

Utility of Corrosion Inhibitors for the Corrosion Protection of Materials in Hostile Environments

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Abstract

The term “inhibitor” refers to a material that reduces the rate of corrosion in an environment when added in trace amounts. As a result, the inhibitor functions as a catalyst for those delays. Inhibitors come in a wide variety of forms and formulations. The two most crucial considerations when choosing materials for industrial applications are cost and safety. Physical criteria are typically simple to achieve, but corrosion resistance presents significant material selection issues. To increase corrosion protection, a variety of organic or inorganic coatings can be applied; however, the financial consequences must be taken into account. Material costs are influenced by machinability, physical properties, and design specifications. Deterioration typically begins with localized corrosion in materials that may otherwise withstand widespread corrosive effects. This localized type of deterioration is particularly harmful since it can accelerate stress corrosion cracking, and only happens in specific situations. Effective monitoring and early detection of localized corrosion require overcoming numerous challenges. Although corrosion-resistant materials are available, their application can be challenging, and their costs are frequently higher. In many cases, adding corrosion inhibitors as a retrofit solution or as part of the original design provides a useful and cost-effective way to deal with corrosion problems.

Keyword: Materials, Corrosion protection, Inhibitors, Catalyst, Organic and inhibitors, Cost and safety.

INTRODUCTION

Classification of Inhibitors

Different types of corrosion inhibitors are distinguished by their chemical and mechanistic characteristics [1]. The corrosion inhibitor attacks the metal’s surface to produce a protective thin barrier layer most of the time. Inhibitor chemistry involves pH regulation, chemical neutralization of dissolved acidic gases, and scavenging for dissolved oxygen to increase constant passivation [2]. Types of inhibitors are recorded in (Table 1).

Adsorption Type Inhibitors

These organic substances limit metal dissolution and reduction processes by adhering to the metal surface. For this type of inhibitors, organic amines are frequently utilized [3].

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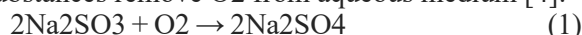
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Scavengers Type Inhibitors

Scavengers work by eliminating corrosive substances from solutions. The compounds N₂H₄ (hydrazine) and Na₂SO₃ are used as such types of inhibitors. The following reactions show how these substances remove O₂ from aqueous medium [4]:



It is observed that the above scavenger inhibitors reduce the concentration of O₂ in solutions and stop the cathodic reaction. These inhibitors are less effective in strong acid solutions.

Table 1. Types of inhibitors.

Type of nature	Inhibition compounds	Function of inhibitors
Anodic	CrO_4^{2-}	Oxidizing deactivator.
	NO_2^-	Oxidizing stabilizer.
	NO_3^-	Oxidizing passivated.
	PO_4^{3-}	Noncorrosive.
	MoO_4^{2-}	Nonreactive.
	WO_4^{2-}	Non-aggressive.
Cathodic	AsO_4^{3-}	cathodic poison.
	CO_3^{2-}	Precipitate of Ca and Mg.
	ZnSO_4	Association as zinc hydroxide.
Deposition	PO_4^{3-}	Anodic/Cathodic.
	SiO_2	Anodic/Cathodic.
O ₂ Scavenger	SO_3^{2-}	Cathodic.
	NH_2NH_2	Cathodic.
Volatile/Vapour phase	$\text{C}_6\text{H}_{11}\text{NH}_2$	Association as NO_2^- salt.
	$\text{C}_4\text{H}_9\text{NO}$	Neutralizing.
Film-forming	Aliphatic & Aromatic amine	Organic/Adsorption.
	R_2CNR	Organic/Adsorption.
	$\text{C}_3\text{H}_6\text{NN}_2$	Organic/Adsorption.
	$[\text{R}_4\text{N}]^+$	Organic/Adsorption.
	$\text{C}_2\text{H}_5\text{OH}$	Organic/Adsorption.

Oxidizers Type Inhibitors

The inorganic substances like CrO_4^{2-} , NO_2^- and Fe^{3+} salts behaves like oxidizer inhibitors in corrosive systems. These oxidizers inhibitors are checked the corrosion of metals and act active-passive transition barrier, for e.g. Fe and its alloys [5].

Vapour Phase Inhibitors

They are high vapour pressure inhibitors. They are used to control the corrosion of metal by sublimation and condensation. These types of inhibitors are useful inside closed packages.

Limitations of the Use of Inhibitors

Since inhibitors have the potential to pollute the environment, they cannot be added to all corrosive systems. The use of many inhibitors in media intended for direct or indirect use in the processing of packed food or other goods that substances will contact with humans is prohibited due to their toxicity. For instance, it is not always possible to employ arsenic salts, which are effective inhibitors of strong acids. The primary applications for inhibitors are in locked systems where the unfriendly atmosphere is either recirculated for an extended length of time. As the environment's temperature and concentration rise, inhibitors quickly lose their potency [6].

Chemistry of Corrosion Inhibitors

Pitting corrosion can be avoided by employing inhibited or active anodic sites. Because they decrease the total current movement in the corrosion reactions and inhibit the reduction reaction instead of directly interfering with the anodic reaction, inhibitors are frequently referred to as "safe" inhibitors. Inhibitors can exhibit anodic, cathodic, or mixed behaviors, which combine anodic and cathodic effects [7].

Adsorption Mechanisms of Inhibitors

In general, adsorption is how organic-based film-forming corrosion inhibitors function. A physisorbed surface film initially accommodates the polar organic compounds or ionic species (according to van der Waals forces). Chemisorption may further solidify the surface film to create a

donor-type bond. The stability of the donor (adsorption) bond is assessed using Lewis acid–base theory. A strong acid will form a bond with a strong base and vice versa according to the HASB (Hard and Soft Acids and Bases) concept [8]. Table 2 provides an example of the principle.

Table 2. HASB (hard and soft acids and bases) principle.

HASB	Basic principles
1. Strong	Low Polarizability. More Electronegativity.
2. Mild	More Polarizability. Less Electronegativity.
3. Strong Acid	Strong Base.
4. Oxides of Fe	Oxygen, Nitrogen.
5. Mild Acid	Mild Base.

Generally, inhibitors show their actions in an acidic medium. The corroded metals are inhibited by the action of cathodic and anodic electrochemical inhibitors. Once inhibitors have deposited on the metal surface [9], they can minimize the corrosion reactions in different processes as shown in (Table 3).

Table 3. The process of minimizing the corrosion reactions.

Protective barrier	Corrosive substances control
1. Development of Physical-Chemical Film	Mitigation diffusion of corrosive ions or molecules.
2. Directly Protection of Anodic and Cathodic reactions	Minimize Corrosive Attacks.
3. Control Intermediate Corrosion reaction Products	Check Corrosion Processes.
4. Stop the Creation of Electrical Double Layers at the Metal Interface	Suppresses Corrosion Reactions.
5. Affect the Rate of Electrochemical Reactions	Neutralised Corrosion Reactions.

FILM FORMATION PROCESSES

The functions of inhibitors are concerned with the presence of O₂ in the process of corrosion. Such inhibitors fall within the category of cathodic inhibitors. Also referred to as the cathodic inhibitor, the cathodic oxygen-reduction process favors deposition at cathodic regions of different salty compounds, causing inhibition. The most prevalent salts in this class are calcium and magnesium carbonates, and insoluble hydroxides of magnesium and zinc, where the inhibition action can be started right away by changing the pH values. The precipitated coatings may also have some anodic nature because they cover a metal surface. In these circumstances PO₄³⁻ and SiO₃²⁻ belong as non-oxidizing passivators, which can play an important role in inhibitor action [10].

Passivation Mechanisms

The action of inhibitors is attached with O₂ in the completion of corrosion reactions. These molecules fall within the category of cathodic inhibitors. Also referred to as the cathodic inhibitor, the cathodic oxygen-reduction process favors consumption at the cathodic region of various salt compounds and is known as the inhibition process. The most prevalent salts in this class are calcium and magnesium carbonates, and insoluble hydroxides of magnesium and zinc, where inhibition takes place right away by changing the pH values. The precipitated coatings may also have some anodic nature because they cover a metal surface. Inhibitors like PO₄³⁻ and SiO₄⁴⁻ act as non-oxidizing inhibitors; deposition can safely perform considerable behavior with a mixed-type inhibitor because of the metal's absorption of atomic hydrogen. The passivating inhibitor can be broadly defined as an unstable condition that typically results in pitting corrosion when inhibitors are available above a threshold amount and potential shifts between the active and passive regions. This idea undoubtedly holds true even if anodic inhibitors differ significantly in the fundamental criterion of inhibition brought on by an anodic shift in corrosion potential [11].

Synergistic Effects

Commercial corrosion inhibitors can be used as certain surfactant/solvent combinations that complement one another. One instance of synergism is the inhibition of mild steel by zinc molybdate combinations, which reduces the corrosion rate when both components are present in solutions, as opposed to when they are present separately. When two ions work together to delay the cathodic reduction of O_2 , inhibition results. In oilfield applications, organic film-forming corrosion inhibitors can have comparable effects on corrosion rate. Altering the solvent package or adding or removing the surfactant will produce these results. The physicochemistry is being altered or modified via synergism. The surfactant improves the metal surface's adsorption capacity. The active concentrations in solution are controlled by the corrosion-inhibitor species present in the solvent package, which also influences the inhibitor's dispersibility and/or partitioning [12].

Raw Materials for Inhibitor Synthesis

Long-chain aliphatic fatty acids ($R(CH_2)_nCOOH$), naphthenic acid ($C_{10}H_7COOH$), fractions of oxidized petroleum, ammonia, and aliphatic or aromatic amines are the fundamental raw ingredients used to make inhibitors. Amines are also synthesized using α -olefins and acrylonitrile [13].

Fatty Acids

Organic acids that range in molecular weight from low to high include C8 and C24 carboxylic acids. Fatty amines are produced by higher molecular weight acids, whereas amines are frequently only salted with low-molar-mass acids to form dispersible or water-soluble compounds. The most often used fatty acids are saturated and unsaturated organic acids like $C_{12}H_{24}O_2$ (lauric acid), $C_{18}H_{36}O_2$ (stearic acid), $C_{18}H_{34}O_2$ (oleic acid), $C_{18}H_{30}O_2$ (linoleic acid), and linolenic acid. These acids are obtained from both vegetable and animal fats, including tallow, coconut oil, and tall oil. Polymerization of unsaturated fatty acids can result in polycarboxylic acids [14].

Amines

These amines include high-molecular-weight ethyleneamines and ammonia (NH_3). The reaction of ethylene dichloride with ammonia is one method of producing ethylene amines. Imidazolines and amidoamines can be produced from the reaction product, ethylenediamine. Additionally, it may react with ethylene dichloride to produce higher-molecular-weight forms of ethyleneamines and diethylenetriamine [15].

Fatty Amino Acids

Fatty acids and ammonia react to make amides, which are further hydrogenated to produce primary fatty amines. Alpha-olefins can also be converted into primary amines. Alpha-olefins can also be converted into secondary and tertiary amines, which can then undergo further reactions to form amides, quaternaries, and other compounds [16].

Diamine

It is formed when acrylonitrile is treated with a primary fatty amine, as followed by hydrogenation.

Imidazolines and Amido-amines

They are obtained by reacting certain organic fatty acids with amines like diethylenetriamine or N-aminoethyl piperazine. The number of nitrogens in polyamines can vary from two to six or more in complicated polyamines [17]. A hydroxyl group that gives polyamines some water solubility may be present.

Oxyalkylated Amines

Ethylene oxide can react with amidoamines, primary amines, and imidazolines to render them soluble in water. Depending on the required oil-water partition and level of water solubility, several moles of butylene, propylene, or ethylene oxide can be used. Tertiary amines, which can be quaternized, are created when amines are combined with alkylene oxides [18].

Quaternaries

Tertiary amines such as oxylated or dimethyl fatty amines are used to make quaternary ammonium salts, and an organic sulfate or benzyl chloride is frequently employed.

Other Amino Derivatives

To enhance adsorption to the metal surface, amines can be altered by including sulfur, phosphorus, or other elements into the molecule. To increase molecular weights, they could undergo further reactions with urethanes, epoxides, and other crosslinking agents. To accomplish branch-bonding of the inhibitors on the metal interface, the amines are subsequently combined with dimerized fatty acids and so on. To make them water-soluble or dispersible, they can be mixed with organic and low-molecular-weight inorganic acids. Surface passivation can be accomplished by adding phosphate and nitrite groups [19].

Formulation of Corrosion Inhibitors

To produce a usable or “finished” product, the appropriate molecules must be selected or synthesized and then mixed. Amines must be diluted using the appropriate solvent because they are viscous liquids or solids. An aqueous mixture of alcohol, water, or coupling agents could be used for the solubility of water for examples of coupling agents such as RCH_2OH (alcohols), RCO_2R (esters), $RCOR$ (ketones), $RCH_2OCH_2CH_2COCH_2R$ (glycol ethers), and $HOCH_2CH_2OH$ (glycols) [20]. These substances are used to form a durable solution of amine and other ingredients having a suitable amount of water and brine solubility. The inhibitor must also meet the requirements for pour point and flash point.

Organic Solvents

For either oil-soluble or water-dispersible inhibitors, a hydrocarbon solvent will be utilized. Due to their superior solvating capabilities over aliphatic solvents, aromatic solvents are recommended. Due to their high cost, pure aromatics like xylene and toluene are rarely employed; instead, certain gas oils, light cycle oils, BTX units from cumene manufacturing, and byproduct aromatic solvents from still bottoms are utilized. Pour point needs to be taken into account because they can contain some polycyclic elements and anthracenes [21]. Aliphatic solvents like diesel will be used in some situations.

Additives

To help disperse inhibitors, avoid emulsification, and reduce the time it takes for amines to “wet” the metal surface, the formulations might include a unique kind of surface-active chemical. On the underlying metal, they might also help penetrate loose deposits. These could include oxyalkylated substances such as aliphatic amines, phenols, organic fatty acids, aromatic amides, amphoterics, sulfonic acids, and sulfonates [22], and so forth. To strengthen the film, substances such as fatty acids will be applied in addition to amine. To achieve water solubility or dispersibility, hydroxyl acids and low-molecular-weight organic acids are used. To aid nitrogen-containing organic compounds in interacting with the metal surface, wetting agents may be used. To ensure inhibitors form a dispersion solution in fluids, an emulsifying surfactant or dispersant may be added. Instead, to avoid formation of oil-water emulsion that could disrupt manufacturing and processing facilities, a demulsifier might be used. Low-molecular-weight amines such as triethylamine, diethylamine, and ethylamine are examples of vapor-phase inhibitors. They are combined with inhibitors to produce an anticorrosive product because of their high vapor pressures and low boiling points [23].

Stability Considerations

For every particular use, the inhibitor must fulfill certain requirements, including durability against corrosive materials, time, temperature, and exposure. It must be simple to use and work at low concentrations. Each application requires a different set of solubility characteristics, and the inhibitor needs to be conveyed at the system temperature. It can fulfill performance requirements and be compatible with other compounds being used. It needs to prevent rusting [24]. Additionally, it must not interfere with the system it is used with and be compatible with it.

ENVIRONMENTAL AND TOXICITY FACTORS

The flash point needs to be within the allowed range, and the inhibitor cannot be overly toxic. Manufacturing processes must be controllable and reproducible, and raw materials must be easily accessible and reasonably priced. The monitoring procedures must be simple and easy to follow, and it must be compatible with the application techniques that are already available. The creation of inhibitors must be guided by each of these factors. To minimize expenses and development time, all material testing and selection must be rigorously based on the criteria.

This chapter has presented a comprehensive overview of the chemistry of corrosion inhibitors [25] for protecting steel, covering fundamental corrosion mechanisms, inhibitor classification, formulation strategies, and application methods. Several key conclusions can be drawn:

Corrosion Mechanism Understanding

The electrochemical nature of corrosion provides the foundation for developing effective inhibition strategies. Different types of corrosion require specific inhibitor approaches.

Inhibitor Classification

Corrosion inhibitors work through various mechanisms including adsorption, film formation, passivation, and precipitation. Understanding these mechanisms is crucial for proper inhibitor selection.

Formulation Considerations

The effectiveness of an inhibitor depends not only on the active components but also on proper formulation with appropriate solvents, surfactants, and additives to ensure stability and compatibility with the environment [26].

Application-Specific Selection

No single inhibitor is suitable for all corrosion scenarios. Inhibitor selection must be based on the specific metal, environment, operating conditions, and system design [27].

TESTING AND MONITORING

Comprehensive testing protocols and ongoing monitoring are essential to ensure the continued effectiveness of corrosion inhibitor programs [28].

For future development and implementation of corrosion inhibitors, the following recommendations are proposed:

Environmental Considerations

Continue the shift toward environmentally friendly “green” inhibitors that maintain performance while reducing environmental impact.

Integrated Protection Strategies

Develop comprehensive corrosion management plans that combine inhibitors with other safety methods like cathodic protection, material selection, and coatings.

Advanced Delivery Systems

Invest in research on smart delivery systems that can provide targeted inhibition where and when it is needed most.

Standardized Testing Protocols

Establish industry-wide standardized testing protocols that enable better comparison between different inhibitor formulations.

CONCLUSION

Inhibitors are used to mitigate corrosion of materials in corrosive environments. Implement life cycle assessment approaches to evaluate both the economic and environmental impacts of corrosion inhibitor

programs. The major role of corrosion inhibitors is cost effectiveness, and their applications are broad and extensive, signifying technology in different fields. The essential perception about inhibition has benefited mostly from the applications of electrochemical tools and their performance. It has promoted an enhanced level of sophistication in the development of commercial corrosion inhibitor products and practicability. The majority of organic-based inhibitors are on the market, and they occupy larger areas in commercial applications. The ongoing research and development in this field, particularly in the areas of green chemistry, nanotechnology, and smart delivery systems, promises to further enhance the effectiveness, efficiency, and environmental compatibility of corrosion inhibitors for steel protection in the coming years.

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