Corrosion
Part 5 – Corrosion Inhibitors

Keywords

Corrosion; Inhibitors

Summary

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. 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

Anodic 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

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.

The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

Mixed Inhibitors

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 hexamethylene-amine 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.

Evaluation of Corrosion inhibitors

Electrochemical methods are used routinely for the evaluation of the efficiency of corrosion inhibitors. The advantages of electrochemical methods are short measurement time and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new inhibitors.

Electrochemical Characterisation of anodic inhibitor

Benzoic acid was chosen as an example anodic inhibitor to illustrate the use of electrochemical methods for the characterization of inhibitors. A polished 3 mm diameter CK 45 steel rod embedded in epoxy was used as the working electrode. The Autolab RDE (rotating disc electrode) system was used to maintain a constant rpm of 800 for the experiments. The experiments were conducted in the AUTOLAB Corrosion Cell.

The efficiency of the inhibitor was studied by adding 0.5 M benzoic acid to 0.1 M Na_2SO_4 solution. The electrolyte was deaerated for 30 minutes by N_2 purging prior to the start of the experiment. Reference measurements were done on 0.1 M Na2SO4 solution without inhibitor. The pH of the solution was adjusted to 6.5 with NaOH and H_2SO_4 prior to the start of the experiment. A platinum sheet electrode (6.0305.100) was used as the counter electrode and Ag/AgCl (6.0733.100) was used as the reference electrode.

The linear sweep voltammetry (LSV) experiments were conducted using an AUTOLAB PGSTAT302N controlled by the NOVA software. The potentials were scanned from -1.2 V to 0.6 V (vs. Ag/AgCl). Beginning the experiments at cathodic potentials ensured that any oxide layer present prior to the start of the experiments was reduced. A 2.5 mV potential step and a slow scan rate of 2 mV/s were used.

Figure 1 shows the polarization curves for solutions with and without inhibitor are shown. The anodic part of the polarization curve without inhibitor is typical for active metal dissolution.
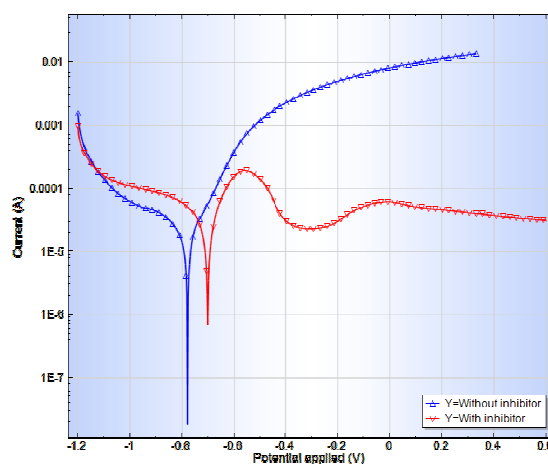

Figure 1 – Linear polarization measurement in the absence and presence of a corrosion inhibitor

The results shown in the figure illustrate when an anodic inhibitor is added to the solution there is a shift of the corrosion potential in the anodic direction and a reduction in the anodic current. The corrosion inhibitor also results in the formation of the passive film evidenced by the appearance of the passivation plateau.

References

- P. Agarwal, D. Landolt, Corrosion Science, 260 (1998), 673-691

Date

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