Inhibitors for Corrosion Control

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INTRODUCTION

Over 40 years ago, the late President Hoover set forth a creed which is perhaps even more applicable today than when he said:

"It is only through the elimination of waste and the increase in our national efficiency that we can hope to lower the cost of living, on the one hand, and raise our standards of living, on the other. The elimination of waste is a total asset. It has no liabilities."[1]

This is the creed by which we in the oil industry are trying to live when we attack the problem of corrosion losses or waste in oil and gas producing equipment. A cynic might say that we in the chemical industry are merely trying to increase our sales and profits while you in the producing industry are merely trying to reduce your lifting costs thereby increasing your profits. Such a statement would be true, of course, and what better way is there to "increase our national efficiency?"

Economics

The economics of the corrosion problem in this country is difficult to define. Fifteen years ago an estimate of six billion dollars per year in economic loss due to corrosion was given.[2] This figure was only for direct costs and did not estimate indirect costs such as loss of production, loss of life, and other intangible factors. Undoubtedly, because of our increased industrial growth in the past 15 years, this estimate would be low today.

We are primarily concerned with corrosion losses in the oil industry, which is a significant portion of the total annual loss in the United States. Some authorities have estimated the oil industry's corrosion loss at 100 million dollars per year, while some estimates have gone as high as 250 million dollars annually.[3]

DESCRIPTION OF CORROSION

Corrosion has been defined simply as the destruction of a metal by chemical or electrochemical reaction with its environment. For practical consideration, corrosion in oil production equipment can be classified into four main types:

(1) Sweet corrosion, which occurs in the presence of carbon dioxide and organic acids.
(2) Sour corrosion, which occurs as a result of the presence of even trace quantities of hydrogen sulfide.
(3) Oxygen corrosion, which occurs wherever equipment is exposed to oxygen either in the atmosphere or in solution.
(4) Electrochemical corrosion, which occurs as the result of a measurable electrical current flow due to a potential difference between two or more areas on a metal in the presence of an electrolyte.

Others have described the mechanism of these various forms of corrosion.[3] We will concern ourselves with methods of alleviating corrosion by the use of corrosion inhibitors.

An inhibitor may be defined for our purposes as a chemical agent which, when added in small amounts to a corrosive environment of a metal, substantially reduces the corrosion rate. A large number of chemical materials have been and are being used as corrosion inhibitors. These include both organic and inorganic chemicals.

HISTORY OF CORROSION INHIBITORS

Chemical treatment of producing oil wells for corrosion control began in the early 1920's. These early treatments were based on the principle of neutralizing the acidic constituents of the produced fluids. Caustic soda, ammonia, and other inorganic chemicals were used with varying degrees of success. By the late 1930's various organic materials were being investigated. Formaldehyde was used rather extensively during this period. Some of the results of these investigations indicated the importance of surface adsorption, which opened the door to a new class of chemicals, the so-called "film-formers." Further research efforts and field developmental studies in the years that followed eliminated a number of organic materials and directed the main effort toward organic nitrogenous compounds which are still the most significant inhibitors in use today.

TYPES OF INHIBITORS

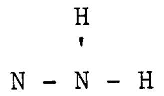
Of the two classes of inhibitors, organic and inorganic, the inorganic inhibitors such as arsenic or chromium compounds are used only to a limited extent in treatment of corrosion in the oil field. These inhibitors are toxic to warm blooded animals and have detrimental effects on refinery catalysts. The mechanism of corrosion inhibition using these inorganic inhibitors is linked to two processes:

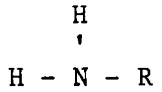
(1) Formation of a phase oxide film or insoluble anodic reaction products of the metal and inhibitor which prevents further reaction of the metal with its environment.
(2) Adsorption of the inhibitor on the metal surface, thereby changing the nature of the metal surface in such a way that the reactivity of the metal is significantly reduced.

The first process is considered by most authorities to be the most acceptable. Since in this process corrosion inhibition depends on the continuity and integrity of the film produced at the anode, it becomes obvious that partial or imperfect coverage will result in accelerated localized attack. For this reason anodic inhibitors are considered dangerous to use, because they must be present in sufficient concentration to assure complete and continuing film integrity to avoid accelerated localized attack. Inhibitors of this type are useful in recirculating cooling water systems where the higher concentrations required are not uneconomical.

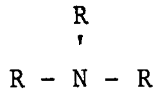
Organic inhibitors, particularly the organic nitrogenous compounds, have been found to be the least expensive and most effective chemicals for use in treating oil and gas producing systems when properly selected and applied. These compounds are available in a wide variety of formulations and solubility characteristics.

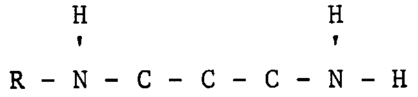
Amines are the basic chemicals used in these formulations. They are substituted organic ammonium compounds and are classified as primary amines, secondary amines, tertiary amines, and quaternary amines (or quaternary ammonium compounds).

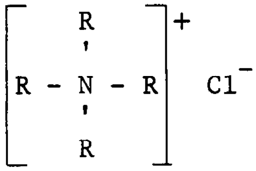
(1) 
$N - \overset{H}{N} - H$ (NH_3) Ammonia

(2) 
$H - \overset{H}{N} - R$ Primary Amine

(3) 
$H - \overset{R}{N} - R$ Secondary Amine

(4) 
$R - \overset{R}{N} - R$ Tertiary Amine

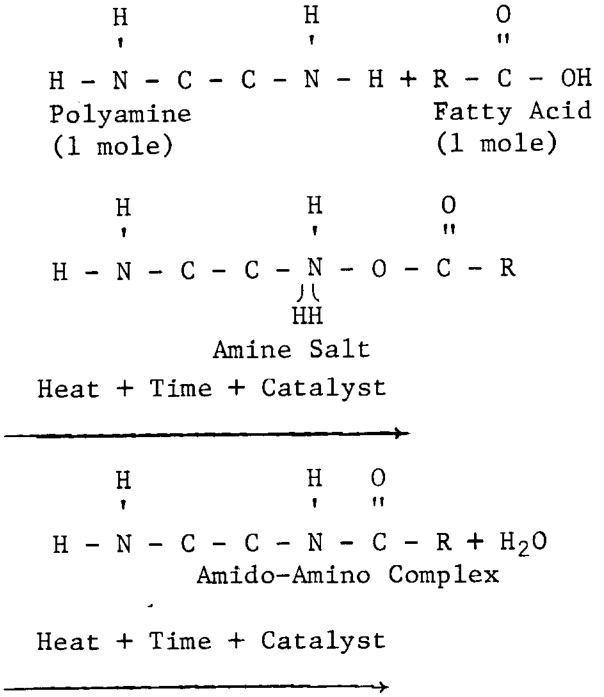
(5) 
$R - \overset{H}{N} - C - C - C - \overset{H}{N} - H$ Diamine

(6) 
$\left[R - \overset{R}{\underset{R}{N}} - R \right]^{+} Cl^{-}$ Quaternary Amine

(R = hydrocarbon group)

The hydrocarbon group can vary in chain length and complexity.

When polyamines are reacted with various amounts of organic acids under different conditions of temperature, pressure and time, materials called partial amides — partial amines (amido-amino compounds) and imidazolines are formed as in the following reactions:



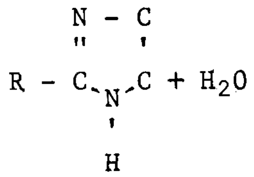
$$\underset{\text{Polyamine (1 mole)}}{H - \overset{H}{N} - C - C - \overset{H}{N} - H} + \underset{\text{Fatty Acid (1 mole)}}{R - \overset{O}{\overset{\|}{C}} - OH} \quad (1)$$

$$\underset{\text{Amine Salt}}{H - \overset{H}{N} - C - C - \underset{HH}{\overset{H}{N}} - O - \overset{O}{\overset{\|}{C}} - R} \quad (2)$$

$$\xrightarrow{\text{Heat + Time + Catalyst}}$$

$$\underset{\text{Amido-Amino Complex}}{H - \overset{H}{N} - C - C - \overset{H}{N} - \overset{O}{\overset{\|}{C}} - R} + H_2O \quad (3)$$

$$\xrightarrow{\text{Heat + Time + Catalyst}}$$



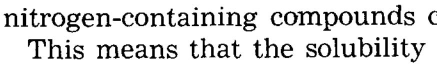
$$\begin{array}{l} \quad\;\; N - C \\ \quad\;\; \| \quad\;\; | \\ R - C \backslash_{N} / C + H_2O \\ \qquad\;\; | \\ \qquad\;\; H \end{array} \qquad (4)$$

Imidazoline

You will note that the amido-amino complex in equation 3 contains an additional primary amine that can be further neutralized with organic or inorganic acids. If two moles of fatty acid had been used, a full amide would have been formed. While amides are usually highly temperature stable, they are not very good corrosion inhibitors. It should be noted that the amine salt in equation 2 could undergo this conversion under some conditions, particularly in a high downhole temperature environment and thus lose its value as an inhibitor.

By varying the type of materials (there are many polyamines and many, many acids available), ratios, temperatures, pressures and catalysts, an almost infinite number of aliphatic or cyclic nitrogen-containing compounds can be prepared. This means that the solubility of the compounds can be varied widely by the choice of the amine or acid to be used. As the hydrocarbon chain length increases, the materials become decreasingly water soluble and increasingly oil soluble. The chain length, degree of unsaturation of the chains, i.e., double bonding, and degree of amidation or imidozoline formation will also control the solubility of the amido-amino complexes or the imidazolines. When higher order polyamines are used in the preparation of imidazoline, then much more complex and much higher molecular weight materials result. Some of these supposedly contain several cyclic structures. Even after these compounds are formed, subsequent neutralization of any unreacted amine groups can also vary their solubility characteristics. A generalization on the solubility characteristics due to neutralization is structurally represented below:

(1)



Long Chain, high mol. wt. Amine (Oil soluble)	Short Chain, organic acid (Water soluble)

End product is oil soluble/water dispersible

(2)

Short Chain, low mol. wt. amine (Water soluble)	Long Chain, high mol. wt. organic acid (Oil soluble)

End product is oil soluble/water dispersible

(3)

Short Chain, low mol. wt. amine (Water soluble)	Short Chain, low mol. wt. organic acid (Water soluble)

End product is water soluble/oil insoluble

(4)

Long Chain, high mol. wt. amine (Oil soluble)	Long Chain, high mol. wt. organic acid (Oil soluble)

End product is oil soluble/water insoluble.

Solubility characteristics can be altered in other ways. The use of surfactants is well known. By adding the right type and concentration of surfactant the solubility properties of nitrogen derivatives can be further varied. When water soluble surfactants are used for this purpose, the tendency of the surfactant to promote water-wetting of a metal surface sometimes tends to override the effect of the amine corrosion inhibitor.

One of the most common ways to increase water solubility of amines is to react the amine with ethylene oxide. The more ethylene oxide reacted with the amine the more water soluble the end product. If propylene oxide is used, the amine will tend to become more oil soluble. When a reaction of this nature is made, the polarity and inhibition properties of the amine are decreased.

Because oil field waters vary greatly in mineral salt concentration and the chemical composition of the hydrocarbon also varies and the ratios of these fluids to one another vary, it is evident that many inhibitors are needed. Other variants such as temperature, pressure, completion techniques, etc., require an even wider choice of inhibitors.

The two most common inhibitor materials on the market today are based on diamines and imidazolines.

HOW INHIBITORS WORK

In order to explain how inhibitors work, we will very briefly review the mechanics of electrochemical corrosion. The elements necessary are an anode, a cathode, an electrolyte, and a return path for electrons, usually by a direct metallic connection between the anode and cathode. Corrosion occurs at the anode where metal ions go into solution and give up electrons that migrate to the cathode. Positively charged hydrogen ions from the water accept these electrons at the cathod forming a protective hydrogen film. In this state the cathode is polarized, and the corrosion reaction stops. If this protective film of hydrogen is removed by erosion, formation of hydrogen gas, reaction with oxygen or by bacterial action, corrosion will continue.

The mechanism of inhibition of these nitrogenous compounds is still subject to some controversy. These compounds are polar or "semipolar" and one end of the molecule contains the nitrogen atom which is usually adsorbed on the metal surface. In other words, the inhibitor molecules align themselves with respect to the surface of the metal in much the same way as a compass needle aligns itself to lines of magnetic force. At the same time, the long hydrocarbon chain of the molecule which is oriented away from the metal surface and which is normally hydrophobic tends to repel water and attract an oil layer. This mechanism, in theory, forms a uniform oil-wet film over the metal surface which effectively insulates the metal from its environment, thus stopping the corrosion reaction. These nitrogen containing compounds are thought to be attracted to both anodic or cathodic areas. It is thought that this adsorption can be viewed as general, involving physical and chemical forces.[4]

Further theories about the adsorption characteristics involve the fundamental law of crystal chemistry which deals with the forces binding a crystal together. The deformation of the crystalline structure of iron which occurs at the surface tends to set up charges in the crystal that strongly attract the inhibitor molecule. Still another mechanism is that of the surface imperfections of the metal which results in potential differences on the surface. This erratic distribution of energy may result in strong adsorption on the "active" areas. Laboratory work using radioacitve tagged amine-acid salt inhibitors has indicated that the inhibitor film is not static but migrates over the surface. Some evidence showed that the "active" areas on the metal surface shifted, causing a redistribution of the inhibitor.[5]

Regardless of the nature of the adsorption mechanism, the tendency of an inhibitor to oil-wet the metal surface is an important consideration in the effectiveness of the inhibitor. This phenomenon could perhaps be more accurately described as oil attraction to the film. Oil enters the adsorbed layer of molecules and attaches itself to the inhibitor film. The resulting double layer provides the inhibiting properties.

Since these amine based inhibitors have the ability to adsorb readily to most surfaces, it is apparent that for them to function effectively, they must be able to make contact with the surface needing protection. For the most part the inhibitor cannot tell the difference between the surface to be protected and suspended particles or corrosion products in the system. Most amine corrosion inhibitors exhibit detergent or surface active properties (or can have such properties added) and can, with time, remove corrosion products, dirt, mill scale, etc. from the metal surface. It can readily be seen why maximum corrosion inhibition will not be achieved during this "cleaning up" period. It is quite often advisable to chemically or even mechanically clean up a system prior to beginning a corrosion inhibition program.

FACTORS TO CONSIDER IN CHOOSING AN INHIBITOR

Let us look now at some of the desirable qualities of a corrosion inhibitor for field use and some of the factors affecting these qualities. This is by no means intended to be a complete listing of all the desirable qualities, and it will become apparent that many of these qualities are interrelated.

First, a corrosion inhibitor should give a high degree of protection. This quality involves the structure of the molecule, its ability to adsorb strongly to a surface and form a uniform film. Second, a corrosion inhibitor should have film persistence or an ability to resist the effects of erosion. Third, a corrosion inhibitor should have solubility features to enable it to go where it is needed. Fourth, a corroison inhibitor should not cause adverse secondary effects in the treated system.

Consideration should be given to the possibility of forming emulsions in the producing secondary recovery or water disposal systems.

Naturally, the inhibitor should not contain compounds which will poison refinery catalysts. The degree of protection is affected by many factors, the composition of the fluid environment, composition of the metal or alloy surface in addition to the molecular structure of the inhibitor molecule, etc. Film persistence is affected by fluid velocity, temperature of the system, type of surface, length of time the inhibitor is in contact with the metal and composition of the fluid environment.

Solubility is affected by the temperature of the system, composition of the fluid, and structure of the inhibitor molecule. Adverse secondary effects are dependent upon the method of production, water-to-oil ratios in the system and compositions of the fluid as well as the inhibitor formulation.

These oversimplifications readily show that no single inhibitor presently known could have all these qualities in every application because of the wide variety of producing methods, oil-water ratios, and produced fluids encountered in the oil field. However, an understanding of the complexity of the problem along with a basic knowledge of the properties of the many available corrosion inhibitors will assist in the proper selection of an inhibitor for a specific problem.

INHIBITOR TESTING

Inhibitor testing is probably one of the most confusing aspects of a corrosion program. This is a major problem to both the chemical supplier and the chemical user. There are many testing methods and techniques, each having their advocates. In this still highly controversial area one is tempted to say, "A plague on both your houses." However, most of the commonly used tests do have merit and at the very least furnish valuable information concerning the properties of an inhibitor under specific conditions.

Field "screening" tests are used in many instances to "screen out" or eliminate inhibitors which obviously do not have the desired degree of inhibition or film persistence in a specific fluid. The copper ion test is a prime example of this screening test. A steel specimen is immersed in inhibited and uninhibited well fluid, rinsed and immersed in a copper sulfate solution. That part of the steel specimen which does not have an inhibitor film will begin to corrode, displacing copper from solution. The copper "plates out" on the steel specimen on the area where no film is present. The degree of copper plating is an indication of lack of protection. There are many modifications of this test including using fluid from an inhibited well to determine if sufficient inhibitor is present in the fluid to achieve the desired level of protection, etc.

Another field method of inhibitor screening is the use of prestressed bearings to determine an inhibitor's value in protecting against hydrogen embrittlement. In this test, bearings are stressed with a 40,000 pound load before being placed in the well fluid to be tested. If the fluid causes hydrogen embrittlement, the bearings will crack, sometimes within a few minutes. Other samples of the fluid containing inhibitors are set up and bearings placed in the fluid. Inhibitors which significantly retard or prevent the cracking of the bearings are considered effective against this type of corrosion attack.

Numerous laboratory screening tests are in use ranging from static tests to rather sophisticated dynamic tests. Actual well fluids are used in some instances and in others an artificial brine with a refined hydrocarbon may be used. In these tests not only the degree of inhibition but the film persistency may be measured. Perhaps the best known and most widely used of these tests is the "wheel test." In this test a series of bottles or containers is set up. Well fluid in prescribed oil-water ratios and with varying concentrations of different inhibitors and a pre-weighed metal specimen are all placed in the container. The container is then rotated at constant speed at a prescribed temperature and for a given time. The coupons are then reweighed and a rating of the various inhibitors used in the test can be ascertained. This test, too, has many modifications and variables which can be changed. Properly designed tests will show the limitations of inhibitors. A proper testing program will include more than one test and should be designed to show the limitations of the chemical rather than relying solely on the chemical's capabilities in terms of per cent protection.

TREATING METHODS

In order to protect the metal surfaces with an amine inhibitor it is not necessary to treat the fluid. Treatments can be done by "batch" or "slug" methods, by continuous treatment, or by a combination of the two. Obviously, the best treating method to use is the one which gives the most protection at the least cost. Quite often the method of completion of the well limits the treating procedure.

When continuous treatment is used, an initial heavy treatment is required. This treatment tends to penetrate scale of corrosion products, which are generally on the metal surface, and initiate film formation. Continuous treatment at relatively low concentrations then continues to repair or replace the film which has been lost due to erosion or solubility effects.

In the "batch" or "slug" treatment, the weekly or monthly requirement of inhibitors based on continuous treatment, is injected in the well in one batch. Successful treatment in this manner is dependent upon injecting the optimum amount of inhibitor for best film formation. The film life should be at least equal to the time between treatments.

A method which combines "batch" treatment with continuous treatment is the inhibitor squeeze technique.[6] This technique utilizes a large volume of inhibitor solution pumped back into the formation. As it is being pumped through the tubing, it contacts the metal surfaces and forms a film. When it enters the formation, in theory, the inhibitor is adsorbed on the solids in the producing formation and slowly desorbed as the well is produced, thus in effect providing continuous treatment. Recent studies indicate the need for proper inhibitor selection and carrier to inhibitor ratios as well as overflush volumes for maximum squeeze life.[7,8]

It is possible in the limited time and space available to cover only a few of the concepts involved in using inhibitors to control corrosion. If a message is intended, it is that corrosion inhibition is not an art but a science, albeit a young science with many questions still unanswered. The complexity of corrosion problems in the oil field requires sound engineering practices to develop an efficient corrosion control program. Such a program will increase profits.

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