University of Pardubice, Czech Republic
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New concept for metallic protection against corrosion: V-active VCI

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Ph.D. Thesis

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DECLARATION

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A skeptic does not mean "one who doubts", but who investigates or research, opposite to that which asserts and thinks that he discovered (Mr. Miguel de Unamuno).

Ambition and knowledge is the way to success. Persistence and perseverance are the vehicles to get there (Mr. Bill Eardley).

Who is brave does not evade the battles of life; we all have our struggles, but only those who know how to win support them. Tackle life as it appears, with its joys and sorrows, and never think of running away cowardly (anonymous).

TITLE

New concept for metallic protection against corrosion: V-active VCI

ANNOTATION

Volatile Corrosion Inhibitors (VCI) are being extensively used as a powerful tool for corrosion inhibition in metals and their alloys. VCI are active compounds able to eliminate certain causes of corrosion such as acidity etc., forming a protective monomolecular layer on the metal inside a packing.

This thesis describes a new concept of corrosion inhibitors and the conditions for their application. The technology is based on volatile corrosion inhibitors, active substances building upon a new concept of using water as a carrier, either in liquid or in gas phase. The developed products carry a generic name in this work: The VCI-active.

As opposed to the literature and to current practice which recommend avoiding the contact of water with the surface of the metal to be protected, in this thesis water is employed as an active carrier of corrosion inhibitors. It bases on the fact that the majority of volatile corrosion inhibitors distill/evaporate with water steam, thus in liquid as well as in gas phase they form a protective film on the surface of metal (in this thesis, iron) products, which very effectively prevents corrosion.

The thesis presents the principles of this development together with actual cases demonstrating and proving the anti-corrosive effect in metals in laboratory as well as in industrial applications. Thanks to positive results of this new concept, further investigations can now focus on application in industrial scale.

KEYWORDS: Corrosion, Corrosion Inhibitors, Volatile Corrosion Inhibitors (VCI)

NÁZEV PRÁCE

Nový koncept ochrany kovů před korozí: V-aktivní VCI

ANOTACE

Těkavé inhibitory koroze (VCI) jsou používány ve velké míře jako účinný nástroj pro inhibici koroze kovů a jejich slitin. VCI jsou sloučeniny, které jsou schopné odstranit některé příčiny koroze (kyselost, a podobně), tvoříce uvnitř uzavřeného obalu na povrchu ochranou monomolekulární vrstvu.

Tato disertační práce popisuje novou technologii inhibitorů koroze a podmínek jejich použití. Tato technologie je obecně založena na těkavých inhibitorech koroze, účinných látkách, kde se jedná o novou koncepci, kde základem jsou těkavé inhibitory koroze (VCI) a voda jako přenašeč, a to jak v kapalné fázi, tak i v plynné fázi. Vyvinuté výrobky nesou v této práci generický název: V-aktivní VCI.

Na rozdíl od literatury a dosavadní praxe, kde se doporučuje, aby povrch chráněného kovu nepřišel do styku s vodou, v této práci se naopak voda využívá jako aktivní přenašeč inhibitorů koroze. Vychází se zde z faktu, že většina těkavých inhibitorů koroze těká/destiluje s vodní parou, takže jak v kapalné fázi, tak i v plynné fázi se na povrchu kovových (v této práci železných) výrobků vytváří ochranný film, který velmi účinně zabraňuje korozi.

Tato disertační práce představuje principy tohoto vývoje, stejně jako skutečné případy, které demonstrují prokázaný účinek inhibice koroze kovů, a to jak v laboratoři, tak i v průmyslových aplikacích. Na základě pozitivních výsledků této nové koncepce je nyní možné se zaměřit na další aplikace v průmyslovém měřítku.

Klíčová slova: Koroze, Inhibitory koroze, Těkavé inhibitory koroze (VCI)

AIMS OF WORK

- The introduction and the test of new concept of application of chemical compounds as corrosion inhibitors that use the water as medium and carrier in transfer process to act on metallic surface;
- The development of new chemical compounds formulations with anticorrosion properties, where no nitrites, nitrates, sulfates, chromates, heavy metals or other chemical compounds, that are toxic or harmful to the environment, will be presented;
- The application and testing of these new formulations in different means and substrates;
- The performance test simulations of these new chemical compounds using the comparative methods:

$$Fe^{0} \xrightarrow{[\,O_2\,]} \underset{\text{(grey)}}{Fe^{+2}} \xrightarrow[{[\,H_2O\,]}]{[\,O_2\,]} \underset{\text{(red-brown)}}{Fe^{+3}}$$

- The development of new chemical compounds with property of O_2 expelling from water and with an affinity to the Iron (Fe0, Fe^{+2} and Fe^{+3});
- The use of VCI compounds and formulations as a base of these new products, that has the same property and mechanisms of metallic corrosion protection;
- The development of products that have proven quality, performance and respect to the clients and in favor to the environment;
- The use of VCI technology in another application means.

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- To my wife Andrea R. Madi Genovez, who knew how to help, support and understand all the situations caused by this work.

- To my dear son Rodrigo Madi Genovez, that much was sacrificed due to the constant absence of his father. He always knew how to encourage me to win more and more.

- To my parents and sisters, who with sapience and education have always supported me in order to be able to achieve this goal. In honor "post-mortem" to my mother, who has always been a person who believed that "education is the best way to thrive and succeed". I'm sure where she is now, she is proud of this achievement.

- To my supervisor Prof. Ing. Radim Hrdina, CSc. and his wife Marcela Hrdinová, due to scientific, professional and personal support during all these years of long collaboration and friendship.

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- In particular to Luiz Henrique Araujo of VCI Brasil, who always believed in my personal and professional competence, and his entrepreneurial vision, encouraged in every way these achievements.

- I thank the company VCI Brasil and directors, which released its laboratories, equipment and financial resources for the development of this work.

- To all friends for their friendship and support, and all those who directly or indirectly contributed in one way or another to the development of this work.

1 Index

2 Biography of MSc. Mário Celso Genovez

Brazilian, graduated in Chemistry at University of Campinas (Unicamp) 1990, São Paulo State, Brazil, Master's degree in Textile Technology, Textile Chemistry at the University of Minho, Portugal 1994.

Chemical Responsible of Development and Product, for VCI Brasil Company since February 1996.

Member of the Brazilian Association of Corrosion ABRACO since 1996; NACE International (National Association of Corrosion Engineer USA) member since 1998; member of the Brazilian Committee of Corrosion Inhibitors since 1999. Annual participation in Corrosion Congress with several lectures since 1998, including Cobrascorr (Brazil) and NACE (USA).

Responsible for the development of all corrosion inhibitors, either in the vapor phase (VCI) or liquid phase (Metal Working Fluids) for VCI Brasil company and responsible for the implementation of products in customers. Responsible for technical support for all customers and representatives of VCI Brasil in Brazil, Argentina, United States, Europe, Turkey, Asia (Singapore) and Australia (Oceania)

3 Introduction

At the beginning of this dissertation, it must be said that in the course of the last two decades, a cooperation between the Faculty of Chemical Technology, University of Pardubice, Czech Republic (www.upce.cz) and VCI Brasil Ltd. (Bauru, Brazil, www.vcibrasil.com.br) in the area of development and application of anticorrosion compounds has been established.

Since prof. Radim Hrdina was the supervisor of my master studies in Portugal (University of Minho, Portugal, 1992-1994), after my joining the VCI Brasil (1996) it was decided that I would continue my studies by attending distance Ph.D. courses in the field of Organic Technology, program Chemistry and Chemical Technologies at the Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice. This study took place in the years 2009 – 2016.

During my tenure in the company VCI Brasil Ltd. I became the head of the Chemical and Development Department that I had built and I have developed and launched a number of products in the field of anticorrosion products and their use.

In this development, the above-mentioned cooperation with the Institute of Organic Chemistry and Technology, University of Pardubice has helped me very much. The cooperation has also greatly contributed to the promotion of both the institutions as well as of the newly launched anti-corrosive products.

4 Theoretical Part

4.1 Corrosion Concept

Corrosion is the deterioration of materials by chemical or electrochemical action of the medium, whether or not associated with mechanical stress.

When considering the use of materials in construction equipment or facilities requires that they resist the action of the corrosive medium, and provide sufficient mechanical properties and suitable manufacturing characteristics.

Corrosion can focus on various types of materials, whether metal such as steel or copper alloy, for example, or non-metallic, such as plastic, ceramic or concrete. The emphasis here will be described on the corrosion of metallic materials. This corrosion is called here metallic corrosion.

Depending on the type of action of the corrosive medium on the metal material, corrosive processes can be classified into two major groups, covering all cases deterioration from corrosion [1]:

- electrochemical corrosion;
- chemical corrosion.

The electrochemical corrosion processes are more frequent in nature and are characterized primarily by:

- necessarily in the presence of water in liquid state;
- temperatures below the dew point of water, the great majority at room temperature;
- formation of a battery or corrosion cell with the electron flow in metal surface.

Due to the requirement of the electrolyte liquid contains water, the electrochemical corrosion is also called corrosion in aqueous medium.

In corrosion processes, the metals react with non-metallic elements present in the medium, O_2, S, H_2S, CO_2, among others, producing compounds similar to those found in nature, to which they have been extracted, in which case, corrosion corresponds to inverse of metallurgical processes [1] (Figure 1).

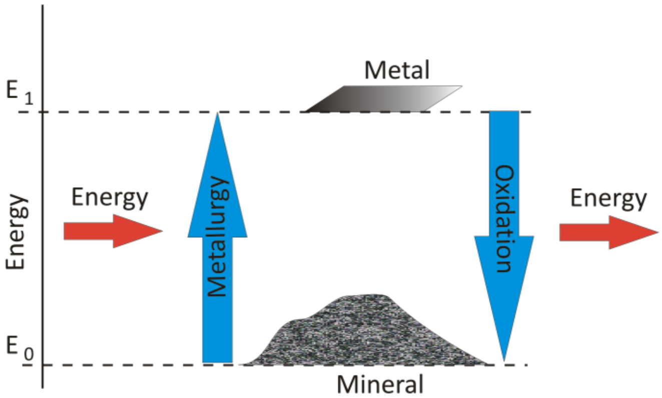


Figure 01 – Oxidation cycle - energy

Corrosion is defined as the transformation of a metal or alloy by chemical or electrochemical interaction with the environment in which it is for example the atmosphere. The damage caused by physical means not call corrosion, but erosion, abrasion and wear.

Many metals and alloys have corrosion or oxidation process. Depending on the intensity level, the materials may lose only the aesthetic appeal or to the mechanical loss of the metal component.

As a result of a chemical transformation of metal oxidation to obtain a characteristic oxide, for example in the steel is formed Hydrated Iron oxide, commonly known as 'Rust'. In Zinc white powder is formed (Zinc Oxide), on copper and its alloys (brass piece) formed the verdigris or Zinabre green color (copper oxide), Silver are formed dark spots losing brightness (silver-oxide), etc.

Atmospheric Corrosion

The chemical transformation (corrosion of a metal and / or metal alloy) by the action of the atmosphere occurs mainly during the storage and / or transportation. The physical and chemical aspects of the atmosphere greatly influence the corrosion rate: moisture, composition of the atmosphere (O_2, CO_2, SO_2, etc.), temperature, the presence of water on the metal surface, etc. The acidity and basicity and others can accelerate the corrosion process

The main types of atmosphere are [1]:

- Sea atmosphere: on the sea and near the sea coast; it contains large amounts of salts, mostly sodium chloride (table salt - strong electrolyte) as crystals dissolved in water droplets;
- Industrial atmosphere: in industrial areas contaminated by gases and ash (O_2, CO_2, SO_2 - acid gases, soot - highly oxidizing);
- Rural atmosphere: far from sources of pollution of air, low in pollutants;
- Urban atmosphere: the major population centers, containing impurities in the form of gases, mainly CO, CO_2, SO_2, SO_3, NO_2.

From a corrosion point of view the sea, urban and industrial atmospheres are the most aggressive, respectively.

Battery (Cell) of Electrochemical Corrosion

The electrochemical corrosion cell consists of four basic elements [1].

- Anode area: area where corrosion is found (oxidation reactions);
- Cathodic area: protected surface where is no corrosion (reduction reactions);
- Electrolyte: ionic conductor or conductive solution that involves both the anodic and cathodic areas;
- Electrical connection between the anodic and cathodic areas.

The appearance of corrosion cells is the result of different electrode potentials at two points on the metal surface, due to the potential difference between them.

An important concept applicable to batteries is corrosion and oxidation reduction reaction. The reactions of the electrochemical corrosion always involve redox reactions.

In the area where the anodic corrosion processes oxidation reactions to occur, the major one being metal passage of reduced form to an ionic form.

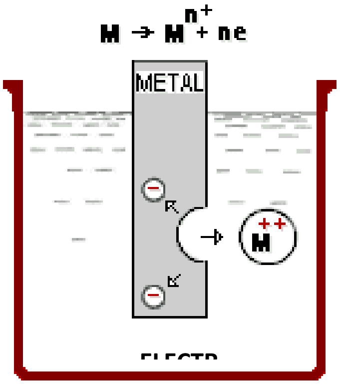


Figure 02 – Anodic reaction

The cathodic area is a protected area (does not occur corrosion), the reactions are reduction of the ions of the corrosive medium, where the main reactions are:

- In aerated media - normal case of sea water and natural.

$$H_2O + 1/2\ O_2 + 2e^- \rightarrow 2\ OH^-$$

- In a non-aerated - common case in industrial fresh water.

$$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$$

4.2 Corrosive Media

Corrosive media in electrochemical corrosion are responsible for the appearance of the electrolyte. The electrolyte is an electrically conductive solution composed of water containing salts, acids or bases [1].

Main Media Corrosive and Respective Electrolytes

- Atmosphere: the air contains moisture, suspended salts, industrial gases, dust, etc. The electrolyte is made up of water that condenses on the metal surface in the presence of salts or gases in the environment. Other constituents such as dust and various pollutants can accelerate the corrosion process:

- Soils: contain moisture, minerals and bacteria. Some soils are too acidic or basic. The electrolyte mainly consists of water with dissolved salts;

- Natural waters (rivers, lakes and underground): these waters may contain minerals, possibly acids or bases, industrial waste, bacteria, various pollutants and dissolved gases. The electrolyte is comprised mainly of water-dissolved salts. The other components can accelerate the corrosion process;

- Seawater: these waters contain an appreciable amount of salts. An analysis of sea water has on average the following constituents in grams per liter of water. The seawater due to the marked presence of an electrolyte salt is par excellence. Other constituents such as dissolved gases may accelerate the corrosion process;

- Chemicals: since contact with water or moisture, form an electrolyte, which can cause electrochemical corrosion.

Reactions in Corrosive Process and Corrosion Products

The reactions that occur in the electrochemical corrosion processes are oxidation and reduction reactions [1].

The reactions in the anodic area (corrosion cell anode) are oxidation reactions.

The most important reaction and responsible for the degradation of the material is the metal transition from reduced form to ion (combined).

$$M \rightarrow M^{n+} + ne^- \quad \text{(degradation of the material)}$$

Reactions in the cathodic area (cathode of the corrosion cell) are reduction reactions.

The reduction reactions are carried out with ions or corrosive environment, where appropriate, with metal ions from solution.

The main reactions in the cathodic area are:

a)	$2H^+ + 2e^- \rightarrow H_2$	neutral or acidic media, not aerated
b)	$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$	acids media, aerated
c)	$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$	neutral or basic media, aerated
d)	$M^{3+} + e^- \rightarrow M^{2+}$	ions present in solution in more oxidized state
e)	$M^{n+} + ne^- \rightarrow M$	ion reduction of more noble metal

Most common cathodic reactions in the corrosive processes are "a", "b" and "c" reactions "d" and "e" are less frequent; the last reaction appears only in chemical or electrolytic reduction process.

Will be detailed following the cathodic reactions previously reported that take place at neutral or aerated media and not aerated [1].

- cathodic reactions in aerated neutral medium

$$H_2O \leftrightarrow H^+ + OH^-$$
$$H^+ + e^- \rightarrow H$$
$$H^+ + 1/2\ O_2 + e^- \rightarrow 2\ OH^-$$
$$\overline{H_2O + 1/2\ O_2 + 2e^- \rightarrow 2\ OH^-}$$

- cathodic reactions in non-aerated neutral medium

$$2\ H_2O \leftrightarrow 2\ H^+ + 2\ OH^-$$
$$2\ H^+ + 2e^- \rightarrow H_2$$
$$\overline{2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2}$$

The above cathodic reactions can draw some important conclusions:

- Cathodic region becomes basic (there is a rise in the pH in the vicinity of the cathodic area).

- In a non-aerated a release of H_2, which is absorbed into the surface and responsible for overvoltage or overvoltage of hydrogen. This phenomenon causes the delay of the corrosion process and is called cathodic polarization.
- In aerated media's consumption of H_2 by O_2, not having the overvoltage of hydrogen.

In this case there is no cathodic polarization and will consequently accelerating the corrosion process.

The composition of the electrolyte in the vicinity of the cathode is oxygen diffusion dependent on the media and the electrolyte refresh rate. Thus it is possible the occurrence of reaction “ao" in aerated media, if the flow of electrons reaching the cathode is very high. An example is the case of cathodic overprotection in sea water where the reaction "c", which usually occurs, can be overcome by the reaction "a". A serious drawback is the possibility of occurrence of embrittlement phenomenon by hydrogen producing cracks and / or the decrease in fatigue life.

Note:

In acidic media there will be a decrease in acidity in the vicinity of the cathode area and basic means there will be an increase of alkalinity in the vicinity of the cathodic area. The corrosion products in electrochemical processes are usually resulting from the formation of insoluble compounds between the metal ion and hydroxyl ion. The corrosion product is therefore in most cases the rusted metal hydroxide or metal oxide hydrate. When the corrosive medium contains other ions may be the formation of other insoluble components and the corrosion product may consist of sulfides, sulfates, chlorides, among others.

4.2.1 Corrosion Forms

The ways in which corrosion can manifest are mainly defined by the appearance of the corroded surface, the main ones being [1]:

- Uniform corrosion: when corrosion proceeds of approximately uniformly across the rusted surface. This form is common in metals that do not form protective films as a result of attack;
- Corrosion plates: occurs when corrosion products are formed on plates that come off gradually. It is common in metal forming a film that is initially protective but to become thick, fracture and lose grip, exposing the metal to fresh attack;
- Alveolar corrosion: When the degradation caused by corrosion occurs in localized form, with the appearance of craters. It is common in metal forming semi protective films or when there is corrosion deposit, as in the case of differential aeration corrosion;
- Pitting corrosion: when degradation occurs very localized and high intensity, usually deeper than the diameter and angular edges. Pitting corrosion occurs in metals that form protective films, usually passive layers, which under the action of certain aggressive agents are destroyed in localized spots, which become active sites, enabling very intense corrosion. Common example is represented by austenitic stainless steels in media containing chlorides;

- Intergranular corrosion or intercrystalline: when the attack is manifested in the grain boundary, as in the case of austenitic stainless steels sensitized, exposed to corrosive media;
- Transgranular corrosion or transcrystalline: when the phenomenon manifests itself in the form of cracks which propagate through the interior of the grains of the material, as in the case of stress corrosion cracking of austenitic stainless steel.

4.3 Expansion of Corrosion Resistance and Corrosion Protection

Methods to Improve Corrosion Resistance

Certain materials with very industrial use have low corrosion resistance in most media. This resistance can be enhanced, magnified or even obtained at its highest level, using techniques or corrosion protection methods that promote passivation or polarization of the material. Among these techniques or methods can be mentioned coatings, corrosion inhibitors, the middle modification techniques, cathodic and anodic protection or control the project [2,3,44].

4.3.1 Coating

The coatings are in film interposed between the metal and the corrosive environment, increasing the corrosion resistance of the metal material. This film can give the material a noble behavior, as is the case of the cathode metal layer to the base metal, or protect it by galvanic action, or even constitute a barrier between the metal and the environment and thus increase the contact resistance of the anodic and cathodic areas of corrosion cells.

The coatings can be made by: metallic, inorganic or organic non-metallic and their use can increase the resistance to atmospheric corrosion and immersion corrosion by soil.

4.3.2 Corrosion Inhibitors

The increase of corrosion resistance by the use of corrosion inhibitors is in one widely used technique, especially when the liquid is a corrosive medium and works in closed circuit.

The inhibitors are chemical compounds added to the media that promote the anodic or cathodic polarization, or are film formers which increase the contact resistance of the anodic and cathodic areas of corrosion cells.

This theme will be explored in more detail later.

4.3.3 Modification Techniques of Corrosive Media

In addition to inhibitors that act through the corrosive medium there are other important technical modification of the environment, among them the deaeration and control of pH.

The deaeration is the removal of oxygen from the middle, and one oxygen depolarizing agent, with the withdrawal favors the cathodic polarization with the consequent decrease in the intensity of the corrosion process.

Oxygen removal process may be chemical or mechanical. The chemical process is carried out by oxygen scavengers, while the mechanical removal process is performed in a deaeration drag of oxygen with another gas, usually steam, or in a vacuum chamber where the decompression facilitates the exit of gases.

The pH control is intended to promote passivation of metals which become passive to slightly basic pH. Special care should be taken with amphoteric metals lose corrosion resistance in very basic means and precipitation of calcium and magnesium compounds that become insoluble at high pH and can bring fouling problems.

These two methods for improving the corrosion resistance are much used in cooling water systems, boiler water, water for injection into oil wells in various fluids such as oil well drilling and the complementation.

May be mentioned as methods to reduce corrosion rates, the speed control on metal / electrolyte and temperature control.

4.3.4 Cathodic and Anodic Protection

Cathodic protection is a method of increasing the corrosion resistance, which consists of making the structure to protect the cathode in an electrochemical or electrolytic cell, forcing a high degree of cathodic polarization.

Cathodic protection is used for buried or submerged structures. It can be used for overhead structures, due to the need for a continuous electrolyte, which is not achieved in the atmosphere.

The anodic protection is a method of increasing the corrosion resistance which comprises applying an anodic current to the structure to be protected.

The anodic current promotes passivation of the material giving it resistance to corrosion.

The anodic protection is successfully employed only for metals and alloys that form protective layers, especially titanium, chromium, iron-chromium alloy, iron-chromium-nickel alloys.

Its use is of most interest to highly aggressive electrolytes (strong electrolyte), such as a metal tank for storing acids. The anodic protection not only promotes the formation of the protective film but mainly maintaining the stability of this film.

The anodic protection of employment is still very limited in Brazil, but has wide application in other countries in the chemical and petrochemical industry.

4.3.5 Corrosion Control in Design Phase (Project)

Increased corrosion resistance through corrosion protection practices in the design phase is one of the most important forms of corrosion control.

This increased resistance could be obtained in two ways, first by adopting practices that minimize corrosion problems and the second using the corrosion protection techniques.

4.4 Temporary Protection

Some metal products require a temporary protection because after some time of storage and / or transport, must have a surface without changes. The "temporary" term applies in order to be easily removable and not for the period to be protected [1,3,50].

The main corrosion media are:

- contamination of corrosive products (manufacture and handling);
- packages containing corrosive substances;
- atmospheric corrosion.

In addition to suitable packaging, it is often necessary to take precautions through the interior of the package, sometimes requiring a temporary protective. The temporary protection is usually obtained by cooling the medium, use of anticorrosion substance by formation of protective films, use of special packaging containing corrosion inhibitor or combination thereof.

4.4.1 Environmental (Media) Control

The formation of a layer of water on metal surfaces (condensation of air humidity) is the main contributor to the corrosion process [1].

The main protection methods for the reduction of water condensation are:

- Ventilation: applied in places where it is difficult to control the humidity and temperature. Is done through natural ventilation (air currents) or forced (fans), and in parallel, leaving the samples at least 1 meter away from walls and suspended.
- Heating: applicable only in places where there is a large temperature range, i.e. when it is cold during the night and daytime heat. The heating is effected to control the relative humidity (at close to 40%). For the heating indoor environment is used heaters placed on top of the walls and the bottoms hoods, so that there is an actual exchange of air. One should be careful with the type of heater to use as some combustion heaters emit gases such as CO2, SO2, etc., which are very corrosive gases. It is necessary to monitor the moisture with the aid of a hygrometer.
- Dehumidification: is only applied when the other two factors do not solve the moisture problem by itself. The most common dehumidification processes are those obtained by cooling, by adsorption (silica) and absorption (lithium chloride).
- Elimination of air impurities: applied to environments with large amounts of combustion products (CO_2, SO_2, etc.), acid vapors, etc.

4.4.2 Film Formers

It is based on obtaining a surface film that prevents contact of the metal surface with moisture and corrosive substances. The layer or film formed has a large thickness, which is dependent on the protective intensity.

They are usually derived from petroleum materials, oil or grease, containing substances which form uniform layers, and corrosion inhibiting chemicals. Its major disadvantage is the removal process, which often becomes difficult, costly, unhealthy and inefficient. For removal of corrosion inhibitor are used highly toxic organic solvents to humans and the environment, for example, chlorinated solvents and / or aromatic (benzene).

These protective are basically composed of [50]:

- film forming materials: oils, greases, resins, petroleum jelly, etc.;
- solvents: water, organic substances, etc.;
- corrosion inhibitors: polar compounds of sulfur and nitrogen;
- acid neutralizers.

They were divided into groups:

- water-miscible - emulsifiable in water and water soluble chemicals;
- oily;
- organic solvents - oily or fatty, waxy, type varnish and plastic type;
- hot applied - vaseline, wax and thermoplastic.

4.4.3 Special Packages

It is the most used medium because of its versatility and applicability, with excellent mechanical and corrosion protection agent, both storage and transportation.

The anti-corrosive packaging differ mainly for their protective content [50]:

- Against mechanical agents;
- With desiccant: chemical compounds that act eliminating the internal moisture of the package and may be by adsorption (silica) or absorption (lithium chloride). Applied in cases where it is not possible to put other types of protective due to chemical incompatibilities or only as reinforcement, as in the case of electronic products;
- Contact inhibitors: products work only when they are in direct contact with the metal surface; It contains inorganic salts impregnated on paper usually based on sodium nitrite;
- Volatile inhibitor: chemical substances used tend to volatilize reaching the metal surface where they are adsorbed as an invisible film. VCI "Volatile Corrosion Inhibitors".

4.5 Corrosion Costs and Preventive Strategies Study

Despite the developments in corrosion resistant alloys over the past few decades, carbon steel still constitutes an estimated 99% of the material used in the oil industry. It is usually the most cost effective option, being a factor of 3 to 5 times cheaper than stainless steels. Yet its corrosion resistance is poor in aggressive environments, and the cost savings can only be realized by adding a corrosion inhibitor to the environment or applying a protective coating to the steel. Inhibitors are used in a wide range of applications, such as oil pipelines, domestic central heating systems, industrial water cooling systems and metal extraction plants [4,60].

A particular advantage of corrosion inhibition is that it can be implemented or changed in situ without disrupting a process. The major industries using corrosion inhibitors are the oil and gas exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry, water treatment facilities, and the product additive industries. The largest consumption of corrosion inhibitors is in the oil industry, particularly in the petroleum refining industry. The total consumption of corrosion inhibitors in the United States has doubled from approximately $600 million in 1982 to nearly $1.1 billion in 1998 (2000 NACE Study).

4.6 Corrosion Inhibitors

The inhibitors are chemical compounds that, when added to the corrosive media, decrease its aggressiveness by one of the following mechanisms [4,50].

- Anodic inhibition (anodic inhibitors): these are compounds which form insoluble products in the anodic areas, producing an anodic polarization. These inhibitors are also called passivating. Example: hydroxides, carbonates, phosphates, silicates, alkali metal borates, sodium nitrite and potassium and sodium chromate.
- Cathodic inhibition (cathodic inhibitors): these are compounds which form insoluble products in the cathodic areas, producing a cathodic polarization. Example: zinc sulphate, magnesium or nickel.
- Inhibition barrier (adsorption inhibitor): are compounds which have the property of forming films by adsorption to the metal surface, creating a protective film on the anodic and cathodic areas. Example: heavy metal soaps, amines, urea, etc.
- Oxygen scavengers: these are compounds which react with oxygen promoting the deaeration means. Example: Sodium Sulfite ($Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$), Hydrazine ($N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$).

The main applications of inhibitors are:

- oil distillation;
- water treatment (boiler, cooling and injection);
- chemical cleaning and acid pickling;
- oil and gas pipeline systems;
- hydrostatic testing;
- packaging system;
- drilling and production area-fluids and acidification.

The basic criteria for selection of inhibitors are:

- must be compatible with the process;
- must be soluble, stable (including temperature and pressure);
- should not form waste or foam;
- should not be polluting and toxic;
- low cost, including disposal.

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection (see corrosion costs study findings). Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by either [4,50]:

- Increasing the anodic or cathodic polarization behavior (Tafel slopes);
- Reducing the movement or diffusion of ions to the metallic surface;
- Increasing the electrical resistance of the metallic surface.

The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance.

Various authors have classified inhibitors differently. Some authors, for example, prefer to group inhibitors by their chemical functionality. However, by far the most popular organization scheme consists in regrouping corrosion inhibitors in a functionality scheme.

ORGANIC INHIBITORS

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as 'film-forming', protect the metal by forming a hydrophobic film on the metal surface [2,3].

The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate, or 0.2% sodium cinnamate, is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

4.7 Volatile Corrosion Inhibitors – VCIs

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values. In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used [2], for example.

On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds, fast action wanting high volatility while enduring protection requires low volatility.

It can be stated, that VCIs are among the most efficient and cost-effective classes of means used to protect metals from atmospheric corrosion. The physicochemical aspects of VCI protective action are covered in a number of reviews [5, 6, 7, 8, 9].

From the technological point of view, very important is review published in 2013, where is a search of the patent literature [10].

The information considered in patent documents allows stating the following general conclusions [10].

1. **The following compounds can be used as VCIs**:

a) inhibitors of atmospheric corrosion with vapor pressure above 10–5 mmHg, including compounds and formulations of compounds belonging to the following classes:

- nitrogen-containing bases of various nature (including various amines, quaternary ammonium bases, Schiff bases, Mannich bases, *etc*.),
- salts of nitrogen-containing bases and some inorganic (including nitrous, carbonic, chromic, molybdenic, *etc*.) or organic acids (including various mono- and dicarboxylic acids, phenols, *etc*.),
- organic nitro compounds (including nitrophenol, aliphatic nitro compounds, *etc*.),
- esters of organic and inorganic acids (including carboxylic acids, chromic acid, phosphoric acid, *etc*.),
- heterocyclic nitrogen-containing compounds (triazoles, imidazoles, thiazoles of various nature, *etc*.);

b) non-volatile compounds and formulations that can release compounds of the above types upon hydrolysis (including hexamethylenetetramine, urea, their mixtures with sodium nitrite, *etc*.).

2. **VCIs for temporary protection can be used as**:

a) active compounds,
b) solutions (aqueous or non-aqueous),
c) packaging materials (including papers, polymer films, specialized containers, *etc*.),
d) porous emitters (including those based on foamed and porous plastics, silica gels, zeolites, *etc*.),
e) inhibited air,
f) special forms intended for the protection of a specific product type.

3. **VCIs can be used for permanent protection of metal articles within**:

a) polymer coatings (paints, etc.),
b) working liquids (hydraulic, cooling liquids, *etc*.).

4.8 Inhibitor Efficiency

By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of that inhibitor is thus expressed by a measure of this improvement [3]:

$$\text{Inhibitor Efficiency (\%)} = 100\cdot(CR_{\text{uninhibited}} - CR_{\text{inhibited}}) / CR_{\text{uninhibited}}$$

where:
$CR_{\text{uninhibited}}$ = corrosion rate of the uninhibited system
$CR_{\text{inhibited}}$ = corrosion rate of the inhibited system

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration, e.g. a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%.

Through the years, sophisticated corrosion inhibitor test methods, typically designed to reproduce the extreme conditions in a system, have been employed to improve inhibitor capabilities. New and better corrosion inhibitors have been developed as a result of their performance in elaborate laboratory apparatus, yet many have not achieved comparable performance in the field. The inability to transfer inhibitor performance from the laboratory to the field remains a challenge today. However, correlation of laboratory and field performance may be possible once key factors involved in inhibitor chemistry and corrosion theory are considered.

4.9 Selection of Corrosion Inhibitors

Rules, equations or theories to guide inhibitor development or use are very limited. A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations. The first step in selecting an inhibitor system is to consider was is usually adopted.

Table 1 - Some corrosive systems and the inhibitors used to protect them [2]:

System	Inhibitor	Metals	Concentration
Acids			
HCl	Ethylaniline	Fe	0.5%
..	Mercaptobenzotriazole	..	1%
..	Pyridine + phenylhydrazine	..	0.5% + 0.5%
..	Rosin amine + ethylene oxide	..	0.2%
Sulfuric	Phenylacridine	..	0.5%
Phosphoric	Sodium iodide	..	200 ppm
Others	Thiourea	..	1%
..	Sulfonated castor oil	..	0.5-1.0%
..	Arsenic Oxide	..	0.5%
..	Sodium arsenate	..	0.5%
Water			
Potable	Calcium bicarbonate	Steel, cast iron	10 ppm
..	Polyphosphate	Fe, Zn, Cu, Al	5-10 ppm
..	Calcium hydroxide	Fe, Zn, Cu	10 ppm
..	Sodium silicate	..	10-20 ppm
Cooling	Calcium bicarbonate	Steel, cast iron	10 ppm
..	Sodium chromate	Fe, Zn, Cu	0.1%
..	Sodium nitrite	Fe	0.05%
..	Sodium phosphate monobasic	..	1%
..	Morpholine	..	0.2%
Boilers	Sodium phosphate monobasic	Fe, Zn, Cu	10 ppm
..	Polyphosphate	..	10 ppm
..	Morpholine	Fe	variable
..	Hydrazine	..	O2 scavenger
..	Ammonia	..	neutralizer
..	Octadecylamine	..	variable
Engine coolants	Sodium chromate	Fe, Pb, Cu, Zn	0.1-1%
..	Sodium nitrite	Fe	0.1-1%
..	Borax	..	1%
Glycol/water	Borax + MBT	All	1% + 0.1%
Oil field brines	Sodium silicate	Fe	0.01%
..	Quaternaries	..	10-25 ppm
..	Imidazoline	..	10-25ppm
Seawater	Sodium silicate	Zn	10 ppm
..	Sodium nitrite	Fe	0.5%
..	Calcium bicarbonate	All	pH dependent
..	Sodium phosphate monobasic + Sodium nitrite	Fe	10 ppm + 0.5%

4.10 Corrosion Mechanism

Modern corrosion science has its roots in electrochemistry and metallurgy. Electrochemistry contributes an understanding of the mechanism that is basic to the corrosion of all metallic objects. Metallurgy provides knowledge of the characteristics of metals and their alloys as well as the methods of combining the various metals and working them into the desired shapes [1,2,3].

The type of corrosion mechanism and its rate of attack depend on the exact nature of the environment (air, soil, water, seawater, etc.) in which the corrosion takes place. In today's industrial setting, the waste products of various chemical and manufacturing processes find their ways into the air and waterways. Many of these substances, often present only in minute amounts, act as either catalysts or inhibitors of the corrosion process. The corrosion engineer then needs to be on the alert for the effects of these contaminants.

Many of the coatings used to prevent or slow corrosion can have specific vulnerabilities that need to be understood. The first step in preventing material corrosion understands its specific mechanism. The second and often more difficult step is designing a type of prevention. Some metals produce corrosion products that are insoluble, about the same size molecularly as the parent metal, and that crystallize in the same type of lattice structure. These are often able to become attached to the metal surface and form a protective coat against further corrosion. The patina that forms on copper is an example of this type of coating.

The existence of anodic and cathodic sites on the surface of a piece of metal implies that differences in electrical potential are found on the surface. These potential differences have a number of causes. One important mechanism is oxygen concentration in cell corrosion, in which the oxygen concentration in the electrolyte varies from place to place. An underground pipe that passes from clay to gravel will have a high oxygen concentration in the gravel region and almost no oxygen in the impermeable clay. The part of the pipe in contact with the clay becomes anodic and suffers damage.

A similar situation is found where a pipe passes under a road. The section under the road (which is the more difficult to get at for repair) is oxygen deprived and will suffer the greatest damage. The cure for this is cathodic protection, which involves the use of a sacrificial anode such as zinc or aluminum. In this situation, the metal to be protected is connected electrically to a piece of scrap metal that will take its place as the anode. The anode is destroyed by the corrosion reaction, leaving the cathode intact. This technique is still used extensively to protect underground gas and water pipelines [2].

Concentration cells may also be formed where there are differences in metal ion concentration. A copper pipe in contact with copper ion solutions of different concentrations will corrode at the part in contact with the more dilute solution. This is an obvious problem when copper pipes are used to carry flowing water. Parts of the copper surface in contact with the more quickly moving fluid will be more negative and therefore anodic. This phenomenon plays an important part in the erosion corrosion of copper and its alloys.

Although most metals are crystalline in form, they generally are not continuous single crystals, but rather are collections of small grains or domains of localized order. Metal objects are formed from melts in which microcrystals form as the liquid cools and solidifies. In the final state, these microcrystals have different orientations with respect to one another. The edges of the domains form grain boundaries, which are an example of planar defects in metals. These defects are usually sites of chemical reactivity. The boundaries become anodic, while the grains themselves are the cathodes. The boundaries are also weaknesses, the places where stress cracking begins [2].

Perhaps the best known of all corrosion types is galvanic corrosion, which occurs at the contact point of two metals or alloys with different electrode potentials. An example of this might be brass detail in contact with copper hot-water pipes. The brass becomes anodic and suffers the loss of its zinc atoms. Brass in contact with galvanized steel is protected, while the zinc coating on the steel is first dissolved, leaving the steel open to attack for the same reason. An obvious area of concern is the use of one type of metal as bolts, screws, and welds to fuse together pieces of another metal. The combination to be desired is the large anode-small cathode combination. Bolts, screws, and so on should be made of the metal less likely to be oxidized so that the bolt or weld is cathodically protected.

Similar electrical potentials may also be developed between two areas of a component made of a single metal as a result of small differences in composition or structure or of differences in the conditions to which the metal surface is exposed. That part of a metal component which becomes the corroding area is called the "anode"; that which acts as the other plate of the battery is called the "cathode" and does not corrode, but is an essential part of the system. In the corrosion systems commonly involved in buildings there may often be only a single metal involved, with water containing some salts in solution as the electrolyte. Corrosion may even take place with pure water, provided that oxygen is present. In such cases oxygen combines with the hydrogen generated at the cathode, removing it and permitting the reaction to go on.

Other agents, notably certain bacteria in the soil that remove hydrogen, can also act as depolarizing agents and thus promote the corrosion reaction. Steel, because of its low cost together with its many desirable properties, is the most common metal used in buildings. It can often be protected adequately by the application of suitable coatings. For certain purposes other metals more resistant to corrosion may be a better choice, depending on initial cost and expected service life. Metal components used in buildings can be grouped for purposes of discussing corrosion into four general categories [1,2,3]:

1) those used on the exterior as cladding, roofing and flashings,
2) those incorporated in the construction as structural and reinforcing steel, masonry ties and damp courses,
3) those used in the services to a building as piping, storage tanks for hot water, drains and heating ducts,
4) those buried in the ground.

Of great importance is the conductivity of the corroding solution. When large areas of the surface are in contact with a water solution of high conductivity, such as seawater, the attack on the anodic metal may spread far from its contact point with the cathodic metal. This is a less severe situation than that which occurs in soft water or under atmospheric conditions in which the attack is localized in the vicinity of the contact. In the absence of dissolved oxygen or hydrogen ions to maintain the cathode process, galvanic corrosion does not occur. It is possible to combine different metals such as copper and steel in closed hot-water systems with little corrosion.

Other preventive measures involve the use of protective coatings and modification of the environment. Some trace impurities can significantly reduce the rate of corrosion and can be added in low concentration to the surrounding medium. Paint is the most common coating used to slow the rate of atmospheric corrosion. Many other materials, such as plastics, ceramics, rubbers, and even electroplated metals, can be used as protective coatings. The corrosion resistance of a metal can be greatly increased by the proper choice of alloys. For example, aluminum added to brass will increase its corrosion resistance.

4.11 Evaluation of Corrosion Inhibitors

In choosing between possible inhibitors, the simplest tests should be done first to screen out unsuitable candidates. The philosophy of initial screening tests should be that poorly performing candidates are not carried forward. An inhibitor that does poorly in early screening tests might actually do well in the actual system, but the user seldom has the resources to test all possible inhibitors. The inhibitor user must employ test procedures that rigorously exclude inferior inhibitors even though some good inhibitors are excluded [3,46,47].

Inhibitor selection begins with the choice of physical properties. Must the inhibitor be a solid or liquid? Are melting and freezing points of importance? Is degradation with time and temperature critical? Must it be compatible with other system additives? Are specific solubility characteristics required? This list can be extensive, but is important because it defines the domain of possible inhibitors. It must be the first step of the inhibitor evaluation for any new system. These physical measurements are those routinely done as part of minimal quality acceptance testing.

The challenge in inhibitor evaluation is design of experiments that simulate the conditions of the real world system. The variables that must be considered include temperature, pressure, and velocity as well as metal properties and corrosive environment chemistry. System corrosion failures are usually localized and attributed to micro conditions at the failure site. Adequate testing must include the most severe conditions that can occur in the system and not be limited to macro or average conditions. Examples of microenvironments are hot spots in heat exchangers and highly turbulent flow at weld beads.

4.11.1 Metal for Testing

Test specimens should be the same metal as that to be protected; even very small differences in metal chemistry can make major differences in inhibitor performance. Inhibitor performance can vary greatly on different metals and thus inhibitor rankings based on one metal are not universal. Much less obvious are differences between the "same" metal. These nonchemical differences include grain size and orientation, residual stresses, and surface condition. Surface preparation should, to the extent possible, provide a surface comparable to that in the system that is being modeled. Except in special tests, minimal cleaning includes a solvent wash to degrease the sample. More vigorous cleaning such as bead blasting or acid activation can markedly affect inhibitor response even while improving reproducibility of tests. Many experimenters activate test specimens in acid when doing electrochemical measurements. The purpose is to remove any protective or passive oxide layer so that metal solution equilibrium is reached rapidly. Methods for preparing specimens can be found in ASTM G 1, Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens [2].

4.11.2 Transportability of Inhibitor

Corrosion inhibitors are generally described by terms such as oil soluble, water soluble, oil soluble-water dispersible, etc. Such terms are generalizations, not rigorous descriptions. An oil soluble inhibitor, for example, in reality partitions between the liquid hydrocarbon phase and the water phase as do all other inhibitors; all that can be assumed is that it likely partitions more to the oil phase [3].

Partitioning of a single compound between two phases is clearly defined. Many commercial corrosion inhibitors, however, are not single compounds but complex mixtures of many compounds, each with its own unique partitioning coefficient. Thus a commercial corrosion inhibitor has no unique partitioning coefficient but rather one for each of the multiple components. Organic inhibitors are generally more soluble in aromatic hydrocarbons than aliphatic ones and more soluble in long chain aliphatics than short chain ones. The result is that partition coefficients must be measured for each "oil" of interest [2].

4.11.3 Corrosion Protection Tests

Corrosion rates are most commonly reported as penetration rates. The usual way of reporting protection efficiency is in terms of percent protection. Although this reporting method is useful for comparing inhibitor performance, it obscures the actual number of interest the inhibited corrosion rate.

Film persistency tests are more complex than constant concentration experiments. The test metal is exposed to an inhibited test solution for a fixed period, and then the corrosion rate is determined in a similar solution containing no inhibitor. Test variables include inhibitor concentration in the initial filming solution and the number of rinse solution repetitions. A typical experiment might film for one hour with 1000 ppm inhibitor, rinse one time for an hour, and finally measure the corrosion rate in a third solution. Film, rinse, and corrode solution are the same composition except for inhibitor in the filming step.

4.11.3.1 Metal Loss Methods

Metal loss can be determined gravimetrically, volumetrically, or radiometrically; all are a direct measure of corrosion. Of these, gravimetric or weight loss methods are most used for inhibitor testing [2]. Volumetric methods are associated with inspection or monitoring techniques such as ultrasonic inspection and electric resistance (ER) probe monitoring, although both are sometimes used in long-term inhibitor evaluations. Radiometric methods are used as monitoring methods such as in thin layer activation but could be used for inhibitor evaluation. The corrosion wheel test used to evaluate oilfield inhibitors is an example of weight loss testing.

Coupons from weight loss experiment should be examined visually for localized corrosion seen as pits or edge attack. Analysis can be as simple as "none, some, or lots" or as detailed as counting and depth measurement. ASTM G 46 (Practice for Examination and Evaluation of Pitting Corrosion) provides a complete procedure for evaluating pitting attack.

4.11.3.2 Electrochemical Methods

Electrochemical testing has two major benefits, one major limitation, and one lesser limitation. The benefits are short measurement time and mechanistic information. The severe limitation is the requirement for a conductive corrosive environment. Less troublesome from a testing perspective is the requirement for a corrosion model. Rapidity of measurement makes these techniques useful in characterizing inhibitor performance. Corrosion rates can be determined electrochemically in minutes while weight loss methods can take days. With the near instantaneousness of electrochemical methods, changes of inhibitor performance with time are readily measurable. Questions about inhibitor persistence and incubation time are thus experimentally accessible and experiments concerned with velocity effects become less cumbersome [2]:

- Potentiodynamic polarization methods
- Linear polarization resistance (LPR)
- Electrochemical impedance spectroscopy (EIS)
- Electrochemical noise (EN)

4.11.3.3 Potentiodynamic Polarization Methods

Polarization methods such as potentiodynamic polarization, potentiostaircase, 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 that is produced as a function of time or potential [2].

- 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 polarization 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 [2]:

- **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 to measure 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, as described in the next section.

4.11.3.4 Linear Polar Resistance (LPR) and the Stern-Geary Equation

With this widely used technique in corrosion monitoring, the polarization resistance of a material is defined as the slope of the potential-current density (DE/Di) curve at the free corrosion potential, yielding the polarization resistance R_p that can be related (for reactions under activation control) to the corrosion current by the Stern-Geary equation [2]:

$$R_p = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)}_{\Delta E \to 0} \qquad \mathrm{B} = \frac{\mathrm{b_a} \cdot \mathrm{b_c}}{2.3(\mathrm{b_a} + \mathrm{b_c})}$$

where:

- R_p is the polarization resistance
- i_{corr} the corrosion current
- The proportionality constant , B, for a particular system can he determined empirically (calibrated from separate weight loss measurements) or, as shown by Stern and Geary, can be calculated from b_a and b_c, the slopes of the anodic and cathodic Tafel.

The Tafel slopes themselves can be evaluated experimentally using real polarization plots. The corrosion currents estimated using these techniques can be converted into penetration rates using Faraday's law or a generic conversion chart.

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 [2]:

- **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).

4.11.3.5 Electrochemical impedance spectroscopy (EIS)

EIS has been successfully applied to the study of corrosion systems for thirty years and been proven to be a powerful and accurate method for measuring corrosion rates. But in order to access the charge transfer resistance or polarization resistance that is proportional to the corrosion rate at the monitored interface, EIS results have to be interpreted with the help of a model of the interface [2].

An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal, usually a voltage between 5 to 50 mV, is applied to a specimen over a range of frequencies of 0.001 Hz to 100,000 Hz. The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system. Depending upon the shape of the EIS spectrum, a circuit model or circuit description code and initial circuit parameters are assumed and input by the operator.

The program then fits the best frequency response of the given EIS spectrum, to obtain in fitting parameters. The quality of the fitting is judged by how well the fitting curve overlaps the original spectrum. By fitting the EIS data it is possible obtain a set of parameters which can be correlated with the coating condition and the corrosion of the steel substrate.

Amongst the numerous equivalent circuits that have been proposed to describe electrochemical interfaces only the following apply in the context of a freely corroding interface at or close to kinetic equilibrium [2]:

- Simplest RC representation of an electrochemical interface
- One relaxation time constant with extended diffusion
- Two relaxation time constants
- Impedance of pitting processes of Al based materials.

4.11.3.6 Electrochemical Noise (EN)

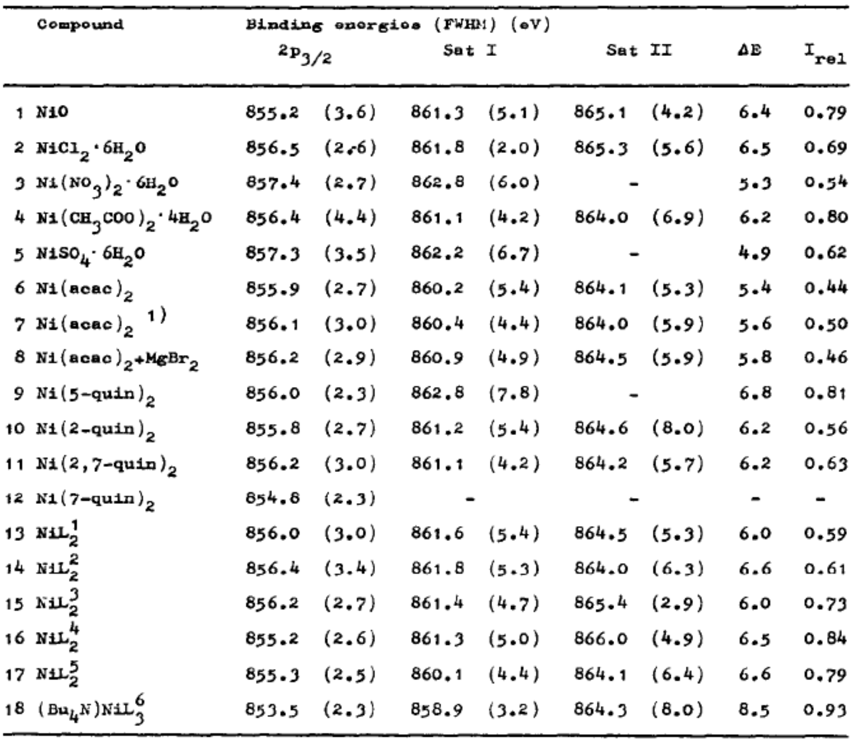
The non-intrusive use of EN for corrosion monitoring is very attractive, e.g. aircraft corrosion and gas scrubbing tower monitoring examples. Fluctuations of potential or current of a corroding metallic specimen are well known and easily observable phenomenon and the evaluation of EN as a corrosion tool has increased steadily since Iverson's paper in 1968 [2].

The extensive development in the sensitivity of the equipment for studying electrochemical systems has rendered the study of oscillations in electrochemical processes that translate into measurable EN, increasingly accessible. The study of corrosion potential fluctuations was applied, for example, to monitor the onset of events characterizing localized corrosion such as pitting or stress corrosion cracking (SCC), exfoliation, erosion-corrosion in either laboratory or diverse and complex industrial environments. No other technique, electrochemical or otherwise is even remotely as sensitive as EN to system changes and upsets.

During localized corrosion, EN is believed to be generated by a combination of stochastic processes, such as passivation breakdown and repassivation events, and deterministic processes that can be caused by film formation or pit propagation processes.

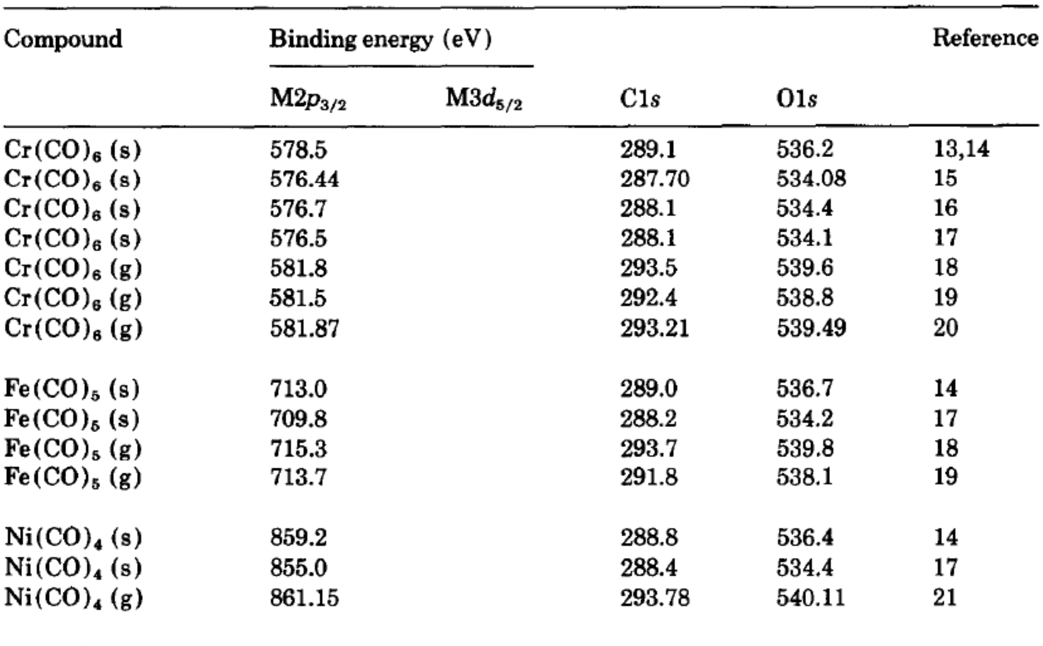
4.11.3.7 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is widely applied in the investigation of transition metal complexes to determine the geometric and electronic structure including charge distribution, the bonding interaction between metal d orbital and the valence orbitals of the ligands, the metal ligand bonding on Ni 2p photoelectron spectra of various paramagnetic nickel chelates and of diamagnetic compound in table 2 [44]. The charge values show that the metal to ligand electron donation is strong for $Ni(CO)_4$, initially with the metal in a d10 configuration, completely filled with electrons, and therefore with a high’’back donation’’ capacity [45], table 3 . The nickel (II) amine complex binding energy shift with the amine N-H, the inductive and steric effect of amine substitution, ligand to metal electron delocalization, coordination of the counter-ion to the metal [46].



Compound	Binding energies (FWHM) (eV)				
	$2p_{3/2}$	Sat I	Sat II	ΔE	I_{rel}
1 NiO	855.2 (3.6)	861.3 (5.1)	865.1 (4.2)	6.4	0.79
2 $NiCl_2 \cdot 6H_2O$	856.5 (2.6)	861.8 (2.0)	865.3 (5.6)	6.5	0.69
3 $Ni(NO_3)_2 \cdot 6H_2O$	857.4 (2.7)	862.8 (6.0)	-	5.3	0.54
4 $Ni(CH_3COO)_2 \cdot 4H_2O$	856.4 (4.4)	861.1 (4.2)	864.0 (6.9)	6.2	0.80
5 $NiSO_4 \cdot 6H_2O$	857.3 (3.5)	862.2 (6.7)	-	4.9	0.62
6 $Ni(acac)_2$	855.9 (2.7)	860.2 (5.4)	864.1 (5.3)	5.4	0.44
7 $Ni(acac)_2$ 1)	856.1 (3.0)	860.4 (4.4)	864.0 (5.9)	5.6	0.50
8 $Ni(acac)_2$+$MgBr_2$	856.2 (2.9)	860.9 (4.9)	864.5 (5.9)	5.8	0.46
9 $Ni(5\text{-}quin)_2$	856.0 (2.3)	862.8 (7.8)	-	6.8	0.81
10 $Ni(2\text{-}quin)_2$	855.8 (2.7)	861.2 (5.4)	864.6 (8.0)	6.2	0.56
11 $Ni(2,7\text{-}quin)_2$	856.2 (3.0)	861.1 (4.2)	864.2 (5.7)	6.2	0.63
12 $Ni(7\text{-}quin)_2$	854.8 (2.3)	-	-	-	-
13 NiL^1_2	856.0 (3.0)	861.6 (5.4)	864.5 (5.3)	6.0	0.59
14 NiL^2_2	856.4 (3.4)	861.8 (5.3)	864.0 (6.3)	6.6	0.61
15 NiL^3_2	856.2 (2.7)	861.4 (4.7)	865.4 (2.9)	6.0	0.73
16 NiL^4_2	855.2 (2.6)	861.3 (5.0)	866.0 (4.9)	6.5	0.84
17 NiL^5_2	855.3 (2.5)	860.1 (4.4)	864.1 (6.4)	6.6	0.79
18 $(Bu_4N)NiL^6_3$	853.5 (2.3)	858.9 (3.2)	864.3 (8.0)	8.5	0.93

Table 2 – Binding energies for nickel chelates and of diamagnetic compound



Compound	Binding energy (eV)				Reference
	$M2p_{3/2}$	$M3d_{5/2}$	C1s	O1s	
$Cr(CO)_6$ (s)	578.5		289.1	536.2	13,14
$Cr(CO)_6$ (s)	576.44		287.70	534.08	15
$Cr(CO)_6$ (s)	576.7		288.1	534.4	16
$Cr(CO)_6$ (s)	576.5		288.1	534.1	17
$Cr(CO)_6$ (g)	581.8		293.5	539.6	18
$Cr(CO)_6$ (g)	581.5		292.4	538.8	19
$Cr(CO)_6$ (g)	581.87		293.21	539.49	20
$Fe(CO)_5$ (s)	713.0		289.0	536.7	14
$Fe(CO)_5$ (s)	709.8		288.2	534.2	17
$Fe(CO)_5$ (g)	715.3		293.7	539.8	18
$Fe(CO)_5$ (g)	713.7		291.8	538.1	19
$Ni(CO)_4$ (s)	859.2		288.8	536.4	14
$Ni(CO)_4$ (s)	855.0		288.4	534.4	17
$Ni(CO)_4$ (g)	861.15		293.78	540.11	21
$Mo(CO)_6$ (g)		234.57	293.16	539.26	20

Table 3: Binding energy data

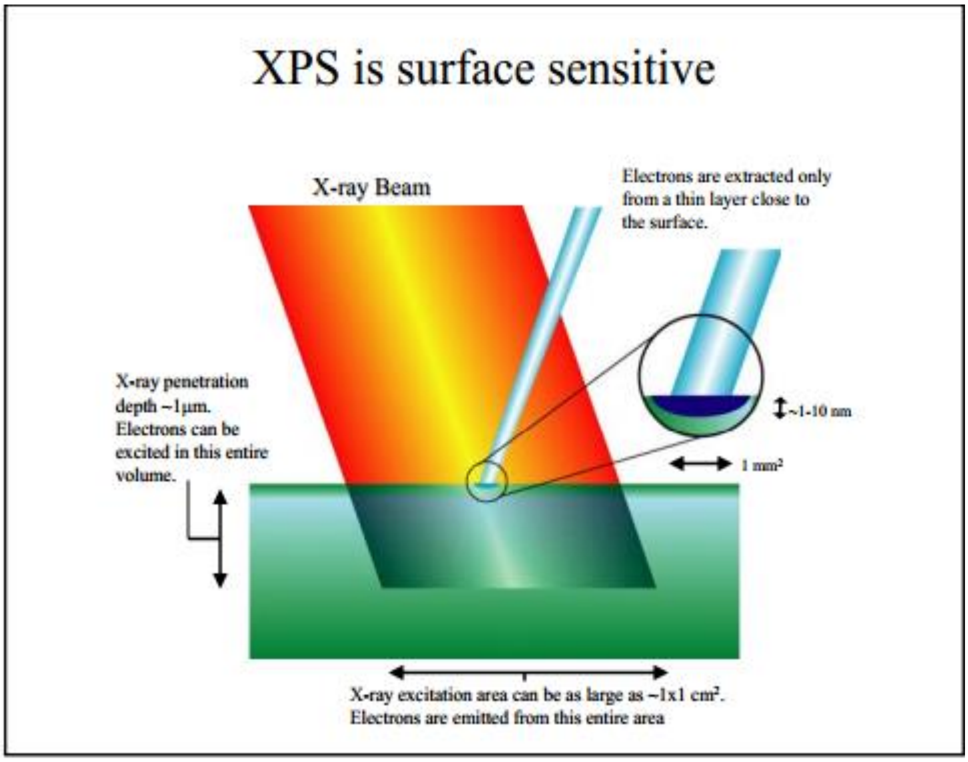


Figure 03 – X-ray photoelectron spectroscopy (XPS)

4.12 Effects of Inhibitors on Corrosion Processes

In acid solutions, the anodic process of corrosion is the passage of metal ions from the oxide-free metal surface into the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen gas. In air-saturated acid solutions, cathodic reduction of dissolved oxygen also occurs, but for iron, the rate does not become significant compared to the rate of hydrogen ion discharge until the pH exceeds a value of 3. An inhibitor may decrease the rate of the anodic process, the cathodic process or both processes [2,3].

The change in the corrosion potential on addition of the inhibitor is often a useful indication of which process is retarded. Displacement of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control), whereas displacement in the negative direction indicates mainly retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

The following discussion illustrates the usage of anodic and cathodic inhibitors for acid cleaning of industrial equipment. The combined action of film growth and deposition from solution results in fouling that has to be removed to restore the efficiency of heat exchangers, boilers and steam generators.

Pourbaix or E-pH diagrams indicate that the fouling of iron-based boiler tubes, by Fe_3O_4 and Fe_2O_3, can be dissolved in either the acidic or alkaline corrosion regions. In practice, inhibited hydrochloric acid has been repeatedly proven to be the most efficient method to remove fouling. Four equations are basically needed to explain the chemistry involved in fouling removal. Three of those equations represent cathodic processes [2]:

- **$Fe_2O_3 + 4\,Cl^- + 6\,H^+ + 2\,e^- \text{-->} 2\,FeCl_{2(aq)} + 3\,H_2O$ ... (A)**
- **$Fe_3O_4 + 6\,Cl^- + 8\,H^+ + 2\,e^- \text{-->} 3\,FeCl_{2(aq)} + 4\,H_2O$ ... (A')**
- **$2\,H^+ + 2\,e^- \text{-->} H_2$ ... (A'')**

and one anodic process, i.e. the dissolution of tubular material

- **$Fe + 2\,Cl^- \text{-->} FeCl_{2(aq)} + 2\,e^-$ ... (C)**

These equations indicate that the base iron functions as a reducer to accelerate the dissolution of iron oxides. Since it is difficult to determine the end point for the dissolution of fouling oxides, an inhibitor is generally added for safety purpose. Both anodic and cathodic inhibitor could be added to retard the corrosion of the bare metal after dissolution of the fouling oxides. This is illustrated in two figures showing the action that could be played by either an anodic inhibitor or a cathodic inhibitor. It can be seen that while the anodic inhibitor retards the anodic dissolution of iron at the end point, it concurrently decreases the rate of oxide dissolution permitted by the chemical system.

On the other hand, the cathodic inhibitor retards both the reduction of protons into hydrogen and the dissolution of the base metal while the reduction of the fouling oxides is left unaffected. The E-pH diagrams also indicate that the dissolution of the fouling oxides is also possible in alkaline solutions. However, the kinetic of anodic and cathodic reactions in high pH environments is much slower and therefore these reactions less useful.

5 Volatile Corrosion Inhibitors

Atmospheric corrosion can be defined as vapor phase corrosion (VPC) which is promoted by individual and combined action of oxygen, moisture, and atmospheric pollutants. Additional contributors to VPC are rain, snow, dust, soot, ash, wind, and radiation (light, heat, etc.). Both acids and bases, depending upon the metal, may accelerate the rate of VPC.

An effective and relatively inexpensive method of controlling VPC in closed environments is through the use of volatile corrosion inhibitor (VCI) or vapor phase corrosion inhibitors (VpCI) [11].

VCI is a compound that has the ability to vaporize and condense on a metallic surface making it less susceptible to corrosion by the formation of a thin protective unimolecular film layer [12,13,14].

VCI compounds are defined as temporary protective and one of the characteristics that distinguish them from the permanent ones, such as paints and metal coatings, is the readiness that they are removable from the surface. Another advantage of VCI's is that the volatized molecules can reach the hard-to-reach spaces [9]. These features make these inhibitors the most economical and also powerful tool in the protection of metals and alloys against the atmospheric corrosion damage [11].

The VCI product was originally denominated due to its physical-chemical property or VPI "Vapor Phase Inhibitor". Later, changed its name to VCI, "Volatile Corrosion Inhibitor", a name that was given based on its application. It creates an invisible and monomolecular protective film over the metallic surface which inhibits corrosion.

These inhibitors are generally composed of organic and inorganic salts which are applied on paper or plastic that gradually volatize, that is, low vapor pressure is its main characteristic. In generic and applied terms, vapor pressure indicates the quantity at which a certain organic salt will become vapor for a determined period.

This characteristic is fundamental to conduct the formulation of acting chemical products. Normally, according to the metal to be protected and the time it will take for the inhibitor to act, several chemical products with different pressure values are mixed, causing a synergetic effect among the compounds.

Duration of protection on metal is closely linked to packaging conditions. VCI Paper is efficient for a period of 24 months or more when the packaging is tightly shut.

Such products are used in order to obtain optimization, efficiency and suitability for the transport and storage of metallic materials, aiding in the elimination of corrosion processes, which frequently occur.

The chemical compounds present in VCI are volatile. When a metal part is packaged with VCI, the product volatizes in the packing environment, creating a monomolecular film on the metallic surface, that protects it from corrosive agents such as oxygen, sulfuric and carbonic gases, salt, dust, etc.

VCI offers a wide range of products that can guarantee the necessary protection, long or short term, for products in storage as well as those that have been transported. When the package is opened, the protective film immediately starts to dissipate and the metal is clean, without corrosion, ready for use. It is not necessary to perform any cleaning processes, which are often unhealthy.

VCI is a technology that can be defined as clean, economical and efficient for it does not require special preparation or any cleaning afterwards, and it has a substantial cost/benefit ratio.

GENERAL COMPOUNDS USED AS VCIS

Organic nitrites

Nitrites of cyclohexylamine, dicyclohexylamine (DICHAN), isopropylamine (ISLAN), diisopropylamine (DISLAN), diisobutylamine, triethylamine, hexylamine and dibenzylamine [11,12,13,14,16] are good inhibitors for carbon steel [11,13,15,16,18]. DICHAN is also a good inhibitor for tin and tin alloys, but may be aggressive to copper and copper alloys [13], magnesium, cadmium, zinc and lead [12]. DISLAN attacks copper, silver and aluminium [13,20].

Mixes of sodium nitrite and urea are good inhibitors for ferrous and non-ferrous metals [22,21]. Organic carbonates. Carbonates of monocyclohexylamine (CHC) [12,13,19,23,24,25], ethylamine [13,26], guanidine [27,28] and dibutylamine [28,29] are good inhibitors for steel. CHC also is a good inhibitor for copper, zinc, tin and tin alloys [30]. Nevertheless, CHC may attack copper and its alloys [12].

Organic benzoates

Benzoates of monocyclohexylamine, dicyclohexylamine (DICHAMIN), isopropylamine, ISLAN, amylamine, diethylamine, triethylamine, dibutylamine, naphthylamine, dibenzylamine, ethylamine and ethylmorpholine are good inhibitors for steel [19,25]. It should be noted that sodium benzoate is a good VCI for steel [25,31], though it provides less protection than DICHAN or CHC inhibitors [12,19].

Organic chromates

Though with certain environmental limitations, some organic chromates are good VCIs, for instance cyclohexylamine and DICHAMIN chromate protect brass [23].

Organic phosphates

Phosphates of alkyl and hexamethylamine are good inhibitors for aluminium [15,32]. Thiurea derivatives can be used as VCIs for steel, copper, brass and aluminium [33].

Triazoles

Compounds derived from triazoles are good inhibitors for copper and its alloys [15, 34,35,36,37,38,39,40]. BTA is also a good VCI for copper and its alloys [36,37,38,41,42,43].

Here it can be seen that most of these compounds is in any way restricted to use, according to the general rules on VCIs such as TRGS, VDA, ECHA, etc.

REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals.

The European Chemicals Agency (ECHA), negative list of chemical products Annex XV of SVHC (Substance of Very Hight Concern), TRGS (Technical Rule for Hazardous Substances) from Federal Institute for Occupational Safety and Health (BAuA-Germany), VDA (Verband der Automolindustrie) Association of Automotive Industry – Germany.

Following these concepts have been developed new classes of VCI that follow these standards and do not have in formulation such restricted chemicals.

5.1 Advantages

- ✓ There is no deposition of materials on the metallic surface (clean technology);
- ✓ It is not necessary the use of protective oil;
- ✓ It is not necessary to have parts cleaned after opening (it is not necessary to use toxic organic solvents);
- ✓ Metallic parts will have a good visual presentation after being stored and transported, ready to be used;
- ✓ Easy to apply: flexible;
- ✓ Offers chemical and mechanical resistance;
- ✓ Low cost: fewer steps in the packing and unpacking of the metallic material;
- ✓ It does not present any hazard to Human Health nor to the environment.
- ✓ Biodegradable, almost entirely non-toxic and some of the products are recyclable.

5.2 VCI Process Inside Package

- ➲ Closing of the package containing Volatile Inhibitor (VCI);
- ➲ Volatilization of VCI;
- ➲ Closed environment containing VCI;
- ➲ Migration of VCI to any cavities in, and places on the metal part;
- ➲ Condensation of VCI on the metallic surface;
- ➲ Adsorption of VCI on the metallic surface;
- ➲ Creation of a mono-molecular film over the metallic surface;
- ➲ Neutralization of the corrosion chain;
- ➲ Saturation of the environment with VCI (Balance).

5.3 Action Mechanism inside Package

The organic base works as a “passive and active carrier” that, when volatized, carries an inorganic or organic anion with it. Its natural tendency is to settle on metallic surface creating a uniform and invisible film.

Equilibrium is established after the vapor has been concentrated to a certain level, which causes a perfect exchange between the inhibitor in the packaging and the inhibitor on the metal surface, that is, the condensation mechanism acts with the same speed as the vaporization mechanism, as seen on the schematic below:

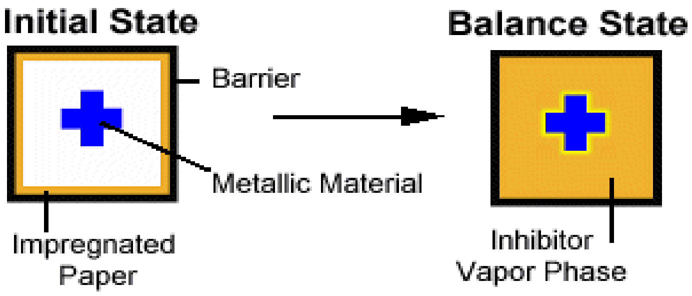


Figure 04 – Schematic representing the VCI action mechanism

For the protection to take place in an ideal system, the packaging must be closed airtight, providing equilibrium in the system. In this case, the duration of VCI’s corrosive protection tends to be infinite. If there is an exchange between this environment and the outside environment (small leaks or openings), said environment will constantly be “renewing” itself, causing consumption and consequently, a wearing down of the VCI applied to the system. The inhibitor film on the metallic surface is preserved as long as the packaging is kept closed. The protection mechanism assures that the parts will be ready for immediate use and will not need to be cleaned or washed with solvents.

This complementary cleaning depends upon the final application of the particular metal. Metallic corrosion starts when humidity (which contains electrolytes) condenses on the metal surface, causing a flow of electrons between the metal surface and the electrolyte.

VCI’s molecules do not impede the deposition of electrolytes, however, they do direct the flow of the existing chain to a satisfactory point where there is no metal oxidation. Depending on the metal and the inhibitor, the thin film that was created impedes physical contact between the electrolytes and the metal.

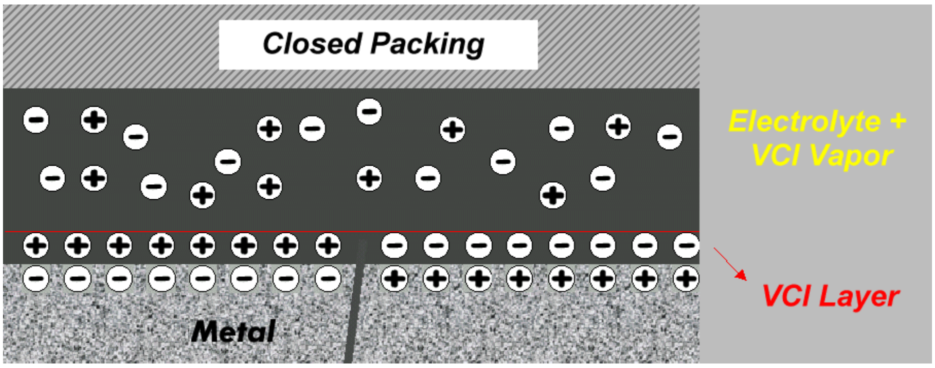


Figure 05 – Graphic representation of VCI acting inside a closed packaging.

In other words, organic salt (VCI) sublimates through convection and diffusion, reaching the packaged metal surface, creating a protective "chemical barrier". This barrier impedes any metal oxidation reaction, protecting it against corrosion. Vapor does not create any residue or film over the metal, avoiding costly, long, unhealthy and polluting methods of application and removal of conventional greasy protectors.

One other VCI advantage is that the metal to be protected can be of any shape (straight or grooved surfaces, or surfaces with voids and crevices) because since we are dealing with a vapor phase, condensation will take place on any part of the metal surface, which is impossible to happen with other kinds of protectors such as oily and greasy products.

5.4 VCI Activation Mechanism on Metallic Surface

The rate of metal corrosion can be reduced using corrosion inhibitors in two distinct ways: reduction in the density of the exchange chain of cathodic and / or anodic reactions, and reduction in the cathodic and / or anodic active areas by creating a barrier between the metal and the environment. This can be done through the inhibitor's reaction with the oxidizer or with the liquefied metal, or through inhibitor adsorption by the metallic surface. Prior to this, the studies conducted to track the activation mechanism for corrosion inhibitors were done by polarization curves.

The following figure demonstrates the effect that an anodic inhibitor has on a metal surface [7].

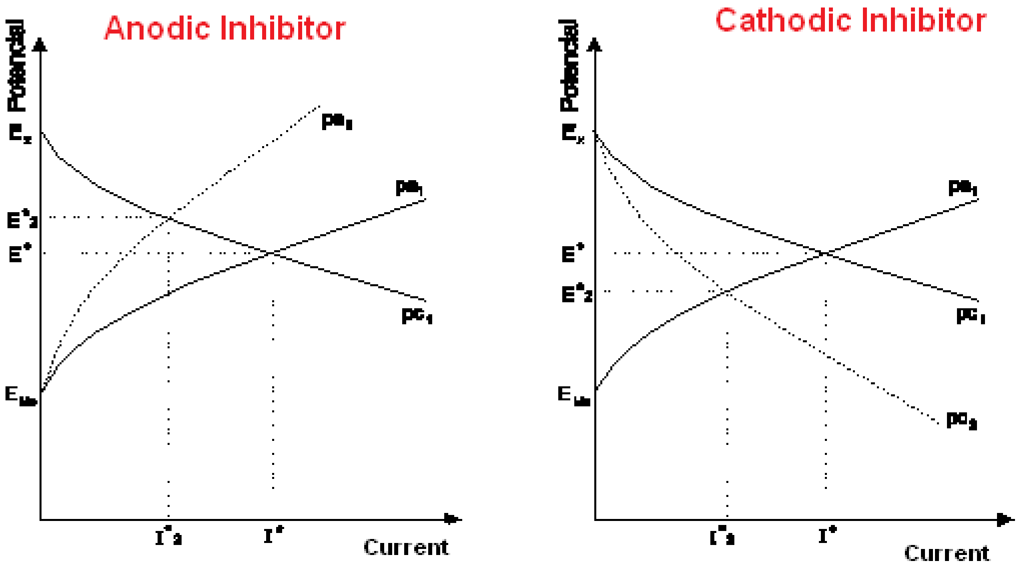


Figure 06 – Graphic representation of the anodic and cathodic effects, with a reduction in the corrosion chain and a shifting of the corrosion potential

Without the presence of the corrosion inhibitor, the potential for corrosion in the system is represented by E*, and the corrosion chain by I*, defined by cathodic (pc1) and anodic (pa1) polarization curves.

In the anodic inhibition process, the anodic polarization curve changes from pa1 to pa2, altering the corrosion state, and the corrosion potential shifts in a prime direction (E*2), causing a reduction in the corrosion chain from I* to I*2. In the cathodic inhibition process, a shift in the corrosion potential toward a less prime direction occurs, creating a reduction in the corrosion chain.

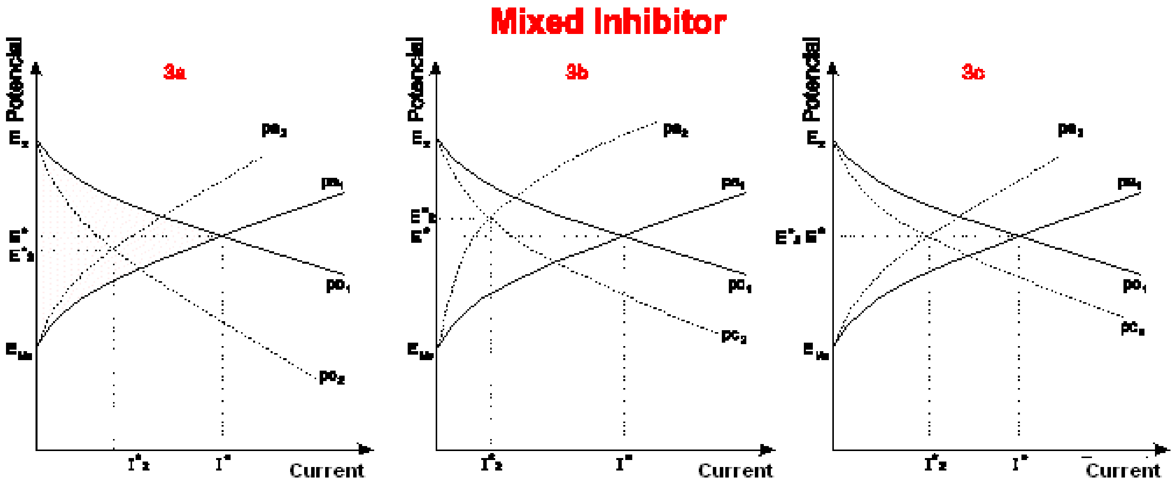


Figure 07 – Graphic representation of the effect caused by mixed inhibitors, with a reduction in the corrosion chain and a shift in the corrosion potential.

With the use of mixed inhibitors, alterations will occur in the anodic, as well as in the cathodic, polarization curve, and in both cases a reduction in the corrosion chain, with variation only in the corrosion potential shift, can be observed: in a less prime direction, figure A; and in a prime direction, figure B; with no alteration, figure C.

As already mentioned, the metallic corrosion starts when humidity (which contains electrolyte) condenses on the metal surface causing a flow of electrons between the metal surface and the electrolyte.

5.5 VCI Applications

VCI products can be formed in several ways. For example, a VCI may be mixed with a carrier such as liquid and sprayed onto the substrate to be protected. The liquid evaporates and leaves a thin layer of VCI on the substrate. Alternatively, a VCI may be applied to a carrier such as paper, thin plastic or another material with relatively high surface area. Typically VCIs applied in this manner have a solvent (such as ethanol/water) as the carrier. The VCI is mixed with the solvent and then coated, impregnated or otherwise applied to the carrier. Also, it is common for vapor-phase or volatile corrosion inhibitor master batches or concentrates to be formed and used in manufacture of poly films, VCI impregnated paper, molded plastic, and other packaging materials which incorporate VCIs.

VCI products can be formed where the VCI is incorporated in to the carrier, as when mixed into a binding matrix such as a resin. For example, a volatile corrosion inhibitor emitting device can be readily molded or cast, which allows the emitting device to form a shape that fits a particular application. This is advantageous in that the device can be custom fitted to an enclosure, a packaging container or the items being protected from corrosion. Emitters may be formed as a narrow cylinder to protect gun barrels, fish-shaped to protect tackle boxes, a bolt to protect tool boxes, a blue shield to protect ferrous based metals, a red shield to protect electrical boxes, a thin strip emitter comprising a resin with the VCI mixed into the plastic, etc.

As already mentioned, VCI mixture can be presented in several ways, depending on its purpose. In addition to VCI paper and film there are other forms to present volatile inhibitors: liquid form (spray) and powder (sachet).

VCI Plastic Film: this can have, for example, a polyethylene basis. A “stretch” film is used as support and is more applied as the package final layer. Due to large demand of its direct customers, a packaging system which use stretch in tapes containing volatile inhibitor, being it applied directly over the surface to be protected.

VCI Paper: is presented in several forms (tubes, sheets, bags, plastic paper, Raffied paper, etc.) and contains a chemical formulation based on compounds of organic salts, which are transferred to the support paper. According to the end use of the product, desired mechanic resistance can be given to VCI paper, which guarantees a perfect metal conditioning in the packaging.

Sachet/Powder Use: VCI sachet is placed inside any kind of packages or between empty spaces of an equipment; and must be as close as possible to the metallic parts. As this use demands more amount of VCI than the use of VCI paper, a packing supplement of VCI paper usually is added in order to reinforce the environment.

5.6 Use Durability

Durability of VCI Paper is directly linked to the conditions of protection of the package. For the protection to take place in an ideal system, the package must be airtight shut, providing equilibrium in the system. In this case, durability of VCI's corrosive protection tends to be infinite.

The exact reproduction of the above conditions is impossible. There is an exchange between the package environment and the outside environment (small leaks or openings), and said environment will constantly be "renewing" itself, causing consumption and consequently a wearing down of the VCI amount applied to the system.

VCI Packaging material contains the needed amount of active product to support some damages on the protection package, but it is necessary to take precautions.

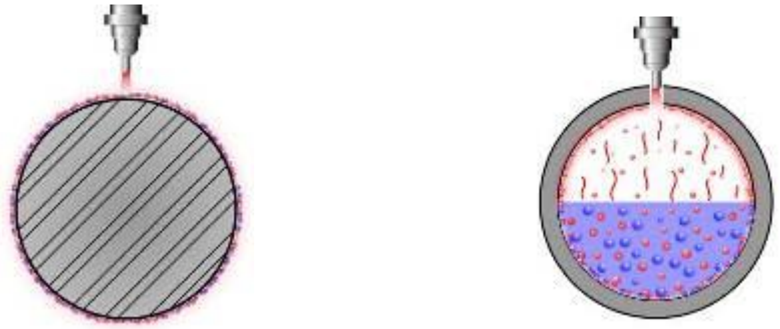
6 Results and Discussion – Mechanisms of V-active VCI

V-ACTIVE VCI: TECHNOLOGY AND CONCEPT

Using the concept of dissociation of the VCI salt promoted by the presence of water (as explained on VCI Chapter 4), has been developed a new formulation of chemical inhibitors that use water medium as the application method, and these new inhibitors/formulation have the property of "neutralize" the oxidizing power of the water, transformed it into the way of application and propagation. In addition to this property, these inhibitors named V-active maintains the property of volatile inhibitor. Thus these compounds are generically called up by **V-active VCI**. Active = the chemical compounds have electrical activity on metal surface and VCI because the base of activity was VCI mechanisms and have activity on liquid and vapor phase.

This chemical formulation (in this case a mixture of various salts of “fatty amine” and organic carboxylic acid, without any inorganic salt), when in the presence of water or aqueous contaminant, migrates to this medium and promotes its dissociation. This generates electrically active products, which interfere with the polarization current of the metal present.

For example, if in a diesel tank happens the water contamination (common evidence), the water sinks to the bottom of the tank and promotes the oxidation of the metal, and oxidizes the parts of the empty tank - top. The inhibitor V-active VCI, if added to diesel fuel prior to the oxidation process, which is also soluble in diesel, migrates to the aqueous medium and inhibit the oxidation process, both in the liquid phase (bottom) and in the vapor phase (void volume tank - top).



External protection,
film-forming with chemical activity

Internal protection
into liquid phase and vapor phase - VCI

Figure 08 – Graphical representation of the mechanism of action of the V-active VCI

This property enabled a variety of applications, which allows formulating new products according to the medium of desired protection.

To prove the protective efficiency of V-active VCI corrosion inhibitors were developed some testing procedures, both in the laboratory and in the industrial field. For this it selected a number of conditions that represent the application of reality through the difficulties.

Thus, we used techniques recognized as the EIS to study the influence of the amine group and was elaborated laboratory methods, including the JAR test, immersion and steam test, etc.

Field tests have also been developed for applying V-active VCI technology in the industrial field, in particular the pre-painting surface cleaning (Hydrojetting), cleaning and preservation diesel tanks, the inerting medium in transport containers, among others.

Presented below all the methods used to demonstrate the protective efficiency of water corrosion inhibitors "V-active VCI", as well as technical reasons that prove the proposed using water as a means of propagation of the corrosion inhibitor.

7 Practical Developments, Results and Comments

Following are the developments and behavioral studies of basic chemicals and formulations (mixtures), in the laboratory and in actual cases applications.

Chemicals and formulations (ratio) presented below, are described as generic formulas for being part of the company's authoring secret affects (VCI Brasil). Remember that the objective is not only to demonstrate the chemicals, but its effect on the metal surface and the positive results of corrosion inhibition in aqueous media.

7.1 Development of V-active VCI compounds - Formulation

It is known that from long use (since 1996 when I began to study and develop corrosion inhibitors) that the best products using the VCI technology are formed by mixtures of carboxylated amines, they are easily dissociated into cations and anions, which to adsorb on the metal surface, have electric activity. This property makes it possible to decrease the bias current and increase corrosion inhibition.

Many salts of carboxylate amines may be obtained and used as a VCI, with the compound having a sufficient vapor pressure to volatilize at room temperature, but should also be noted that many chemicals have, as mentioned, its use restricted by some international standards to "use restriction of chemicals". As an example of restricted substances, it is possible to mention a few primary and secondary amines, among them morpholine, ethylamine, cyclohexylamine, and phosphate salts, chromate and the use of heavy metals.

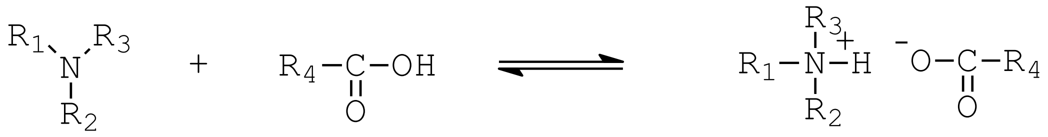
In addition to observing these restrictions chemical substance uses, should assess whether the product obtained after the reaction (or chemical mixture) are toxic or not. This that meets the legal requirements of use and do not affect the operators and the environment during use.

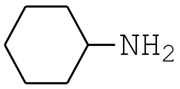
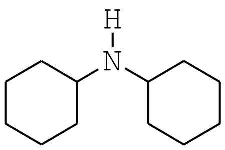
Thus, the following formulations used were designed to meet all usage specifications and still be effectively positive in the sense of corrosion protection.

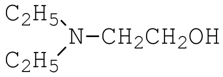
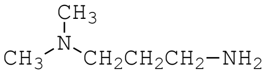
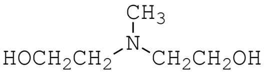
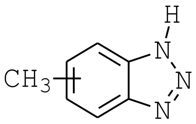
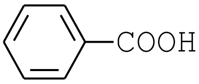
1. Salt from diethylethanolamine and caprylic acid: 10 to 50%, preferable 20-30% - named VCI1 (DEAC)
2. Salt from diethylethanolamine and benzoic acid: 5 to 30%, preferable 10-20% - named VCI2 (DEAB)
3. Salt from dicyclohexylamine and caprylic acid: 10 to 50%, preferable 20-30% - named VCI3 (DCAC)
4. Salt from dicyclohexylamine and benzoic acid: 10 to 50%, preferable 20-30% - named VCI4 (DCAB)
5. Salt from 3-dimethylaminopropylamine and caprylic acid: 10 to 50%, preferable 20-30% - named VCI5 (DMAPAC)

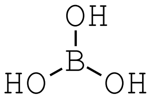
6. Salt from 3-dimethylaminopropylamine and benzoic acid: 10 to 50%, preferable 20-30% - named VCI6 (DMAPAB)
7. Salt from 2,2'-(methylimino)diethanol and caprylic acid: 10 to 50%, preferable 20-30% - named VCI7 (MDEAC)
8. Salt from 2,2'-(methylimino)diethanol and benzoic acid: 10 to 50%, preferable 20-30% - named VCI8 (MDEAB)
9. Salt from monocyclohexylamine and caprylic acid: 10 to 50%, preferable 20-30% - named VCI9 (MCHAC)
10. Salt from monocyclohexylamine and benzoic acid: 10 to 50%, preferable 20-30% - named VCI10 (MCHAB)
11. Salt from dicyclohexylamine and boric acid: 10 to 50%, preferable 20-30% - named VCI11 (DCBO)
12. 1-H-4/5 Methylbenzotriazol - all formulation have 1 – 10%, preferable 2 – 5%, named TTZ

From the chemical point of view, the mixing of aliphatic or aromatic amine (primary, secondary, tertiary) with a carboxylic acid leads to the formation of salt and an equilibrium:



Name	Formula	Data
Monocyclohexylamine		Melting point = -17.7 °C Boiling point = 134.5 °C Vapor pressure = 11 mm Hg (20° C) Acidity (pK_a) = 10.64 LD_{50} = 156 mg/Kg (rat, oral)
Dicyclohexylamine		Melting point = -0.1 °C Boiling point = 255.8 °C Vapor pressure * Acidity (pK_a) = 11.43 (predicted at 25 °C) LD_{50} = 373 mg/Kg (rat, oral)

Diethylethanolamine		Melting point = -70 ^{o}C Boiling point = 161.1 ^{o}C Vapor pressure = 100 Pa (at 20 ^{o}C) Acidity (pK_a) = 14.74 (predicted at 25 ^{o}C) LD_{50} = 1300 mg/Kg (rat, oral)
3-Dimethyl-aminopropylamine		Melting point = -70 ^{o}C Boiling point = 123 ^{o}C Vapor pressure = 0.7 – 2.4 KPa Acidity (pK_a) = 10.13 (predicted at 25 ^{o}C) LD_{50} = 1870 mg/kg (rat, oral)
2,2'-(Methylimino)-diethanol		Melting point = -21 ^{o}C Boiling point = 247.1 ^{o}C Vapor pressure = 1 Pa (at 20 ^{o}C) Acidity (pK_a) = 14.41 (predicted at 25 ^{o}C) LD_{50} = 1945 mg/kg (rat, oral)
Methyl benzotriazol		Melting point = 82^{o}C Boiling point = 210^{o}C LD_{50} = 1600 mg/kg (rat, oral)
Caprylic acid	C_7H_{15}-COOH	Melting point = 16.7 ^{o}C Boiling point = 239.7 ^{o}C Vapor pressure = 0.25 Pa Acidity (pK_a) = 4.89 LD_{50} = 10.08 g/kg (rat, oral)
Benzoic acid		Melting point = 122.41 ^{o}C Boiling point = 249.2 ^{o}C Acidity (pK_a) = 4.202 LD_{50} = 1700 mg/Kg (rat, oral)

Boric acid		Melting point = 170.9 °C Boiling point = 300 °C Acidity (pK_a) = 9.24; 12.4; 13.3 LD_{50} = 2660 mg/Kg (rat, oral)

CRC Handbook of Chemistry and Physics, 78th Edition 1997-1998.

When formulating a chemical product, the final expected behavior alone cannot match the expected protective efficiency because there is a chemical interaction between the various products, which is generally called chemical synergy. That is, a particular chemical may not have a protective efficiency when considered in isolation, but in conjunction with a proportional relationship to another chemical, presents certain chemical protection. For this reason, a study of the substance is presented alone, by EIS technique (Electrochemical Impedance Spectroscopy), which refers to the study isolate each substance formulation and behavior (mixture) evaluated for practical applications.

7.2 Study of Amine Salts Using EIS

(Special thanks to Prof. Dr. Antonio Carlos Dias Angelo and UNESP Bauru - Faculty of Science - Chemistry Department – paper presented on The Electrochemical Society Meeting – Hawaii)

Volatile Corrosion Inhibitors (VCIs) have been presented as efficient inhibitors against atmospheric corrosion on metals. These compounds usually have high vapor pressure that enables them to strongly adsorb on the metallic surface in closed systems. The resulted adsorbed film protects the metallic surface against the aggressive action of compounds present in the atmosphere.

Despite the advantageous uses of this class of inhibitors, over grease and protective oils for protecting metallic stored materials, there has not been found a practical method to evaluate their action. The methods usually employed are commonly complex, time spending and non-reproducible. In this regard, we have recently proposed the use of the Electrochemical Impedance Spectroscopy (EIS) to qualitatively evaluate the action of the inhibitor [5].

The action of the VCI in aqueous solution is based on the electrosorption of the inhibitor molecules on the metal. The electrosorption is the organic molecules adsorption on the metallic surface by replacing the solvent molecules [6] that can be represented by equation (1) as follows:

$$R + M - nH_2O_{ads} \rightarrow M - R_{ads} + nH_2O \tag{1}$$

where R represents the organic molecule and M represents adsorption surface metallic site.

Volatile Corrosion Inhibitors are characterized by exhibiting strong interaction with the metallic surfaces [7]. In this case one can suppose that the changing in the Gibbs free energy (ΔG_{ads}) should be depicted in terms of the chemical potential of the species involved in the electrosorption process [6]:

$$\Delta G_{ads} = (\mu_{M-R} - \mu_R) - n(\mu_{M-nH_2O} - \mu_{H_2O}) \tag{2}$$

Due to strong interaction between the organic molecule and metallic surface, it is realistic to consider that the chemical potential of the organic molecule adsorbed is smaller than the chemical potential of such specie in the bulk solution. On the other hand, the replacement of the water molecules adsorbed on the metallic surface by the organic molecule is an entropy favorable process that enables us to consider that the chemical potential of adsorbed water molecules is greater than the chemical potential of this specie in the bulk solution. On these assumptions ΔG_{ads} becomes negative suggesting that the electrosorption of the inhibitor molecules is a spontaneous process in aqueous solution, which allows the evaluation of the VCIs in aqueous solution.

The aim of this work is to investigate the action of organic compounds usually employed as VCI, in aqueous solution, by using *EIS* technique.

Mild steel VC1020 (0.25% C; 0.15-0.30% Si; 0.80-1.20% Mn; 0.04% P, 0.05% S and 0.20% Cu) disc samples (surface geometric area = 3,14cm^2), were polished with grade 2000 emery paper (Imperial Wetordry 401Q, 3M), and afterward polished with alumina suspension (QM, 0.3μm) to achieve a mirror finishing and followed by degreasing with acetone. After polishing, the samples were submitted to ultrasonic bath (Thornton, T7C), in deionized water (Barnstead, 18MΩ), in order to remove surface impurities and alumina residues. The samples were mounted in a copper rod conductor and sealed with epoxy resin and tube shrinkable.

The corrosion inhibitors used were the following compounds: dicyclohexylamine caprilate (DCAC), monocyclohexylamine caprilate (MCAC), diethylethanolamine caprilate (DEAC), diethylethanolamine borate (DEBO) and diethylethanolamine benzoate (DEAB), all in ethanol solution 50% (w/v). The first three compounds were studied to evaluate the influence of the cation while the three last compounds were studied to investigate the influence of the anion on the corrosion inhibition process. Those compounds were synthesized and characterized in our laboratories. The inhibitor was added to the electrolyte solution up to a concentration of 0.01g L^{-1}, which, from our previous experimental findings, showed to be the minimal concentration necessary to achieve equilibrium between the inhibitor on the metallic surface and the inhibitor in the bulk solution and to provide a protective action.

Electrochemical studies were performed in a glass corrosion cell using a high surface area carbon rod as counter electrode and a Saturated Calomel Electrode (SCE, Analion E1768) as reference. All potentials cited in this paper are referred to the SCE. The corrosion cell was filled with 5% w/w NaCl solution prepared with deionized water.

The evaluation of the inhibitor performance was investigated by EIS. All EIS studies were performed, in the frequency range of 10KHz to 0.05 Hz (withan amplitude of 10 mV), at a determined electrode potential. This technique was applied by using the electrochemical system consisting of a Potentiostat/Galvanostat (EG&G - PAR, mod. 283) and a Frequency Response Detector (EG&G-PAR, mod. 1025) controlled by a Personal Computer.

Cation Influence

From the representative impedance plots for the anodic process occurring on mild steel VC 1020 and with added MCAC, DEAC and DCAC. MCAC and DCAC produced one semi-circle for lower overpotentials range and for higher overpotentials it can be observed an inductive loop in low frequencies range. DEAC presented for higher overpotentials range a second semi-circle. Mild steel impedance plot presented an inductive loop in lower frequencies range. It must be point out that the inductive loop is usually related to iron dissolution process [8]. Furthermore, the presence of the inhibitor has effectively increased the resistance of charge transfer from the metallic surface. EIS data was mathematically adjusted by using the Boukamp program [8] and by considering the simplest equivalent circuit that is able to represent the electrode interphase. Results shows the dependence of the estimated charge transfer resistance (R_{ct}) on the electrode overpotential for all studied systems. The main feature to point out from this study is the remarkably increase in the R_{ct} values for the anodic process in the presence of the inhibitors that can be related to the protective action of the organic film adsorbed on the metallic surface through electrosorption. The investigated inhibitors have minimized the corrosion of the mild steel mainly for overpotentials up to 150 mV. It is possible to suggest that overpotentials higher than the cited value are able to damage the protective film. From the same study one could obtain the influence of the anodic overpotential on the double layer capacitance (C_{dl}). From the plots the corresponding estimated data. In this study it was considered that the electrode interphase could be represented by a parallel plates capacitor, which can be represented by equation (3) as follow [9, 10]:

$$C_{dl} = \varepsilon . \varepsilon_f . \frac{A}{d} \tag{3}$$

where ε is the dielectric constant in vacuum; ε_f is the dielectric constant of the protective film; A is surface area and d the thickness of the film on the electrode surface. From the adopted experimental conditions it should be suggested that C_{dl} is dependent on the dielectric constant of the film produced on the electrode surface for different inhibitors. All remaining parameters in the equation were considered unchanged. In this regard the more close packed or dense structure of the film ought to a better inhibition against corrosion. From the data depicted it is difficult to assert the exact influence of the protective film on the inhibition process. However, one can be observe that the DEAC has presented the smallest capacitance value among all the organic compounds investigated. Furthermore, it is reasonable to take into account that a combinatory influence of the changing in the film dielectric constant and thickness should be implicated in the obtained results. Table 5 summarizes the EIS parameters obtained from the performed study. It is suggested that the compound DEAC presented the highest inhibitory action (under this experimental conditions), that can be observed from the biggest R_{ct} and the smallest C_{dl} values.

Table 5 – Impedance parameters (Rct and Cdl) for mild steel in 5% p/p NaCl at 25ºC and with the inhibitors DEAC, MCAC and DCAC.

SAMPLE	η/mV	C_{dl} (mF/cm^2)	R_{ct} (Ohm cm^2)
Mild steel	157	16.65	2.03
DCAC	135	28.95	314.18
DEAC	160	21.68	545.98
MCAC	154	43.55	427.50

These results must be rationalized due to the structure of the adsorbed film on the metallic surface. The DEAC differentiates from the other compounds by the absence of cyclic substituents in its structure. Consequently, DEAC is able to adsorb on the metal surface in a denser package compared with the other compounds. This denser film may be result in higher corrosion inhibition.

Anion Influence

Through the results, displays some representative complex plane impedance plots for the anodic process occurring on mild steel VC 1020 and in the presence of the inhibitors DEAC, DEAB and DEBO. DEAB presented an inductive loop in lower frequency range in almost the whole explored overpotential range. For DEBO it was observed two semi-circles in the whole overpotential range. Furthermore, the presence of inhibitor has effectively increased the resistance of charge transfer from the metallic surface. Through the results, it is possible observe the dependence of the electrode capacitance and the charge transfer resistance on the electrode overpotential. Table I6 show the representative impedance parameters for the investigated systems. From the results obtained, one can propose that the compound with caprilate anion presented the highest corrosion resistance.

Table 6 – Impedance parameters (R_{ct} and C_{dl}) for mild steel in 5% p/p NaCl at 25ºC and with the inhibitors DEAC, DEAB and DEBO.

SAMPLE	η/mV	Cdl (mF/cm2)	Rct (Ohm cm2)
Mild steel	157	16.65	2.03
DEAC	160	21.68	545.98
DEAB	180	3.637	2.53
DEBO	185	111.50	7.89

Figure 9 - Cell

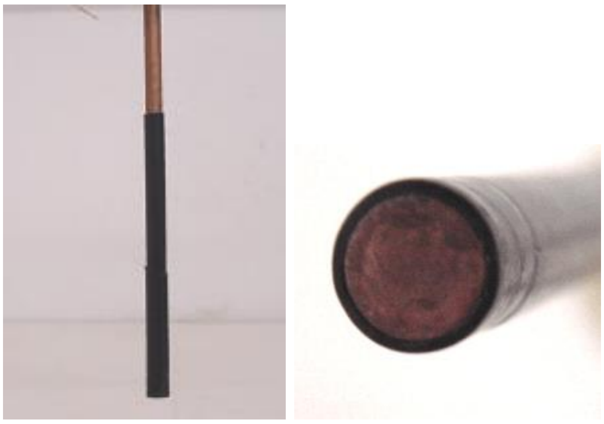


Figure 10 – Electrode test with metal coupon

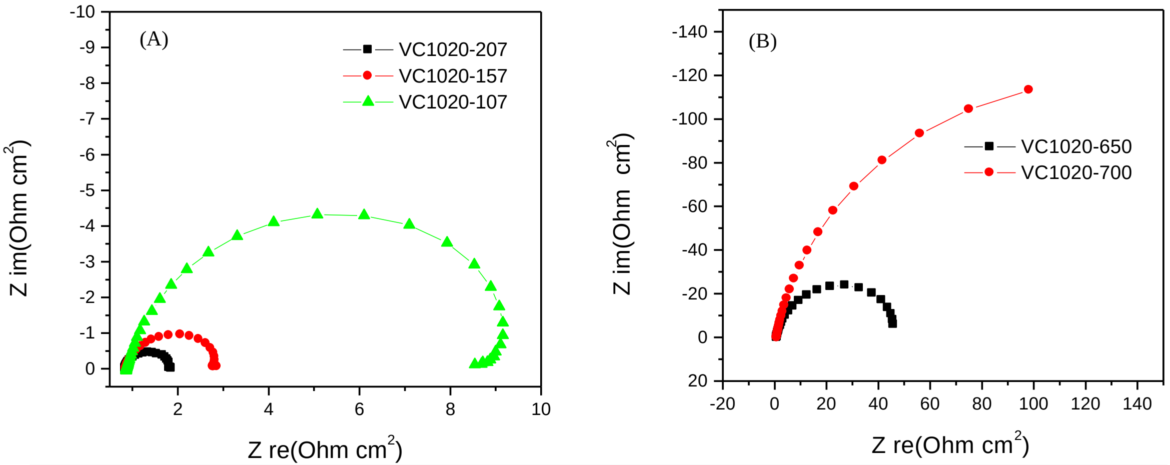


Figure 11 – Anodizing impedance chart for steel VC1020 in NaCl 3% at room temperature

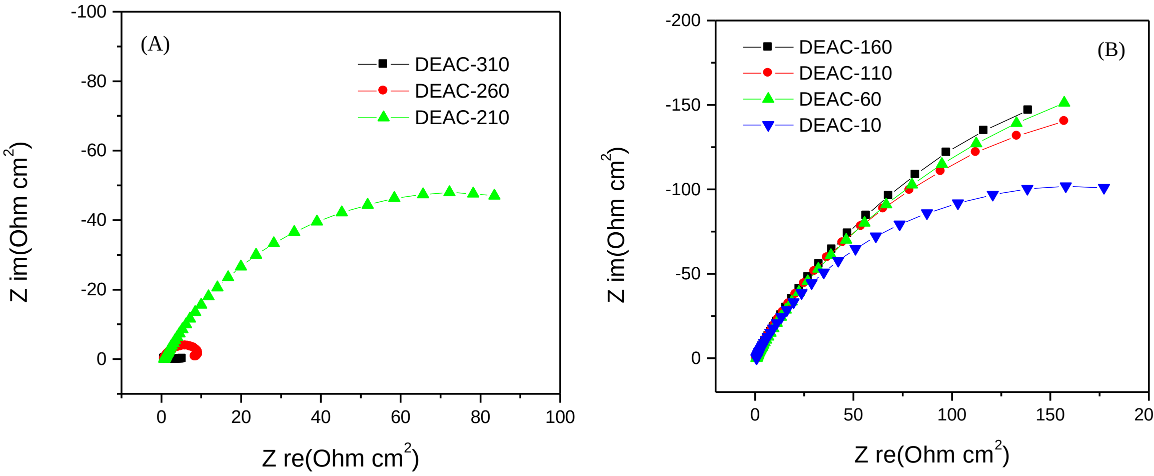


Figure 12 – Anodizing impedance chart for steel VC1020 in NaCl 3% at room temperature + DEAC corrosion inhibitor

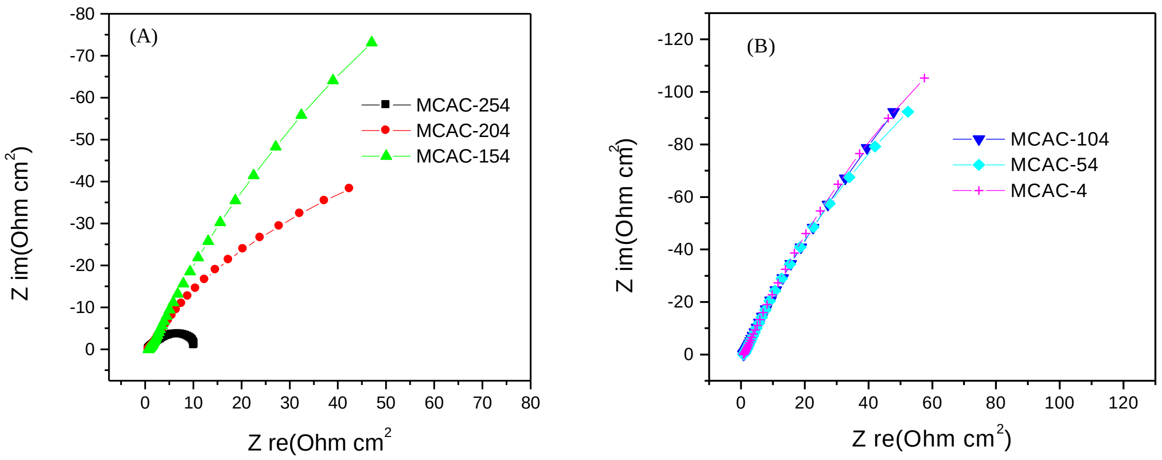


Figure 13 – Anodizing impedance chart for steel VC1020 in NaCl 3% at room temperature + MCAC corrosion inhibitor

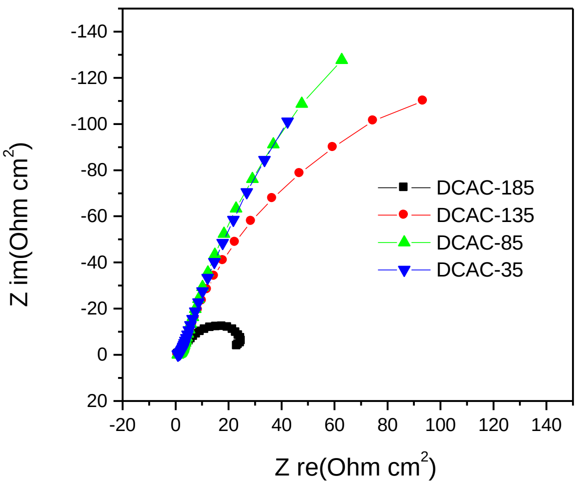


Figure 14 – Anodizing impedance chart for steel VC1020 in NaCl 3% at room temperature + MCAC corrosion inhibitor

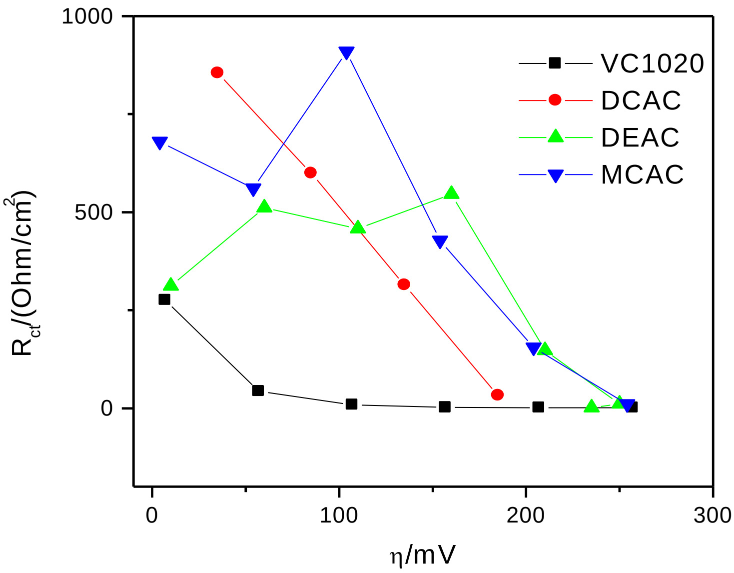
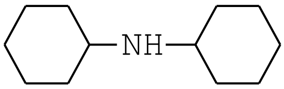
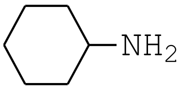
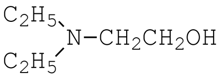
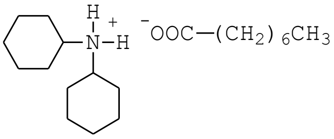
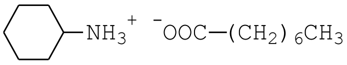
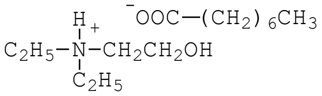


Figure 15 – Charge transfer resistance (Rct) dependent on the electrode overpotential in NaCl 3% at room temperature + 0.01g/L corrosion inhibitor

Acid	Caprylic acid $CH_3(CH_2)_6COOH$		
Base	Dicyclohexylamine 	Cyclohexylamine 	Diethylethanolamine $(C_2H_5)_2N-CH_2CH_2OH$
Salt	Dicyclohexylamine caprylate [90] 	Cyclohexylamine caprylate [91] 	Diethylethanolamine caprylate [10] $C_2H_5-\overset{H\,+}{N}(C_2H_5)-CH_2CH_2OH\ \ ^-OOC-(CH_2)_6CH_3$

EIS has provided useful information about the inhibitory action of some compounds that can be used as VCI. The obtained results suggested that diethylethanolamine cation produces a denser film, which is most effective for surface protection. On the other hand, the investigation on the anion influence confirmed that the caprilate derivative could be an effective inhibitor for corrosion.

7.3 Development of Water Based Protective Products

Using the concept proposed that water is the means of transport of the corrosion inhibitor, specific formulations (mixtures of chemicals) were prepared for the fluid containing the V-active VCI corrosion inhibitors. These fluids are generally used in metallurgical processes: water based metal working fluids.

Among these products (formulations) are mentioned: cutting fluids (machining), degreasing fluids, protective water based, etc. Besides the technical function that is desired to the product, giving it a corrosion inhibiting effect, ie it is possible to use the V-active VCI technology in these products, by adding the corrosion inhibitor property.

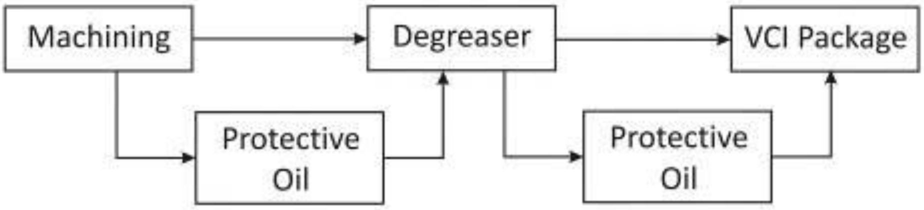
The current technology for "process fluids" comes from each stage of the process as a separate step, that is, it appears the machining process without assessing the previous or subsequent stage. With this new product chain water-based, known generically as MVAqua, there is the whole process, proposing changes in the production chain, always observing the result of corrosion protection as a primary objective and cost reduction and reduction of environmental liability. This enables process gains, elimination phases and therefore costs, reduce environmental and labor liabilities (problems associated with the use of products based oil and solvent).

When working out a process that proposes sending of metal materials with the use of VCI packaging is required before assessing the initial condition of the metal surface, as any contaminants can interfere with the protective efficiency (the contaminant can prevent direct VCI action in metal surface). The process steps and the products used interfere with the desired protective effect against corrosion.

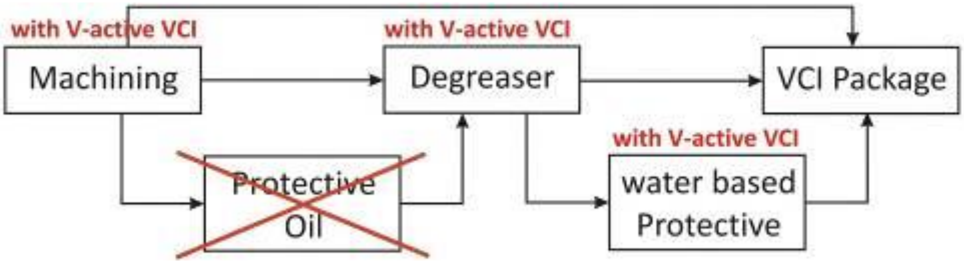
Thinking thus, before the indication of the use of VCI packaging, it is recommended to evaluate each step of the process and check what kind of chemicals the metal surface may be contaminated. If the product applied processes already contain compatible corrosion inhibitors or the same chemical base, the VCI packaging can be easily applied without the need of previous cleanings.

In the present process, the whole process is dependent on the applied chemicals and time needed for the next step.

Example: After the process of machining the metal part will go to another stage of the process, but will remain in stock closed for at least 15 days. In this condition the part needs to be protected against corrosion and applies a protective oil, unhealthy to the user and the environment. Prior to use, in another step of the process, the metal part should be cleaned and undergo a decontamination using a degreaser. Some regular market degreasers are highly alkaline and generate a residue on the metal part, which interferes with the protective efficiency of the VCI present on packaging. Thus, it is recommended to check the chemical basis of each degreasing.



In this example, it is possible to indicate the use of a machining fluid which contains a protective V-active VCI, eliminating the use of oil based protective and hence without requiring the use of a degreaser to decontaminate. With these changes and the use of V-active VCI, are eliminated two-step correction, maintaining the integrity of the metal piece and compatibility with the use of a VCI packaging, noting that the main purpose of using a VCI packaging is be clean and dry parts, for immediate use without the need for cleaning procedures before use.



The use of industrial products (metal working fluids) containing the V-active VCI inhibitors, generically called MV Aqua, allows the elimination of process steps and show big gains in process costs, protective efficiency, reduction of environmental liabilities and labor. As besides the cost analysis assesses primarily the result of the protective efficiently generated with the use of V-active VCI corrosion inhibitors obtains complete and compatible processes, with effective results protection without the need for treatment and decontamination before use.

Formulation Example: Water Based Protective with V-active VCI

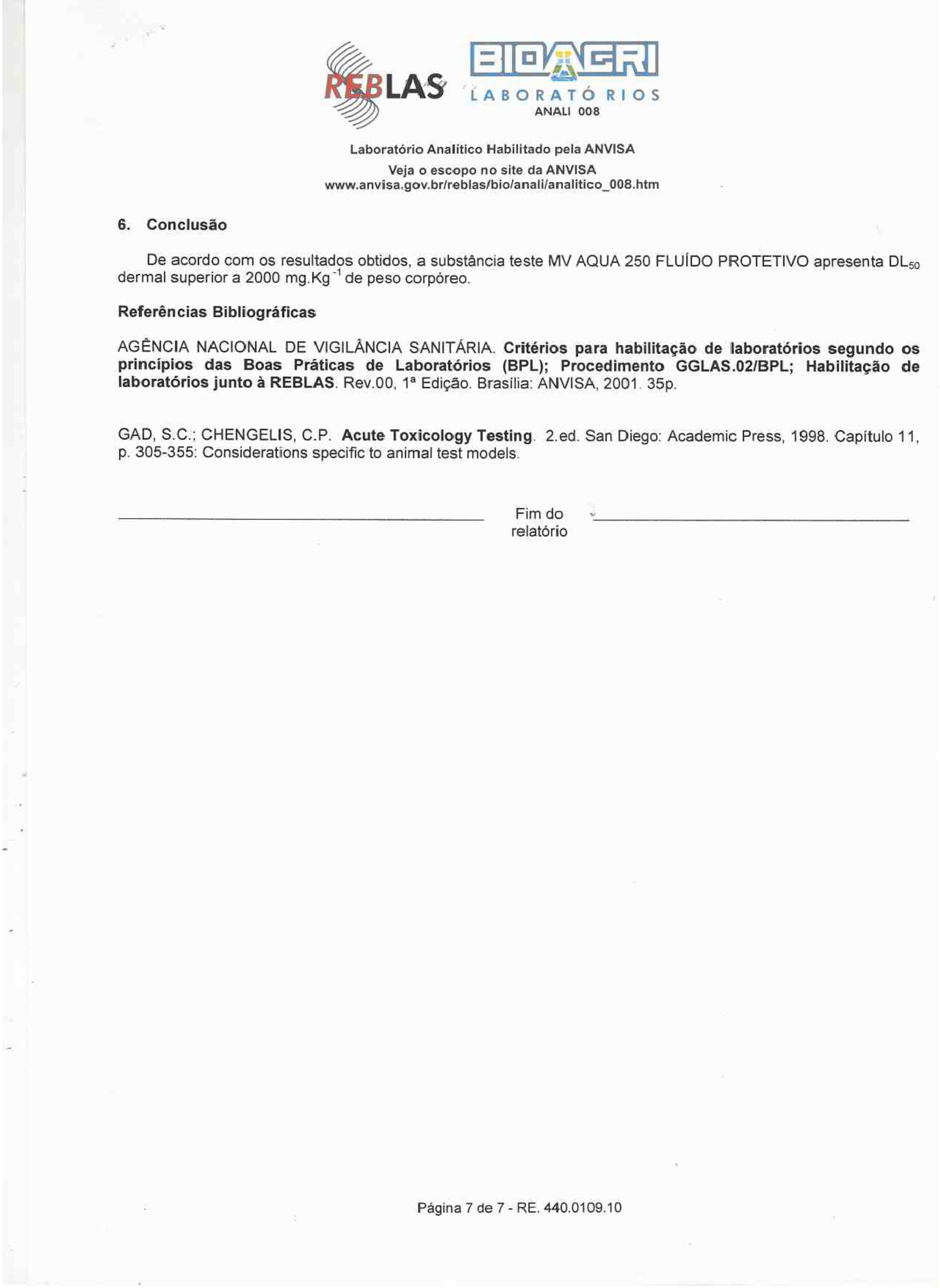
- Film Forming (10% up to 20%)
- Tension Surface regulator (15% up to 25%)
- Water Based Additive – V-active VCI compounds (20% up to 30%)
- Bactericidal (0.5 up to 1.0%)

This product, which has the generic name "Corrosion Inhibitor water-based", should be applied from 10% to 30% dissolved in water (industrial), depending on the initially estimated protection time before application. This level of concentration allows an effective concentration of inhibitor on the metallic surface 2% to 9%.

As previously mentioned, an important feature to be evaluated is the toxicity and biodegradability of each formulated product. All products formulated using the V-active VCI technology were subjected to toxicity and biodegradability tests, being regarded as "practically non-toxic" and biodegradable.

The following are examples of results of toxicity test (oral, dermal and inhalation) obtained by analysis of a commercial product MVAqua 250.

Conclusion: According to the results, the product has reported Dermal LD50 greater than 2000 mg/kg.



6. Conclusão

De acordo com os resultados obtidos, a substância teste MV AQUA 250 FLUÍDO PROTETIVO apresenta DL_{50} dermal superior a 2000 $mg.Kg^{-1}$ de peso corpóreo.

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GAD, S.C.; CHENGELIS, C.P. **Acute Toxicology Testing**. 2.ed. San Diego: Academic Press, 1998. Capítulo 11, p. 305-355: Considerations specific to animal test models.

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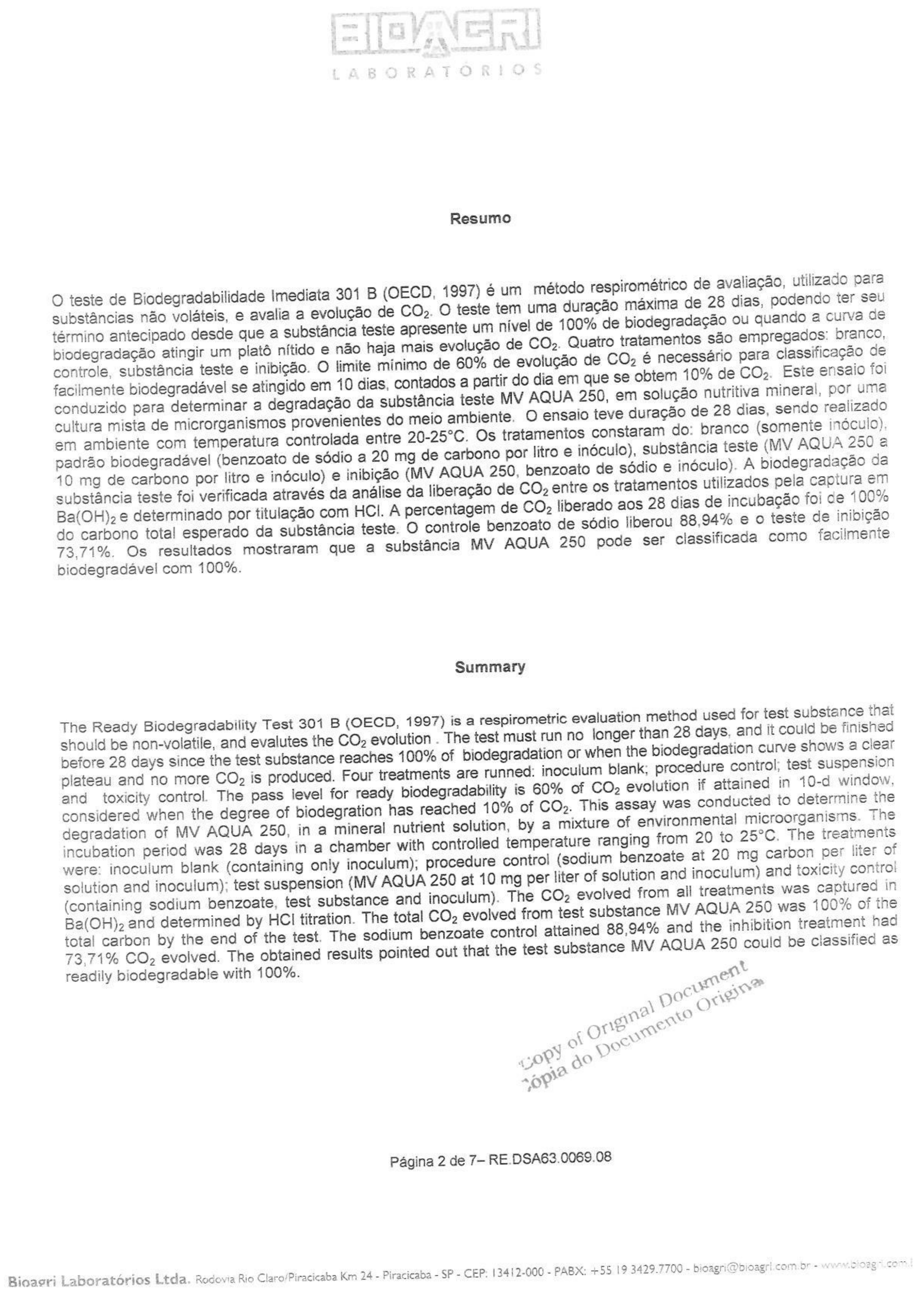

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Resumo

O teste de Biodegradabilidade Imediata 301 B (OECD, 1997) é um método respirométrico de avaliação, utilizado para substâncias não voláteis, e avalia a evolução de CO_2. O teste tem uma duração máxima de 28 dias, podendo ter seu término antecipado desde que a substância teste apresente um nível de 100% de biodegradação ou quando a curva de biodegradação atingir um platô nítido e não haja mais evolução de CO_2. Quatro tratamentos são empregados: branco, controle, substância teste e inibição. O limite mínimo de 60% de evolução de CO_2 é necessário para classificação de facilmente biodegradável se atingido em 10 dias, contados a partir do dia em que se obtem 10% de CO_2. Este ensaio foi conduzido para determinar a degradação da substância teste MV AQUA 250, em solução nutritiva mineral, por uma cultura mista de microrganismos provenientes do meio ambiente. O ensaio teve duração de 28 dias, sendo realizado em ambiente com temperatura controlada entre 20-25°C. Os tratamentos constaram do: branco (somente inóculo), padrão biodegradável (benzoato de sódio a 20 mg de carbono por litro e inóculo), substância teste (MV AQUA 250 a 10 mg de carbono por litro e inóculo) e inibição (MV AQUA 250, benzoato de sódio e inóculo). A biodegradação da substância teste foi verificada através da análise da liberação de CO_2 entre os tratamentos utilizados pela captura em $Ba(OH)_2$ e determinado por titulação com HCl. A percentagem de CO_2 liberado aos 28 dias de incubação foi de 100% do carbono total esperado da substância teste. O controle benzoato de sódio liberou 88,94% e o teste de inibição 73,71%. Os resultados mostraram que a substância MV AQUA 250 pode ser classificada como facilmente biodegradável com 100%.

Summary

The Ready Biodegradability Test 301 B (OECD, 1997) is a respirometric evaluation method used for test substance that should be non-volatile, and evalutes the CO_2 evolution . The test must run no longer than 28 days, and it could be finished before 28 days since the test substance reaches 100% of biodegradation or when the biodegradation curve shows a clear plateau and no more CO_2 is produced. Four treatments are runned: inoculum blank; procedure control; test suspension and toxicity control. The pass level for ready biodegradability is 60% of CO_2 evolution if attained in 10-d window, considered when the degree of biodegration has reached 10% of CO_2. This assay was conducted to determine the degradation of MV AQUA 250, in a mineral nutrient solution, by a mixture of environmental microorganisms. The incubation period was 28 days in a chamber with controlled temperature ranging from 20 to 25°C. The treatments were: inoculum blank (containing only inoculum); procedure control (sodium benzoate at 20 mg carbon per liter of solution and inoculum); test suspension (MV AQUA 250 at 10 mg per liter of solution and inoculum) and toxicity control (containing sodium benzoate, test substance and inoculum). The CO_2 evolved from all treatments was captured in $Ba(OH)_2$ and determined by HCl titration. The total CO_2 evolved from test substance MV AQUA 250 was 100% of the total carbon by the end of the test. The sodium benzoate control attained 88,94% and the inhibition treatment had 73,71% CO_2 evolved. The obtained results pointed out that the test substance MV AQUA 250 could be classified as readily biodegradable with 100%.

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7.4 Effectiveness – Laboratory Study

Because all MV Aqua is a water soluble product and use a new technology, it becomes impossible to apply the common tests used by accredited laboratories and described in standard as the Salt Spray test (ASTM B117-11 Standard Practice for Operating Salt Spray (Fog) Apparatus) and Humid Chamber test (ASTM D2247 - 11 Standard Practice for testing water Resistance of Coatings in 100% Relative Humidity) because both tests dissolve the water based product, preventing a conclusive analysis.

These ASTM practices provide a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber. That is, these tests use a water mist that deposits on the surface of the treated metal. Since the V-active VCI products are water soluble, all of it is dissolved by deposition of the mist (saline or not), precluding the use of these standard methods as study reference. It would be that water from the equipment, "wash" the V-active VCI from the metal surface.

To analyze the possible efficiency of V-active VCI products, it was essential to develop (adapt) a method to assess their protective efficiency. For this we used the Brazilian standard NBR 15109 (VCI efficiency test) as a base, making a change to the proposed in standard adapting to a device for the metal plate treated with V-active VCI, could stay all time during the test as immersed and part in the vapor phase.

Cleaning Metal Test Specimens (Metal Coupons)

For this step, it was used as a reference the Standard NBR 6210: 2008 “Atmospheric corrosion - Metallic materials - preparation, cleaning and determination of corrosion rate bodies of the test piece for corrosion tests”.

One of the most important steps is the selection of the "Metal Coupons" and the cleaning process. For all laboratory methods described below, was used for steel plates tests in 1020 (called by MCs, obtained from a flat steel maker CSN Brazil). These MCs were degreased with the use of neutral detergent, rinsed with deionized water several times with friction to remove the excess detergent, sanded with coarse sandpaper (480) and fine sandpaper (220) for perfect polishing. After further cleaning with detergent and rinsing with deionized water immediately MCs were immersed in pure acetone, and then dried over neutral paper. These MCs were then stored in a desiccator containing silica gel. In the process of manipulation of MC were used Neoprene surgical gloves in order to eliminate possible contaminations that human skin can impart the metal surface.

7.4.1 Jar Test

Standard ABNT NBR 15109 refers to the use of a 1L flask with a specific support for evaluating the VCI product. For the standard test after preparation, one should place the apparatus in a oven at a temperature of 65 ± 2 ° C for 1 hour, long enough to obtain a relative humidity near 100%. After this period, the apparatus is removed, and it remains for 30 minutes at room temperature. Repeat this cycle temperature and humidity for 3 times, observing the surface condition of metal. This test is relative and not absolute, that is, you should always make a test in parallel with a bottle without VCI, so you can evaluate relative to a metal unprotected and compare the difference.

To adapt the method and possible assessment used the same apparatus and same conditions of temperature (65 ± 2 ° C), but the evaluation time extends (16hs at 65°C - 8hs at 23°C). A new support has been prepared in order to keep part of the immersed metal and elsewhere in the vapor phase.

Figure 16 – Standard ABNT NBR 15109 – original apparatus

Figure 17 – New support and adaptation for testing

For each assay were prepared varying concentrations of product V-active VCI (mass / mass), and by simple dissolution of the product mass in deionized water. The cleaned and dried MCs were then placed in the apparatus, always remaining part of the MC immersed in the solution and partly in the vapor phase. As a means of comparison, we used the same apparatus and MCs, but used only deionized water.

This assembly was then placed in a oven at a temperature of 65 ± 2 ° C for a period of 16hs and removed to ambient temperature 23°C during 8hs being referred to as “one cycle”.

Figure 18 – Oven and apparatus

It was observed that in the process without protection, the MCs are oxidized, as expected, while in the liquid phase there was an almost immediate oxidation and vapor deposition was observed and oxidation after the first cycle.

For other MCs and conditions, we observed a long time of protection, both in the vapor phase and the liquid phase. It is also noted that in small concentrations such as 0.10% took 10 cycles to start oxidation in the vapor phase, while remaining intact and free of oxidation when immersed in the solution. For concentrations of 0.20%, 0.25% and 0.50% was observed after beginning of oxidation 15, 25 and 40 cycles, respectively. For other concentrations of 1%, 2%, 5% and 10% no rust was observed in both the liquid and vapor phase during the course of the test.

Test Apparatus – no inhibitor

Figure 19 – Test apparatus for liquid and vapor phase – no inhibitor

Test Apparatus – V-active VCI inhibitor

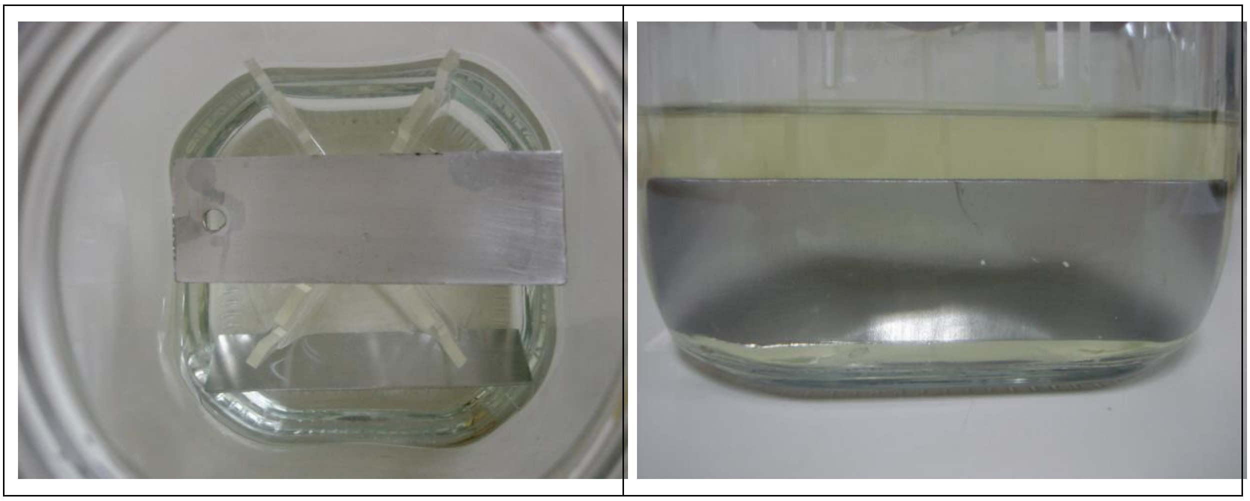


Figure 20 – Test apparatus for liquid and vapor phase – no inhibitor

After 60 cycles (days) Removal of the heating phase at 65 ± 2 ° C while maintaining the vial under test for 200 days at room temperature (approximately 23 ° C). No changes or oxidation was found. A result observed in the vial containing only deionised water (kept closed) was the formation of widespread microorganisms. In the flasks containing the V-activeVCI solutions (corrosion inhibitor), we were not observed any microorganisms, in any of the tested concentrations (0.10 to 10.0%). This result was observed in other tests as well (such as wood boxes, cartons, various aqueous solutions).

Although it is not the purpose of the product, it was possible to prove that the V-active VCI product maintains stability in aqueous solution without the proliferation of microorganisms. Additional tests conducted in independent laboratories confirm this property.

7.4.2 Glass Vasel

It tested the water-based inhibitor dissolved at 2% in deionized water, keeping part of the MC immersed in the solution and part of the air, in a capped glass vial. These sets, with and without V-active VCI inhibitor, were kept under room temperature (range 15 to 30 ° C) for 12 months.

To date description and presentation of this work, metallic materials were in perfect condition, even in the vapor phase.

For the implementation of this test was elaborated four glass bottles, shaped aquarium (approximately 5L or $0.05m^3$), containing no fixed caps. Was selected in a tube 1020 steel industry, 4 inch diameter samples were cut in 2 parts. One of 1020 steel bar was selected, 2 inches in diameter and were machined 2 metal parts with thread designs and deep cuts. These metal parts are extensively used in industrial piping, particularly in the manufacture of fluid transmission lines in the oil and gas industry.

Through the results it was possible to prove the effectiveness of protective corrosion inhibitor developed. In the bottle without corrosion inhibitor, intense oxidation was observed both in the vapor phase and the liquid phase of the metal piece. In the set containing the inhibitor dissolved in water, not observed any oxide formation during the time of 1 year.

It was also observed an intense formation of condensed water during the evaluation time, showing activity also be in the vapor phase, which assists the activity of the V-active VCI corrosion inhibitor also in vapor phase.

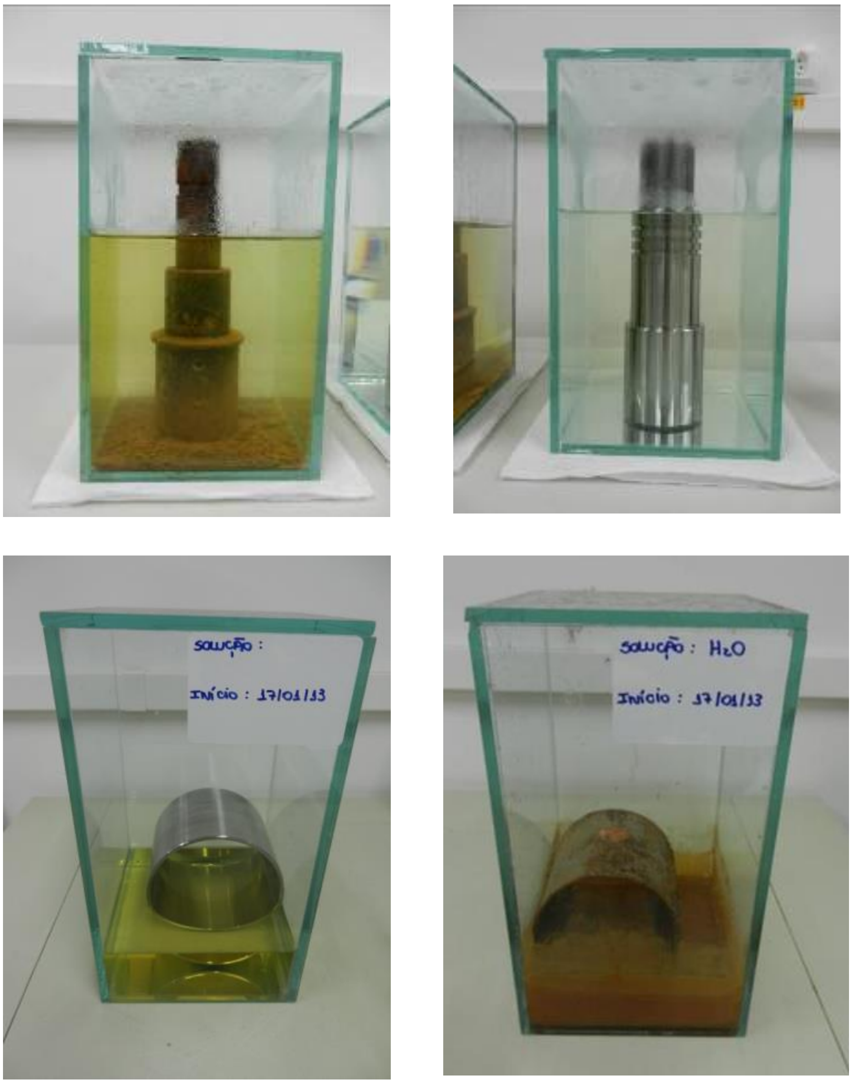


Figure 21 – Glass Vasels with and without V-active VCI

7.4.3 Woodboxes – Chemical Treatment

To inhibit the action of the acidity of the humid wood, when in contact with the metallic part, and prevent oxidation of metallic material.

Figure 22 – V-Active VCI Treatment – by spray

After the formulation of a V-active VCI solution in water and ethanol at the concentration of 57%, this solution was applied by spraying inside wooden crates. These wooden boxes are specially designed for testing, always taking care to be no gaps that allow the entry or exit of contaminants. The wood used is of greater use in export processes, being made from reforested pinewood.

Figure 23 – Fitting metal plates (for contact and vapor analysis)

Conditions of the tests:

Placing 10 boxes on the roof of the building, covered with polyethylene film with anti-UV treatment for a period of 12 months.

Placement of 2 boxes inside oven at 60°C, making the heating and cooling cycles - 60°C and 16hs 8hs at room temperature. Placed inside the boxes cups with water to increase indoor humidity.

Figure 24 – Results for metal plates (no V-Active VCI)

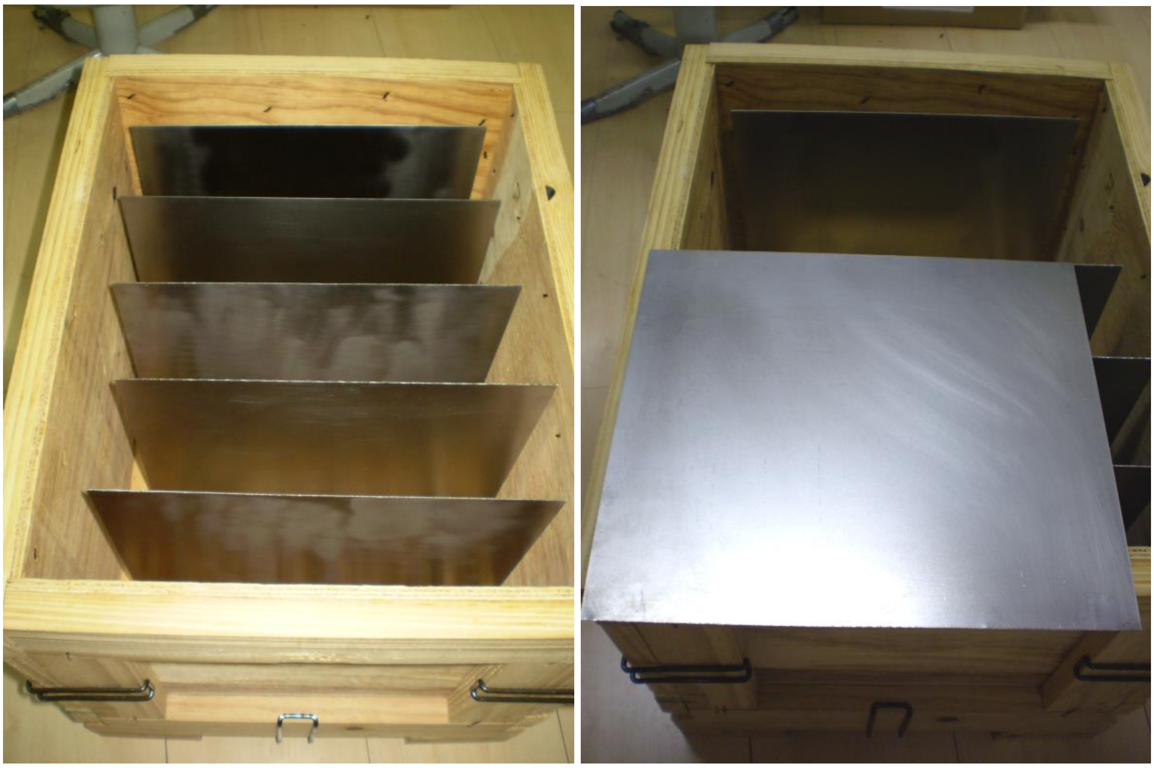


Figure 25 – Results for metal plates (with V-Active VCI)

The excellent results show the expected: efficiency against corrosion in the vapor phase (by volatilization of VCI) and the metal contact with the wood, showing that VCI treatment eliminates the influence of acid pH when damp wood comes into contact with the metal.

An important observation is on the quality of wood after treatment and high humidity. After this period of 12 months, the wood exposed and without V-activeVCI treatment was all degraded and with lot of fungus (mold) and bacteria (visually observed by dark green and black). The boxes treated with V-activeVCI and subjected to the same environmental conditions, is presented whole and without any visually detectable bacteria or fungus.

7.4.4 Diesel Fuel Tanks

In order to prove the protective efficiency and migration of the inhibitor from the solvent phase to the liquid phase, carried out 2 kinds of tests: simulation mini tanks steel and 200L pilot in drum.

In sequence, performed is a more complete work in real diesel tanks in the industry.

In all cases formulated were applied corrosion inhibitors, called V-active VCI 1061 .

7.4.4.1 Diesel Mini Tanks

SUBJECT

- Protecting internally stationary diesel tanks, by adding protective MVOil900 with V-active VCI1061.
- Test conducted using customer samples: diesel and iron ore
- Simulate the fuel behavior in the tanks, with evaluation of the influence of possible contaminants.
- The final application comprises tanks protect against oxidation and it is considered that they will be cleaned and prepared for the protective proposed method. During use the diesel should be filtered.

TEST CONDITIONS:

- Mini tanks (500 mL) sanded and degreased;
- Added 250 mL of diesel;
- Added 25 mL of fresh water;
- Added MVOil900 with V-active VCI1061 (0.5%; 1.0%; 1.5% e 2.0%);
- Evaluation of protective effect of corrosion inhibitor inside mini tanks, closed, inside oven at 40°C.

EVALUATIONS:

- Keep in oven at 40°C until the mini tanks called "blank" has changed significantly, and the minimum period 7 days;
- Efficiency inhibiting corrosion in the vapor phase and contact (in the aerated - inside top cover and in contact diesel in contact with water and interstitial part water / diesel);
- Efficiency inhibiting formation of microorganisms and aerobic and anaerobic bacterial action;
- Keep the residual fluid samples after testing for further analysis;
- Define the best protective and concentration condition of MV Oil 900.

PRATICE:

- Internal and external sanding with sandpaper # 220 and # 480 with water;
- Cleaning of tanks with degreaser MV Aqua 200 10%; exhaust rinsed with water to remove the protective;
- Conservation ethanol 98%

1. 12.5 mL deionised water
2. 250 mL of diesel fuel (from customer) type S 500;
3. 2.5 g of Iron Ore
4. 0.25 g of commercial steel wool without protective;
5. Adjustment of the oven with air circulation under temperature 40 °C during 30 days.

Figure 26 – Mini tanks made with steel 1020

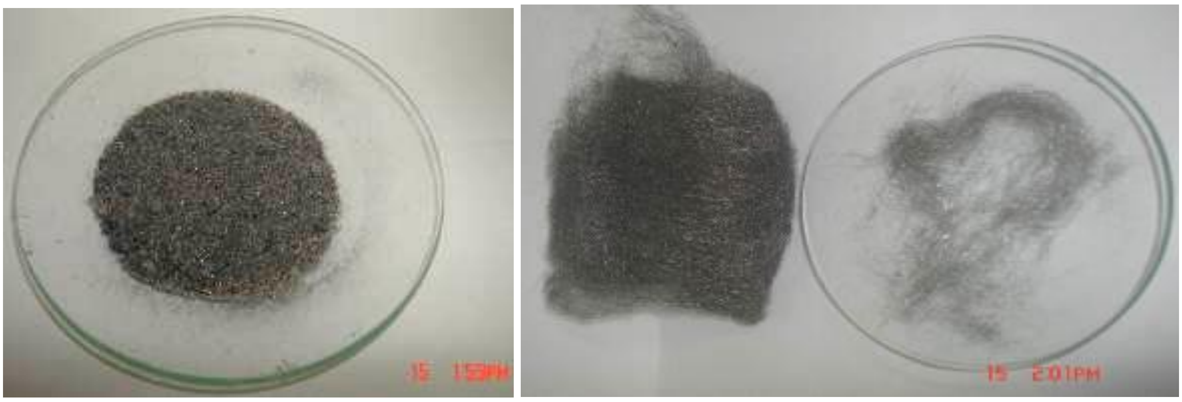


Figure 27 – Iron ore and steel wool samples

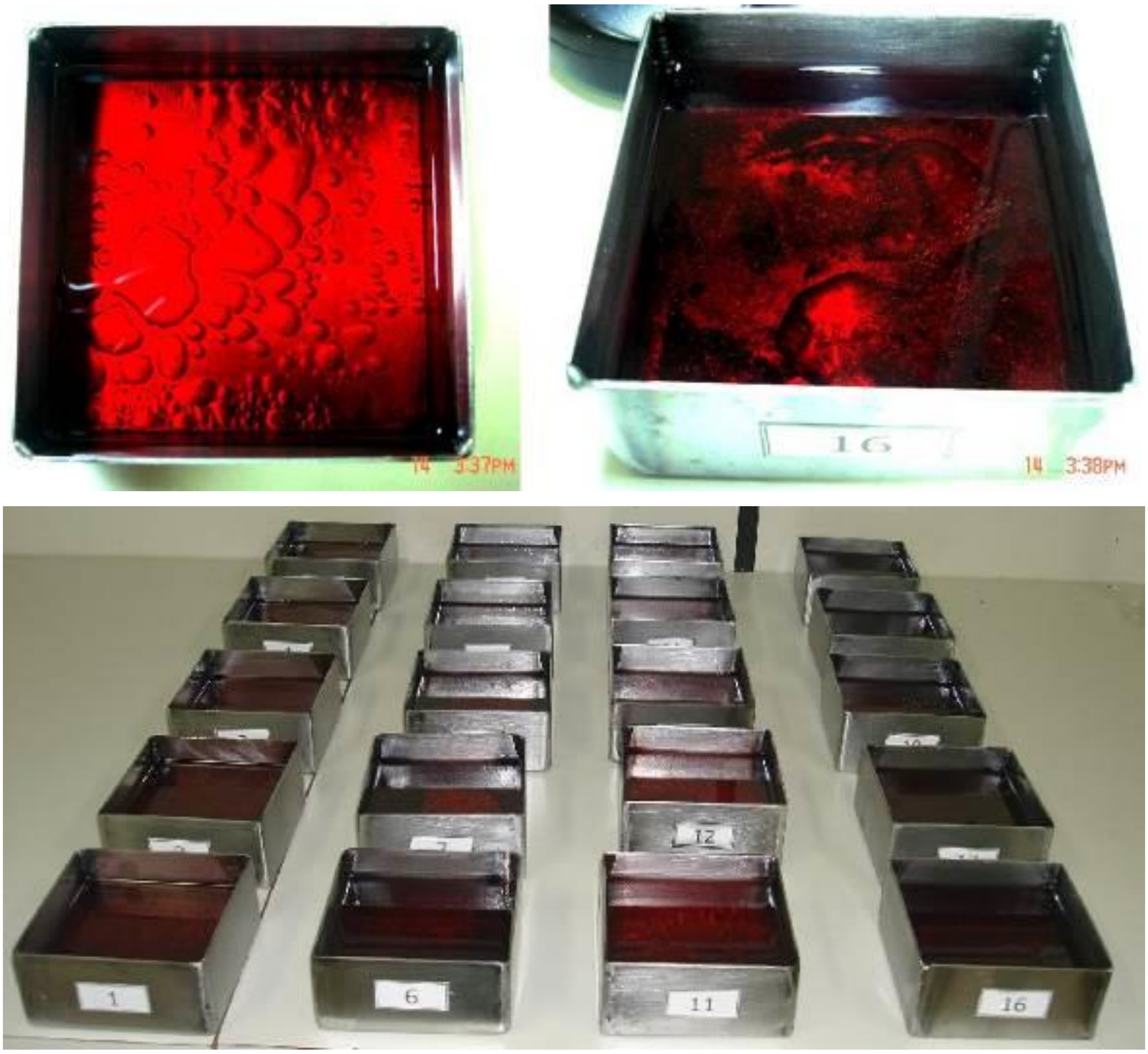


Figure 28 – Mini tanks, with 250mL of diesel fuel, added with MVOil900, water, Iron ore and steel wool

Figure 29 - Oven at 40 °C – during 30 days

CONDITIONS AND RESULTS – PART 1

1. Inhibitor efectiveness – without contaminants

Tank 1 – WITHOUT INHIBITOR 	Tank 2 – 0.5% MV Oil 900 	Tank 3 – 1% MV Oil 900 
Tank 4 – 1.5% MV Oil 900 	Tank 5 – 2% MV Oil 900 	Diesel samples in mini tanks, without contaminants, which was only evaluated the performance of MV Oil 900 inhibitor. Best condition = 1.5% From formulation 1.5% of MV Oil 900 with 0.375% of active inhibitor V-active 1061

Figure 30 – Results sequence for mini tanks with diesel and without contaminants and MV Oil 900

2. Inhibitor effectiveness – with 1 g iron ore

Tank 6 – WITHOUT INHIBITOR 	Tank 7 – 0.5% MV Oil 900 	Tank 8 – 1% MV Oil 900 
Tank 9 – 1.5% MV Oil 900 	Tank 10 – 2% MV Oil 900 	Diesel samples in mini tanks, with Iron Ore contaminants, which was only evaluated the performance of MV Oil 900 inhibitor. Observed reduced water activity in the oxidation (all iron ore was oxidized by water, reducing the active quantity). Better condition 1.5%

Figure 31 – Results sequence for mini tanks with diesel and with Iron Ore contaminant and MV Oil 900

3. Inhibitor effectiveness – with 0.25 g steel wool

Tank 11 – WITHOUT INHIBITOR 	Tank 12 – 0.5% MV Oil 900 	Tank 13 – 1% MV Oil 900 
Tank 14 – 1.5% MV Oil 900 	Tank 15 – 2% MV Oil 900 	Diesel samples in mini tanks, with 0.25g Steel wool contaminants, which was only evaluated the performance of MV Oil 900 inhibitor. Better condition 1.5%

Figure 32 – Results sequence for mini tanks with diesel and with 0.25 g of steel wool and MV Oil 900

4. Inhibitor effectiveness – with 1 g of iron ore and 0.25 g of steel wool

Tank 16 – WITHOUT INHIBITOR 	Tank 17 – 0.5% MV Oil 900 	Tank 18 – 1% MV Oil 900 
Tank 19 – 1.5% MV Oil 900 	Tank 20 – 2% MV Oil 900 	Diesel samples in mini tanks, with 0.25g Steel wool and 1% Iron Ore contaminants, which was only evaluated the performance of MV Oil 900 inhibitor. Better condition 1.5%

Figure 33 – Results sequence for mini tanks with diesel and with Iron ore and with 0.25 g of steel wool contaminant and MV Oil 900

OBSERVATIONS:

The corrosion inhibitor MV Oil 900 containing V-active VCI 1061 has protective efficiency when added to diesel;

It is observed by comparing the tanks 1, 6, 11 and 16, which in the absence of inhibitor oxidation is severe;

In the tank 2 to 5 there is an increasing corrosion inhibition to the extent of 1.5% inhibitor; the same is seen in other tanks with the addition of contaminants, such as iron ore and steel wool;

The presence of contaminants reduces the water activity as an oxidizer, however there is the protective efficiency of the inhibitor;

Definition of use of MV Oil 900 inhibitor to 1.5%. In this condition there is an effective V-active VCI 1061 content of 0.375%.

It gave the sequence in the test without the presence of contaminating = worst condition - more intense oxidation.

CONDITIONS AND RESULTS – PART 2

- Mini Tanks (500 mL) sanded and degreased;
- New sample Diesel S500 to test sequence in the optimal concentration of V-active VCI 1061 = 0.375%
- Addition of pure V-active VCI 1061 directly to diesel in concentrations of 0.10%, 0.25%, 0.375% and 0.50%;
- 12.5 mL deionized water
- 250 mL of diesel fuel (from customer) type S 500;
- Adjustment of the oven with air circulation under temperature 40 °C during 30 days.

5. Inhibitor efectiveness – without contaminants

Tank 21 – WITHOUT INHIBITOR 	Tank 22 – 0.1% 1061 	Tank 23 – 0.2% 1061 
Tank 24 – 0.375% MV 1061 	Tank 25 – 0.5% 1061 	Diesel samples in mini tanks, without contaminants, which was only evaluated the performance of V-active VCI1061. Better condition Higher than 0.2% V-active VCI1061

Figure 34 – Results sequence for mini tanks with diesel and without contaminates, with pure corrosion inhibitor V-active VCI1061

FINAL OBSERVATIONS:

- The additive V-active VCI1061 inhibitor has protective corrosion efficiency when added to diesel;

- This consideration is performed when a comparison is made in the tank without the presence of the inhibitor, wherein the oxidation is severe;
- Tanks 22 to 25 there is a growing improvement to the limit of 0.5% of inhibitor;
- Definition of use of V-active VCI1061 inhibitor at a concentration of 0.375%.

7.4.4.2 Diesel 200 L Drums

SUBJECT:

To evaluate the protective efficiency of V-active VCI1061 corrosion inhibitor added directly to diesel, in liquid and vapor phase, in carbon steel tanks.

The diesel has, among other additives, a certain amount of sulfur (S500 in this case - fuel trucks) and has the property of hygroscopic (absorb water). These two components, water and sulfur promote the microbiological degradation of diesel by sulfate-reducing bacteria, forming an organic mass and an acidic due to the formation of sulfuric acid and subsequent chemical attack to the surface of the tank. Furthermore, there is also the oxidizing effect of water on the tank walls.

In concept, the corrosion inhibitor was dissolved in the Diesel, thereby preventing the absorbed water promotes the oxidation of the steel tank, both contact (water goes to the tank bottom) and the vapor phase (by evaporation and condensation effect).

Materials

- 0.3 L V-active VCI 1061 additive applying inside Diesel Drums
- 120 L Commercial Diesel fuel S500 (500 ppb of Sulfur)
- 2 Commercial Metal Drums 55GL (200L) – was cleaned by detergent, rising and dry
- One drum with Diesel and Additive; other drum with Diesel and without additive
- Start: 21/Feb/2008
- Last analysis: 10/Mar/2012 (after 4 years).

Figure 35 – 200L Drums with diesel with and without V-active VCI1061

Experimental

- In each 200 L Drum was added 60 L of commercial Diesel S500;
- Inside one 200 L Drum was added 0.5% of V-active VCI 1061 (0.3 L)
- Closed the drums with regular tap, using a tube to control internal pressure (simulating real fuel tanks).
- Maintained inert during the time of the experiments.

Results

1. Drum – No Additive – after 4 years

Figure 36 – 200L Drum with diesel and without corrosion inhibitor

Drum inner surface is completely oxidized, proving the existence of water internally and the subsequent attack on the steel surface.

At the bottom of this drum, there is degradation and formation of an organic mass.

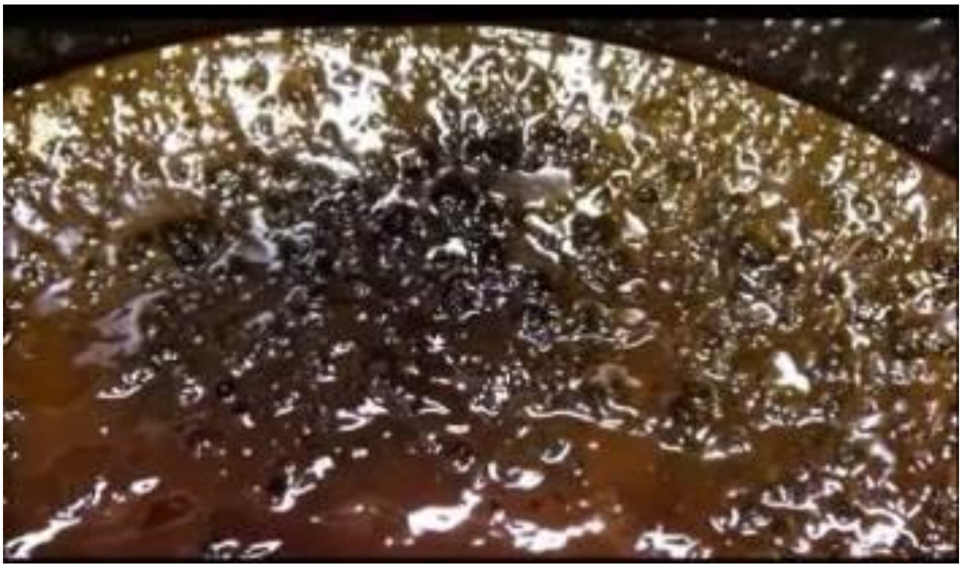


Figure 37 – 200L Drum with diesel and without corrosion inhibitor: formation of an organic mass at the botton.

In the upper part (top) susceptible to condensation of water is observed intense oxidation.

Figure 38 – 200L Drum with diesel and without corrosion inhibitor: intense corrosion at the upper (top).

2. Drum with 0.5% of V-active VCI 1061 Additive – after 4 years

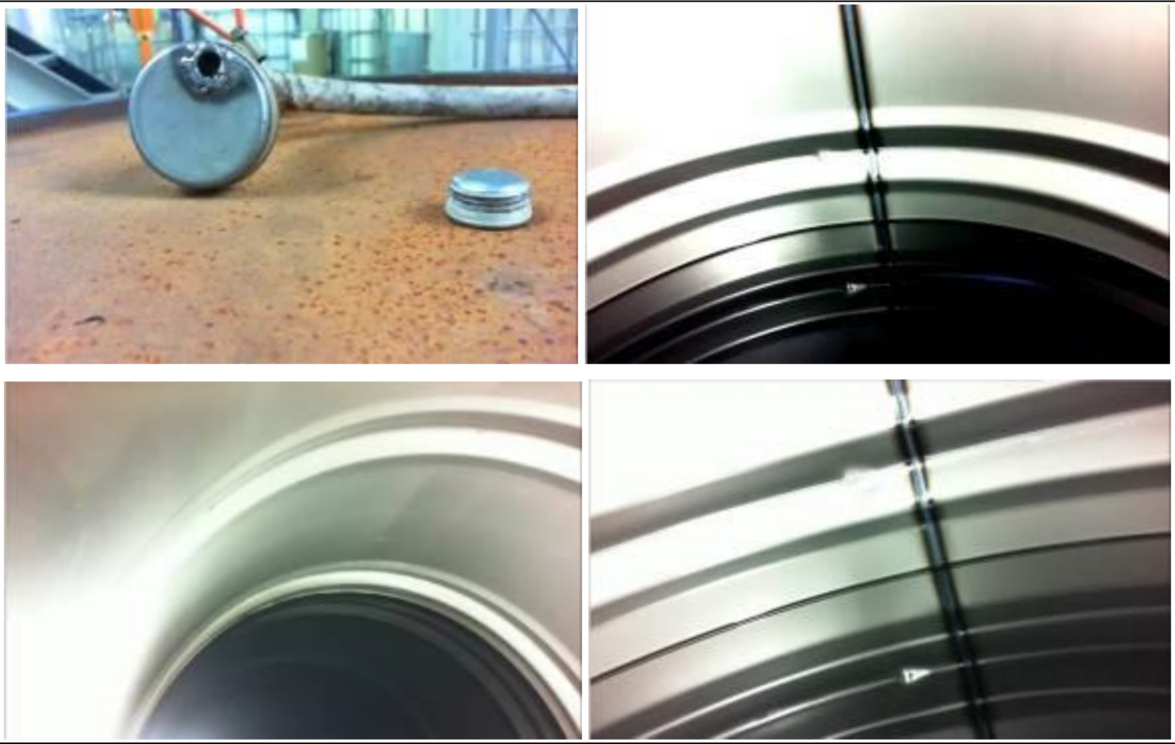


Figure 39 – 200L Drum with diesel and with 0.5% of V-active VCI1061 corrosion inhibitor

Note the inner surface completely free of oxide, with condensation stains, proving the existence of water internally and the consequent inhibition of the attack on the steel surface by V-active VCI1061 inhibitor.

At the bottom of the 200L Drum, is not observed the degradation and formation of organic mass, just showing the natural sedimentation of diesel waste stopped for 4 years and completely free of oxidation

Figure 40 – Botton of the Drum with diesel and with 0.5% of V-active VCI1061 corrosion inhibitor

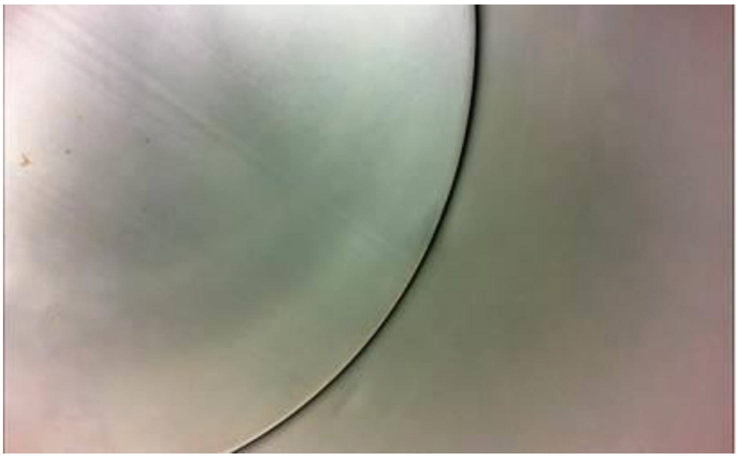


Figure 41 – Top of the Drum with diesel and with 0.5% of V-active VCI1061 corrosion inhibitor – clean

The diesel samples were characterized before and after the test, showing that the addition of the V-active VCI does not change the rheological characteristics of diesel.

Table 7 – Test results for Diesel Analysis – with and without corrosion inhibitor, before and after test.

PARAMETER	**METHOD**	**RESULTS**			
		WITHOUT VCI		**WITH VCI 1061**	
		DIESEL NEW	AFTER TEST	DIESEL NEW	AFTER TEST
Viscosity 40°C cSt	ABNT NBR-10441/07	3,99	3,54	3,99	3,54
Density a 20°C g/ml	ABNT NBR-14065/06	0,8297	0,8277	0,844	0,8298
Flash Point ºC	ABNT NBR-11341/08	53	52	54	54
Carbon Residual %	IT-LTV-017/06-Ver.05	0,01	0,02	0,01	0,01
Ash %	ABNT NBR 9842	0,002	0,006	0,001	0,002
Corrosivity Cu 3h 50°C	ABNT NBR 14359	1A	1A	1A	1A
Ketane Index	ABNT NBR 14759	44	44	44	42
Water and Sedments %	ASTM D 2709/01	0,025	1	0,025	1
Filter Restriction Cold ºC	ABNT NBR 14747	-8	-2	0	-9
Particles - particles/mL	ISO 4406/87-NAS 1638				
2 µm		10114,8	25566	18210,2	26432,5
5 µm		1541,9	23428,7	1460	24257,2
15 µm		217,2	9411,2	148	8194,6
25 µm		15,7	1339,2	47,1	117,7
50 µm		1,2	38,9	7	0,3
100 µm		0,1	0,8	0,1	0

As it was expected, higher water content was found. Also was found an increase in sediment and solids, determined by the size of the particles.

7.5 Real Cases of Application

Many were and are the cases of application for these corrosion inhibitors. Here are present some of these cases, when considering water as medium for the spreading (in liquid and vapor form), being applied during the process or by spray vaporization.

In all case studies presented here and in others, the biggest problem is the technical conviction of those involved. In concept, when it is desired corrosion inhibition, all technical people tend to eliminate the presence of water, using desiccant means, substituting water for protective oil, or "obtaining the inert medium" with the use N_2 (nitrogen gas).

7.5.1 Flash Rust Protection in Hydrojet Metal Cleaning

In this part of the work is reported the application of water-surface metal cleaning by hydrojet. Under current conditions of surface preparation, as a rule should not expect more than 2 hours to paint after washing with water (hydrojet). This occurs because the oxidation of the metal part and the whole preparation process is lost. This stage of work demonstrates that it is possible to eliminate or reduce the oxidizing action of the water, extending the waiting time for painting, using a new concept of corrosion inhibitor that does not interfere in the final quality of painting. This action increases the metal surface that can be cleaned and prepared, reducing labor costs, and products, mainly reduces water consumption in the preparation process.

For this application, has developed a corrosion inhibitor capable of dissolving in water and, after application, forming a protective film (imperceptible to the eye), using the technology V-active VCI. In this formulated product was given the name reference: V-active VCI 1712 SPH.

7.5.1.1 Hydrojet Metal Surface Cleaning

7.5.1.1.1 Real Case – Application – Offshore Condition

Anti-Corrosion Methods and Materials 62/1 (2015) 53–58 – A new concept of corrosion protection in the presence of water: V-active VCI: Concept and Application

In this process, the water is used in ultra-high pressure (30 to 35 Mpsi) with rotation over the metal surface. This process eliminates oxide residues and paints leaving the metal bare and exposed. The temperature on the surface of the metal reaches approximately 80 °C, which makes easier the drying process and consequently speed up the oxidation process.

After a few minutes, the surface recently cleaned has already oxide patches on the surface and in 2 hours is completely oxidized.

The painting processes, for example in shipyards, usually begin with the elimination of the oxide residues and salts contamination from the metal surface followed by the application of the first protective layer (primer). This is performed with one more washing with water at low pressure. In some occasions the protective paints used can be applied to wet surfaces. The process becomes slow and requires the operation to prepare and paint the hull of the ship in small parts.

Comparative tests were performed in laboratory and pilot test was performed in a major shipyard in the northeastern of Brazil (humid and saline environment – seaside bay). The results of this pilot test are presented below.

a. Dissolution of the chemical inhibitor:

The chemical inhibitor V-active VCI V-active VCI 1712 SPH was directly dissolves in the water tank of the hydrojet, in concentration of 2% (10.000L).

Figure 42 – Preparation of the 10,000L water solution with 2% V-active VCI1712SPH

b. Procedure of the cleaning process by "Hydrojet"

The samples of metal plates to be cleaned and treated had the same origin and surface conditions were similar. In order to obtain the best possible conditions to perform the test was used 10 plates with the same dimension.

b.1 – Initial condition of the metal surface:

Figure 43 – Steel plates – same as used in the construction of hulls of large crude oil ships

b.2 – hydrojeting using 2% V-active VCI 1712 SPH (9:00 am)

After the addition of the inhibitor in water the formation of foam was observed during the application, without any interference on the final quality of cleaning.

Figure 44 – Steel plates – after hydrojeting using 2% V-active VCI 1712 SPH

b.3 – hydrojeting using fresh water (9:15 am) - blank test – reference

Standard procedure was used, consisting in the application of a water jet under a pressure of 35,000 Psi on the metal surface. It was enough to remove any encrustations on the surface, including other forms of protection as paint and scale.

Figure 45 – Steel plates – after hydrojeting using fresh water

c. Sampling - results

After the cleaning had been done, the drying was done by natural process (the time counting already was running). The samples were submitted to the tests proof, where the time of protection or oxidation and influence on the adherence of paint (pull off) was measured.

Figure 46 – Steel plates – after hydrojeting – 5 hs later – without corrosion inhibitor presence of flash rust

The results showed that after 2 hours the plates cleaned by hydrojet, with water only, already had been completely oxidized (oxidation process starts immediately after the application, observing spots while the surface get dried), while the plates cleaned by hydrojet with V-active VCI V-active VCI 1712 SPH additive remained for up to 48 hours without oxidation. Samples were kept in the humid and saline environment of the hydrojet rooms.

The temperature on the surface due to friction reaches 80 °C, doing easier the drying process and speed up the oxidation process.

The samples that have been hydrojeted with V-active VCI 1712 SPH 2% solution formed a uniform film, imperceptible to the human eye, showing no residues on surface after complete drying.

d. Procedure of the Painting Process (by Petrobras standard procedure)

To the continuation of the test, using part of the treated material, has been employed the Petrobras standard procedure of painting (used by the shipyard). It has been measured the influence of the inhibitor on the painting process and consequent influence on the adhesion test.

It was used paints usually applied without any surface preparation beyond hydrojet cleaning. According to the collected information, this primer paints (with red color) is prepared to be used on slightly oxidized and wet surfaces (the paints should not detach from the surface any residues after touch). The painting was performed with foam rollers due to the painting area being too small for application by spray paint gun.

In another samples it was applied the usual paints (white) in layers from to 300 μm.

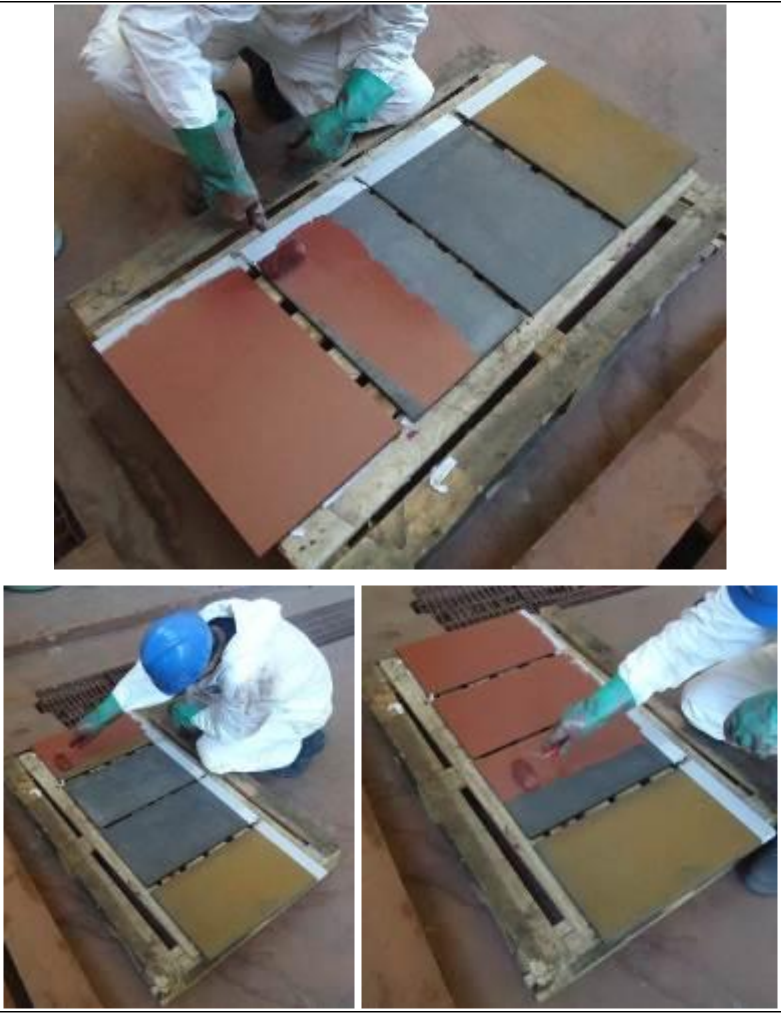


Figure 47 – Steel plates – after hydrojeting – painting process

e. Adherence Test - Pull off (Petrobras standard procedure)

15 days after the application of paints, it was performed a standard procedure for adhesion test generally called “Pull off”. This process consists in gluing the specific pin (bolt) of the equipment (glue, bolt) and drying time specified in the standard) and applies a given force to pull out the bolt.

Figure 48 – Steel plates – after hydrojeting – adherence “pull-off” test

The results have shown there is no influence on the paint adhesion when compared with and without additive. In both cases the results in absolute numbers of the equipment were above 100 PSIG, demonstrating to be above the specification of Petrobras.

This work allows proving the proposed technology: V-active VCI uses water as carrier to promote inhibition of metallic corrosion.

7.5.1.1.2 Hydrojet – Lab and Standard Tests

Anti-Corrosion Methods and Materials Accepted June 2016 - Applying a new concept of corrosion protection in the presence of water: Hydrojetting application – effectiveness lab test

Using the concept of dissociation of the VCI salt promoted by the presence of water, a new formulation of chemical inhibitors has been developed that use the moisture itself as the application medium, and these new inhibitors have the capability to transform the moisture into the route for application and propagation of the inhibitor. Such inhibitors, known generically as V-active VCIs retain the properties of a volatile inhibitor. Their chemical formulation, when in the presence of water or aqueous contaminant, migrates to the medium and this promotes its dissociation. The inhibitor V-active VCI migrates to the aqueous medium and inhibits the corrosion process, both in the liquid phase and in the vapor area (the void volume).

As main objective is to investigate the performance of the corrosion inhibitor additive for water high pressure jetting as a pretreatment for painting, with respect to:

- soluble salts;
- the time interval for the formation of initial oxidation (flash rust);
- influencing the performance of a coating system applied.

2 EXPERIMENTAL

Teste Description	Standard - Method
Time for formation of flash rust	SSPC-VIS 4 (NACE VIS 7)
Soluble salts	ISO 8502-6
Cyclic corrosion test type III (20 cycles)	N 2680 Petrobras
Test Methods for Cathodic Disbonding (30 days)	ASTM G-8
Test Method for Pull-Off Strength of Coatings	ASTM D 4541, ABNT NBR 15877

2.1 SAMPLES

Product tested: V-Active VCI SPH 1712 – Organic Corrosion inhibitor for water jetting, called SPH1712. Concentration used: 2% w/w in deionized water

Metallic substrate

Base material: Carbon Steel SAE 1012.

Surface treatment: Abrasive Jet Sa 2 ½.

Surface profile (µm): 50-80.

Dimensions of the specimens (Coupons) mm: 150 x 100 x 4.25.

2.3 PRE-TREATMENT METHODS AND CONDITIONS OF SUBSTRATES

Description	Surface Treatment
Jet	Abrasive blasting
H_2O	Abrasive blasting followed by wetting of the substrate by immersion in deionized water
SPH1712 wet	Abrasive blasting followed by immersion in 2% solution SPH1712
SPH1712 dry	Abrasive blasting followed by immersion in 2% solution SPH1712, allowed to dry for 5 hours in the laboratory (25 °C, 60% RH)

2.4 METHODOLOGY

2.4.1 Surface Preparation

The surface of the Metal Coupons were degreased with xylene and then abrasive blasting to SA 2 ½ according to ISO 8501-1, or WJ-2 as NACE VIS 7 / SSPC-VIS 4.

The roughness measurement was made with dial Digimess.

The resulting degree of cleaning after abrasive blasting and blown with compressed air for removing dust in the process, was obtained by passage of tape method as described in ISO 8502-3 Standard.

The content of soluble salts on the metallic surface was verified as Bresle method according to ISO 8502-6 Standard.

In the case of the specimens (MCs) with V-active VCI SPH1712, was observed drying the surface of a panel after immersion in solution 2% w/w, about three hours apart, to perform the test.

The conductivity of a 2% solution of V-Active VCI SPH1712 and deionized water was also measured with a conductivity meter Horiba B-173.

Painting System (WEG Paint Wet System)

1th layer/coat – EPOXI PRIMER 76 WS N 2680 – DFT = 150μm

2nd layer/coat – EPOXI PRIMER 76 WS N 2680 – DFT = 150 μm

3rd layer/coat – EPOXI FINISHING 76 WS N 2680 – DFT = 150 μm

DFT: Dry Film Thickness

2.4.2 Soluble Salts on Metal Surface

Reading the content of salts in the conditions of "Jet" and "dry SPH1712" was made according ISO 8502-6. The conductivity of the solution 2% SPH1712 and deionized water were also read.

2.4.3 Time for Formation of Flash Rust

Three specimens (Metal Coupons) prepared under conditions “Jet”, “H_2O” and “SPH1712 dry” were exposed in a climatic chamber at 60 °C and 100% RH for 70 hs at an angle of 20 ± 5° from the vertical, favoring the condensation on the surface of test.

The flash rust degrees were determined according to SSPC-VIS 4 (NACE VIS 7).

The specimens (Metal Coupons) under conditions “H_2O” and “SPH1712 dry” were prepared by immersion in heated fluids respective at 80 °C, where they remained for 5 minutes.

After this, made it natural drying in laboratory conditions (25 °C, 60% RH) during about 5 min before exposure in the chamber condition.

2.4.4 Performance of the Coating System

The paint system was applied to the specimens under the conditions: “Jet”, “H_2O”, “SPH1712 wet” e “SPH1712 dry”.

Paint: WEG EPOXI PRIMER 76 WS N 2680

Description	1th Coat/Layer	2nd Coat/Layer	3rd Coat/Layer
Batch – Component A	1020573	1020573	1020573
Batch – Component B	1017155	1017155	1017155
Mixing Ratio	3 x 1	3 x 1	3 x 1
Application Equipment:	Airless Spray Gun Graco, model Xforce HD		
Application Equipment:	Pressure 8		

Description	1th Coat/Layer	2nd Coat/Layer	3rd Coat/Layer
Application Equipment:	spray nozzle 521		
Air Temperature (ºC)	28.5	26.6	26.0
R.H. (%)	71.0	79.5	78.5
Metal Surface Temperature (ºC)	29.3	28.5	29.6
Dew Point (ºC)	22	22	22

2.4.5 Parameters for Evaluation

For analysis and designation of corrosion points and eventually blisters observed on the painted samples, ISO 4628-3 and ISO 4628-2 standards were adopted, respectively.

On the metal coupons used for the cyclic corrosion test III (ECC3), after painting process and dry, a longitudinal incision was made in the paint layer, by exposure of the base metal, about 1 mm wide, 50 mm long and 70 mm from the edge lower.

As for the Test Methods for Cathodic Disbonding (30 days) ASTM G-8, an intentional defect milling was carried out until the interface metal / coat with a diameter of 7 mm, centered relative to the width and 50 mm from the bottom edge. For electrical contact with the circuit panels were fitted on the back at the top.

3 RESULTS

3.1 Soluble Salts - ISO 8502-6

"Condition"	Soluble Contaminants (mg/m^2)
Jet	15.3
SPH1712 dry	33.0
Deionised Water	2.4
SPH1712 2% Solution (w/w)	201.78

3.2 Time for formation of flash rust 60°C and 100% R.H. - SSPC-VIS 4 (NACE VIS 7)

Condition	**Sample**	***Flash rust* degree after (hs)**			
		0	**3 hs**	**7hs**	**70hs**
Jet	1	A WJ-1	A WJ-1 M	A WJ-1 M	A WJ-1 H
	2	A WJ-1	A WJ-1 M	A WJ-1 M	A WJ-1 H
	3	A WJ-1	A WJ-1 M	A WJ-1 M	A WJ-1 H
H_2O	1	A WJ-1 L	A WJ-1 L	A WJ-1 L	A WJ-1 M
	2	A WJ-1 L	A WJ-1 L	A WJ-1 L	A WJ-1 M
	3	A WJ-1 L	A WJ-1 L	A WJ-1 L	A WJ-1 M
SPH1712 Dry	1	A WJ-1	A WJ-1	A WJ-1	A WJ-1
	2	A WJ-1	A WJ-1	A WJ-1	A WJ-1
	3	A WJ-1	A WJ-1	A WJ-1	A WJ-1

Notes: Light *flash rust* **(L),** Moderate *flash rust* **(M),** High *flash rust* **(H)**

Classification of the *Flash rust* – SSPC-VIS 4/ NACE VIS 7 (adapted):

No flash rust: the surface seen through the eyes without magnifier aid, do not shown flash rust.

*Light flash rust **(L)**: the surface seen through the eyes without magnifier aid, displays small amount of a yellow / brown rust layer. Corrosion or discoloration may be optionally concentrated or distributed, but is strongly adherent and not easily removed.*

*Moderate flash rust **(M)**: the surface seen through the eyes without magnifier aid, displays a yellow oxide layer / brown that covers the original steel. Corrosion can be eventually distributed or concentrated, but is reasonably well adherent.*

*High flash rust **(H)**: the surface seen through the eyes without magnifier aid, displays a red oxide layer / intense brown to yellow / brown hiding the initial condition of the surface completely. Corrosion can be eventually distributed or concentrated, but it is very adherent.*

Flash Rust – Inicial (time 0)

Figure 49a – Condition Jet – 1, 2 and 3 – flash rust test – initial (time 0)

Figure 49b – Condition H_2O – 1, 2 and 3 – flash rust test – initial (time 0)

Figure 49c – Condition SPH1712 dry – 1, 2 and 3 – flash rust test – initial (time 0)

Images for flash rust 60°C and 100% R.H. - SSPC-VIS 4 (NACE VIS 7) – after 70hs

Figure 50a – Condition Jet – 1, 2 e 3 – flash rust test – after 70 hs

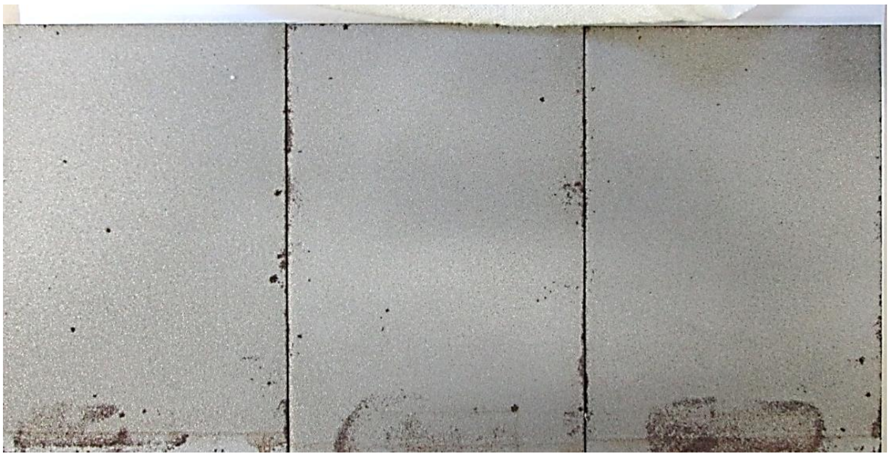


Figure 50b – Condition H_2O – 1, 2 e 3 – flash rust test – after 70 hs

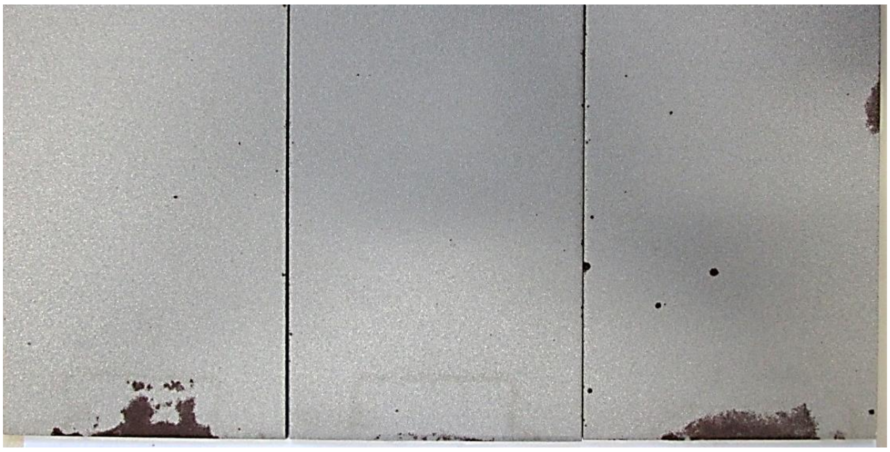


Figure 50c – Condition SPH1712 dry – 1, 2 e 3 – flash rust test – after 70 hs

3.3 Cyclic corrosion test type III (20 cycles) – N2680 Petrobras Standard

Condiction	Sample	Coat (µm)	Oxidation degree	Blister	Corrosion on longitudinal incision (mm)
Jet	57584 - 69	460 – 529	Ri 0	0 (S0)	29,1
	57584 - 70	478 – 510	Ri 0	0 (S0)	21,2
H_2O	57587 - 01	402 – 470	Ri 0	0 (S0)	24,3
	57587 - 02	420 – 463	Ri 0	0 (S0)	20,4
	57587 - 03	417 – 475	Ri 0	0 (S0)	20,3
SPH1712 wet	57587 - 04	400 – 511	Ri 0	0 (S0)	20,8
	57587 - 05	376 – 477	Ri 0	0 (S0)	23,3
	57587 - 06	400 – 520	Ri 0	0 (S0)	19,4
SPH1712 dry	57587 - 07	403 – 486	Ri 0	0 (S0)	18,4
	57587 - 08	407 – 475	Ri 0	0 (S0)	12,8
	57587 - 09	457 – 513	Ri 0	0 (S0)	16,8

Images for cyclic corrosion test type III (20 cycles)

Figure 51a – Samples 69 and 70 (Jet condition without inhibitor) – after 20 cycles Cyclic Corrosion Test

Figure 51b – Samples 01, 02 and 03 – Condition H_2O – after 20 cycles Cyclic Corrosion Test

Figure 51c – Samples 04, 05 and 06 (SPH1712 wet) – after 20 cycles Cyclic Corrosion Test

Figure 51d – Samples 07, 08 and 09 (SPH1712 dry) – after 20 cycles Cyclic Corrosion Test

3.4 Test Methods for Cathodic Disbonding (30 days) – ASTM G-8

Condiction	Sample	Coat (µm)	Oxidation degree	Blister	Cathodic Disbonding (mm)
Jet	57584 – 76	435 – 470	Ri 0	0 (S0)	6,6
	57584 – 77	440 – 461	Ri 0	0 (S0)	9,2
	57584 – 81	402 – 525	Ri 0	0 (S0)	10,1
H2O	57587 – 10	478 – 570	Ri 0	0 (S0)	32,3
	57587 – 11	434 – 493	Ri 0	0 (S0)	26,0
	57587 – 12	443 – 498	Ri 0	0 (S0)	37,8
SPH1712 wet	57587 – 13	428 – 484	Ri 0	0 (S0)	25,3
	57587 – 14	432 – 505	Ri 0	0 (S0)	18,7
	57587 – 15	430 – 496	Ri 0	0 (S0)	19,3
SPH1712 dry	57587 – 16	407 – 473	Ri 0	0 (S0)	9,7
	57587 – 17	420 – 483	Ri 0	0 (S0)	10,6
	57587 - 18	457 – 478	Ri 0	0 (S0)	10,5

Images for Cathodic Disbonding – ASTM G-8

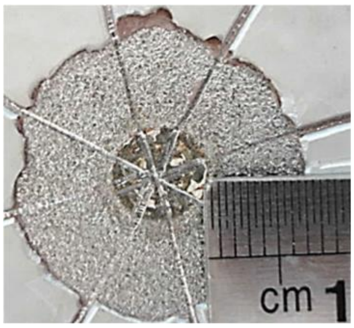
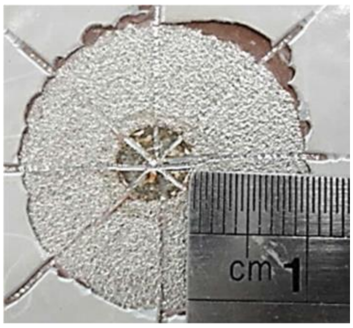
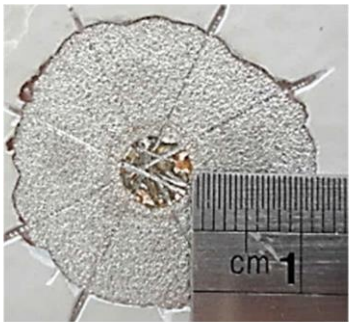
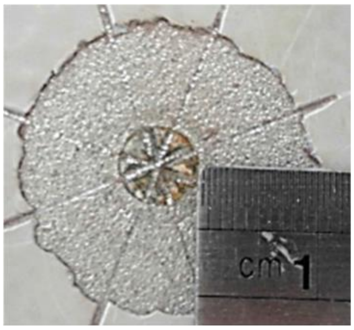
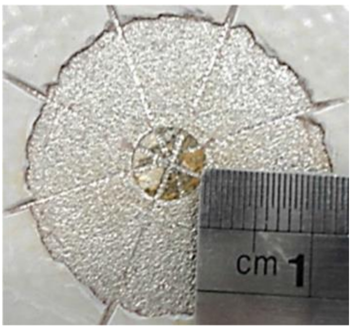
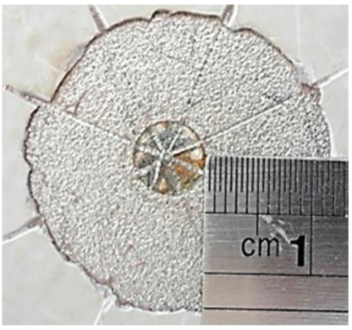
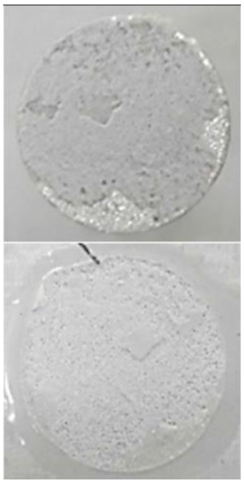
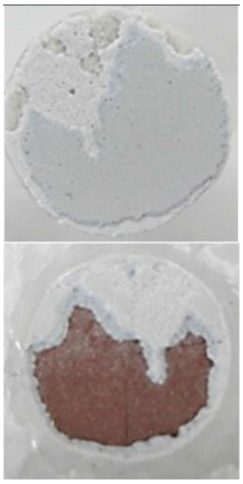
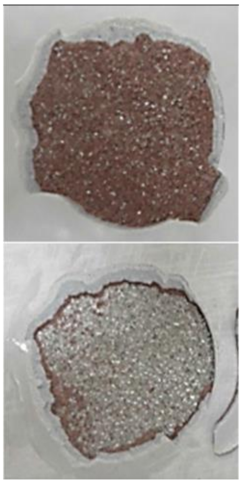
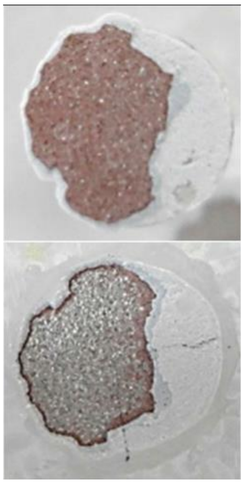
		
57584 – 76 (Jet)	57584 – 77 (Jet)	57584 – 81 (Jet)
		
57587 – 10 (H_2O)	57587 – 11 (H_2O)	57587 – 12 (H_2O)
		
57587 – 13 (SPH1712 wet)	57587 – 14 (SPH1712 wet)	57587 – 15 (SPH1712 wet)
		
57587 – 16 (SPH1712 dry)	57587 – 17 (SPH1712 dry)	57587 – 18 (SPH1712 dry)

Figure 52 – Images for Cathodic Disbonding – ASTM G-8

3.5 Test Method for Pull-Off Strength of Coatings – ASTM D 4541 – method D; ABNT NBR 15877

Condiction	**Sample**	**Coat (µm)**	**Adhesiveness (MPa)**	
			Dolly 01	*Dolly* 02
Jet	57854 - 85	435 – 475	18,7 80% D; 10% D/Y; 10% Y/Z	21,2 20% D; 80% B/C
H_2O	57857 - 19	463 – 546	13,0 100% A/B	16,2 25% D; 75% A/B
SPH1712 wet	57857 – 20	465 – 554	19,9 5% B; 80% D; 15% B/C	17,0 85% D; 10% A/B; 5% Y/Z
SPH1712 dry	57857 - 21	407 – 455	20,5 100% D	22,0 50% D; 25% C/D; 25% D/Y

Images for Pull-Off Strength of Coatings – ASTM D 4541 – method D; ABNT NBR 15877

			
Dolly 01	Dolly 02	Dolly 01	Dolly 02
57854 – 85 (Jet)		57854 – 19 (H_2O)	

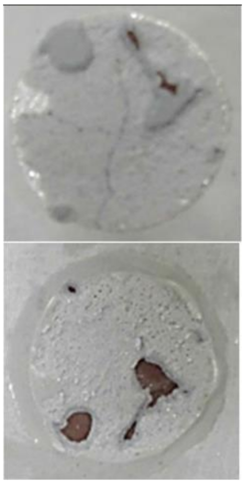
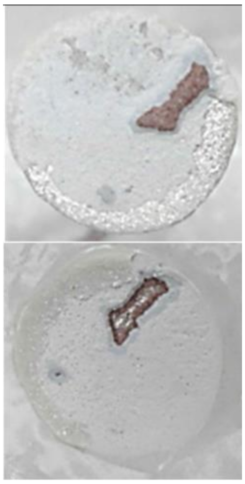
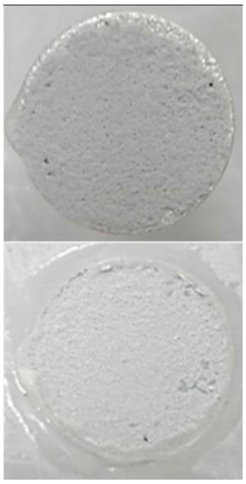
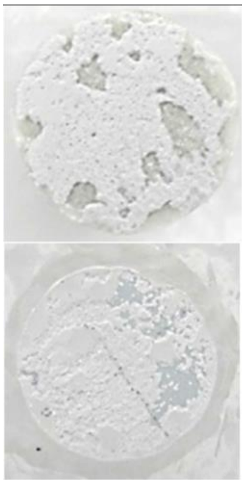
			
Dolly 01	Dolly 02	Dolly 01	Dolly 02
57854 – 20 (SPH1712 wet)		57854 – 21 (SPH1712 dry)	

Figure 53 – Images for Pull-Off Strength of Coatings – ASTM D 4541 – method D; ABNT NBR 15877

The influence of water base corrosion inhibitor on application of water-surface cleaning by hydrojet is reported in this paper. Typical conditions of surface preparation generally should not allow more than 2 hours for paint application after washing with water (hydrojetting). This is because oxidation of the metal will occur and the whole benefit of the preparation process is lost.

The results demonstrate that it is possible to eliminate or reduce the oxidizing action of the water, extending the acceptable waiting time before painting, using a new concept of corrosion inhibitor that does not interfere in the final quality of the painting. This action increases the metal surface that can be cleaned and prepared at any one time, thereby reducing labor and product costs, and reduces the consumption of fresh water during the preparation process. For this application, an organic corrosion inhibitor has been developed that is capable of dissolution in water and, after application, forming a protective film (imperceptible to the eye), using the V-active VCI technology. This formulated product was given the name reference: V-active VCI 1712 SPH (a mixture of various salts of “fatty amine” and organic carboxylic acid, with a film forming component, without any inorganic salt). The results have shown there is no negative influence on the paint adhesion when comparing coatings that have been applied to cleaned metal surfaces with and without the additive. The samples, that were hydrojeted with 1712 SPH 2% solution, had a uniform film on their surface, imperceptible to the human eye. No residues were on surface after complete drying retaining a clean and no corroded surface.

The investigation demonstrated the effectiveness of the V-active VCI technology: V-active VCI uses water as carrier to promote inhibition of metallic corrosion.

From the results collected in the testing protocol performed in this work, it was observed that the addition of V-active VCI SPH1712 showed no negative interference in the performance of the paint system in question (simulation of surface treatment on the offshore environment) while increasing efficiency in corrosion protection in pre-painting, as goals of this document.

The excellent results obtained, both in pull-off testing as in cathodic disbondment, indicate that the inhibitor V-active VCI SPH1712 shows protective effect against corrosion and film formation, not interfering with adhesion properties and protection of the paint layer.

Regarding the inhibition of flash rust, the same inhibitor showed a potential to increase time before the application of paint systems after jetting, with a significant increase in time that the clean metal remains on hold “waiting” for painting. This enables resizing times between cleaning and the execution of the painting, reducing hand labor, material and water consumption, as it enables to extend the areas that will be subject to cleaning.

However, it is noteworthy that, in theory, an increase in salinity levels on the metal surface (33 mg/m^2 near the maximum acceptable limit of 30 mg/m^2) concerning the use of corrosion inhibitor in question, which can represent other types of failures in different tests and conditions of service, which may obviate the need for further evaluation or execution of more specific tests. Adding that in practice, the salt content is associated herein, the content of chloride salts, mainly in offshore sea areas (location of major manufacturing and maintenance for the oil & gas company).

In practice for preparation of pre-painted metal surface, the salt content is associated with bubble formation and migration by the presence of water, which has been tested and the inhibitor SPH1712 (dry condition) is also effective in preventing bubble formation. It is intended to extend the tests for more specific analyzes and to evaluate the influence of salt content in the paint layer (bubble formation), since it is not able to observe here the loss of these properties due to the high salt content.

The means of painting, quality levels and specifications used in this document represent the reality of usage for systems offshore painting. Tests in other paint systems and for paint with different chemical natures, also specific tests are recommended.

The results also demonstrate that it is possible to develop corrosion prevention systems using simple and proven biodegradable products that are practically non-toxic and which respect the environment and human health.

7.5.2 Controlled Humidity (Dispenser)

INTERNAL PROTECTION OF THE ENVIRONMENT INSIDE 40" CONTAINER. CONTROLLED ENVIRONMENT USING VCI SPRAY – DISPENSER.

PROTECTION OF PACKED STEEL CORD COILS – ARCELOR MITTAL BRAZIL

IN SHIPPING FROM BRAZIL TO TURKEY – 27/APRIL/2011

The company produces and export the steel wire coils. This steel is used to produce "steel nets" used in the manufacture of tires. Upon receiving and due to the care process, there may be no oxidation point in the wire and any other liquid product on the metal surface. The metal must be clean and dry.

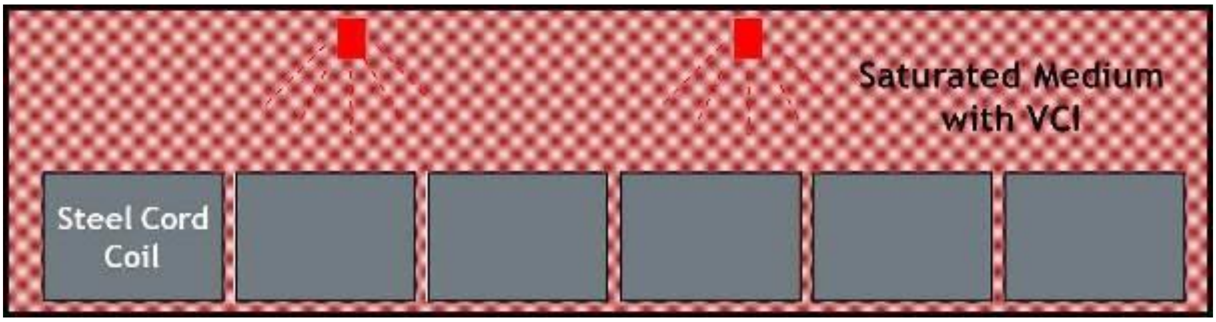
Even with the packaging of coils, small portions of water penetrating into the package, providing some rust points or produce spots or loss of gloss. This development made possible to achieve very positive results and a significant reduction of complaints and customer's disposal.

SUBJECT:

- To evaluate the effect of modifying the internal corrosive environment when transported in containers by sea, using steel coupons;
- To evaluate the changes in relative humidity and temperature inside the container;
- To evaluate the changes in relative humidity and temperature inside the coil packing of steel cord;
- To evaluate the protective efficiency of the group: coil wrapped and change the medium

CONCEPT:

- The volatile corrosion inhibitor is sprayed from a dispenser, which consists of a VCI spray, coupled to a system containing a timer, which vaporizes at scheduled times a certain amount of VCI in the middle.
- The internal environment of the container contains contaminants such as water, which can penetrate and attack the steel packaging, promoting its oxidation. VCI uses the water in vapor form to dissociate into charges, and by saturation of the air, tends to leave the inert medium.



Other possible contaminants such as salt (sodium chloride that penetrate in the medium) can accelerate the corrosion of steel. The VCI, because of its high concentration, tends to "neutralize" this action.

With this pilot test aims to assess the protective efficiency of the medium generated in a system, that today has an incidence of rust due to penetration of contaminants in the packed coils. At this condition of controlled environment, if the contaminants enter into the coils, there will be not the oxidation of steel.

The VCI amount needed in the medium was calculated as the volume of container only, because the steel coils remain packed. We intend inerted the aggressive medium with the use of VCI and to prevent the action of external contaminants through the coils.

Container MSCU 947740

Figure 54 – Images of the container conditions

Figure 55 – Storage condition of the wire steel coils before loading of the containers

SCHEME OF ARRANGEMENT OF THE EQUIPMENTS INSIDE CONTAINER MSCU 947740

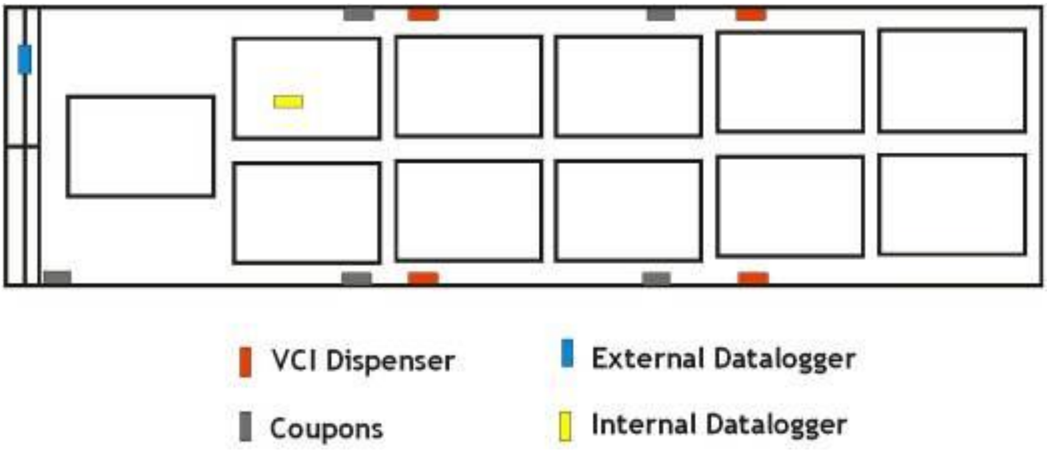


Figure 56 – Scheme of the of coils wrapped with PR VCI579 tape and FM8 after loading - 11 steel coils

🟥 Dispenser

Dispenser is an electronic device that contains a VCI spray can and a timer that promotes temporal spray action, scheduled to jet a spray every 36 minutes. With the internal volume of the spray can, and this time of 36 minutes between each application, can obtain a Dispenser activity within 60 days.

Figure 57 – Timer Dispenser and mounting location within the container

Four Dispensers units were placed and programmed to jet every 36 minutes. Fixed with adhesive and plastic strap through the hook, just in case and not fall off. Turned Off when received at destination.

Internal Datalogger

Placed inside the wire steel coil, between metal and external coil packed. Scheduled to reading every 60 minutes.

It is located on the 2nd row of coils in the coil to the left side.

To evaluate the variation of humidity and temperature inside the coil.

Start = 17hs day 27/04/2011 – To collect data when receiving the container at destination

Figure 58 – Internal datalogger – inside steel coil

External Datalogger

Placed on top of the access door on the left side. Fixed with adhesive. Scheduled to reading every 60 minutes. To evaluate the variation of humidity and temperature inside the container, the external coils. Start = 17hs day 27/04/2011 To collect data when receiving the container at destination.

Figure 59 – External datalogger

Coupons

To evaluate the protective effect. Placed on top of the container, adapted with plastic strap and numbered from 1 to 5. Where: two on each side of the container and 1 (number 5) placed at the door, right side, halfway up.

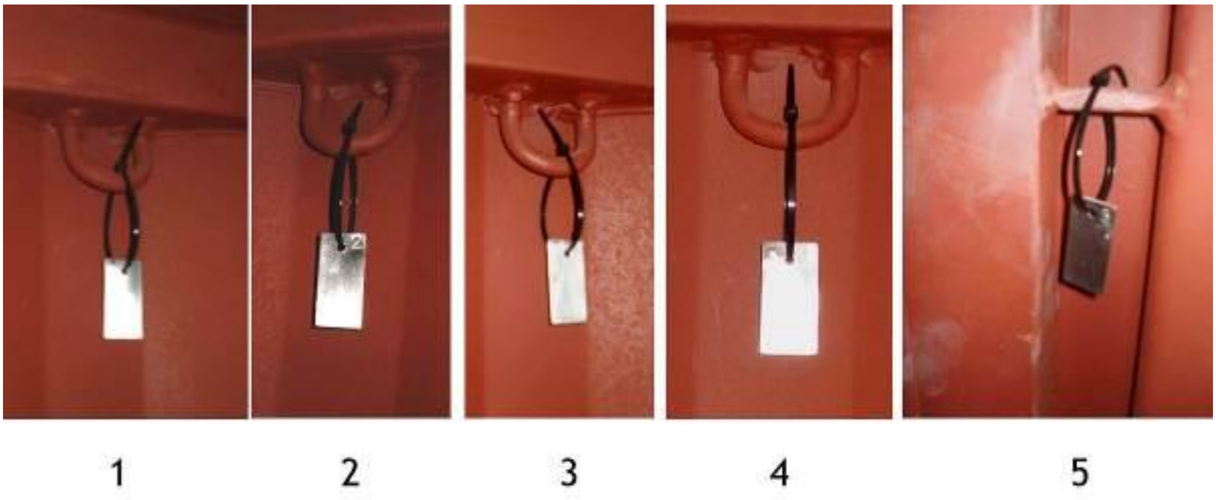


Figure 60 – Steel Metal Coupons

RESULTS AFTER SHIPPING THE CONTAINER FROM RIO DE JANEIRO (BRAZIL) TO GEBZE (TURKEY) – 11 WIRE IRON ROD COILS INTO A 40' CONTAINER EQUIPED WITH VCI AUTOMATIC SPRAY DIFUSOR (DISPENSER):

- Opening was made on June 09, 2011 (43 days):

The inspection of the container, performed by Captain of the Gezbe Port el Port Captain of the MARTY, Mr. Hasan Kabakci Logistic Director Arcelor Mittal in Turkey, in coordination with Mr. Danio Mirelli – Sea Land Logistics & Customer Care ArcelorMittal Milan.

- Reception conditions of the container (Gezbe - Turkey) and Coils Condition after transport

The coils have not been movement during transport. The tie-down straps are not broken. The interior of the container was in great condition (without condensation stains).

Figure 61 – Opening of the container after shipping period

INTERNAL DATA LOGGER

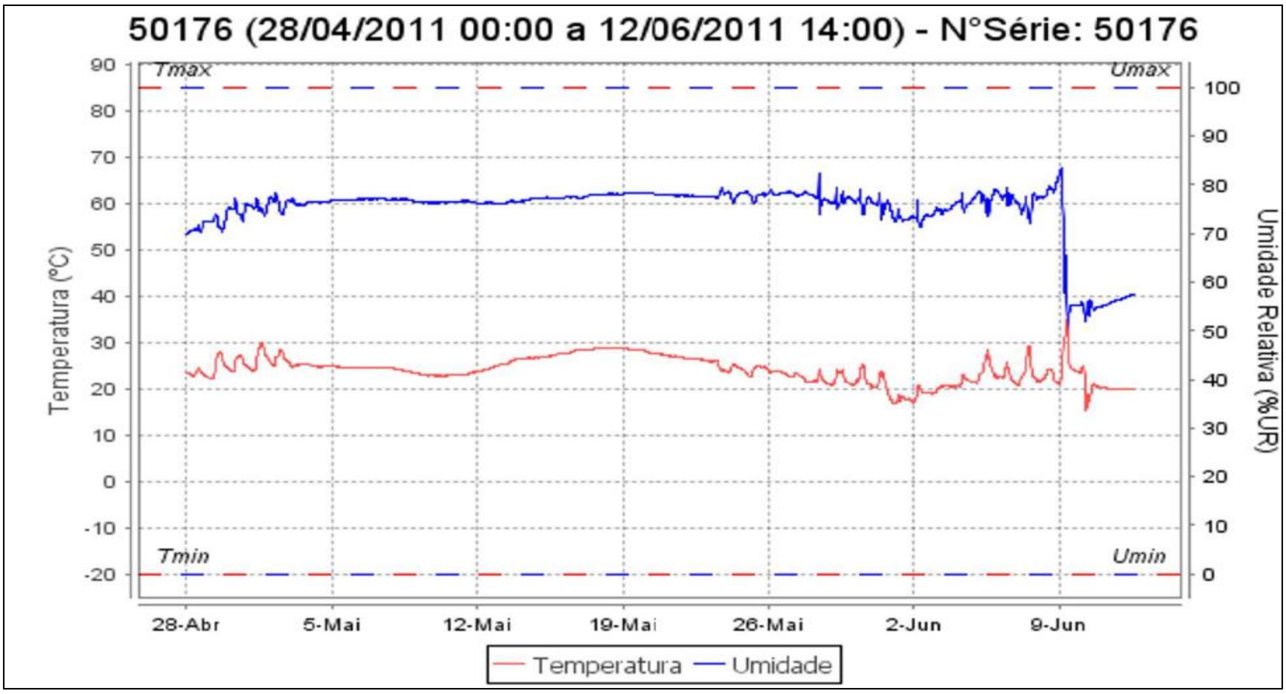


Figure 62 – Data from Internal Datalloger:

EXTERNAL DATA LOGGER

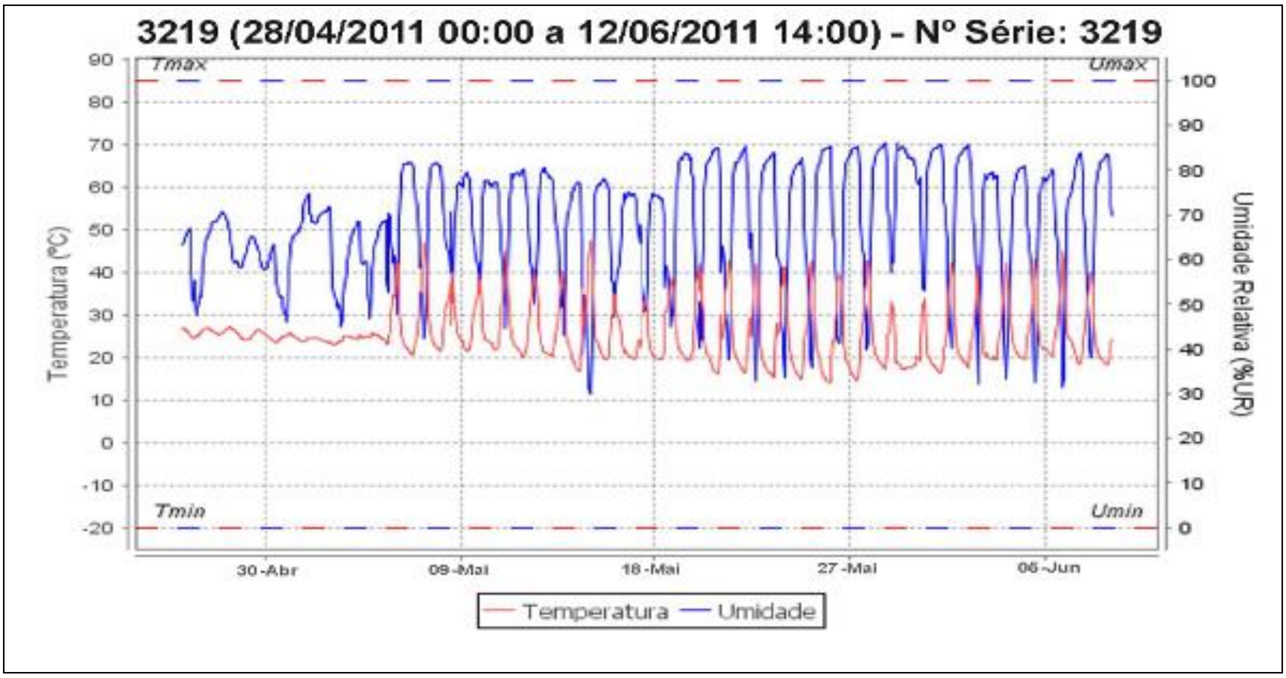


Figure 63 – Data from External Datalloger:

Dispenser Condition after Transport:

The VCI Dispenser was disabled (Turned off). Each Spray was removed and kept to be analyzed in laboratory. After laboratory analysis found that was used on average 78% of the volume in 43 days or 129 g of active VCI compounds. The Disperser VCI has 60 days activity or 165 g per each spray can.

Figure 64 – Dispenser apparatus after 43 days

Superficial Coupons Conditions:

The Coupons were retired using gloves for not contaminating them. Each coupon was packed in the VCI Bag (VCI Film + VCI Paper) to transport and to prevent oxidation.

Figure 65 – Metal coupons after 43 days:

After laboratory analysis found that the 5 coupons were no spots of oxidation (both side). We conclude that the medium was adequately protected during the closing time and transportation back to Brazil by courier.

Figure 66 – Metal coupons after lab analysis

Metal Surface Condition after Transport:

Figure 67 – Opening the package for inspection after 43 days

The metal is bright and oxide free. The right side doesn't present any dot of oxidation.

Figure 68 – Wire Steel Coil after 43 days - No oxide inside the coil.

Bottom – free oxide. Small grooves due to the lashing strap without oxide. The coil was raised and proven free of oxide.

Figure 69 – Wire Steel Coil after 43 days – bottom condition

Side of the coil clean, bright and oxide free.

Figure 70 – Wire Steel Coil after 43 days – side condition

Observations:

The appearance of the rolls is perfect thoroughly analyzed from the point of view of absence of oxidation; the surface of the metal is clean, bright and oxide free. Any oxide stains on the metal surface in all 11 coils were not found.

The normal points of friction between coils and vibration due to friction between the fastening strips and wire were clean of rust. Through observation of coupons, we can say that, even under high humidity, there was no oxide formation, proving that the environment is protected. There was no entry of salt water inside the container, nor the entry of water condensation inside the coils.

Important to note that this process is to control moisture in the air and saturate the environmental with VCI; for the success of this process should always keep out water inside the container and prevent tearing of the packaging during handling. For the success, the condition of the container before shipment is very important too.

This pilot test confirmed that automatic VCI dispenser can prevent corrosion of wire steel rolls during the transport.

7.5.3 Preservation and Hibernation of Oil & Gas Equipment

During the assembly process of an oil platform, the equipment and materials are purchased and metal parts are in stock and partly goes to the assembly line. This stage is called commissioning.

As this assembly takes more than five years, it is necessary to maintain the integrity of the materials and equipment using inhibition of corrosion processes. If this is not done, the material must be recovered before use or in some cases, the material is lost due to improper condition.

With several formulated protective products, always containing based V-active VCI corrosion inhibitor, a list of actions applied to the preservation of equipment and structure in the Oil & Gas industry was created. This procedure is proposed to be initially corrosion protection to avoid costly recovery processes. The term preservation and hibernation are part of the comprehensive action technician conviction of those involved.

To achieve these goals were created several product lines complement each other, such as water-based inhibitors (MV Aqua), the protective base oil (MV Oil), protective resin (MV Skin), cleaners and surface passivating (LQS500), VCI packing materials (Polyethylene Film and Paper VCI), VCI Releasing (Dispenser), etc.

GENERAL INDICATIONS OF USE OF V-ACTIVE VCI PRODUCTS – PRESERVATION AND HIBERNATION

1. **External surfaces** "unpainted'': tubes, spools, cable trays, stainless steel trays, flanges, shafts of pumps, compressors, turbines, screws, nuts, pipes, plates, welded areas

Protective MV Oil 800 or MV Oil 802, depending on the exposure to which is subjected the metal material. These products form a waxy film (MV Oil 800 thicker)

- Wash with cloth or degreaser, without any residue;
- Application by brush, cloth or spray (depending on the location and ease of application);
- If you need to remove, use solvent;
- If extend the period for a further 6 months is necessary, semiannual reapplication
- Monthly inspections

It could also be used the MV Skin (V-active VCI removable resin) - it is recommended to use in small areas of protection as "bezel“ in tubes, "curves" of pipes, flanges and external screws, welds, etc..

- Wash with cloth or degreaser, without any residue;
- Apply with a brush liquid resin with VCI without nitrite and with UV protection;
- Drying in 10 minutes. Reapplication (layers) with 10 minute intervals;
- Inspect each month;
- Reapply every six months;

Figure 71 – Oil & Gas – External protection

2. **Internal areas** with access and permission of the manufacturer, clean and free of oxidation: pipes, tanks, vessels, heat exchangers, valves, pumps, etc.

- Verify the initial internal surface condition of the material, it may need cleaning/decontamination;

- Pulverization of a solution composed by 20% of MV AQUA 250 (protective industrial fluid with VCI without nitrite) and 80% of water:

- With the pneumatic pistol or costal pump,

- Close hermetically all possible entries of contaminants,

- Necessary one liter of solution per cubic meter to be preserved,

- Expected period of preservation: for 12 months,

- Monthly inspections.

Note 1: As the product is water based, do not mix with oil, if the equipment contains waste of oily preservation, it should degrease using for such the protective degreaser MV AQUA 200 at 5%.

Note 2: in case of equipment subject to calibration with oil:

- After the test, drain the calibration oil,

- With pneumatic pistol, spray the MV Oil 902. Being a liter for each cubic meter of internal volume.

Figure 72 – Oil & Gas – Internal protection

3. **Internal reservoirs** of lubricant oils, hydraulic fluids and turbines:

Without lubricant: internal pulverization of MV OIL 902 (industrial protective fluid with nitrite-free VCI), with pneumatic pistol, or deposit internally. Requiring one liter of solution per cubic meter to be preserved.

Install coupons on entries (CPs steel plates 1020, for periodic inspections).

With Lubricant (or internal oil) add MVSQ V-ACTIVE VCI 1061 additive (protective industrial additive with nitrite-free VCI), without dilution, in the proportion of 4% of the volume of lubricant.

Figure 73 – Oil & Gas – Internal protection of tanks with oil

4. **Fuel Reservoirs**:

Without fuel: dissolve MVSQ V-ACTIVE 1061 additive (protective industrial fluid with nitrite-free VCI) in the fuel tank at the rate of 2-4%. Apply this solution internally by pulverization or deposition, being necessary one liter of protective solution for each cubic meter to be preserved.

With fuel: add the fuel with MVSQ V-ACTIVE 1021 (protective industrial additive with nitrite-free VCI), without dilution and in the proportion of 2-4% of its volume.

Figure 74 – Oil & Gas – Internal protection of fuel tanks

5. **Fuel Reservoirs**:

If the tanks are contaminated and/or oxidized, it is recommended a chemical cleaning using the LQS500 product at a concentration of 10 to 30%, passivation with MV Aqua 350 and addition of V-active VCI 1021 in the proportion of 4% of fuel volume.

Figure 75 – Oil & Gas – Internal protection of tanks – cleaning process

6. **Electric Engines**:

- Axes and unpainted external areas, use the protective MV OIL 800. This product forms a waxy film;

- Can also be applied to small areas, using a brush, the MV SKIN product, a drying liquid resin nitrite-free with VCI and with UV protection. Drying in 10 minutes.

- Pack with VCI P579 76g/m2 paper impregnated with VCI (absorbs excess moisture), superimpose with shrinkable film VCI FPE691 White UV (with UV protection);

- Inspect the integrity of packages weekly;

- Redo closure of the packaging in case of damages or openings for inspection.

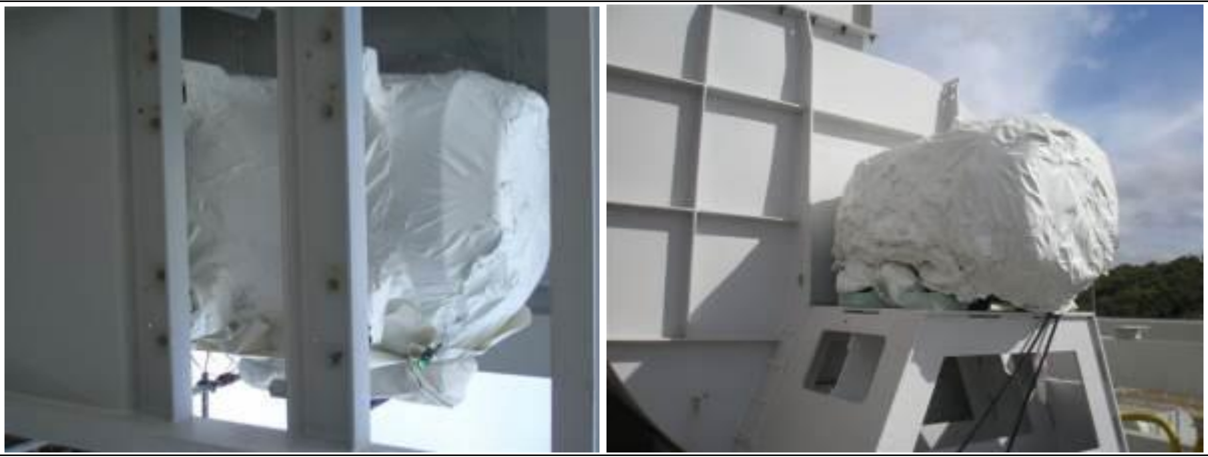


Figure 76 – Oil & Gas – electric engines

7. **New electric panels** without oxidation:

- Contacts preservation – spray the contacts with MV CLEANER. Install MV PANEL 8 (8 pieces per cubic meter to be preserved). Durability of 6 months. Sometimes, it is applied a sheet of VCI579 Paper, fixing it inside the door.

- Access doors and cabinets - spray external metal parts with MV OIL 807, set VCI P579 76g/m2 Paper and superimpose with Bubble VCI FBL691 70/80 g/m2 Film or Shrinkable VCI FPE691 White UV Film (with UV protection).

- Inspect monthly the packaging;

- Semiannually open the package for inspection of the material;

- Redo packaging;

- Having the heating system, it should remain operational.

Figure 77 – Oil & Gas – electric panel

8. **Instruments**:

- Spray external metal parts with MV OIL 807, pack with VCI 76g/m2 P579 Paper (absorbs excess moisture). Superimpose with Shrinkable VCI FPE691 White UV Film or Bubble VCI FPE691 Film (with UV protection);

- Inspect monthly packaging;

- Semiannually open the packages for inspection of the material;

- Redo packaging.

Figure 78 – Oil & Gas – general instruments

9. **Light Fixtures**

- Insert plates of CELLULOSE LINTER LC579 96 x 126 mm impregnated with VCI;
- Monthly inspections;
- Semiannual Exchange.

Figure 79 – Oil & Gas – light fixtures

10. **Wood boxes** containing equipment:

- In closed boxes, apply internally on surface the Wood active VCI, using brush or spray.

- If it is equipment of small dimensions, wrap them with VCI579 76 g /m² Paper.

- If there is risk of excessive moisture in the box, at transport or storage: the equipment can be involved with Bubble VCI691 70/80 g /m² Film or Shrinkable VCI FPE691 White UV Film.

- For the cases of boxes with large equipment, apply MV Oil 807 on unpainted parts, involving with VCI579 76 g /m² Paper. Bubble VCI691 70/80 g /m² Film is optional in case of mechanical protection.

Figure 80 – Oil & Gas – wood boxes treatment

11. **Equipment stored in container**

20 feet: install 02 units of Dispenser VCI

40 feet: install 04 units of Dispenser VCI

- Regulate for every 36 minutes spray (usually changing the refill and batteries occurs every 60 days).

- Install, 01 carbon steel SAE 1020 coupon, brushed (it should be replaced every 30 days and sent to VCI Brasil, for analysis). With such steps accomplished, it is possible to monitor the degree of protection of the stored materials.

Figure 81 – Oil & Gas – Dispenser VCI

12. **General Application**

Figure 82 – Oil & Gas – Trucks and heavy equipment

Figure 83 – Oil & Gas – FPSO – Singapore

Figure 84 – Oil & Gas – Comperj Pre-Salt Petrochemival Pole – Rio de Janeiro Brazil

Figure 85 – Oil & Gas – Comperj Pre-Salt Petrochemival Pole – Rio de Janeiro Brazil - Pre-Salt Petrobras – CO_2 Gas Generators

8 Conclusions

We learned in school that the problem of corrosion occurrence is the water contact with the metal, and that we must eliminate by whatever methods, the presence of water. Here in this paper proposes a new concept and mechanism of action of a new corrosion inhibitor model. Here in this document can be said that: water is not an enemy of the metal, use it to protect against corrosion.

For various methods and applications described herein may be shown and complete protective effect against corrosion, when a new class of inhibitor is added to water, and migrates to the water when the water is present in the medium. In other words, this new class of inhibitor, in particular V-active VCI neutralizes oxidant action when in the presence of metal.

The results obtained in laboratory tests and the tests applied in the production field, it was possible to verify the protective efficiency of V-active VCI inhibitor dissolved in water, both liquid phase and vapor phase.

Thus, it can be concluded that through the many results presented here, the corrosion inhibitor dissolved in water, be it in liquid phase or in the vapor phase, dissociates into positive and negative loads and starts to have electrical activity. This enables neutralizing the metal bias current (transition to a state of lower energy, as for example by an oxide in the case of iron), preventing its oxidation.

The purpose of this study was to develop and present an innovative product corrosion inhibitor and a new concept of performance of this in the middle and the metal surface. These results were fully found in various ways and conditions. With this, a new technology for inhibiting corrosion was proposed and very well accepted by the techno-scientific and techno-industrial community. With the perfect understanding of the proposed, which requires more than 10 years of experience in this regard, new products and applications can also be developed. With this new concept, where water is a problem of corrosion, the V-active VCI inhibitor may contribute to its elimination.

This paper (thesis) describes a new concept of development of corrosion inhibitors, using as a basis the proposed mechanisms of action of volatile corrosion inhibitors (VCIs). The use of water as the vehicle and means of chemical, either in liquid phase and vapor phase. Here refers to this technology and product, the generic name: V-active VCI.

This paper (thesis) presents the principles of this new development, as well as actual cases that demonstrate the effect of metal corrosion inhibition, either in the laboratory or in applied projects and proven.

In the literature there are several references mentioning that for metal protection against corrosion, especially metals and alloys containing iron (such as steel, cast iron, etc.), should eliminate contact of the metal surface with water (liquid or vapor phase). Here we propose to use water as a means of protection through the use of a new range of chemical and mixtures thereof dissolved or applied.

These chemical compounds affect the metal surface and have an action on the surface, preventing its oxidation, as comproved using the technical analysis XPS (X-Ray Photonelectron Spectroscopy). They enable the inhibition of the medium, through its vaporization and elimination of deleterious effects of water vapor. Thus, these inhibitors have inhibitory action in both the liquid phase and vapor phase.

Based on obtained positive results for these efficient inhibitors is possible to target several applications, namely “use the water as medium to transport and apply corrosion inhibitor”, the modification of the media conditions by controlling the parameters as humidity, acidity, quantity of used inhibitors and their uniform deposition on the metal surface in liquid phase and vapor phase, also by the setting volatility of prepared protective formulation can be influenced the lasting of the protection.

With these results and technical aspects is introduced the concept of "preserve to not recovering”. It is possible, with a depth and detailed case study and research, to obtain preservation systems using simple and proven biodegradable products, practically non-toxic, which respect the environment and human health.

In addition to the results presented for the additives water-based V-active VCI (1727, 1712, etc.), as proof of the success of these V-active VCI inhibitors it was possible to make various commercial products (belonging to VCI Brasil company), called MV Aqua®, such as protective metalworking fluids (MVAqua100, MVAqua102), protective degreasing fluids (MVAqua200, MVAqua203), protective fluids water-based (MVAqua250, MVAqua300, MVAqua350). It was also possible to formulate protective oils containing inhibitor V-active VCI corrosion, called MVOil, including the Protective Oils – film formers (MVOil800, MVOil802, MVOil807), protective for motorcycle chains (MVOil808), protective diesel tanks (MVOil902, MVNautic).

At the end of this work it can be stated, that the concept of water or steam as a carrier of volatile corrosion inhibitors (VCI) has proven both in the laboratory and in industrial practice. The practical result of this work is the manufacture and marketing of following products, anti-corrosion agents.

1. Protective Metalworking Fluids (Machining)

MV AQUA	**Characteristics**	**Specification**	
		Min	**Max**
MV Aqua 100	Spec. gravity (g/mL)	0.966	1.181
	pH	9.0	11.0
MV Aqua 102	Spec. gravity (g/mL)	0.956	1.169
	pH	8.0	10.0

2. Protective Degreasers ferrous and nonferrous materials

MV AQUA	**Characteristics**	**Specification**	
		Min	**Max**
MV Aqua 200	Spec. gravity (g/mL)	0.935	1.143
	pH	10	12.0
MV Aqua 203	Spec. gravity (g/mL)	0.942	1.152
	pH	10.0	12.0

3. Water-based Protective fluids

MV AQUA	**Characteristics**	**Specification**	
		Min	**Max**
MV Aqua 250/300	Spec. gravity (g/mL)	0.933	1.140
	pH	7.0	9.0

4. Protective oils – Film-formers (gallon and spray)

MV Oil	**Characteristics**	**Specification**	
		Min	**Max**
MV Oil 753	Spec. gravity (g/mL)	0.750	0.860
MV Oil 800	Spec. gravity (g/mL)	0.750	0.890
MV Oil 802	Spec. gravity (g/mL)	0.800	0.920
	Viscosity 40°C (cSt)	10.0	20.0
MV Oil 807	Spec. gravity (g/mL)	0.800	0.940
	Viscosity 40°C (cSt)	50.0	80.0

5. Protective for motorcycle chains (gallon and spray)

MV Oil	**Characteristics**	**Specification**	
		Min	**Max**
MV Oil 808	Spec. gravity (g/mL)	0.840	0.930

6. Protective diesel tanks: **MV Oil 902 and MV Nautic**

7. Protective applied inside Woodbox: **MV Woodactive**

8. Additive for oil-based product: **V-active VCI 1061**

9. Additive for water-based product: **V-active VCI 1727**

10. Additive for Hydrojecting: **V-active VCI 1712**

The results of this study were also published in both the scientific journal impact factor, as well as at international and national scientific conferences.

Journal with impact factor

Genovez M.C., Hrdina R., Pinto T., Araujo L.H.: *New concept of corrosion protection in the presence of water: V-active VCI. Concept and Application*.
Anti-Corrosion Methods and Materials, 62/1, 2015. Impact Factor: 0.414.

Genovez M.C., Hrdina R., Pinto T., Araujo L.H: *Applying a new concept of corrosion protection in the presence of water: Hydrojetting application – effectiveness lab test.*
Anti-Corrosion Methods and Materials, ACMM-03-2015-1509.R1. Accepted 2016. Impact Factor: 0.414.

Conferences

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Genovez M., Hrdina R.: *Inibidor de Corrosão Utilizando a Tecnologia V-active VCI*: Preservação e Hibernação (*Corrosion Inhibitor using V-active VCI Technology: Preservation and Hibernation of Metallic Materials*).
27º Congresso Brasileiro de Manutenção 2012 (*27º Brasilian Congress of Maintenance 2012*) – Rio de Janeiro Brazil – 10 to 14 September.

Other procedures of implementation was reported and new applications are under study, such as preservation of internal tubes and pipes, Hydrostatic Test processes and cleaning with water, diesel tanks contaminated with water, etc.

It means where there is a contamination caused by the water (as vapor phase or liquid), it can be promoted internal protection of equipment and metal parts.

9 Future work

Future work in this area can be divided into two parts - scientific and practical (new product development).

From a scientific perspective, we would like to find out first, which compound is actually adsorbed on the surface of iron products (VCI inside a closed container) since start from the fact that only amines (aliphatic or aromatic) volatilize/steam distilled. The most appropriate method for this investigation appears to us X-ray photoelectron spectroscopy. Secondly, for hygienic and ecological reasons, we would like to replace amines with the oxygen compounds.

Regarding the development of new products, we intend to build on recent work, where we have developed a new corrosion surfactants (soluble in water) [46] that are readily biodegradable.

Furthermore, new applications are underway and that will have major impact on scientific and industrial applied: replacement of heavy oils of wire drawing of an aqueous solution containing V-active VCI. This change will contribute to the elimination of environmental contamination and the elimination of the use of oils that harm the environment and humans. In addition, it makes it possible to eliminate the use of protective oils to keep the wire and metal bars longer in stock and without oxidation.

New applications and studies are underway, demonstrating there is a wide range of possible applications, providing environmental and economic gains very evident, proving that technology and developed products have a clear and effective application against corrosion.

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