10

Corrosion Inhibitors

Corrosion of metallic surfaces can be controlled or reduced by the addition of chemical compounds to the corrodent. This form of corrosion control is called *inhibition* and the compounds added are known as *corrosion inhibitors.* These inhibitors will reduce the rate of either anodic oxidation, cathodic reduction, or both. The inhibitors themselves form a protective film on the surface of the metal. It has been postulated that the inhibitors are adsorbed onto the metal surface either by physical (electrostatic) adsorption or chemisorption.

Physical adsorption is the result of electrostatic forces between the organic ions and the electrically charged metal surface. Chemisorption is the transfer, or sharing, of the inhibitor molecule's charge to the metal surface, forming a coordinate-type bond. The adsorbed inhibitor reduces the corrosion rate of the metal surface either by retarding the anodic dissolution reaction of the metal, by the cathodic evolution of hydrogen, or both.

Inhibitors can be classified in many different ways according to:

1. Their chemical nature (organic or inorganic substances)
2. Their characteristics (oxidizing or nonoxidizing compounds)
3. Their technical field of application (pickling, acid cleaning, descaling, cooling water systems, etc.)

The most common and widely known use of inhibitors is their application in automobile cooling systems and boiler feed waters.

By considering the electrochemical nature of corrosion processes, constituted by at least two electrochemical partial reactions, inhibition may be defined on an electrochemical basis. Inhibitors will reduce the rates of either or both of these partial reactions (anodic oxidation and/or cathodic reduction). As a consequence, there can be anodic, cathodic, and mixed inhibitors.

Inhibitors can be used in electrolytes at different pH values, from acid to near-neutral or alkaline solutions. Because of the very different situations created by changing various factors such as medium and inhibitor in the system, metal/aggressive medium/inhibitor, various inhibition mechanisms must be considered.[1–6]

An accurate analysis of the different modes of inhibiting electrode reactions, including corrosion, was carried out by Fisher.[7] He distinguished among various mechanisms of action such as:

- Interface inhibition
- Electrolyte layer inhibition
- Membrane inhibition
- Passivation

Subsequently, Lorenz and Mansfield[8] proposed a clear distinction between interface and interphase inhibition, representing two different types of retardation mechanisms of electrode reactions, including corrosion. Interface inhibition presumes a strong interaction between the inhibitor and the corroding surface of the metal.[1, 7, 9] In this case, the inhibitor adsorbs as a potential-dependent, two-dimensional layer. This layer can affect the basic reactions in different ways:

- By a geometric blocking effect of the electrode surface because of the adsorption of a stable inhibitor at a relatively high degree of coverage of the metal surface.
- By blocking the effect of the surface sites because of the adsorption of a stable inhibitor at a relatively low degree of coverage.
- By reactive coverage of the metal surface. In this case, the adsorption process is followed by electrochemical or chemical reactions of the inhibitor at the interface.

According to Lorenz and Mansfield,[8] interface inhibition occurs in corroding systems exhibiting a bare metal surface in contact with the corrosive medium. This condition is often realized for active metal dissolution in acid solutions.

Interphase inhibition presumes a three-dimensional layer between the corroding surface and the electrolyte.[7, 10, 11] Such layers generally consist of weakly soluble corrosion products and/or inhibitors. Interphase inhibition is mainly observed in neutral media with the formation of porous or nonporous layers. Clearly, the inhibition efficiency strongly depends on the properties of the formed three-dimensional layer.

10.1 Inhibitor Evaluation

Because there may be more than one inhibitor suitable for a specific application, it is necessary to have a means of comparing the performance of each. This can be done by determining the inhibitor efficiency according to the following correlation:

$$I_{eff} = \frac{R_O - R_i}{R_O} \times 100$$

where I_{eff} is the efficiency of the inhibitor (%), R_0 is the corrosion rate of the metal without inhibitor present, and R_i is the corrosion rate of the metal with inhibitor present. R_0 and R_i can be determined by any of the standard corrosion testing techniques. The corrosion rate can be measured in any unit, such as weight loss (mpy), as long as the units are consistent across both tests.

10.2 Classification of Inhibitors

Inhibitors can be classified in several ways, as previously indicated. Inhibitors will be classified and discussed under the following headings:

1. Passivation inhibitors
2. Organic inhibitors
3. Precipitation inhibitors
4. Vapor phase inhibitors

10.2.1 Passivation Inhibitors

10.2.1.1 Mechanism of Passivation

Passivators in contact with a metal surface act as depolarizers initiating high current densities at residual anodic areas that exceed $i_{(critical)}$ for passivation. The only ions that can serve as passivators are those that have both an oxidizing capacity in the thermodynamic sense (noble oxidation-reduction potential) and that are readily reduced (shallow cathodic polarization curve (Figure 10.1). Hence, SO_4^- or ClO_4^- ions are not passivators for iron because they are not readily reduced, nor are NO_3^- ions compared to NO_2^-, because nitrates are reduced less rapidly than are nitrites, the former reducing too sluggishly to achieve the required high value of $i_{(critical)}$. The extent of chemical reduction on initial contact of a passivator with metal, according to this viewpoint, must be at least chemically equivalent to the amount of passive film formed as a result of such reduction. For the passive film on iron, this is on the order of 0.01 coulomb/cm^2 of apparent surface. The total equivalents corresponding to chemical reduction of chromates is found to be of this order and is probably also the same for other passivators acting on iron. The amount of chromate reduced in the passivation process derives

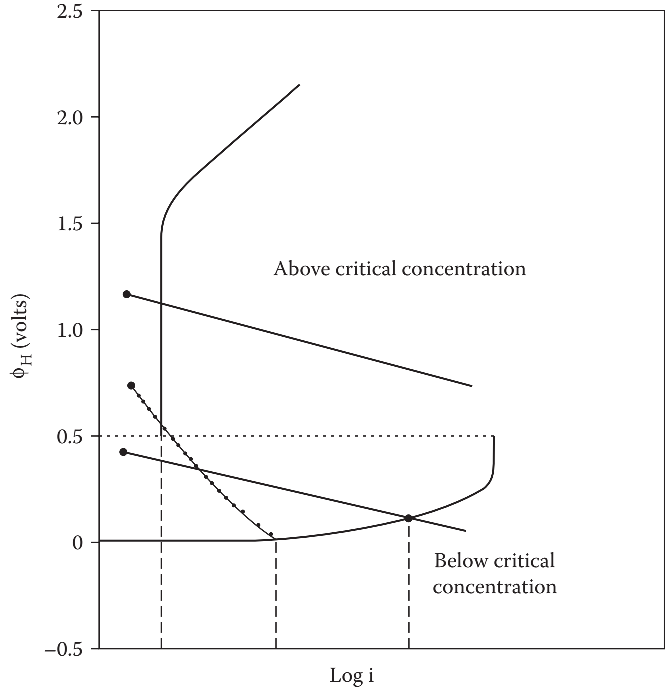

FIGURE 10.1
Polarization curves that show effect of passivator concentration on the corrosion of iron. An oxidizing substance that reduces sluggishly does not induce passivity (dotted cathodic polarization curve).

from measurements[12–14] of residual radioactivity of a washed iron surface after exposure to a chromate solution containing Cr 51. The following reaction applies, assuming, as measurements appear to substantiate,[15] that all reduced chromate (or dichromate) remains on the metal surface as adsorbed Cr[13] or as hydrated Cr_2O_3:

$$Cr_2O_7^{-2} + 8H^+ + \text{Fe surface} \rightarrow 2Cr^{3+} + 4H_2O + O_2O\,(\text{adsorbed on Fe})$$

$$E^0 = 0.79\,\text{volt}$$

Residual radioactivity accounts for 3×10^{16} Cr atoms/cm^2 (1.5×10^{-7} equivalents or 0.515 coloumb passive film substance/cm^2). The above equation assumes an adsorbed passive film structure, but the same reasoning applies whatever the structure.

Reduction of the passivator continues at a low rate after passivity is achieved in the absence of dissolved oxygen to the value of $i_{passive}$ slowly forming iron oxide and reduction products of chromate. From the observed corrosion rates of iron in contact with chromate solutions (<0.0001 ipy), it is estimated that $i_{passive}$ is less than 0.3 µamp/cm^2. The rate of reduction increases with factors that increase $i_{passive}$ such as the H^+ concentration, temperature, and Cl^- concentration. It is found in practice that less chromate is consumed as exposure time increases, which may be caused, in part, by a secondary film of oxides eventually covering the metal, thereby exposing less surface at which the passive film requires repair.

For optimum inhibition, the concentration of passivator must exceed a certain critical value. Below this concentration, passivators behave as active depolarizers and increase the corrosion rate in localized areas (pits). Lower concentrations of passivator correspond to more active values of the oxidation-reduction potential and eventually the cathodic polarization curve intersects the anodic curve in the active region instead of in the passive region (Figure 10.1).

The critical concentration for CrO_4^{2-}, NO_2^-, MoO_4^{2-}, or WO_4^{2-} is about 10^{-3} to 10^{-4} M.[16] A concentration of 10^{-3} M Na_2CrO_4 is equivalent to 0.016%, or 160 ppm. Chloride ions and elevated temperatures increase $i_{critical}$ as well as $i_{passive}$, which in effect raise the critical passivator concentration to higher values.

Should passivator concentration fall below the critical value in stagnant areas (e.g., at threads of a pipe or at crevices), the active potential of such areas in galvanic contact with passive areas elsewhere of noble potential promotes corrosion (pitting) at the active areas (passive-active cells). For this reason, it is important to maintain the concentration of passivators above the critical value at all portions of the inhibited system by the use of stirring, rapid flow rates, and avoidance of crevices or of surface films of grease and other dirt. Because consumption of passivators increases with an increase in chloride and sulfate ions, it is also essential to maintain as low a concentration of these ions as possible.

This is the most effective, and consequently, the most widely used type of inhibitor. Chromatics are the least expensive inhibitors for use in water systems and are widely used in the recirculating-cooling systems of internal combustion engines, rectifiers, and cooling towers. Sodium chromate in concentrations of 0.04 to 0.1% is used for this purpose. At higher temperatures or in freshwater that has chloride concentrations above 10 ppm, higher concentrations are required. If necessary, sodium hydroxide is added to adjust the pH to a range of 7.5 to 9.5. If the concentration of chromate falls below a concentration of 0.016%, corrosion will be accelerated. Therefore, it is essential that a periodic colormetric analysis be conducted to prevent this from happening.

Recent environmental regulations have been imposed on the use of chromates. They are toxic, and in prolonged contact with the skin can cause a rash. It is usually required that the Cr^{6+} ion be converted to Cr^{3+} before discharge. The Cr^{3+} ion is insoluble and can be removed as a sludge, whereas the Cr^{6+} ion is water soluble and toxic. Even so, the Cr^{3+} sludge is classified as a hazardous waste and must be constantly monitored. Because of the chromate ions cost of conversion, the constant monitoring required, and the disposal of the hazardous waste, the economics of the use of these inhibitors are not as attractive as they formerly were.

Because most antifreeze solutions contain methanol or ethylene glycol, chromates cannot be used for this application because they have a tendency to react with organic compounds. In these applications, borax ($Na_2B_4O_7$ $10H_2O$) that has added sulfonated oils to produce an oily coating and mercaptobenzothiazole are used. The latter material is a specific inhibitor for copper.

Nitrates are also used in antifreeze-type cooling water systems because they have little tendency to react with alcohols or ethylene glycol. Because they are gradually decomposed by bacteria, they are not recommended for use in cooling tower waters. Another application for nitrites is as a corrosion inhibitor for the internal surfaces of pipelines used to transport petroleum products or gasoline. Such inhibition is accomplished by continuously injecting 5 to 30% sodium nitrite solution into the line.

At lower temperatures, such as in underground storage tanks, gasoline can be corrosive to steel as dissolved water is released. This water, in contact with large quantities of oxygen dissolved in the gasoline, corrodes the steel and forms large quantities of rust. The sodium nitrite enters the water phase and effectively inhibits corrosion.

Nitrites are also used to inhibit corrosion by cutting-oil-water emulsions used in the machining of metals.

Passivating inhibitors can usually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential that constant monitoring of the inhibitor concentration take place.

Chromates are applied mostly as inhibitors for recirculating the cooling water of internal combustion engines, rectifiers, and cooling towers. The concentration of Na_2CrO_4 used for this purpose is about 0.04 to 0.1%, the higher concentrations being employed at higher temperatures or in freshwaters of chloride concentrations above 10 ppm. The pH is adjusted, if necessary, to 7.5 to 9.5 by the addition of NaOH. Periodic colormetric analysis is required to ensure that the concentration remains above the critical 10^{-3} M or 0.016% Na_2CrO_4. Sometimes, combinations of chromates and polyphosphates or other inhibitors permit the concentration of chromates to fall below the critical level. This results in some sacrifice of inhibiting efficiency but with adequate protection against pitting for the treatment of very large volumes of water employing cooling towers.

Corrosion rates of mild steel as a function of chromate and chloride concentration at various temperatures are shown in Table 10.1 Such data in the region of the critical chromate concentration are not readily reproduced because of erratic pitting behavior.

Nitrites are inhibitors only above about pH 6.0. In more acidic environments, they tend to decompose, forming volatile nitric oxide and nitrogen peroxide. In common with other passivators, they tend to induce pitting at concentrations

TABLE 10.1

Effect of Chromate Concentration, Chlorides, and Temperature on Corrosion of Mild Steel

Velocity of Spec: 37 cm/s: 14-day tests					
$Na_2Cr_2O_7 \cdot 2H_2O$ (g/L)		0	0.1	0.5	1.0
%NaCl	Temp. (°C)	Corrosion Rate (ipy)			
0	20	0.021	0.0001	0.0001	0.0000
	75	0.036	0.014[a]	0.0004	0.0002
	95	0.017	0.011[a]	0.0004	0.0000
0.002	20	0.026	0.0006	0.0000	0.0000
	75	0.067	0.005[a]	0.0002	0.0000
	95	0.021	0.017[a]	0.005[a]	0.0003
0.05	20	0.031	0.0012	0.0015	0.0008
	75	0.085	0.002	0.003	0.002
	95	0.023	0.007[a]	0.005[a]	0.002
3.5	20	0.024	0.0017	0.0016	0.0015
22.0	20	0.007	0.0009	0.0006	0.0013

[a] Pitted.

near the critical value in the presence of Cl^- or SO_4^{2-} ions. In this regard, nitrites are less sensitive to Cl^- than to SO_4^{2-} contrary to the situation for chromates.

Zinc molybdate has been suggested as an inhibiting pigment for paints, being white instead of the characteristic yellow of chromates. It is also said to be less toxic than chromates.

10.2.2 Organic Inhibitors

A variety of organic compounds are used as inhibitors. Common among them are amines, imines, thiourea, mercaptans, guanidine, and aldehydes. These compounds are chemisorbed on the metal surface, forming a monolayer that interferes with both the anodic and cathodic processes, although in many cases the effect is equal. The chemisorption is effected through the presence of a polar group in the molecular structure by which the molecules can attach themselves to the metal surface. These include sulfur, nitrogen, amine, phosphorous, and hydroxyl groups.

Cationic inhibitors (such as amines) or anionic inhibitors (such as sulfonates) will be adsorbed preferentially, depending on whether the metal is negatively or positively charged with respect to the solution. Amines show better performance as inhibitors for steel in phosphoric acid in the presence of iodides. The explanation for this synergism is that the adsorption of iodide ions shifts the surface charge of steel to more negative values, where the adsorption of positively charged amines is favored. The fact that a certain

TABLE 10.2

Inhibition Efficiency of Some Pyridinium Derivatives at the Same Molar Concentration (1×10^{-4} M) on Armco Iron in Hydrochloric and Sulfuric Acid Solutions at 12°C

	Inhibition Efficiency (%)	
Additive	**1 N HCl**	**1 N H_2SO_4**
n-Decylpyridinium bromide	87.6	20.0
n-Decyl-3-hydroxypyridinium bromide	94.8	57.5
n-Decyl-3-carboxypyridinium bromide	92.7	76.5
n-Decyl-3-5-dimethylpyridinium bromide	92.5	30.2

10.3.2 Chemisorption

Another type of metal/inhibitor interaction is chemisorption. This process involves charge sharing or charge transfer from the inhibitor molecules to the metal surface in order to form a coordinate type of bond.

The chemisorption process takes place more slowly than electrostatic adsorption and with a higher activation energy. It depends on the temperature, and higher degrees of inhibition should be expected at higher temperatures. Chemisorption is specific for certain metals and is not completely reversible. The bonding occurring with electron transfer clearly depends on the nature of the metal and the nature of the organic inhibitor. In fact, electron transfer is typical for metals having vacant, low-energy electron orbitals. Concerning inhibitors, electron transfer can be expected with compounds having relatively loosely bound electrons. This situation may arise because of the presence in the adsorbed inhibitor of multiple bonds or aromatic rings, whose electrons have π character. Clearly, even the presence of heteroatoms with one lone pair of electrons in the adsorbed molecule will favor electron transfer. Most organic inhibitors are substances with at least one functional group regarded as the reaction center for the chemisorption process. In this case, the strength of the adsorption bond is related to the heteroatom electron density and to the functional group polarizability. For example, the inhibition efficiency of a homologous series of organic substances differing only in the heteroatom is usually in the following sequence:

$$P > Se > S > N > O$$

An interpretation may be found in the easier polarizability and lower electronegativity of the elements on the left in the above sequence. On this basis, a surface bond of a Lewis acid-base type, normally with the inhibitor as the electron donor and the metal as the electron acceptor, has been postulated.

Dicyclohexylamine nitrite is a widely used vapor inhibitor that is often impregnated in the waxed paper or cardboard used for wrapping and packaging. One gram of this inhibitor saturates about 550 M^3 of air and the protection to steel is provided over years. Cyclohexylamine carbonate has a higher vapor pressure and is used in packages that must be opened and closed repeatedly.

The mechanism of inhibition is not the same for all vapor-phase inhibitors. Nitrite ions and benzoate ions in association with oxygen present passivate the steel surface. Carbonate provides alkalinity to the environment and the organic amine portion of the inhibitor effectively provides protection through adsorption.

While the vapor-phase inhibitors, in general, are effective in the prevention of corrosion in steel, they accelerate the corrosion of some nonferrous metals. The vapor-phase inhibitors based on nitrobenzoate organic compounds have been reported to protect ferrous, copper, and other alloy systems.

10.3 Inhibition in Acid Solution

The inhibition of corrosion in acid solutions can be accomplished using a variety of organic compounds. Among those used for this purpose are triple-bonded hydrocarbons, acetylenic alcohols, sulfoxides, sulfides, and mercaptans; aliphatic, aromatic, or heterocyclic compounds containing nitrogen; and many other families of simple organic compounds and of condensation products formed by the reaction between two different species such as amines and aldehydes.

Incorrect choice or the use of organic inhibitors in acid solutions can lead to corrosion stimulation and/or hydrogen penetration into the metal. In general, stimulation of corrosion is not related to the type or structure of the organic molecule. Stimulation of iron's corrosion has been found with mercaptans, sulfoxides, azoles, and triazole derivatives, nitrites, and quinoline. This adverse action depends on the type of acid. For example, bis(4-dimethylamino-phenylantipyrilcarbinol and its derivatives at a 10^{-4} concentration inhibited attack of steel in hydrochloric acid solutions but stimulated attack in sulfuric acid solutions. Much work has been done studying the inhibiting and/or stimulating phenomena of organic compounds on ferrous as well as nonferrous metals. Organic inhibitors have a critical concentration value, below which inhibition ceases and stimulation begins. Therefore, it is essential that when organic inhibitors are used, constant monitoring of the solution should take place to ensure that the inhibitor concentration does not fall below the critical value.

organic compound acts as a good inhibitor for some metals but not others is explained from this specific electronic interaction of the polar groups with the metal surface.

The molecular structure and size of the organic compound influence their inhibitive action. The structures with benzene rings are particularly effective inhibitors. Primary amines become more effective as the chain length increases. This is presumably because of the steric effect (i.e., diffusion barrier) provided by long chains. However, for mercaptans and aldehydes, the efficiency decreases with the increasing chain length. The sharp decrease in corrosion rate with organic inhibitors is shown in Figure 10.2.

Sodium benzoate, sodium cinnamate, and sodium pyrophosphate are examples of nonoxidizing compounds that effectively passivate iron in the near-neutral range, apparently by facilitating the adsorption of dissolved oxygen. As little as 10^{-4} M sodium benzoate (0.0014%) effectively inhibits in aerated distilled water, but inhibition is not observed in deaerated water.

Organic inhibitors find application as pickling inhibitors. Acid pickling of hot-rolled steel is necessary to remove mill scale. Pickling inhibitors resist corrosion of the substrate metal. These inhibitors are used for acid cleaning

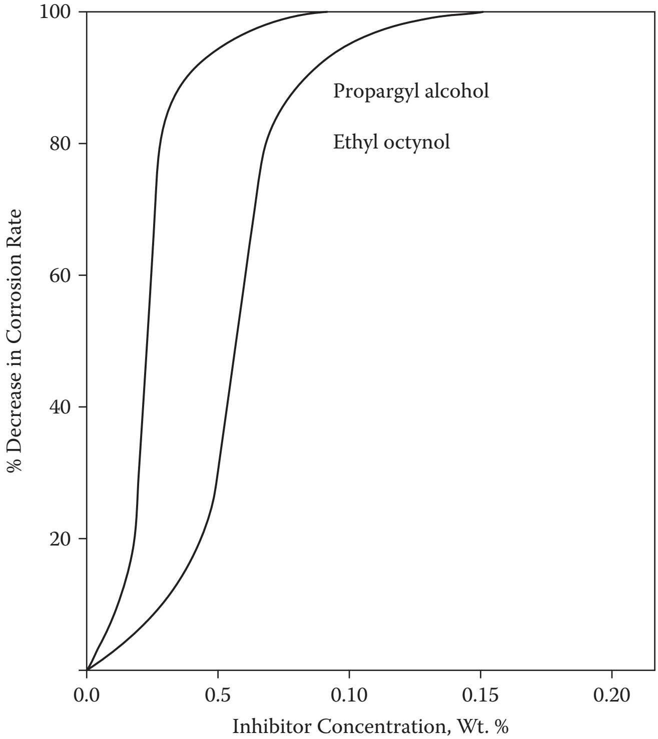

FIGURE 10.2
Effect of concentration of organic inhibitors on corrosion rate.

It is generally assumed that the first stage in the action mechanism of inhibitors in aggressive acid media is adsorption of the inhibitors onto the metal surface. This adsorption process is influenced by the nature and surface charge of the metal, by the chemical structure of the inhibitor, and by the type of aggressive electrolyte. Physical (or electrostatic) adsorption and chemisorption are the principal types of interaction between an organic inhibitor and a metal surface.

10.3.1 Physical Adsorption

Physical adsorption is the result of electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. The surface charge of the metal is due to the electric field at the outer Helmholtz plane of the electrical double layer existing at the metal/solution interface. The surface charge can be defined by the potential of the metal (E_{corr}) vs. its zero charge potential (ZCP) ($E_{q=0}$).[12] When the difference $E_{corr} - E_{q=0} = ø$ is negative, carbon adsorption is favored. Adsorption of anions is favored when ø becomes positive. This behavior is related not only to compounds with formal positive or negative charge, but also to dipoles whose orientation is determined by the value of the ø potential.

According to Antropov,[16] at equal values of ø for different metals, similar behavior of a given inhibiting species should be expected in the same environment. This has been verified for adsorption of organic charged species on mercury and iron electrodes at the same potential for both metals.

In studying the adsorption of ions at the metal/solution interface, it was first assumed that ions maintained their total charge during the adsorption, giving rise in this way to a pure electrostatic bond. Lorenz[17–19] suggested that a partial charge is present in the adsorption of ions; in this case, a certain amount of covalent bond in the adsorption process must be considered. The partial charge concept was studied by Vetter and Schulze,[20–22] who defined as electrosorption valency the coefficient for the potential dependence and charge flow of electrosorption processes. The term "electrosorption valency" was chosen because of its analogy with the electrode reaction valency that enters into Faraday's law as well as the Nernst equation.

Considering the concepts discussed above in relation to corrosion inhibition, when an inhibited solution contains adsorbable anions, such as halide ions, these adsorb onto the metal surface by creating oriented dipoles and consequently increase the adsorption of the organic cations on the dipoles. In these cases, a positive synergistic effect arises; therefore, the degree of inhibition in the presence of both adsorbable anions and inhibitor cations is higher than the sum of the individual effects. This could explain the higher inhibition efficiency of various organic inhibitors in hydrochloric acid solutions compared to sulfuric acid solutions (see Table 10.2).

of the pipes clogged with rust or to remove limestone crust from inside the boiler tubes. Typical examples of pickling inhibitors are quinolin ethiodide, *o*- and *p*-tolythiourea, hexamethylene tetramine, formaldehyde, and *p*-thiocresol. They are added in concentrations of 0.01 to 0.1%. Organic inhibitors are also added to oils, greases, and waxes used as slushing compounds to temporarily protect steel surfaces from rusting during shipment or storage.

10.2.3 Precipitation Inhibitors (Cathodic Inhibitors)

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Cathodic inhibitors interfere with the cathodic processes and the rate of corrosion thereby decreases. They fall into three catergories: cathodic precipitates, oxygen scavengers, and hydrogen evolution poisons.

Calcium and magnesium carbonates, which are often present in natural waters, can be precipitated to form protective cathodic deposits with the adjustment of pH. The addition of zinc also inhibits corrosion by precipitating insoluble $Zn(OH)_2$ at increased alkalinity on the cathodic areas according to the reaction:

$$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$$

Hydrogen evolution poisons interfere with the formation of hydrogen gas ($2H_{ads} \rightarrow H_2$) to retard the overall rate of the cathodic reaction of hydrogen evolution. The corrosion rate consequently decreases. Sulfides, selenides, and compounds (usually oxides) of arsenic, antimony, and bismuth act as hydrogen evolution poisons. They are effective inhibitors in strong acids where the hydrogen evolution rate is controlling in the corrosion process. One difficulty is caused by these inhibitors: they cause blistering and hydrogen embrittlement in certain grades of steel because of the entry of atomic hydrogen into the metal. Also, arsenic, being toxic, is restricted in use.

10.2.4 Vapor-Phase Inhibitors

Vapor phase inhibitors (VPIs) are compounds with low vapor pressures (0.0002 to 0.4 mm Hg). In a closed system, they volatilize and the vapor condenses on the metal surface to provide protection. In boilers, volatile basic compounds such as morpholine and ethylenediamine are transported with steam to the condenser tubes; this prevents corrosion of the tubes by neutralizing carbonic acid and making the environment alkaline. In closed containers and packages, volatile solids such as nitrite, carbonate, and benzoate salts of dicyclohexylamine, cyclohexylamine, and hexamethylene imine are used for temporary protection of critical machine parts, ball bearings, cold-rolled steel coils, etc. during storage or transportation.

Chelating agents of the surface-active variety also act as efficient corrosion inhibitors when insoluble surface chelates are formed. Various surface-active chelates recommended for corrosion inhibition of different metals are shown below.

Chelating agents used as corrosion inhibitors in near-neutral solutions include:

Chelating Agent	Type of Metal Protected
Alkyl-catechol derivatives, sarcosine derivatives, carboxymethylated fatty amines, and mercaptocarboxylic acids	Steel in industrial cooling systems
Azo compounds, cupferron, and rubeanic acid	Aluminum alloys
Azo derivatives and alkyl esters of thioglycolic acid	Zinc and galvanized steel
Oximes and quinoline derivatives	Copper
Cresolphthalexon and thymolphthalexon derivatives	Titanium in sulfuric acid solutions

10.5 Inhibition of Alkaline Solutions

All metals whose hydroxides are amphoteric and metals covered by protective oxides that are broken in the presence of alkalies are subject to caustic attack. Localized attack may also occur as a result of pitting and crevice formation.

Organic substances such as tannions, gelatin, and agar-agar are often used as inhibitors for the protection of aluminum, zinc, copper, and iron. Other materials also found effective include thiourea, substituted phenols, β-diketones, 8-hydroxyquinoline, and quinalizarin.

10.6 Temporary Protection with Inhibitors

Occasions arise when temporary protection of metallic surfaces against atmospheric corrosion is required. Typical instances are in the case of finished metallic materials or of machinery parts during transportation and/or storage prior to use. When ready for use, the surface treatment or protective layer can be easily removed.

It is also possible to provide protection by controlling the aggressive gases or by introducing a vapor-phase inhibitor. This latter procedure can only be

It is well known that pitting depends not only on the concentration of the aggressive anions in the solution, but also on the concentration of the nonaggressive anions. For this reason, special attention must be paid to the effect of inhibitor anions in the aggressive solution. The presence of nonaggressive anions produces different effects:

1. Shifting the pitting potential to more positive values
2. Increasing the induction period for pitting
3. Reducing the number of pits

It has been found that pit nucleation on iron electrodes in phthalate buffer containing chloride ions was prevented by pictate ions. The pitting potential of iron in borate buffer containing chloride ions is enhanced by the presence of capronate. On the other hand, sulfate ions can reduce the current density at the pit bottom area, inhibiting the propagation stage of pitting corrosion.

Dezincification is the most common example of selective leaching. It is usually prevented by using less-susceptible alloys. The phenomenon can also be minimized by reducing the aggressive of the environment with corrosion inhibitors. The addition of surface-active substances such as saponin, dextrin, or benzotriazole can inhibit dezincification of single-phase and dibasic brass in 0.5 N NaCl and HCl solutions. The highest inhibition efficiency was obtained by benzotriazole.

Mild steels are susceptible to SCC in nitrate, caustic, and carbonate solutions. It has been demonstrated that the presence of inorganic ions (e.g., nitrate or chromate) or organic chemicals (e.g., acetate, benzoate) can inhibit the localized attack.

Research on SCC inhibition with austenitic stainless steels in magnesium chloride solutions has been performed by Lee and Uhlig[27] and Pinard[28]. In the presence of small concentrations of piperidine, n-decylamine, and other nitrogen-containing substances, it was possible to noticeably lengthen the failure time of AISI 304 wires under constant load in boiling chloride solutions.

The influence of some organic substances on the stress corrosion cracking of austenitic stainless steels in sulfuric acid solutions containing chlorides or in dilute hydrochloric acid solutions at room temperature has also been studied. Very promising results have been obtained with benzonitrile, 2-mercaptobenzimidazole, 2-mercaptobenzothiozole, and thiourea deratives, depending on the type of aggressive medium. The overall results support the idea that SCC of austenitic stainless steels in acid chloride media occurs on the alloys in the active state and is related to the presence of an adsorbed layer of chloride ions. The stress brings “bare” metal areas, which are more active than the surrounding areas, into contact with the solution. A very localized attack can thus occur with the consequent formation of a crack. In this way, only organic substances able to rapidly adsorb onto the surface

In most neutral solutions, the corrosion process of metals results in the formation of sparingly soluble products, such as oxides, hydroxides, or salts. The cathodic partial reaction is oxygen reduction.

Inorganic or organic compounds as well as chelating agents are used as inhibitors in near-neutral aqueous solutions. Inorganic inhibitors can be classified according to their mechanisms of action:

1. Formation and maintenance of protective films can be accomplished by the addition of inorganic anions such as polyphosphates, phosphates, silicates, and borates.
2. Oxidizing inhibitors, such as chromates and nitrites, cause self-passivation of the metallic material. It is essential that the concentration of these inhibitors be maintained above a “safe” level. If not, severe corrosion can occur as a result of pitting or localized attack caused by an oxidizer.
3. Precipitation of carbonates on the metal surfaces forming a protective film. This usually occurs because of the presence of Ca^{2+} and Mg^{2+} ions usually present in industrial waters.
4. Modification of protective film properties is accomplished by the addition of Ni^{2+}, Co^{2+}, Zn^{2+}, or Fe^{2+}.

The sodium salts of organic acids such as benzoate, salicylate, cinnamate, tartrate, and azelate can be used as alternatives to the inorganic inhibitors, particularly in ferrous solutions. When using these particular compounds in solutions containing certain ions such as chlorides or sulfates, the inhibitor concentration necessary for effective protection will depend on the concentration of the aggressive anions. Therefore, the critical pH value for inhibition rather than the critical concentration must be considered. Other formulations for organic inhibition of near-neutral solutions are shown in the following table:

Organic Inhibitors for Use in Near-Neutral Solutions

Inhibitor	**Type of Metal Protected**
Organic phosphorus-containing compounds, salts of aminomethylenephosphoric acid, hydroxyethllidenediphosphoric acid, phosphenocarboxylic acid polyacrolate, poly-methacrylate	Ferrous
Borate or nitrocinnamate anions (dissolved oxygen in solution required)	Zinc, zinc alloys
Acetate or benzoate anions	Aluminum
Heterocyclic compounds such as benzotriazole and its derivatives, 2-mercaptobenzothiozole, 2-mercaptobenzimidazole	Copper, copper-based alloys

accomplished in a closed environment such as sealed containers, museum showcases, or silmiar enclosures.

Organic substances used as contact inhibitors or vapor inhibitors are compounds belonging to the following classes:

1. Aliphatic, cycloaliphatic, aromatic, and hetrocylic amines
2. Amine salts with carbonic, carbamic, acetic, benzoic, nitrous, and chromic acids
3. Organic esters
4. Nitro derivatives
5. Acetylenic alcohol

10.7 Inhibition of Localized Corrosion

Corrosion inhibitors are usually able to prevent general corrosion but their effect on localized corrosion processes is limited. Generally, a higher inhibitor concentration is required to prevent localized corrosion processes than is necessary to inhibit general corrosion.

Staehle[25] examined the possibility of inhibiting localized attack that does not depend on metallurgical structures. He considered phenomena related to:

- Geometric effects, such as galvanic corrosion and crevice corrosion
- Simple localization of the attack, such as pitting and dezincification
- Effects of relative motion, such as erosion and cavitation

The application of organic inhibitors to control galvanic corrosion presents several problems. It is well known that an inhibitive treatment efficient on a single metal, because of the specific action of the inhibitor, may fail to control corrosion if dissimilar metals are in contact. The behavior of a zinc-steel couple in sodium benzoate solution was studied by Brasher and Mercer.[26] Steel is protected in benzoate solution but usually it corrodes when coupled to zinc, as in galvanized iron, in that solution. An interpretation of the phenomena was given, emphasizing that rusting of steel coupled to zinc in benzoate solution can be prevented by bubbling air through the solution for 1 or 2 days immediately after immersion. After this time, the system should have become stabilized and no corrosion of the steel should take place when the air stream is discontinued. In the study of the steel-copper combination in a hot-water system, the best inhibitor efficiency was obtained using a mixture of benzoate and nitrite.

10.3.3 Interactions between Adsorbed Inhibitors

When the coverage of the metal surface by the adsorbed inhibitor species increases, lateral reactions between inhibitor molecules may arise, thereby influencing efficiency.

Attractive lateral interactions usually give rise to stronger adsorption and higher inhibition efficiency. This effect has been shown in the case of compounds containing long hydrocarbon chains, because of attractive van der Waals forces. In the presence of ions or molecules containing dipoles, repulsive attractions may occur, thus weakening the adsorption and diminishing the inhibition efficiency.

10.3.4 Relationships between Inhibitor Reactivity and Efficiency

The nature of the inhibitor initially present in acid solutions may change with time and/or electrode potential as a consequence of reduction reactions, polymerization reactions, or the formation of surface products. The inhibition because of the reaction products is usually called secondary inhibition, whereas primary inhibition is attributed to the compound initially added to the solution. Secondary inhibition may be higher or lower than primary inhibition, depending on the effectiveness of the reaction products.

An example of inhibitors undergoing electrochemical reduction is that of sulfoxides, the most important being dibenzyl sulfoxide, whose reduction gives rise to a sulfide that is more effective than the primary compound.

On the contrary, the reduction of thiourea and its alkyl derivatives gives rise to HS^- ions, whose accelerating effect is known. In some instances, the reduction reaction may be followed by polymerization reactions at the metal/electrolyte interface. This mechanism of action is generally accepted for acetylenic derivatives. Electrochemical measurements on iron electrodes in sulfuric acid solutions inhibited by alkynes showed that acetylenic compounds act as cathodic inhibitors, giving rise to a surface barrier phenomenon. Duwell et al.[24] found hydrogenation and dehydration reaction products in heptane extracts of acid/iron powder/ethynylcyclohexan-1-ol. According to Duwell et al., the efficiency of ethynylcyclohexan-1-ol as a corrosion inhibitor apparently depends on the properties and rates of formation of the reaction products.

10.4 Inhibition of Near-Neutral Solutions

Because of the differences in the mechanisms of the corrosion process between acid and near-neutral solutions, the inhibitors used in acid solutions usually have little or no inhibition effect in near-neutral solutions. In acid solutions, the inhibition action is due to adsorption on oxide-free metal surfaces. In these media, the main cathodic process is hydrogen evolution.

zones where the layer is destroyed by the mechanical stress can block the fissuring attack by inhibiting the anodic process of metal dissolution.

With regard to corrosion fatigue, there are two principal ways to mitigate the phenomenon: (1) by lowering the stress amplitude or (2) by reducing the corrosivity of the medium. The latter can be achieved by varying pH, decreasing temperature, or adding inhibitors.

10.8 Summary

Corrosion inhibitors are usually able to prevent general or uniform corrosion. However, they are very limited in their ability to prevent localized corrosion such as pitting, crevice corrosion, galvanic corrosion, or stress corrosion cracking. Additional research work is being undertaken in the use of inhibitors to prevent these types of corrosion. The importance of these studies is realized when it is taken into account that only about 30% of all failures because of corrosion in chemical plants result from general corrosion. The remaining 70% is due to stress corrosion cracking, corrosion fatigue, and erosion corrosion. Attack on metals by general corrosion can be predicted and life spans of the equipment determined and/or the corrosion rates reduced by the use of inhibitors. This is not the case with other types of corrosion.

The use of inhibitors can be advantageous in certain cases. However, before using inhibitors, it is essential that the efficiency of the inhibitor to be used be determined to ensure that inhibition will take place.

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