Protection of Iron by Corrosion Inhibitors

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Iron is a widely used metal due to its low cost and availability, but it is susceptible to corrosion in many circumstances. This corrosion can result in economic and environmental losses, and negatively affect the physical and chemical properties of the metal.

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1. Introduction

The high cost of annual material degradation has prompted the use of protection methods to save materials and energy, and to meet new requirements, such as the use of non-toxic products.

The protection of materials from corrosive environments can be achieved through various actions at the metallurgical, structural, electrochemical, and environmental levels. Three degrees of action are identified ^[1]:

- Actions on the material, such as modifying its composition or microstructure or isolating it from its environment through a metallic or organic coating or anodization.
- Actions on the environment, such as incorporating corrosion inhibitors or avoiding moisture accumulation in the structure.
- Actions on the electrochemical corrosion process, such as cathodic protection.

The protection of metal heritage requires consideration of both preservation of surface information and protection against corrosion. Organic coatings, such as varnishes and waxes, can provide protection. Anodic, cathodic, and galvanic protection, as well as the use of inhibitors, are common and effective methods of protection.

2. Background

The Romans were aware of corrosion and its effects on metal objects. Pliny the Elder, a Roman naturalist and historian, mentioned in the first century A.D. the use of oil or bitumen for protecting bronze and pitch, gypsum or ceruse for iron from corrosion.

This shows that even in ancient times, people were aware of the need for protection against corrosion and sought methods to preserve their metal objects.

The study of corrosion has a long history, dating back to the 17th century. However, it was not until the 19th century that the means of protecting against corrosion were studied scientifically. The number of references dealing with corrosion inhibitors increased rapidly after 1945, with numerous articles written on the subject in various fields such as aviation, oil refining, and diesel engines. In recent years, there has been a significant increase in works on corrosion inhibition, reflecting technological advancements in the field ^[2].

3. Definition

A corrosion inhibitor is a substance added to a corrosion system to slow down the corrosion rate of a metal without significantly altering the concentration of corrosive agents in the environment. The definition used by the National Association of Corrosion Engineers (NACE) states that an inhibitor is a substance that retards corrosion in low concentration. The international standard ISO 8044 defines an inhibitor as a chemical substance added to the corrosion system in a chosen concentration to decrease the corrosion rate of the metal. The properties of an effective inhibitor include lowering the corrosion rate, stability in the presence of other constituents, stability at temperatures of use, effectiveness at low concentrations, compatibility with non-toxicity standards, and cost-effectiveness [3][4].

4. Classification

Inhibitors can be classified based on different criteria such as mechanism of inhibition, application, or chemical nature. This classification helps in better understanding the working of inhibitors and selecting the right inhibitor for a particular corrosion problem. The different classifications of inhibitors provide a comprehensive understanding of the different types of inhibitors and their uses in various corrosion scenarios ^[5].

The classification of inhibitors based on their field of application is a useful way to differentiate between inhibitors used in different environments. For example, inhibitors used in acidic media are mainly used to prevent electrochemical attack during pickling processes and in drilling fluids in the oil industry. Inhibitors for neutral media are mainly used to protect cooling circuits. In organic media, a large number of inhibitors are used in engine lubricants and gasoline to protect against corrosion caused by the presence of water and ionic species. This classification helps in selecting the appropriate inhibitor for a specific corrosion problem and ensures maximum protection against corrosion [6].

Inhibitors for paints and gas phases are used to temporarily protect various packaged objects from corrosion during transport and storage. Electrochemically, inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on their effect on the rate of oxidation and reduction reactions. Anodic inhibitors slow down the oxidation of the metal, cathodic inhibitors slow down the reduction of the oxidant, while mixed inhibitors affect both anodic and cathodic domains. The electrochemical effect of inhibitors on the surface can be explained by various physico-chemical mechanisms. In some cases, the inhibitor forms a physical barrier between the metal and the corrosive medium, as in the case of thick coatings such as waxes and varnishes. In other cases, the inhibitor operates

through a pH or redox buffer effect, which can passivate the metal and reduce the corrosion rate. The mode of action of an inhibitor can also involve the formation of surface films due to the precipitation of inorganic salts or poorly soluble organic complexes. These films reduce the accessibility of oxygen to the metal surface and partially block the anodic dissolution [7].

The technique of removing the corrosive agent from the medium is only applicable in closed systems, such as in the closed hot water circuits of thermal power stations. Additionally, it is important to note that many inhibitors act through multiple mechanisms simultaneously, which can increase their effectiveness in preventing corrosion ^[8].

5. Inhibitors Specific to Ferrous Metals in an Acid Medium

Different corrosion inhibitors can effectively protect ferrous metals from corrosion in acidic environments, either individually or in combination. The selection of the appropriate inhibitor depends on various factors such as the type of metal, environment, and specific conditions ^[9].

5.1. Synthetic Inhibitors

Organic inhibitors contain elements such as nitrogen, sulfur, and oxygen that can exchange electrons with the metal and protect it from corrosion. These inhibitors work through a chemical process called spontaneous adsorption and provide good results in inhibiting steel corrosion in acidic medium ^[10]. Organic inhibitors have several advantages over inorganic inhibitors, as they provide uniform passivation on the metal surface for maximum protection, while inorganic inhibitors form brittle and porous films that can lead to localized corrosion ^[11].

The addition of organic compounds to the acid solution generally reduces its aggressiveness, however, these compounds are toxic and harmful to the environment, leading to the need for alternative, eco-friendly, and efficient inhibitors. One such alternative is the use of natural substances, including vegetable oils ^[12].

5.2. Corrosion Inhibitors Based on Natural Substances

The use of natural substances such as vegetable oils is attractive due to their low cost and abundant availability as environmentally friendly and biodegradable compounds. The use of plant extracts as corrosion inhibitors dates back to 1930, with the use of Chelidonium majus and other plants in a pickling bath of H_2SO_4 . The first patent on corrosion inhibition was granted to Baldwin, who used molasses and vegetable oils for pickling steel sheets in acidic media ^[13].

Currently, many research groups around the world are exploring the use of plant products as corrosion inhibitors for metals and alloys in various corrosive environments ^[14]. There is an increasing number of publications addressing this topic, as shown in **Table 1**, which details some of the main green inhibitors for the corrosion of ferrous metals in acidic medium.

Table 1. Literature review on the use of natural substances as corrosion inhibitors.

Non-Toxic Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
Henna, <i>L. inermi</i> s	Cathodic	92.1	HCI (1 M)	Mild steel	Chemisorption	[15]
N. fruticans Wurmb	Mixed	75.1	HCI	Mild steel	Physisorption	[<u>16</u>]
Eugenol derivatives	Mixed	91	HCI (1 M)	Steel	Chemisorption	[<u>17</u>]
Khillah extract (seeds (A. <i>visnaga</i>))	Mixed	99.3	HCI (2 M)	Steel SX 316	Chemical adsorption	[<u>18</u>]
Natural oil extracted from pennyroyal mint (<i>Mentha</i> <i>pulegium</i> , PM)	Cathodic	80	HCI (1 M)	Steel	Simple blocking of the available surface, intermolecular synergistic Active molecules of this oil	[<u>19]</u>
Plant extract of Z. alatum	Cathodic	95	HCI (5%)	Mild steel	Chemisorption	[<u>17</u>]
Flavonoids (Monomers)	Cathodic	>70	HCI (0.5 M) aerate d	Steel	Chemisorption	[<u>20]</u>
Succinic acid (SA)	Anodic	97.5	HCI (1.0 M) aerate d unstirred	Low carbon steel	Film of inhibitor adsorbed on electrode surface	[21]
Aqueous extract of olive leaves (<i>O. europaea</i> L.)	Mixed	91	HCI (2 M)	Carbon steel	Physical adsorption	[22]
T. occidentalis, (TO)						
A. indica, (AI)	Cathodic	91–	HCI (1 M)	Mild	Physisorption	[23]
H. sabdariffa, (HS)	Outriouio	97		steel	1 Hysisorption	
G. kola (GK) seed extract						
Extract from <i>J. gendarussa</i> (JGPE)	Mixed	93	HCI (1 M)	Mild steel	Physisorption	[<u>24]</u>
Extracts of leaves and seeds of <i>P. amarus</i>	Mixed	80.1– 94.1	HCI (2 M)	Mild steel	Chemisorption	[<u>25</u>]

Non-Toxic Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
		77.6	HCI (2 M)		Chemisorption	
L. albus L.	Mixed	85	H ₂ SO ₄ (1 M)	Steel	Physisorption	[<u>26</u>]
Pennyroyal oil from <i>M.</i> pulegium	Cathodic	80	HCI (1 M)	Steel	Chemisorption	[<u>19</u>]
Zest of (Mango, Orange, Passion, Cashew)	Mixed	80– 95	HCI (1 M)	Carbon steel	Adsorption of organic compounds present in the extracts on the active sites of the electrode surface	[27]
Juniperus phoenicea (Cupressaceae) essential oil	Mixed	83	HCI (1 M)	Mild steel	adsorption of aromatic compounds on the metal surface	[28]
Methanolic extract of A. Pallens	Mixed	96.5	HCI (4 N)	Mild steel	Formation of a very tightly adhering adsorbent film on the metal surface	[<u>29]</u>
Guar gum	Mixed	93.6	H ₂ SO ₄ (1 M)	Carbon steel	Formation of passive, active and continuously propagating centers.	[<u>30]</u>
Chamomile (<i>C. mixtum</i> L.)						
Halfab ar (C. proximus)		90.2	H ₂ SO ₄ (1 M)	Steel	Adsorption of the stable complex to the steel surface	[21]
Black cumin (<i>N. sativa</i> L.)	Mixed					[31]
Kidney bean (<i>P. vulgaris</i> L.)						
Berberine	Mixed	98	H ₂ SO ₄ (1 M)	Mild steel	Chemical adsorption	[<u>32</u>]

Non-Toxic	Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
Fenugreek lea	aves (AEFL)	Mixed	88.3		Mild steel	Chemical adsorption of inhibitor molecules on mild steel	[<u>33</u>]
Black pepp	er extract		90	H_2SO_4			[<u>34</u>]
Saffron-	0 (SO)		65				[<u>35</u>]
Alizarin Yel	llow (GG)	Mixed	85	H ₂ SO ₄ (2 M)	Mild steel	Physisorption	[<u>36</u>]
Caffeio	e acid		83.9	H ₂ SO ₄ (0.1 M)			[<u>37</u>]
Lignin extracte liquor of the paper in	ed from black e pulp and dustry	Cathodic	95	H ₂ SO ₄ (0.5 M)	Mild steel	Adsorption of more lignin molecules on the metal surface, preventing the electrochemical corrosion process	[<u>38]</u>
Galactomanna from Caro (Ceratonia	an extracted b seeds a <i>Siliqua</i>)	Mixed	86.6	HCI (1 M)	Archaeological iron	Establishment of inhibitor film on iron substrate surface	[<u>39]</u>
Formulations based on oils	Opuntia ficus indica (OTH)	Mixed	99.6	Acid rain- simula ted enviro nment pH = 3.6	Archaeological iron	Establishment of inhibitor film on iron substrate surface	[40]
extracted from the seeds of	Nigella sativa (FBN)		99.3				<u>[41]</u>
Jati Cu (J Cera Siliq (F0	Jatropha Curcas (JAC)		97				[<u>42</u>]
	Ceratonia <i>Siliqua L.</i> , (FCSL)		98.6				[<u>43]</u>
	Aleurites moluccana (ALM) LU Decemb)	97				[44]

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Non-Toxic Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
Орипtia Dillenii Control; E	sterdam,	99	i. III Philopies therlands, 200	ь от сотгозюг)6; pp. 352–3	і ⊑пушеенну а 881.	(<u>45)</u> a D

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