

CORROSION INHIBITORS

Edited by

C. C. NATHAN



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CONTENTS

| | Page | | Page |
|--|------|---|------|
| Scope and Importance of Inhibitor Technology <i>Norman E. Hamner</i> | 1 | Inhibitors for Potable Water <i>George B. Hatch</i> | 114 |
| Theoretical Aspects of Corrosion Inhibitors and Inhibition <i>Olen L. Riggs, Jr.</i> | 7 | Inhibition of Cooling Water <i>George B. Hatch</i> | 126 |
| Methods of Evaluation and Testing of Corrosion Inhibitors <i>E. Schaschl</i> | 28 | Inhibitors in Desalination Systems <i>Billy D. Oakes</i> | 148 |
| Corrosion Inhibitors in Refineries and Petrochemical Plants Part 1 | 42 | Inhibitors in Acid Systems <i>George Gardner</i> | 156 |
| Part 2—Control of Fouling | 55 | Application of Inhibitors in Automobiles and Their Environment <i>Leonard C. Rowe</i> | 173 |
| <i>C. C. Nathan</i> | | Inhibitors in Organic Coatings <i>Norman E. Hamner</i> | 190 |
| Corrosion Inhibitors in Petroleum Production Primary Recovery <i>Al Nestle</i> | 61 | Inhibition and Corrosion Control Practices for Boiler Waters <i>J. H. Metcalf</i> | 196 |
| Corrosion Inhibition in Secondary Recovery <i>A. K. Dunlop</i> | 76 | Inhibitors for Temporary Protection Part 1—Oil and Grease Coatings | 220 |
| Control of Internal Corrosion of Pipelines Carrying Refined Petroleum Products | 89 | Part 2—Vapor Phase Corrosion Inhibitors | 224 |
| Control of Internal Corrosion of Pipelines Carrying Crude Oil | 95 | <i>D. F. Knaack and D. Brooks</i> | |
| Inhibition of Natural Gas Pipelines | 96 | Microbiological Corrosion and Its Control <i>J. M. Sharpley</i> | 228 |
| Inhibition of Tanks and Other Structures Handling Crude Petroleum <i>Ivy M. Parker</i> | 98 | Controlling Corrosion in Pulp and Paper Mills <i>A. J. Piluso</i> | 236 |
| Inhibition of Tankships Transporting Refined Petroleum Products | 100 | Inhibition of Aluminum <i>A. H. Roebuck</i> | 240 |
| Controlling Corrosion in Petroleum Drilling and in Packer Fluids <i>H. E. Bush</i> | 102 | Inhibition of Corrosion From Caustic Attack <i>A. H. Roebuck</i> | 245 |
| | | Application of Inhibitors in Miscellaneous Environments <i>Norman E. Hamner</i> | 251 |
| | | Index | 261 |

Scope and Importance of Inhibitor Technology

NORMAN E. HAMNER*

Introduction

Information about inhibitors is scattered throughout the corrosion literature and frequently is concealed under a poultice of semantics so thick that only the most vigorous digging brings it to light. Also, like many other technical words, "inhibitor" labors under the difficulty that not everyone agrees on exactly what an inhibitor is and few agree on all aspects of the manner in which inhibitors function.

The definition of inhibitor favored by the National Association of Corrosion Engineers is:

A substance which retards corrosion when added to an environment in small concentrations.¹

While this is not a perfect definition, it will be one of the bases on which this book on inhibitors is oriented. There are temporary excursions around the limits of this description, but most discussions will center on this definition.

The subject of mechanisms by which inhibitors work will be discussed elsewhere in this work, but it is useful to paraphrase a statement about the fundamentals of inhibitor mechanisms found in a recent publication.² The statement is that inhibitors function:

1. By adsorption as a thin film onto the surface of a corroding material.
2. By inducing formation of a thick corrosion product.
3. By changing characteristics of the environment either by producing protective precipitates or removing or inactivating an aggressive constituent so that it does not corrode the material.

Sometimes more than one of these effects takes place.

These mechanisms cover most of the observed effects and form the bases for experimental work leading to the development of inhibitors as well as schemes for their use. It also is the main premise of the book "Corrosion Inhibitors," by J. I. Bregman, which this volume attempts to succeed.

It will be useful also to consider the contents of Dr. Bregman's book and to understand the philosophy of the present work. Because Dr. Bregman's book has been out of print for some time, there has been some urgency to get a successor volume into circulation for those involved in inhibitor technology.

Contents of Predecessor Book

By agreement with J. I. Bregman, the National Association of Corrosion Engineers has prepared a successor to his book for publication. The association's aims, set forth in greater detail later in this chapter, were to bring his book up to date with technology developed since its preparation and to increase the scope of this work to cover many areas of inhibitor importance that he did not cover.

Dr. Bregman's book was limited intentionally to "problems caused by water in certain aqueous and petroleum systems." As a result, many of the industrial areas in which inhibitors are commonly used either are not mentioned or are discussed only superficially by him. Because the scope of the present work is broader, it is obvious that a number of persons must contribute to this volume because no one person could expect to have sufficient competence in the diverse areas in which inhibitors are used to do justice to all of them.

Active work on this book began late in 1969. Its comprehensiveness is a tribute to the editor and a credit to numerous collaborators, not all of whom are listed in the author index.

Objectives of This Edition

The main objectives of this edition are, in approximate order of their importance:

1. To produce a book essentially comprehensive of the whole field of inhibition.
2. To bring up to date the excellent work of Dr. Bregman.
3. To provide a base on which improved editions of this book may be issued in the future.

If these aims are met to a significant degree, it should be possible for both newcomers and experienced practitioners alike to use this edition to advantage. The opportunity has been taken to set down in one place a large volume of information which, although available elsewhere, is scattered among a large number of sources. Some of these sources are not readily available and others are available only at great expenditure of time, expense and effort.

Not the least of the aims of NACE is the provide a good summary of the subject matter and a large number of references to other works for those who wish to go into a subject in greater depth. Even in this aim it will be necessary to limit the information given, because in NACE magazines alone, there are hundreds of references to inhibitors and inhibitor technology.

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The numerous developments since 1963 in the technology of inhibitor related to the petroleum field will be considered under several headings. In some cases, such as in connection with oilwell sucker rods, existing information on inhibitor protection has been collected into a report³ published by NACE. Other similar data will be included among the several chapters relating to petroleum.

Among the references in this and other chapters and in the bibliography following this chapter, a considerable volume of additional information on many inhibitor applications will be found.

History of Inhibition

As is the case with other technology, there is no certain way to determine exactly when inhibition began to be considered as a separate technology. It has been observed for many years that the calcareous coating formed inside pipes carrying certain natural waters is protective of the pipes. It is common practice for water supply operators to so adjust the mineral content of their water that this beneficial coating is deposited to protect them.

This coating is so common in potable water piping that it and its benefits often are overlooked. This leads to such consequences as the multiple leaks that occurred in the water system of a city into whose mains the low solids water derived from a desalination plant was introduced. The high purity water dissolved the calcareous lining from the inside of the pipes, thus exposing numerous holes which previously had been blocked by the lining. It was necessary to treat the desalination plant water with calcium to protect the piping.⁴ Lime treatment was a well known practice over 65 years ago. Current practice is described in a book.⁵

H. E. Waldrip in an article in 1948 *Corrosion*⁶ referred to a 1943 report in his discussion of the inhibition of oilwells. Treatments using hexametaphosphates in water, inhibitors in coatings, in product pipelines, in acid systems and elsewhere were well established practices before NACE was founded in 1945.

The 10-Year Index to Corrosion covering 1945-54, contains references to inhibition in aircraft, aluminum process equipment, boilers, diesel engines, cooling water, street deicing salt, petroleum refineries, tankships and numerous others. The articles published during these years indicate a highly developed technology.

Extent to Which Inhibitors Are Used

There is little question that inhibitors are widely used. There is some evidence that their use is growing and there is ample reason to believe that sophisticated methods are available for the evaluation, application and assessment of the merits of inhibitors in a wide range of environments. While the nature of inhibitors is such that they are far more common in aqueous environments, extensive use in hydrocarbon, high temperature, gaseous, liquid metal and other environments is evident.

As pointed out by Dr. Bregman, it is difficult, if not impossible, to determine the dollar value of inhibitors used in the United States. This is so not only because many

products used as inhibitors are not necessarily so classed, but also because financial information is not readily obtained from either producers or users. In some cases the dollar value of the material used as an inhibitor is unimportant, if not trivial, as is the case of 0.5 percent water that passivates titanium exposed to chlorine.⁷

Dr. Bregman estimated some large installations may spend as much as \$100,000 annually for inhibitors. There is no reliable way to determine how accurate this is nor any way to extrapolate it to an overall figure for all industry today. It is sufficient and probably accurate to say that many millions of dollars are spent annually not only for the inhibitor materials themselves, but also for the equipment used to apply them and for the labor and supervision required for their successful use.

To the extent that the statistics are significant, an examination of the abstract literature⁸ shows that there has been a gradual increase in the number of abstracts of articles and books on inhibition during the past eight years. In 1962 there were 38 abstracts and in 1969, 91. Total abstracts in the eight years was 647. By contrast, there were 29 abstracts in the 1945 *Bibliographic Survey of Corrosion*.

If the NACE definition is accepted, the main types of inhibition may be, from one point of view, substantially as follows:

1. Adsorptive.
2. Bulk film formers.

From another point of view, they can be classified as

1. Anodic.
2. Cathodic.
3. Mixed.

In the latter schedule they are classed as to whether they interfere with the corrosion reaction by preferentially attaching themselves to anodic or cathodic areas or whether they attach to both.

There is no completely satisfactory way to categorize inhibitors. This is readily understood when one of the mechanisms for protection of steel is considered: Changing pH of the environment into the alkaline range in which steel does not corrode. The effect of alkaline media probably is to stifle the corrosion reaction because iron's lower oxides are sparingly soluble in alkaline solutions.⁹

Conversely, tungsten and molybdenum, whose oxides tend to be stable in acid, are active in alkaline solutions.⁹ Oxides of some metals such as zinc and aluminum are active over a wide range of pH.

There is no unimpeachable classification for water as in the case of titanium cited except to say that oxygen in water apparently forms a stable layer on titanium which is protective against chlorine. Similarly, halides of fluorine, bromine, chlorine and iodine (usually corrosive elsewhere, help to inhibit the corrosion of steel in sulfuric acid.²⁰

How Inhibitors are Used

In liquid environments, inhibitors may be introduced:

1. In slugs (that is, large quantities at once).
2. Continuously (that is, in metered amounts).

The choice of an application method usually is a function of one of the main parameters of inhibitor

performance, persistence. An inhibitor is said to be persistent when it tends to resist detachment from the surface it protects or to remain in the environment in sufficient concentration to be protective.

Examples of slug treatment in oil wells, for example, include those in which a measured amount of inhibitor is forced by pressure (squeezed into an underground producing formation from which it gradually is released to maintain an effective film on surfaces subject to corrosion. Technique is important in the successful application of inhibitors. In many oilwells, the surfaces to be protected must be coated with an effective film of inhibitor before the "squeeze" into the formation. The squeezed inhibitor reemerges to replenish this film as it is gradually worn off by produced fluids.

Continuous application is used frequently in such environments as those requiring large volumes of cooling water. The complex environment of cooling water systems, especially when open to the atmosphere, involves the use of biological agents (which may be corrosive); pH adjusting chemicals (sulfuric acid, for example) and other chemicals, such as flocculants. In such systems, not only is there a continuous application of the various chemicals, but often also a continuous monitoring system permitting operators to check on the water condition. Among books in the bibliographic references at the end of this chapter are several that discuss water inhibition skillfully and in great depth.

Materials Problems Associated With Inhibition

Because there are three principal avenues to solution of a corrosion problem, or similarly three avenues to prevention of or control of corrosion before it occurs, it is desirable to consider them separately. Although these approaches will be detailed in succeeding chapters, a few observations about them are appropriate.

The approaches are

1. Change the materials in the system.
2. Change the environment.
3. Put a barrier between the materials and the environment (a coating, for instance).

One or more of the above can be combined.

Select Corrosion Resistant Materials

Materials in a system are obviously of primary importance. Because of economics, however, freedom to select noncorrosive materials, or those which are sparingly corrosive, is limited. More often than not as a consequence, prevention of corrosion or solution of a corrosion problem involves alterations in the environment, or more specifically alteration of conditions at the interface between environment and material. It is at the interface—a zone of the infinitely small—that many studies of inhibitor reactions are made. These reactions are taken into account when selecting an inhibitor for a specific function.

Nevertheless, in some circumstances, such as for atomic reactors and as in heat exchangers in electric power plants, selection of the proper materials is the best way to prevent corrosion. A few examples will illustrate why this is so.

Stainless Steel in Nuclear Ship

Several analyses of stainless steel were used in the Nuclear Ship Savannah's main propulsion plant so that the volume of corrosion and other foreign matter circulating would be kept to a minimum.¹¹ Selection of these materials did not entirely eliminate the necessity for chemical treatment of the circulating water, however. Timer-actuated feeder pumps metered injections of morpholine, di and tri-sodium phosphate and sodium sulfite into the secondary water system to control corrosion there. The system was also charged with hydrazine to keep the pH at 8 to 9.5.

Cupronickel (consisting essentially of copper and nickel) alloys selected for tubing in heat exchangers used to cool exhaust steam from power plant turbines using salt water contain a small percentage of iron (usually 0.40 to 1.75) because the iron significantly improves their corrosion resistance to salt water and boiler feedwater.¹²

Chemical Treatment of Environment

As is apparent from the preceding discussions, inhibition usually involves addition of chemicals to the environment. It is useful, however, to avoid the misconception that aqueous environments are the only ones in which inhibitors (or inhibiting practices) are employed. So, the following examples are in order.

Hot Salt Corrosion of Titanium

Various hot salts (sodium chlorides, sodium bromide, sodium iodide, among others at 650 to 750 F (343 to 399 C) cause stress corrosion cracking of titanium alloys.¹³ It was discovered that water is a prime factor in making these hot salts aggressive. Environments in which hot salt environments are found include gas turbines, especially those operating in aircraft over oceans where sodium chloride and bromine can be concentrated from the atmosphere. In this case, where it is feasible to do so, excluding water will prevent or reduce corrosion damage from these hot salts.

Vanadium Pentoxide as Corrodent

Vanadium pentoxide, which by itself and in combination with other byproducts of the combustion of certain fuels, is aggressive at high temperatures, is amenable to treatment with certain chemicals (inhibition is one sense of the word) which limit its corrosivity. One method involves absorbing the pentoxide in a copper-magnesium oxide when the conditions are oxidizing and another involves using reducing agents, such as ammonium ions when the conditions are reducing (i.e., non-oxidizing).¹⁴

Chemical Treatment in Aqueous Environments

The subject of chemical treatment in aqueous environments will be covered in detail under numerous headings in other chapters. The environments considered range from the very simple (i.e., very pure water such as that used in nuclear reactors) to heavily contaminated liquids, such as those found in solutions of hydrochloric acid used to clean chemical equipment. Inhibitors markedly reduced the corrosion rate of steels cleaned by hydrochloric acid

solutions, but the inhibition rate is strongly influenced by corrosion products, such as hydrogen sulfide.¹⁵

Because oxygen is the most common corrosive in aqueous environments, many inhibitors are designed to counteract its attack. In a similar manner, such elements as sulfur, because they combine readily with oxygen, are soluble in water and are aggressive also, frequently are targets for inhibitors. The Battersea and Bankside electric generating stations in England remove sulfur dioxide from stack gases in a water scrubber then neutralize (inhibit) the resulting sulfurous acid with chalk.¹⁶

Succeeding chapters will discuss inhibition by chemicals in detail, so no further treatment is needed here.

Barriers to Separate Materials From Environments

Although it is outside the scope of this book, barriers between the environment and the material are the third control method. An example is the use of coatings inside piping used to transport salt water, especially when the volume of water is great and when it contains large quantities of dissolved oxygen. In this case, when a non-corroding material (such as a fiber reinforced plastic) cannot be substituted for steel and when the volume of inhibitor that would be required to effectively control corrosion is prohibitively expensive, then a coating on the pipe surface may be a remedy.

Other Influences on Performance

In common with other reactions in the corrosion process, the usefulness and efficiency of inhibitors is affected by numerous other conditions of the environment and of the materials. This discussion of these influences is introductory only. Each of them is treated fully in other chapters.

The most common conditions are temperature and velocity. Conditions of pressure or vacuum are known to have some influence on inhibitor performance in some cases. Instances when this is true apparently are infrequent, however, because they are rarely mentioned in the literature. Consequently, neither of these latter effects is mentioned to any significant extent in this book.

Effect of Temperature

It is generally conceded that the effectiveness of inhibitors usually is adversely influenced by increases in temperature. This is true in inhibited cleaning acids¹⁵ and is usually true in other environments. The extent to which temperature affects inhibitor efficiency often can be determined only after tests in the actual corrosive medium being studied. In some cases, the properties of organic inhibitors have been so fully explored that maximum operating temperature limits for their use are well known.

The temperature factor is always important and always is a design consideration.

Effect of Velocity

Because of the inherent properties of chemical compounds, velocity effects are important in inhibition, especially when they are considered in relation to performance.

While many effects at the metal-environment interface are comparatively stable, many others are not. Performance of inhibitors usually is affected adversely by high velocity. On the other hand, performance of certain inhibitors in some environments is adversely affected by low velocity.

An example of adverse influence by increased velocity is seen in tests with hot carbonate systems used to remove carbon dioxide from natural gas. Tests showed that the metavanadate ion improved the passivation of mild steel in hot carbonates at 100 C, but that this ion was ineffective when the carbonate impinged on material at high velocity, as it did at an elbow.¹⁷

The reverse of this effect is reported in tests of a water system in which it was found that corrosion of copper tubing at 6 ft/sec was superficial, but that pitting and surface attack occurred when the same solutions moved at only 2 ft/sec. This effect may be attributed to well known effect of the presence or absence of oxygen in the environment.

Techniques for Inhibitor Testing

Testing, to be considered in detail in a later chapter is important in inhibitor technology. Various means have been developed by NACE and other organizations to test the inhibitor efficiency before a selection is made. These are two main types of tests: Laboratory and on-site (or service). Laboratory tests usually involve screening inhibitors to weed out those obviously unsuited. Laboratory tests also permit a measure of judgment of relative merit when inhibitors are compared to others of known efficiency and performance.

NACE has published reports concerning static testing of inhibitors for oilfield service.^{18,19} Other organizations, notably the American Society for Testing and Materials, have published others.

A large volume of information about inhibitor testing will be found in the NACE magazine *Materials Protection*. An example of this is an article concerning inhibition of alkanolamine-carbon dioxide systems in which an effective inhibitor was reported to make substantial reduction in corrosion rates.²⁰ Other reports concern special problems and merit study by those who have similar problems. The data are located readily through the subject indexes in December issues in NACE journals.

Scientific and Practical Inhibitor Development

The development of scientific methods of inhibitor development have accelerated in recent years. These developments have been both by associations and scientific groups such as the American Chemical Society, NACE, ASTM and by individuals and companies.

The scientific approach is exemplified by the work of electrochemists who pursue reactions at the material-environment interface with a number of sophisticated instruments, deriving data useful in the technology both directly and indirectly. An example of the scientific approach is found in an article recently published describing the concept of developing an inhibitor by designing the molecules of which it is composed.²¹ In these studies the

kinetics of the reaction and electric double layer are evaluated. They also permit considering the principal types of inhibitor adsorption and the role of molecular architecture, nature of metal to be protected, corrosion solution composition, mechanism of inhibitor action, molecular designing of corrosion inhibitors and other factors.

Indicative of another type of approach is the recent NACE report surveying quality control practices of major oil field inhibitor manufacturers.²² This report is assumed to cover about 90 percent by volume of the inhibitors manufactured in the United States. The survey showed a high level of control over quality.

Individual companies also issue reports on tests of inhibitors such as one recently published on the performance of 48 organic inhibitors designed for oilfield use.²³ In this report the inhibitors are rated by one of three classifications: Superior, intermediate or dubious.

Other similar developments are occurring continuously throughout industry. The findings in these studies permit a more precise choice of materials for specific conditions and selection of the best among several inhibitors recommended for a given use. The economics of inhibitor application are continuously improving as more is learned about initial choice, application techniques and testing for results.

Scope of This Book

As has been indicated, the scope of this book has been expanded to cover essentially the whole field of inhibition. For the most part, the presentations will be industry oriented. In spite of the inevitable overlaps in such a scheme, it is believed that the method is useful and practical. Cross indexing permits locating information on subjects dispersed in a number of the chapters.

Authors chosen for the chapters are among those known to be active in the specific fields on which they are writing. The editor of this book and the National Association of Corrosion Engineers believe that this method produces the greatest volume of useful information on the subject.

Authors used their own sources of information both specified and otherwise. In addition, numerous references are listed for those who wish to pursue in greater depth some topic that is not fully treated in the text.

NACE Activities in Inhibition

From its beginning NACE has had a deep and continuing interest in inhibition and inhibitors. Among the early technical committee reports published by NACE was a reference list of corrosion inhibitors.²⁴ Technical committee activity has continued to be comprehensive, with attention given to acid cleaning solutions, cooling waters, hydrocarbon streams, high temperature, high purity water and numerous other environments.

NACE members will be found working on inhibitor problems in many major industries, so their contributions make up the bulk of the literature published by NACE and a significant part of that published elsewhere. Inhibitor topics are a continuing feature of NACE meetings at every level and the data generated constitute a significant segment

of the total available. Because of membership is diverse industries, there is a useful interchange of information across traditional lines. This is beneficial not only to NACE members, but to industry as a whole, which has free access to NACE technology.

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Theoretical Aspects of Corrosion Inhibitors and Inhibition

OLEN L. RIGGS, JR.*

Introduction

When metals are reduced from their ores, one of nature's fundamental reactions is reversed. In most environments, metals are not inherently stable, but tend to revert to compounds which are more stable; a process which is called corrosion. Corrosion is derived from the Latin "corrosus," meaning gnawed away. Corrosion may be further defined as a gradual destruction of a material, a substance, or an entity, usually by solution or other means attributed to a chemical process.¹

Metallic corrosion reactions are so extensive it is unlikely that a single set of mechanisms can explain all cases. Generally, the corrosion of metals in aqueous environments is caused by electrochemical processes. These processes occur on the metal surface and/or at the metal/solution interface. Organic corrosion inhibitors also may function by:

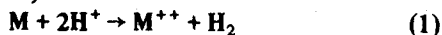
1. Chemisorption of the molecule on a metallic substrate;
2. Complexing of the molecule with the metal ion which remains in a solid lattice;
3. Neutralizing the corrodent; and
4. Absorbing the corrodent.

Corrosion is a heterogeneous reaction which is often diffusion controlled. In order for the reaction to proceed electrochemically, there are three necessary conditions which must be met simultaneously:

1. There must be a potential difference;
2. Mechanisms for charge transfer between electronic and electrolytic conductors must exist; and
3. A continuous conduction path must be available.

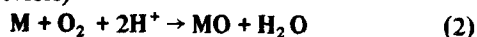
The corrosion reaction can be expressed as simply:

(Reduction Processes)



and/or

(Oxidation Processes)



Because corrosion reactions result from the inherent thermodynamic instability of most metals (gold, platinum, iridium and palladium excepted) or as the result of stray

external electrical currents, a change in free energy satisfies the requirements of Condition 1. Whether the metal's corrosion is controlled by the cathodic or anodic reaction, the rate, in most cases, is limited by the first transfer step. The discrete oxidation and reduction reactions, typified by Equations 1 and 2, are the charge transfer mechanisms. While other reactions can occur, they usually will satisfy Condition 2 also.

Condition 3 is satisfied when metal ions discharged into an electrolyte provide a conductive path through it to complete the electrical circuit.

Anodic and cathodic reactions occur as the result of differences in free energy states between reacting sites when all other conditions essential for a corrosion reaction are met. This is typified by the situation created when a piece of iron is partially immersed in brine, for example, when differences in the surface states of zones at the gas-liquid interface and those deeper in the brine cause reactions between these zones. Corrosion usually is accelerated at the interface zone.

Differences in the oxygen content of liquid in a crevice between two metals and the bulk electrolyte outside the crevice also can result in accelerated corrosion. An electrochemically identical reaction occurs when scale produced by reactions on a metal surface is broken or removed, thus exposing zones differing in free energy states from the remainder of the undisturbed surface.

The Electrical Double Layer

Exhaustive theoretical treatment has been given by electrochemists and others to the reactions that occur at the metal-electrolyte interface. While the complexities of these studies are such that a full exposition is outside the main objectives of this chapter, nevertheless, a general description of what is presumed to take place at the corroding interface is useful. Those who wish to investigate these phenomena in detail are referred to the several discussions about them, including the exhaustive treatment by Delahay.²

For the purposes of this discussion, it is sufficient to say that the reactions take place at what has been termed by Delahay and others as the "compact" double layer "comprised between the electrode and the plane of closest approach," and the "diffuse" double layer extending "from the plane of closest approach to the bulk of the solution." The double, or Helmholtz layer, and some of the other

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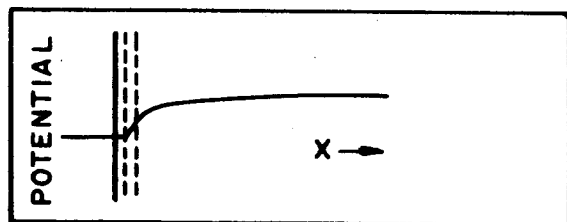
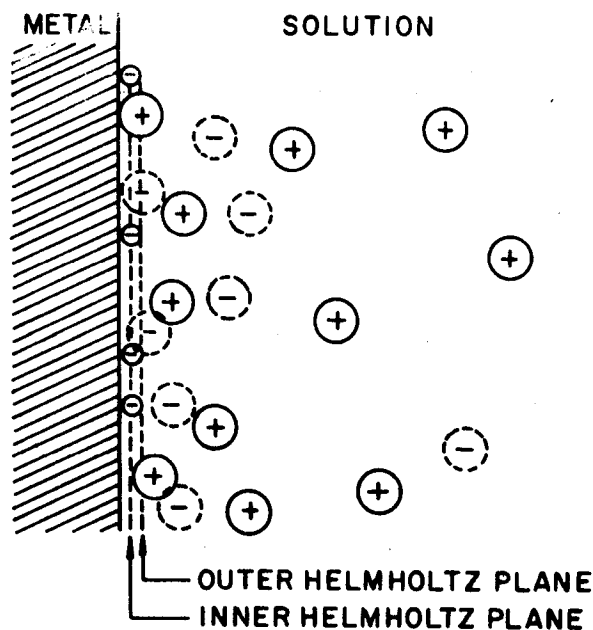


FIGURE 1 - Schematic representation of the electrical double layer at the potential of the electro-capillary maximum. Small circles represent adsorbed ions. Dotted circles represent "ghosts", ions which would be present if the double layer were not there. (D. Grahame)

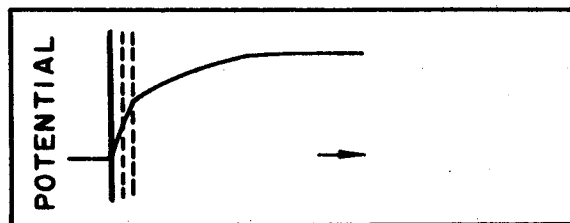
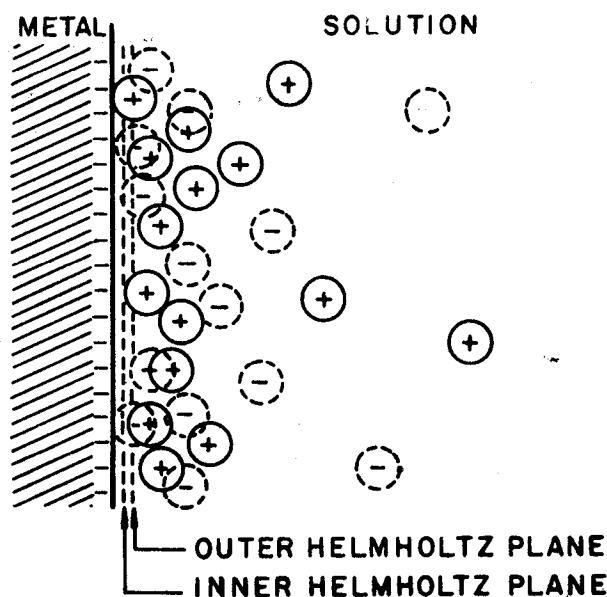


FIGURE 2 - Schematic representation of the electrical double layer with negative polarization. Note absence of adsorbed ions and increased concentration of positive ions as compared with Figure 1. The concentration of "ghosts" is also increased. (D. Grahame)

characteristics of this hypothesis are graphically displayed in Figures 1, 2 and 3.

A simplified explanation of what happens is that ions approaching or entering the Helmholtz layer participate in reactions with the electrons of metal exposed to the electrolyte. These concepts will be broadened by discussions of corrosion processes, inhibitors and inhibition in terms of the metal-solution interface, the inhibitor molecule, corrosion inhibition and measurement techniques.

In Figures 1 through 3,³ the large circles represent an excess of solvated ions. The dotted circles represent deficiencies of an ion type. The small circles (Inner Helmholtz Plane) represent the nonsolvated excess ions. The positive or negative signs on the metal represent either electron deficiencies or electrons. The change in potential as a function of distance is shown schematically in the boxes below each figure. Figure 1 diagrams the electrical double layer at zero charge potential of the metal surface. Figures 2 and 3 show schematically the double layer, with negative and positive polarization, respectively. This description of the composition of and states in or near the Helmholtz layer is more or less the same as that given by

Fouroulis⁴ discussing surface phenomena related to inhibitor action.

These comparisons are schematically presented in Figure 4, illustrating the relationship of both potential position and structure for the negative and positive surfaces with respect to the zero charge potential surface. The processes (electron discharge and ionization) are related to the ion transition from a "hydrate" (aqua ion) to a surface adsorbed atom and the reverse. The electrical field within the double layer controls these directional processes. Levine⁵ gave a detailed review of the electrical double layer, with attention focused on the discreteness of charge, or discrete ion effect.

Free Energy

All changes in the nature of materials are caused by their tendency to reach a state of maximum stability. Once this state of equilibrium has been reached, the tendency to change further is reduced and the system is said to be stable. The tendency towards change is greater, the greater the difference between the free energy state of the material and the equilibrium state.

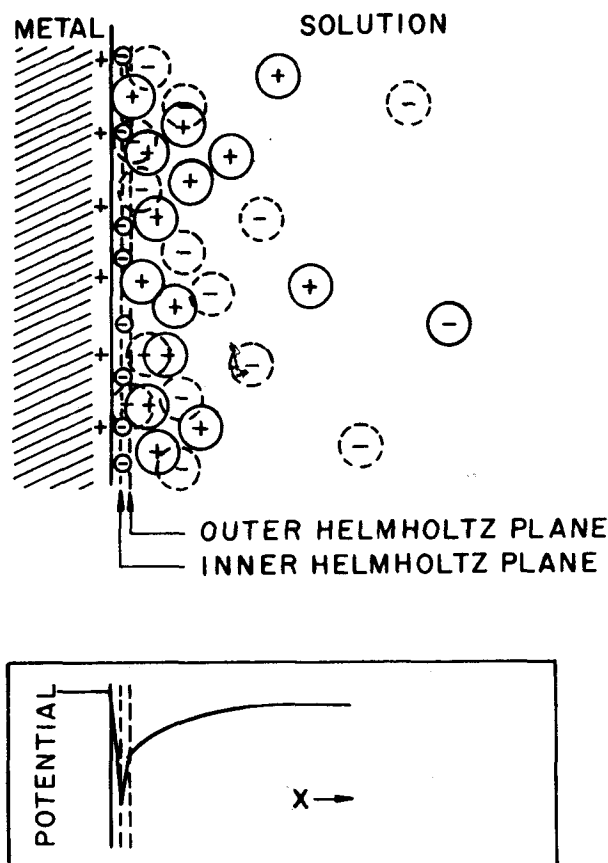


FIGURE 3 - Schematic representation of the electrical double layer with positive polarization. Note presence of adsorbed anions. Diffuse double layer is identical with that depicted in Figure 2. (D. Grahame)

Considering that a chemical system and its constituents are charged electrically (ions or electrons), any effort to effect a change in the charge distribution will require work. The system can perform maximum work only when the change is carried out reversibly. The force that causes the change is the maximum work difference between the final and initial states, which is the greatest energy available from the process.

Every chemical entity has chemical free energy, G . The electrically charged entity also contains electrical energy $g\phi$, so the total energy can be expressed as:

$$\bar{G} = G + g\phi \quad (3)$$

The electrical potential, ϕ , is the work expended in moving a unity positive charge from infinity. The electrical charge is g . The quantity, G , is the chemical free energy. A complete derivation is available from several sources.⁶⁻¹⁰ Morse curves effectively profile the chemical free energy of ions pulled out of the metal surface and then solvated.

Figure 5 illustrates the metal dissolution process when an ion (M) is "pulled out" of the surface into a polar solvent (water). The deep energy well for the metal ion bound to its lattice is shown with a second energy well for the metal ion surrounded by the primary solvation sheath. The M^{Z+}_{aq} (aqua ion) can have up to six solvating water

molecules, depending on the kind of solvent, i.e., hydroxyl, ammonia, sulfate hydrate, hypophosphite, cyano, and others. The compressed solvation sheath is rigidly oriented about the metal ion and in this manner tends to shield it from further complexing ions. This is the type of metal surface boundary that occurs during metallic corrosion and

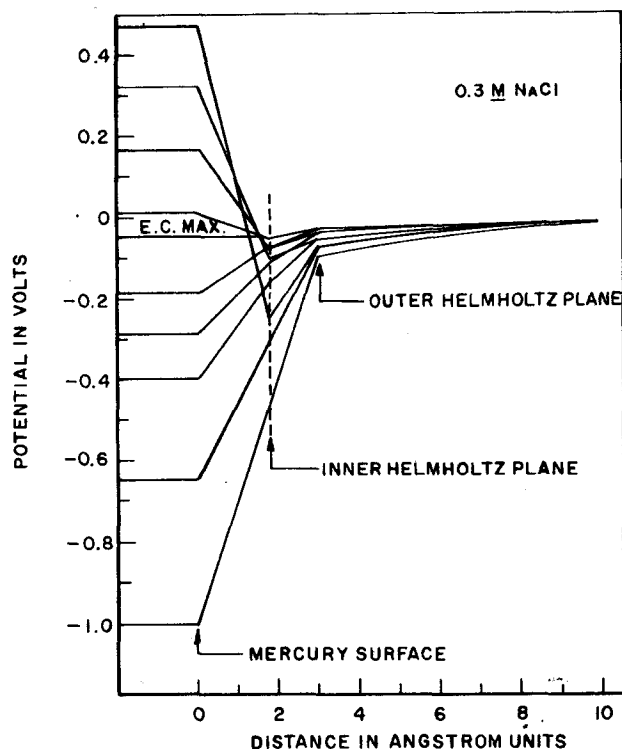


FIGURE 4 - Potentials in the electrical double layer between mercury and aqueous 0.3M sodium chloride solutions at 25 C at various polarizing potentials. Note that the potential of the inner Helmholtz plane reaches a maximum as the polarizing potential is varied from one extreme to the other. (D. Grahame)

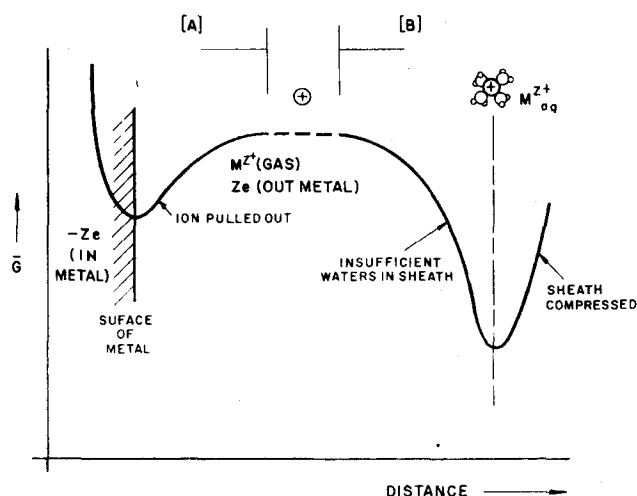


FIGURE 5 - A schematic Morse curve showing the chemical free energy of ions pulled out of the metal (A) and subsequently solvated (B). (From West)

represents the electrical charges which must be accommodated for polarization (inhibition).

Use of Polarization Diagrams

An understanding of polarization diagrams is useful in the study of inhibitors. Data from laboratory test programs may be plotted to indicate the relative efficiency with which inhibitors control corrosion reactions. Because most theories of inhibition involve concepts relating to the electronic affinities of substances with surfaces and the reactions among inhibitive species, metal surfaces and electrolyte properties, it is useful to review some of the main points about these diagrams.

Because the purposes of this discussion do not include an exhaustive treatment, it will be sufficient to present essential information only. Those who wish to do so will find thorough treatment in the references.

In 1905, Tafel¹¹ reported an empirical relationship between current density and overvoltage. He discovered:

$$\eta = a + b \log i_p \quad (4)$$

Where (a) is an empirical constant and (b) is the slope. Detailed derivations¹²⁻¹⁵ of the electrochemical kinetics of activation polarization are reduced for simplicity and understanding of the mathematical determination of Tafel slopes from experimental data to:

$$\frac{d\eta}{d \log i_p} = \beta \quad (5)$$

The Tafel slope (β) is obtained by plotting the log of applied current, i_p , versus the reference potential, η . These slopes can be measured for either the cathodic polarization (β_c) or the anodic polarization (β_a) (Figure 6).

When a metal electrode is in equilibrium with the electrolyte surrounding it, the anodic (i_a) currents and cathodic (i_c) currents are equal and no net reaction occurs. If this equilibrium is altered by an external EMF, the metal surface becomes polarized. The metal can be either anodically polarized (electrons are withdrawn from the metal and a net anodic current will flow), or cathodically polarized (electrons are pushed into the metal).

Polarization is associated with two processes: A net flow of current and a net shift of the electrode potential from equilibrium. These phenomena are the basis of the electrochemical kinetics of corrosion. It follows that electrochemical polarization can be divided into

1. Activation polarization,
2. Concentration polarization, and
3. Resistance polarization.

Another term pertinent to the electrochemistry of the corrosion process is polarization resistance (R) (not to be confused with resistance polarization). This resistance is related to the ease with which an electron may be transferred across a solution-electrode interface.

Stern¹⁵ published an equation which expresses β_a , β_c

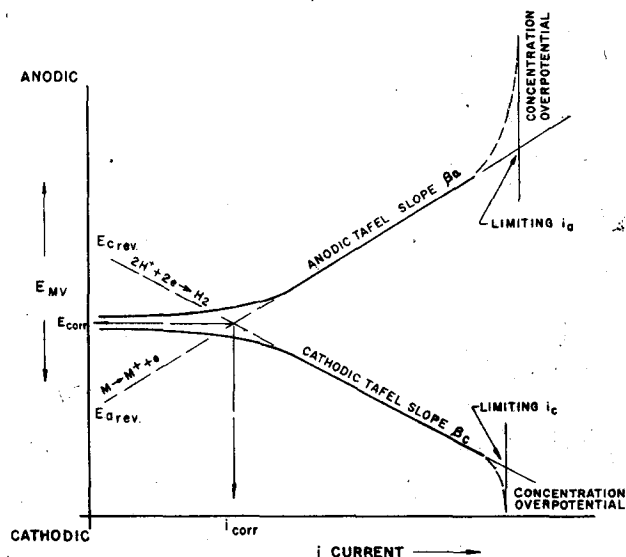


FIGURE 6 - Schematic activation polarization curves showing the pertinent processes for the metal/solution under impressed EMF conditions.

and R as pertinent functions in determining corrosion current (i_{corr}).

$$I_{corr} = \frac{\beta_a \beta_c}{2.303(R) (\beta_a + \beta_c)} \quad (6)$$

For a given metal-solution interface, the Tafel slopes (β_a and β_c) can be assumed to be constants and the corrosion current to be proportional to the reciprocal of the polarization resistance, $1/R$.

The various functions are schematically shown in the polarization curves of Figure 6.

The rates of the cathodic and anodic corrosion reactions have been defined by Hackerman and Hurd¹⁶ as:

$$i_{c,H} = k_{c,H} a_{H_3O^+}^y \exp \left\{ - \frac{F}{RT} [\alpha_{c,H} \varphi_c + (1 - \alpha_{c,H}) \psi] \right\} \quad (7)$$

for the cathodic reaction of the hydrogen ion discharge, and as indicated in Equation (8) for the anodic oxidation of iron.

$$i_{a,Fe} = k_{a,Fe} a_{OH^-}^x \exp \left[\frac{F}{RT} \alpha_{a,Fe} n (\varphi_a - \psi) \right] \quad (8)$$

$i_{c,H}$ and $i_{a,Fe}$ expressed in electrical units are the rates of the cathodic and anodic corrosion reactions;

$\alpha_{c,H}$ and $\alpha_{a,Fe}$ are the transfer coefficients;

ψ is the potential drop in the outer boundary of the electrochemical double layer;

φ_c or φ_a is the electrode potential with respect to the solution potential;

$a_{H_3O^+}$ and a_{OH^-} are the activities of the H_3O^+ and OH^- species; and

Y and X are the electrochemical reaction orders with respect to H_3O^+ and OH^- .

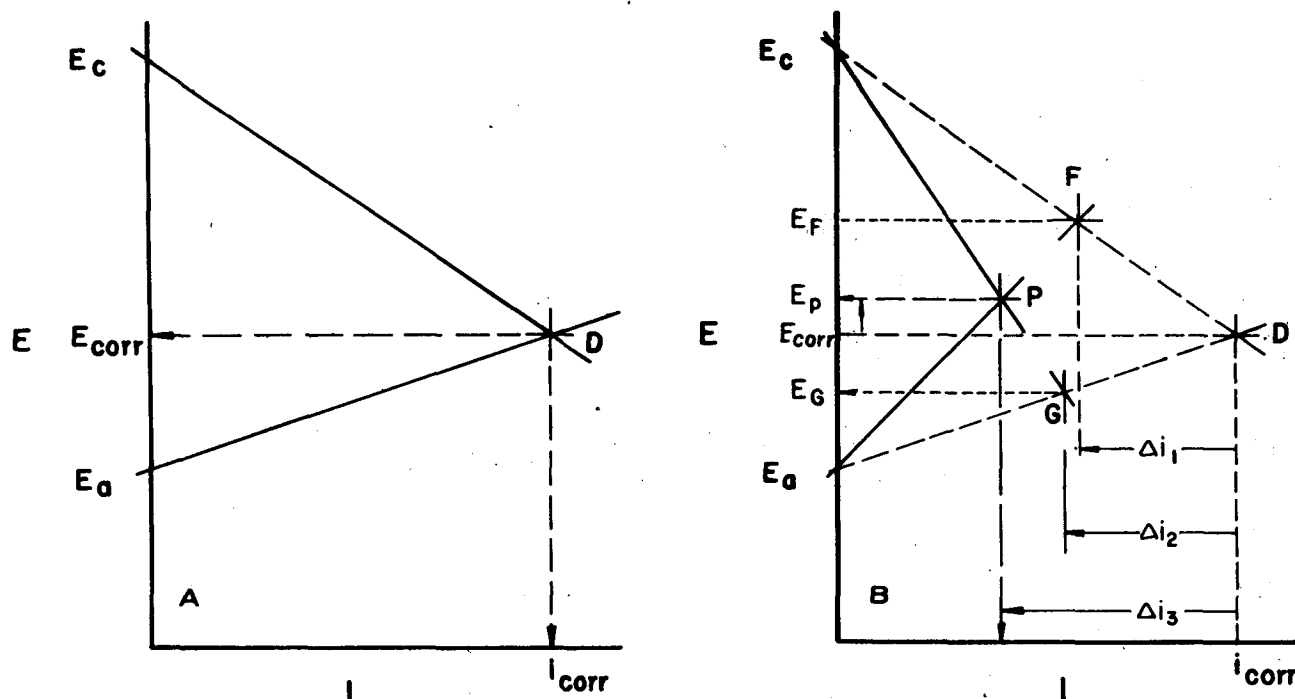


FIGURE 7 - Anodic and cathodic polarization curves. A-Illustrates significant terms for freely corroding metal. B-Schematic diagram showing relation of metallic corrosion, protection and inhibition.

A very useful review and derivation were published by Makrides.¹⁷ The chemical portion of the standard free energy of activation is included in terms k_c and k_a of Equations (7) and (8).

Figure 7A illustrates the significant terms for a freely corroding metal. The line E_aD represents the anodic reactions; line E_cD represents the cathodic reactions. The point of intersection of anodic and cathodic reactions (D) establishes the open circuit corrosion potential (E_{corr}) of the metal and indicates the magnitude of corrosion at i_{corr} (corrosion current).

Figure 7B is a schematic diagram showing the relation of metallic corrosion (D), protection (F and G) and inhibition (P). Generally, the immersed metal may be corroding by reactions under anodic control (E_aF) by use of anodic type inhibitors; under cathodic control (E_cG) by use of cathodic type inhibitors; or by mixed control (E_a-E_cP) where the inhibitor controls both anodic and cathodic reactions. It is readily apparent that an inhibitor which can control both reactions is more effective. Note that both anodic and cathodic type inhibitors reduce the corrosion current (anodic: Δi_1 ; cathodic: Δi_2), and that the "mixed" control inhibitor reduces the corrosion current more effectively (Δi_3).

Inhibitors

An inhibitor is a chemical substance which, when added in small concentrations to an environment, effectively checks, decreases, or prevents the reaction of the metal with the environment. Corrosion inhibitors are added to many systems including: Cleaning pads, cooling sys-

tems, various refinery units, pipelines, chemical operations, steam generators, ballast tanks, oil and gas production units and many products that are marketed to the general public. The corrosion inhibitor is of major significance for the preservation of metals. To be used effectively, the inhibitor must be compatible with the expected environment, economical for the operation amenable to treatment, and one which will contribute the greatest desired effect.

Inhibitors fall into several classes:¹⁸ Passivators, precipitators, vapor phase, cathodic, anodic, neutralizing and absorbants. While inorganic chemicals are certainly useful for controlling corrosion and can be classified as referenced above, this discussion will be limited to organic chemicals because of their primary importance as inhibitors and their wide acceptance for preventing metallic corrosion.

An organic corrosion inhibitor can be classified as anodic, cathodic, or both. Its classification depends primarily on its reaction at the metal surface and how the potential on the metal is affected. The chemical structure of the inhibitor molecule plays a significant role and often determines whether or not a compound will effectively inhibit a specific system.

Some organic inhibitor structures are presented in the Appendix as examples of several generic classifications. These are by no means comprehensive because the number of inhibitor chemicals is legion. Even within this list, combinations of one structure with another (formation of salt, or reaction product) can produce an inhibitor which is even more effective than either chemical alone.

Effectiveness of inhibitors has been determined in

1. Aniline



a. Ortho and/or Para

R, C, thru C₆, or S
 NHCOR
 NCOR
 N(COR)₂
 X(Halogen)

(CH)_(2n-1)COOH
 n = 1,2,3
 C_(2n-1)O₂R
 n = 1,2,3
 CONH₂

CONR₂
 CONHR

SH (or Se, Te in place of S)

Addition made with o, m, p groups
 until steric hindrance prevents!

b. Meta

NHR
 NH₂
 NR₂
 (CH₂)_nCOOH
 n = 0,1,2,3

CH₂CN
 NO₂
 SO₃H
 CHO
 COR

C_{2n}O₂R
 n = 1,2,3
 COX
 CX₂
 CH₂X

Note: Same list as above replacing N with P, Sb, or As.
 Replace N in example aniline structure with P, Sb, or As.
 Also, aniline (N) could have these substitutions: HR, HX, R₂,
 X₂, or RX in place of H₂.

2. Thiobenzene



All director groups apply to thiobenzene only, but positions they occupy on the aromatic structure are different. The group listed under aniline as "ortho and para" now become meta directors attached to thiobenzene. Likewise, the meta directors for aniline will be the ortho and para groups for thiobenzene. Also, the S in thiobenzene can be replaced with selenium (Se), or tellurium (Te).

FIGURE 8 - Constructions based on aniline and thiobenzene.

many ways and conclusions have been drawn as to the determining factors contributing to effectiveness. Some general concepts are:

1. The size of the organic molecule.
2. The aromaticity and/or conjugated bonding.
3. Carbon chain length.
4. Bonding strength to metal substrate.
5. The type and number of bonding atoms or groups in the molecule (can be either π or σ).
6. Ability for layer to become compact, or cross link (molecules effectively cover extra metal area through shielding).
7. The ability to complex with the atom as a solid within the metal lattice, as recently learned.

Although all of these properties are important, none is as significant as one property which is a prerequisite if an inhibitor is to be effective: The structure must offer efficient solubility. In this way, the inhibitor can be

effective at very small concentrations and at a minimum surface saturation.

Theoretical Aspects of Inhibition

Classifications

Corrosion inhibitors are not universally applicable, a fact supported in some degree by the large number of compounds used and also by the fact that an inhibitor effective in one system may not be effective in another. These complexities account in part for differing views about types. One such division could be:

1. Those that form layers of considerable thickness.
2. Those that form films by reactions with the protected substrate, and
3. Those which function by surface adsorption, with no significant reaction with the substrate.

The first two types are similar in that they may describe reactions that occur naturally, as in the formation of rust on iron or oxides on aluminum of chromium. In both of these types, the protective layer involves an exchange of energy between the substrate and some component in the electrolyte. For example, dissolved oxygen in water combines readily with iron; iron may not corrode at all in water with no dissolved oxygen. These two reactions are concerned mainly with inorganic materials. Organic inhibitors usually are believed to inhibit by adsorption.

It is universally accepted that the organic molecule inhibits corrosion by adsorbing at the metal-solution interface. However, the modes of adsorption are dependent upon:

1. The chemical structure of the molecule;
2. The chemical composition of the solution;
3. The nature of the metal surface; and
4. The electrochemical potential at the metal-solution interface.

There are three principal types of adsorption associated with organic inhibitors:

1. π -bond orbital adsorption;
2. Electrostatic adsorption; and
3. Chemisorption

Adsorption of organic inhibitors usually involves at least two types of adsorption simultaneously.

In addition to this classification is a recently discovered mechanism by which an organic molecule prevents the corrosion reaction: *Organo metallic complex layer*. For example, the inhibitor is an organic molecule which, when dissolved in hydrochloric acid, complexes with the steel surface and forms a combination chemical-metal layer which provides both physical and chemical protection.

Inhibitor reactions are accomplished at low molecular concentrations and may reduce steel corrosion in the range of 99%. This will be discussed further in inhibitor performance sections.

Influence of Temperature

Like most chemical reactions, the corrosion of iron and steel by oxygen in aqueous solutions increases with increased temperature in closed systems. In open systems, after an initial rapid increase the rate drops off after the system reaches about 90 °C because of the reduced solubility of oxygen in the water. Nevertheless, an increase in temperature will produce an increase in the corrosion rate in most systems. Sieverts and Lueg¹⁹ attributed diminished effectiveness of inhibitors under the influence of increasing temperatures to diminished coverage by the inhibitor. Their premise is based on the assumption that metal dissolution occurs on that part of the surface free of adsorbed molecules. Riggs and Hurd²⁰ took exception to this premise and suggested that the measured corrosion rate is expressed more accurately as the sum of two rates:

$$\frac{-d(\text{Fe})}{dt} = K_1 (1-\theta) + K_2 \theta \quad (9)$$

Where

θ is the fraction of the surface covered by the adsorbed inhibitor,

K_1 is the rate constant for the uninhibited reaction, and

K_2 is the rate constant for corrosion of the completely covered surface.

They developed rate equations based on the Langmuir adsorption isotherm and used these as means of determining the temperature coefficient of corrosion inhibition.

Practical Application Considerations

Practical parameters to be considered before using the organic molecule as an inhibitor include:

1. Compatibility of the inhibitor molecule with the system.
2. A desirable, effective solubility.
3. Temperature of system.
4. The solution pH.
5. Diffusion rate through boundary layer.
6. Various side effects.
7. Economic analysis.

Knowledge of the system's chemistry eliminates much of the difficulty associated with the use of the organic inhibitor molecule. Following are abbreviated descriptions of substances commonly found in many industrial environments which substances can affect the compatibility of the organic inhibitor with its aqueous environment.

1. Metal Cations—Monovalent cations have no measurable effects on inhibitors. Divalent cations may be used with bicarbonates to form protective precipitates. At high concentrations, divalent cations interfere with inhibition by precipitating inhibitors such as phosphate (PO_4^{3-}), silicate (SiO_3^{2-}) and organic molecules such as the sulfonates (RSO_3^-).

2. Alkali, (OH^-) — Corrosion of steel in alkaline solutions is controlled by the rate of oxygen diffusion. Steel is easily passivated. Aluminum, zinc and lead corrode slowly at low alkali concentrations, but above pH 9.0, their rates are accelerated and inhibition is needed.

3. Chloride, (Cl^-) — Chloride ions are strongly adsorbed by steel, making it difficult to passivate. Therefore, the higher the concentration of the chloride ion, the higher the concentration of passivating inhibitor required.

4. Sulfate, (SO_4^{2-}) — The effects of sulfate are not as severe and in many cases more beneficial than chlorides on passivity. The sulfates may contribute to depassivation if permitted to concentrate (precipitate). Sulfates cause coagulation of certain aliphatic (long hydrocarbon chain) bactericides and corrosion inhibitors.

5. Bicarbonate, (HCO_3^-) — In hard waters, bicarbonates offer natural inhibition by forming mineral scales. In soft waters, corrosion inhibitors must be used due to the acidic condition produced by excess carbon dioxide.

6. Sulfides, (S^{2-}) — Many metal ions are precipitated by sulfides. Oxidizing inhibitors are reduced by sulfide converting the sulfide to form free sulfur, so they can be effective only if used in large concentrations. However, corrosion can be accelerated under these conditions.

7. Oxygen, (O_2) — If oxygen is lowered to less than 0.1 ppm, this alone is sufficient corrosion control for most systems. Oxygen can support passivation of steel. Organic inhibitors are not generally effective against oxygen-caused corrosion unless they contain passivating groups such as benzoates or sulfonates.

8. Acid, (H^+) — Corrosion rates are increased by increased hydrogen ion concentration. Passivating inhibitors are used in sulfuric (H_2SO_4) and phosphoric acids (H_3PO_4) but not in hydrochloric (HCl). Nonpassivating organic or cathodic inhibitors (e.g., guanidine, propargyl alcohol and pyridines are preferred in pickling acids).

9. Naphthenic Acids, (R-COOH) — In basic waters, these substances can support natural inhibition. In acidic systems, inhibitors are generally added to control metallic corrosion. They affect interfacial tensions.

Designing Inhibitors

A careful examination of the literature (see bibliography) will inform anyone familiar with corrosion processes and organic chemistry as to pertinent factors in designing an organic corrosion inhibitor. The theoretical explanations of inhibitor function are in common agreement that adsorption phenomena involve:

1. Proton acceptors;
2. Electron acceptors; and
3. "Mixed" molecules.

1. Proton Acceptors — The organic structures that fit this group can be generally considered as cathodic site adsorbers. Materials in this group accept the hydrogen ion or proton and migrate to the cathode. Organic inhibitors used in various acidic environments are included. Examples are: Anilines, quinolines, ureas and aliphatic amines.

2. Electron Acceptors — Materials in this group are generally effective at anodic sites. They function as inhibitors due to their ability to accept electrons, and are most effective for corrosion reactions under anodic control. In addition to anodic inhibitors, passivating inhibitors are found within this group. Examples are: Organic peroxides,