Chapter 3. Methods of corrosion prevention

Introduction

The fight against corrosion is a constant concern in many industrial fields; it must be taken into consideration from the start of a project until its completion.

Preventive measures taken at the right time help avoid corrosion many problems when it comes to guaranteeing a certain lifespan of an object, therefore the prevention of corrosion must be considered from the design phase.

In general, protection against corrosion can be performed based on two main principles, and all various methods employed, adhere to these two concepts.

- To cover with protective coating that is more resistant to corrosion than the metal it is covering.
- Alter the electrical condition of the system in order to safeguard the metal.

Preventive measures

Preventive measures taken at the right time, making it possible to avoid many corrosion problems at no additional cost:

- An adapted shape of the metal parts.
- Judicious choice of materials.

1. Adapted shape of the metal parts

It is possible to reduce the risk of corrosion by giving metal parts a shape adapted to the conditions of use, and thus significantly influence their lifespan. For example, tanks and containers are designed taking into account the flow rate of the fluid and the absence of depressions, cracks and closed corners.

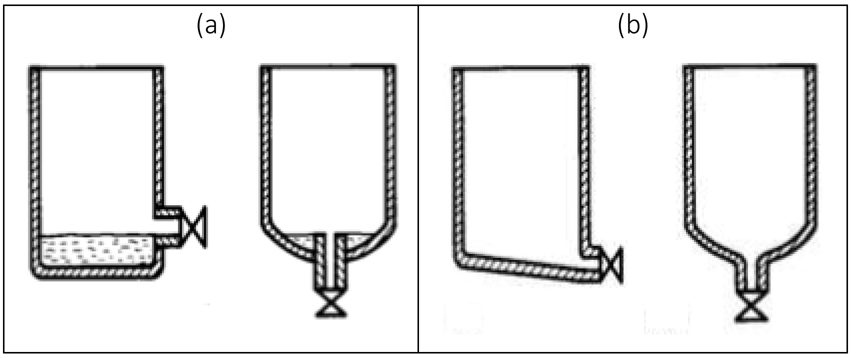

Figure 1. Prevention by container shape (a) inappropriate, (b) adequate

2. Judicious choice of metal or alloy

The hazards of corrosion can be effectively mitigated by selecting materials wisely. The selection of materials considers factors such as the specific application, the type and intensity of mechanical and thermal forces, as well as the cost and accessibility of materials. No metals or alloys possess complete immunity to corrosion, just pure metals are generally characterized by better corrosion resistance than impure metals, but they are very expensive, taking into account the mechanical properties such as hardness and impurities of these metals (Gold and platinum). The following table displays the corrosion resistance of specific pure metals in various conditions.

Table 1. Corrosion resistance of metals in corrosive environments.

Medium	Fe	Cr	Ni	Cu	Al	Zn	Ti
Humid air	-	+	+	+	+	+-	+
Aerated natural water	+-	+	+	+	-	+	+
Sea water	-	+	+	+-	+-	-	+
High temperature oxidation	+-	+	+	-	-	-	+-

(+) good ; **(-)** bad ; **(+-)** medium

Corrosion protection

Due to the variety of types of corrosion, each with its own preferred conditions and distinct characteristics, it is necessary to use different methods to prevent the different types of corrosion that can occur. Therefore, to effectively combat corrosion, a variety of protection methods are used which include :

- Protection by coating.
- Protection by inhibitors.
- Electrochemical protection.

1. Protection by coating

The coatings serve as a physical barrier that separates the metal to be protected from the aggressive environment, they are a thin layer that is unchangeable and impermeable, ensuring that the metal remains isolated from the harsh environment. They extends the life of components and improves performance as well as their decorative appearance. However, prior the use of these coating, it is important to properly prepare this surface : - Removing grease - Removing coatings and perhaps Polishing.

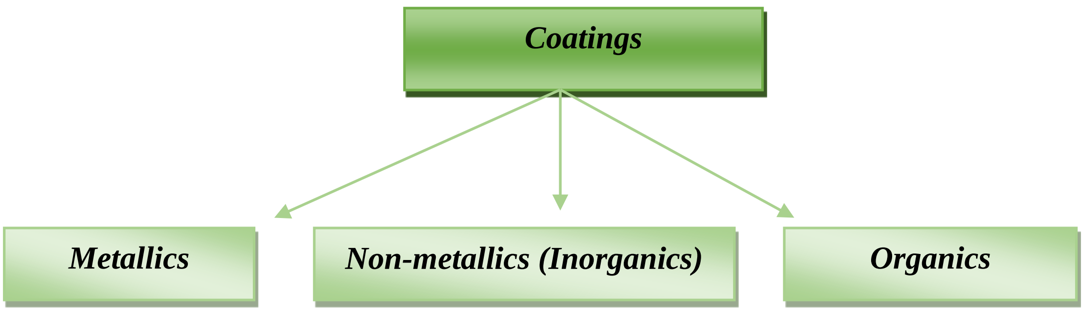

Figure 2. Types of coatings

1.1. Metallic coatings

Metallic coatings refer to layers of metal that are applied onto various substrates, including metal, plastic, glass, or other materials. These coatings are widely used for corrosion protection due to their ability to provide a barrier against environmental factors. The selection of the appropriate coating depends on factors such as the type of metal substrate, environmental conditions, desired durability, and cost considerations. we will distinguish two types of metal coverings:

a. **Anodic coatings :** In this case the protective metal is less noble than the metal to be protected (zinc coating). If there is a flaw in the coating, a local pile forms and the latter corrodes while cathodically protecting the base metal. Hence, the thickness is an important element in this type of coating, generally it varies between 100 and 200 µm.

b. **Cathodic coatings :** The protective metal is nobler than the metal to be protected (nickel or copper coating on steel).

1.1.1. Processes for producing metal coatings

Various techniques are used to obtaine metal coatings, and the main ones are : Immersion, Diffusion, Metallization, Plating and Electrolysis.

1.1.2. Examples of metallic coatings

Each metallic coating has its advantages, limitations, and specific applications. The selection of the appropriate coating depends on factors such as the type of metal, environmental conditions, desired durability, and cost considerations. Here are some common types of metallic coatings used for corrosion protection :

Hot-Dip Galvanizing : Involves dipping steel or iron into molten zinc to create a thick, durable layer of zinc coating. Hot-dip galvanizing provides excellent corrosion protection, particularly in harsh environments such as marine or industrial settings.

Zinc Plating : Zinc electroplating deposits a thin layer of zinc onto the surface of a metal substrate, providing corrosion protection through sacrificial protection.

Nickel Plating : Nickel electroplating forms a protective layer on the metal surface, providing corrosion resistance and improving wear resistance.

Chromium Plating : Chromium electroplating provides corrosion resistance and enhances the appearance of the metal surface. It is commonly used in decorative applications.

Hot-Dip Aluminizing : Involves dipping steel into molten aluminum to create a layer of aluminum coating. Aluminizing provides excellent corrosion resistance and heat resistance, making it suitable for high-temperature applications.

Tin Plating : Tin electroplating deposits a thin layer of tin onto the surface of a metal substrate, providing corrosion resistance and enhancing solderability. Tin coatings are commonly used in the food packaging industry and electronics industry.

Cadmium Coating : Cadmium electroplating provides excellent corrosion resistance, particularly in harsh environments. However, due to environmental concerns related to cadmium toxicity, its use has been restricted in many applications.

Zinc-Nickel Alloy Coating : Zinc-nickel alloy coatings provide enhanced corrosion protection compared to pure zinc or nickel coatings. The alloy composition offers improved corrosion resistance and sacrificial protection.

Copper Plating : Copper electroplating provides corrosion resistance and improved electrical conductivity. It is commonly used in electronic components and decorative applications.

Silver Plating : Silver electroplating offers excellent corrosion resistance, electrical conductivity, and solderability. It is used in various industries, including electronics, telecommunications, and aerospace.

Gold Coatings : Gold electroplating provides superior corrosion resistance and electrical conductivity. It is used in high-end electronic components, connectors, and decorative applications.

1.2. Non-metallic (Inorganic) coatings

The inorganic and non-metallic coatings are protective layers applied to the surface of materials to protect them against corrosion. These coatings are composed of materials such as polymers, ceramics, oxides and non-metallic composites. They work by forming a physical barrier between the material and its surroundings, preventing corrosive agents from penetrating and damaging the metal substrate. Different methods can be used depending on the specific properties of the coating materials and the requirements of the final application, including :

Physical Vapor Deposition (PVD) : In this technique, materials in vapor form are deposited on the surface of the substrate to form a coating. Common PVD methods include sputtering, vacuum evaporation, and ion beam deposition.

Electrochemical deposition (electrodeposition) : This process involves passing an electric current through a solution containing metal ions, resulting in the formation of a layer of metal on the surface of the substrate.

Dip-coating : This method involves dipping the substrate into a solution containing the coating materials, followed by a drying and curing process to form the coating.

Spray-coating : Coating materials are sprayed in particle form onto the substrate surface using a spray device. The coating is then hardened to form a protective layer.

1.3. Organic coatings

Organic coatings are protective layers applied to the surface of materials to protect them against corrosion. These coatings are composed primarily of organic compounds such as resins, polymers, solvents and additives. They can be applied in liquid form (paints, lacquers, varnishes), in powder form (powder coatings) or in the form of an adhesive film.

Organic coatings work by forming a physical barrier between the material and its surroundings, preventing corrosive agents from penetrating and causing damage. They also provide aesthetic benefits by allowing coloring and customization of surfaces, as well as specific properties such as electrical insulation, chemical resistance and heat resistance.

These coatings are widely used in various industries such as automotive, construction, aerospace, furniture and many others, to protect metallic and non-metallic surfaces and extend their useful life.

2. Protection by inhibitors

2.1. Definition

A corrosion inhibitor is a chemical substance added to a corrosive medium to reduce or prevent corrosion of metals. These inhibitors work by forming a protective layer on the metal surface, which limits or blocks contact with corrosive agents present in the environment.

Corrosion inhibitors can be used in various fields, including the oil and gas industry, chemical industry, water treatment, and other sectors where corrosion protection is essential to extend the life of equipment and infrastructure.

2. 2. Classification of inhibitors

Generally, inhibitors are classified in several ways (Figure 1), depending on their fields of application, their nature (organic or inorganic inhibitors), their electrochemical mechanisms of action (anodic, cathodic or mixed inhibitors) and their interface mechanisms and principles of action (adsorption on the metal surface and/or formation of a protective film).

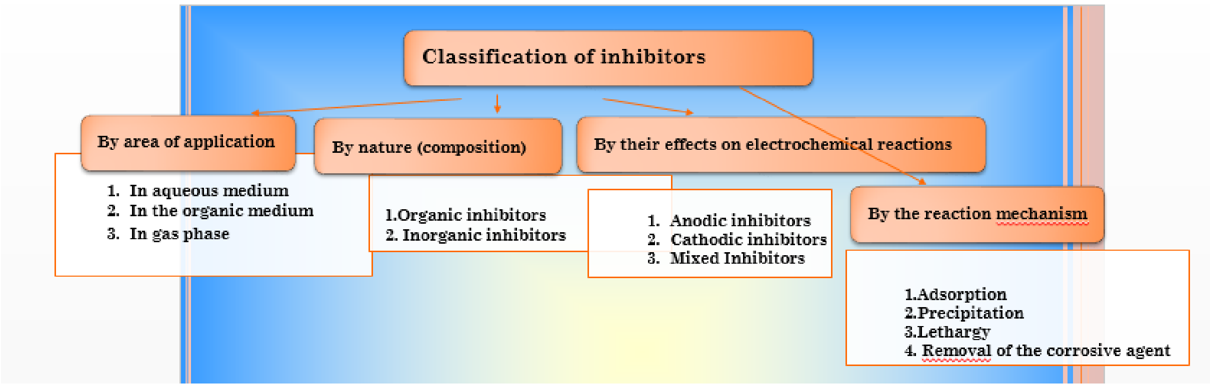

Figure 3. Differents class of inhibitors

2.2.1. By area of application

Inhibitors are commonly categorized based on their specific application area. These areas include the aqueous medium, organic medium, and gas phase [1].

1. In aqueous medium

Inhibitors for acidic environments : Are used to prevent electrochemical phenomena attacking steel during pickling. In the oil industry, they are added Drilling fluids.

Neutral medium inhibitors : Are mainly used to protect circuit cooling.

Inhibitors for basic environments : Are used to inhibit corrosion in the pores of reinforced concrete.

2. In the organic medium : These corrosion inhibitors are used in engine lubricants and in fuels.

3. In gas phase : These inhibitors are used to protect sensitive and delicate devices and also electronic parts during transportation or storage.

2.2.2. By nature (composition)

The inhibitors can be classified based on their compositions, and we can identify two distinct categories of inhibitors (organic and inorganic inhibitors).

1.Organic inhibitors

Organic inhibitors are chemical substances composed of carbon chains that contain active centers such as oxygen (O), nitrogen (N), and sulfur (S). The efficacy of these inhibitors relies on their strong adsorption onto the metal surface.

Nitrogen compounds : Nitrogen compounds, such as amines and azoles, have the ability to create complexes with the metal surface, resulting in the formation of a protective layer. This layer acts as a barrier, preventing corrosive chemicals from directly contacting the metal. This layer can also promote the development of passivation, which is a thin layer of oxide or carbonate that provides additional protection to the metal against corrosion. In addition, nitrogen compounds have the ability to function as corrosion inhibitors by altering environmental factors, such as pH or the concentration of metal ions, so creating an environment that is less conducive to corrosion. Nitrogen compounds are commonly employed in refrigerants, heating systems, and water circulation circuits.

Sulfur compounds : Sulfur compounds, including both organic and inorganic sulfides, have the ability to create protective coatings on metal surfaces. These compounds are less commonly utilized than the previous ones, although they can be largely as effective, particularly at elevated temperatures. Their major disadvantage is the risk of decomposition with the formation of hydrogen sulphide, in an acidic environment promoting the penetration of hydrogen and the weakening of steels.Sulfur compounds are commonly employed in drilling fluids, lubricants and fuels.

Oxygen compounds : Certain oxygen compounds have the ability to function as corrosion inhibitors by creating protective coatings on metal surfaces. Corrosion inhibitors that contain oxygen are commonly introduced into operational fluids in many industrial systems to safeguard metal equipment from corrosion.

2. Inorganic inhibitors

Inorganic inhibitors, often known as mineral inhibitors, they are chemicals obtained from mineral sources that do not contain carbon in their structure. Mineral (inorganic) inhibitors can function in several ways : by passivating the metal, which means they build or stabilize the oxide layer on the metal's surface, by creating insoluble protective coatings, or by making the medium more alkaline. Below are some examples of commonly used inorganic corrosion inhibitors :

Chromates : Chromates are widely used as corrosion inhibitors for metals such as aluminum and zinc.

Phosphates : Phosphates are used as corrosion inhibitors in cooling systems and water treatment systems.

Nitrites : Nitrites are often used as corrosion inhibitors in engine cooling systems and heating systems.

2.2.3. According to their effects on electrochemical reactions

Based on their impact on the speed of partial electrochemical reactions, inhibitors can be classified into three types : (anodic, cathodic or mixed inhibitors)

1. Anodic inhibitors

Anodic inhibitors are substances that are used to prevent or slow down the corrosion of metals by inhibiting the anodic reaction, they act by interfering with the oxidation reactions that occur at the anode during the electrochemical corrosion process.

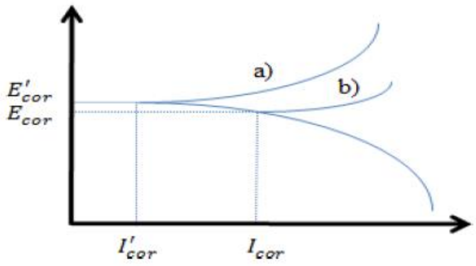

Figure 4. Polarization curve with and without the anodic inhibitor **a** and b respectively

2. Cathodic inhibitors

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface.

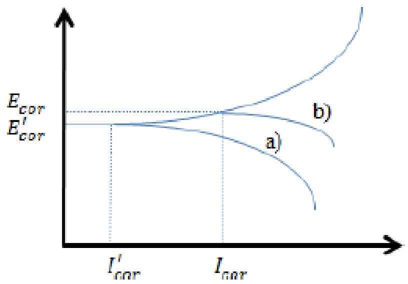

Figure 5. Polarization curve with and without the cathodic inhibitor **a** and b respectively

3. Mixed Inhibitors

Mixed inhibitors work by reducing both the cathodic and anodic reactions.

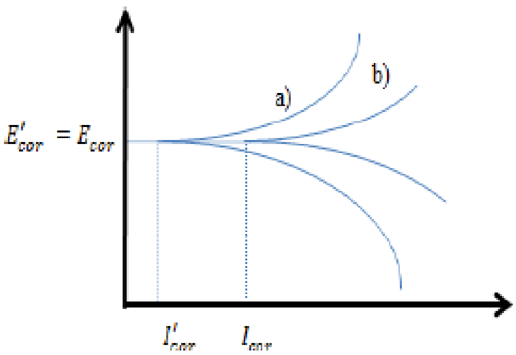

Figure 6. Polarization curve with and without mixed inhibitor

2.2.4. According to the reaction mechanism (inhibition)

According to the reaction mechanism, we can describe inhibition in terms of the response mechanism inhibition and it can be categorized as follows : - Inhibition by adsorption - Inhibition by passivation - Inhibition by precipitation of a film - Inhibition by removal of the corrosive substance.

1. Adsorption

In this type, inhibitors are organic compounds that are are introduced into a corrosive environment, and they become adsorbed on the surface of the metal exposed to corrosion, preventing it from interacting with the surrounding medium. These substances are distinguished by the presence of active sites, which form a strip at the level of the surface of the metal as a result of their adsorption. Adsorption inhibitors are typically employed in acidic environments, adsorption can be classified into two categories : physical and chemical adsorption.

2. Precipitation

Precipitation is a process where mineral salts or organic complexes that have low solubility in corrosive substances are deposited on the surface of the metal.

3. Lethargy

Chemically inert deposits are formed on the corrosive medium as a result of the interaction of the inactive inhibitors with the surface of the metal causing lethargy. As a result, the metal becomes inert and the rate of corrosion slows down. For example, chromates and nitrates are examples of this class of inhibitors that alter the medium's pH.

4. Removal of the oxidant or corrosive agent

In this case, we add a material that quickly consumes the oxygen in the hostile setting. Examples of such inhibitors include sodium sulfide.

2. Electrochemical Protection

Controlled manipulation of the corrosion process's oxidation and reduction reactions is the essence of electrochemical protection. The actual process of this procedure is done by shifting the electrode potential in the positive or negative direction until its attack speed is extremely low or inexistant. These methods are widely used to protect metals against corrosion in the soil and in aqueous environments.

2.1. Anodic Protection

Anodic protection is an electrochemical technique employed to mitigate the corrosion process. Corrosion protection is achieved by the creation of a metal oxide layer on the metal surface, which acts as a barrier against corrosive substances, effectively isolating the metal and safeguarding it from their detrimental effects. This technique is accomplished by administering an exogenous electrical current. This approach is utilized for metals that demonstrate the phenomena of negative, such as iron (Fe), nickel (Ni), chromium (Cr), and their alloys.

Anodic protection of aluminum metal and its alloys is a widely used industrial procedure. The presence of aluminum oxide, Al2O3, forms a solid, cohesive, and impermeable coating that effectively blocks the entry of oxygen and water vapor into the metal, so serving as a protective barrier against corrosion.

2.2. Cathodic Protection

Cathodic protection is a method employed to manage the corrosion of a metal surface by converting it into the cathode of an electrochemical cell. This is commonly accomplished by linking the metal that needs protection to a sacrificial metal that is more prone to corrosion, serving as an anode.

Cathodic protection is employed to safeguard metal constructions, such as steel, gas pipelines, oil pipelines, water pipes, tanks, metal piers of jetties, ships, oil platforms, and reinforced concrete structures, against corrosion. There exist two main types of cathodic protection.

2.2.1. Cathodic protection by sacrificial anode

Cathodic protection by sacrificial anode is a method used to prevent corrosion of metal structures, such as pipelines, ships, offshore platforms, and underground tanks. In this technique, a more active, less noble metal is electrically connected to the structure to be protected.

This sacrificial anode are metals or alloys attached to the hull that have a more anodic, i.e. less noble, potential is electrically connected to the structure to be protected. This sacrificial anode supply the cathodic protection current, but will be consumed in doing so and therefore require replacement for the protection to be maintained.

When selecting sacrificial anodes, various types are available, each with distinct characteristics and suitable applications. For example, For the steel protection, anodes made of zinc, aluminum, or magnesium are employed.

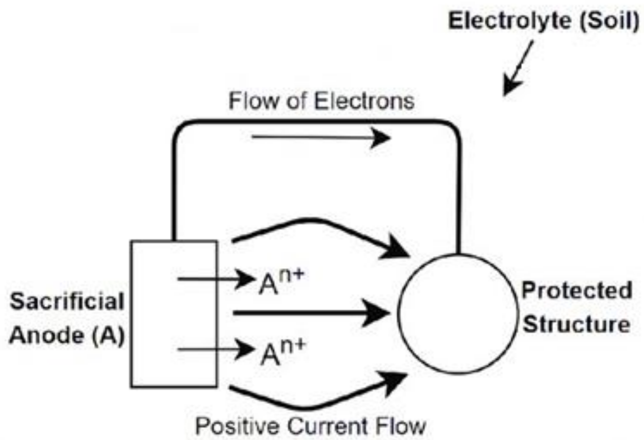

Figure 7. Schematic diagram of Sacrificial Anode

2.2.2. Cathodic protection by impressed current

In cases when the installations are larger or has inadequate mechanical insulation due to low-quality coating, sacrificial anodes may not provide sufficient current for optimal protection.

In impressed current systems, anodes are subsequently linked to a permanent or cyclic direct current generator. The anodes are either tube or compact rods, designed to facilitate oxygen degassing. They are constructed from several specialized materials such as steel, cast iron, graphite, metal oxides, platinum-coated wires, and niobium.

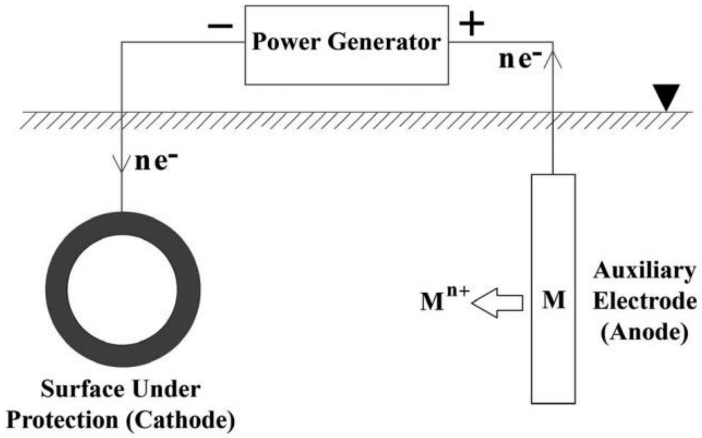

Figure 8. Schematic diagram of impressed current