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# Use of Corrosion Inhibitor in Solid Form to Prevent Internal Corrosion of Pipelines and Acidification Process

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## Abstract

**Use of corrosion inhibitors in solid form promotes the development of a new technique for internal corrosion protection of oil & gas pipelines and operations of oil wells acidification, because the controlled dissolution of the corrosion inhibitor forms a surface on metallic parts, a protective film that prevents or minimizes undesirable reactions to corrosion. In addition, this technique has important social and environmental benefits, ensures the operator has a lower risk of contamination when handling the product, changes the type of industrial packing, facilitates transportation, reduces solvent use and consequently reduces the waste that normally results from the use of inhibitors. The purpose of this article is to present a class of solid corrosion inhibitor tested in the laboratory and offer proposals for its application in industrial pipes such as gas and oil pipelines.**

## Keywords

**Corrosion, Corrosion Inhibitor, Petroleum, Acidification, Pipeline**

## 1. Introduction

The study of the modification of polymers obtained by condensation or addition is of growing interest in several industrial segments because of the function of the reactive groups present in the polymers' structure. In general, this type of modification targets the synthesis of polymers with physico-chemical properties for industrial application as in the formulation of corrosion inhibitors. Obtaining the polymer: poly (2-vinyl-2-oxazoline), PEOX, in solid form is such an application. The solid characteristics of this substance make possible its use in acidification (stimulation) in oil wells and could result in benefits in terms of controlled dissolution and ease of packag-

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ing and transport packaging.

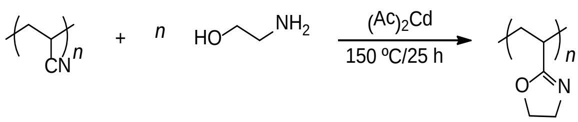
Corrosion inhibitors aim at the protection of metals and alloys, preventing or retarding corrosion reactions through formation of a monomolecular film-adsorbed surface exposed to corrosive medium [1] [2].

The modified polymers in the form of solids can be used as corrosion inhibitors, but they must possess, inter alia, the following features: anti-corrosion protection capability, proper consistency to use controlled dissolution rate and chemical compatibility with the material, corrosive medium and other additives used in petroleum industry operations.

This work aims at presenting a corrosion inhibitor in solid form for use in the hydrochloric acid solutions commonly used in oil well stimulation and proposing solid inhibitor application techniques for use in segments of the petroleum industry such as oil and gas pipelines.

## 2. Characteristics of Corrosion Inhibitor Based on the Poly (2-Vinil-2-Oxazoline)

The polymer poly (2-vinyl-2-oxazoline) was obtained by the reaction of polyacrylonitrile with 2-amino-ethanol, in the presence of catalyst cadmium acetate, $[(Ac)_2Cd]$, under reflux to 150˚C for 25 hours, as shown in the following reaction. After reflux, the reaction mixture was distilled to eliminate excess amino-ethanol, filtered, purified and dried under vacuum [3] [4].




This polymer has oxazolinic rings hanging on the main chain in place of nitrile groups and, consequently, the polymer thus formed will have the characteristics of a paraffin-like appearance associated with the properties of oxazoline-2-substituted. This substance was dark brown, solid, and elastic and its molecular weight was valued at 1000.

When a steel plate is immersed in a solution of hydrochloric acid the preferential reactions (anodic and cathodic) that occur on the metallic surface are:

$Fe - 2e^{-} \rightarrow Fe^{2+}$ (anodic reaction).

$2\,H^{+} \rightarrow H_2 - 2e^{-}$ (cathodic reaction).

The $Fe^{2+}$ ion formed by the attack of the acid on the carbon steel leaves the metal (Fe) for the solution, and consequently there is a migration of $H^{+}$ ions from the concentrated acid to the metal surface to form atomic hydrogen (H) and, soon afterwards, molecular hydrogen ($H_2$). The addition of an organic inhibitor-type system non-oxidizing acid reaction can lead to partial or even total with the $H^{+}$ ions dissociated in acidic solution, having spontaneously captured the positive charges by the inhibitor molecule, a process called protonation [2] [5] [6].

Consequently there is intense competition between $H^{+}$ ions and protonated inhibitor molecules moving into areas where they can accumulate cathode electrons. Although the ionic mobility of the $H^{+}$ ions is much greater (because of the smaller size of the ion) than that of the protonated molecular inhibitor, there is an adsorption of the stable inhibitor on the metallic surface, which forms a barrier that prevents migration of $H^{+}$ ions to capture the electrons, thus preventing the formation of atomic hydrogen (H) and detachment of molecular hydrogen ($H_2$).

The adsorptive inhibitors or films are generally organic substances of high molecular weight that form a monomolecular film on the metal surface, preventing the development of electrochemical reactions.

Considering the protonation in acid medium the most likely mechanism is the adsorption of the oxazolinic rings on the metallic surface which forms a protective film and reduces or prevents the cathodic reactions.

### Corrosion Laboratory Test and Results

In this paper, the corrosion coupons to represent the pipeline were made from an AISI 1020 steel sheet measuring 45 × 15 × 1.2 mm. They were prepared with three different sandpapers: 150, 320 and 400, in that order. Then they were degreased with acetone, washed with deionized water and anhydrous alcohol and were finally dried with hot air and stored in desiccators for use in the tests. They were then weighed to the nearest 0.0001 g.

In laboratory experiments hydrochloric acid solution 10% (% mass) was used as a corrosive medium. The basic substances used as corrosion inhibitors were poly (2-vinyl-2-oxazoline) concentrations of 1000 mg/L, 2000 mg/L, 3000 mg/L and 4000 mg/L.

Gravimetric assays (weight loss) were performed in a glass vessel resistant to temperature variation with a capacity of 300 mL. The corrosion coupons were completely immersed in 150 mL of acid solution, leaving the remaining capacity of the vessel for the evolution of hydrogen ($H_2$) resulting from acid attack.

The glass vessel was kept at the correct temperature via a thermostatically controlled bath. The temperature was set at 60˚C. The time for testing was 1 hour after exposure. Immediately after completion of the test, the corrosion coupons were removed from the corrosive medium, rinsed in water and alcohol and quickly dried in hot air, before being weighed with the same accuracy. The weight loss was determined according to ASTM G 31 - 72 [7].

The corrosion rate (CR) and the efficiency of corrosion inhibitors (E %) are defined by the following expression:

Corrosion rate = CR = $(W_o - W_i)/S.t$ ($mg/cm^2 \cdot h$).

Efficiency = E % = $100 (W_o - W_i)/W_o$.

where:

$W_o$ and $W_i$ are the weight loss in the absence and presence of the inhibitor;

S = area ($cm^2$);

t = exposure time, h.

The results of the laboratory tests carried out on four carbon steel coupons immersed in hydrochloric acid solution 10% (% mass) and corrosion inhibitor poly (2-vinyl-2-oxazoline) in concentrations of 1000 mg/L, 2000 mg/L, 3000 mg/L and 4000 mg/L are presented in **Table 1** and the graph of **Figure 1**.

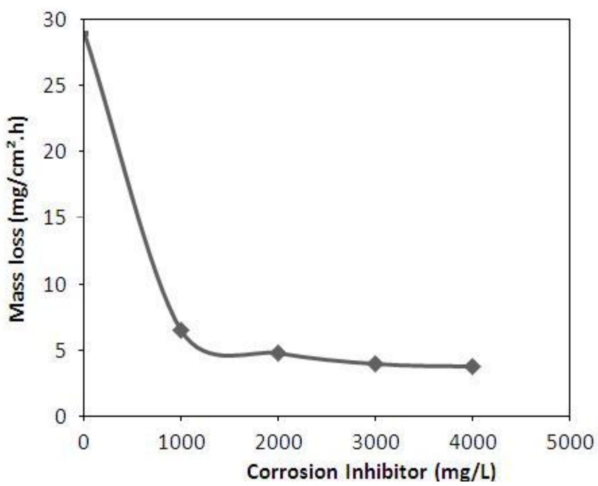



**Figure 1.** Corrosion of carbon steel in hydrochloric acid (10% mass) after additions of corrosion inhibitor at a temperature of 60˚C and immersion for one hour.

**Table 1.** Corrosion rate of carbon steel in hydrochloric acid (10% mass) after additions of corrosion inhibitor at a temperature of 60˚C and immersion for 1 hour.

| Concentrations: poly (2-vinyl-2-oxazoline, mg/L | Loss of mass ($mg/cm^2 \cdot h$) | Efficiency (%) |
|---|---|---|
| 0 | 29.10 | ------- |
| 1000 | 6.57 | 77.40 |
| 2000 | 4.80 | 83.50 |
| 3000 | 3.98 | 86.30 |
| 4000 | 3.80 | 87.90 |

## 3. Application of Corrosion Inhibitors in Oil Pipelines, Gas Pipelines and Acidification Systems

The use of corrosion inhibitors in internal protection of pipes is a technique widely used in the production and transportation of oil and its derivatives. Applications are usually in liquid or emulsion form, and are organic and inorganic substances, or both.

The solvent has is physicochemistry characteristics of each inhibitor formulation. Solvents used for organic substances are toluene, glycols, alcohols (from methanol to hexanol) and kerosene. In the case of inorganic substances water is generally the solvent although alcohols are also used.

These formulations may also be associated with the demulsifying agent, antifoaming, dispersant, etc. The literature over the years has shown that most substances used are potentially toxic and the use of aromatics such as benzene has carcinogenic potential. Therefore less toxic substitutes are desirable [1].

In the case of pipelines, gas pipelines and acidification systems the injection of corrosion inhibitors for internal protection is in liquid form with solvents such as the BTX family (benzene, toluene and xylene). The idea of using a solid corrosion inhibitor is to reduce or minimize the risk of contamination to humans (during packaging or operation) and the environment, as it requires no solvent.

Dissolution tests performed with the solid substance poly (2-vinyl-2-oxazoline) presented on the graph in **Figure 1** show an order of efficiency of 87%.

Consequently the following proposals for the application of a corrosion inhibitor in solid form are made:

- Small spheres, pellets or soluble capsules injected into the pipe with special equipment;
- Compressed cylindrical rod, consumable and adapted equipment.

### 3.1. Small Spheres, Pellets or Soluble Capsules Injected with Special Equipment

Corrosion inhibitors can be manufactured in spherical or oval form or packaged in soluble capsules and injected by a gun into a gas pipeline, oil pipeline or acidification system. The mechanism drawn in **Figure 2** shows that the small spheres dissolve in the flux to form a film adsorbed on the metallic surface parts for the necessary corrosion resistance.

Another way to use the inhibitor is to pack its solid particles in soluble capsules, as shown in **Figure 3**, in such a way that it will form a protective film on the metallic surface.

The injection system consists essentially of a pressurized tank attached to a valve and welded to a pipe flange, as shown in **Figure 4**. The pressurized reservoir containing the spheres or capsules of the inhibitor is controlled and programmed to release mode, so gradually the spheres or capsules adhere to the inside of the pipe.

### 3.2. Pressed Cylindrical Rod, Consumable and Adapted Equipment

This is a simple system, consisting essentially of a cylindrical rod which is introduced inside the pipe through a flange welded on the outside, as shown in **Figure 5**. The cylindrical rod dissolves and releases particles as a function of flow of the corrosive medium. The cylindrical rod is compressed continuously and controlled for the interior of the pipe as if wearing.

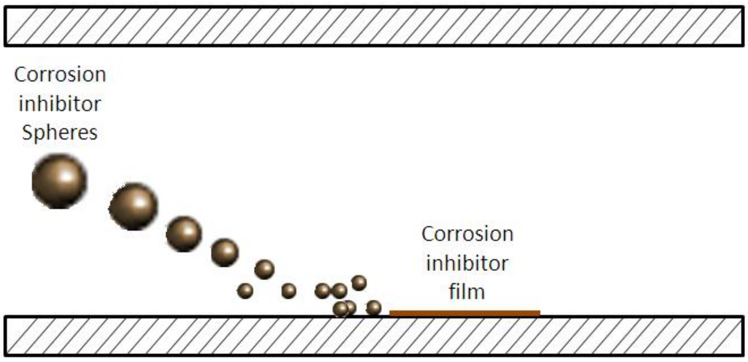



**Figure 2.** Mechanism of corrosion inhibitor.

Figure 3. Soluble capsules with solid corrosion inhibitor.

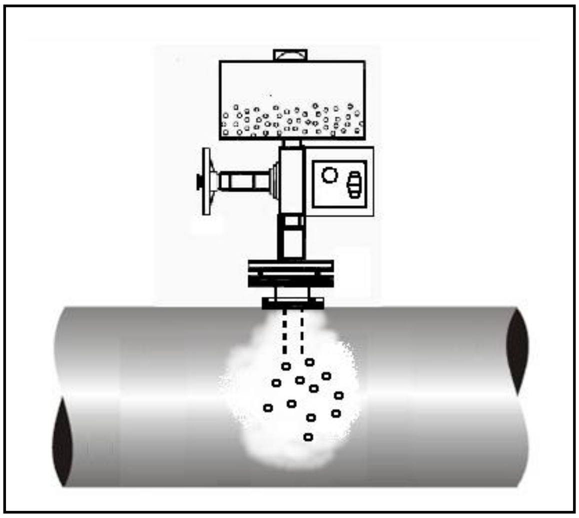


Figure 4. Injection system welded in pipe.

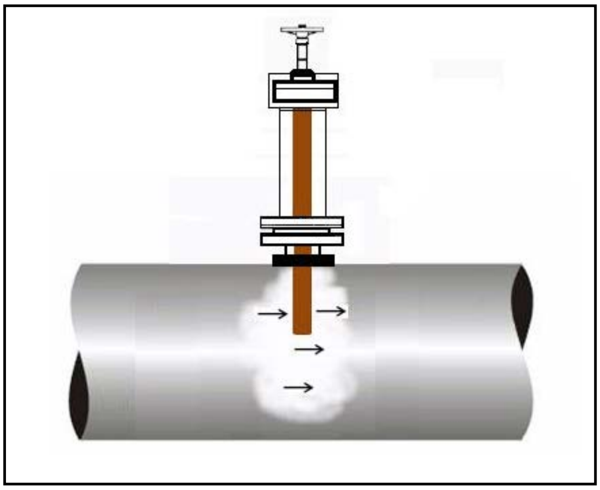


Figure 5. Corrosion inhibitor in the form of a cylindrical rod inside the pipe.

## 4. Conclusions

- Laboratory testing with hydrochloric acid solution showed that the inhibitor constituted of poly (2-vinyl-2-oxazoline) presented 87% efficiency in corrosion protection of carbon steel coupons. It is an excellent example of a corrosion inhibitor in solid form.
- The use of a corrosion inhibitor in solid form opens the door to new uses as there is no need for toxic organic solvents. This technology increases the operational safety of the worker handling the product and reduces environmental contamination.
- The use of a corrosion inhibitor in solid form as small spheres, packaged as a soluble capsule in the form of a compressed cylindrical rod, provides a new anti-corrosion technique that is easy to operate, particularly in gas and other pipelines and acidification systems.

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