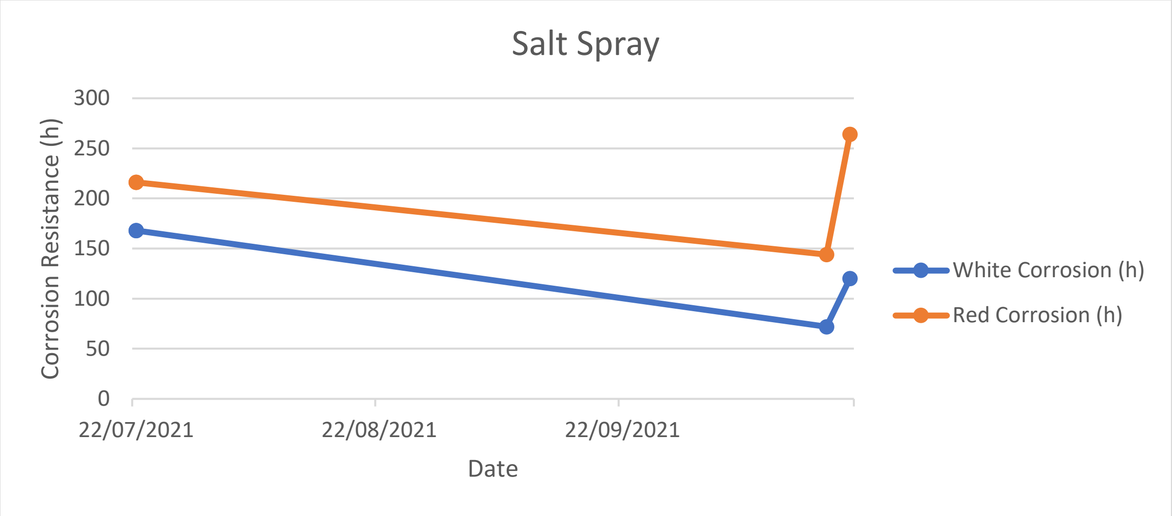


Figure 85 - NSS corrosion resistance of all sample that performed the passivation with IYCC2+ Sealer

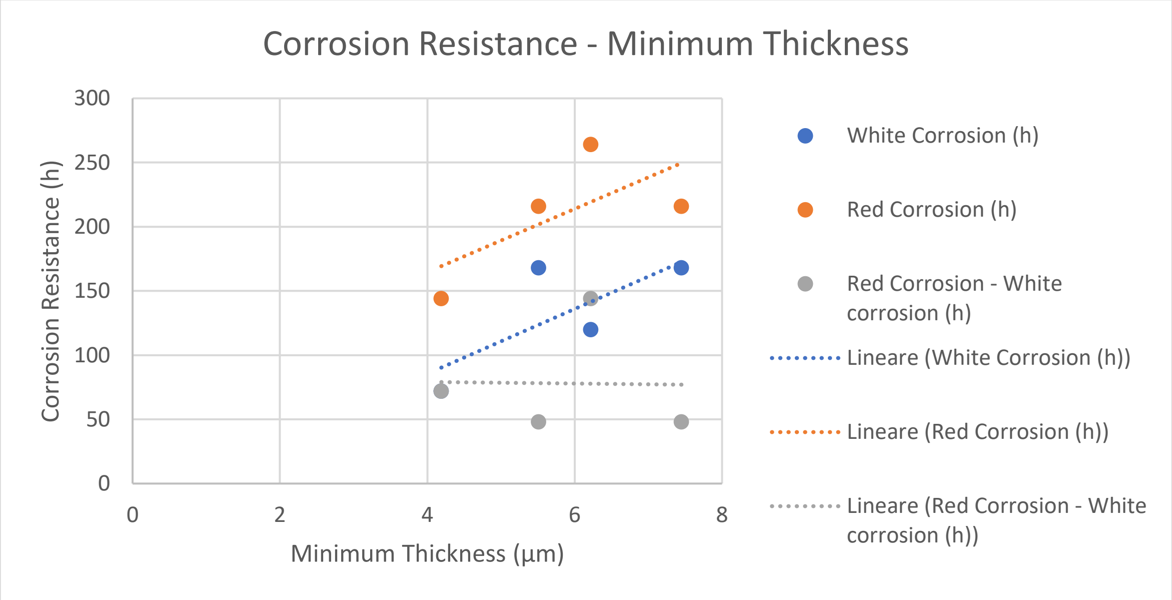


Figure 86 - NSS corrosion resistance vs minimum thickness of all sample that performed the passivation with IYCC2+Sealer

The white corrosion resistance increases with the increase of the zinc layer thickness (Figure 86). This should be considered a coincidence, because as written previously the white corrosion resistance is only related to the conversion coating and so is to be related only to the quality of the passivation layer. Moreover, the red corrosion resistance has the same tendency of the white one. Therefore, the resistance of the zinc layer doesn't increase with the layer thickness, probably because of a non-optimal zinc layer in the samples.

It is important to take in consideration that these observations are done with a small amount of data and that can be wrong for that reason.

4.6. Hull cell test

In this section, there are the images of the metal sheet used in the hull cell test. It is important to remember that the left side of the sheet is the one that is in high current density and the right in low current density during the test.

Figure 87 - Metal sheet of the Hull cell test of 22/07/2021

From Figure 87 is possible to see that the sample is almost totally bright, with the exception of the left side and on all the top sheet that have some dull parts (on the right side there are some finger print). The dull parts on top are probably due to a bad cleaning of the metal sheet.

Figure 88 - Metal sheet of the Hull cell test of 26/07/2021

From Figure 88 it is notable a beginning of burn at the left end of the metal sheet and dull zinc layer in the high current zone and at the extremity of the low current zone.

Figure 89 - Metal sheet of the Hull cell test of 29/07/2021

From Figure 89 it is of immediate notice the burn on the high current and the large dull zone in almost all the left side and at the extremity of the right side.

Figure 90 - Metal sheet of the Hull cell test of 03/08/2021

From Figure 90 it is notable a slight burn on the left extremity, a corroded zone in the middle that should not be considered because is to be implied to the environment where this samples are stored (slightly aggressive environment) and a zone on the right with the strip. The strip is glue that has been dropped on the sample by accident.

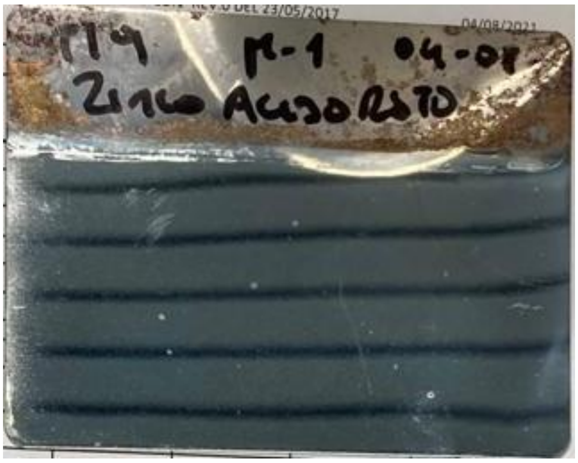


Figure 91 - Metal sheet of the Hull cell test of 04/08/2021

From Figure 91 it is possible to see a burn in the high current and diffused in all the sample a deposit of what probably is organic component (the additive).

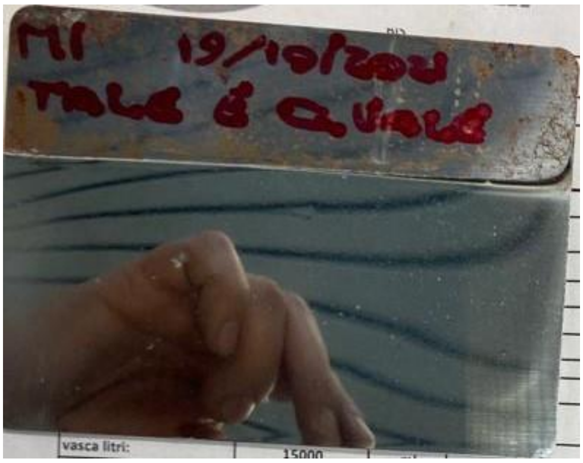


Figure 92 - Metal sheet of the Hull cell test of 19/10/2021

From Figure 92 it is notable a slight burn in the high current and diffused in all the sample a deposit of what probably is organic component (the additive).

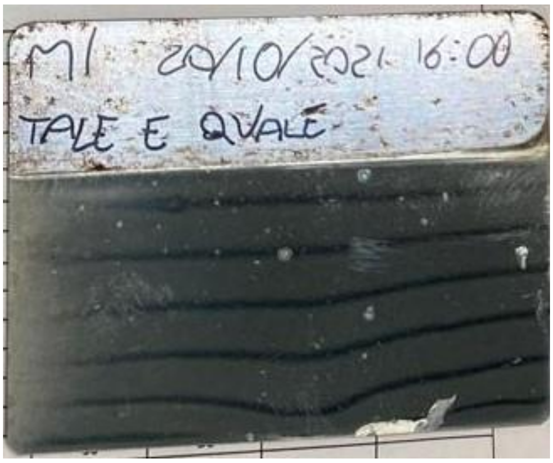


Figure 93 - Metal sheet of the Hull cell test of 20/10/2021

From Figure 93 it is possible to see a burn in the high current, the rest of the sample is bright.

Figure 94 - Metal sheet of the Hull cell test of 21/10/2021

From Figure 94 it is possible to see a slight burn in the high current, the rest of the sample is bright.

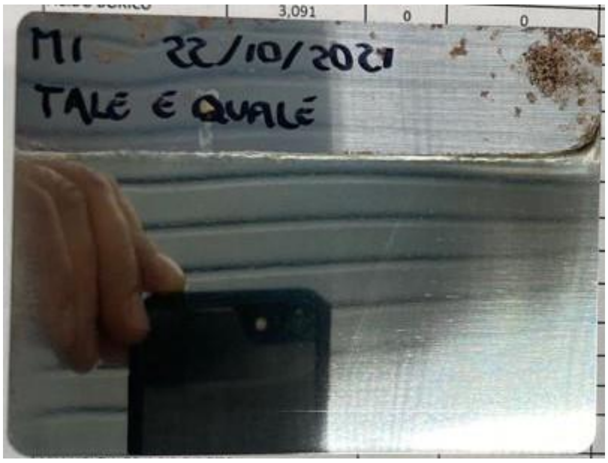
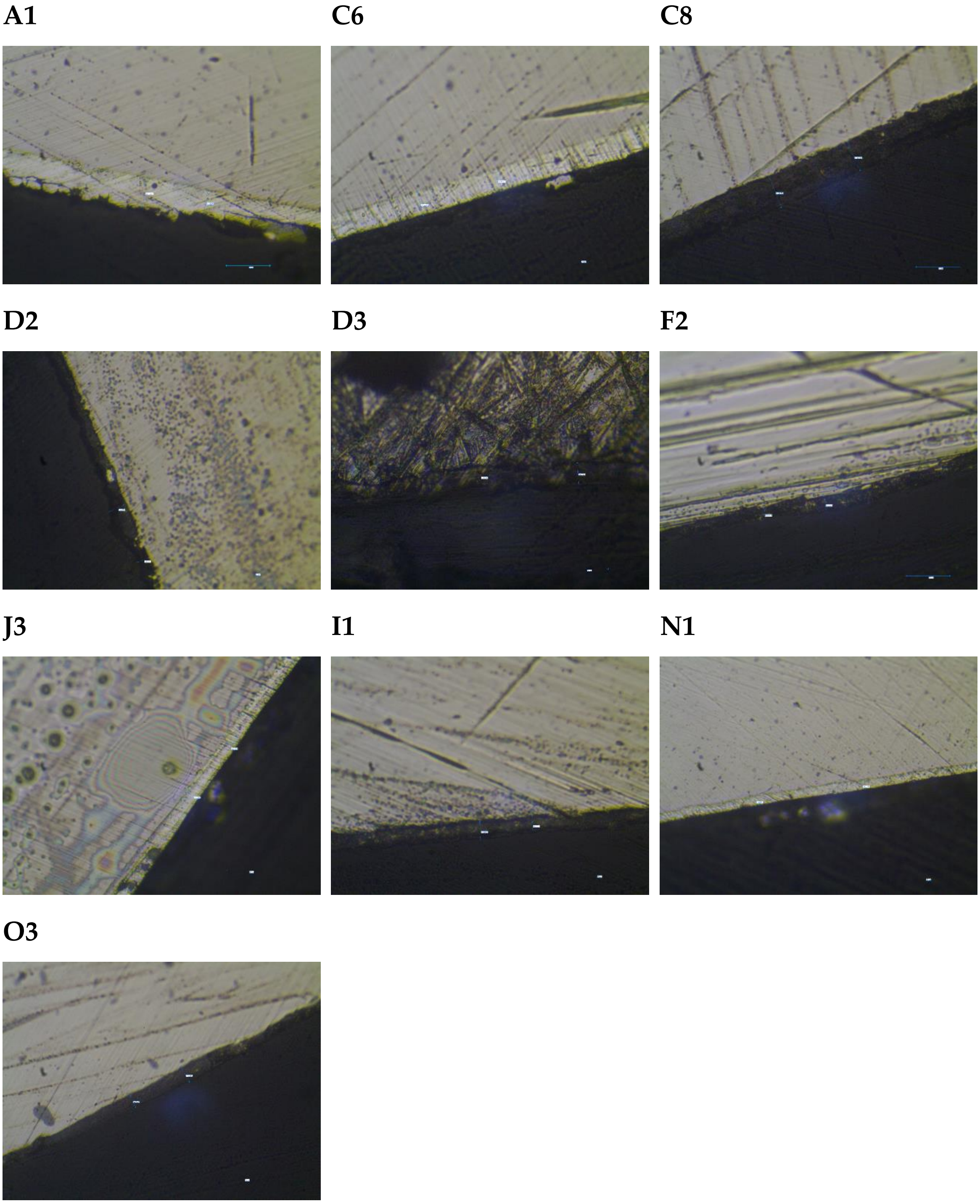


Figure 95 - Metal sheet of the Hull cell test of 22/10/2021

From Figure 95 it is possible to see a start of burn in the high current, the rest of the sample is bright.

4.7. Optical microscopy analyses



A1 C6 C8 D2 D3 F2 J3 I1 N1 O3

Figure 96 - Photos of sections of zinced samples obtained with an optical microscopy

The Figure 96 represent the section of some of the samples. The images have been obtained with an optical microscopy.

During the cutting of some samples, to obtain the section to analyze, the zinc layer was badly damaged or in some parts completely removed. This can be clearly seen in sample D2 (Figure 96).

The fact that samples A1, C6, J3 and N1 have the zinc layer colored in white, while the samples C8, D2, D3, D3, F2, I1 and O3 have the zinc layer colored in black is most certainly due to a slightly different lighting in the microscopy when the images were taken.

4.8. SEM analyses

The Figure 97 shows a part of the section of sample C8. It is of immediate notice the presence of cracks on the zinc layer perpendicular to the surface.

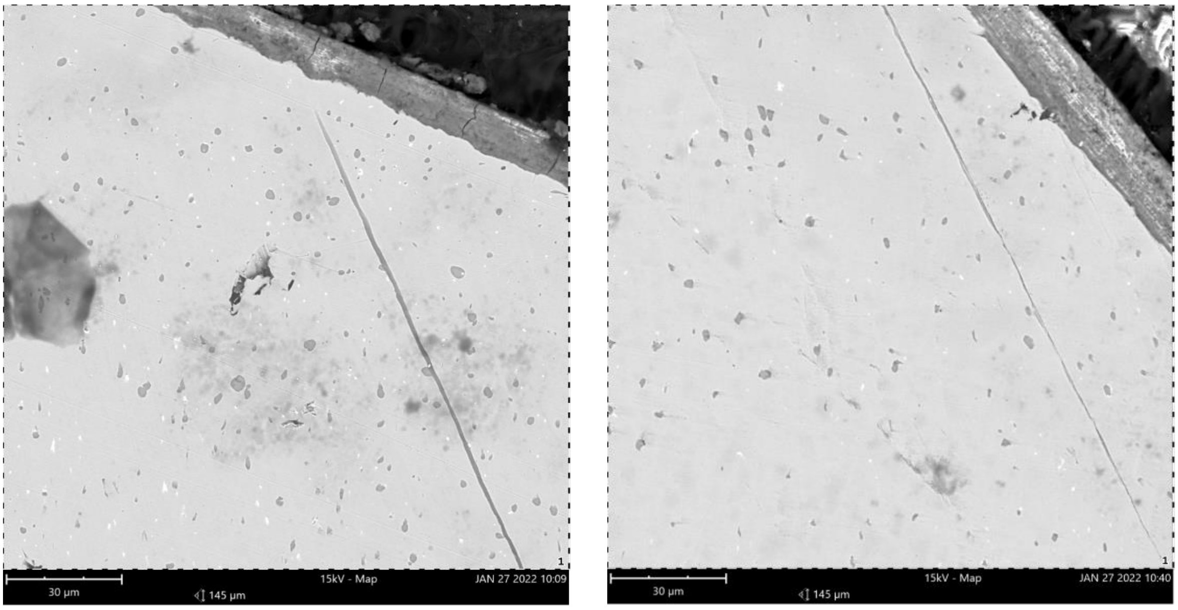


Figure 97 - Sections of sample C8 obtained with SEM

The cracks on the zinc surface are to imply to the cutting process because the sample has one of the best performance in the salt spray test, moreover many other samples during the cutting process lost the zinc layer or had sustained several damage in the zinc layer, as it is possible to see in Figure 98.

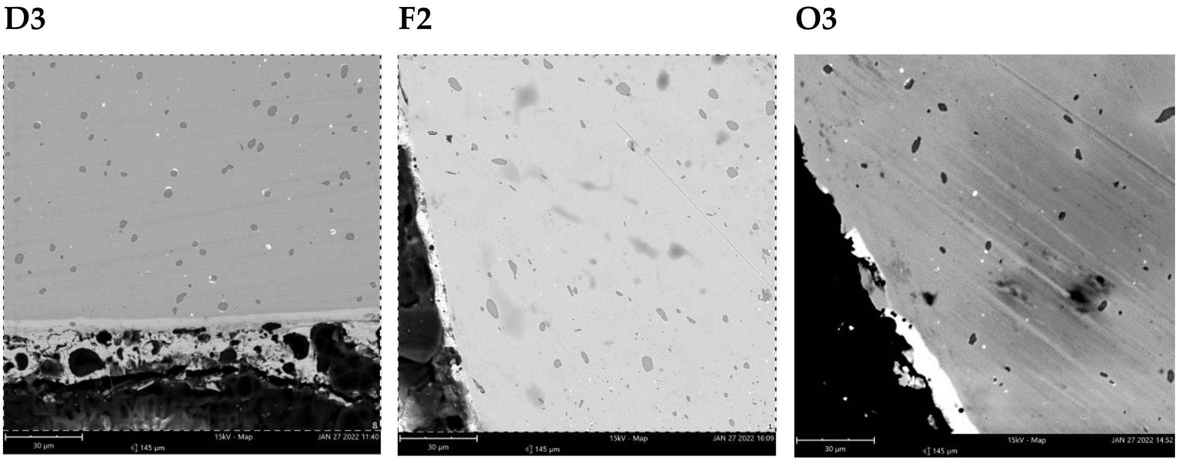


Figure 98 - Sections of samples D3,F2 and O3 with damaged zinc layer obtained with SEM

In Figure 99 is easy to see the zinc layer (light blue), but there is no trace of chromium or silicon (the sealer used is based on silicon). The reason for this is the fact that the analyzed part should contain a very small percentage of both element, so in the spectrum their peak are not visible.

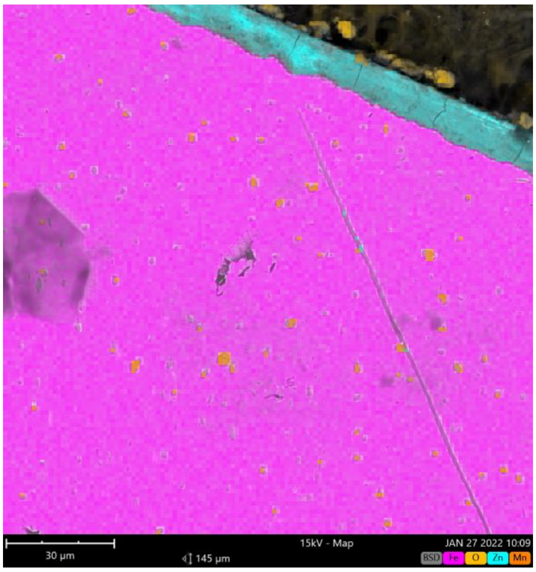


Figure 99 – Elemental map of C8 sample section obtained with SEM

Table 22 - Elemental composition of Figure 99

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
26	Fe	Iron	86.06	92.49
8	O	Oxygen	10.32	3.18
30	Zn	Zinc	2.51	3.16
25	Mn	Manganese	1.11	1.17

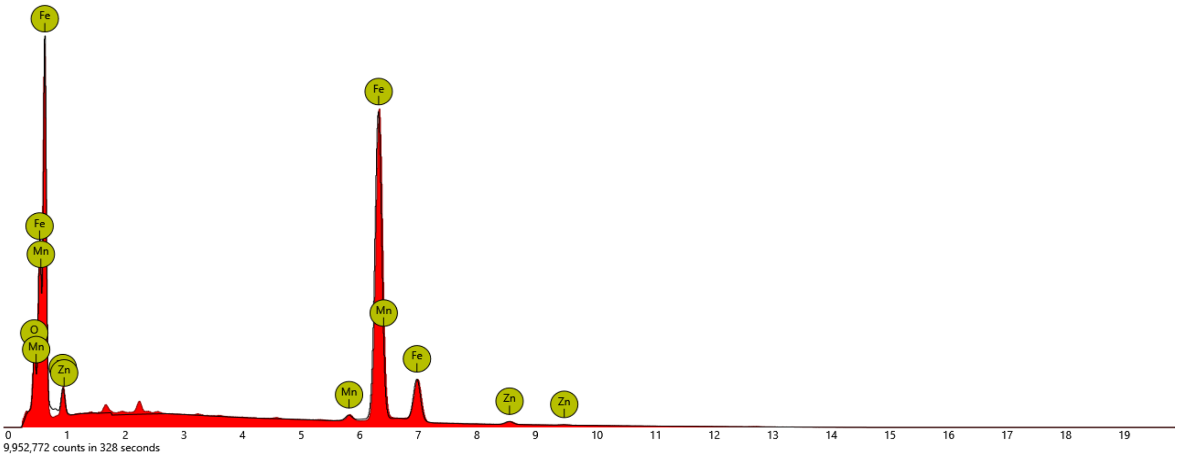


Figure 100 - Spectrum of the section in Figure 99 (Disabled elements: B, Dy, Yb)

The presence of oxygen in the sample is expected since the cutted sample remained in atmosphere condition for some time before the SEM analysis, leading to a start of oxidation.

To try to observe chromium and silicon an analysis along the perpendicular of the zinc layer has been performed (Figure 101).

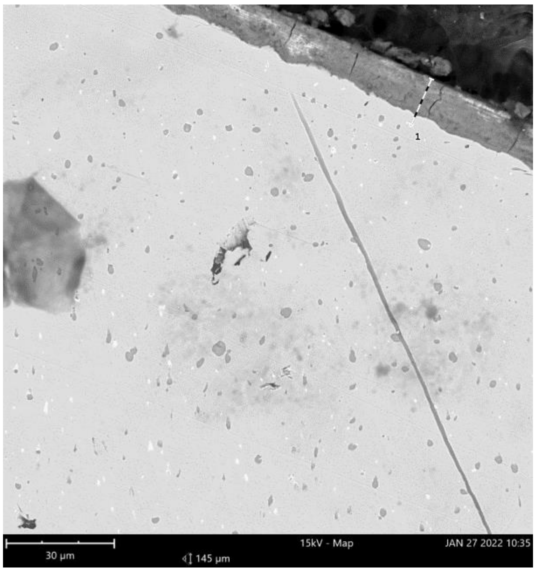


Figure 101 - Section of C8 sample with indicated the direction (black and white line) of the analysis of the zinc layer

Table 23 - Elemental composition along the direction in Figure 101

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
30	Zn	Zinc	29.78	51.60
26	Fe	Iron	17.43	25.80
8	O	Oxygen	52.56	22.29

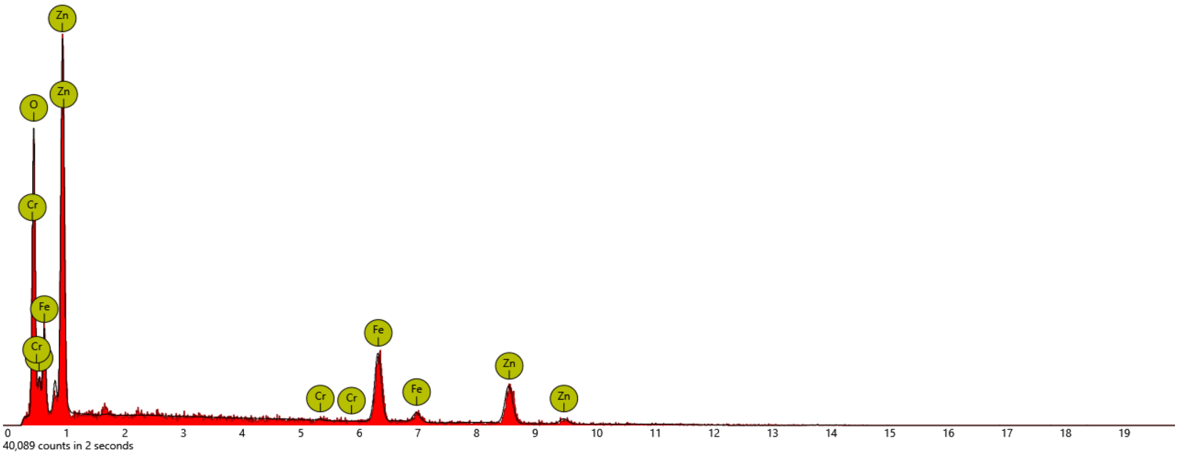


Figure 102 - Spectrum along the direction in Figure 101 (Disabled elements: B, Dy, Yb)

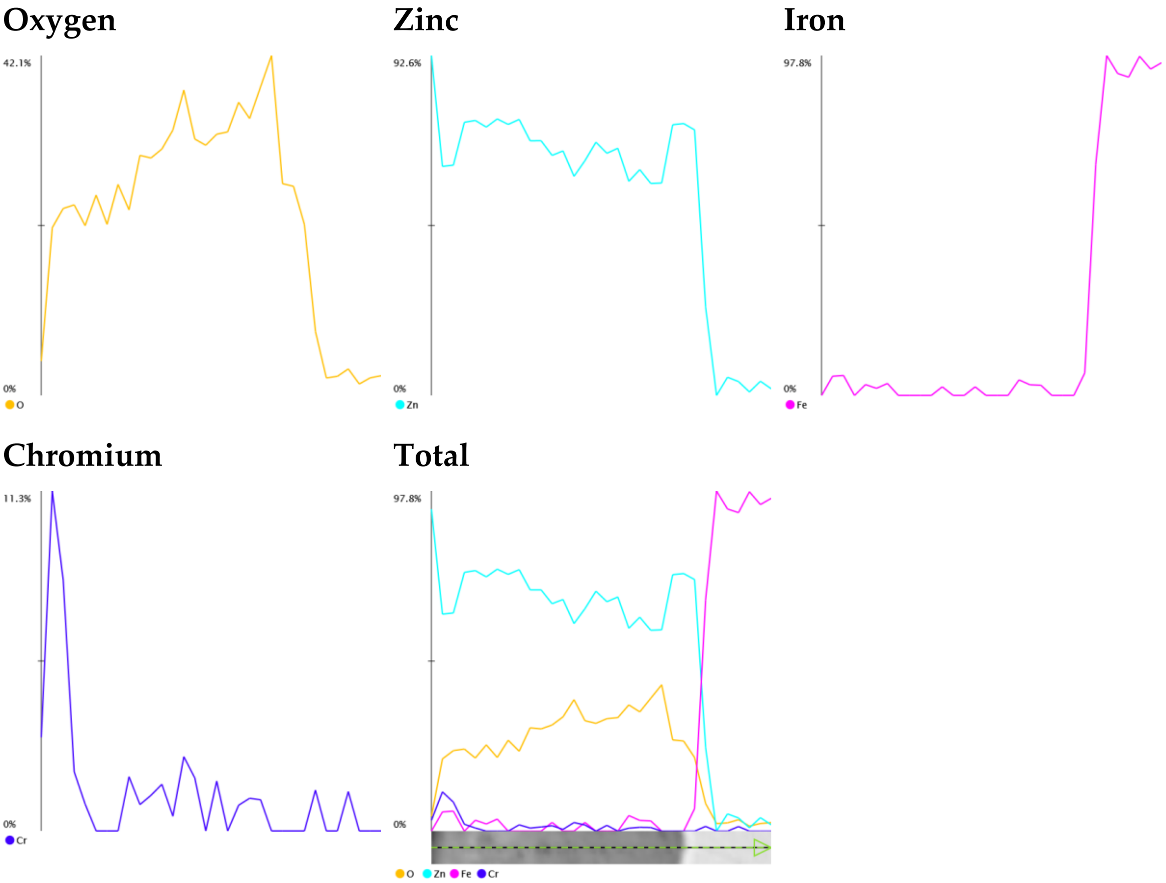


Figure 103 - Graphs with the percentage of oxygen, zinc, iron and chromium along the direction represented in Figure 101

From the analysis (Figure 103) is easy to observe a chromium peak at the start of the zinc layer as one should expect, instead there is still no trace of silicon, probably because the percentage of silicon is too small or maybe during the cutting process was removed.

5 Conclusion and future developments

In this work, analysis of a real acid barrel zinc plant was done, with the goal of improving the quality of the final products. Chemical analysis of the pretreatment and of the zinc bath were performed, instead the analysis of the passivation were performed weekly by the supplier. Moreover thickness of the zinc layer and corrosion resistance of final product samples were evaluated. Finally the most significant samples were selected to be analyzed and observed through optical microscopy and SEM.

From the results, it is possible to observe that for parts treated in the same way the thickness of the zinc layer is not the only parameter involved in the corrosion resistance, in fact in some cases thicker coating resulted in a lower corrosion resistance. Although it is important to say that there is a general trend to increase the corrosion resistance with the thickness of the coating, as one would aspect. Moreover, it is possible to observe a better corrosion resistance of the final product when the sample from the hull cell test have a better appearance (no burn or at least not so severe burn at high current density, absent or small dull zone and no additive deposit).

Furthermore, it was tried to observe with optical microscopy and SEM the zinc layer on some significant samples, but due to difficulty during the cutting process of the samples, most of the zinc layer detached from the substrate or sustained severe damage.

Finally, the pretreatments baths and the zinc baths can remain within the pre-established parameters with not too much difficulty if the “ordinary” corrections provided in the supplier's documents and the “extraordinary” corrections obtained from the analyses are carried out correctly. It is not needed to say that when errors happen it is, most of the time, because of human factor. To prevent these errors the only solutions are a more accurate attention during the procedure by the operators or an automated systems, but the last one is not of simple application.

References

[1] M. Ormellese, *Lecture notes.*

[2] M. Pushpavanam, S. Natarajan, K. Balakrishnan and L. Sharma, “Corrosion behaviour of electrodeposited zinc-nickel alloys.pdf,” *JOURNAL OF APPLIED ELECTROCHEMISTRY,* vol. 21, pp. 642-645, 1991.

[3] B. Tamagnini, *Electrodeposition of Zn – Cr alloys: a coating for corrosion protection,* 2021.

[4] L. Magagnin, *Lecture notes.*

[5] M. Fourez, D. F. Gheno and P. E. White, “The Application of Zinc-Aluminium Flake Non-electroytic Surface Coatings,” *Transaction of the IMF,* pp. 21-25, 1993.

[6] J.-M. Mataigne, “Key mechanisms in galvanization of steel sheets,” *La Revue de Métallurgie,* vol. 106, pp. 27-33, 2009.

[7] M. Guttmann, “Diffusive Phase Transformations in Hot Dip Galvanizing,” *Materials Science Forum,* Vols. 155-156, pp. 527-548, 1994.

[8] J. Culcasi, P. Sere´, C. Elsner and A. D. Sarli, “Control of the growth of zinc–iron phases in the hot-dip galvanizing process,” *Surface & Coatings Technology,* vol. 122, pp. 21-23, 1999.

[9] P. Bicao, W. Jianhua, S. Xuping, L. Zhi and Y. Fucheng, “Effects of zinc bath temperature on the coatings of hot-dip galvanizing,” *Surface & Coatings Technology,* vol. 202, pp. 1785-1788, 2008.

[10] [Online]. Available: https://en.wikipedia.org/wiki/Sherardising.

[11] F. Natrup and W. Graf, “Sherardizing: corrosion protection of steels by zinc diffusion coatings,” in *Thermochemical Surface Engineering of Steels*, 2015, pp. 737-750.

[12] D. Wortelen, R. Frieling, H. Bracht, W. Graf and F. Natrup, “Impact of zinc halide addition on the growth of zinc-rich layers generated by sherardizing,” *Surface & Coatings Technology,* vol. 263, pp. 66-77, 2015.

[13] Volume 5 Surface Engineering, 1994.

[14] Z. Long, Y. Zhou and L. Xiao, “Characterization of black chromate conversion coating on the electrodeposited zinc-iron alloy,” *applied surface science,* vol. 218, pp. 123-136, 2003.

[15] J. Handley, L. Wing and J. O'Grady, “Corrosion Resistance Without Hexavalent Chromium - New Zinc Plating Systems,” 2002.

[16] J. Garcìa-Antòn, R. Fernàndez-Domene, R. Sànchez-Tovar, C. Escrivà-Cerdàn, R. Leiva-Garcià and A. U. V. Garcià, “Improvement of the electrochemical behaviour of Zn-electroplated steel using regenereted Cr (III) passivation baths,” *Chemical Engineering Science,* vol. 111, pp. 402-409, 2014.

[17] “Non-Chromate Conversion Coating Treatments For Electrodeposited Zinc-Nikel Alloys,” *Transactions of the IMF,* pp. 210-213, 2017.

[18] T. Bellezze, G. Roventi and R. Fratesi, “Electrochemical study on the corrosion resistance of Cr III-based conversion layers on zinc coatings,” *Surface & Coatings Technology,* vol. 155, pp. 221-230, 2002.

[19] X. Zhang, W. Sloof, A. Hovestad, E. v. Westing, H. Terryn and J. d. Wit, “Characterization of chromate conversion coatings on zinc using XPS and SKPFM,” *Surface & Coatings Technology,* vol. 197, pp. 168-176, 2005.

[20] I. Haque, I. Sadiq and N. Ahmad, “Durability of Passivation in Zinc Electroplating,” *Jour. Chem. Soc. Pak.*, vol. 25, no. 1, 2003.

[21] Tecnochimica S.p.A., *TECNOLIQUID NEODET.*

[22] Tecnochimica S.p.A., *CROMOZINK.*

[23] Tecnochimica S.p.A., *TRIDIP EVO.*

[24] Tecnochimica S.p.A., *TRIDIP PULSAR.*

[25] Tecnochimica S.p.A., *SpectraMATE 25.*

[26] Tecnochimica S.p.A., *ATC 500.*

[27] Tecnochimica S.p.A., *LATHROSEAL.*

[28] Tecnochimica S.p.A., *TECNOSEAL 300.*

[29] Tecnochimica S.p.A., *Io07-08 Zinco acido 14.*

[30] Tecnochimica S.p.A., *Io07-39 Decapaggio 14.*

[31] Tecnochimica S.p.A., *Alcalinità Totale.*

[32] T. McColm and J. Evans, "A modi®ed Hull cell and its application to the electrodeposition of zinc," *Journal of Applied Electrochemistry,* vol. 31, pp. 411-419, 2001.

[33] Tecnochimica S.p.A., *CELLE DI HULL Bonaccina.*

[34] *UNI EN ISO 9227:2017.*

[35] *ASTM B 117/97.*

[36] F. Altmayer, "Critical Aspects Of the Salt Spray Test," *Plating & Surface Finishing,* 1985.

[37] N. Barbabietola, *Quale resina per quale campione?,* 2006.

[38] B. Inkson, “Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization,” in *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*, 2016, pp. 17-43.

[39] W. Zhou, R. P. Apkarian, Z. L. Wang and D. Joy, “Fundamentals of Scanning Electron Microscopy”.

[40] A. A. Azad MOHAMMED, “SCANNING ELECTRON MICROSCOPY (SEM): A REVIEW,” in *Proceedings of 2018 International Conference on Hydraulics and Pneumatics - HERVEX*, Băile Govora, 2018.

[41] A. Ul-Hamid, A Beginners’ Guide to Scanning Electron Microscopy, 2018.

[42] M. Amuda, O. Subair and O. Obitayo, “Study of Optimum Conditions for Zinc Plating On Mild Steel,” *International Journal of Engineering Research in Africa,* vol. 2, pp. 31-39, 2010.

List of Figures

List if Tables