

59 Corrosion Inhibitors

S. PAPA VINASAM

CANMET Materials Technology Laboratory
Ottawa, Ontario, Canada

A. INTRODUCTION

A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion [1].

Corrosion inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, required, for example, to prevent corrosion that may result from accumulation of small amounts of an aggressive phase. One example is brine, in a nonaggressive phase, such as oil. An efficient inhibitor is compatible with the environment, is economical for application, and produces the desired effect when present in small concentrations.

Inhibitor efficiency, P , is given as

$$P = (w_0 - w/w_0) \times 100 \quad (1)$$

where w_0 is the corrosion rate in the absence of inhibitor, and w is the corrosion rate in the same environment with the inhibitor added.

B. CLASSIFICATION OF INHIBITORS

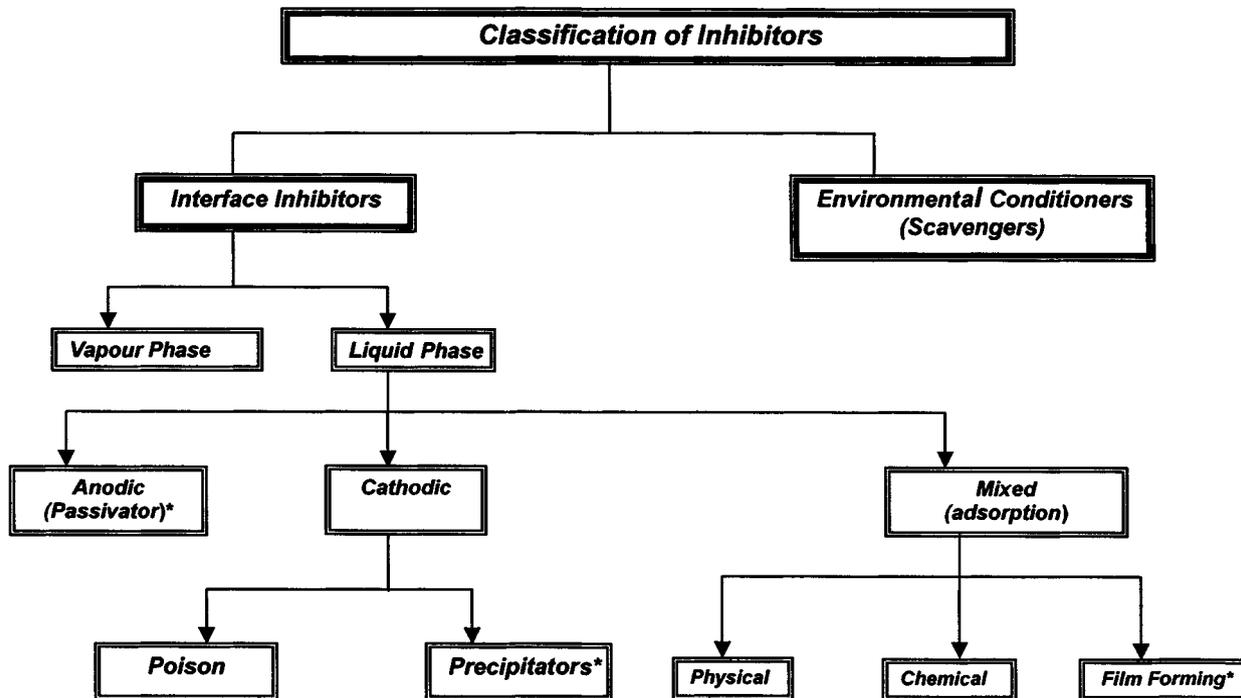
Inhibitor selection is based on the metal and the environment. A qualitative classification of inhibitors is presented in Figure 1. Inhibitors can be classified into environmental conditioners and interface inhibitors.

1. Environmental Conditioners (Scavengers)

Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers. In near-neutral and alkaline solutions, oxygen reduction is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using scavengers (e.g., hydrazine [2]).

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*Form three-dimensional layers at the interface, so they are classified collectively as interphase inhibitors

FIGURE 1. Classification of inhibitors.

2. Interface Inhibitors

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid- and vapor-phase inhibitors.

2.1. Liquid-Phase Inhibitors Liquid-phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on whether they inhibit the anodic, cathodic, or both electrochemical reactions.

2.1.1. Anodic inhibitors. Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. They form, or facilitate the formation of, passivating films that inhibit the anodic metal dissolution reaction. Anodic inhibitors are often called passivating inhibitors.

When the concentration of an anodic inhibitor is not sufficient, corrosion may be accelerated, rather than inhibited. The critical concentration above which inhibitors are effective depends on the nature and concentration of the aggressive ions.

2.1.2. Cathodic inhibitors. Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators).

Cathodic poisons, such as sulfides and selenides, are adsorbed on the metal surface; whereas compounds of arsenic, bismuth, and antimony are reduced at the cathode and form a metallic layer. In near-neutral and alkaline solutions, inorganic anions, such as phosphates, silicates, and borates, form protective films that decrease the cathodic reaction rate by limiting the diffusion of oxygen to the metal surface.

Cathodic poisons can cause hydrogen blisters and hydrogen embrittlement due to the absorption of hydrogen into steel. This problem may occur in acid solutions, where the reduction reaction is hydrogen evolution, and when the inhibitor poisons, or minimizes, the recombination of hydrogen atoms to gaseous hydrogen molecules. In this situation, the hydrogen, instead of leaving the surface as hydrogen gas, diffuses into steel causing hydrogen damage, such as hydrogen-induced cracking (HIC), hydrogen embrittlement or sulfide stress cracking.

Cathodic precipitators increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface. The most widely used cathodic precipitators are the carbonates of calcium and magnesium.

2.1.3. Mixed inhibitors. About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte.

Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation. Physical (or electrostatic) adsorption is a result of electrostatic attraction between the inhibitor and the metal surface. When the metal surface is positively charged, adsorption of negatively charged (anionic) inhibitors is facilitated (Fig. 2).

Positively charged molecules acting in combination with a negatively charged intermediate can inhibit a positively charged metal. Anions, such as halide ions, in solution adsorb on the positively charged metal surface, and organic cations subsequently adsorb on the dipole (Fig. 3). Corrosion of iron in sulphuric acid containing chloride ions is inhibited by quaternary ammonium cations through this synergistic effect [3].

Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface.

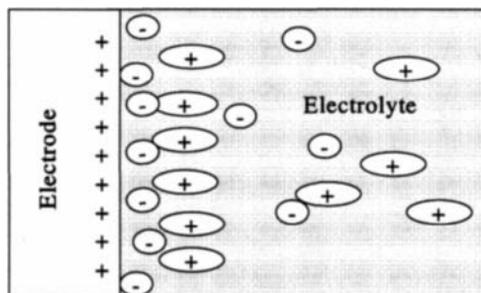
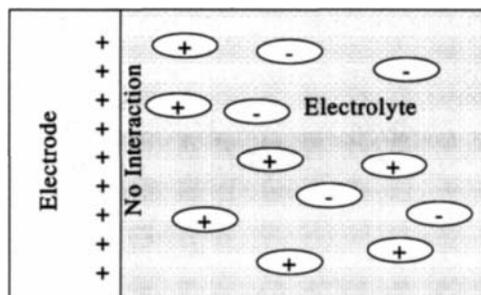
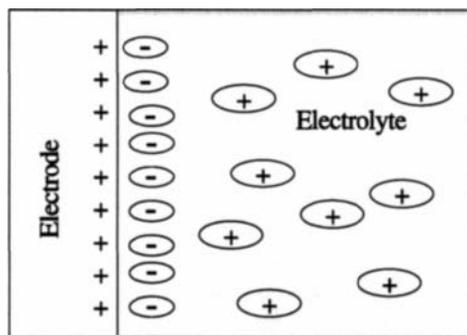


FIGURE 2. Adsorption of negatively charged inhibitor on a positively charged metal surface.



(a)

FIGURE 3(a). Positively charged inhibitor molecule does not interact with positively charged metal surface.



(b)

FIGURE 3(b). Synergistic adsorption of positively charged inhibitor and anion on a positively charged metal surface.

Chemisorption takes place more slowly than physical adsorption. As temperature increases, adsorption and inhibition also increase. Chemisorption is specific and is not completely reversible [4].

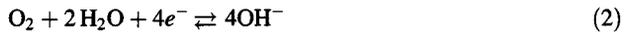
Adsorbed inhibitor molecules may undergo surface reactions, producing polymeric films. Corrosion protection increases markedly as the films grow from nearly two-dimensional adsorbed layers to three-dimensional films up to several hundred angstroms thick. Inhibition is effective only when the films are adherent, are not soluble, and prevent access of the solution to the metal. Protective films may be nonconducting (sometimes called ohmic inhibitors because they increase the resistance of the circuit, thereby inhibiting the corrosion process) or conducting (self-healing films).

2.2. Vapor-Phase Inhibitors Temporary protection against atmospheric corrosion, particularly in closed environments can be achieved using vapor-phase inhibitors (VPI). Substances having low but significant pressure of vapor with inhibiting properties are effective. The VPIs are used by impregnating wrapping paper or by placing them loosely inside a closed container [5]. The slow vaporization of the inhibitor protects against air and moisture. In general, VPIs are more effective for ferrous than non-ferrous metals.

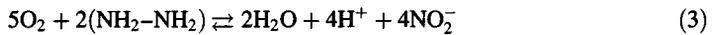
C. MECHANISTIC ASPECTS OF CORROSION INHIBITION

1. Environmental Conditioners (Scavengers)

In near-neutral solutions, the common cathodic reaction is oxygen reduction:



Scavengers deplete the oxygen by chemical reaction; for example, hydrazine removes oxygen by the following reaction [2]:



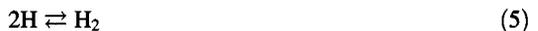
2. Anodic Inhibitors (Passivators)

The mechanism of anodic inhibition can be explained using the polarization diagram of an active-passive metal (Fig. 4) [6].

In the absence of inhibitors, the metal corrodes in the active state at a rate corresponding to point A in Figure 4. As the concentration of inhibitor is increased, the corrosion rate also increases until a critical concentration and a critical corrosion rate (point B, Fig. 4) are reached. At the critical concentration, there is a rapid transition of the metal to the passive state, and the corrosion rate is decreased (point C).

3. Cathodic Inhibitors

In acid solution, the cathodic reaction is, typically, the reduction of hydrogen ions to hydrogen atoms, which combine forming hydrogen molecules:



In alkaline solution, the cathodic reaction is typically oxygen reduction [Eq. (2)].

Cathodic inhibitors impede reduction reactions. Substances with high overpotential for hydrogen and those that form precipitates at the cathode are effective in acid and alkaline solutions, respectively. The effect of a cathodic inhibitor on the polarization curves is shown in Figure 5. In this case, the slope of the anodic polarization curve is unaffected, but the slope of the cathodic polarization curve is changed [7].

4. Mixed Inhibitors (Adsorption)

Adsorption occurs as a result of electrostatic forces between the electric charge on the metal and the ionic charges or dipoles on the inhibitor molecules.

The potential at which there is no charge on the metal is known as the zero-charge potential (ZCP) (Table 1) [8]. The charge on a metal surface in a given medium can be determined from the

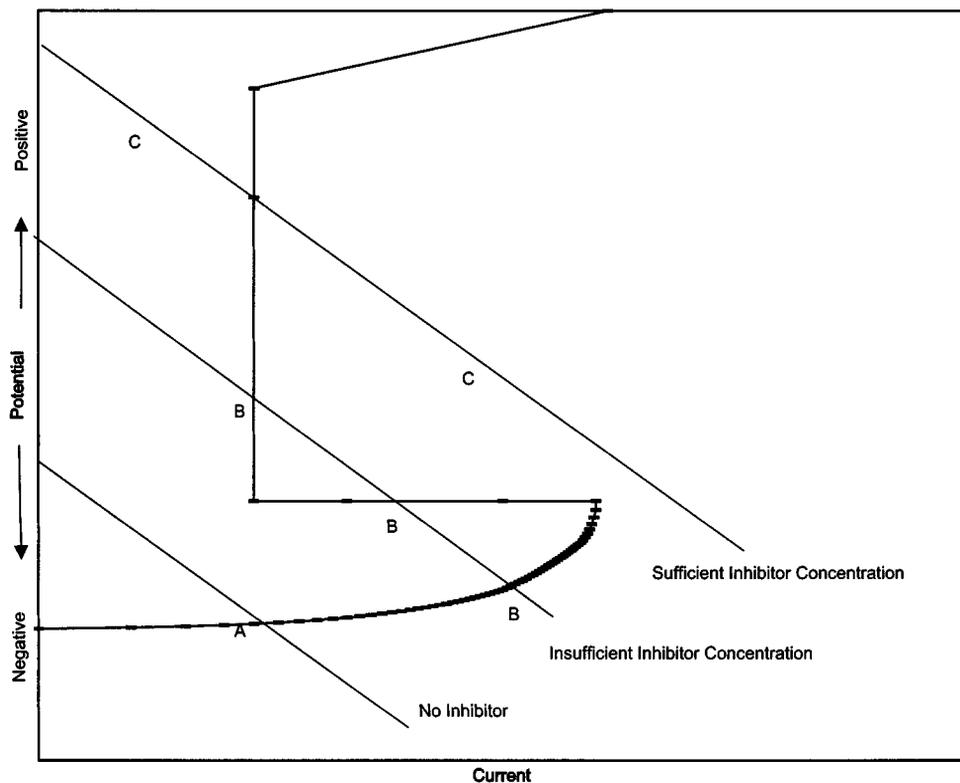
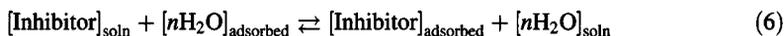


FIGURE 4. Polarization diagram of an active-passive metal showing the dependence of the current on concentration of passivation-type inhibitor [7].

corrosion potential (E_{CORR}) and zero-charge potential. When the difference, $E_{\text{CORR}} - \text{ZCP}$, is negative, the metal is negatively charged and adsorption of cations is favored. When $E_{\text{CORR}} - \text{ZCP}$ is positive, the metal is positively charged and adsorption of anions is favored.

The charge on inhibitors depends on the presence of loosely bound electrons, lone pairs of electrons, π -electron clouds, aromatic (e.g., benzene) ring systems, and functional groups containing elements of group V or VI of the periodic table. Most organic inhibitors possess at least one functional group, regarded as the reaction center or anchoring group. The strength of adsorption depends on the charge on this anchoring group [rather on the hetero atom (i.e., atoms other than carbon including nitrogen, sulphur) present in the anchoring group]. The structure of the rest of the molecule influences the charge density on the anchoring group [4].

Water molecules adsorb on the metal surface immersed in an aqueous phase. Organic molecules adsorb by replacing the water molecules:



where n is the number of water molecules displaced by one inhibitor molecule.

The ability of the inhibitor to replace water molecules depends on the electrostatic interaction between the metal and the inhibitor. On the other hand, the number of water molecules displaced depends on the size and orientation of the inhibitor molecule. Thus, the first interaction between inhibitor and metal surface is nonspecific and involves low activation energy. This process, called "physical adsorption," is rapid and, in many cases, reversible [9].

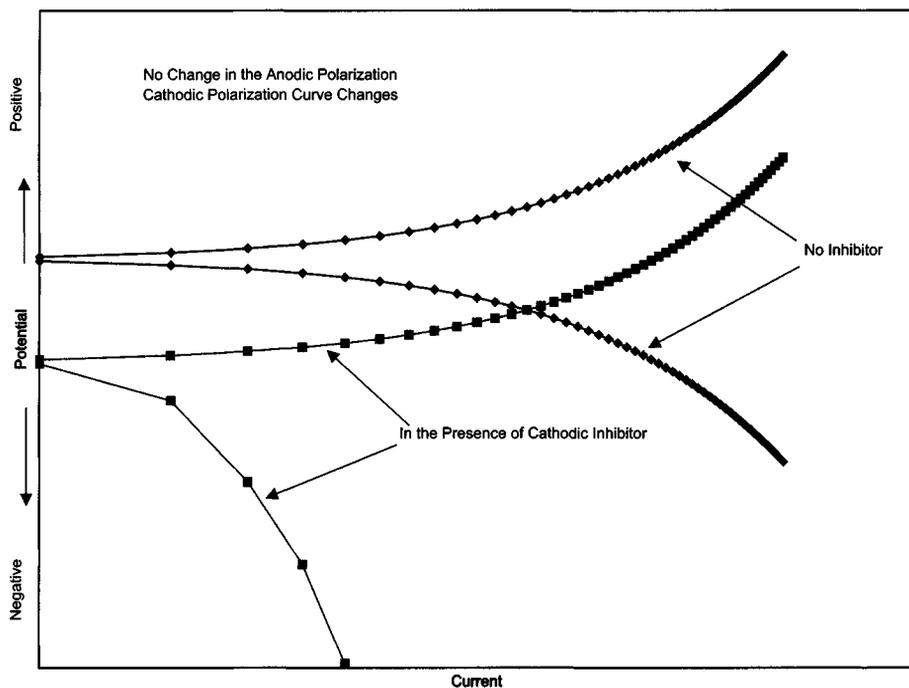


FIGURE 5. Polarization curve in the presence of cathodic inhibitor [7].

TABLE 1. Values of Zero Charge Potentials^a

Metal	Zero-Charge Potential, mV (SHE)
Ag	- 440
Al	- 520
Au	+ 180
Bi	- 390
Cd	- 720
Co	- 450
Cr	- 450
Cu	+ 90
Fe	- 350
Ga	- 690
Hg	- 190
In	- 650
Ir	- 40
Nb	- 790
Ni	- 300
Pb	- 620
Pd	0
Pt	+ 20
Rh	- 20
Sb	- 140
Sn	- 430
Ta	- 850
Ti	- 1050
Tl	- 750
Zn	- 630

^a See [8].

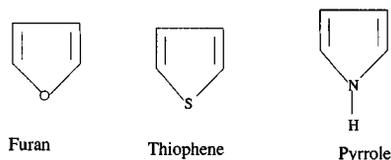


FIGURE 6. Homologous series of organic molecules (the molecules differ only in the hetero atom).

Under favorable conditions, the adsorbed molecules involved in chemical interaction (chemisorption) form bonds with the metal surface. Chemisorption is specific and is not reversible. The bonding occurs with electron transfer or sharing between metal and inhibitor. Electron transfer is typical for transition metals having vacant, low-energy electron orbitals.

Inhibitors having relatively loosely bound electrons transfer charge easily. The inhibition efficiency of the homologous series of organic substances differing only in the heteroatom is usually in the following sequence: $P > S > N > O$. An homologous series is given in Figure 6. On the other hand, the electronegativity, that is, the ability to attract electrons, increases in the reverse order.

Adsorption strength can be deduced from the adsorption isotherm, which shows the equilibrium relationship between concentrations of inhibitors on the surface and in the bulk of the solution. Various adsorption isotherms to characterize inhibitor efficiencies are presented in Table 2 [10–13]. To evaluate the nature and strength of adsorption, the experimental data (e.g., corrosion rate) are fitted to the isotherm, and from the best fit, the thermodynamic data for adsorption are evaluated.

The principle of soft and hard acids and bases (SHAB) has also been applied to explain adsorption and inhibition [14]. The SHAB principle states that hard acids prefer to coordinate with hard bases and that soft acids prefer to coordinate with soft bases. Metal atoms on oxide-free surfaces are considered to be soft acids, which in acid solutions form strong bonds with soft bases, such as sulfur-containing organic inhibitors. By comparison, nitrogen- or oxygen-containing organic compounds are considered to be hard bases and may establish weaker bonds with metal surfaces in acid solutions.

Whatever may be the mechanism of adsorption, the electron density of the functional groups, polarizability and electronegativity are important parameters that determine inhibition efficiency.

5. Vapor-Phase Inhibitors

The process of vapor-phase inhibition involves two steps: transport of inhibitor to the metal surface and interaction of inhibitor on the surface. A VPI may vaporize either in the molecular form or it may first dissociate and then vaporize. Amines vaporize in the undissociated molecular form. Subsequent reaction with water, present as moisture at the surface, dissociates the inhibitor. On the other hand, dicyclohexylamine nitrite dissociates liberating amine and nitrous acid, which deposit on the metal

TABLE 2. Adsorption Isotherms^a

Name	Isotherm ^b	Verification Plot
Langmuir	$\theta/(1 - \theta) = \beta \cdot c$	$\theta/(1 - \theta)$ vs. $\log c$
Frumkin	$[\theta/(1 - \theta)]e^{f\theta} = \beta \cdot c$	θ vs. $\log c$
Bockris–Swinkels	$\theta/(1 - \theta)^n \cdot [\theta + n(1 - \theta)]^{n-1}/n^n = c \cdot e^{-\beta/55.4}$	$\theta/(1 - \theta)$ vs. $\log c$
Temkin	$\theta = (1/f) \ln K \cdot c$	θ vs. $\log c$
Virial Parson	$\theta \cdot e^{2f\theta} = \beta \cdot c$	θ vs. $\log(\theta/c)$

^a See [10–13].

^b θ , %P/100, surface coverage; β , $\Delta G/2.303RT$; ΔG , free energy of adsorption; R , gas constant; T , temperature; c , bulk inhibitor concentration; n , number of water molecules replaced per inhibitor molecule; f , inhibitor interaction parameter (0, no interaction; +, attraction; and -, repulsion); K , constant; and %P = 1-inhibited corrosion rate/uninhibited corrosion rate.

TABLE 3. Some Anchoring (Functional) Groups in Organic Inhibitors

Structure	Name	Structure	Name
-OH	hydroxy	-CONH ₂	Amide
-C≡C-	-yne	-SH	Thiol
-C-O-C-	epoxy	-S-	Sulfide
-COOH	carboxy	-S=O	Sulfoxide
-C-N-C-	amine	-C=S-	Thio
-NH ₂	amino	-P=O	Phosphonium
-NH	imino	-P-	Phospho
-NO ₂	nitro	-As-	Arsano
-N=N-N-	triazole	-Se-	Seleno

surface [15]. Both in molecular and in dissociated forms VPIs adsorb either physically or chemically on the metal surface to inhibit corrosion.

D. EXAMPLES OF CORROSION INHIBITORS

Inhibitors used in practice are seldom pure substances, but are usually mixtures that may be byproducts, for example, of some industrial chemical processes for which the active constituent is not known. Commercial inhibitor packages may contain, in addition to the active ingredients for inhibition, other chemicals, including surfactants, deemulsifiers, carriers (e.g., solvents) and biocides.

The active ingredients of organic inhibitors invariably contain one or more functional groups containing one or more hetero atoms, N, O, S, P, or Se (selenium), through which the inhibitors anchor onto the metal surface. Some common anchoring groups are listed in Table 3. These groups are attached to a parent chain (backbone), which increases the ability of the inhibitor molecule to cover a large surface area. Common repeating units of the parent chain are methyl and phenyl groups. The backbone may contain additional molecules, or substituent groups, to enhance the electronic bonding strength of the anchoring group on the metal and/or to enhance the surface coverage. The outline of the constitution of an organic inhibitor is presented in Table 4.

1. Inhibitors Containing the Oxygen Atom

Benzoic acid and substituted benzoic acids are widely used as corrosion inhibitors [16]. Adsorption and inhibitor efficiencies of benzoic acids depend on the nature of the substituents. Electron-donating substituents increase inhibition by increasing the electron density of the anchoring group (-COOH group); on the other hand, electron-withdrawing substituents decrease inhibition by decreasing the electron density. Percent inhibition as a function of substituents is presented in Figure 7.

TABLE 4. Constitution of an Organic Corrosion Inhibitor

Anchoring Group ^a	Backbone	Substituent Groups ^a
Binds onto the metal	Bears anchoring and substituent groups Provides surface coverage	Supplements electronic strength and surface Coverage

^a Anchoring and substituent groups are interchangeable, that is, the substituent group through which the inhibitor anchor onto the metal surface depends on the electron density, charge on the metal and the orientation of the molecule in a particular environment.

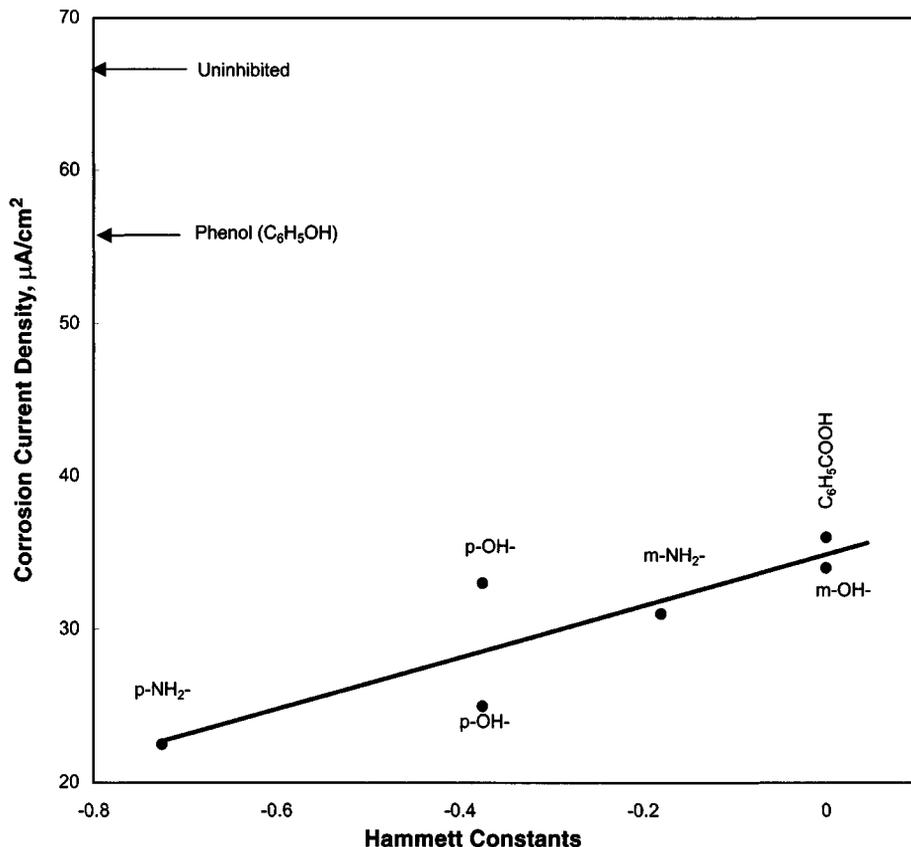


FIGURE 7. Variation of inhibitor efficiency as a function of substituents (benzoic acid) (substituents with negative Hammett constants will attract electrons from the anchoring $-\text{COOH}$ group, thereby decreasing the efficiency) [16]. (Hammett constant is a measure of ability of the substituents to attract or repel electrons).

2. Inhibitors Containing the Nitrogen Atom

Benzotriazole (BTA) and its derivatives are effective inhibitors for many metals, especially copper, in a variety of conditions [17]. At low concentrations, BTA is adsorbed slightly on the surface. At sufficiently high solution concentrations, bulk precipitation of the complex on the surface occurs, inhibiting corrosion. Formation of this complex is a slow process and, as a result, the inhibitor efficiency of BTA increases with time (Fig. 8).

3. Inhibitors Containing the Sulfur Atom

Thiourea and its derivatives are used as corrosion inhibitors for a variety of metals [18]. They are nontoxic and are not an environmental hazard. The variation in the inhibitor efficiencies of various derivatives of thiourea depends on the molecular weight. By using lower concentrations of large molecules, higher inhibitor efficiencies can be obtained (Table 5).

4. Electronically Conducting Polymers

In situ polymerisation of heterocyclic compounds, such as pyrrole and thiophene (structures in Fig. 6) and aniline, produces homogeneous, adhesive films on the metal surface [19]. These films are

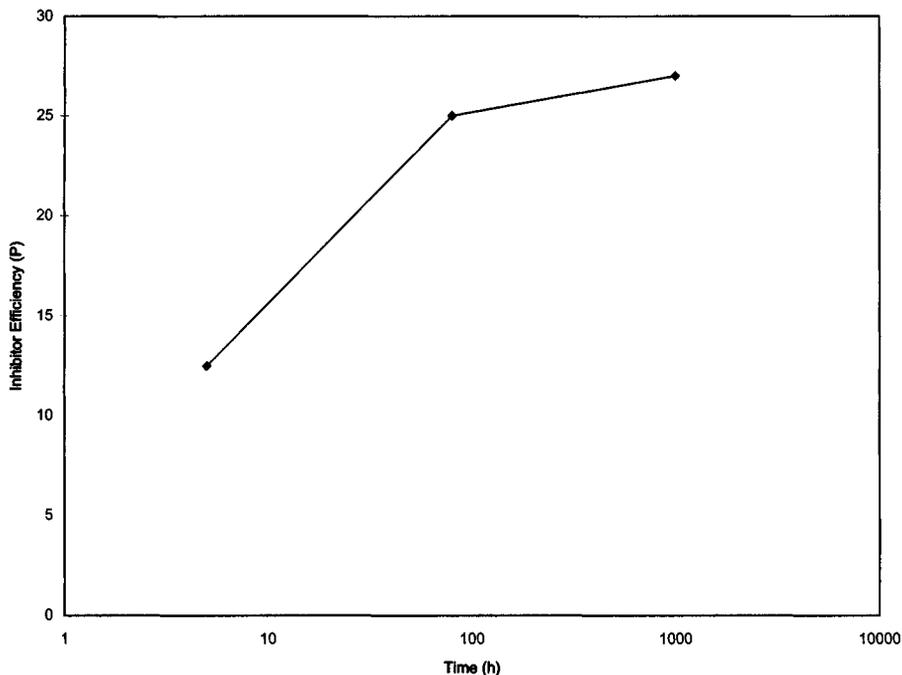


FIGURE 8. Dependence of inhibitor efficiency on time (benzotriazole on copper) [17].

TABLE 5. Concentrations of Substituted Thioureas Required to Produce 90% Inhibition^a

Inhibitor	Chemical Structure	Concentration, (mol/L)	Molecular Weight
Thiourea	$\text{H}_2\text{N}-\text{CS}-\text{NH}_2$	0.1	76.13
Allyl thiourea	$\text{H}_2\text{N}-\text{CS}-\text{NH}-\text{CH}_2\text{CH}=\text{CH}_2$	0.1	116.19
<i>N,N</i> -Diethyl thiourea	$\text{C}_2\text{H}_5\text{HN}-\text{CS}-\text{NHC}_2\text{H}_5$	0.003	132.23
<i>N,N</i> -diisopropylthiourea	$\text{C}_3\text{H}_7\text{HN}-\text{CS}-\text{NHC}_3\text{H}_7$	0.001	160.28
Phenyl	$\text{H}_2\text{N}-\text{CS}-\text{NH}-\text{C}_6\text{H}_5$	0.001	152.21
Thiocarbamide	$\text{C}_6\text{H}_5\text{HN}-\text{CS}-\text{NHC}_6\text{H}_5$	0.0006	228.38
Symdiotolythiourea	$\text{CH}_3\text{C}_6\text{H}_4\text{NH}-\text{CS}-\text{NHC}_6\text{H}_4\text{CH}_3$	0.0004	256.35

^a See [18].

electronically conducting and have the advantage of tolerance to microdefects and minor scratches. Conductivity can be up to 100 S/cm and can be varied depending on the extent of oxidation, from semiconductor to metal. Because of these properties, the films repassivate any exposed areas of metal where there are defects in the passive film. Conducting polymers are now used as inhibitors for metal corrosion.

5. Coordination Complexes

A variety of chelants provide either corrosion inhibition or corrosion acceleration, depending on the structure and functional groups. The chelants displaying high surface activity and low solubility in solution are effective corrosion inhibitors. If they do not have these characteristics, they stimulate corrosion.

The 8-hydroxyquinoline molecule satisfies the structural requirements for surface chelation, but formation of a nonadherent film is a distinct disadvantage (Fig. 9). On the other hand, pyrocatechols

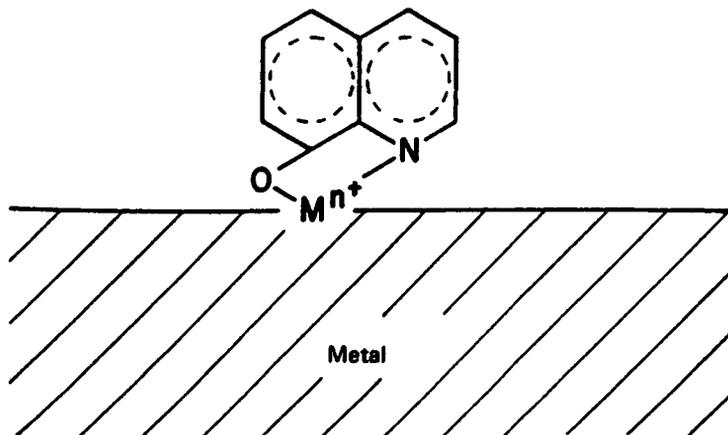


FIGURE 9. 8-Hydroxyquinoline surface chelation (Stable chelate complex is formed, but is soluble in aqueous medium—no corrosion inhibition) [20]. Copyright NACE International. Reprinted with permission.

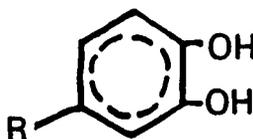


FIGURE 10. Pyrocatechols (forms insoluble chelate complex with the metal. Efficient corrosion inhibitor; also refer to Table 6) [20].

(Fig. 10), forming adherent chelants on the metal surface, are effective inhibitors. Inhibition efficiency can be increased by decreasing the solubility through alkylation (increase in chain length) (Table 6) [20].

E. INDUSTRIAL APPLICATIONS OF CORROSION INHIBITORS

1. Petroleum Production

Corrosion in the hydrocarbon industries may be divided into two types, “wet corrosion” and “dry corrosion.” At low temperature (i.e., below the boiling point or dew point of water), material corrodes due to the presence of an aqueous phase (wet corrosion). At higher temperature (above the boiling point of water), corrosion occurs in the absence of an aqueous phase (dry corrosion).

Wet corrosion is influenced by pressure, temperature, and compositions of aqueous, gaseous, and oil phases. In refineries and petrochemical plants, the amount of water is usually small, but the

TABLE 6. Dependence of Inhibitor Efficiency of Pyrocatechol on Chain Length^a

Inhibitor	Substituent (<i>R</i> value in Fig. 10)	% Inhibition
Pyrocatechol	—H	— 14
4-Methylpyrocatechol	—CH ₃	84
4- <i>n</i> -butylpyrocatechol	—(CH ₂) ₃ CH ₃	93
4- <i>n</i> -hexylpyrocatechol	—(CH ₂) ₅ CH ₃	96

^a See [20]. Copyright NACE International. Reproduced with permission.

corrosivity is high and is localized at regions where the aqueous phase contacts the metal. The water may contain dissolved hydrogen sulfide (H_2S), carbon dioxide (CO_2), and chloride ions (Cl^-). Corrosion may occur even when the produced water content is as low as 0.1%, or corrosion activity may not begin until after several years of production.

Refineries and petrochemical industries employ a variety of film-forming inhibitors to control wet corrosion. Most of the inhibitors are long-chain nitrogenous organic materials, including amines and amides. Water-soluble and water-soluble–oil-dispersible type inhibitors are continuously injected, or oil-soluble and oil-soluble–water-dispersible type inhibitors (batch inhibitors) are intermittently applied to control corrosion.

Film-forming inhibitors anchor to the metal through their polar group. The nonpolar tail protrudes out vertically. The physical adsorption of hydrocarbons (oils) on these nonpolar tails increases film thickness and the effectiveness of the hydrophobic barrier for corrosion inhibition [21].

Because inhibitors are interfacial in nature, they are active at liquid–liquid and/or liquid–gas interfaces and can lead to emulsification. As a result, foaming is sometimes experienced in the presence of inhibitors.

2. Internal Corrosion of Steel Pipelines

Gathering pipelines, operating between oil and gas wells and processing plants, have corrosion problems similar to those in refineries and petrochemical plants. The flow regimes of multiphase fluids in pipelines influence the corrosion rate. At high flow rates, flow-induced corrosion and erosion–corrosion may occur, whereas at low flow rates, pitting corrosion is more common.

Corrosion is related to the amount and nature of sediments. High-velocity flow tends to sweep sediments out of the pipeline, whereas low velocity allows sediments to settle at the bottom, providing sites for pitting corrosion. Internal corrosion of pipelines is controlled by cleaning the pipeline (pigging) and by adding continuous and/or batch inhibitors.

3. Water

Potable water is frequently saturated with dissolved oxygen and is corrosive unless a protective film, or deposit, is formed. Cathodic inhibitors, such as calcium carbonate, silicates, polyphosphates, and zinc salts, are used to control potable water corrosion.

Water is used in cooling system in many industries. In a recirculating system, evaporation is the chief source of cooling. As evaporation proceeds, the dissolved mineral salt content increases. Cooling systems may consist of several dissimilar metals and non-metals. Metals picked up from one part of the system can be deposited elsewhere, producing galvanic corrosion. Corrosion is controlled by anodic (passivating) inhibitors including nitrate and chromate as well as by cathodic (e.g., zinc salt) inhibitors. Organic inhibitors (e.g., benzotriazole) are sometimes used as secondary inhibitors, especially when excessive corrosion of copper occurs [22].

4. Acids

Acids are widely used in pickling, in cleaning of oil refinery equipment and heat exchangers, and in oil well acidizing. Mixed inhibitors are widely used to control acid corrosion.

5. Automobile

Inhibitors are used in an automobile for two reasons: (1) to reduce the corrosivity of fluid systems (internal corrosion), and (2) to protect the metal surfaces exposed to the atmosphere (external corrosion). Internal corrosion is influenced by the coolants, flow, aeration, temperature, pressure, water impurities and corrosion products, operating conditions, and maintenance of the system. Some common inhibitors dissolved in antifreeze are nitrites, nitrates, phosphates, silicates, arsenates, and

chromates (anodic inhibitors); amines, benzoates, mercaptans, and organic phosphates (mixed inhibitors); and polar or emulsifiable oils (film formers) [23].

Atmospheres to which automobiles are exposed contain moist air, wet SO₂ gas (forming sulfuric acid in the presence of moist air) and deicing salt (NaCl and CaCl₂). To control external corrosion, the rust-proofing formulations that are used contain grease, wax resin, and resin emulsion, along with metalloorganic and asphaltic compounds. Typical inhibitors used in rust-proofing applications are fatty acids, phosphonates, sulfonates and carboxylates.

6. Paints (Organic Coatings)

Finely divided inhibiting pigments are frequently incorporated in primers. These polar compounds displace water and orient themselves in such a way that the hydrophobic ends face the environment, thereby augmenting the bonding of the coatings on the surface. Red lead (Pb₃O₄) is commonly used in paints on iron. It deters formation of local cells and helps preserve the physical properties of the paints. Other inhibitors used in paints are lead azelate, calcium plumbate and lead suboxide [24].

7. Miscellaneous

Inhibitors are used to control corrosion in boiler waters, fuel oil tanks, hot chloride dye baths, refrigeration brines, and reinforcing steel in concrete, and they are also used to protect artifacts.

F. OTHER FACTORS IN APPLYING INHIBITORS

Some factors to be considered in applying inhibitors are discussed in the following paragraphs.

1. Application Techniques

A reliable method should be applied for inhibitor application. A frequent cause of ineffective inhibition is loss of the inhibitor before it either contacts the metal surface or changes the environment to the extent required. Even the best inhibitor will fail if not applied properly.

If the inhibitor is continuously applied in a multiphase system, it should partition into the corrosive phase, usually the aqueous phase. This partitioning is especially important when using water-soluble, oil-dispersible inhibitors.

In batch treatment, the frequency of treatment depends on the film persistency. It is important that the corrosion rates are measured frequently to ensure that a safe level of inhibition is maintained. It is also important that the inhibitor contacts the entire metal surface and forms a continuous persistent film.

When using volatile inhibitors, care must be taken in packaging to prevent the loss of inhibitor to the outside atmosphere.

Inhibitors are added to the primers used in paint coatings. When moisture contacts the paint, some inhibitor is leached from the primer to protect the metal. The inhibitor should be incorporated in such a way that it protects the areas where potential corrosion can take place, and not leach completely from the primer during the service life.

2. Temperature Effects

Organic molecules decompose at elevated temperatures. In general, film-forming inhibitors that depend on physical adsorption become less effective at elevated temperatures, so that larger treatment dosages may be required to maintain protective films. Chemisorption, on the other hand, increases with temperature due to the strengthening of chemical bonds. As a result, inhibitor efficiency increases with temperature up to the temperature at which decomposition of the inhibitor occurs.

3. Poisoning

Inhibitors for hydrogen damage should reduce not only the corrosion rate, but also the rate of absorption and permeation of hydrogen into the steel. For example, corrosion rate of steel in sulfuric acid is decreased [25], while hydrogen flux through a steel membrane is increased by adding thiourea [26]. Although thiourea inhibits corrosion, it poisons the hydrogen recombination reaction, so that much of the hydrogen produced at the steel surface enters the steel, causing hydrogen damage, rather than recombining with other hydrogen atoms to form bubbles of hydrogen that escape from the system.

4. Secondary Inhibition

The nature of the inhibitor initially present in acid solutions may change with time as a consequence of chemical or electrochemical reactions. Inhibition due to the reaction products is called secondary inhibition. Depending on the effectiveness of the reaction products, secondary inhibition may be higher or lower than primary inhibition. For example, diphenyl sulfoxide undergoes electrochemical reaction at the metal surface to produce diphenyl sulfide, which is more effective than the primary compound [27]. On the contrary, the reduction of thiourea and its alkyl (e.g., methyl, ethyl) derivatives gives rise to HS^- , which accelerates corrosion.

5. Synergism and Antagonism

In the presence of two or more adsorbed species, lateral interaction between inhibitor molecules can significantly affect inhibitor performance. If the interaction is attractive, a synergistic effect arises, that is, the degree of inhibition in the presence of both inhibitors is higher than the sum of the individual effects. For example, because of this synergistic effect, the inhibition efficiency of a mixture of formaldehyde and furfuralimine is higher compared to the inhibition efficiency when these inhibitors are used separately (Fig. 11). On the other hand, when narcotine and thiourea are

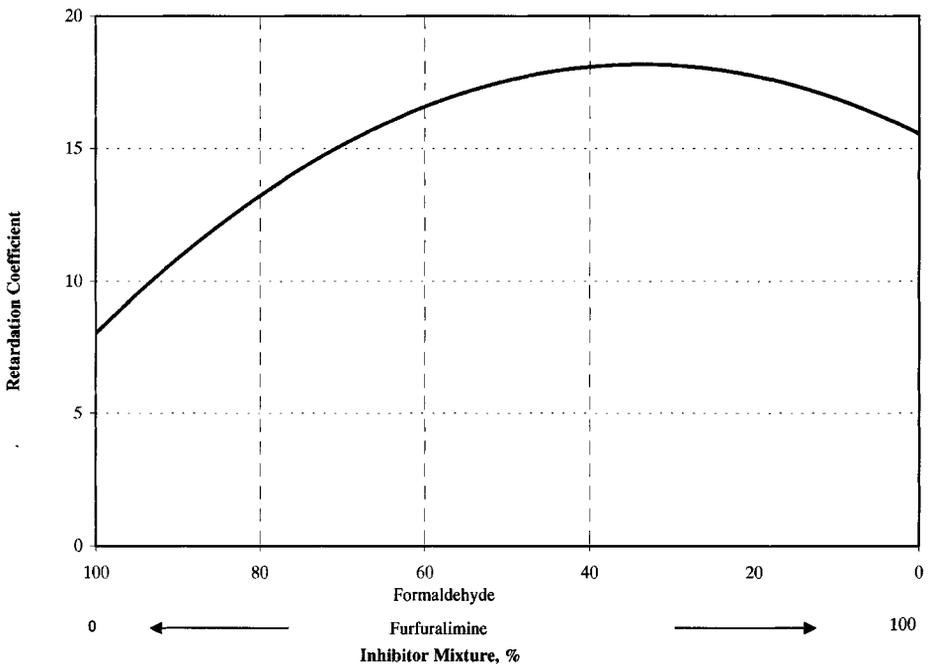


FIGURE 11. Synergistic effect of mixing formaldehyde and furfuralimine [28].

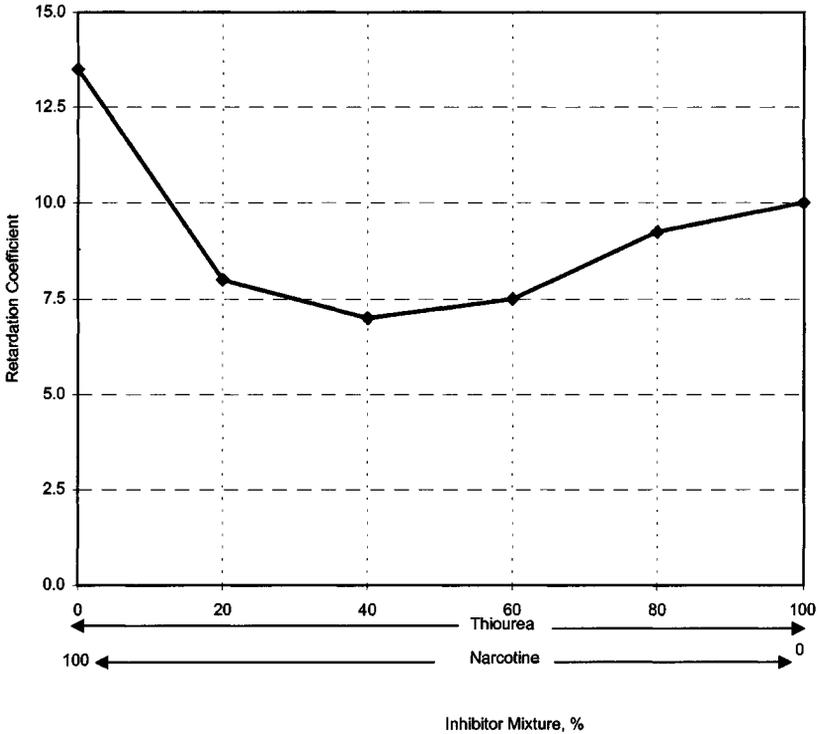


FIGURE 12. Antagonistic effect of mixing narcotine and thiourea [28].

used as mixed inhibitors, there is an antagonistic effect and a decrease in inhibitor efficiency compared to that which exists when these inhibitors are used separately (Fig. 12) [28].

6. Green Inhibitors

Environmental concerns worldwide are increasing and are likely to influence the choice of corrosion inhibitors in the future. Environmental requirements are still being developed, but some elements have been established.

The biodegradation, or biological oxygen demand (BOD), should be at least 60%, and inhibitors should be nontoxic [29]. The BOD is a measure of how long the inhibitor will persist in the environment. Toxicity is measured as LC₅₀ or EC₅₀³⁰. LC₅₀ is the concentration of the inhibitor needed to kill 50% of the total population of the test species. The results are quoted as milligrams of

TABLE 7. Toxicity of Corrosion Inhibitors^a

Compound	LC ₅₀ , (mg/kg)
Propargyl alcohol	55
Hexynol	34
Cinnamaldehyde	2200
Formaldehyde	800
Dodecylpyridinium bromide	320
Naphthylmethylquinolinium chloride	644
Nonylphenol-ethylene oxide surfactants	1310

^a See [30].

chemical per liter of fluid (or LD₅₀, milligrams per kilogram) for exposure times of 24 and 48 h. The EC₅₀ is the effective concentration of inhibitor to adversely affect 50% of the population. In general, EC₅₀ values are lower than LC₅₀ values because the former are the concentrations required to damage the species in some way without killing it. Some chemicals are excellent inhibitors, but are quite toxic and readily adsorbed through the skin. Toxicity of some inhibitors is presented in Table 7.

There is a growing demand for corrosion inhibitors that are less toxic and biodegradable compared to current formulations. Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in the future.

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