POLITECNICO DI MILANO

III School of Engineering (Ing. III - PRO)
Master of Science degree in Materials Engineering

ELECTROCHEMICAL ASSESSMENT OF INNOVATIVE PRETREATMENTS FOR AUTOMOTIVE PAINTING ON ALUMINUM

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Academic Year 2011/2012

Acknowledgements.

I would like to thank my academic advisor Luca Magagnin, I am sincerely grateful to him, he led me and my colleagues on this multi-disciplinary research project, stimulating my interest, and for all the invaluable advices, the encouragement, comments and suggestions he gave me during the course of this work, being all of this, crucial for the successful completion of this study.

I also would like to thank Swerea IVF AB and Volvo Personvagnar Surface Treatment Center for choosing Politecnico di Milano, in specific the Chemistry, Material and Chemical Engineering Department "Giulio Natta" (CMIC) as a partner of this challenging research.

And of course to al the members of the research group and dear friends for the assistance and hard work throughout this research period; Renata Gutierrez and Renato Brioschi, thank you for being part of the team from the beginning and for all the support, encouragement and good time we shared; Luigi Sironi, Samuele Pellegatta, Daniele Zambello, Riccardo Ciapponi and Alessandro Amodio thank you for everything you have done to make the lab being such a nice place to work and the big influence you had in the experimental part of the project in order to finish it on time.

And more personally I would like to show the most sincere and deepest gratitude to my parents and sisters, for all their sacrifices and the truly sincere devotion they have shown since the beginning of this road, for letting me always have the freedom to choose, giving me the necessary guidance that only advices can achieve, all of this is possible because of you; thank you very much for having faith on me and my ability and talent to fulfill my goals, also to all my friends at home and at my second home, Italy; and the people who in every part of my life have been of considerable importance. Thank you all for sharing with me and letting me share with you.

Abstract.

The present thesis work is part of the European research project call: “Environmentally acceptable Pretreatment System for Painting Multi Metals”, with the acronym name of “ENABLE” and type of funding scheme: FP7-SME-2010-1. In which Politecnico di Milano is taking part in alliance with Swerea IVF AB and Volvo Personvagnar Surface Treatment Center.

From a production development point of view there is a need for accelerated corrosion methods in order to obtain fast results of the performance of new concepts in pre treatment or paint development. Ideally, accelerated corrosion tests would provide data that could be correlated to actual in-service performance. However, by the very nature of accelerated corrosion tests, these procedures can rarely (if ever) be used to confidently predict service life. In general, actual corrosive environments are more complex and less carefully controlled than accelerated laboratory tests. Therefore, at best, the latter can be used to measure the relative field performance in terms of a particular corrosion mechanism/mode, which during the research of this thesis were assessed by different tests of the Electrochemical kind, including Potentiodynamic, Cyclic Voltammetry and Galvanostatic pulse.

Therefore the problem that the project addresses is to replace the “standard” pre-treatment process for out-door use with a new process, although the knowledge concerning the corrosion performance of paint system in Aluminum based on a new pretreatments ZEC 888 is limited; there is however, a great need for further testing in order to establish an accelerated corrosion test that is known to correlate with field testing for the new pre treatment systems. The corrosion protection properties and correlation to process conditions have to be understood in order to be able to improve the corrosion inhibition properties.

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Introduction.

Painting of metal surfaces used in outdoor applications is necessary in order to protect the final product from external and environmental factors that can cause corrosion, and also to increase the esthetical value. The corrosion protection performance is dependent on the quality of the paint coating and on the pre-treatment of the metal surfaces i.e. the cleaning and the pre paint coating.

The surface coatings industry consists to a large extent of small and medium companies which operate as workshops, coating many different products made out of different materials (e.g. aluminum steel and galvanized steel). When these substrates are mixed in a product or treated in the same process they are called multi metal.

Zinc phosphating has been used since the beginning of the 1970's as pre-treatment of metal surfaces for out-doors use. It is a chemical process with a high consumption of high quality water and energy and with use of potentially toxic chemicals like nickel and zinc. Changing from zinc phosphating to the new pretreatment process has the objective to reach: energy and water savings, less sludge, phasing out nickel, reduced total costs.

Today many different new pretreatment processes based on silanes, zirconium, titanium and/or zinc are now being introduced in the industry. They are used on products with lower demands on corrosion protection compared with the demands from the vehicle industry. During the last 3-5 years many new systems have been launched for the pretreatment of multi-metals.

The problem that the project addresses is to replace the "standard" pre-treatment process for out-door use, zinc phosphating with a new process.

This thesis work is a part of an extensive European research project , code named ENABLE, in which the Dipartimento di Chimica, Materiali e Ing. Chimica "Giulio Natta" Politecnico di Milano is taking part in alliance with Swerea IVF AB and Volvo Personvagnar Surface Treatment Center.

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The most used test method to evaluate the corrosion protecting properties of paint systems is the Neutral Salt Spray test (NSS). This test method has however not been able to show correlation with results from real life.

Cars are an example of complex products that are subject to varying environments throughout the world. This has to be taken into account when corrosion tests are designed. The most advanced and reliable accelerated corrosion tests have been developed by the car manufacturers. As an example Volvo Cars has developed a well-known accelerated corrosion tests called VICT and now recently with a new Accelerated Corrosion Test - ACT, which is a 6 weeks chamber test. The development and adjustments of accelerated tests are continuously going on, in order to faster obtain reliable results.

The knowledge concerning the corrosion performance of paint systems based on new pretreatments is limited. It has, so far, been difficult to achieve as good corrosion results with the new pretreatments as with zinc manganese phosphating. This is especially the case with steel. Galvanized material has better possibilities to reach the requirements that are set.

Besides accelerated corrosion tests and their correlation to field tests it is possible to perform electrochemical corrosion tests. These tests were made at the Dipartimento di Chimica of Politecnico di Milano and are subjects of this thesis work. The electrochemical tests that were performed are: potenziodynamic, cyclic voltammetry and galvanostatic pulse.

The aim of this work is to investigate the corrosion resistance of the Zinc Protector ZEC 888 pretreatment.

The thesis is organized in six chapters:

In chapter one Materials, after a brief description of the materials that are being used in the automotive industry, we deeply analyzed the properties and requirements of the Aluminum used in this case of study.

In chapter two Pretreatment, is given a general description of the state of the art and innovative pretreatment Zinc Protector ZEC 888.

In chapter three Painting, all the most important industrial painting techniques have been illustrated. Organic coatings add different properties to the metal on which they are applied but they also require particular substrate and surface conditions. All of these has been discussed in this chapter. A description of the paint used in this evaluation is also given, in terms of its properties, thickness and its applying technique.

Chapter four Electrochemistry of corrosion is focused on the electrochemical techniques which during the experimental processes were the main tools, their description, the method and parameters used, as well as the samples and cell preparation, these techniques are Potentiodynamic test, Galvanostatic Impulse test and EIS (Electrochemical Impedance Spectroscopy).

Chapter five Result, shows the results obtained at the end of the experimental process, considering the tests performed and the measurement of physico-chemical properties of the materials and coatings such as composition, surface characteristics , resistance and capacitance; the latter calculated with the impulse technique.

In chapter seven Conclusions

1 Materials.

1 Materials.

Aluminium is a global commodity. The economic advantage of hydropower has shifted production sites to countries rich in hydroenergy resources. Stability of supply and price is a dominating criteria for use of materials in product models built over a long period of time. Recycled aluminium alloys are presently being used predominantly for production of castings. Sorting by alloys is needed for wrought products.

Why care for aluminium resources?

- Aluminium is having a growing potential for mass produced cars.
- The materials decisions are taken well in advance of the actual production runs.
- Car models are produced over a period of many years.
- Wrought and cast aluminium alloys rely on different raw materials resources.

Therefore, the criteria for materials selection, availability and supply must include the assured continuity of resources

At about 7.5% of the earth's crust aluminium is the most abundant metal and the third most abundant element in the earth's crust. Approximately 22 million tonnes of "primary" aluminium were produced worldwide in 1998, with another 5 million tonnes "secondary" (recycled) aluminium. Approximately 30% of the consumption of aluminium goes to transportation applications - a rapidly growing market and a significant source for recycled aluminium.

Beyond the question of reliable raw materials resources the sustainability of the industrial production processes of materials and the deposition of industrial wastes are further criteria in materials selection.

While aluminium is sometimes used in its commercially pure form, most applications involve the addition of small quantities of other metals to create alloys with special properties. Certain alloying elements will increase strength or corrosion resistance, while others enhance such properties as machinability, ductility, weldability and strength at high temperatures.

Alloying elements include manganese (strength and formability), magnesium and silicon (strength and corrosion resistance), copper and zinc (higher strength), titanium and chromium (grain size control), etc.

Molten aluminium is cast into ingots of various shapes depending upon the type of equipment that will be used to process the metal. For example, ingots for rolling into plate, sheet and foil are typically rectangular and can weigh up to 30 tonnes or more. Aluminium ingots for extrusion are usually cylindrical, while those for rolling into rod/wire are square.

Aluminium for remelting can be cast into large blocks called sows, as well as tri- lock shapes or T- ingots designed for efficient and secure handling.

A large proportion of aluminium ingots (in particular for sheet and extrusion applications) are cast by the semi- continuous, vertical direct- chill casting process (DC Casting), where water is directly sprayed onto a solidifying ingot installed on a descending platten.

Unalloyed, pure aluminium is very soft and ductile. For structural and other uses alloying elements are added to impart desired properties, such as strength, toughness, corrosion resistance and physical properties.

According to the theories of metallurgical thermodynamics alloying elements can enter the crystal structure as solid solution or build various constituent phasesdepending on composition, temperature and on the kinetics of nucleation and growth processes. The types of phases existing in an alloy of given composition and at various temperature regimes are mapped inphase diagrams.

The parameters of the complete chain of thermo- mechanical processes in the production of a cast or wrought product influence the type and distribution of alloying elements and constituent phases in the microstructure and thereby determine the properties and behaviour of the product.

Improvement of cold formability, ductility or strength by heat treatments depends on the constitution of the individual aluminium alloys and their products.

1.1 Basic Aluminum alloy groups.

Casting alloys & wrought alloys: It is useful to distinguish between casting and wrought alloys, since their constitution is typically different according to the respective requirements of castability (fluidity, solidification characteristic and resistance to hot cracking) and hot formability (homogeneous a- solid solution for optimum behaviour during hot rolling, extruding and forging).

Accordingly and traditionally, there is a different designation system for these two groups of aluminium alloys in various national and international standards.

Age-hardening alloys & strain- hardening alloys: Wrought alloys and casting alloys may be also distinguished by their prevalent strengthening mechanism, which is reflected by the temper designation:

· Non- age- hardening alloys are solid solution strengthened. Wrought alloys may be further strengthened by work- hardening (H- tempers).

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The alloy composition also reflects the type of processes used to manufacture the casting or the semi-finished wrought product. Alloys are specifically designed for a particular casting method (sand, die, high- pressure die casting, etc.) as well as for the type of hot (and cold) forming methods (rolling, extruding, forging).

Most alloying elements have limited solubility in solid Al. Beyond the limit demarcated by the solvus on the phase diagram, further amounts lead to formation of intermetallic phases.

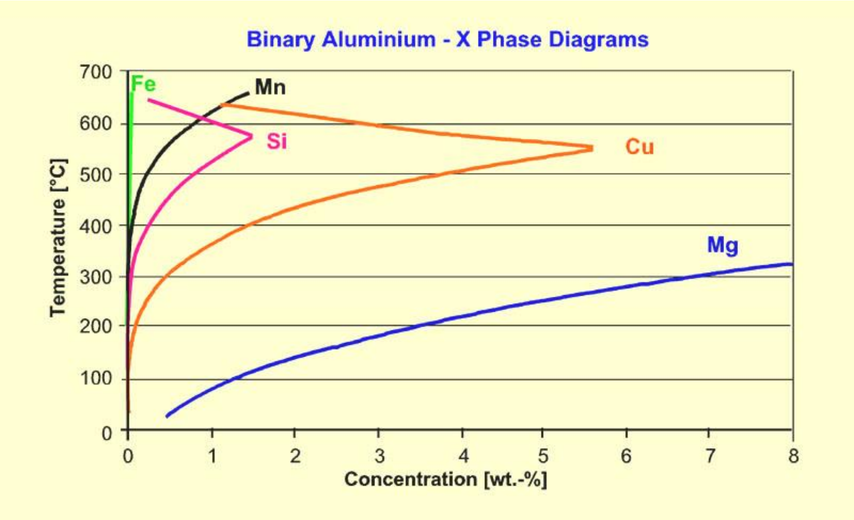


Figure 1 Solubility of different alloying elements in solid Al.

Alloying elements are added in Al for different purposes. Si is added to improve the fluidity of molten Al and Ti (on its own or as TiB2 or TiC grain refiners) are added to improve castability. Most other elements are added to improve strength of the final product in different ways.

The figure show the effect of strengthening of different alloying elements in super pure binary Al alloys.

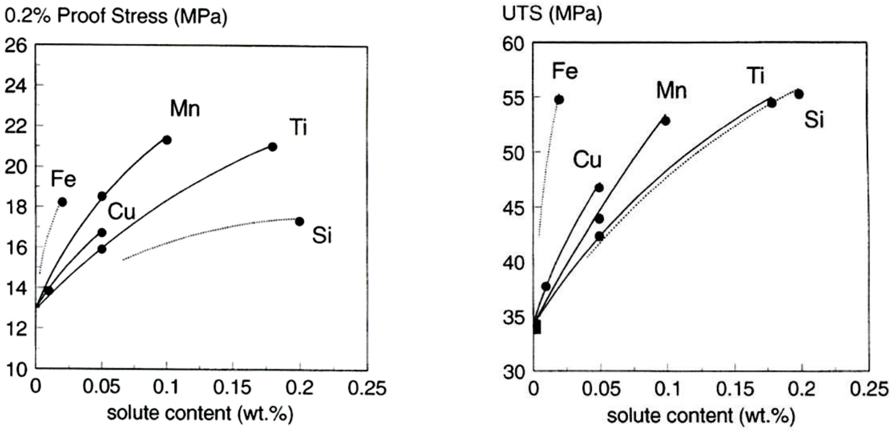
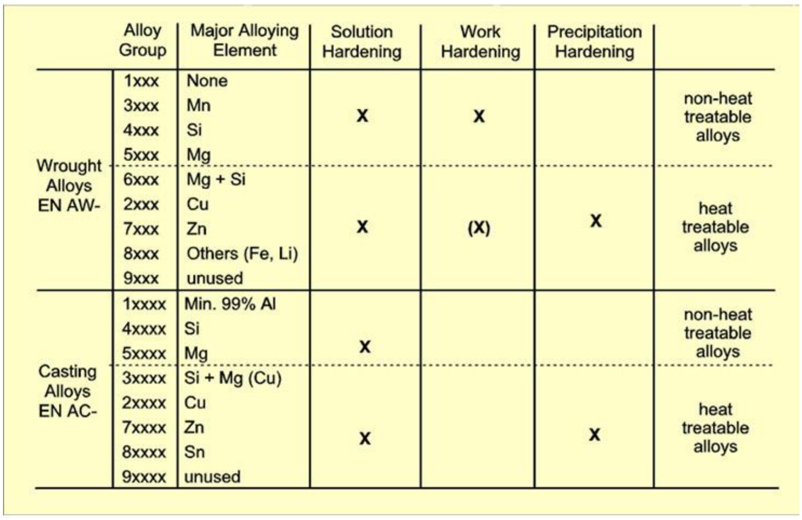


Figure 2 Effect of strengthening of different alloying elements in super pure binary Al alloys.

Major alloying elements are specially added to the alloy to introduce certain specific properties (solid solution strengthening, strain hardening, precipitation or age hardening, ease of casting etc.) during use.

Minor alloying additions usually those with low solid solubility - form coarse and fine intermetallic phases and indirectly affect properties, e.g. by grain refining during casting or heat treatments.



	Alloy Group	Major Alloying Element	Solution Hardening	Work Hardening	Precipitation Hardening	
Wrought Alloys EN AW-	1xxx	None	x	x		non-heat treatable alloys
	3xxx	Mn				
	4xxx	Si				
	5xxx	Mg				
	6xxx	Mg + Si	x	(X)	x	heat treatable alloys
	2xxx	Cu				
	7xxx	Zn				
	8xxx	Others (Fe, Li)				
	9xxx	unused				
Casting Alloys EN AC-	1xxxx	Min. 99% Al	x			non-heat treatable alloys
	4xxxx	Si				
	5xxxx	Mg				
	3xxxx	Si + Mg (Cu)	x		x	heat treatable alloys
	2xxxx	Cu				
	7xxxx	Zn				
	8xxxx	Sn				
	9xxxx	unused				

Figure 3 Major and minor alloying elements.

As an example of Major alloying elements in 6XXX automotive wrought alloys Al- Mg- Si and Al- Mg- Si-Cu are described next.

Mg, Si and **Cu** are the major alloying elements in Al automotive alloys. Mg and Si combine to form Mg2Si which affects natural ageing behaviour (slightly) and all three affect paint bake response during curing of 6XXX alloys, the natural (T4) and artificial (T6/T8) ageing response of body sheet alloys.

AA6016 and AA6111 are shown in Figures. Cu confers additional strength to the 6XXX automotive alloys. T4 refers to as supplied sheet. The paint bake response is measured by testing the sheet after subjecting it to a 2% elongation followed by heating to 180 °C for 30 minutes (T8X).

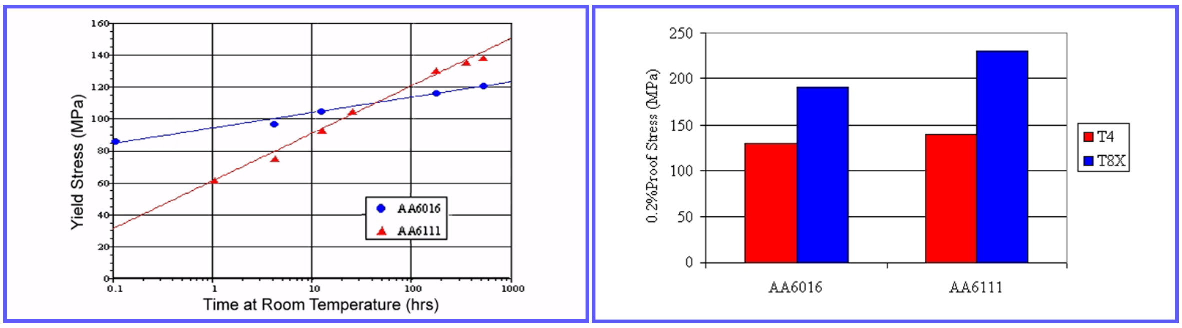


Figure 4 Paint bake and natural ageing on AA6016 and AA6111 .

Mg also increases strain hardening, tensile strength (0.2%PS and UTS) and formability (uniform and total elongation). However, these beneficial properties to the sheet must be balanced by increasing difficulty to roll the higher Mg containing alloys as they strengthen on rolling.

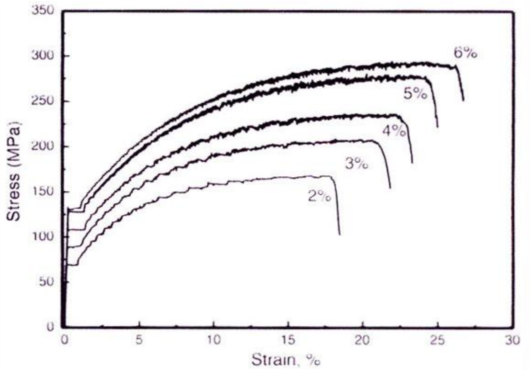


Figure 5 Tensile strength and formability on MG containing alloy.

Elements with low solubility such as Mn and Fe, and minor alloying elements such as Cr, Zr and Ti also have an important role to play in the development of properties of Al automotive alloys. Being of low solubility these elements form relatively coarse intermetallic particles during casting and pre- heating prior to hot rolling. In small quantities, these particles play critical roles in controlling the grain structure which develops during subsequent hot and cold rolling and final gauge annealing of the sheet.

On the other hand, if the levels of these elements are too high, there can be detrimental effects on properties. E.g., Fe levels can influence properties: formability is reduced if higher levels of Fe and hence more Fe containing particles are present. However, low Fe levels are costly to achieve and also impose constraints on the use of recycled alloys. Optimisation of alloy composition must balance the technical requirements of the end application, for example the need to be able to form complex parts, against the commercial considerations and practicalities.

There are about 10 major alloying elements of the Periodic System, which, in concentrations of between 0.1 and a few wt.%, can be used to change signifycantly the properties of pure aluminium according to needs of the producer, fabricator or user. Consequently, there is an abundance of aluminum alloys, which are currently in use. There are about 500 internationally registered wrought and cast aluminum alloy compositions, from which only little more than a dozen are used for the manufacture of automotive components and cars.

To select and specify an alloy with specific properties for a given application, its composition and state of heat treatment (temper) must be defined. This is achieved by a standardized designation system for the alloy composition as well as for the temper.

The global character of the European Market demanded a common designation system in lieu of various national varieties. For its simplicity and flexibility the designation system for wrought alloys created 1954 by the North American Aluminum Association (AA) was adopted in 1970 by the International Organization for Standardization (ISO).

In 1985 the member states of the European Community agreed to adopt harmonised European standards in place of respective national ones. For wrought aluminium, the AA designation system was adopted by the Comité Europeén de Normalisation (CEN), but for cast alloys a separate designation standard was developed.

The usefulness of aluminum as engineering material is fundamentally related to the metal's:

- mechanical properties,

- physical properties and
- chemical properties.

As a rule it is not a single individual property - like e.g. density - which determines its choice for a particular engineering application but a full spectrum of these properties; i.e. heat exchangers, density, thermal conductivity.

On the other hand, properties of aluminum automotive materials and their behavior during fabrication and service are intimately related to alloy constitution and microstructure.

Under tension or compression the slope of the initial part of the stress- strain curve determines the Modulus of Elasticity (Young's Modulus). Mostly, the rounded value of E = 70.000 MPa is used for aluminium and its alloys. It is 1/3 the value of steels. Under torsion the Shear Modulus or Modulus of Rigidity is G = 26.000 MPa for aluminium compared to 82.700 MPa for steel. Poisson's Ratio i.e. lateral strain divided by longitudinal strain is n = 0.33. The modulus of elasticity (and rigidity) is only marginally dependent on alloy composition and temper, varying less than +/-4% from the mean value of 70.000 MPa over the whole range of aluminium alloys.

Due to the lower E- modulus aluminium can absorb elastically the 3- fold amount of energy before plastic yielding compared with steel. This property is significant for crash- relevant components, like bumpers, etc.

1.2 Reference Application Consideration.

A revolution is in progress in the materials industry as a result of strong global competition, spurred on by increasing concern for the environment. The two thrusts driving the materials revolution are the need to tailor materials to meet specific properties at low cost, and the need to minimize the impact of materials production on the environment. The technologies that have been brought to bear on the production of a wide range of metals are indeed highly sophisticated. Unprecedented advances have been made in the processing of metals to yield superior properties at lower costs, which in combination with recyclability, assures their dominance on the global scene in the next century. In 1998, the worldwide production of crude steel, which constitutes 95% by volume of the total output of metals, was 760 million tones and nearly half of the output was in the form of sheet and strip. Steel sheet and strip has a wide range of application in numerous sectors, such as automotive, bridges, pipelines, packaging, tanks, utility poles, and in industrial and residential construction. In tonnage, aluminum is second in volume to steel, and primary aluminum production is estimated to be around 17 million tonnes. Over 85% of fabricated aluminum products are rolled sheet and foil. A major portion of aluminum sheet is utilized to produce can stock for beverage containers, and it is also used in the construction, transportation, printing industry, and industrial distribution markets. Other applications include the production of foil for household and commercial packaging. Impressive gains have been made in the area of recycling of these two metals. The North American steel industry’s overall recycling rate is around 68%, with the rate approaching 96.5% for automobiles. On a worldwide basis, 80% of the beverage cans are made of aluminum with a recycling rate of 55%, while the automotive industry recycles 85-90% of the aluminum used in vehicles.

The automotive industry’s demand for materials with properties aimed at reducing vehicle weight has generated intense competition between the aluminum and steel industry, a reason for this weight reduction is because it is key to cutting carbon emissions and impoving fuel economy, while maintaining safety. In key automotive components, aluminum can reduce vehicle weight safety by as much as 40 percent, compared to only 11 for high-strengh steel.

The reason the potential weight reduction using high-strength steel is so small, is that nearly 40 percent of the parts analyzed simply cannot be made thinner regardless of the grade of steel used. If high-strength steel were to be used to downweight these parts, their stiffness would actually be reduced and the car’s performance would suffer, whereas, aluminum could be used without reducing stiffness or causing the car’s performance to suffer. This varies and some options include maintaining a steel body with aluminum closures, hang-on and mounting parts, hybrid or multi-material designs for the body and full aluminum body.

1.2.1 General Processing Considerations.

This section describes the processes for production of major semi- finished automotive products; the purpose is to illustrate the production processes, which lead to special qualities and shapes and to a variety of surface finishes, as background for material selection and fabrication. When specifying or designing such products, it is important -for economic reasons- to consider the characteristics of the production processes.

Semi-finished automotive products are specialty materials with closely controlled properties and tolerances for specific customer requirements and are to be distinguished generally from standard mill products and stock materials for general purpose applications.

In order to comply with the requirements of the car manufacturer aluminium automotive sheet materials have been developed with special property profiles, which are the result of combined characteristics of:

· the base material and

· the sheet surface (*s. figure at right*).

Sheet production comprises several discrete steps:

· ingot casting,

· hot rolling,

· cold rolling and

· finishing (heat treatment, surface preparation and/or cutting).

1.2.1.1 Cast House.

Raw metal for production of ingots: mixture of primary aluminium and sorted fabrication scrap or secondary aluminium gained by melting of scrap from recycled products.

Casting:

- alloying elements are added (when needed) to the melt to attain precise composition control.
- The molten Aluminium is filtered and degassed immediately before casting.
- DC casting stands for Direct Chill casting.

From ingot to rolling slab: The cast ingots are typical sawn at head and foot to remove head skrinkage and start of cast foot region. The cast surface imperfections and metallurgical inhomogeneities are also removed by scalping the rolling faces to a predefined depth that depends on alloy and product requirements.

Strip casting: It is also possible to produce a coil of aluminium by a semi-continuous route using a block, belt or roll caster. The semi-fabricated product is a coil in the 3 to 10 mm range which would subsequently be cold rolled to final gauge. Casting a thin strip product can have economic advantages but there are metallurgical drawbacks associated with rolling a cast surface, lack of homogenisation and chemical segregation linked to some alloys. For these reasons continuous casters have yet not been adopted for automotive sheet.

1.2.1.2 *Hot Rolling.*

Preheating: the slabs are preheated at 480- 580^{o}C for several hours for homogenization of the microstructure.

Hot rolling: the preheated slabs are hot rolled using exactly defined pass reductions and controlled temperature conditions. In most rolling plants hot rolling is done on a reversing mill (up to ~ 25 mm strip gauge) followed by rolling on a tandem mill. In some rolling plants hot rolling is performed on a reversing mill only. Depending on the hot rolling concept, the gauge of the hot rolled strip can vary between 3- 12 mm. The hot rolled strip is hot coiled and cooled down to RT.

Cold rolling: The hot rolled strip is cold rolled to final gauge in several passes. Cold deformation leads to an increase of the material strength. Therefore, for some alloys an interanneal is performed to allow further rolling.

1.2.1.3 Annealing of cold rolled strip.

At final gauge the strip is annealed to adjust the required material properties:

- heat treatable alloys, such as AlMgSi alloys, are subjected to an anneal in acontinuous annealing furnace with rapid heating to the required metal temperature (MT), short hold at MT followed by quenching. By this solution anneal the main alloying elements Mg and Si are dissolved leading to a good formability of the material (T4 temper).

- AlMg alloys are soft annealed at inter- mediate or final gauge depending on the required temper. Usually the coils are annealed in batch type furnacesfor several hours at 300 to 400 °C.

1.2.1.4 Cutting of panels.

Annealed strip is supplied in coil or is cut longitudinally or into individual panels depending on customer needs. For certain parts, e.g. hoods, the strip is cut into panels with special shape. This offers the advantage that production costs and scrap can be saved.

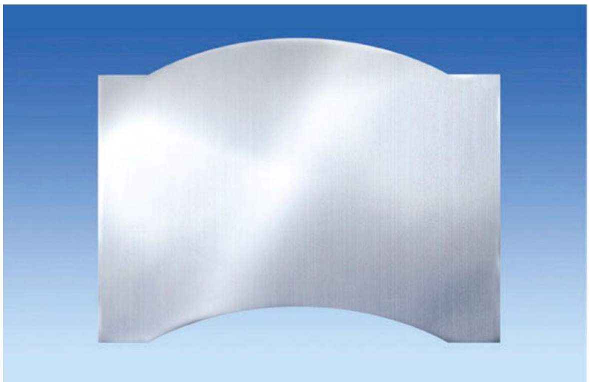


Figure 6 Automotive sheet.

1.2.1.5 Surface Topography.

The sheet surface topography affects

- the formability of the material and
- the appearance of the panels after lacquering.

Special topographies have been developed for automotive sheet; the required topography usually is transferred during the last cold rolling pass from carefully prepared work rolls to the strip surface using controlled rolling conditions. In Europe the established surface quality is EDT (Electric Discharge Texturing). To produce this topography the roll surface is textured by means of electric discharge; transfer to the strip requires a special rolling practice.

In North America the established surface is mill finish which is achieved without special work roll topographies and using standard rolling practices.

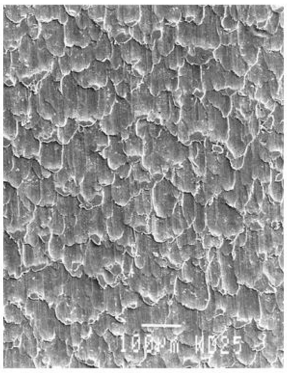


Figure 7 EDT surface of strip.

1.2.1.6 Chemical & electrochemical pre-treatment.

Reasons for pre-treatment of strip:

- remove residues from rolling: oils and aluminium debris: Degreasing)
- generate an oxide layer with homogeneous properties: Etch cleaning (pickling)
- pre-treatment and corrosion protection of adhesive bonds: Conversion or anodising layer
- interlayer before application of a primer or lacquer: Conversion or anodising layer

These pre-treatment are performed in coil coating lines.

The contact with the chemical agents can be achieved by means of spray or immersion. The conversion treatment is, mainly due to environmental reasons, preferably performed in a No Rinse process, i.e. without rinsing after treatment.

The conversion treatment can be done by means of a roll coater or by means of spraying or immersion followed by squeezing of excess chemical agents.

Degreasing: Degreasing of aluminium strip is preferably performed using mild alkaline agents that do not attack aluminium.

Etch Cleaning (Pickling): Aluminium is covered by a natural oxide layer that can vary in thickness and composition depending on the alloy type and processing conditions. The oxide layer protects the aluminium against corrosion, because it is passive over pH ~4.5 to ~8.5.

The surface properties of the material are strongly influenced by its oxide layer, e.g.:

- the surface resistance has a considerable effect on the spot weldability; a low, homogeneous surface resistance is of advantage
- the chemical composition of the oxide layer influences the performance of adhesive bonds and the adhesion of primers and lacquers.

In order to achieve homogeneous surface characteristics a pickling process is done usually by means of acidic agents.

1.2.1.7 Conversion treatments.

Presently two main types of conversion treatment are applied, a thin stabilising pretreatment used mainly for closure sheets and a structural layer used when adhesive bonding is required. For a stabilising pre-treatment the natural oxide layer is removed and replaced by a chemically modified layer (<10 nm thick). Suitable for this process are e.g. agents based on titanium- and/or zirconium-fluoride or on silicates. For environmental reasons chromating is not used any more. Thicker layers can be used for aluminium sheet where structural bonding is required. An example of this type is a silicate based system with a 50 nm layer.

1.2.1.8 Pre-coatings.

In order to protect the relatively soft aluminium surface for transport, the strip surface is usually covered with a thin film of a corrosion protection or deep drawing oil or alternatively with a dry lubricant film.

Panels that are supplied for exterior applications sometimes still are covered for surface protection with interleave paper instead of a lubricant.

The oil and dry lubricant usually are applied by means of roll coating or spraying.

The use of dry lubricated sheet has the main advantage that automation is facilitated during pressing of panels in the press shop.

1.2.1.9 Primers.

Aluminium sheet can be coated with an organic primer before supply to the OEM. The primers fall into two categories, electrical conducting primers that are electro-coat compatible and non-conductive primers that are electro-coat replacements with multiple layers up to the clear coat. The application of a primer offers a number of advantages:

- surface protection during transport and handling
- improved formability
- in mixed metal constructions a primer coating can protect against galvanic corrosion of the aluminium
- good bondability and long term stability of adhesive bonds
- appearance after lacquering comparable to that of steel panels

Primers are applied on the strip surface by means of a roll coater process after degreasing and conversion treatment. For curing of the primer the strip has to be heat treated.

1.2.1.10 Application of Primers to aluminum sheet.

Both types of primers require special processing equipment to produce a high quality product. Following the final metallurgical heat treatment, the aluminium strip is first cleaned/degreased, then conversion treated for adhesion promotion and then coated with a primer. The organic based primer is typically roll coated but then has to be heat treated to harden the film. The temperature of bake hardening can be as a high as 240°C depending on the system chosen. For multiple coating layers a sequence of roll coating and baking steps is needed. The most efficient processing is achieved using an integrated line to perform all steps in sequence and indeed, when coupled to the metallurgical heat treatment, all finishing operations can be economically completed.

Pre-lacquers are applied on the strip by means of a roll coater after degreasing and conversion treatment.

Each lacquer layer has to be cured by heat treatment.

Rolled products as plate, sheet, foil or welded tubes are the second largest fraction of aluminium in automobile applications. They are used for many different components to reduce weight and enhance part performance.

Special alloys and tempers have been developed and are in use that provide the properties needed to meet the specific quality requirements of the various parts.

Sheet products are provided with special surface topographies, claddings as well as with pre- treatments for lubrication, joining and painting by coil coating processes.

Aluminum alloys of the non- heat treatable Al- Mg (EN AW- 5xxx series) and the heat treatable Al- Mg- Si (EN AW- 6xxx series) alloy system were especially tailored by suitable variations in chemical composition and processing for various applications, e.g.

- for use in chassis the Al- Mg alloys were optimised for optimum strength and corrosion resistance.
- In the field of carbody sheets the Al- Mg- Si alloys are frequently applied and have been improved for formability, surface appearance and age- hardening response.

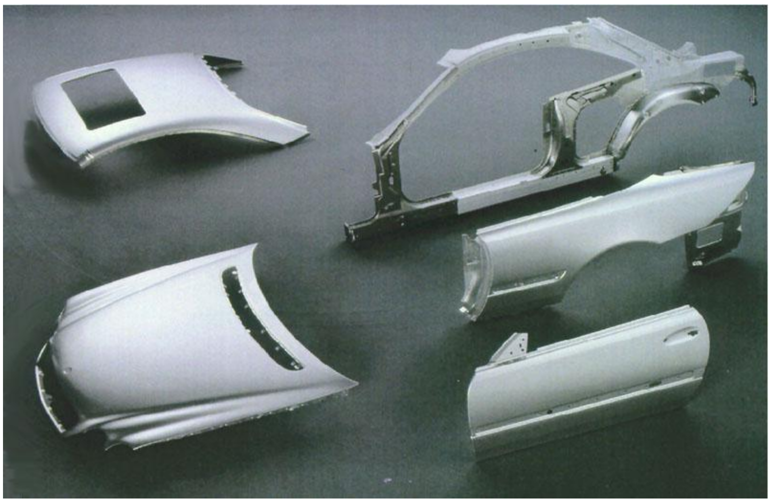


Figure 8 Manufactured parts of Body in white.

The reported materials for the project “Enable” are mainly three that will be discussed in two different thesis , since they are divided in two big families: Steel, and Aluminum since as mentioned before those are the main materials used in the automotive industry for the production of the of car body panels .

The principal materials that will be analyzed in the present thesis will be Aluminium.

2 Pretreatments.

2 Pretreatments.

Organic coatings protect metallic structures from corrosion by both inhibition and barrier effects. The barrier effect depends on the adhesion to the under-layer but also the non.conducting properties of the coating. Penetration of water or ions is a major cause for loss of the barrier, which may lead to delamination of the coating and under-film corrosion.

In general the coating consist of four basic elements:

- Binder: forms the polymeric matrix of the coating in which all other components may be incorporated.
- Pigments and fillers: improves the corrosion protection properties and provide the coating with almost any color.
- Additives: it has a variety of functions; e.g. thickeners, UV-absorbers, anti fungi and so forth.
- Solvent: reducing the viscosity of the binder and other components to enable a homogeneous mixing.

A coating provides protection by forming a physical barrier between the metallic substrate and an aqueous corrosive environment. These physical properties are limited as all organic coatings are known to be permeable water and ions to certain extent. When the adhesion of the coating to a metal surface is perfect there will not be any under-film corrosion. This is however impossible as a result of the irregularities in the coatings as well as one metal surface. Loss of adhesion may be caused by permeated water that causes blisters (Figure 9). Phenomena as swelling of the coating due to water, the presence of voids or ions in the coating, wet adhesion problems, poor adhesion properties are some of the reasons why blisters are formed. These blisters are perfect starting places for corrosion reactions. Good knowledge of the water permeability gives information related to:

- Polymer structure and composition.
- Loss of adhesion.
- Under-film corrosion.

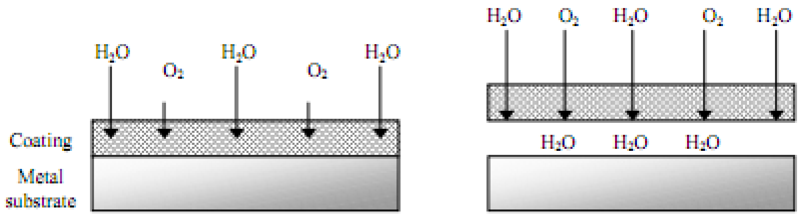


Figure 9 Initiation of a blister under an intact organic coating.

A new coating was investigated during the experiments with the samples, this coating is in recent development and due to this fact, there is very few information available about it. The coating on the materials is herewith described.

2.1 Glomax Zinc Protector ZEC 888.

The ZEC-COAT 888 is a perfectly chromium-free corrosion inhibitive coating for galvanized parts. Designed to correspond with the Regulations of Chromium; when it is applied upon a galvanized steel parts having a sacrificial corrosion inhibitive effect, it remarkably improves the corrosion inhibitive performance.

The corrosion inhibiting mechanism of Zinc Protector ZEC-Coat 888 is estimated as follows.

In cases when Zinc Protector ZEC-Coat 888 is applied upon a galvanized surface, two layers are formed. One is a siliceous top coated layer and the other is a reaction layer at the interface containing zinc, siliceous and oxygen.

When a slight amount of water moisture gets to the reaction layer through the nano-sized pores of siliceous top coating, it is speculated to generate invisible nano-sized white rusting caused by the water moisture. Although the white rusting would be generated in the reaction layer, surrounding siliceous matrix suppresses the growth of the white rusting and it extends the time period until the white rusting grows to be visible. The white rusting generated in the reacting layer properly acts as a passivation film together with the reaction layer.

Due to the water shielding effect of the passivation film composed of nano-sized white rusting and the reaction layer, the zinc-dissolution process (sacrificial corrosion inhibitive effect) would be kept for an extended period, and hereby able to protect steel substrate for a long time.

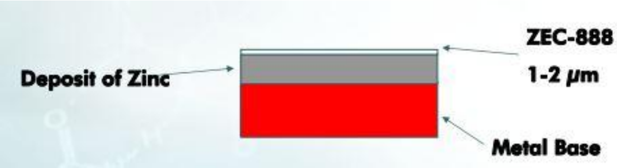


Figure 10 Zinc Protector ZEC 888.

ZEC 888 is suitable for electrolytic zinc, zinc/nickel alloy, zinc die-cast, zinc flake, and it is a good replacement of chromium conversion coatings.

2.1.1 Chemistry.

The main additive is a silicon based molecule, which is polymerized through a sol-gel process in alcoholic solution.

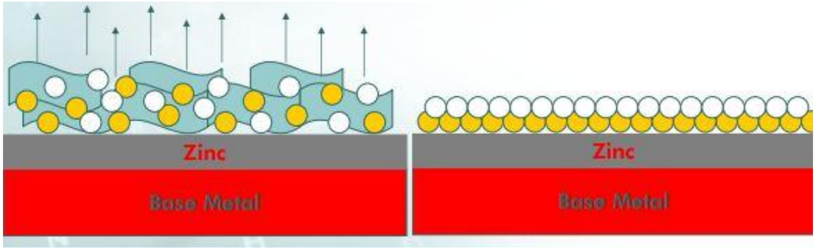


Figure 11 Main additive silicon based molecule.

There is a physico-chemical bond between silicon based compound and zinc substrate, as well as reticulation of coating and formation of a compact layer that forms a barrier.

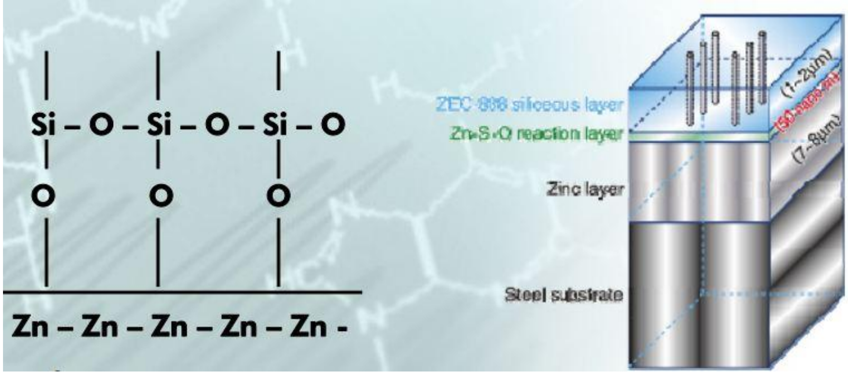


Figure 12 Physico-chemical bond between silicon based compound and zinc substrate.

It also features a self-healing property in which there is a dispersion of the silicon based compound; this happens as follows, on an scratched surface; the silicon based compound shifts into the scratch, covering it and by doing so there is a re-establishment of the barrier effect. The migration of Si based occurs in condition of moisture

Figure 13 Self-healing property in scratch.

2.1.2 Process.

The process can be briefly described; after zinc plating it is necessary and essential to dry the working piece and it is also important not to apply ZEC 888 on top of other coating.

ZEC 888 is possible to dilute on parts with chromic conversion and the thickness is not affected by the time of conversion.

It is suitable for Dip & Spin, centrifuge pieces after immersion without dilution, Dip & drain (2-4 times dilution) and Spray Electrostatic (2-4 times dilution).

The recommended environmental conditions are to have less than 60%RH of moisture and a room temperature around 25°C. This condition must be observed from the immersion to the entrance in the oven; which must be able to keep the temperature at 120°C for a period of 15 to 20 minutes. A longer period does not increase or decrease the properties.

There are some variations in the Surface Treatment Procedure of ZEC

1. GALVANIZING (without chromate treating) + ZINC PROTECTOR ZEC-COAT 888.
2. GALVANIZED + TRIVALENT CHROMIUM TREATMENT + ZINC PROTECTOR ZEC-COAT 888.
3. GALVANIZED + PHOSPATING + ZINC PROTECTOR ZEC-COAT 888.
4. ZINC FLAKES + ZINC PROTECTOR ZEC-COAT 888.
5. ZONC DIE-CASTED PARTS + ZINC PROTECTOR ZEC-COAT 888.

2.1.2.1 *CORROSION INHIBITIVE COATING, GALVANIZING (without chromate treatment) + Z.P. ZEC-COAT 888.*

Hexavalent chrome (or chromate treatment) has been commonly used as a corrosion inhibitive treatment for galvanized parts, but in the near future the chromate treatment must be stopped under the control of ELV and RoHS regulations. At present trivalent chrome treatment is considered as an alternative treatment, but trivalent chrome components must partly change to hexavalent chrome components in equilibrium.

Zinc Protector ZEC-Coat 888 is an innovative Chromium-free surface treating material particularly potential for treating galvanized parts (substituting chromate treating).

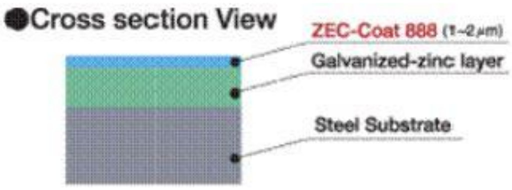


Figure 14 Cross section Galvanized + ZEC-Coat 888 treatment

Aspect and Capability

- Perfectly chromium free.

- Visual appearance: clear (glossy).

- Good self-repairing capability.

- Friction coefficient: nearly equivalent to colored chromate treated surface.

- Waste water treatment is unnecessary due to the chromium free treatment.

- Very good adhesiveness.

Characteristics

- Process available: Spray coating (include electrostatic spray coating), dip-spin and dip-drain coating.

- Thickness: 1-2 µm.

- ZINC PROTECTOR ZEC-888: Alcohol solution of a particular silicate compound.

Treating and Coating Procedure

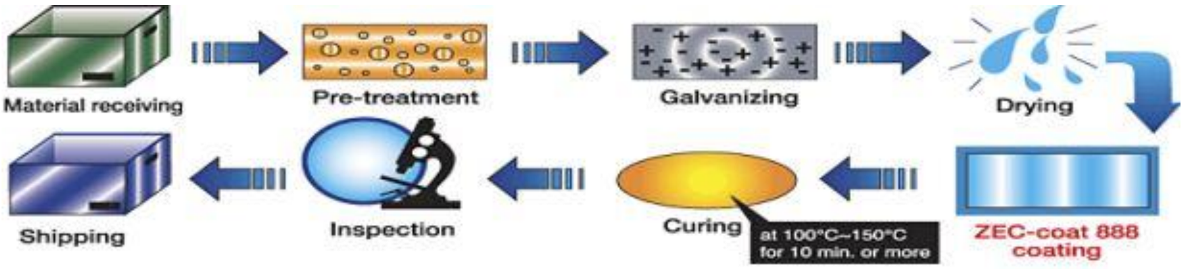


Figure 15 Treatment and coating procedure Galvanized + ZEC-Coat 888

2.1.2.2 CORROSION INHIBITIVE COATING, GALVANIZING + CHROMIUM TREATMENT + Z.P. ZEC-COAT 888.

Black Trivalent chromium treated galvanized surface is known to have a highly dispersed poor rust inhibiting properties. In order to improve and stabilize the rust inhibitive properties of black trivalent chromium treated items, application of Zinc Protector ZEC-Coat 888 is effective. Herewith, rust inhibitive properties of black trivalent chromium treated items can be improved by leaps and bounds.

This process can be used also on other chromium treatment like yellow, green and blue chromates improving their resistance to corrosion.

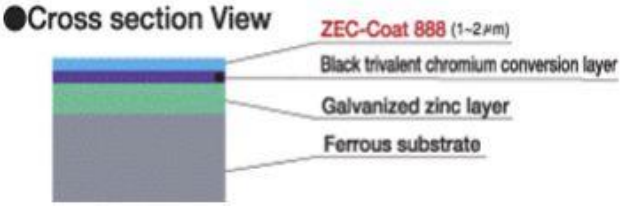


Figure 16 Cross section Galvanizing + chromium treatment + ZEC-Coat 888

Aspect and Capability

- Improves highly dispersed rust inhibitive properties of black trivalent chromium treated items and steps up their rust inhibitive properties remarkably.

- Visual appearance: eliminates interference colors and puts some gloss.

- Good self-repairing capability.

- Friction coefficient: nearly equivalent to colored chromate treated surface.

- Rust inhibitive properties are not influenced by those of adopted galvanizing bath.

Characteristics

- Process available: Spray coating (electrostatic spray coating), dip-spin and dip-drain coating.

- Thickness: 1-2 μm.

- ZINC PROTECTOR ZEC-888: Alcoholic solution of a particular silicate compound.

Treating and Coating Procedure

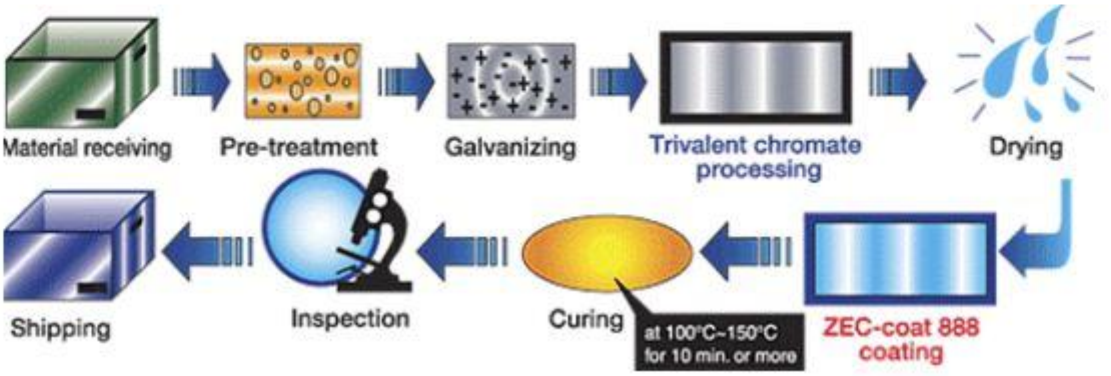


Figure 17 Treating and Coating Procedure Galvanizing + chromium treatment + ZEC-Coat 888

2.1.2.3 CORROSION INHIBITIVE COATING, GALVANIZED + PHOSPHATING + Z.P. ZEC-COAT 888.

In this method, galvanizing is performed on metal parts, and followed by chemical conversion coating, then Zinc Protector ZEC-Coat 888 is applied as the final surface treatment process. Although the corrosion inhibiting property of Zinc Protector ZEC-Coat 888 coated galvanized parts is excellent, this coating system would improve corrosion inhibiting property against white rusting.

Obtained corrosion inhibiting property with this method is impervious to be influenced by the galvanizing conditions. Visual appearance has a kind of frosted glass.

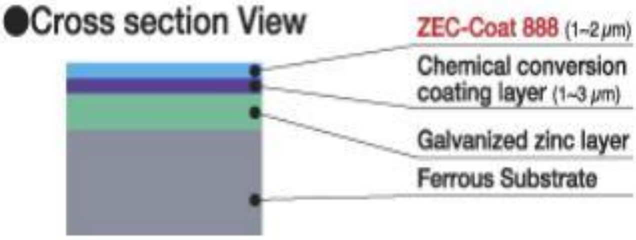


Figure 18 Cross section galvanized + phosphating + ZEC-Coat 888

Aspect and Capability

- Perfectly chromium free.

- Visual appearance: frosted glass.

- Good self-repairing ability.

Characteristics

- Process available: Spray coating (include electrostatic spray coating), dip-spin and dip-drain coating.

- Thickness: 1-2 µm.

- Chemical Conversion coating is usually zinc phosphate type.

- Zinc Protector ZEC-Coat 888: Alcoholic solution of particular silicate compound.

Treating and Coating procedures

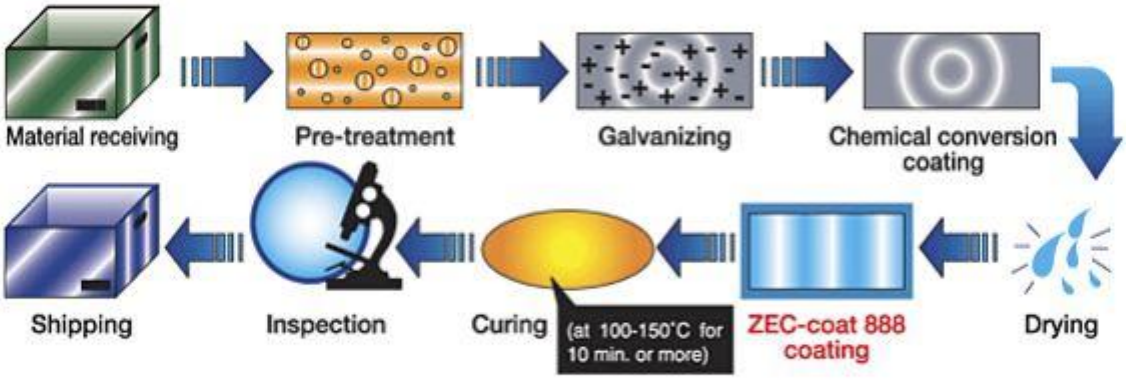


Figure 19 Treating and Coating procedures galvanized + phosphating + ZEC-Coat 888

2.1.2.4 CORROSION INHIBITIVE COATING, ZINC FLAKES + ZINC PROTECTOR ZEC-COAT 888.

Zinc Flake is a chromium-free coating material (or zinc rich paint) composed of dispersed metal-zinc flakes in an aqueous or alcoholic binder solution. Steel parts are coated with this coating material usually by dip-spin method. After that the parts are baked in a furnace at 320°C. During the baking process, the binder material would be solidified to form a configured coating layer having parallel multilayered metal-zinc flakes adhered to each other. Rust inhibitive mechanism of Zinc Flakes + Zinc Protector ZEC-Coat 888 is composed of both the self-sacrificial rust protection effect of metal zinc flakes and the improving rust inhibitive effect of Zinc Protector ZEC-Coat 888 coating, and hereby an excellent rust inhibitive property is obtained.

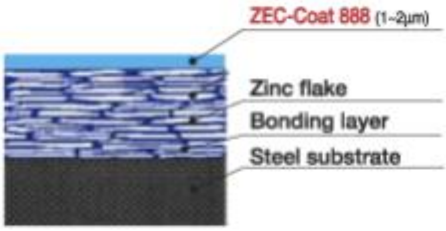


Figure 20 Cross section Zinc Flakes + ZEC-Coat 888

Aspect

- Perfect chromium-free.

- Aqueous or alcoholic binder system (Zinc Flake).

- No hydrogen brittleness.

- Process available: Spray coating and dip-spin method.

- Coating easiness: Excellent.

- Appearance: Good.

Capability

- Good sacrificial rust protection effect.

- No peeling for cross-cut adhesion test (100/100) **

-Self healing properties.

Treating and Coating procedures

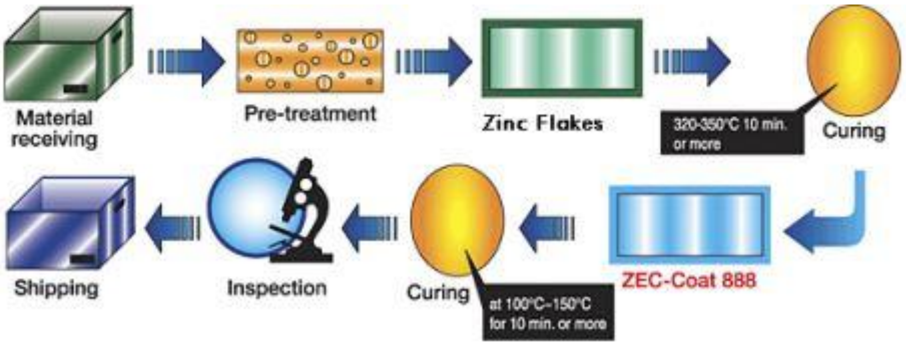


Figure 21 Treating and Coating procedures Zinc Flakes + ZEC-Coat 888

2.1.2.5 CORROSION INHIBITIVE COATING, ZINC DIE-CASTED + COAT 888.

White rusting would be significantly inhibited by treating zinc parts with Zinc Protector ZEC-Coat 888. It can also be applied upon aluminum die-casted parts. This Zinc Protector ZEC-Coat 888 treated parts will exhibit better rust inhibitive performance compared with conventional chromate parts.

The process can also be used on zinc die-casted or aluminum die-casted parts treated with chromate solutions, with this treatments the corrosion resistance is improved significantly.

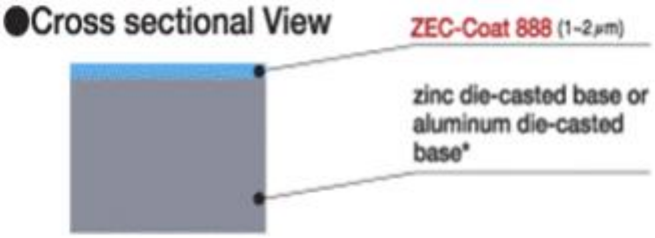


Figure 22 Cross section Zinc Die-casted + ZEC-Coat 888

Aspect and Capability

- Zinc Protector ZEC-Coat 888 treating needs no conventional galvanizing chromate treatment.

- Visual appearance: clear.

- Good self-repairing capability.

- Friction coefficient: nearly equivalent to colored treated surface.

- Perfectly chromium-free.

- Adhesiveness: very good.

- Waste water treatment is unnecessary due to the chromium-free treatment.

Characteristics

- Process available: Spray coating (include electrostatic spray coating), dip-spin and dip-drain coating.

- Thickness: 1-2 µm.

- Zinc Protector ZEC-Coat 888: Alcoholic solution of a particular silicate compound.

Treating and Coating Procedure

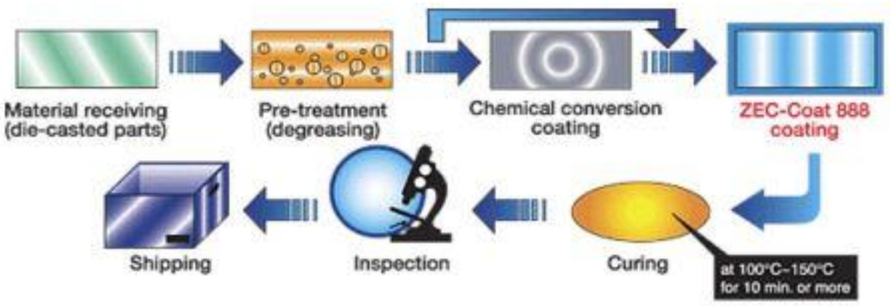


Figure 23 Treating and Coating procedure Zinc Die-casted + ZEC-Coat 888

3 Painting.

3 Painting.

Painting is a generic term for the application of a thin organic coating to the surface of a material for decorative, protective, or functional purposes. Painting offers the following advantages over other processes used for the protection or decoration of metal parts and assemblies:

- The equipment required for applying paint is usually less expensive to buy and install, is simpler to operate, and requires less control.
- Material and labor costs per unit area of surface coated often are much lower;
- Organic coatings are available in a wide range of pigments and vehicles and can meet practically any coating requirement for color, gloss, or surface texture.
- Paints have been developed that can withstand most corrosive conditions, and unlike many metallic protective coatings, organic films can simultaneously resist more than one corrosive condition, such as combinations of marine atmosphere and acid fumes.
- Conventional paint films have good dielectric properties, which enable them to inhibit galvanic action between dissimilar metals. Conversely, paints are available that contain special pigments to provide conductivity suitable for grounding induced or static electricity.
- Paints have been developed to meet newer environmental regulations.

3.1 Type of Paints.

The general terms "paint" and "organic coating" are essentially interchangeable and are used to designate certain coatings having an organic base. Most organic coatings are based on a film former or binder that is dissolved or dispersed in a solvent or water. This film-forming liquid constitutes the vehicle in which pigments are dispersed to give color, opacity, and other properties to the dried film. Many other ingredients can be added to the vehicle to achieve specific film properties. These would include such things as driers to aid curing, plasticizers to impart flexibility and other properties, and stabilizers to lessen the deleterious effects of heat or sunlight. A wide variety of film-forming materials is available and includes oils, varnishes, synthetic resins and polymers such as cellulose, vinyl, epoxy, and polyester. In general, major performance characteristics depend on the binder used.

3.1.1 Enamels.

Enamels are topcoats characterized by their ability to form a smooth surface that is typically of high gloss, but may also include lower degrees of gloss such as flat enamels. Enamels may air dry or bake. Air-dry enamels are cured essentially by a combination of solvent evaporation and oxidation. Baking enamels incorporate catalysts and cross-linking agents that require heat for polymerization.

3.1.2 Lacquers.

Lacquers are compositions based on natural or synthetic thermoplastic film-forming materials dissolved in organic solvent. These dry primarily by solvent evaporation. Lacquers are generally characterized by fast drying properties. Typical lacquers include those based on nitrocellulose, other cellulose derivatives, vinyl resins, and acrylic resins. A natural lacquer resin, based on secretions of the lac beetle, is called shellac.

3.1.3 Water-Borne Paints.

Water-borne paints are dilutable with water. There are three principal types: solutions, colloidal dispersions, and emulsions. Solution coatings are based on water-soluble binders. Many conventional binders (alkyds, acrylics, and epoxies) can be made water soluble by chemically attracting polar groups such as carboxyl, hydroxyl, and amide, which are strongly hydrophilic. Some hydrocarbon solvents are usually necessary, up to 20% of the total, to improve solubility.

Colloidal dispersions are very small particles of binder, less than 0.1µm in diameter, dispersed in water. Normally, these dispersions contain water-soluble polar groups to partially solubilize a portion of the resin. Emulsions, or latexes, are water dispersions that differ from colloidal dispersion by having much larger particle size on the order of 0.1 µm or larger. They are made by precipitation in water and therefore do not need to be dispersed.

Pigments must be compatible with water. Metallic particles are usually coated before being mixed into the paint to prevent chemical reaction with water, which would cause the mixture to generate gas. Water-reducible paints have a low volatile organic content (VOC) and comply with most environmental regulations. The advantages of water-bore paints include:

- Low flammability.
- Reduced toxicity and odor.
- Easy cleanup with water.
- Good film continuity, with continuous film similar to conventional solvent systems.
- Good mechanical stability; can be pumped in all types of equipment similar to conventional solvent paints.
- Application by air spraying, dipping, flow coating, electrodeposition, and roller coating.

The disadvantages of water-borne paints include:

- Application by electrostatic spraying requires complete electrical isolation because of the water conductivity.
- Coatings require a longer flash tunnel before curing.
- Temperature must be raised more slowly to evaporate water at a slow enough rate to prevent the coating from blistering.
- Coatings are more susceptible to dirt pickup.
- Proper temperature and humidity control are vital. If the humidity is too high or the temperature too low, coating can sag or run off the workpiece.

3.1.4 Electrophoretic Paints.

Electrophoretic paints are special water-reducible paints. Resin and pigment materials are shipped and stored as concentrates to be added to the production tank as needed. Electrophoretic films are always deposited from a dip tank. The operating bath consists of resin concentrate and pigment concentrate mixed with deionized water and small amounts of solubilizers and defoamers. The concentration of nonvolatile solids in the bath varies from about 10 to 20%, depending on type and composition. Paint films are deposited on the work by electrophoretic action. Immediately after the film has been deposited, the work is removed from the bath and rinsed with water to remove the excess paint bath, leaving a uniform, tightly adhering film of paint on the workpiece. The workpiece is then baked. Paints can be prepared to deposit films on either the anode or cathode. The resins used most frequently are epoxies and acrylics, including numerous modifications and hybrids. For more information on this process, see the section on electrocoating in this article.

3.1.5 Autophoretic Paints.

Autophoretic paints are water-reducible paints deposited on metal surfaces by the catalytic action of the metal on the paint materials in the bath. Currently, only ferrous surfaces activate the autophoretic paints available commercially. Tubular automotive frames are coated with this method, because the entire length of the tubing can be coated inside and outside with equal ease.

3.1.6 High-Solids Paints.

High-solids paints contain 70% or more solids by volume. One method of obtaining high-solids paints is to use lower molecular weight polymers, which require less solvent to attain the desired application viscosity. Another method of reducing viscosity of high-solids paints is by heating the paint material to a temperature of about 32 to 52°C. Many two-component systems use a catalyst to increase the rate of the curing reaction. Fast-reacting two-component systems are usually applied with special spray guns that mix the two components at the spray nozzle. Single-component resins in high-solids paints include epoxy, acrylic, polyester, and alkyd; whereas two-component resins may be urethanes, acrylic-urethane, or epoxy-amine. The advantages of high-solids paints include:

- Color control and color matching is no more difficult than with conventional solvent paints.
- These paints can be applied by higher speed (6000 to 30,000 rev/min) electrostatic bells and disks requiring minimum facility conversion from existing bell or disk systems.
- Performance properties are equivalent to those of conventional solvent paints.
- Applied cost per square foot is lower than that of conventional solvent paints.
- In many cases, these paints require less energy for curing than conventional solvent paints.
- VOC compliance is more readily attained because of reduced solvent use.

The disadvantages of high-solids paints include:

- High-solids paints require specialized pumping and transport equipment.
- Cleanup of overspray is much more difficult than with conventional solvent paints.
- Toxicity of the isocyanates used with urethanes and amines used with epoxies can be a problem.
- Drying and/or curing times may be longer than those for conventional solvent paints unless the coatings are baked.

3.1.7 Powder Paint.

Powder paint consists of plastic resins, color pigments, and additives. In a mixing and grinding unit, the ingredients are combined in a homogeneous mixture that is heated to the melting point. The molten material is extruded into a thin sheet, which is cooled and crushed. The chips are pulverized to a fine powder of carefully controlled particle size, ensuring optimum fluidity and efficient flow through the finishing system.

3.2 Substrate and Surface Conditions.

The type of substrate must be considered. A coating capable of giving excellent performance on one metal may fail badly on another. Smoothness, porosity, dimensional stability, and corrodibility affect the choice of a proper finishing system. Smooth, clean metal surfaces that cannot be phosphate coated lack sufficient "tooth" for good adhesion of some air-dried coatings. ("Tooth" is the coarse or abrasive quality of a substrate that facilitates the application and adhesion of a coating).

No special primer coats are required on surfaces containing small quantities of tightly adhering rust, if the finished parts are intended for indoor service in a mildly corrosive atmosphere. Attractive and durable finishes can be obtained over such surfaces with a single coat of a special paint that produces a textured finish, such as wrinkle finishes and pebble finishes. These paints are relatively inexpensive and hide surface irregularities with their own irregular appearance.

On parts intended for outdoor use where tightly adhering rust is present and not economically removable, a rust-inhibiting primer with good penetrating qualities must be used to prevent, or at least substantially retard, further rusting in service. Parts with heavy rust or mill scale should not be painted unless the loose rust and mill scale are removed.

The diverse requirements of substrate and environment often necessitate a dual or multiple coating systems. In these systems, a primer with one composition is used to satisfy substrate adhesion and corrosion resistance, and a coating with a different composition is used as a topcoat to withstand environmental conditions, for example, a vinyl wash primer followed by an epoxy primer with an acrylic topcoat.

3.3 Basic Functions.

Coatings may be applied for appearance, to meet functional requirements, or to meet combined function and appearance needs. If the basic purpose is appearance, the gloss, color, and retention of these properties in service are emphasized. In some applications, functional requirements are of equal importance to appearance. On office furniture, for example, paint films must provide attractive appearance and resist marring and abrasion. On automobiles, paint films must be attractive in appearance, easily applied, and readily repaired, but be resistant to abrasion, marring, and impact as well as capable of protecting the underlying metal from corrosion. In other applications, such as corrosion protection of tanks or chemical equipment, the functional requirements of the paint film are of prime concern. Corrosion resistance is the most important of functional requirements.

Paint coatings are not completely water-resistant; in fact they might absorb water and oxygen, increasing the sub-corrosion. The corrosion speed control might be Ohmic type if the coating electrical conductivity is low. The conductivity depends first on the absorbed water quantity which depends itself on the chemical physical properties of the paint; the electrical conductivity depends also on the solution saltiness.

The presence of ionic groups produced from hydrolysis phenomena caused by absorbed water makes the paint really selective in terms of negative and positive ions migration, giving it the typical characteristic of semi-permeable membrane. The salt concentration in many coating decreases going from the external to the internal layers, for this reason at the metal-paint interface the electrical conductivity is very low. Some factors may increase this conductivity such as the presence of corrosion products on the metallic surface and the presence of electrolytes in the paint itself.

3.4 Industrial Paint Application Technologies.

Paint application technology depends on the type of coating and the nature of the substrate. The major types of coatings (liquid, powder, etc.) are all applied using different methods. Choice of technique can also be determined by the specific application. Liquid coatings can be applied with brushes, using spray technology, or via continuous methods such as roll, curtain, and air knife technology. The application of powder coatings is typically done via electrostatic spray technology. No matter what the coating type or the application methodology, transfer efficiency and uniformity remain the critical parameters that continue to be addressed by research and development efforts.

3.4.1 Spray Painting.

The major methods for applying liquid paints for industrial applications include spraying (both traditional and electrostatic) for substrates with complex shapes and roll or web, curtain and knife techniques (continuous operations) for less complicated parts. With spray techniques, the transfer efficiency and uniformity of the coating that is applied remain the critical aspects of the coating process. For continuous processes, line speed is also an issue. Transfer efficiency relates to the percentage of paint sprayed that actually adheres to the substrate. The current standard is 65% or better.

The introduction of HVLP spray guns within the last 10 years has been a response to the need for improved transfer efficiencies and waste minimization. These spray guns use lower pressure to spray a higher volume of the paint. As a result, the spray area is more concentrated and a greater percentage of the paint can be applied to the substrate.

Spray technology is ideal for many industrial applications where parts are three-dimensional and have many nooks and crannies that are difficult to reach. The automotive industry is one such example, where most of the parts have irregular shapes. In these cases, robots have found great utility as the technology for control of fine movement has rapidly advanced.

3.4.2 Electrostatic Attraction Painting.

Powder coatings are applied to metal surfaces using electrostatic attraction of the paint particles to the metal surface. For nonconductive surfaces such as wood, plastic, and composites, a "prep-coat" is often applied that provides the necessary conductivity. In other cases, moisture in the wood or conductive additives added to a molded part can serve as the source of conductivity. Electrostatic spray provides significantly enhanced transfer efficiency over air-spray without electrostatic attraction.

One of the newest technologies to be introduced to the market is the Pulse Power powder coating system. The pulse power system can significantly improve transfer efficiency, particularly on complex parts with "Faraday Cage" areas. Customers have been able to reduce powder consumption by up to 35%, while others have been able to eliminate a touch-up operator. Other benefits include smoother finishes with reduced orange peel and back ionization. Very thick coatings can be applied using the pulse power system, and metallic powder coatings react the same as standard powders.

Besides transfer efficiency and the desire for uniform coatings, the main issue for application of powder coatings has revolved around the need for faster color changes. A full color change can take 15 to 20 minutes and requires two operators to manage it. For companies making 60 to 80 color changes per day, that kind of time and investment of resources is unacceptable. This need, combined with the increased cost effectiveness of powder coatings and improved recycling ability, has resulted in a shift to "spray-to-waste" techniques where the guns and lines are blown out after each color is used to clear them for the next.

Production of the powder coatings themselves is also affecting the application of paints. Paint manufacturers have improved the particle size distribution of powder coatings by removing more of the undesirable fines. The narrower distribution has resulted in reduced waste and greater transfer efficiency.

3.5 Samples Dimension and Paint Conditions Used in the Present Case of Study.

We received the materials to be tested directly from the project costumer. For each material and pretreatment combination we received 12 sheets: 6 painted and 6 non painted.

We measured the sheets dimensions using a micrometer for the thickness. The results are presented in Table 1.

	Length [mm]	Width [mm]	Thickness [mm]
Aluminum Painted	80	160	0,93
Aluminum Non Painted	80	160	0,78

Table 1 Metal Sheets Dimensions.

For a further and more accurate analysis we decided to measure the paint thickness using the instrument: Fischer DUALSCOPE® FMP100 (See Figure 24) using the probe FGAB1.3 and following the method of magnetic induction according to the technical standard DIN EN ISO 2178.

Figure 24 Fischer DUALSCOPE® FMP100.

The results of this analysis concur with the one done with the micrometer. In fact the average paint thicknesses are:

- Aluminum: 130 µm (max: 187 µm; min: 27 µm).
-

The type of coating utilized is a powder paint applied with spray technology.

For all the painted metal sheets the two sides have not the same paint level of quality. In fact, in order not to waste too much material, the costumer decided to paint one side very fast; in this way the layer is thin and in some parts, where you can still see the metal substrate, it is not even present. On the other side, on the contrary, the paint layer is very uniform, thick and brilliant. Even if it can sound obvious, we want to underline the fact that the entire test were always done on the better paint side of the metal sheet. In Figure 25 it can be appreciate how the samples look alike.

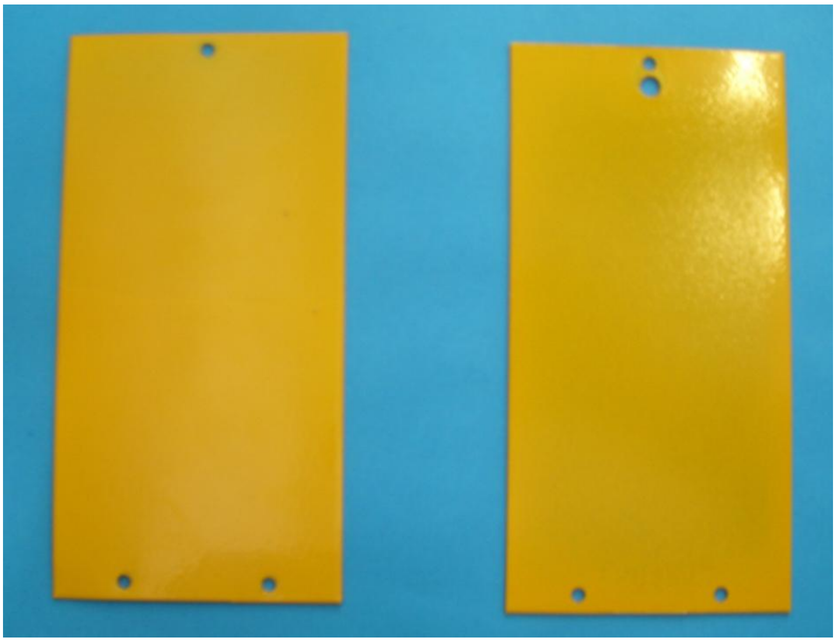


Figure 25 Painted Metal Sheets.

4 Electrochemistry of Corrosion.

4 Electrochemistry of Corrosion.

Metallic corrosion is usually an electrochemical process, which may be defined as destruction by electrochemical or chemical agencies. Corrosion in an aqueous environment and in an atmospheric environment (which also involves thin aqueous layers) is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. It results from the overwhelming tendency of metals to react electrochemically with oxygen, water, and other substances in the aqueous environment. Fortunately, most useful metals react with the environment to form more or less protective films of corrosion reaction products that prevent the metals from going into solution as ions.

While the term corrosion has in recent years been applied to all kinds of materials in all kinds of environments, this thesis will only consider the electrochemistry of corrosion of CRS and HDG in aqueous solutions at ambient temperatures. Electrochemical corrosion occurring under such conditions is a major destructive process that results in such costly, unsightly, and destructive effects as the formation of rust and other corrosion products.

Electrochemical processes require electrical contact and a continuous ionic path (i.e., electrolyte) between anodes and cathodes. The electron flow between the anodic and cathodic areas quantifies the rates of the oxidation and reduction reactions that occur at the surfaces. Factors that govern the theoretical possibility and practical occurrence of corrosion are the following:

- The thermodynamic driving force.
- The kinetic parameters that govern the oxidation and cathodic reduction reaction rates.

The former determines whether anodic oxidation and cathodic reduction reactions are thermodynamically possible and will occur spontaneously, while the latter determines the reaction rate per unit area. Electrochemical reactions are defined as those that involve electron transfer during de-electronization (anodic oxidation) or electronization (cathodic reduction). There are three typical anodic oxidation (i.e., de-electronization) half-cell reactions by which a metal atom (M) in the solid state may be oxidized and transferred into a charged metallic ion in an ionic conducting phase such as an aqueous solution.

$$M(s) = M^{z+}(aq) + ze^{-}(s)$$

$$M(s) + zH_2O(aq) = M(OH)_z + zH^{+}(aq) + ze^{-}(s)$$

$$M(s) + zH_2O(aq) = MO_z^{z-} + 2zH^{-}(aq) + ze^{-}(s)$$

Where z describes the number of electrons transferred from the valence electron shell of the metal in each half-cell reaction and also represents the charge of the metallic cation in the case of the first reaction. Typical cathodic reactions in aqueous solutions involve the reduction of oxygen, proton reduction, and the reduction of water. In these reactions electrons are consumed:

$$O_2(g) + 2H_2O(aq) + 4e^{-}(s) = 4OH^{-}(aq)\ in\ neutral\ or\ alkaline\ solutions$$

$$O_2 + 4H^{+} + 4e^{-} = 2H_2O\ in\ acid\ solutions$$

$$2H^{+} + 2e^{-} = H_2\ in\ acid\ solutions$$

$$2H_2O + 2e^{-} = H_2 + 2OH^{-}\ in\ neutral\ or\ alkaline\ solutions$$

Other cathodic reactions are possible including the reduction of metallic species in solution (e.g., Fe3++ e−=Fe2+). Corrosion occurs spontaneously when the equilibrium half-cell potential, E0, of a relevant cathodic reaction (E0 is determined from knowledge of the standard free energy of the half-cell reaction at unity activity, pressure, and temperature; G=−zFEstd0) is more positive than the equilibrium half-cell potential of the proposed anodic reaction. This situation results in a negative change in free energy associated with the overall reaction at constant pressure and temperature as given by:

$$\Delta G = -zF\left(E_0^{cath} - E_0^{anode}\right)$$

Where F is Faraday's constant, z is the number of electrons transferred in the overall reaction, andE0 are the equilibrium half-cell potentials for the relevant cathode and anodic reactions. Corrosion occurs spontaneously when the change in free energy is negative. The magnitude of ΔG is a measure of the thermodynamic driving force but does not accurately define the kinetics of the reaction.

Laboratory test methods include a number of direct current measurement techniques that are commonly used in electrochemical testing. Specific methods include potentiodynamic polarization, potentiostatic polarization, and galvanostatic polarization. The scan rate in a potentiodynamic test can significantly influence the results obtain. Also, the dynamic nature of these test methods may preclude the natural formations of films on a metal surface, which can cause the distorted results. Potentiostatic and galvanostatic polarization methods are often applied in studying localized corrosion. Electrochemical methods to measure the susceptibility of alloys to pitting corrosion are reviewed elsewhere, and are not study cases of the present thesis. The disadvantages associated with selecting the proper scan rate in the potentiodynamic and selected methods.

4.1 Samples Preparation.

For all the electrochemical tests we decided to prepare the samples in the same way. From the metal sheets we received from the project contractor (3.5 Samples Dimension and Paint Conditions Used in the Present Case of Study.) we obtained smaller samples by cutting them in pieces. The average dimensions of the samples used in all tests are:

- Length: 80 mm.
- Width: 25 mm.
- Thickness: depending on the type of material and on the coating conditions (See Table 1).

After the cutting process it was necessary to clean the samples from dirt and cutting oils. In order not to damage the pretreatment layers or the paint we decided to use only distilled water. In those rare cases when we noticed that the dirt was not removed we proceeded with acetone and ethanol. We repeated this cleaning operation on each sample before running.

For no limiting the current flow on the painted samples it was necessary to remove the paint on a small area on which we attached the croc clip.

We also decide to limit the exposed area on every sample for each test to 1 cm^2. In order to so we cover the sample either with Teflon® or Kapton® tapes. In this way it was possible to do multiple tests on the same sample.

For those types of tests that required the paint to be damaged, we scratched a diagonal line on the exposed area using a cutter.

When all the tests on the sample were over we removed the tape and we labeled the exposed areas for further microscope investigation, as shown in Figure 26.

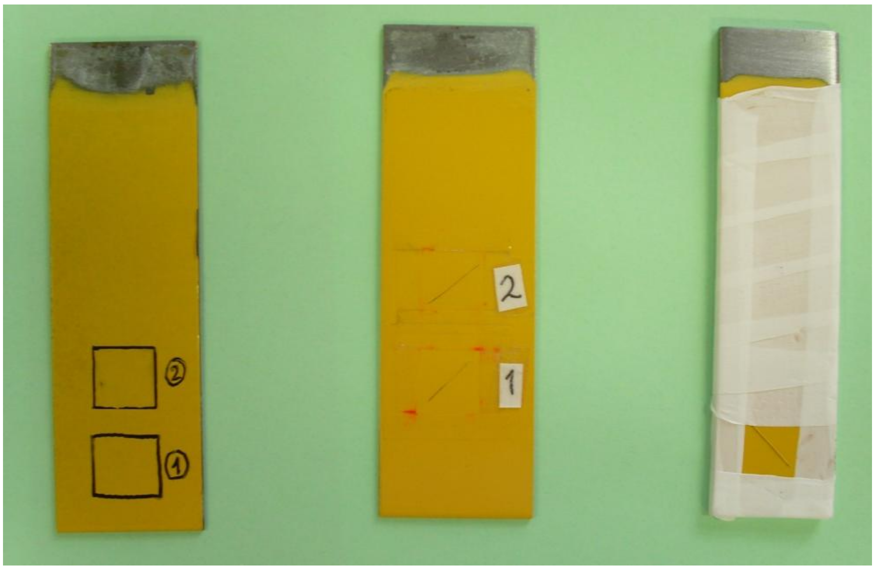


Figure 26 Sample conditions before and after a test.

4.2 Electrochemical Cell Set-Up.

For all the Potenziodynamic (See: 4.3 Potentiodynamic Polarization Corrosion Test.), Galvanostatic pulse (See: 4.5 Galvanostatic and Galvanostatic Pulse Method.), Cyclic Voltammetry (See: 4.4 Cyclic Voltammetry.) and Impedance tests (See: **Error! Reference source not found.**), it was used the same electrochemical cell setup.

The electrolyte solution used during the experimental part was a 3.5%w sodium chloride dissolved in distilled water consideration that was taken after reading the standard ASTM B 117-03, (ASTM Standards, October, 2003).

It was used a three electrode setup. The working electrode was the sample to be tested prepared as described before (4.1 Samples Preparation.).

As counter electrode, a mesh of platinum was used. The area of this mesh was always kept higher than the exposed one on the working electrode.

The Saturated calomel electrode (SCE) was at the end used as reference electrode. This electrode is based on the reaction between elemental mercury and mercury (in liquid phase) chloride. The aqueous phase in contact with the mercury and the mercury (in liquid phase) chloride (Hg_2Cl_2, "calomel") is a saturated solution of potassium chloride in water. The electrode is linked via a porous frit to the solution in which the other electrode is immersed. This porous frit is a salt bridge. The electrode is based on the redox reaction:

$$Hg_2^{2+} + 2e^- \Leftrightarrow 2Hg(l)$$

The potential of the electrodes has been very accurately determined against the hydrogen electrode: its standard potential is:

$$E = 0{,}2412\ V$$

In Figure 27 its well explain the functioning of the SCE electrode.

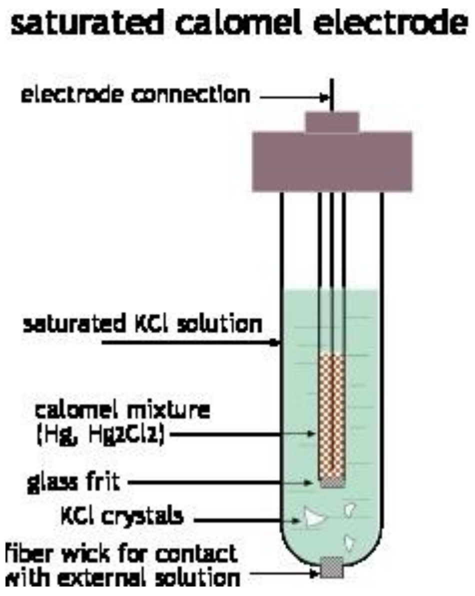


Figure 27 SCE reference electrode scheme.

4.3 Potentiodynamic Polarization Corrosion Test.

Polarization methods such as potentiodynamic polarization and cyclic voltammetry are often used for laboratory corrosion testing. These techniques can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential.

- **Anodic polarization**: the potential is changed in the anodic (or more positive direction) causing the working electrode to become the anode and causing electrons to be withdrawn from it;
- **Cathodic polarization**: the working electrode becomes more negative and electrons are added to the surface, in some cases causing electrodeposition;
- **Cyclic polarization**: both anodic and cathodic polarizations are performed in a cyclic manner.

Several methods may be used in polarization of specimens for corrosion testing. Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. It is probably the most commonly used polarization testing method for measuring corrosion resistance and is used for a wide variety of functions: (reference).

- **Cyclic polarization tests:** These tests are often used to evaluate pitting susceptibility. The potential is swept in a single cycle (or slightly less than one cycle), and the size of the hysteresis is examined along with the differences between the values of the starting open circuit corrosion potential and the return passivation potential. The existence of the hysteresis is usually indicative of pitting, while the size of the loop is often related to the amount of pitting.
- **Cyclic voltammetry:** Cyclic voltammetry involves sweeping the potential in a positive direction until a predetermined value of current or potential is reached, then the scan is immediately reversed toward more negative values until the original value of potential is reached. In some

cases, this scan is done repeatedly to determine changes in the current-potential curve produced with scanning.

- **Potentiostaircase method:** This technique polarizes an electrode in a series of potential steps where the time spent at each potential is constant, while the current is often allowed to stabilize prior to changing the potential to the next step. The step increase may be small, in which case, the technique resembles a potentiodynamic curve, or it may be large.
- **Electrochemical potentiodynamic reactivation (EPR):** This technique allows measuring the degree of sensitization of stainless steels such as S30400 and S30403 steels. This method uses a potentiodynamic sweep over a range of potentials from passive to active (called reactivation).
- **Linear polarization resistance (LPR):** A widely used technique, the polarization resistance of a material is defined as the slope of the potential-current density curve at the free corrosion potential, yielding the polarization resistance.

The study of uniform corrosion or studies assuming corrosion uniformity are probably the most widespread application of electrochemical measurements both in the laboratory and in the field. The widespread use of these electrochemical techniques does not mean that they are without complications. Both linear polarization and Tafel extrapolation need special precautions for their results to be valid. The main complications or obstacles in performing polarization measurements can be summarized in the following categories:

- **Effect of Scan Rate:** The rate at which the potential is scanned may have a significant effect on the amount of current produced at all values of potential. The rate at which the potential is changed, the scan rate, is an experimental parameter over which the user has control. If not chosen properly, the scan rate can alter the scan and cause a misinterpretation of the features.
- **Effect of Solution Resistance:** The distance between the Luggin capillary (of the salt bridge to the reference electrode) and the working electrode is purposely minimized in most measurements to limit the effect of the solution resistance. In solutions that have extremely high resistivity, this can be an extremely significant effect.
- **Changing Surface Conditions:** Since corrosion reactions take place at the surface of materials, when the surface is changed, due to processing conditions, active corrosion or other reasons, the potential is usually also changed. This can have a strong effect on the polarization curves.
- **Determination of Pitting Potential:** In analyzing polarization curves the appearance of a hysteresis (or loop) between the forward and reverse scans is often thought to denote the presence of localized corrosion (pitting or crevice corrosion).

4.3.1 Experimental Set-Up.

In order to perform a potentiodynamic polarization in the systems evaluated with HDG and CRS metal/solution, a number of components must be assembled and appropriately prepared. Prior performing the experiments, the sample surface must be prepared such that the initial condition or starting point, of the measurement is well defined and does not vary from test to test, from the same type of material with the same type of pretreatments and coating. Finally, equipment capable of performing the measurement and acquiring data is been used (EG&G).

For all test it was used an electrolytic solution of 3.5%w NaCl (As mention in: 4.1Samples Preparation.). It is important to remember to monitor the pH of the electrolytic solution during the proceedings of the test, making sure that it is always in the range of neutral.

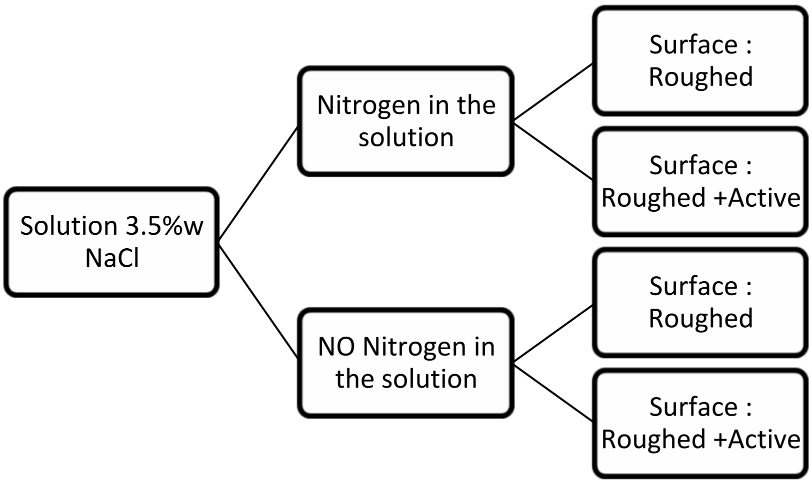


Table 2 Potentiodynamic test considerations.

During the beginning of our research the tests were done at least three times for each different sample to be able to get enough data for our statistical survey that will be presented lather in this thesis; while repeating the tests, it was used different exposed area in the specimen, always a mark of 1cm^2, and the rest of the surface that was exposed to the solution was cover all the time with the appropriate Thread seal tape "Teflon" with thickness of 0.01mm.

The purpose of the present work was to study the application, the reproducibility and the influence of some methodological variables on the results of potentiodynamic polarization corrosion testing applied to the different families of the materials that were presented by the product end-used company. Embedded 8 different specimens of HDG and 8 different specimens of CRS, all types were subjected to anodic polarization scan within the potential range of -250mV to 1V.

4.3.1.1 Activation Procedure.

To activate the surfaces of the specimens must be used for each material:

- **CRS**: Immersion for 1 min in a solution of HCl 20%$_w$;
- **HDG**: Immersion for 1 min in a solution of H_2SO_4 10% $_w$;
- **To clean**: Immersion for 1 min in a solution of NaOH 20%$_w$.

Proceed to rinse with distilled water. Soak for another 1 min in a solution of nitric acid 5%$_w$.

4.3.1.2 Test Parameters.

Scan Rate:	1 mV/sec	*vs. Open Circuit Potential
Start Voltage:	-250 mV vs. OPC	
Finish Voltage:	1 V	

Table 3 Potentiodynamic test parameters.

4.3.1.3 The Test Cell.

The test cell should be constructed to allow the following items to be inserted into the solution chamber: the test electrode also call working electrode, a platinum counter electrode, a reference electrode SCE sat. KCL, and in some cases the inlet for Nitrogen gas. The test cell shall be constructed as shown in Figure 28, with materials that will not corrode, deteriorate, or otherwise contaminate the test solution. (See also: 4.2 Electrochemical Cell Set-Up.)

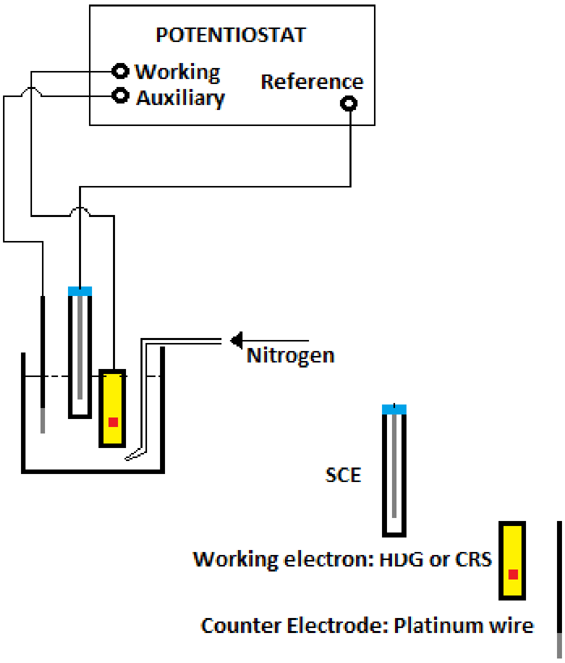


Figure 28 Potentiodynamic test cell.

4.3.1.4 Measuring Instrument.

During the experimental time of the present thesis the instrument that was used because of its capability of measuring in an accurate way was the EG&G Princeton Applied Research: Potentiostat/Galvanostat, Model: 273A (That can be seen in: Figure 29).

Figure 29 EG&G Potentiostat/Galvanostat Model: 273°.

4.4 Cyclic Voltammetry.

Cyclic voltammetry (CV) is when the voltage is swept between two values at a fixed rate, however when the voltage reaches V_2 the scan is reversed and the voltage is swept back to V_1.

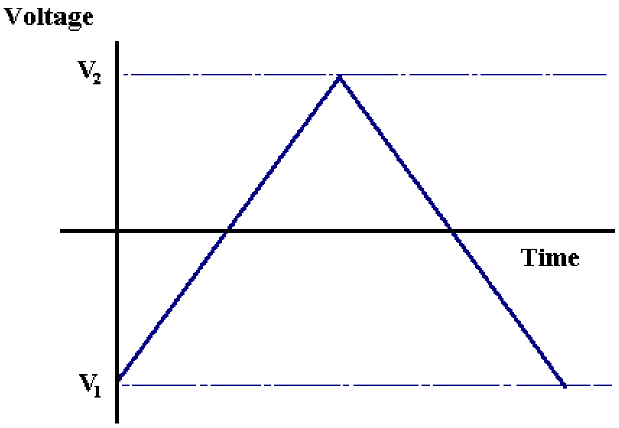


Figure 30 Cyclic Voltammetry Principle.

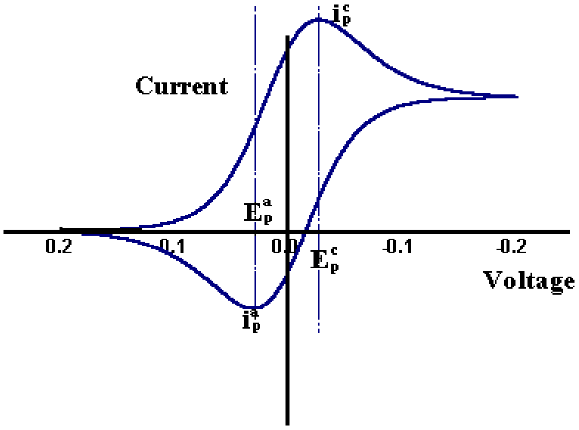


Figure 31 A typical cyclic Voltammogram recorded for a reversible single electrode transfer reaction.

The forward sweep produces an identical response to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product (F^{2+} back to reactant (Fe^{3+}). The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward seep but otherwise the behavior can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

- The voltage separation between the current peaks is:

$$\Delta E = E_p^a - E_p^c = \frac{59}{n} mV$$

- The positions of peak voltage do not alter as a function of voltage scan rate.
- The ratio of the peak currents is equal to one.

$$\left|\frac{i_p^a}{i_p^c}\right| = 1$$

- The peak currents are proportional to the square root of the scan rate.

$$i_p^a \text{ and } i_p^c \propto \sqrt{v}$$

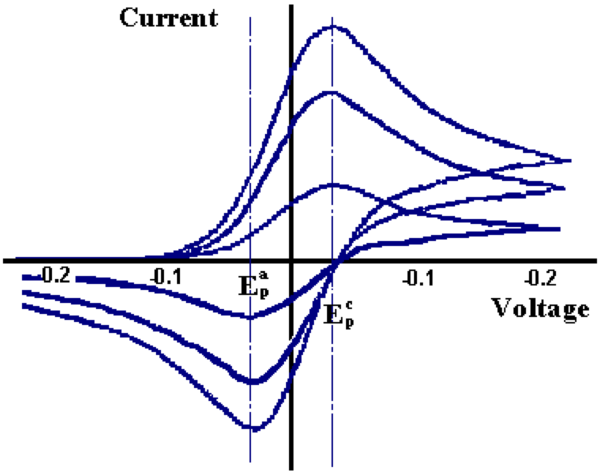


Figure 32 Influence of the voltage scan rate on the current for a reversible electron transfer.

As with LSV the influence of scan rate is explained for a reversible electron transfer reaction in terms of the diffusion layer thickness. The CV for cases where the electron transfer is not reversible show considerably different behavior from their reversible counterparts.

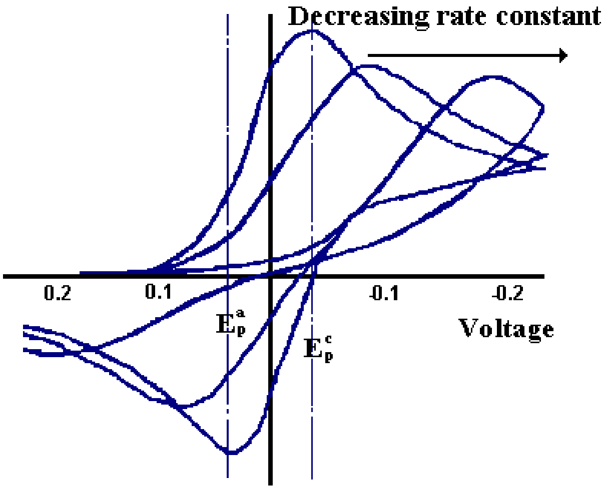


Figure 33 Voltammogram for a quasi-reversible reaction for different values of the reduction and oxidation rate constants.

The first curve shows the case where both the oxidation and reduction rate constants are still fast, however, as the rate constants are lowered the curves shift to more reductive potentials. Again this may be rationalized in terms of the equilibrium at the surface is no longer establishing so rapidly. In these cases the peak separation is no longer fixed but varies as a function of the scan rate. Similarly the peak current no longer varies as a function of the square root of the scan rate.

By analyzing the variation of peak position as functions of the scan rate it is possible to gain an estimate for the electron transfer rate constants.

4.4.1 Experimental Set-Up.

In order to perform a cyclic voltammetry in the systems evaluated with HDG and CRS metal/solution, a number of components must be assembled and appropriately prepared. Prior performing the experiments, the sample surface must be prepared such that the initial condition or starting point, of the measurement is well defined and does not vary from test to test, from the same type of material with the same type of pretreatments and coating. Finally, equipment capable of performing the measurement and acquiring data is been used (EG&G).

For all test it was used an electrolytic solution of 3.5%w NaCl. It is important to remember to monitor the pH of the electrolytic solution during the proceedings of the test, making sure that it is always in the range of neutral.

A different exposed area in the specimen was used, always a mark of 1 cm2, and the rest of the surface that was exposed to the solution was covered all the time with the appropriate Thread seal tape "Teflon" with thickness of 0.01mm.

4.4.1.1 *Test Parameters.*

Potential E_1:	1 V
Potential E_V:	-1.5 V
Potential E_F:	1 V
Scan Rate:	100 mV/s
№ of points:	5001

Table 4 Cyclic voltammetry test parameters.

4.4.1.2 *The Test Cell.*

The test cell should be constructed to allow the following items to be inserted into the solution chamber: the test electrode also call working electrode, a platinum counter electrode, a reference electrode SCE sat. KCL. The test cell shall be constructed of materials that will not corrode, deteriorate, or otherwise contaminate the test solution. In our case of study the evaluation of the samples was done in 2 different ways, first of all in a clean surface without scratch and also in a clean surface with scratch.

4.4.1.3 *Measuring Instruments.*

During the experimental time of the present thesis the instrument that was used because of its capability of measuring in an accurate way was the EG&G Princeton Applied Research: Potentiostat/Galvanostat, Model: 273A. as mention in the potentiodynamic test part.

4.5 Galvanostatic and Galvanostatic Pulse Method.

Galvanostatic pulse method is a rapid non-destructive polarization technique.

In general, the galvanostatic pulse method is characterized by impressing a small amplitude, short interval catholic current pulse, applied galvanostatically with the help of an external counter electrode over the concrete surface and analyzing the resultant change in potential.

The potential transient for a given current step of ΔI to a typical Randles circuit under galvanostatic condition is given by:

$$\eta_t = \Delta IR_c + \Delta IR_p \left[1 - e^{\left(-\frac{t}{CR_p} \right)} \right]$$

where η_t is the total change in the potential of the test electrode, ΔIR_c is the ohmic drop in the concrete, R_p and C are the polarization resistance and electrical double layer capacitance of the corroding interface. Upon the interruption of the current pulse, the ohmic drop contribution ΔIR_c is immediately lost by the electrode potential and a sudden fall of potential to a value within few microseconds gives the actual polarization of the test specimen. In the absence of any further current, the potential decays exponentially with time according to

$$\frac{\eta_t}{\eta_{\max}} = e^{\left(-\frac{t}{CR_p} \right)}$$

Where η_{max} is the maximum polarization at the time of current interruption and η_t is the polarization at any instant of time.

Typical schematic potential transient for a current pulse under galvanostatic condition is shown in Figure 34 where an anodic current pulse catholic of amplitude Δi is impressed between the time $t=t_0$ to $t=t_1$. Upon applying the current pulse, the potential of the system shifts to a value equivalent to ΔIR_c in few microseconds and thereafter increases gradually to a maximum value η_{max}. At the instant of time $t=t_1$ when the current pulse is switched off, the potential value drops suddenly to a value equivalent to ΔIR_c (IR drop) and starts decaying exponentially.

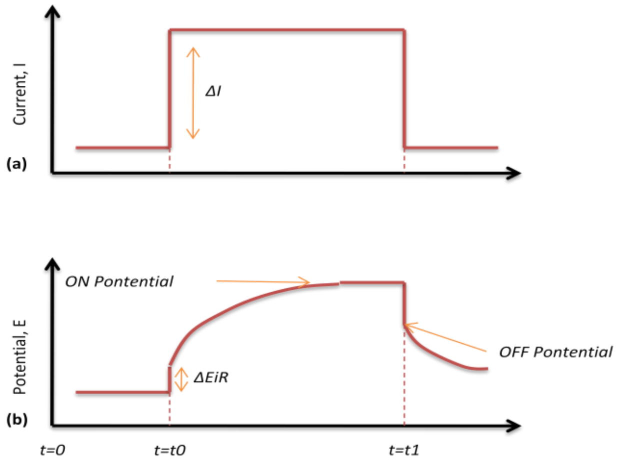


Figure 34 Nature of potential transient of steel in concrete for a galvanostatic current pulse: (a) current input, (b) potential transient for corroding steel.

4.5.1 Experimental Set-Up.

All the samples that were used in this series of tests have been prepared as was described in the paragraph 4.1. Samples Preparation.

In order to be able to see how every metal and every pretreatment reacts to this type of technique we decided to repeat the test on the same exposed area for five times.

In between a test and the following we ran one hour length galvanostatic test.

4.5.1.1 Test Parameters.

IMPULSE TEST	
Segment 1	
Step Time	60 s
Amplitude	50 µA
Segment 2	
Step Time	10 ms
Amplitude	100 µA
Time per point	5 µs
№ of points	2000

Table 5 Galvanostatic pulse test parameters.

GALVANOSTATIC TEST	
Segment 1	
Step time	3600 s
Amplitude	50 µA
Time per point	1,2 s
№ of points	3000

Table 6 Galvanostatic test parameters.

As we described in Table 5 all the pulse test started with a first segment where the current was kept constant for one minute and after that a single electric pulse was given to the sample. The only segment recorded in all tests was the second one representing the pulse.

We did also recorded all the galvanostatic tests and the results will be shown in the following paragraphs even if the attention in this type of analysis was focused on the pulses. In fact those galvanostatic tests were considered functional to highlight the shifting of the pulse curves over time.

Once this characterization was done using these standard test parameters we decided, for few samples, to register the results of a single pulse after 15 hours of exposure. The parameters for this type of analysis are shown in the next table.

IMPULSE TEST	
Segment 1	
Step Time	54000 s
Amplitude	50 µA

Segment 2	
Step Time	10 ms
Amplitude	100 µA
Time per point	5 µs
№ of points	2000

Table 7 Galvanostatic pulse test parameters (15 hours).

4.5.1.2 The Test Cell and Measuring Instrument.

For the one hour galvanostatic test the cell setup has always been the one described in the paragraph 4.2 Electrochemical Cell Set-Up.

A different cell setup was then chosen for the impulse tests. The three electrodes system was still kept but in this case the platinum mesh was used as reference electrode while a small piece of carbon steel play the role of counter electrode. The sample to be tested has been kept as working electrode.

The instrument used in this series of test was the Amel System 5000.

Figure 35 AMEL System 5000.

5 Results.

5 Results.

Before describing in detail the results that will be presented in this chapter it is important that the reader understands the way the results are displayed. The experimental procedure was divided since the beginning in the analysis of samples mainly divided of two different kinds, the first group of samples without paint, and the second one involving samples with paint ENABLE.

As mentioned before, the purpose of study of the present thesis work is limited to electrochemical assessments to evaluate the corrosion rate, which include: Potentiodynamic, cyclic voltammetry, galvanostatic pulse and impedance tests.

The reader will notice in the following pages that in the first part of the results will be shown just schematic representations of the changes according to the test that was done and the different conditions, giving in this way a better understanding to the reader of the theoretical results that are shown in the comparison sub-part of every test analysis.

5.1 NO Paint.

The polarization scan test ran during the experimental part of the present thesis work where from the Anodic scan type.

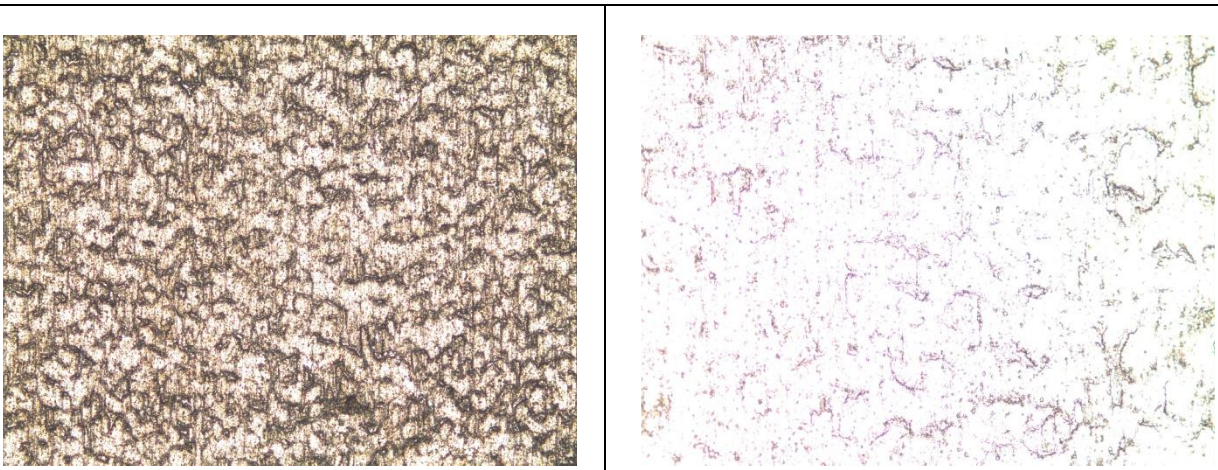
A given polarization scan may have some but not necessarily all, of the features described below. In addition, other features may also present not detailed here. In order to completely understand a system, knowledge of the potential anodic reactions which may take place is essential. A schematic anodic polarization curve as can be seen in Figure 38 where is shown the theoretical anodic polarization scan, the scan starts from point 1 and progress in the positive (potential) direction until termination at point 2. There is a number of notable features on the curve. The open circuit or rest potential is located at point A, at this potential the sum of the anodic and cathodic reaction rates on the electrode surface is zero. Giving as a result, the measured currents which must be applied to achieve the desired level of polarization. As the potential increases, we move into region B, called active region. In this region, metal oxidation is the dominant reaction taking place. Point C is known as the passivation potential, and as the potential increases above the value, the current density is seen to decrease (region D) until a low, passive current density is achieved (Passive region–Region E).

Once the potential reached a sufficiently positive value (Point f, sometimes termed the breakaway potential) the applied current rapidly increases (region G). This increase may be due to a number of phenomena, depending on the alloy/environment combination. For some systems (e.g., aluminum alloys in salt water) this sudden increase in current may be pitting (localized breakdown of passivity), while for others it may be transpassive dissolution. For some alloys, typically those with a very protective oxide, such as cobalt, the sudden increase in current is due to oxygen evolution.

5.1.1 Potentiodynamic Test Results.

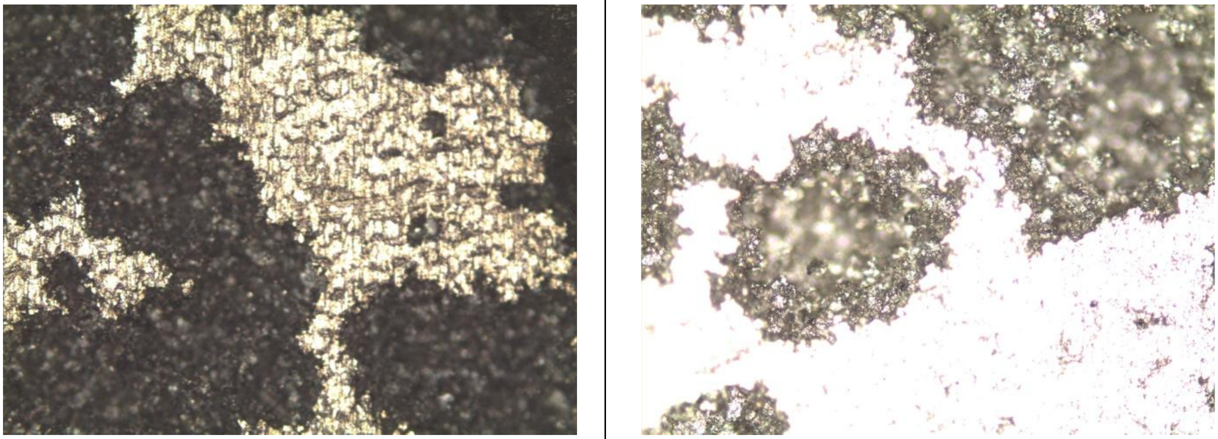
Before showing the potentiodynamic curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for each pretreatment condition. As a general observation, important degradation of the surface in terms of morphology change and formation of corrosion products can be detected.

5.1.1.1 No Pretreatment.



Microscopic image 50x (Aluminum, No Pretreatment, No Paint). Before Potentiodynamic test.

Microscopic image 100x (Aluminum, No Pretreatment, No Paint). Before Potentiodynamic test.

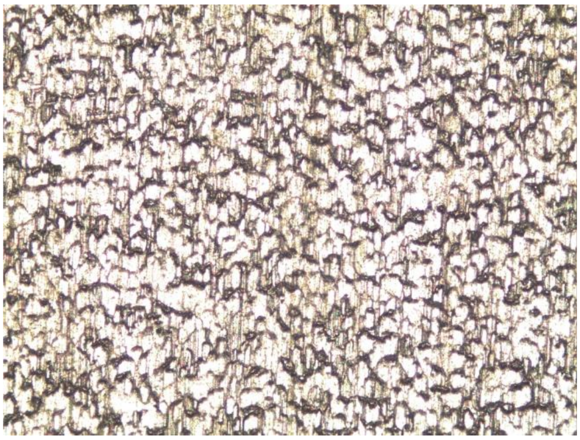


Microscopic image 50x (Aluminum, No Pretreatment, No Paint). After Potentiodynamic test Without Nitrogen.

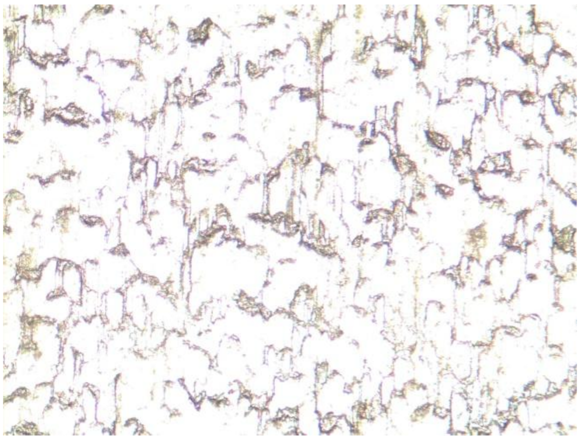
Microscopic image 100x (Aluminum, No Pretreatment, No Paint). After Potentiodynamic test Without Nitrogen.

Figure 36 Comparison of microscopic images of Aluminum, No pretreatment and No paint, before and after Potentiodynamic test.

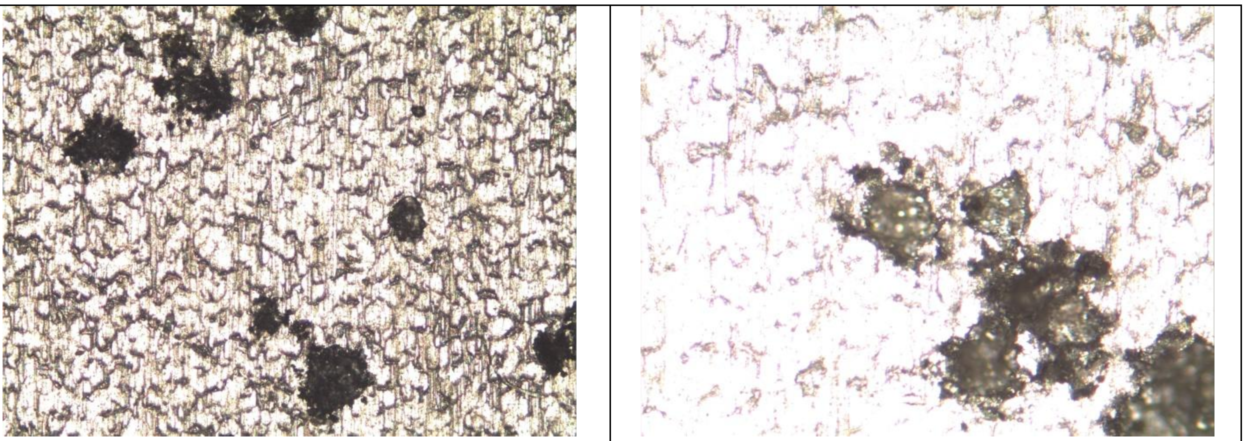
5.1.1.2 ZEC 888.



Microscopic image 50x (Aluminum, ZnPh, No Paint). Before Potentiodynamic test.



Microscopic image 100x (Aluminum, ZnPh, No Paint). Before Potentiodynamic test.



Microscopic image 50x (Aluminum, ZnPh, No Paint).
After Potentiodynamic test Without Nitrogen.

Microscopic image 100x (Aluminum, ZnPh, No Paint).
After Potentiodynamic test Without Nitrogen.

Figure 37 Comparison of microscopic images of Aluminum, ZEC 888 pretreatment and No paint, before and after Potentiodynamic test.

5.1.1.3 Comparison.

As mentioned in 5.1.1., the following image represents the theoretical anodic polarization scan, that as will be observed by the reader, in the graphics obtained during the experimental research, not all of the parts are present, since in the test parameters the potential was limited to 1V, because the active area of the plot and the beginning of the passivation area were important for this case of study; since in the active region is where metal oxidation is the dominant reaction taking place.

The comparison results are based in two different test conditions for each sample without paint and with ZEC 888 pretreatment. In the first part it will be described the behavior of the samples in a solution where the oxygen had been eliminated, as in the second the aqueous environment consist in the regular solution of 3.5%w of NaCl.

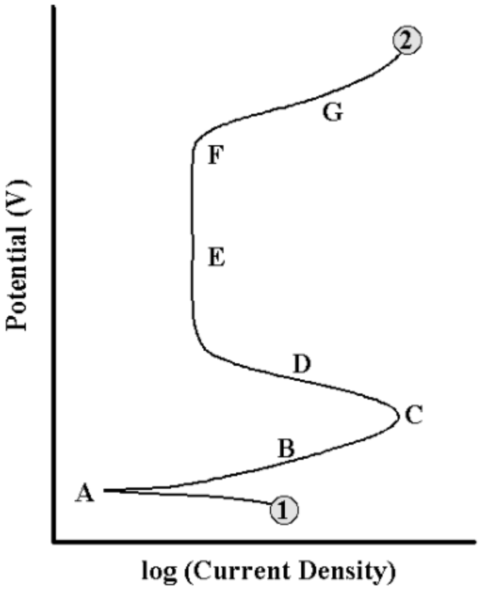
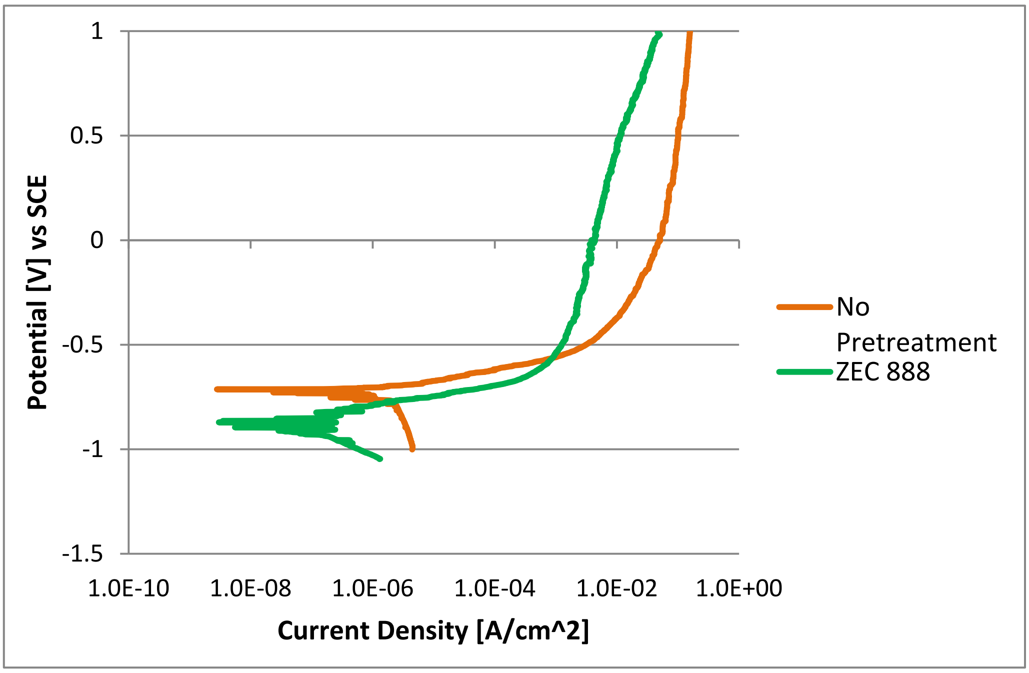


Figure 38 The theoretical anodic polarization scan.

5.1.1.3.1 With Nitrogen.

Regarding to the behavior of Aluminum with ZEC 888 pretreatment after potentiodynamic tests ran without paint. In this first part will be described the behavior of the samples in a solution where the oxygen had been eliminated with the addition of Nitrogen to the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation.

As can be noticed in Graph 1 there is a difference in the behavior of both cases, the starting scan point in the current density axis and the progress in the positive potential. As a second difference in the current density axis exists at the open circuit or rest potential point, and we can see that only the sample with ZEC 888 pretreatment is lower than -1V and it also shows a lower corrosion current density.



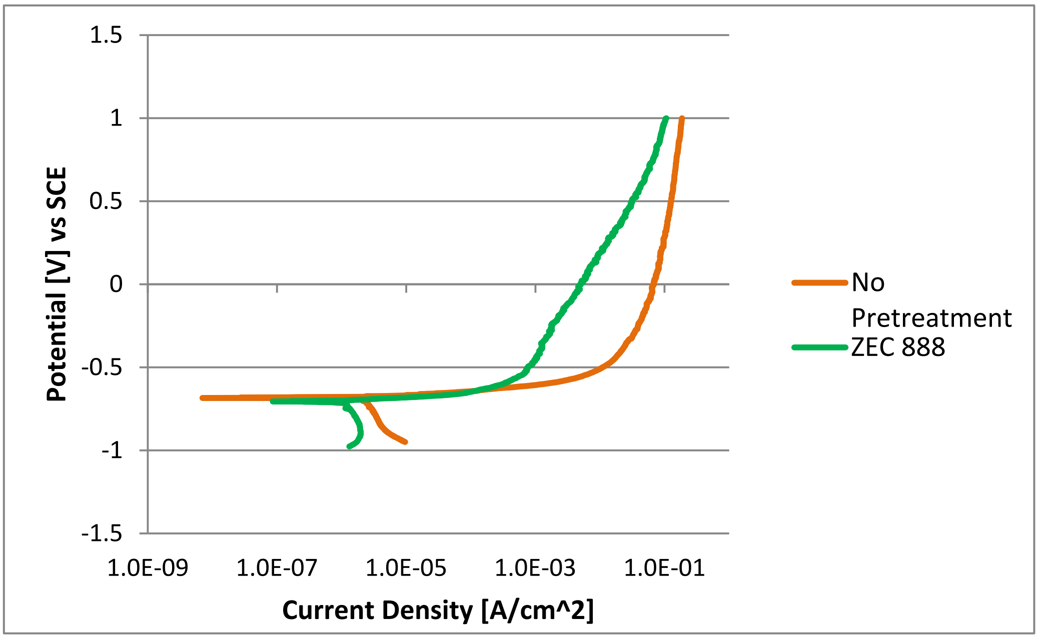
Graph 1 Comparison of the results obtained in the Potentiodynamic test for Aluminum, No paint, with ZEC 888 pretreatment in the surface with Nitrogen in the solution.

5.1.1.3.2 Without Nitrogen.

Regarding to the behavior of Aluminum with ZEC 888 pretreatment after potentiodynamic tests ran without paint. In this part will be described the behavior of the samples in a solution where the oxygen was present in to the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation.

As can be noticed in Graph 2 the behavior is different in both cases, the starting scan point in the current density axis and the progress in the potential are different. A second difference in the current density axis exists at the open circuit or rest potential point.

In a final comparison comment for this test, it can be noticed that under the present conditions, (No paint, without Nitrogen) the ZEC 888 pretreatment shows a good behavior against corrosion, since it shows the lowest corrosion current density.



Graph 2 Comparison of the results obtained after Potentiodynamic test for Aluminum, No paint, with ZEC 888 pretreatment in the surface without Nitrogen in the solution.

5.1.2 Cyclic Voltammetry Test Results.

Cyclic voltammetry provides both qualitative and quantitative information as well as a fast and reliable characterization tool. The important parameters for a cyclic voltammogram are the peak potentials and peak currents, which are measured using the Peak Parameters operation. If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be reversible.

In this case the voltage is swept between two values at a fixed rate, however now when the voltage reaches 1V the scan is reversed and the voltage is swept back to -1.5 V for this case of study, where the scan rate was 100mV/s as mention in the point 4.4.1.1 Test Parameters.

Before showing the cyclic voltammetry curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for each condition. As a general observation, a degradation of the surface in terms of morphology change and formation of corrosion products can be detected.

5.1.2.1 No Pretreatment.

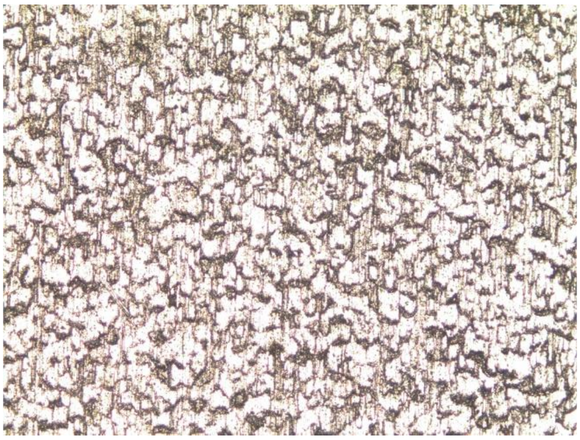
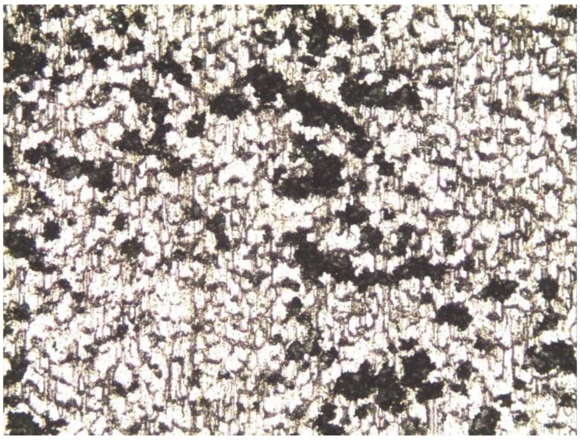
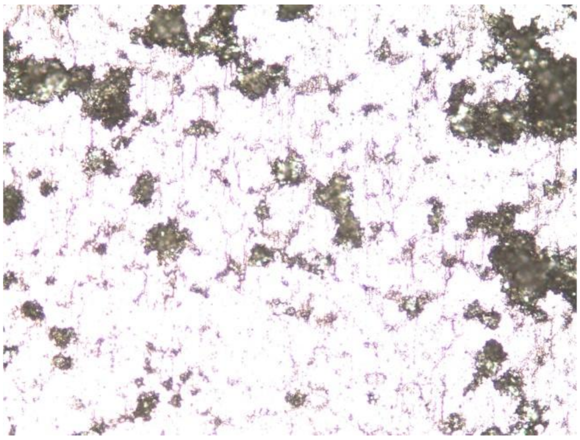
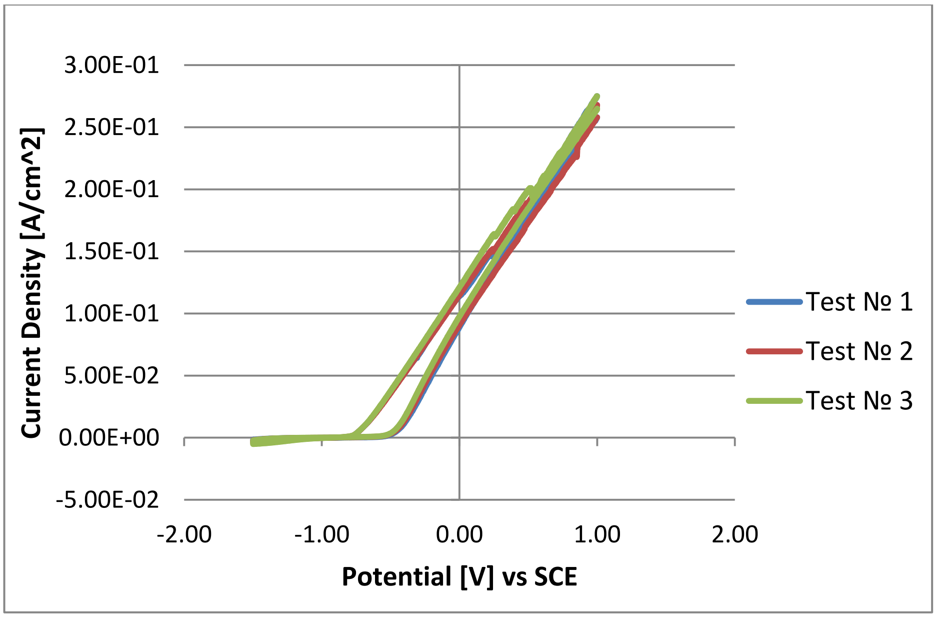
 Microscopic image 50x (Aluminum, No Pretreatment, No Paint). Before CV test.	 Microscopic image 100x (Aluminum, No Pretreatment, No Paint). Before CV test.
 Microscopic image 50x (Aluminum, No Pretreatment, No Paint). After CV test.	 Microscopic image 100x (Aluminum, No Pretreatment, No Paint). After CV test.

Figure 39 Comparison of microscopic images of Aluminum, No pretreatment and No paint, before and after CV test.



Graph 3 CV test representation of the 3 cycles for Aluminum, No pretreatment, No paint.

5.1.2.2 ZEC 888.

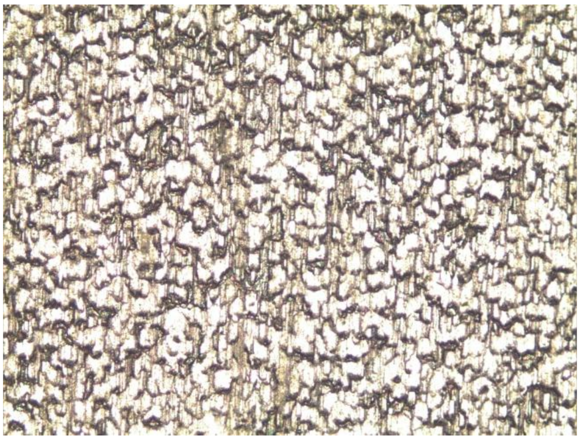
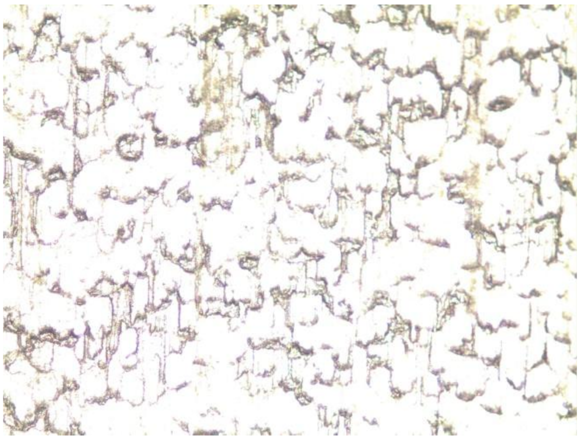
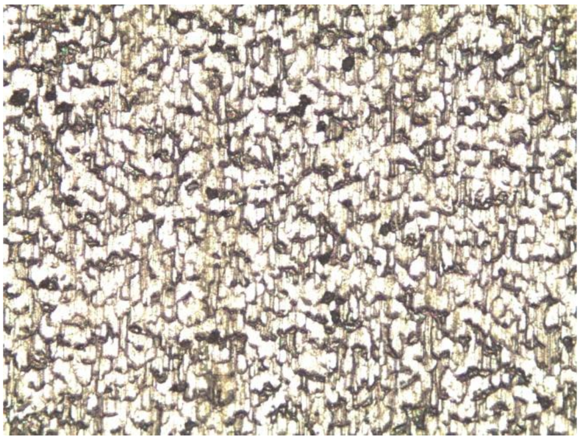
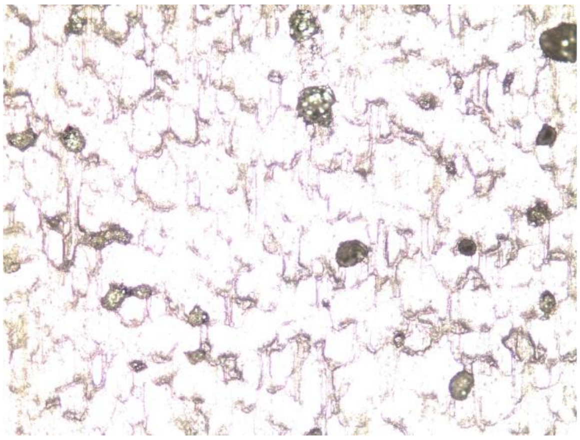
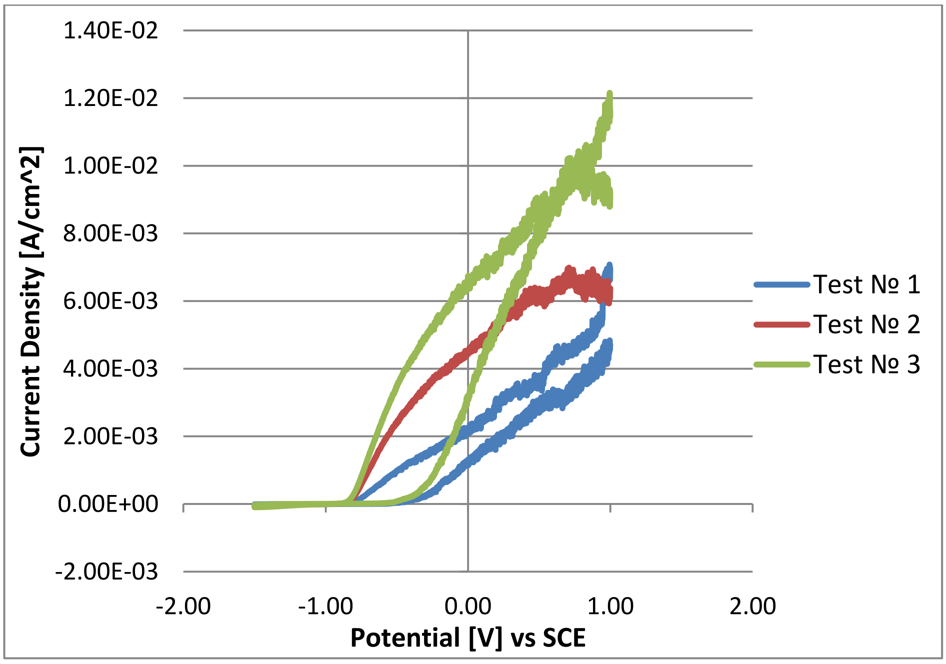
 Microscopic image 50x (Aluminum, ZEC 888, No Paint). Before CV test.	 Microscopic image 100x (Aluminum, ZEC 888, No Paint). Before CV test.
 Microscopic image 50x (Aluminum, ZEC 888, No Paint). After CV test.	 Microscopic image 100x (Aluminum, ZEC 888, No Paint). After CV test.

Figure 40 Comparison of microscopic images of Aluminum, ZEC 888 pretreatment and No paint, before and after CV test.

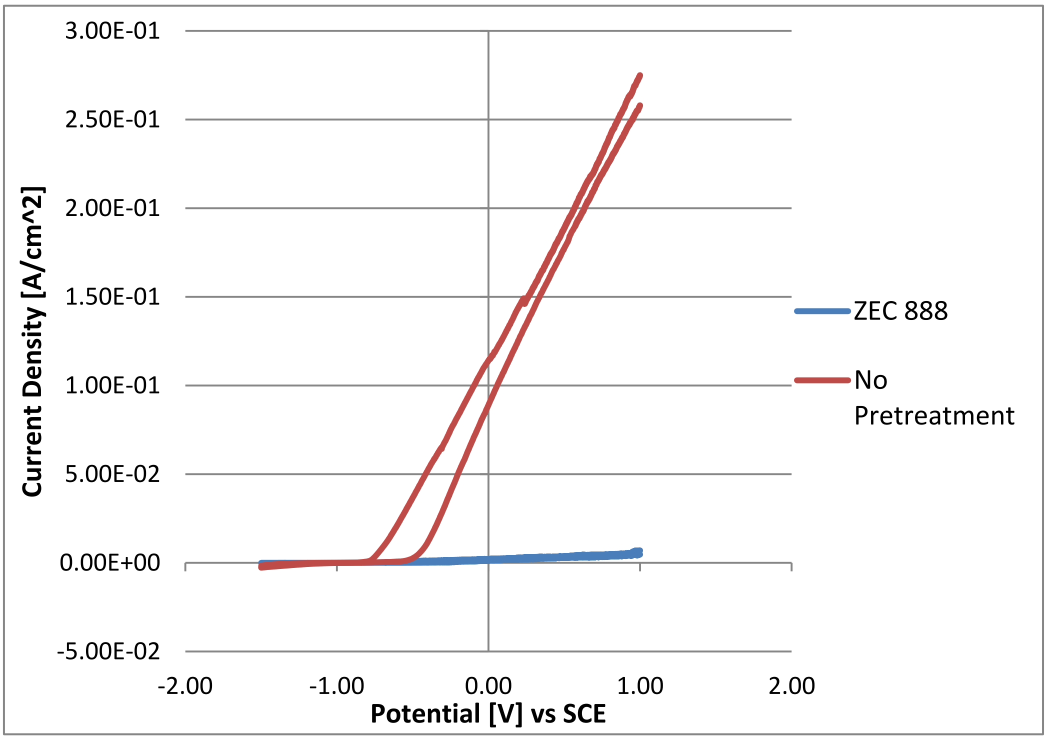


Graph 4 CV test representation of the 3 cycles for Aluminum, ZEC 888 pretreatment, No paint.

5.1.2.3 Comparison.

In the comparison Graph 5 for the first cycle of the exposed areas with and without pretreatment it can be observed that exist an increase in the scan rate behavior in the current density axis, having a lower density the ZEC 888 than the one without pretreatment.

Talking particularly about each sample, it can be described that there is no significant potential at which anodic reactions start for coated samples.



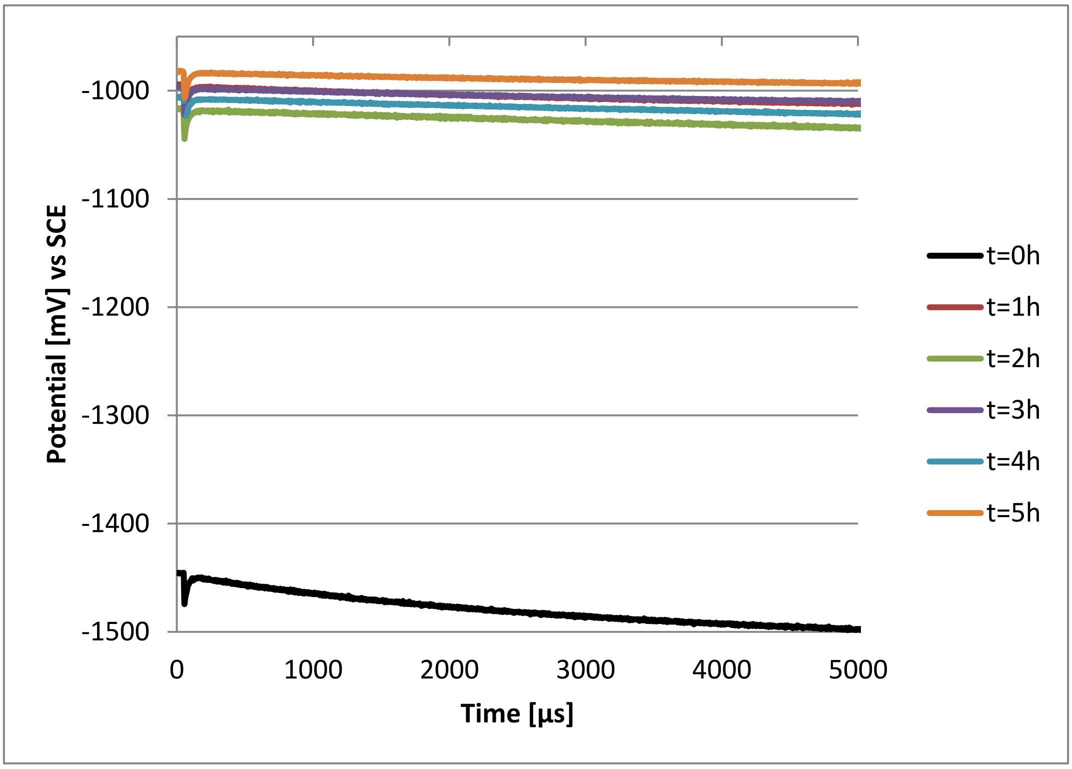
Graph 5 Comparison of the results obtained after CV test of Aluminum, with and without pretreatment, No paint, for the first cycle.

5.1.3 Galvanostatic Pulse Test Results.

In this next section the results of the galvanostatic pulse technique for HDG without paint are shown. The parameters used for this type are the one discussed in the paragraph 4.5 Galvanostatic and Galvanostatic Pulse Method. and in particular in the Table 5 Galvanostatic pulse test parameters.

As the electrical pulse is given the potential is recorded using an SCE reference electrode. The next graphs mean to show, for each pretreatment condition, the variation of the potential both versus the time at the shifting of the curves on the Y axis as the test is repeated every hour.

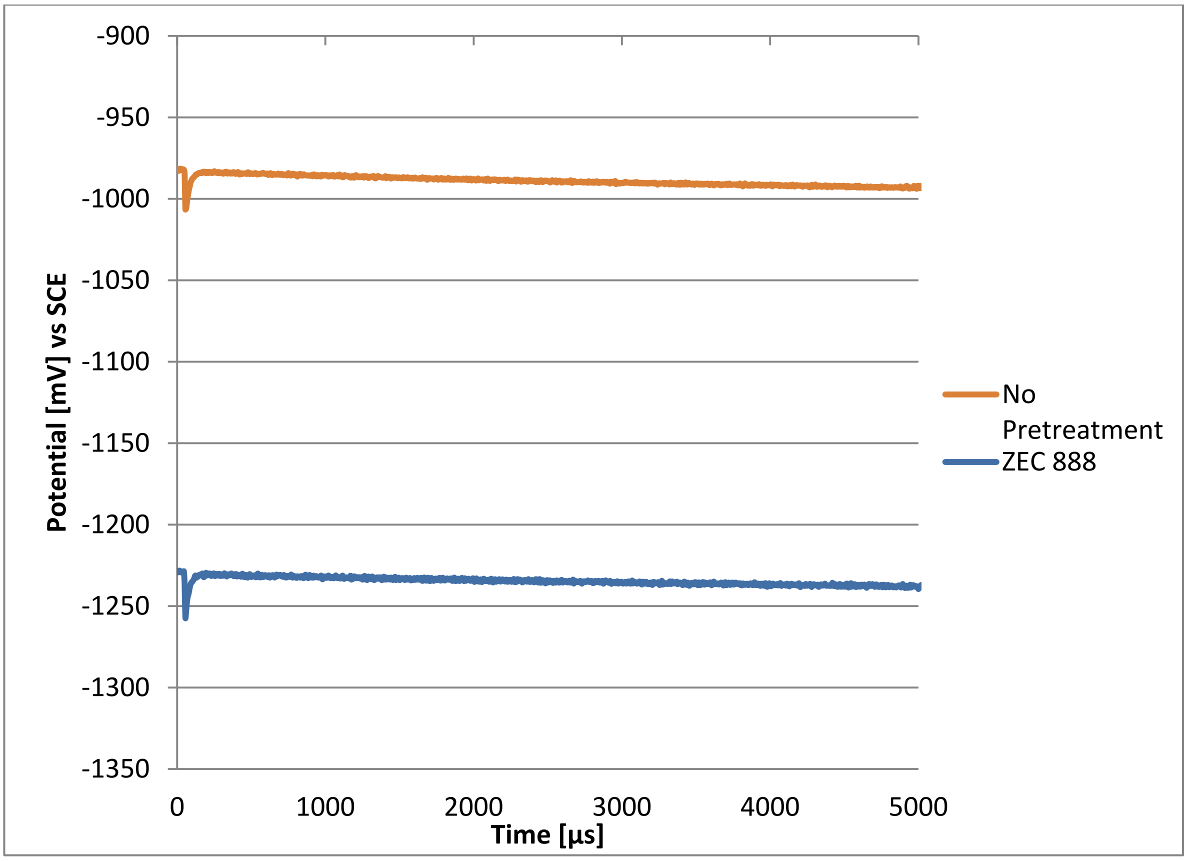
5.1.3.1 No Pretreatment.



Graph 6 Impulse test result for Aluminum without pretreatment and no paint, measured at different exposure times after Galvanostatic test.

5.1.3.2 Comparison.

In Graph 7 are reported the curves for the impulse test at time 5h of exposure for each condition. As it can be seen the curve for ZEC 888 pretreatment is located at a lower potential compared to the one for No pretreatment. In these conditions ZEC 888 acts better because it can offer a sort of cathodic protection to the substrate.



Graph 7 Impulse test comparison result for Aluminum with the different conditions without paint, measured after t=5h exposure after Galvanostatic test.

5.2 Paint ENABLE.

5.2.1 Potentiodynamic Test Results.

Before showing the potentiodynamic curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for the pretreatment condition. As a general observation it can be said it offers good adhesion for the paint and also acts well as protective barrier for the substrate itself.

5.2.1.1 *Without Scratch.*

5.2.1.1.1 ZEC 888.

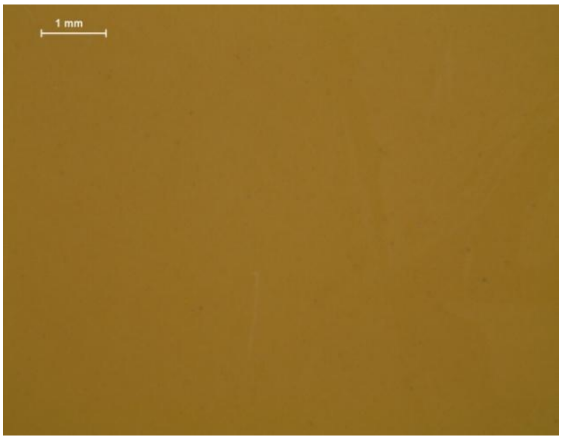
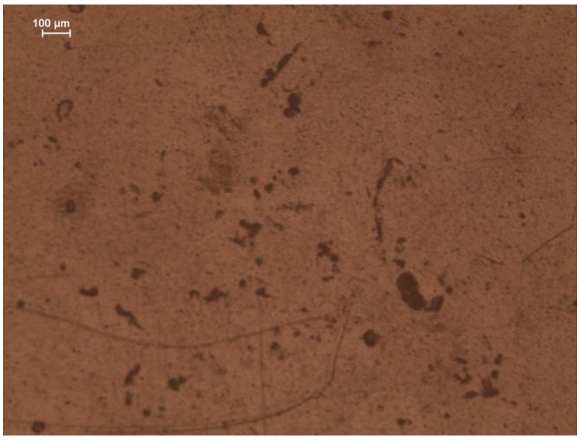
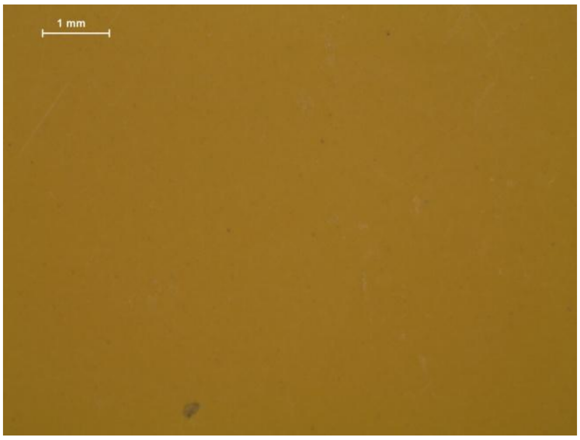
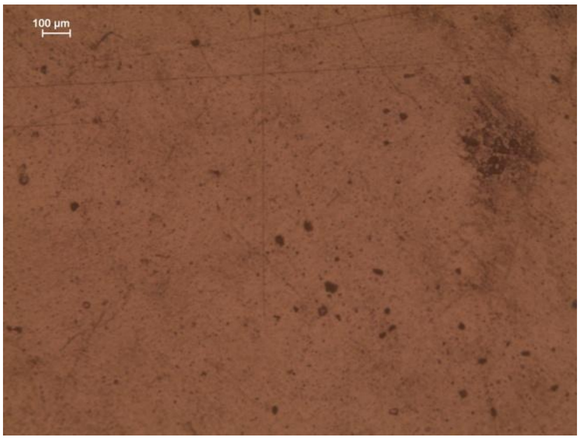
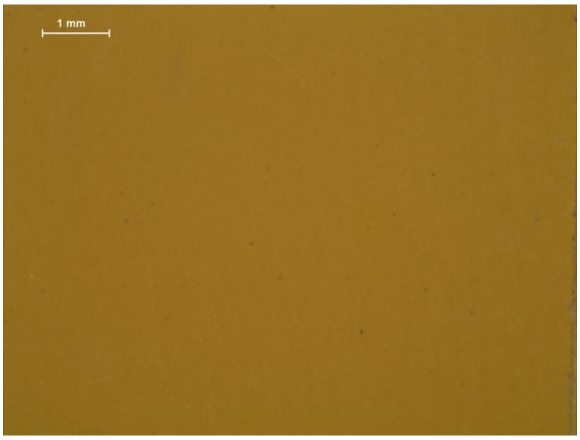
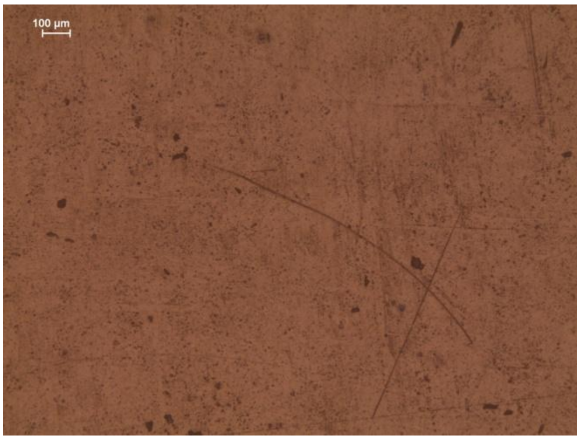
 **Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). Before Potentiodynamic test.**	 **Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). Before Potentiodynamic test.**
 **Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). After Potentiodynamic test With Nitrogen.**	 **Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). After Potentiodynamic test With Nitrogen.**
 **Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). After Potentiodynamic test Without Nitrogen.**	 **Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). After Potentiodynamic test Without Nitrogen.**

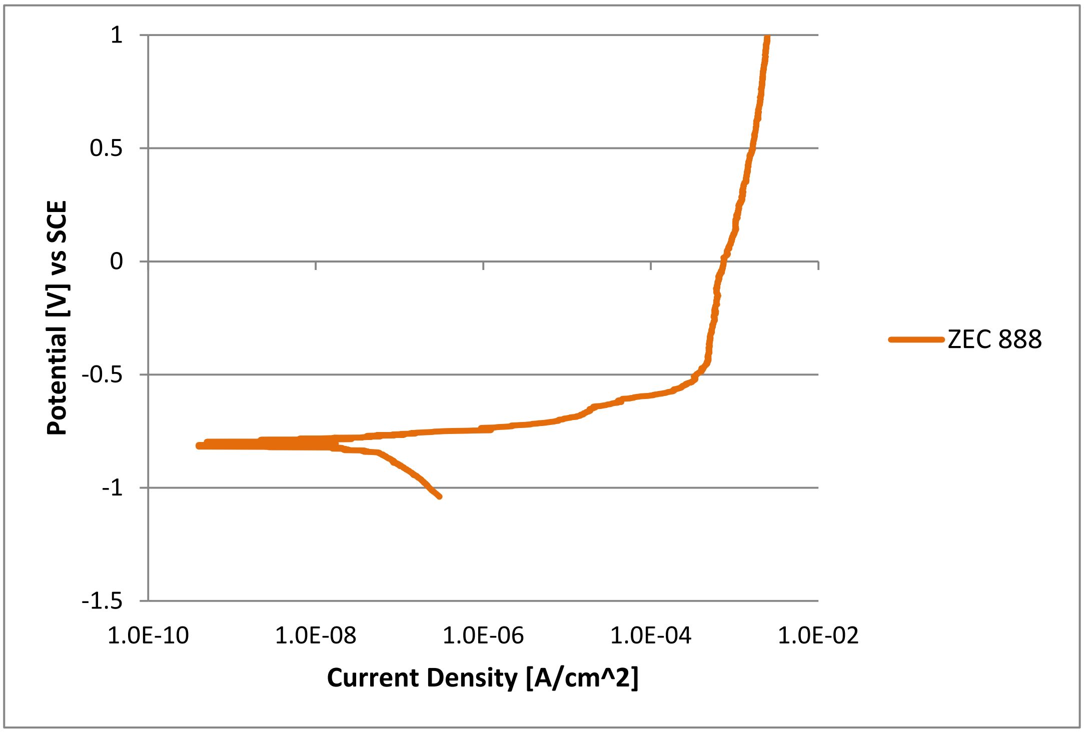
Figure 41 Comparison of microscopic images of Aluminum, ZEC 888 and paint ENABLE, before and after Potentiodynamic test.

5.2.1.1.1.1 With Nitrogen.

Regarding the behavior of Aluminum with ZEC 888 pretreatment after potentiodynamic tests ran with paint ENABLE on top of ZEC 888 pretreatment. In this first part will be described the behavior of the sample in a solution where the oxygen had been eliminated with the addition of Nitrogen to the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation.

As can be noticed in the Graph 8 the behavior is similar to the unpainted samples, the main difference that can be noticed is the smoothest flow of the plot line and the starting scan point in the current density axis and the progress in the positive potential.

In a final comparison comment for this test, it can be noticed that under the present conditions (Paint, with Nitrogen) the pretreatment shows the lowest corrosion current density as was expected, hence having a better behavior against corrosion.



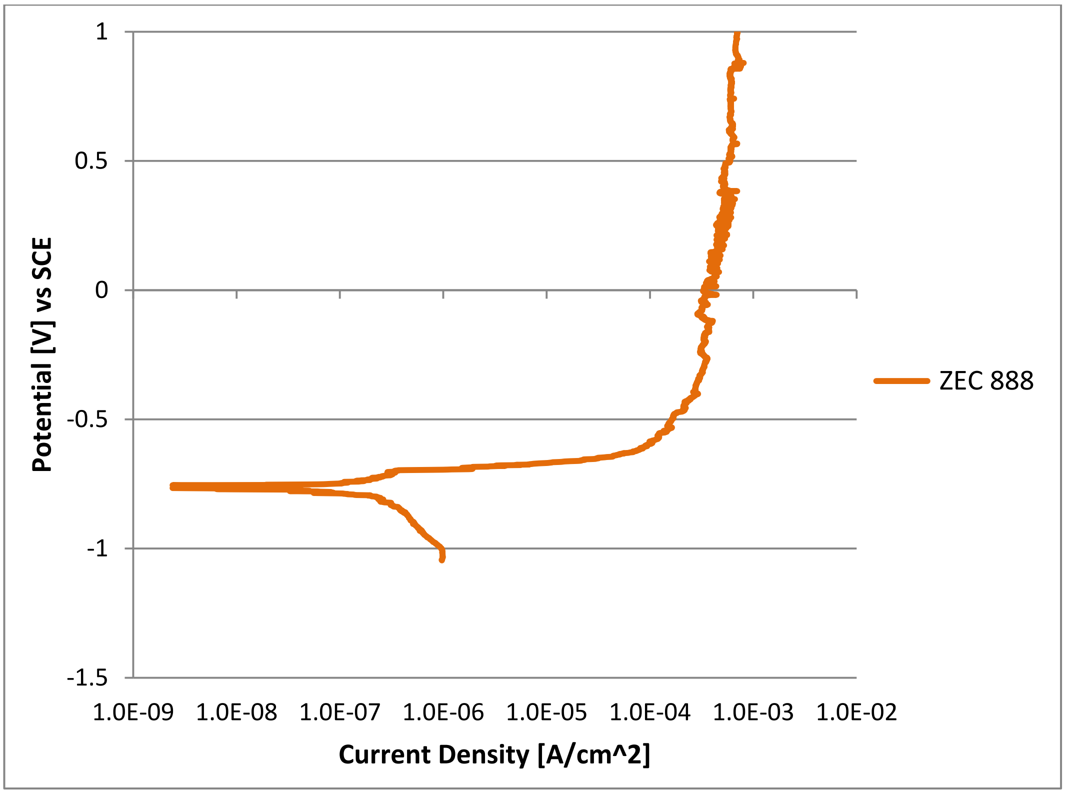
Graph 8 Results obtained in the Potentiodynamic test for Aluminum, paint ENABLE, with ZEC 888 pretreatment in the surface with Nitrogen in the solution.

5.2.1.1.1.2 Without Nitrogen.

Regarding to the behavior of Aluminum with ZEC 888 pretreatment after potentiodynamic tests ran with paint ENABLE. In this part will be described the behavior of the samples in a solution where the oxygen was present into the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation.

As can be notice in the Graph 9 the behavior is similar to the unpainted samples, the main difference that can be noticed is the smoothest flow of the plot line and the starting scan point in the current density axis and the progress in the positive potential.

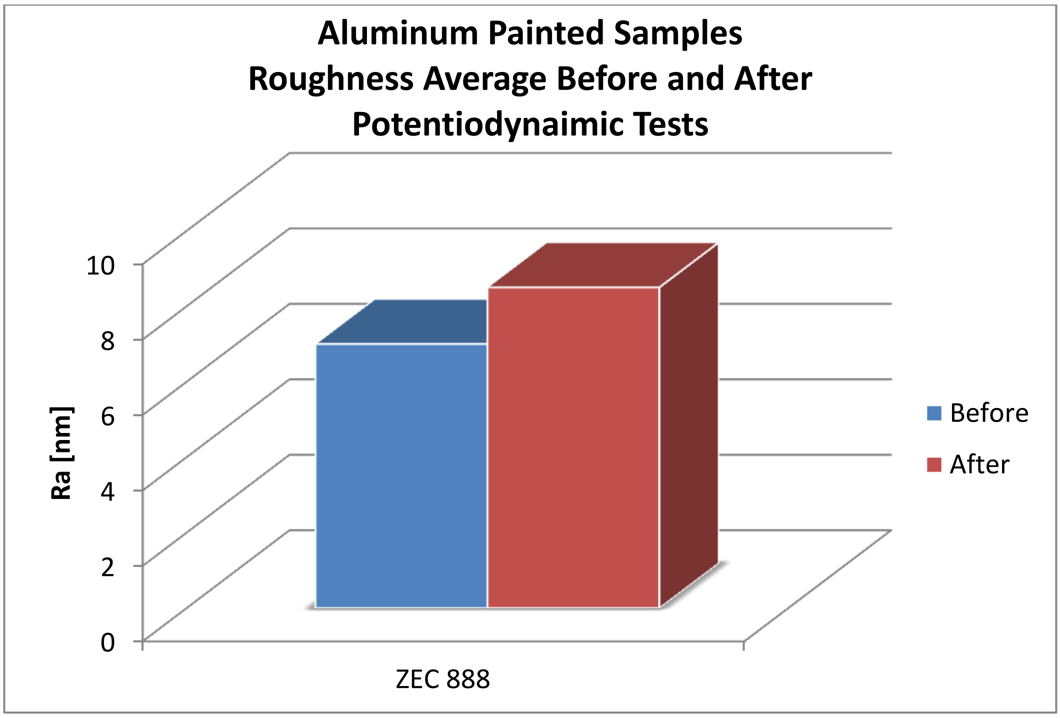
In a final comparison comment for this test, it can be noticed that under the present conditions (Paint, with Nitrogen) the pretreatment shows the lowest corrosion current density as was expected, hence having a better behavior against corrosion.



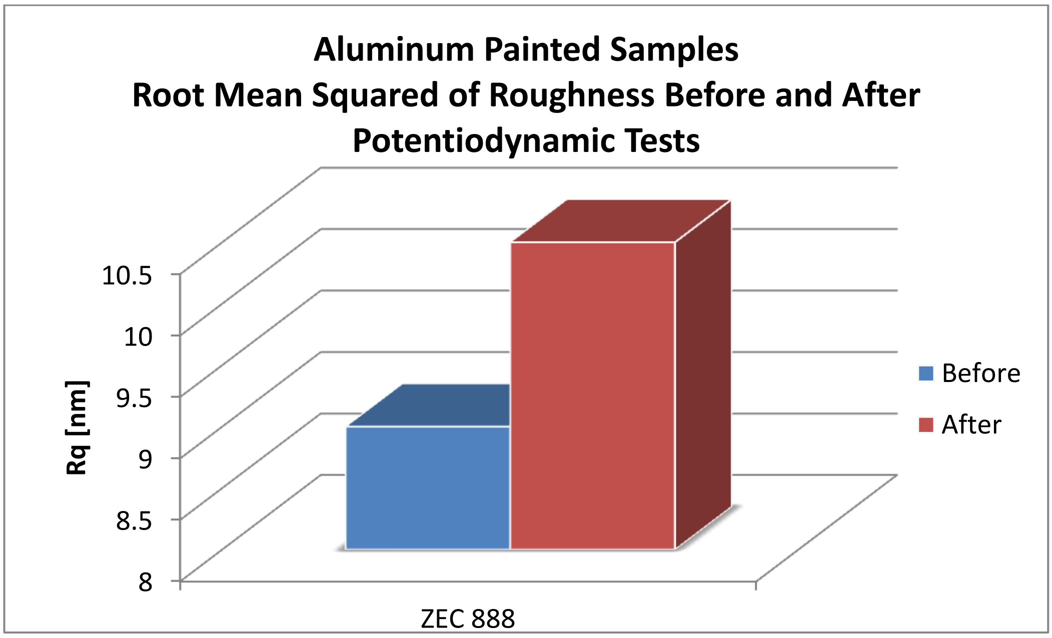
Graph 9 Comparison of the results obtained in the Potentiodynamic test for Aluminum, paint ENABLE, with ZEC 888 pretreatment in the surface without Nitrogen in the solution.

Being important information for this research, Roughness tests were run before and after the potentiodynamic tests, since the quality of machined surface is characterized by the accuracy of its manufacture with respect to the dimensions specified by the designer. Every machining operation, and in this specific case of study, the electrochemical tests ran in the surface of the samples leaves characteristic evidence on the surface. This evidence in the form of finely spaced micro irregularities. Each surface finishes and pretreatment operations impart a specific surface finish. This pattern is known as surface finish or surface roughness and can be measured by a surface profilometer which quantifies the surface roughness i.e. positive deviation from a datum plane (peak) or negative deviation from a datum plane (valley) as well as peaks per inch. The roughness is expressed in RMS (Root Mean Square) values for the present case of study, and the specific value obtained was 116 nm.

In Graph 10 and Graph 11, it can be observed the different behaviors for the samples with the ZEC 888 pretreatment before and after the mentioned potentiodynamic tests. As shown in Graph 10 the Roughness average value for the sample with the pretreatment shows how the value increases.



Graph 10 Comparison of Roughness average value before and after Potentiodynamic tests.



Graph 11 Comparison of the Root Mean Squared of Roughness value before and after Potentiodynamic tests.

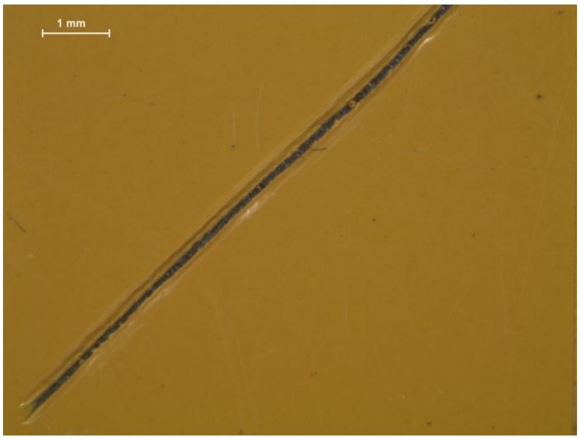
As shown in Graph 11 the Root Mean Squared of Roughness value changes, decreasing considerably.

5.2.1.2 With Scratch.

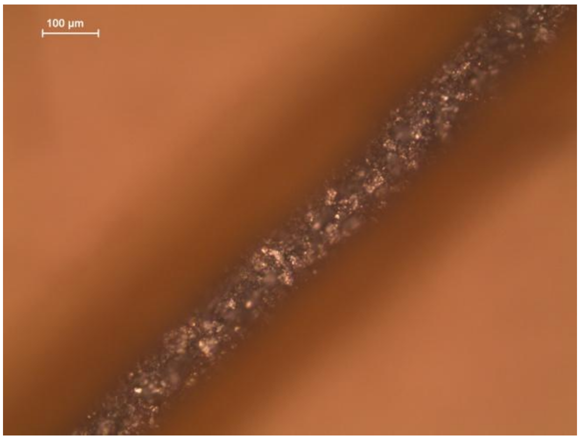
The following tests series include a scratch done on purpose, to evaluate the behavior of the pretreatment on top of the Aluminum sample while at the same time, it was evaluated the effectives of the painting, knowing that the final objective of the case of study will be used in the automotive industry.

The scratch images are now reported. Both before and after polarization test images are reported. In this case both optical and electronic microscope have been used. From the last one are also reported the composition spectra in the damaged areas.

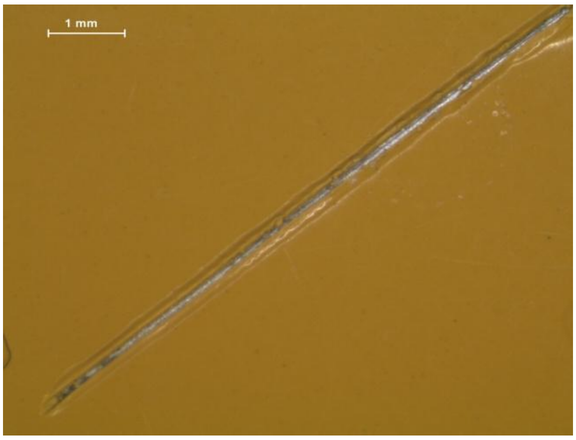
5.2.1.2.1 ZEC 888.



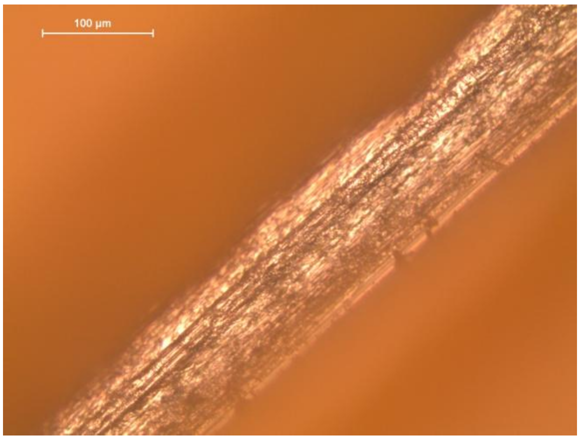
Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE, Scratched).
Before Potentiodynamic test.



Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE, Scratched).
Before Potentiodynamic test.



Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE, Scratched).
After Potentiodynamic test Without Nitrogen.



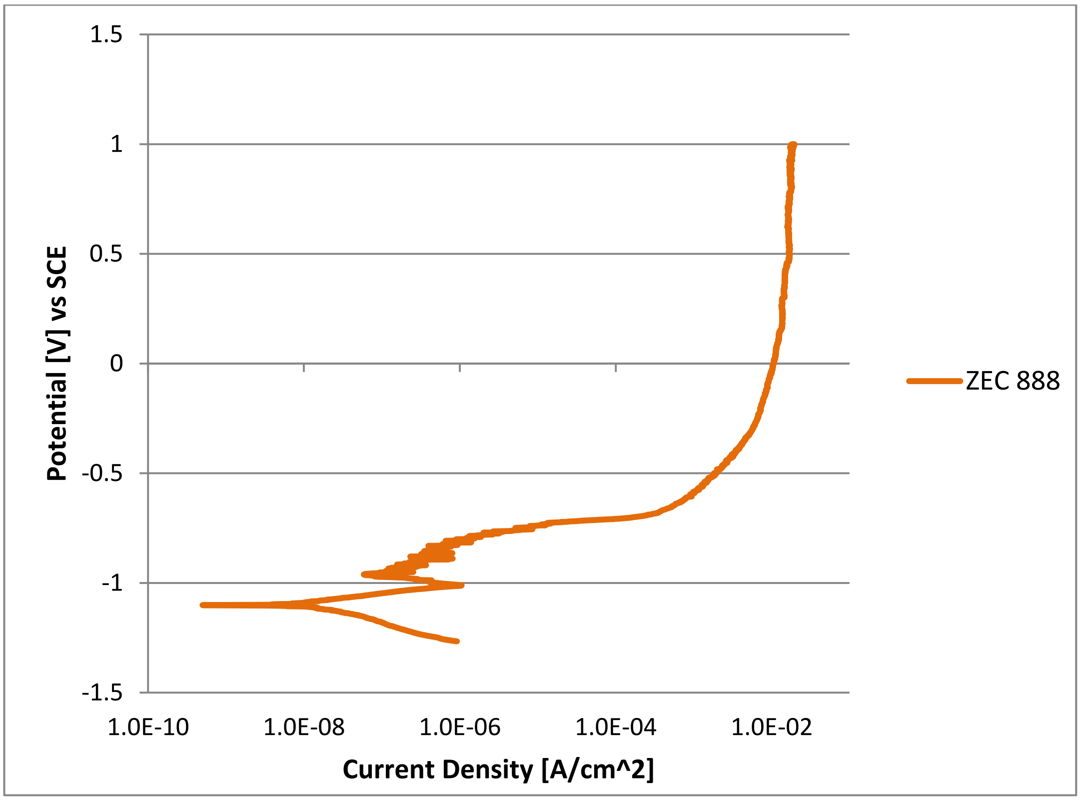
Microscopic image 200x (Aluminum, ZEC 888, Paint ENABLE, Scratched).
After Potentiodynamic test Without Nitrogen.

Figure 42 Comparison of microscopic images of Aluminum, ZEC 888 and paint ENABLE, with Scratch in the surface before and after Potentiodynamic test.

5.2.1.2.1.1 With Nitrogen.

Regarding to the behavior of Aluminum with ZEC 888 pretreatment after potentiodynamic tests ran with paint ENABLE. In this first part will be described the behavior of the samples in a solution where the oxygen had been eliminated with the addition of Nitrogen to the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation with a scratch in the surface.

As can be noticed in the Graph 12 there is a different behavior than on the painted sample without the scratch, there is a lower current density in the rest potential point for the scratched sample, then it shows another peak, though it presents lower potential; but even with the scratch it shows a lower current density than the unpainted samples, this might be due to the recovery feature of the ZEC 888 pretreatment.

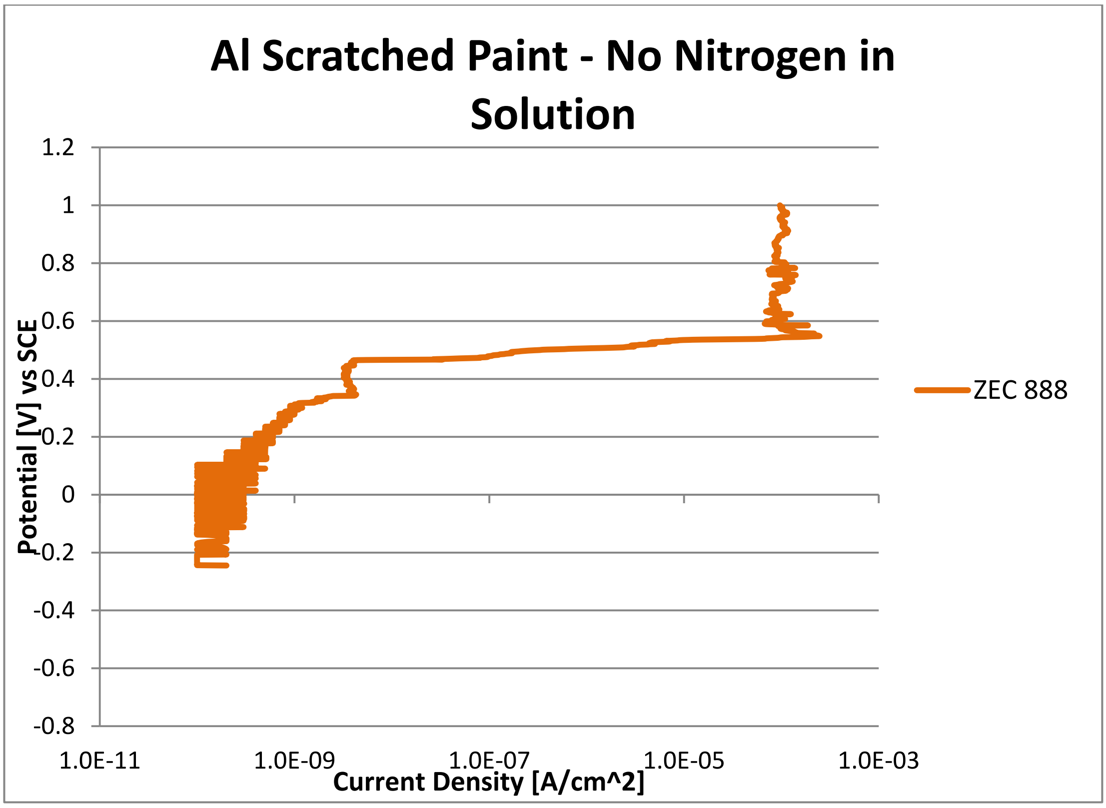


Graph 12 Results obtained in the Potentiodynamic test for Aluminum, paint ENABLE, Scratched with ZEC 888 pretreatment in the surface with Nitrogen in the solution.

5.2.1.2.1.2 Without Nitrogen.

Regarding to the behavior of HDG with the different pretreatments after potentiodynamic tests ran with paint ENABLE and in the different pretreatments. In this part will be described the behavior of the samples in a solution where the oxygen was present in to the aqueous solution of 3.5%w of NaCl during the exposure time of experimentation with a scratch in the surface.

As can be noticed in the Graph 13, difficulties in the measurements were detected when no nitrogen was used.



Graph 13 Results obtained in the Potentiodynamic test for Aluminum, paint ENABLE, Scratched with ZEC 888 pretreatment in the surface without Nitrogen in the solution.

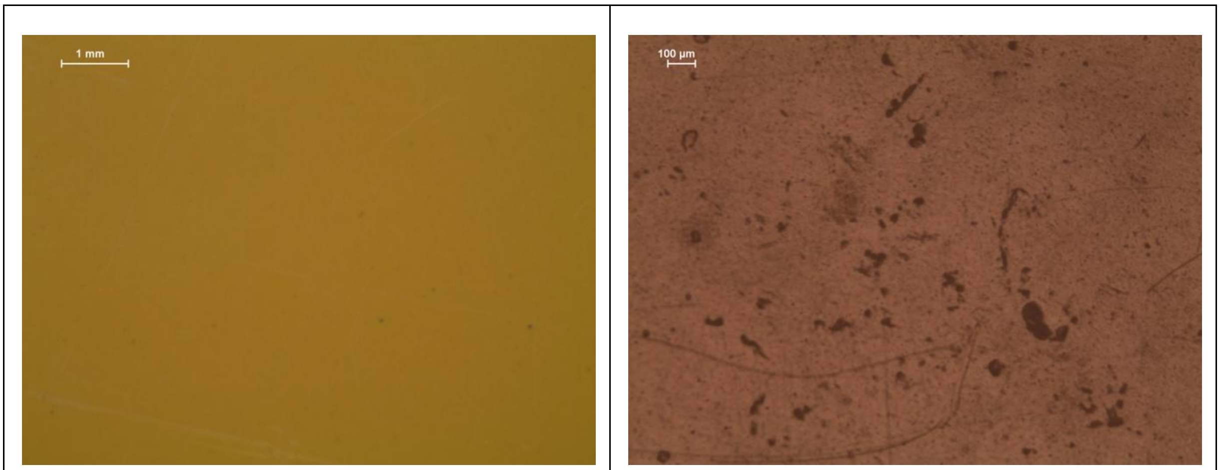
5.2.2 Ciclyc Voltammetry Test Results.

Before showing the cyclic voltammetry curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for each pretreatment condition. As a general observation, it is possible to say that there is not a significant change in terms of the paint color in every sample case. This might be due to the fact that the surface has been exposed for a little time in every electrochemical test.

For this type of test analysis, in this conditions (paint and without scratch), it can be implied that the pretreatment shows a defined anodic peak, which is increasing with each cycle, giving a good explanation that the pretreatment is protecting the surface.

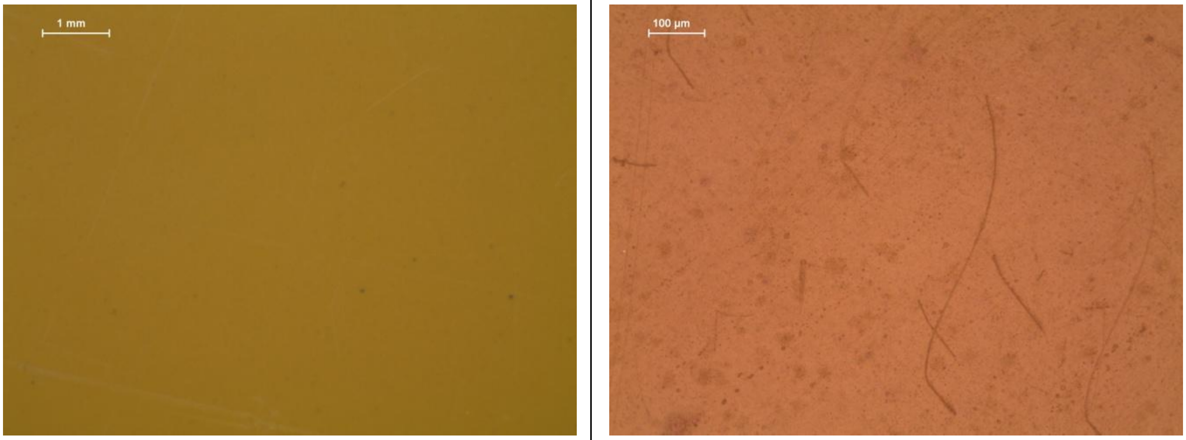
5.2.2.1 Without Scratch.

5.2.2.1.1 ZEC 888.



Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). Before CV test.

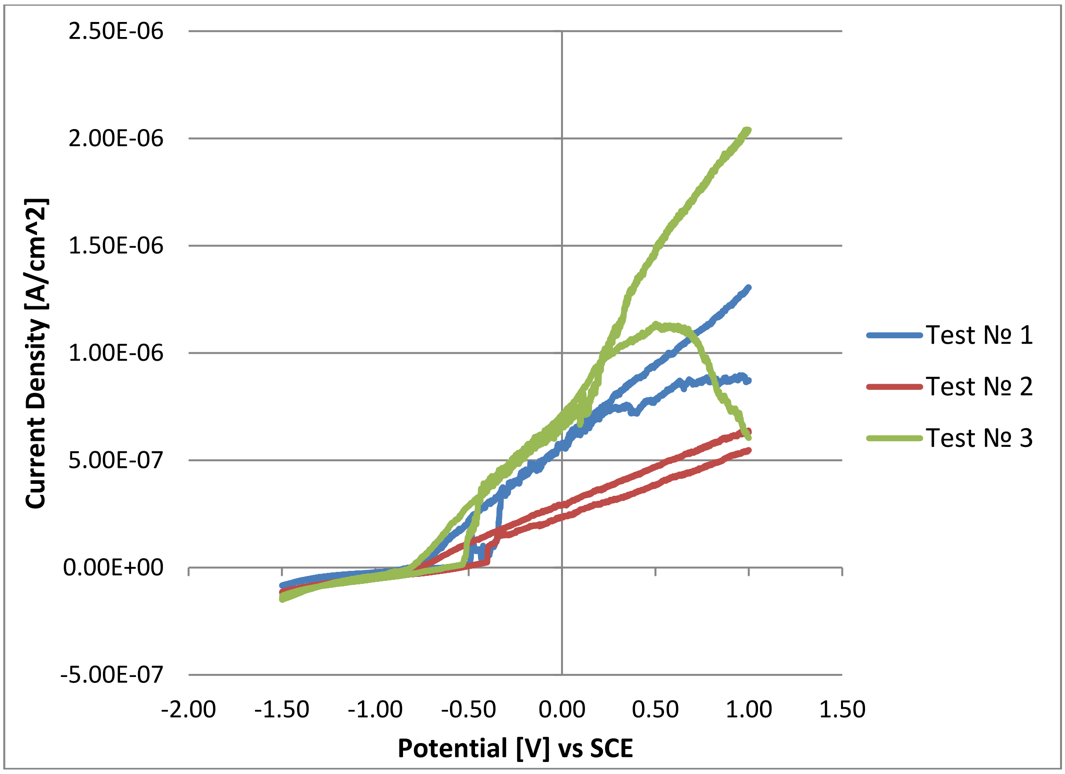
Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). Before CV test.



Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). After CV test.

Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). After CV test.

Figure 43 Comparison of microscopic images of Aluminum, ZEC 888 and paint ENABLE, before and after CV test.

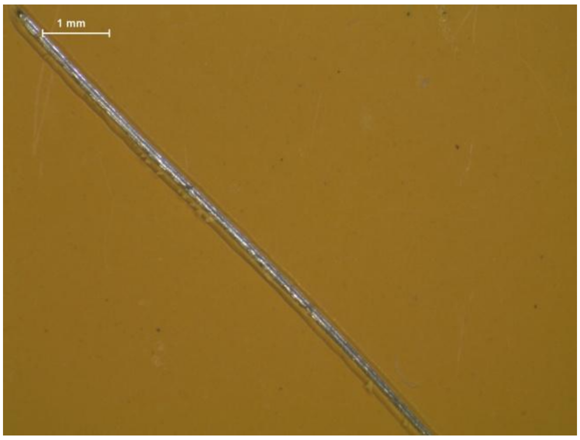
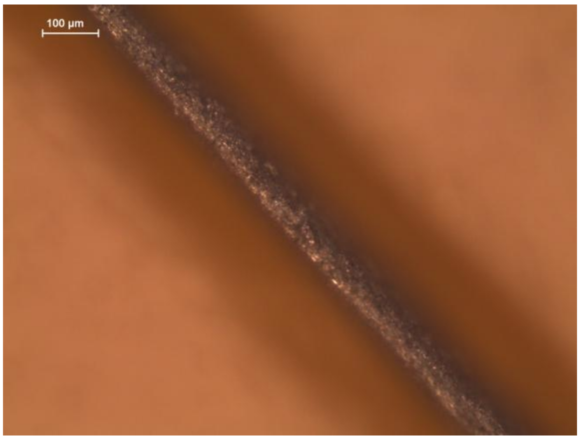


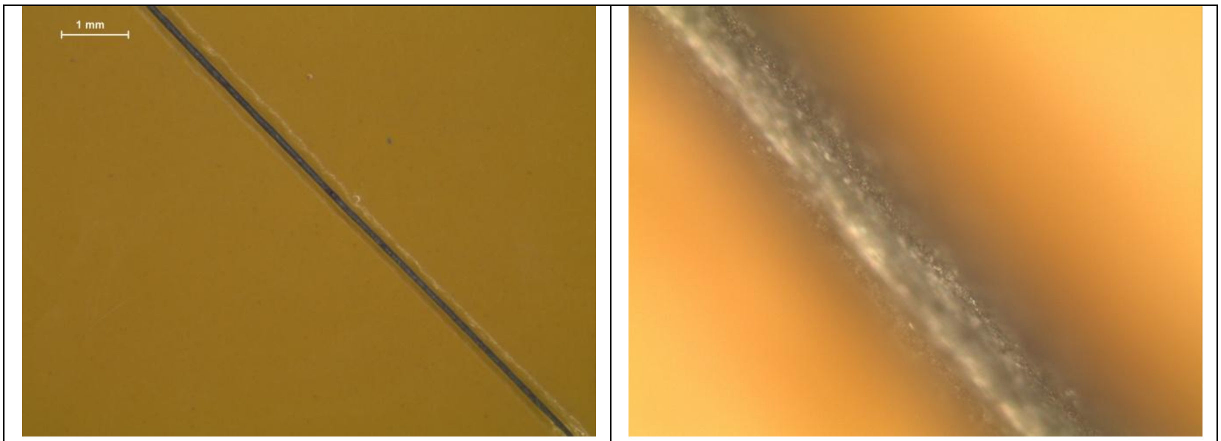
Graph 14 Results obtained after CV test of Aluminum, with ZEC 888 pretreatment, paint ENABLE.

5.2.2.2 With Scratch.

Before showing the cyclic voltammetry curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for each pretreatment condition.

5.2.2.2.1 ZEC 888.

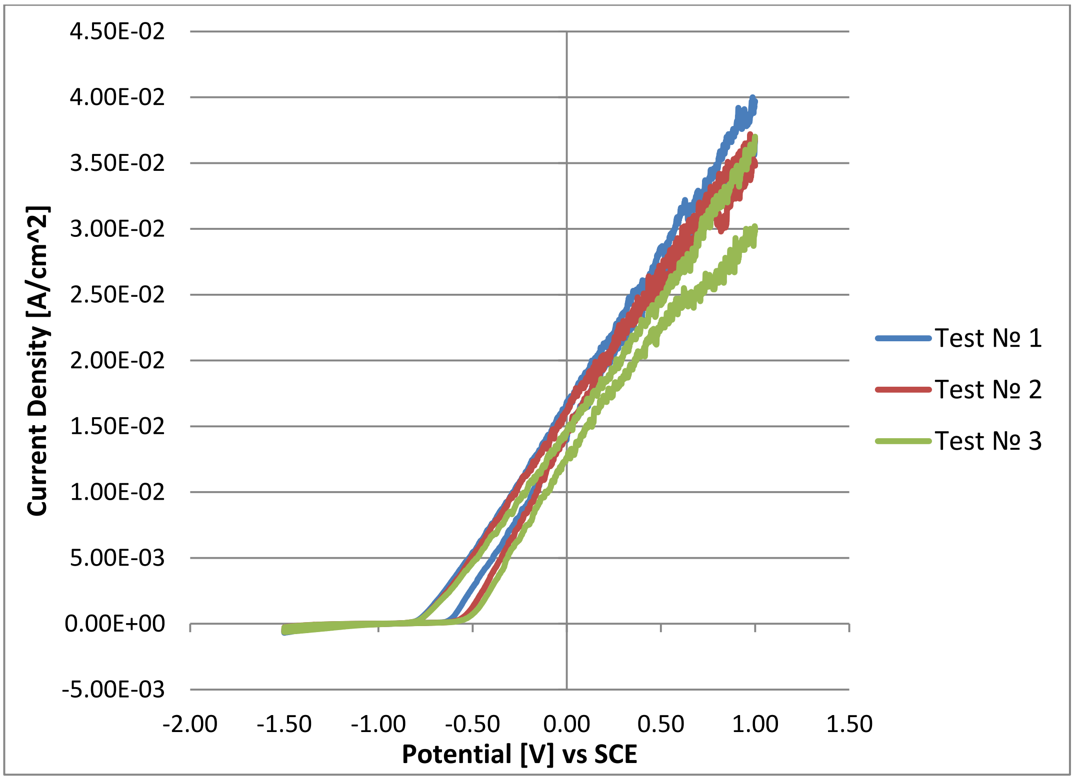
 **Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). Before CV test.**	 **Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE). Before CV test.**



Microscopic image 12x (Aluminum, ZEC 888x, Paint ENABLE, Scratched). After CV test.

Microscopic image 200x (Aluminum, ZEC 888, Paint ENABLE, Scratched). After CV test.

Figure 44 Comparison of microscopic images of Aluminum, ZEC 888, paint ENABLE and Scratched, before and after CV test.



Graph 15 Results obtained after CV test of Aluminum with ZEC 888, paint ENABLE and Scratched surface.

5.2.3 Galvanostatic Pulse Test Results.

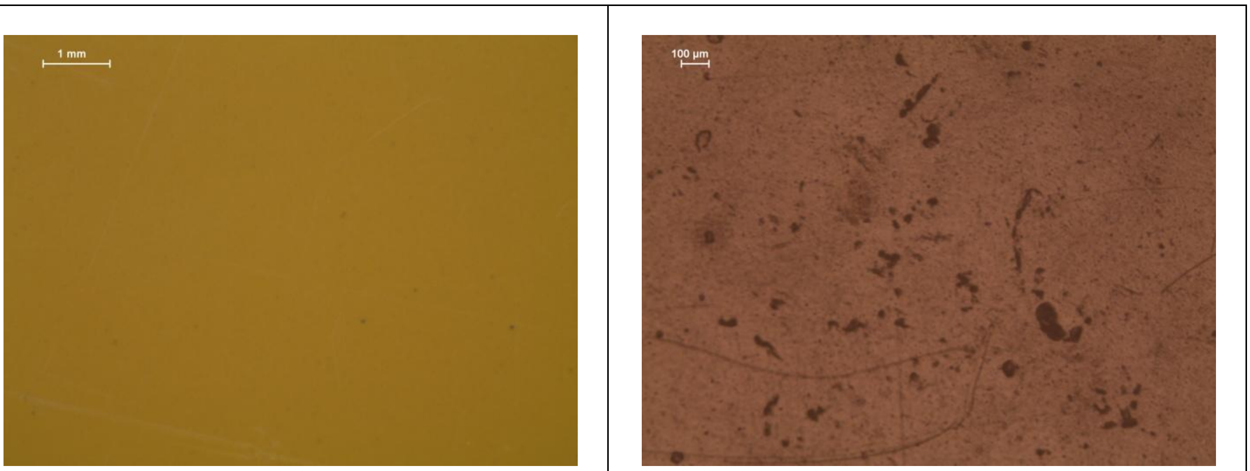
In this next section the results of the galvanostatic pulse technique for HDG with paint are shown. The parameters used for this type are those discussed in the paragraph 4.5 Galvanostatic and Galvanostatic Pulse Method. and in particular in the Table 5 Galvanostatic pulse test parameters.

As the electrical pulse is given, the potential is recorded using an SCE reference electrode. The next plots mean to show, for each condition, the variation of the potential both versus the time at the shifting of the curves on the Y axis as the test is repeated every hour.

5.2.3.1 Without Scratch.

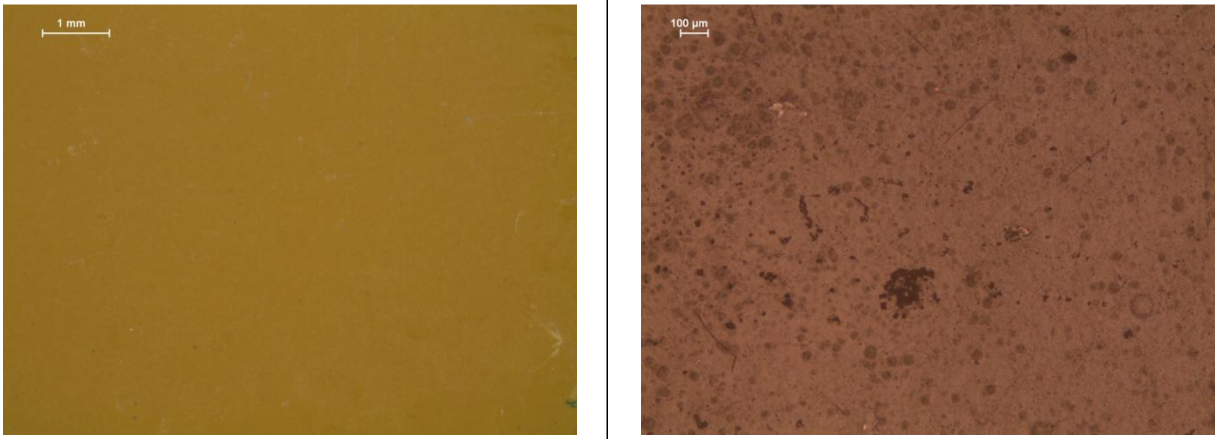
Before showing the pulse curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for ZEC 888 pretreatment.

5.2.3.1.1 ZEC 888.



Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). Before Galvanostatic pulse test.

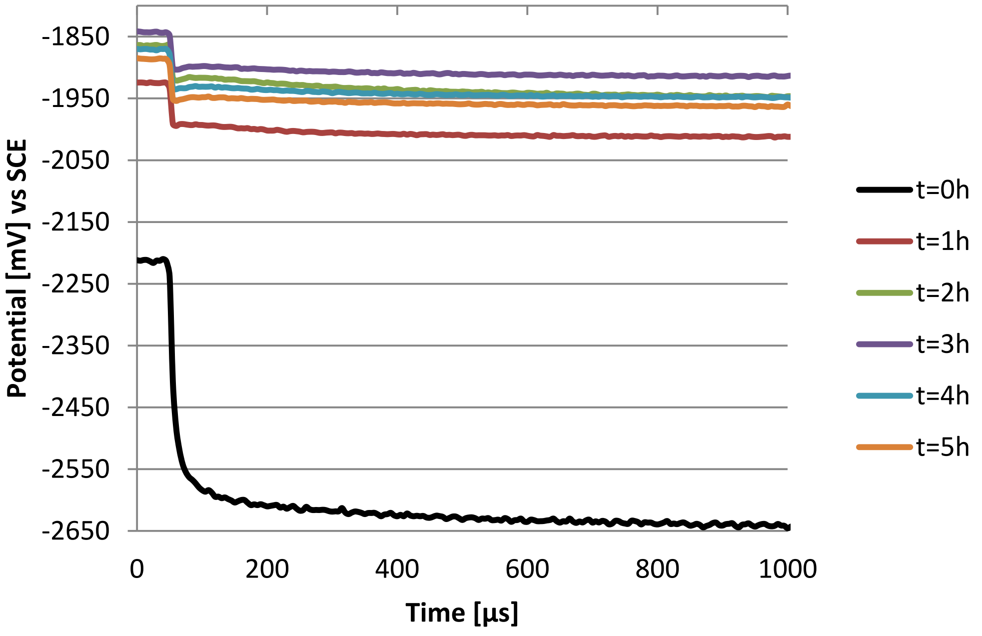
Microscopic image 100x (Aluminum, ZEC 888, Pain ENABLE). Before Galvanostatic pulse test.



Microscopic image 12x (Aluminum, ZEC 888, Paint ENABLE). After Galvanostatic pulse test.

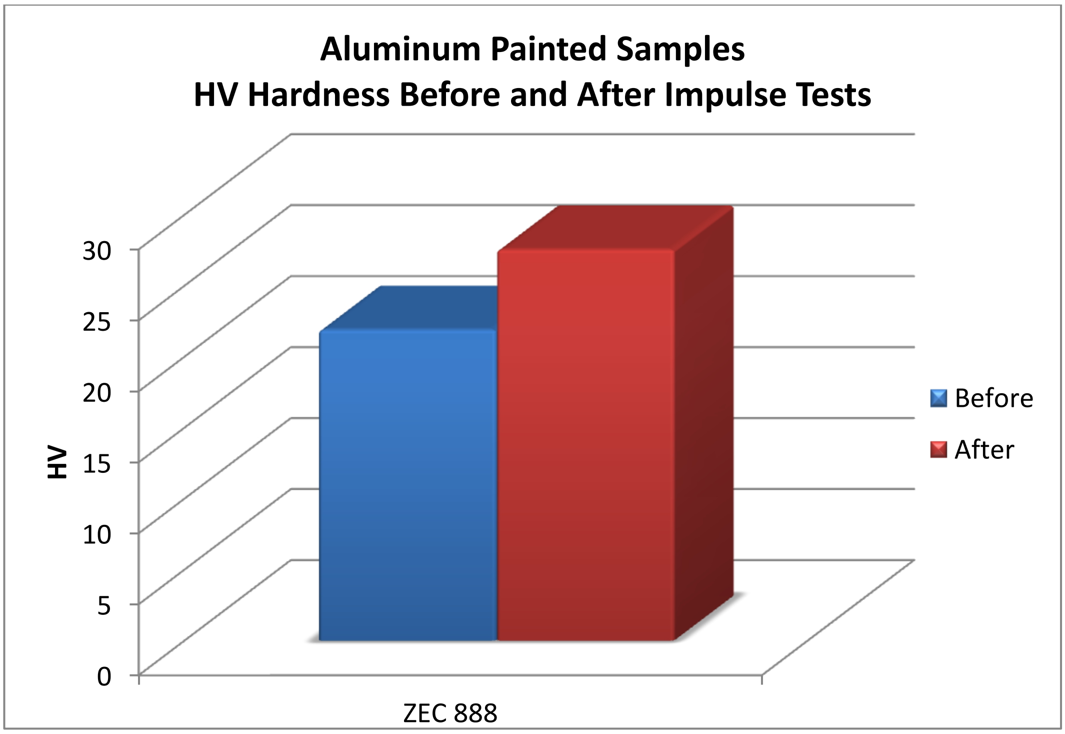
Microscopic image 100x (Aluminum, ZEC 888 , Paint ENABLE). After Galvanostatic pulse test.

Figure 45 Comparison of microscopic images of Aluminum, ZEC 888 and paint ENABLE, before and after exposure of 6 hours to a Galvanostatic pulse test.

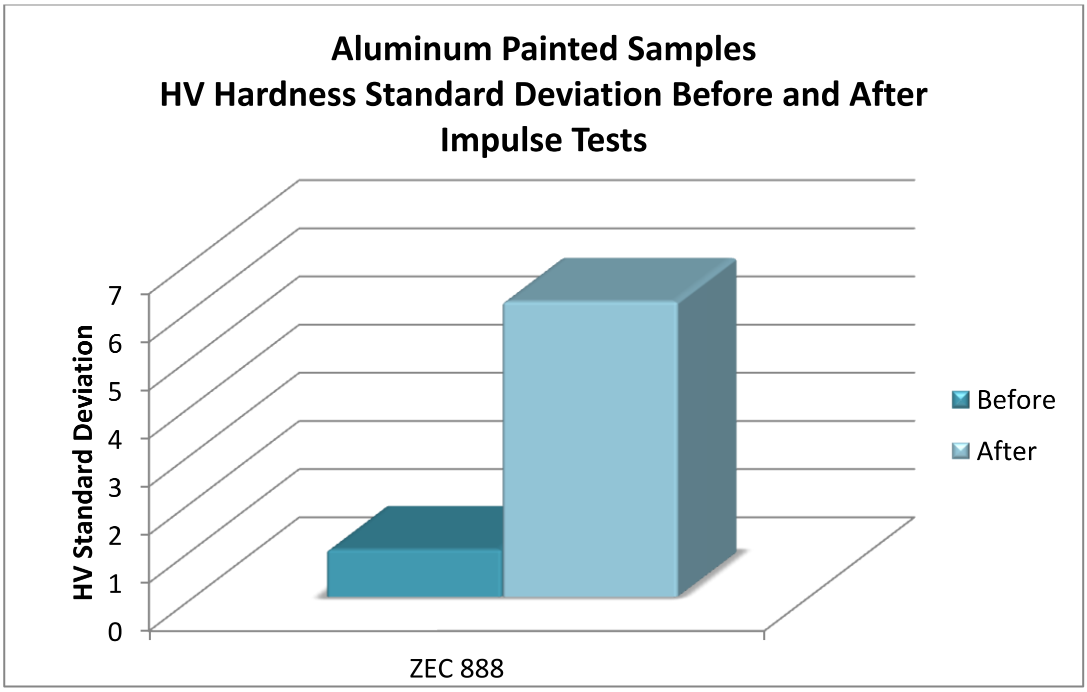


Graph 16 Impulse test result for HDG without pretreatment and paint, measured at different exposure times after Galvanostatic test.

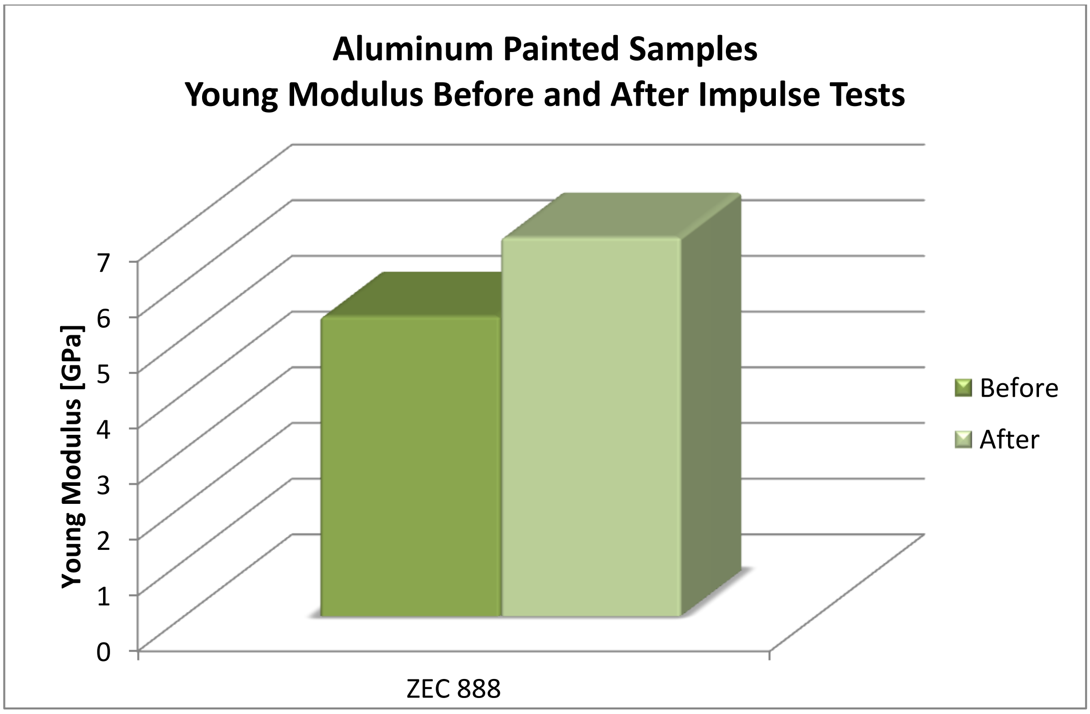
In Graph 17, Graph 18, Graph 19, Graph 20, Graph 21, Are shown the values for HV hardness, HV hardness standard deviation, Young modulus, Roughness average and Root mean square of roughness all taken before and after pulses series tests. As it can be seen in harness the value increases after the test; the Young modulus also increases as well as on the Roughness tests. This last symptom is once again in accordance to what has been seen from the microscopic images.



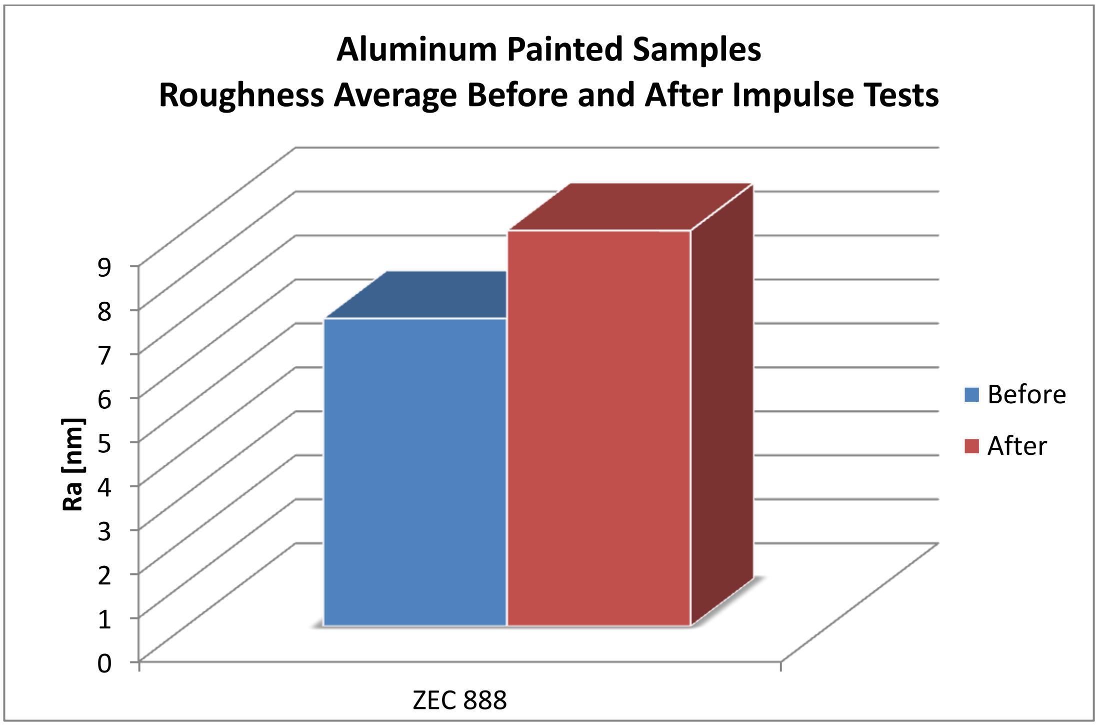
Graph 17 Comparison of the HV Hardness value for Aluminum painted before and after Impulse tests.



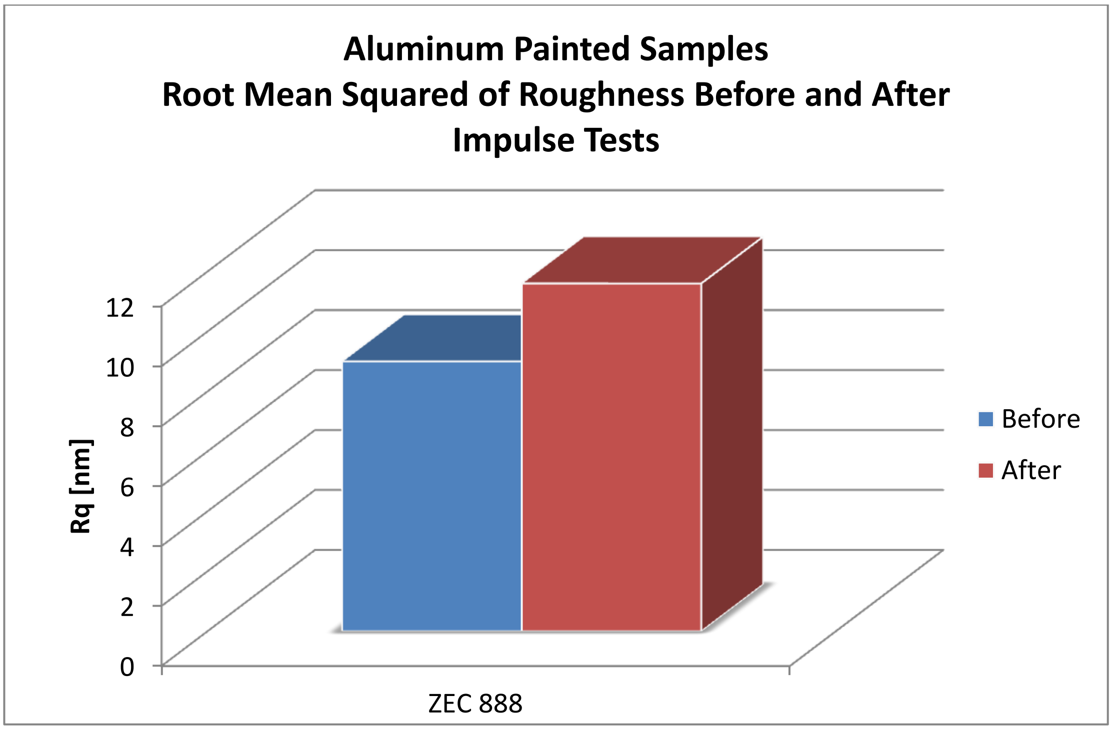
Graph 18 Comparison of the HV Hardness standard Deviation value for Aluminum painted before and after Impulse tests.



Graph 19 Comparison of the Young Modulus value for Aluminum painted before and after Impulse tests.



Graph 20 Comparison of the Roughness average value for Aluminum painted before and after Impulse tests.

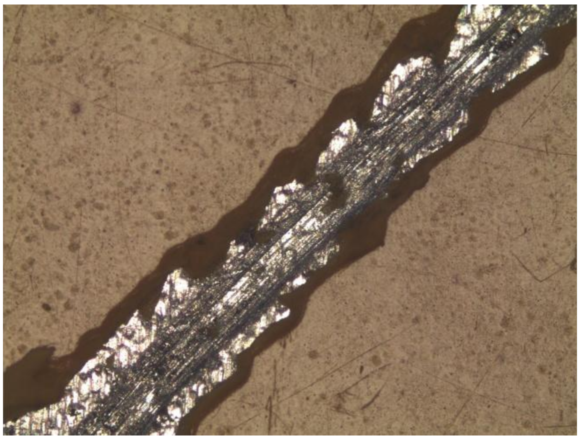
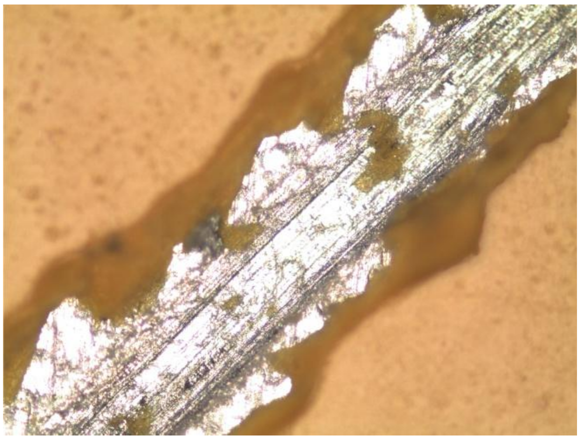


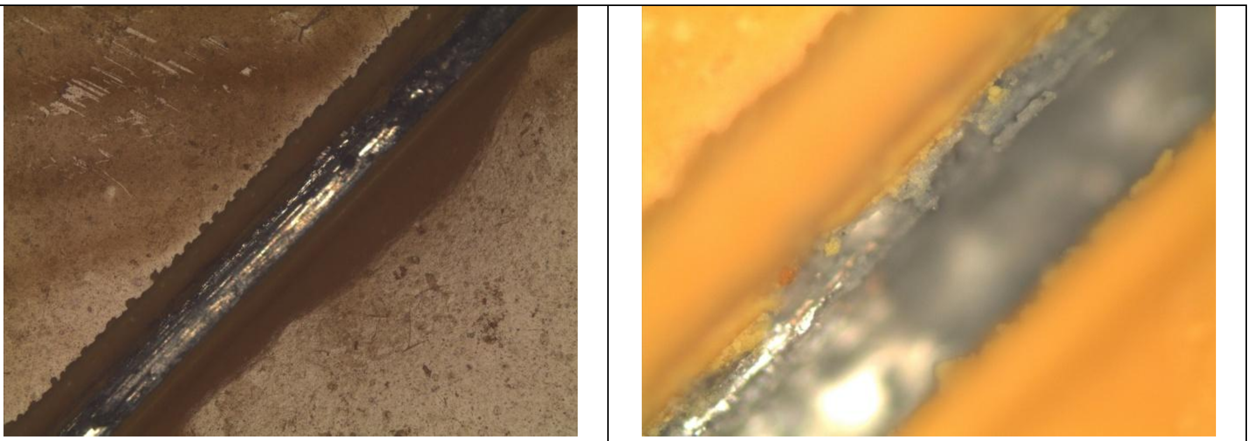
Graph 21 Comparison of the Root mean squared of Roughness value for Aluminum painted before and after Impulse tests.

5.2.3.2 *With Scratch.*

Before showing the pulse curves, it can be useful to evaluate the morphology of surfaces before and after the electrochemical tests. The following figures report the optical microscope images for each pretreatment condition.

5.2.3.2.1 ZEC 888.

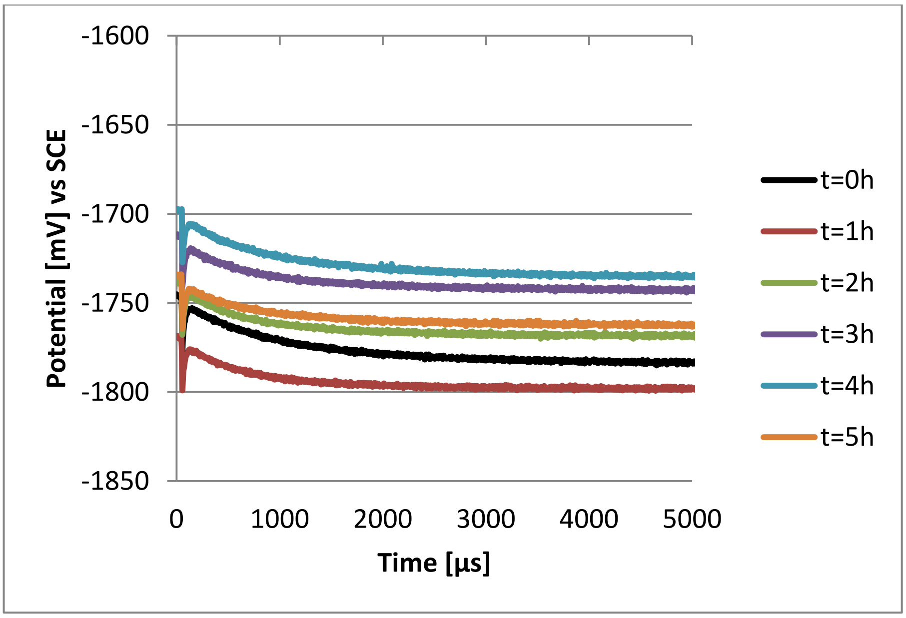
 Microscopic image 50x (Aluminum, ZEC 888, Paint ENABLE, scratched). Before Galvanostatic pulse test.	 Microscopic image 100x (Aluminum, ZEC 888, Paint ENABLE, scratched). Before Galvanostatic pulse test.



Microscopic image 50x (Aluminum, ZEC 888, Paint ENABLE, Scratched). After Galvanostatic pulse test.

Microscopic image 200x (Aluminum, ZEC 888, Paint ENABLE, Scratched). After Galvanostatic pulse test.

Figure 46 Comparison of microscopic images of Aluminum, ZEC 888 and paint ENABLE with Scratch before and after exposure of 6 hours to a Galvanostatic pulse test.



Graph 22 Impulse test result for Aluminum with ZEC 888 pretreatment, paint ENABLE and with a scratch on the surface, measured at different exposure times after Galvanostatic test.

From the pulse tests results, it can be observed that high resistance and low capacitance value can be detected at the beginning of the degradation tests.

With the application of the cathodic current, a decrease of the resistance and an increase of the capacitance were observed, suggesting the loss of the barrier properties for the painted and pretreated layers.

6 Conclusions.

6 Conclusions.

The present thesis work is part of the European research project called: “Environmentally acceptable Pretreatment System for Painting Multi Metals”, with the acronym “ENABLE” and type of funding scheme: FP7-SME-2010-1. In which Politecnico di Milano is taking part in alliance with Swerea IVF AB and Volvo Personvagnar Surface Treatment Center.

This thesis focuses on the characterization of the corrosion resistance of new pretreatments, in particular, the subject of study in the ENABLE project: ZEC 888. On this intent, this new pretreatment has been valued when deposited on Aluminum. In addition, to better simulate the real in use conditions, the samples have been provided after having apply a 100µm thick film of powder paint.

From a production development point of view there is a need for accelerated corrosion test methods in order to obtain fast results of the performance of new technologies in pre treatment or paint development. By the very nature of accelerated corrosion tests, e.g. salt spray tests, CASS Test, etc., these procedures can rarely (if ever) be used to confidently predict service life. This is due to the fact that in general, actual corrosive environments are more complex and less carefully controlled than accelerated laboratory tests.

Therefore the first goal of this research project was to establish a fast laboratory procedure based on electrochemical methods in order to measure the relative field performance in terms of a particular corrosion mechanism/mode. For this reason it was decided to proceed with some standard electrochemical tests that include Potentiodynamic and Cyclic Voltammetry, together with an innovative Galvanostatic pulse test.

As a first conclusion of this thesis work, it was noticed that the results obtained with the Galvanostatic pulse were reliable. What was recorded is that Galvanostatic pulse can be considered a valid method for this purpose.

Under other consideration, the ENABLE project address the future replacement of the “standard” pre-treatment process for out-door use, zinc phosphating with one of the new process. The reason why a replacement is needed today is because it is a chemical process with a high consumption of quality water and energy and with use of potentially toxic chemicals like nickel and zinc. Changing from zinc phosphating to the new pretreatment processes has the objective to reach: energy and water savings, less sludge, phasing out nickel, reduced total costs.

As an specific goal of this thesis, the team as a part of the Dipartimento di Chimica, Materiali e Ing. Chimica “Giulio Natta” Politecnico di Milano needed to give results to the other project partners, marking in this way a new path for research regarding on the characterization of the new pretreatments which will become the next surface technology suitable for automotive quests.

A new pretreatment from Glomax named Zinc Protector ZEC 888 was investigated. The treatment bath in cases when Zinc Protector ZEC-Coat 888 is applied upon a galvanized surface, two layers are formed. One is a siliceous top coated layer and the other is a reaction layer at the interface containing zinc, siliceous and oxygen. The corrosion resistance of treated aluminum was compared to samples treated with ZEC 888 and without treatment, giving in most of the results a favorable behavior as resistance to corrosion; saying this, it is implied that this pretreatment can be considered a viable alternative from the electrochemical point of view.

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