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Eco-friendly Inhibitors for Corrosion Protection of Stainless steel: An Overview

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Abstract.
Corrosion is a major concern in the industrial application of ferrous alloys, this is as a result of the enormous cost involved in damages, maintenance and corrosion control. Stainless steels have high corrosion resistance capacity because of the existence of chromium, which forms a passive film layer of chromium-rich oxide in the presence of oxygen at lower temperatures; this forms a barrier against the surrounding. However, this layer could be damaged in aggressive environments. This necessitates attention from researchers worldwide for novel, cost effective, and environmental friendly corrosion prevention techniques. Inhibitors are extensively applied in the industry to minimize the corrosion degradation of metallic alloys; however, most inhibitors are hazardous and expensive. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. This review briefly discusses some of the eco-friendly substances which are used as corrosion inhibitors for stainless steel in aggressive media.
Keywords: Corrosion inhibitors; Toxicity; Eco-friendly inhibitors; Corrosion inhibition

1. Introduction

Almost all metals and alloys are unstable in the Earth's atmosphere and therefore will always be susceptible to corrosion. Corrosion deterioration of metallic alloys by chemical interaction with their environments is one of the major sources of industry overhead costs due to maintenance and repair of damaged and worn out equipment and parts. In general, a good portion of the loss can be avoided by proper corrosion control and monitoring. One of the best methods to reduce the rate of metallic corrosion is by the addition of inhibitors in which even small concentrations can result in decrease of the corrosion rate of metallic surface [1- 6]. However, there are conditions aiding the selection of a suitable inhibitor substance. These include, the cost and amount of the inhibitor required, long term toxicological effects on the environment, the inhibitors ability to treat the corroded surfaces, the inhibitor's availability and stability in the environments.

Stainless steels are often used in applications for which aluminium and carbon steels provide undesirable results, due to its above average resistance to strong acids, alkalis and cracking resulting from chloride stress corrosion. Stainless steels form surface films, which protects the underlying metal from attack in many environments. This film is very thin, transparent and self-healing; if damaged mechanically or chemically, the protective film will be reformed very rapidly, however, in a situation where the rate of damage is more than the rate of repair, a progressive active corrosion occurs. In spite of advancement in the science and technology of corrosion prevention and control, the phenomenon of corrosion continues to pose a major concern to many industries around the world. It is estimated that with proper corrosion prevention technologies, this loss could be avoided. The adsorption mechanism of organic inhibitors at metal/solution interface may consist of one or more steps for completion. In the first step, adsorption of an organic inhibitor on a metal surface usually involves replacement of one or more water molecules initially adsorbed at the metal surface:

$$Inh_{(sol)} + xH_2O_{(ads)} Inh_{(ads)} + H_2O_{(soln)} \quad (1)$$

Where:

$Inh_{(sol)}$ and $Inh_{(ads)}$ represents the inhibitors in the solution which are adsorbed on the metal surface, x is the number of water molecules displaced by the inhibitor. Subsequently, the inhibitor may then combine with newly generated metal ions M^{+2} on the metal surface as a result of metal oxidation or dissolution process, and by this form metal-inhibitor complex:

$$M \rightarrow M^{+2} + 2^{e-} \quad (2)$$
$$M^{+2} + Inh_{(ads)} \rightarrow [M - Inh]_{(ads)^{+2}} \quad (3)$$

Depending on the relative solubility of the resulting complex, it may further inhibit or catalyse further metal dissolution. It is generally accepted that in the absence of the corrosion inhibitor, the aggressive solution is always in contact with the metal and porous film surface causing corrosion as a result of metal dissolution. Whereas, in the presence of inhibited solution, the active or open sites in the porous film are almost blocked by the adsorption of the inhibitor resulting in a barrier layer which suppresses further corrosion reactions.

Currently, the use of toxic material as corrosion inhibitors has been limited by different agencies [7]. However, different synthetic compounds have been proved as excellent corrosion inhibitors, but most of them are highly toxic in nature having serious threats to both human and environment. In addition, they are often expensive and non-biodegradable in nature [8]. Based on these, the environmental and safety issues of using toxic corrosion inhibitors in industry have become a global concern. Therefore, the use of natural products as corrosion inhibitors has become important because of their advantages such as: low cost, ready availability and environmental friendliness. Organic compounds have been successfully used in the inhibition of general corrosion of materials.The application of inorganic inhibitors for stainless steel corrosion has not received much attention from corrosion researchers, while different organic and inorganic compounds have been successfully reported as excellent inhibitors of general corrosion of other engineering materials. Several compounds including nitrogen have been studied intensively as corrosion inhibitors by many researchers, for example: quaternary ammonium salts[9, 10], imidazole derivatives and benzimidazole[11], cationic surfactant [12], bipyrazole [13, 14], aniline-N-salicylidenes [15], fluconazole [16], phosphorous [17], amino acid, titanium (iv) oxide, gluconates, castor oil, silicon oil. Encouraging results have been attained in this regard.

2. Corrosion prevention of stainless steel

Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration use acidic solutions extensively and as such steel vessels used in these environments are prone to corrosion [18]. Different means of protecting stainless steel against corrosion have been studied and long service life has been guaranteed by corrosion prevention. These methods include: coating, cathodic protection, corrosion inhibitors and use of additive minerals to provide better corrosion control and minimize permeability. The use of corrosion inhibitors among other methods is one of the most effective and suitable method for preventing corrosion of metals and equipment during storage and transportation [8]. The use of many inorganic inhibitors, particularly those containing phosphate, chromate, and other heavy metals, is now being gradually restricted by various environmental regulations because of their toxicity. Synthetic organic inhibitors have also been extensively applied but their use is now being marred by their toxicity and high cost of manufacturing. This has prompted researchers to explore other areas to produce eco-friendly, cheap, and biodegradable green corrosion inhibitors to replace inorganic and synthetic organic inhibitors. Natural products such as plant extract, amino acids, proteins, and biopolymers have been reported as effective inhibitors. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [19]. These natural extracts are analogous to the synthetic organic inhibitors and are being proven to work as much as their synthetic counterparts. This literature review gives an overview of recent work on the inhibitive effect of various inhibitors reported for stainless steel in different media.

The authors [20] investigated 304 stainless steel corrosion inhibition in 2M HCl medium with N-Furfuryl N'- Phenyl Thiourea at varied temperatures. The inhibitor performed excellently for stainless steel 304 in acid solution at different concentrations and temperatures studied. The observed inhibition efficiency was because of protective film formation mechanisms which blocks the effect of the metal surface, eventually reducing the effective area of corrosion attack. The corrosion of austenitic stainless steel in aqueous solution with the addition of amino trimethylidene phosphoric acid was studied by [21] with the aid of polarization resistance, electrode potential monitoring and weight loss methods. Corrosion rate values were observed to decrease progressively with increase in concentration of the inhibitor. The authors found amino trimethylidene phosphoric acid to have a protective effect on austenitic stainless steel surface by forming a protective film layer on the surface of the metal. MPT (1-methly-3-pyridine-2-Y1-thiourea) on austenitic stainless-steel Type 302 in acid environment was carried out by [22]. Results from the research showed that MPT is an effective inhibitor for stainless steel Type 302. Temperature effect of MPT inhibition was also analyzed in their research. Increase in temperature was found to lead to increase in corrosion current densities whereas corrosion potential decreases. Benzyl Triethyl ammonium chloride (BTEAC) was found by [23] to act as an efficient inhibitor for stainless steel Type 430 corrosion due to the positive charge of π electrons and N ions in its molecule adsorbing on the surface of the metal. [24] found the inhibitor less effective with an increase in temperature. The inhibition tendency of 2-Dimethylamino ethanol (DMA) on type 304 austenitic stainless-steel corrosion in dilute hydrochloric acid solution was studied by [25] using potentiodynamic polarization, weight loss and open circuit potential measurement. The authors ascribe the steel protection to the presence of inhibitor on the metal surface which leads to formation of a protective film layer preventing the corrosion process. [26] analyzed the inhibitive behavior of hepta molybdate (HM) ions on stainless steel ASI 304. HM ions were found to be an ionic inhibitor for the stainless steel in 0.5 molar hydrochloric acid solutions. Wei et al. (2003) studied the pitting corrosion of 304 stainless steel using *N*-lauroylsarcosine sodium salt (NLS) as inhibitor in 0.1 molar sodium chloride solutions at neutral pH via surface chemical and electrochemical techniques. NLS was found to increases the pitting resistance of stainless steel at optimum concentration of 30 mM. Adsorption of NLS on stainless steel shows bi-layer coverage and electro-phoretic, mobility data for the studied stainless steel particles show that the steel surface was negative due to the inhibitor adsorption in the sodium chloride solution at neutral pH. The inhibitor mechanism is proposed to be as a result of the blocking effect of the negatively charged NLS adsorption layer. The authors concluded that NLS inhibits pitting corrosion of stainless steel in NaCl solution and the inhibitor efficiency is a function of NLS concentration.

Loto (2017) evaluated the inhibitive efficiency of benzosulfonazole on corrosion inhibition of S40977 stainless steel in 3M H_2SO_4 solution using open circuit potential, potentiodynamic polarization, IR spectroscopy and optical microscopy. The obtained results showed the effectiveness of the inhibitor with identified functional groups of alcohols, phenols, amines, amides, carboxylic acids, aliphatic amines, esters and ethers which were adsorbed onto the stainless steel surface. Cationic adsorption was confirmed to be chemisorption mechanism following the Langmuir, Freundlich and Temkin adsorption isotherms. Severe corroded morphology with corrosion pits was confirmed in the absence of inhibitor which contrast the images obtained with the addition of inhibitor. The author concluded that the benzosulfonazole effectively inhibited the surface oxidation and corrosion of S40977 stainless steel in the studied medium through adsorption onto the stainless-steel surface. [27] studied the corrosion inhibition of stainless steel in 0.9% NaCl solution in the presence of poly vinyl alcohol (PVA) using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electronmicroscopy (SEM) and X-ray photoelectron spectroscopy (XPS) technique. Electrochemical measurements indicated that the presence of PVA in NaCl solution decreases the corrosion current and increases the polarization resistance. In the absence and presence of PVA, SEM images showed that the stainless steel surface was covered with a non-uniform layer and uniform adsorbed film, respectively. XPS analysis indicated that the surface layer of the steel consists of PVA with small amount of other elements, such as Na and Cl. Loto et al. (2015) considered the corrosion of austenitic stainless steel (type 304) in dilute sulphuric acid solutions in addition to recrystallized sodium chloride concentrates in the presence of phenyl amine using polarization resistance technique, electrode potential monitoring and coupon method. Results obtained show the positive influence of the inhibitor with an inhibition efficiency of 97.5% from coupon analysis and 86.10% from polarization test at optimum concentration of the inhibitor. Corrosion rate was found to decrease with increase in phenyl amine concentration. Thermodynamic variables of adsorption showed the interaction with the stainless steel to be physiochemical and spontaneous. Adsorption of amino benzene on the stainless steel obeyed Langmuir's adsorption isotherm. Lidija et al. (2013) worked on nano-structured TiO2 thin films deposited on AISI 304 austenitic stainless steel by sol–gel process and dip coating technique. The influence of number of layers, addition of polyethylene glycol (PEG), morphology and the surface roughness parameters of titania films on corrosion resistance of coated stainless steel were studied in simulated marine environment in 3 wt.% aqueous NaCl solution by electrochemical impedance spectroscopy (EIS) and in 0.5 M aqueous HCl solution by potentiodynamic polarization. After exposure to corrosive media, it was found that the surface of both films exhibits small pores, especially for the film prepared with PEG addition. Corrosion resistance of stainless steel was proved in simulated marine environment in 3 wt.% of NaCl solution. The best corrosion protection results were obtained by sol–gel TiO2 film. Loto (2017) worked on the synergistic effect of corrosion inhibition properties of 2-methoxy-4-formylphenol and sodium molybdenum oxide on the electrochemical property of 3CR12 ferritic stainless steel in 2M H_2SO_4 acid solution through coupon analysis, potentiodynamic polarization technique, IR spectroscopy and micro-analytical technique. Experimental data showed that the combined inhibitor effectively inhibited the stainless steel corrosion with inhibition efficiency of 94.47% and 89.71% from coupon analysis and potentiodynamic polarization. Results from corrosion thermodynamic calculations showed chemisorption adsorption mechanism for the inhibitor. Infrared spectroscopic images exposed the functional groups of the molecules involved for the corrosion inhibition reaction. Micro-analytical images showed sharp contrast in surface morphology between the inhibited and corroded test specimens in 2M H_2SO_4 solution. Cracks, intergranular and pitting corrosion was observed in the uninhibited samples. Inhibitor adsorption of the inhibitor follows the Langmuir isotherm model. Roumaissa et al. (2017) investigated the anti scale properties of aqueous extract of olive (Olea europaea L.) leaves as natural inhibitor for stainless steel in raw water using chronoamperometry (CA), electrochemical impedance spectroscopy techniques and microscopic examination. The results show that the inhibition efficiency increases with increase in the extract concentration which reduced as the temperature increased. Yafa (2015) investigates the effect of Tris-dimethylaminoselenophosphoramide (SeAP) as corrosion inhibitor for AISI 630 and AISI 316L stainless steel in 3 wt. % NaCl using potentiodynamic polarization, SEM and GDOES techniques. With the presence of SeAP at different concentrations in the studied solution, the inhibitor efficiency increases with SeAP concentration. The synthesized inhibitor acts as mixed-type in a merely neutral solution (pH=6.8). The SEM and GDOES analysis signify the presence of protective layer on the surface of AISI 630 and AISI 316L. The corrosion resistance and susceptibility of 12Cr martensitic stainless steel was successfully studied by [28] in acid solution using potassium dichromate as inhibitor. Stainless steel protection in the phosphate fertilizer production industry was studied by (Singh and Kumar, 2015) using 1-(2-bromophenyl) methanamine and 1-(2-chlorophenyl) methanamine with the addition of 15% H_2SO_4 and 15 mM (Millimolar) concentration of inhibitor. The inhibitor was confirmed capable of enhancing electron charge density towards metal corrosion, leading to a protective thin layer on the metal surface. Stainless steel corrosion inhibition using plant extract (*Vernonia amygdalina and Azardirachta indica)* was studied by [29] in 2.5 M HCl, HNO_3 and H_2SO_4. The investigated results revealed that the inhibition behavior of the leave extracts on stainless steel depend on the acid solutions. The extracted fluid from the plant showed the inhibitor effectiveness for stainless steel in HCl and H_2SO_4 solutions. The authors reported analysis in HNO_3 to be unsuccessful in all studied conditions, which was reported to be as a result of corrosive nature of nitric acid. 0.5M Dichromate was studied effectively as inhibitor for stainless steel corrosion in sodium chloride medium by [30]

[31]. Nitrate anions, tetra borate and molybdate dichromate was successfully studied in Bromide medium by [32]. Andrographis panniculata in natural sea water was investigated by [33]. Natural oils in 0.1M NaOH was reported by [34], 2-Cyano-3 hydroxy-4(Ar)-5-anilino thiophene derivatives in 3.5% NaCl has been successfully studied [35]. Indigo carmine and cetyl trimethyl ammonium bromide in 5% HCl was investigated by [36]. Vitamin C in 0.01-5 M HCl has been detailed by [37]. Nitrite anion in Acetic acid with bromide was reported by [38]. Amino acid in 4M HCl solution by [39], N, N Dimethyl amino ethanol in 3M H_2SO_4 by [40], *Lanvandula stoekas* leaves extract by [41]. The anticorrosion effect of agricultural wastes [42, 45] have been reported from our laboratories.

Conclusion

In general inhibitors are excellent inhibitors for stainless steel under a variety of corrosive environments. The non-toxicity of these substances is the major advantages for these inhibitors. Although different authors have proved different green inhibitors as effective against corrosion at different environments, but main drawback efforts are seldom made to pinpoint the active ingredient present in the inhibitor. Therefore, further research efforts are needed to use green inhibitors for preventing stainless steel against corrosion.

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