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# A REVIEW OF GREEN CORROSION INHIBITOR FOR MILD STEEL IN SEAWATER

A. Ismail

Department of Materials and Design Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn
Malaysia, Johor, Malaysia
E-Mail: azzura@uthm.edu.my

## ABSTRACT

Carbon steel is a combination of the carbon (C) and iron (Fe) for which the maximum content of alloy elements. The various uses of carbon steel especially mild steel are depends on the amount of carbon added to the alloy. Mild steel steel are widely used in marine applications, nuclear, fossil fuel power plants, transport, chemical processing, construction, mining and metal processing equipment due to its cost and availability. However, corrosions are likely to attack carbon steel not only in aggressive environment, but also in normal environment. Several choices can be implement to reduce or control the corrosion attack on carbon steel, but inhibitors often play an important role in the oil extraction and processing industries where they have been considered to be the first line of defence against corrosion. However when the environment is of prime concern, as well as oil and gas operations legislation, anything is discharged overboard into the water in offshore operations it should meet the relevant regulatory requirements. Most of the effective inhibitors have an issue concerning biocompatibility, biodegradability, bioaccumulation and toxicity composition that is harmful to the sea habitat. Most issues arise when discharging the waste direct to the sea through bioaccumulation, which can be described as a chemical's tendency to be taken up and stored by living organisms through their environment and diet.Inhibitor can be devided into four types namely; anodic inhibitors, cathodic inhibitors, mixed inhibitors and volatile corrosion inhibitors. The evaluation of inhitors type can be characterised by electrochemical or immersion test by adding identified amount of inhibitor into solutions which are normally seawater. This paper reveals some industrial green inhibitor that has been used as corrosion protection on carbon steel.

**Keywords:** Organic, linear polarisation resistance, corrosion rate, seawater, legislation.

## INTRODUCTION

Mild steel, also know as plain-carbon steel is the most common form of steel due to its relatively low price while provides excellent properties to be accepted in many applications. The most crucial problem for mild steel is when corrosion is likely to attack. While corrosion control is the main key for most industries, in oil production, water and acidic gases ($H_2S$ and $CO_2$), are co-produced with the oil. These gases are known to be associated with the surface corrosion demage that leads to costly failures. One of the established methods of protection against corrosion damage in oil production is the use of corrosion inhibitors. A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment (Roberge, 2000). Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defence against corrosion. Types of corrosion inhibitors includes anodic inhibitors, cathodic inhibitors, mixed inhibitors and volatile corrosion inhibitors. Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic 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. The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging. Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal forming a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required. Volatile Corrosion Inhibitors 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 the 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 dicyclo-hexylamine, cyclohexylamine and hexamethyleneamine are used. When these inhibitors come in 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. Therefore, the use of corrosion inhibitor could control the corrosion attack on carbon steel, however the major change will influence the formulations and will be demanding on environmental legislation and the desire for the offshore industry to show its commitment to preserving the sea and marine ecosystems.

Frequently research by worldwide has proved that the use of inhibitors is one of the best options of protecting metals and alloys against corrosion. With the increased awareness in environmental issues, the concern and pressure not only towards the effectiveness of these new inhibitors, but also their effect towards environment due to its past record of spillage and discharges these have caused the environment. Therefore, this has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are the among the best choice as they are inexpensive, readily available and renewable. This brings the interest of investigations for corrosion inhibiting abilities of tannins, alkaloids, organic,amino acids, and organic dyes of plant origin.

**Corrosion inhibitors**

A corrosion inhibitor is a substance, solid or liquid, which when added in only moderate quantities to a corrosive fluid should significantly reduce the corrosivity of that fluid towards a particular metal (Roberge, 2000). Corrosion inhibitor reduces the corrosion attack in two ways. In some situations, the added inhibitors can alter the corrosive environment into a noncorrosive or less corrosive environment through its interaction with the corrosive species. In other cases, the corrosion inhibitor interacts with the metal surface and therefore inhibits the corrosion of the metal. The inhibitors interact with the metal surface and form a passive film or an adsorbed layer acting as a barrier film. Therefore, base on the mode of interaction, inhibitor can be divided into two broad classes which are environment modifiers and adsorption. Environment modifiers act by simple interaction with the aggressive species in the environment and reduce the attack of the metal by the aggressive species. Adsorption type act by adsorb on the metal surface and inhibit the corrosion (Figure-1). Regardless of their type, most of the inhibitors currently used are either organic or inorganic

chemicals for the retardation of the corrosion progress under different environments. Inorganic compounds must be able to oxidize the metal and form a passive layer on its surface. Its molecules may have a large structure, double bonds, an active centre or group, thus, giving the molecule an ability to cover a large area of metal surface with a firmly attached film.
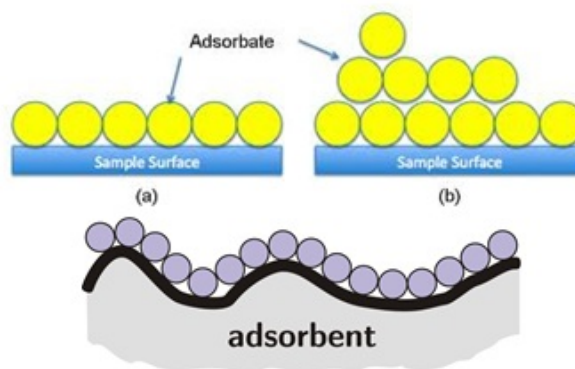


**Figure-1.** Adsorption type inhibitor (Roberge, 2000).

Inhibitor can be designed to act as anodic or cathodic inhibitors depending upon reaction. They are also mixed inhibitors that inhibit both anodic and the cathodic reactions and this type are generally represent by organic compounds. Cathodic inhibitors inhibit the hydrogen evolution in acidic solutions or the reduction of oxygen in neutral or alkaline solutions. Substances with high overpotential for hydrogen in acidic solutions and those that form insoluble products in alkaline solutions are generally effective cathodic inhibitors. Anodic inhibitors are generally effective in pH range of 6.5 – 10.5 (near neutral to basic). Nevertheless, the concentration of inhibitor is the main factor which affects the effectiveness of inhibitor.

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media. In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors (Wanees *et al.* 2003, Khaled 2010). In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by; (i) adsorption of ions/molecules onto metal surface, (ii)increasing or decreasing the anodic and/or cathodic reaction, (iii)decreasing the diffusion rate for reactants to the surface of the metal, (iv)decreasing the electrical resistance of the metal surface and (v)inhibitors that are often easy to apply and have in situ application advantage (Behpour, 2010).

Several factors including cost and amount, easy availability and most important safety to environment and

8711

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its species need to be considered when choosing an inhibitor.

## Green corrosion inhibitors

In the past two decades, the research in the field of "green" corrosion inhibitors has been directed toward the goal of using cheap, effective molecules of low or zero negative environmental impact. Therefore, the use of non-toxic inhibitors has also become one of the major selection requirements. Omanovic and Ghareba (2010) introduce 12-aminododecanoic acid (AA) as a green corrosion inhibitor to carbon steel in $CO_2$-saturated acidic medium also known as sweet corrosion. They identified AA as non-toxic, biocompatible and easily biodegradable molecule and be considered as green corrosion inhibitor. It also can be considered as high efficiency as it inhibits carbon steel from corrosion attack within one hour of application by spontaneous adsorption.

Sethuraman and Kamal (2010) found Spirulina platensis as green inhibitor for mild steel in HCl and $H_2SO_4$ media. They found that inhibition efficiency increased with increasing the inhibitor concentrations. Spirulina platensis inhibits the corrosion of mild steel through adsorption following Temkin isotherm, ΔG. Temkin isotherm, ΔG was calculated by using;

$$\Delta G = -RT \ln (55.5 \ K) \tag{1}$$

relationship where R is universal gas constant (kJ/mol), 5535 is a concentration of water (mol/L) and T is the temperature and K is equilibrium constant value.

The most acid corrosion inhibitors are nitrogen-sulfur and oxygen-containing organic compounds (Lalita, 2005). Saracoglu et at.(2011) used Benzamide (BA) and 4-aminoben-zenesulfonamide (ABSA) to replace Amides Benzotriazole (BTA) which is known toxic and not biodegradable. Figure-2 below shows the structure of BA and ABSA. They found that ABSA more effective than BA and the adsorption of inhibitor are followed Langmuir isotherm model.
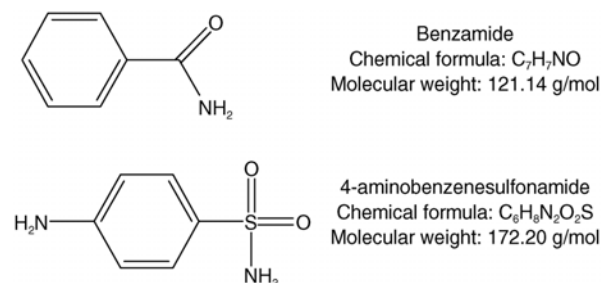


Benzamide
Chemical formula: $C_7H_7NO$
Molecular weight: 121.14 g/mol

4-aminobenzenesulfonamide
Chemical formula: $C_6H_8N_2O_2S$
Molecular weight: 172.20 g/mol

**Figure-2.** Structure of inhibitor molecules (Saracoglu *et al.* (2011).

To claim the inhibitor are "green" for subsea applications, the inhibitor should meet the Norwegian and UK regulatory requirements, such that they can be classed as environmentally acceptable. Regarding the discharge of water overboard in offshore operations, the Norwegian

legislation bodies have drawn up a set of guidelines out of concern for the environment. These guidelines differ from those of the UK sector that require chemicals for field applications to have specific properties in terms of biodegradation, toxicity and bioaccumulation, and, which initially resulted in many of the 'classic' water discharges being discounted. They classified the hazardous into four categories black, red, yellow and green, as shown in Figure-3.



**Figure-3.** Norwegian legislation (Myles *et al.* 2007).

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Delonix regia extracts inhibited the corrosion of aluminum in hydrochloric acid solutions (Ding Rong *et al.*2007), rosemary leaves were studied as corrosion inhibitor for the Al + 2.5Mg alloy in a 3% NaCl solution at 25°C

It is found that ethanol extract of M. sapientum peels (banana) can be used as an inhibitor for mild steel corrosion. The inhibitor acts by being adsorbed on mild steel surface according to classical adsorption models of Langmuir and Frumkin adsorption isotherms. Adsorption characteristics of the inhibitor follow physical adsorption mechanism. It is found that temperature, pH, period of immersion, electrode potential, and concentration of the inhibitor basically control the inhibitive action of M. sapientum peels.

The use of dyes such as azo compounds methyl yellow, methyl red, and methyl orange (Abiola, 2009) as inhibitors for mild steel has been reported (Tirbonod, 1978, Gupta, 1984). The inhibition action of carmine and fast green dyes on corrosion of mild steel in 0.5 M HCl was investigated using mass loss, polarization, and electrochemical impedance (EIS) methods. Fast green showed inhibition efficiency of 98% and carmine 92%. The inhibitors act as mixed type with predominant cathodic effect. Corrosion inhibition of mild steel in acidic solution by the dye molecules can be explained on

the basis of adsorption on the metal surface, due to the donor-acceptor interaction between π electrons of donor atoms N, O and aromatic rings of inhibitors, and the vacant d-orbitals of iron surface atoms (Zheludkevich , 2005). The fast green molecules possess electroactive nitrogen, oxygen atoms, and aromatic rings, favouring the adsorption while the carmine molecules possess electroactive oxygen atoms and electron rich paraquinanoid aromatic rings. In addition, the large and flat structure of the molecules occupies a large area of the substrate and thereby forming a protective coating. The inhibitors were adsorbed on the mild steel surface according to the Temkin adsorption isotherm (Figure-4). Torres *et al.* (2011) studied the effects of aqueous extracts of spent coffee grounds on the corrosion of carbon steel in a 1 mol L−1 HCl. Two methods of extraction were studied: decoction and infusion. The inhibition efficiency of C-steel in 1 mol L−1 HCl increased as the extract concentration and temperature increased. The coffee extracts acted as a mixed type inhibitor with predominant cathodic effectiveness.
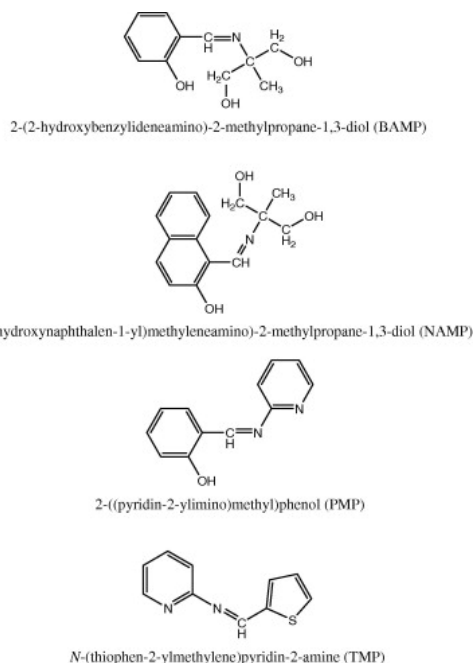


2-(2-hydroxybenzylideneamino)-2-methylpropane-1,3-diol (BAMP)



2-((2-hydroxynaphthalen-1-yl)methyleneamino)-2-methylpropane-1,3-diol (NAMP)



2-((pyridin-2-ylimino)methyl)phenol (PMP)



N-(thiophen-2-ylmethylene)pyridin-2-amine (TMP)

**Figure-4.** The chemical structure of Temkin adsorption isotherm.

**CONCLUSIONS**

        Despite large numbers of organic compounds, the choice of an appropriate inhibitor for a particular system is unfortunately limited due to the variety of corrosion systems and specificity of the inhibitor compounds. The performance of an organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The inhibition could be due to (i) Adsorption of the molecules or its ions on anodic

and/or cathodic sites, (ii) increase in cathodic and/or anodic over voltage, and (iii) the formation of a protective barrier film. Apart of that, some factors that contribute to the action of inhibitors are (i) chain length, (ii) size of the molecule, (iii) bonding, aromatic/conjugate, (iv) strength of bonding to the substrate, (v) cross-linking ability, (vi) solubility in the environment.

**ACKNOWLEDGEMENTS**

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