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# **Corrosion Inhibitors – Principles, Mechanisms and Applications**

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## **1. Introduction**

Corrosion processes are responsible for numerous losses mainly in the industrial scope. It is clear that the best way to combat it is prevention.

Among the various methods to avoid or prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best know methods of corrosion protection and one of the most useful on the industry. This method is following stand up due to low cost and practice method. [1] [2] [3] [4]

Important researches have being conducted with government investment mainly in large areas such as development construction of new pipelines for shale gas and growth in construction. The focus of these researches has being the inhibitors applications in water and concrete for the protection of metals. [5]

Historically, inhibitors had great acceptance in the industries due to excellent anti-corrosive proprieties. However, many showed up as a secondary effect, damage the environment. Thus the scientific community began searching for friendly environmentally inhibitors, like the organic inhibitors. [6] [7] [8] [9] [10] [11] [12] [13]

This chapter presents a revision of the corrosion inhibitors applications mainly the novel compositions environmentally friendly. Is describes the mechanisms of action of inhibitors, main characteristics, environmental impact, technical analysis and calculation of efficiency.

### **1.1. Mechanisms of actions of inhibitors**

Inhibitors are substances or mixtures that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion. [2]

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Generally the mechanism of the inhibitor is one or more of three that are cited below:

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;
- the inhibitor leads a formation of a film by oxide protection of the base metal;
- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex. [4] [14] [15]

## 1.2. Historic review

There are many industrial systems and commercial applications that inhibitors are applicable, such as cooling systems, refinery units, pipelines, chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants, etc. [16]

There are evidences of the use of inhibitor since the early XIX century. On that time they were already used to protect metals in processes such as acid picking, protection against aggressive water, acidified oil wells and cooling systems. Since years 1950's and 1960's, there was significant advances in the development of technology for corrosion inhibitor as the application of electrochemistry to evaluate corrosion inhibitors. [17]

Recent studies estimate that the U.S. demand for corrosion inhibitors will rise 4.1% per year to USD\$ 2.5 billion in 2017. In 2012 they estimated that the market demand of inhibitors was divided on 26.6% to refining petroleum, 16.9% utilities, 16.7% gas and oil production, 15.3% chemical, 9.5% metals, 7.1% pulp and paper and 8.0% other. [5]

Now a days, due to changes occurred on the market of corrosion inhibitors, some industrial corrosion inhibitors are being unused. Due to high toxicity of chromate, phosphate and arsenic compounds, related to various environmental and health problems, strict international laws were imposed. Reducing the use of these and therefore increasing the need for the development of other inhibitor to supply the lack in this area. Should, however, present a similar anti corrosive properties similar than a chromate inhibitor. [18]

An important number of papers have been published with the intention of develop an environmentally friendly corrosion inhibitors and a lot of research has been doing to development of the called "green" corrosion inhibitors.[19] Also, has been increasing research in natural products, such as plant extracts, essential oils and purified compounds to obtain environmentally friendly corrosion inhibitors. [20]

The first evidence of natural product use as corrosion inhibitors is 1930's. When extracts of *Chelidonium majus* (Celadine) and other plants were used on the first time in H<sub>2</sub>SO<sub>4</sub> pickling baths. Successful developments of researches to obtain natural corrosion inhibitors are growing as quickly as the environmental consciousness is gaining ground.[21]

Chromates as active inhibitors are being replaced by other components such as molybdate compounds and rare earth metal salt, like cerium chloride. Also, drugs have been studied as corrosion inhibitors. [22] [23] [24]

## 2. Inhibitors classifications

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by:

- the chemical nature as organic or inorganic;
- the mechanism of action as anodic, cathodic or a anodic-cathodic mix and by adsorption action, or;
- as oxidants or not oxidants. [4]

In general, the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption.

This chapter is subdivided in according to the classification of the inhibitors shown on the Figure 1

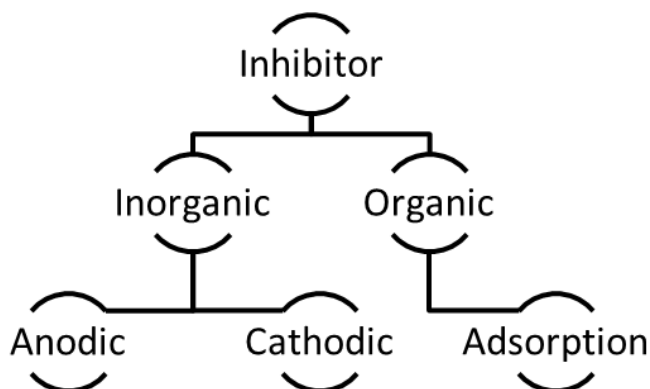


Figure 1. Classification of inhibitors

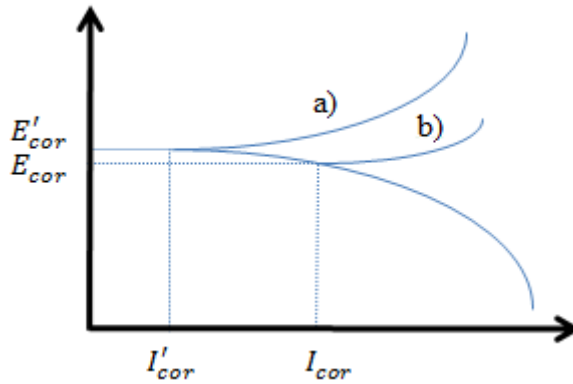
### 2.1. Inorganic inhibitors

#### 2.1.1. Anodic inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is, blocks the anode reaction and supports the natural reaction of passivation metal surface, also, due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface. [4] [24]

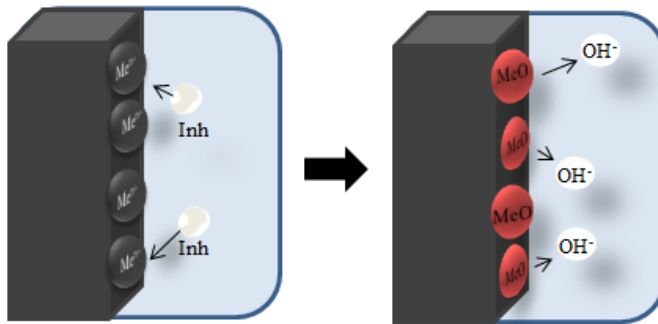
Figure 2 shows a potentiostatic polarization diagram of a solution with behavior inhibitor anodic. The anodic reaction is affected by the corrosion inhibitors and the corrosion potential

of the metal is shifted to more positive values. As well, the value of the current in the curve decreases with the presence of the corrosion inhibitor.



**Figure 2.** Potentiostatic polarization diagram: electrochemical behavior of a metal in a solution with anodic inhibitor (a) versus without inhibitor (b).

The anodic inhibitors reacts with metallic ions  $Me^{n+}$  produced on the anode, forming generally, insoluble hydroxides which are deposited on the metal surface as insoluble film and impermeable to metallic ion. From the hydrolysis of inhibitors results in  $OH^-$  ions. [4] Figure 3 shows how is the mechanism of the anodic inhibitory effect.



**Figure 3.** Illustration of anodic inorganic inhibitors effect and their mechanism of action.

When the concentrations of inhibitor becomes high enough, the cathodic current density at the primary passivation potential becomes higher than the critical anodic current density, that is, shift the potential for a noble sense, and, consequently, the metal is passivated. [25] [26]

For the anodic inhibitors effect, it is very important that the inhibitor concentrations should be high enough in the solution. The inappropriate amount of the inhibitors affects the forma-

tion of film protection, because it will not cover the metal completely, leaving sites of the metal exposed, thus causing a localized corrosion. [4] [25] [26]

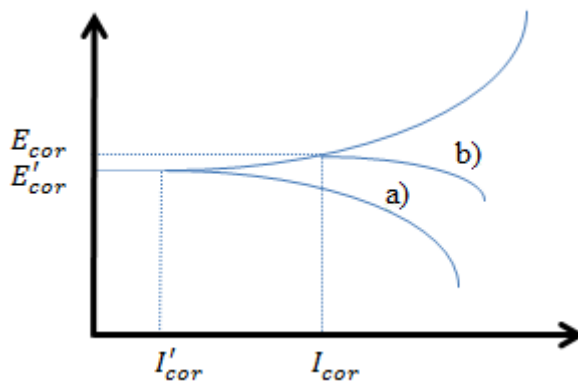
Concentrations below to the critical value are worse than without inhibitors at all. In general can cause pitting, due reduction at the anodic area relative to cathodic, or can accelerate corrosion, like generalized corrosion, due to full breakdown the passivity. [25]

Some examples of anodic inorganic inhibitors are nitrates, molybdates, sodium chromates, phosphates, hydroxides and silicates.

### 2.1.2. Cathodic inhibitors

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors have metal ions able to produce a cathodic reaction due to alkalinity, thus producing insoluble compounds that precipitate selectively on cathodic sites. Deposit over the metal a compact and adherent film, restricting the diffusion of reducible species in these areas. Thus, increasing the impedance of the surface and the diffusion restriction of the reducible species, that is, the oxygen diffusion and electrons conductive in these areas. These inhibitors cause high cathodic inhibition. [4] [24] [27]

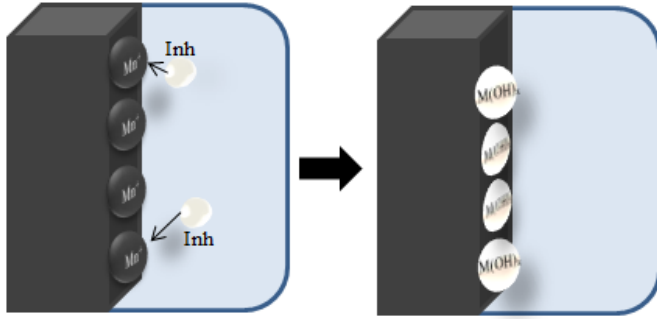
The Figure 4 shows an example of a polarization curve of the metal on the solution with a cathodic inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values.



**Figure 4.** Potentiostatic polarization diagram: electrochemical behavior of the metal in a cathodic inhibitors solution (a), as compared to the same solution, without inhibitor (b).

The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it. Thus, restricts the metal contact with the environment, even if it is completely immersed, preventing the occurrence of the corrosion reaction. Due to this, the cathodic inhibitor is independent of concentration, thus, they are considerably more secure than anodic inhibitor. The Figure 5

shows the illustration of mechanical effect of cathodic inhibitors to restrain the corrosion process. [4]



**Figure 5.** Illustration has shown the mechanism of actuation of the cathodic inhibitors.

Some examples of inorganic cathodic inhibitors are the ions of the magnesium, zinc, and nickel that react with the hydroxyl ( $\text{OH}^-$ ) of the water forming the insoluble hydroxides as ( $\text{Mg}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ) which are deposited on the cathodic site of the metal surface, protecting it. [4] Also can be cited polyphosphates, phosphonates, tannins, lignins [15] and calcium salts as examples that presents the same reaction mechanism.

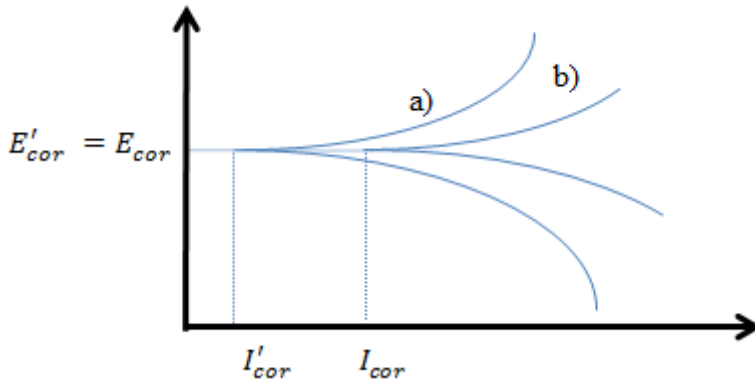
It seen in hard waters a kind of this mechanism of inhibiting, due to the effect of the magnesium or calcium bicarbonate on it. When temporary hard water flows over the metal it can assist on the nucleation of carbonates, allowing the reactions near to the equilibrium and forming precipitations on the metal surface. These precipitations, like a  $\text{CaCO}_3$ , cover the cathodic area, protecting the metal. So these cathodic inhibitor depends only on the chemistry of the water, is not due the metal composition, because of this they are applicable to all metals. [4] [25]

As example, may be mentioned the oxides and salts of antimony, arsenic and bismuth, which are deposited on the cathode region in acid solutions. These cathodic inhibitors minimize the release of hydrogen ions due to a phenomena that can difficult the discharge of the hydrogen, called overvoltage.

## 2.2. Organic inhibitor

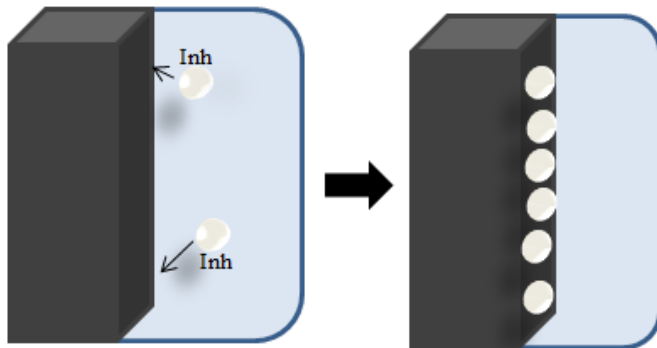
Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or together, as cathodic and anodic inhibitors, nevertheless, as a general rule, act through a process of surface adsorption, designated as a film- forming. Naturally the occurrence of molecules exhibiting a strong affinity for metal surfaces compounds showing good inhibition efficiency and low environmental risk. [28] These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal. [4]

In the Figure 6, that shows a theoretic potentiostatic polarization curve, it can be seen that the effect of the solution containing organic inhibitor on the metal presents an anodic and cathodic behavior. After the addition of the inhibitor, the corrosion potential remains the same, but the current decreases from  $I_{cor}$  to  $I'_{cor}$ .



**Figure 6.** Theoretical potentiostatic polarization diagram: electrochemical behavior a metal on a solution containing a cathodic and anodic inhibitor (a) compared to the same solution without the inhibitor (b).

Is showed in Figure 7 the mechanism of actuation of organic inhibitors, when it is adsorbed to the metal surface and forms a protector film on it.



**Figure 7.** Illustration of the mechanism of actuation of the organic inhibitor: acting through adsorption of the inhibitor on the metal surface. Where the Inh represents the inhibitor molecules.

The efficiency of an organic inhibitor depends of the:

- chemical structure, like the size of the organic molecule;
- aromaticity and/or conjugated bonding, as the carbon chain length;

- type and number of bonding atoms or groups in the molecule (either  $\pi$  or  $\sigma$ );
- nature and the charges of the metal surface of adsorption mode like bonding strength to metal substrate;
- ability for a layer to become compact or cross-linked,
- capability to form a complex with the atom as a solid within the metal lattice;
- type of the electrolyte solution like adequate solubility in the environment. [16]

The efficiency of these organic corrosion inhibitors is related to the presence of polar functional groups with S, O or N atoms in the molecule, heterocyclic compounds and pi electrons, generally have hydrophilic or hydrophobic parts ionizable. The polar function is usually regarded as the reaction center for the establishment of the adsorption process.[4] [28]

The organic acid inhibitor that contains oxygen, nitrogen and/or sulfur is adsorbed on the metallic surface blocking the active corrosion sites. Although the most effective and efficient organic inhibitors are compounds that have  $\pi$ -bonds, it present biological toxicity and environmental harmful characteristics. [29]

Due to the metal surface covered is proportional to the inhibitor concentrates, the concentrations of the inhibitor in the medium is critical. [24] [30]

Some examples are amines, urea, Mercaptobenzothiazole (MBT), benzotriazole e toliotriazol, aldehydes, heterocyclic nitrogen compounds, sulfur-containing compounds and acetylenic compounds and also ascorbic acid, succinic acid, tryptamine, caffeine and extracts of natural substances. [4] [25] [28]

There are still some inhibitors that act in vapor phase (volatile corrosion inhibitor). Some examples are: dicicloexilamônio benzoate, diisopropylammonium nitrite or benzoate, ethanolamine benzoate or carbonate and also the combination of urea and sodium nitrite. [4] [24]

### 3. Techniques for analysis of inhibitors

The most usefully technique to analysis the effectiveness of an inhibitor are weight loss experiment and electrochemical measurements, like polarization curve method and the impedance measurement analyzing. In addition, microscopy techniques are used to characterize the corrosion process.

### 4. Considerations to employ inhibitors

For all types of inhibitors, we should consider some environmental actions factors because some elements such as metals, pH, composition, impurities, agitation, temperature, geometry



of the system, the concentration of inhibitor and the mixture of one or more inhibitors may change the anti-corrosive mechanism. [4] [23] [31] [33]

To employment of the inhibitors is quite satisfying that certain factors should be seen as the real cause of the corrosion, the cost X benefit and possible interactions of the inhibitor with the environment, such as the influence of a catalyst, deposition or contamination. Four fundamental aspects must be analyzed to obtain a satisfactory result from the use of the inhibitor.

## 5. Inhibitor efficiency

The inhibitor efficiency could be measured by the follow equation:

$$E_f = \frac{R_i - R_o}{R_o} \times 100 \quad (1)$$

where,  $E_f$  is inhibitor efficiency (percentage),  $R_i$  is corrosion rate of metal with inhibitor and  $R_o$  is corrosion rate of metal without inhibitor.[38]

## 6. Industrial application

Acid pickling: Prevent the attack in the metal due to the acid solution in which metal gets cleaned of mill scale (bark lamination), and also prevented the subsequent hydrogen evolution inhibitors are added, typically organic, must be soluble or dispersed in the solution. Examples: thiourea and amino and its derivatives, propargyl alcohol. [4]

Oil industry: sodium carbonates or organic amines complex are employed to reduce the corrosive effect of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and organic acids, enabling the use of more cheaper materials and less resistant to corrosion in wells extracting crude oil. Pipes for gasoline and kerosene are employed sulphonated oils, sodium nitrite. Oil well uses up fatty amines, fatty acids, imidazolines and quaternary ammonium salts. Internal pipe corrosion occurs in wet gas transportation due to condensation of water containing dissolved corrosive gases. Corrosion is caused by the dissolution of the corrosive gases, such as carbon dioxide and hydrogen sulfide as well as condensation of acid vapors [42].

Water transmission and distribution systems: is used corrosion inhibitor in combination with pH adjusters and alkalinity control towards an efficient protection [32] The most common inhibitors are phosphates, amines volatiles (cyclohexylamine, morphine) [4]

Concrete: To improve the durability of reinforced concrete structures, which are impaired due the high alkalinity, are used corrosion inhibitors, mixed with cement or concrete paste. An example is phosphate ion. [33]

Boiler: Thermoelectric use, in general, Ammonia, Cyclohexylamine, alkanol and Morpholine as inhibitors in boilers in various processes. The inhibitors, also, are added by the hydrochloric acid used for the solubilization of limescale to prevent the attack on pipes.

## 7. Conclusion

Inhibitors are a great method of preventing corrosion and are easy to apply. Has application in a wide range of sectors

The knowledge of the method of the action, facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.

It is important in the choice of inhibitor, ascertain the subsequent effects of this towards the environment.

The search for environmental friendly inhibitors has shown excellent results, outperforming conventional inhibitors.

Reference organic inhibitors newly developed

alloy	environmental	pH	inhibitor	concentration	efficiency	reference
		7	$K_2Cr_2O_7$	$10^{-4}$ M	97.31	
AA2024-T3	0,1 M NaCl	7	Cerium dibutylphosphate (Ce(dbp) <sub>3</sub> )	$10^{-4}$ M	94.10	[23]
		7	Cerium chloride (CeCl <sub>3</sub> )	$10^{-4}$ M	73.90	
AA5754	3% NaCl	6.3	Laurus nobilis L. oil	50ppm	84.3	[43]
Al	3% NaCl	6.3	Laurus nobilis L. oil	50ppm	89.9	[43]
AA5083	3.5% NaCl	5.5	CeCl <sub>3</sub>	500ppm	297	[44]
			LaCl <sub>3</sub>	500ppm	113	[44]
Steel	1M HCl	-	N. cadamba Bark extract	5mgL <sup>-1</sup>	91.0	[45]
Steel	1 M HCl	-	VSBH (C <sub>31</sub> H <sub>47</sub> O <sub>4</sub> N <sub>2</sub> Br)	400 ppm	95.0	[46]
Steel	88% phosphoric acid	-	Dried Zenthoxylum-alatum plant fruits	2400ppm	98.0	[47]
Steel	0.5 M H <sub>2</sub> SO <sub>4</sub>	-	Polyacrylamide grafted Okra mucilage(O-g-PAM)	100ppm	94.4	[48]
Copper	0.5M HCl	-	Chitosan	$8 \times 10^{-6}$	92.0	[29]
Cu-10Al-5Ni alloy	3.5% NaCl	-	Cysteine	6mM/L	96.0	[49]
			N-acetylcysteine	6mM/L	87.6	[49]

alloy	environmental	pH	inhibitor	concentration	efficiency	reference
			Methionine	6mM/L	76.7	[49]
Cu	0.6M NaCl	-	Cysteine	16mM	76.5	[50]
Cu	1M HCl	-	Cysteine	18mM	84.13	[50]
AZ91D	0.05 wt.% NaCl	9	Paeonol	50ppm by wt	90	[51]
AZ91D	ASTM D1384-87	8.2	8-hydroxyquinoline	Saturated with 8HQ	82	[52]
AZ91D alloy	0.05 wt.% NaCl	6.8	5,10,15,20-tetraphenylporphyrin (TPP)	5ppm	84	[53]

**Table 1.** Inhibitors organics for aluminum, steel, copper, magnesium and its alloys at room temperature.

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