

Inhibitors Used to Control Corrosion of Mild Steel in Crude Oil Recovery

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Abstract

Industries first select construction materials on the basis of safety and cost-effectiveness. Physical requirements can be satisfied easily but corrosion effects seriously complicate the selection of suitable materials. The corrosion-mitigations can be enhanced by the coating of organic and inorganic substance but its costs must also be considered. The cost of material depends upon design and physical requirements of the material. The attractive facial appearance makes the material expensive. Initially materials face localized corrosion which is also known as general corrosion. Localized corrosion is more insidious form of deterioration under certain conditions. It can promote stress corrosion which leads to the cracking of materials. It is very difficult to detect localized corrosion early and to monitor it effectively. The use of corrosion inhibitors is a practical and economical method, which can be designed according to the environmental conditions. Industrial use of the corrosion inhibitors may exceed the budget amount. A recent survey estimated that the US industry spent \$798 M (1.54 M tonne) on corrosion inhibitor chemicals in 1986. This paper attempts to provide details of chemical corrosion inhibitors as a broader introduction.

Keywords: Inhibitor, Design inhibitors, Commercial uses of inhibitor, Localized corrosion.

INTRODUCTION

Oil production and refining industries have the major share of chemical inhibitors [1]. Water is used in excess amount during recovery of crude oil. The biggest market growth of chemical inhibitor is predicated in the sector of oil production/drilling/refining/water treatment [2]. Petroleum industries demands increase lime, chromates and phosphates within the 39% inorganic chemicals inhibitors share of the market whereas amidoamines, imidazolines, fatty acids, phosphonates, alkanolamines and neutralizing amines feature in the 61% organic chemicals' share of the market. Organic chemicals [3] amines (e.g. fatty acid amines, cyclic amines, quaternaries, diethylamines and imidazolines) are used predominantly as corrosion inhibitors in oil and gas production/transmission, refineries, and boiler water return lines. Chemical inhibitors [4] use for water treatment chromates-base zinc salts, phosphates, molybdates and triazoles. Phosphates and some polymers are applied as new corrosion inhibitors. Inorganic based corrosion inhibitors occupy the major percentage share in market for water treatment. However an increasing use of organic corrosion inhibitors is predicted for treatment of

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cooling waters due to a decline in the use of heavy metals (e.g. Cr, Zn). An increased use of neutralizing amines for treatment of boiler water return lines and a decrease in use of oxygen scavengers to treat boiler waters is also seen as significant in shifting the balance towards greater use of organic chemicals [5]. Corrosion inhibitors typically used with anti-freeze formulation [6] include sodium benzoate, borax, benzotriazole and tolyltriazole. However, with the automotive industry's move to multi-metal engines inhibitor formulations are becoming more complex.

Utility of Corrosion Inhibitors in Corrosive Atmosphere

Corrosion inhibitor is a chemical substance which is added in small concentration to reduce the corrosion rate of a metal in a hostile environment. On the basis of mechanistic and chemical considerations corrosion inhibitors are divided into specific types of classes. In the most of cases inhibition is achieved by interaction or reaction between the corrosion inhibitor and the metal surface to form of an inhibitive thin surface film, which directly occurs at the metal surface/environment interface or via precipitation. The chemistry of environment [7] is modified by chemically scavenging uses for dissolved oxygen which chemically neutralizing dissolved acidic gases and adjusting pH to promote stable passivation. Their classification is mentioned in Table 1.

Table 1. Classification inhibitors [8].

Type	Species	Classification
Anodic	Chromate Nitrite Nitrate Phosphate Molybdate Tungsten	Oxidising passivator Oxidising passivator Oxidising passivator Non-Oxidising passivator Non-Oxidising passivator Non-Oxidising passivator
Cathodic	Arsenate Carbonate Zinc sulphate	Cathodic poison Precipitate (Ca & Mg) Precipitate as Zn(OH) ₂
Precipitation	Phosphate Silicate	Anodic/Cathodic effects Anodic/Cathodic effects
O ₂ Scavenger	Sulphite Hydrazine	Cathodic effects Cathodic effects
Volatile/Vapour phase	Cyclohexylamine Morpholine	Passivating (NO ₂ ⁻ salt) Neutralizing
Film-Forming	Amines Imine Imidazolines Quaternaries Acetylenic alcoholols	Organic/adsorption Organic/adsorption Organic/adsorption Organic/adsorption Organic/adsorption

Pitting corrosion [9] is to be avoided by the use of active anodic inhibitors. Sometimes inhibitors are referred as 'safe' because they do not directly interfere with the anodic reaction but reduce the net current flowing in the overall corrosion reaction and inhibiting the cathodic reaction. Inhibitors exhibit anodic, cathodic or mixed behaviors which is combination of both anodic and cathodic effects. The metal substrate is inhibited by paint in corrosive medium. Recent developments using inhibitors-loaded ion-exchange pigments would protect metal. Inhibitor is released for the supporting pigment during an ion-exchange mechanism and corrosion rate dependent on the corrosive properties of its surrounding medium.

Classification of Chemical Inhibitors

Corrosion inhibitors are classified on the basis of mechanism and environment condition [10] in which metals are exposed. Inhibitors are commonly classified as anodic, cathodic, passivation, oxidizing, foil-forming, organic, vapour phase, volatile and safe or dangerous inhibitors. These inhibitors are given in Table 1. Aqueous systems are the most common corrosive environments in which corrosion inhibitors are applied. A corrosion inhibitor affects the electrochemical reactions which combine to describe the corrosion process to be inhibited.

Mixed potential theory [11] of an electrochemical corrosion process expressed graphically in the form of an Evans type polarization diagram is an extremely useful way to picture how an inhibitor works. Figure 1 show a simple corrosion reaction described in this manner defining the steady state free corrosion potential and corrosion current (rate). These results from the mutually polarizing (coupled) partial reactions, anodic and cathodic, which combine to constitute the overall corrosion reaction.

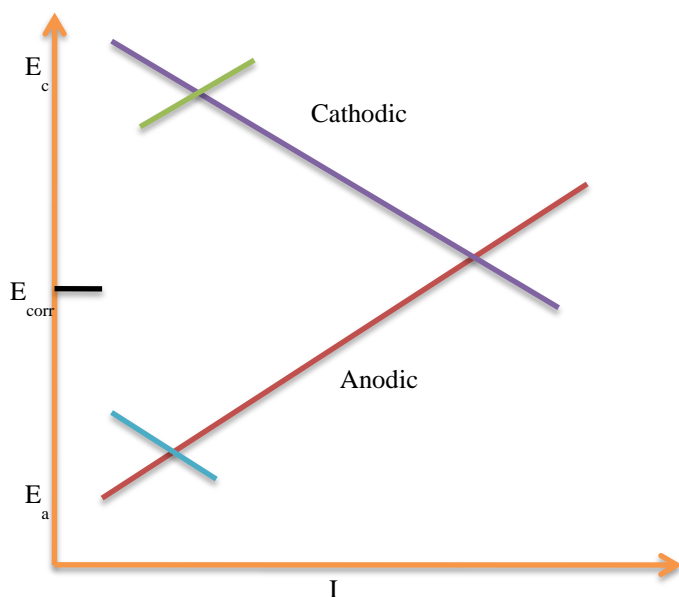
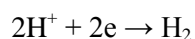


Figure 1. Evans type polarization diagram describing a simple corrosion process.

Anodic reaction



Cathodic reaction Acid



Neutral to alkaline

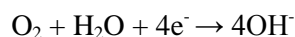
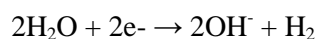
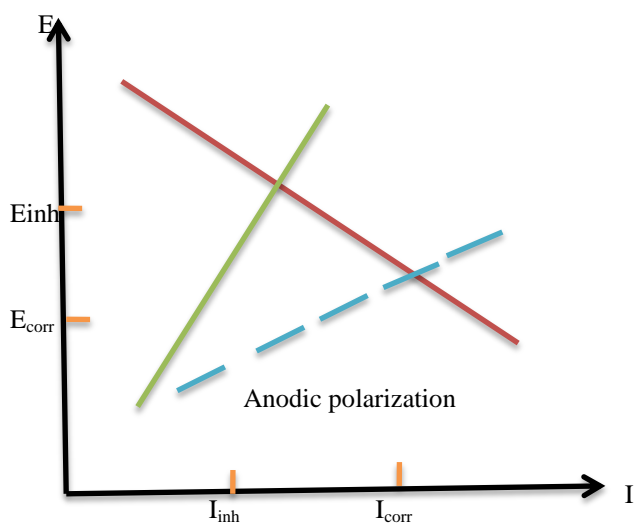


Figure 1 show six basic changes to produce in electrode potential and current density by the addition of inhibitors [12] and several situations are depicted in Figure 2 (a-f). It can be observed that a corrosion inhibitor can either affect the anodic partial reaction, cathodic partial reaction or both so it is classified of anodic, cathodic or mixed inhibitors which depend upon whether they reduce the corrosion current by shifting the corrosion potential anodically (positively),cathodically (negatively) and both directions respectively.

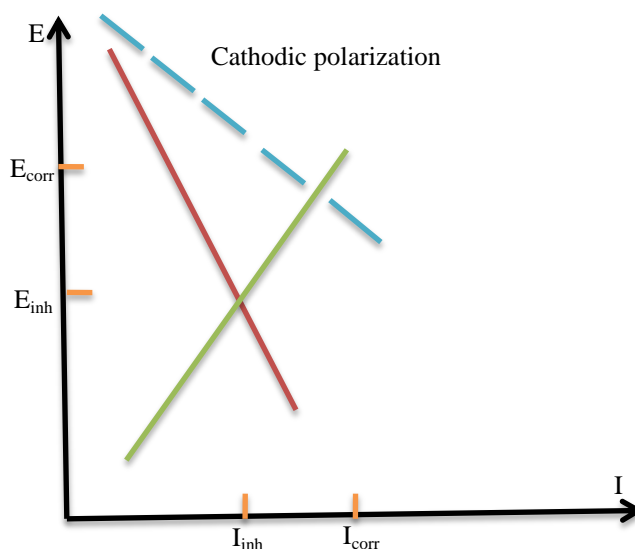
The remaining situation pictured in Figure 2 (a-f) is the presence of an ohmic resistance. This may result naturally form the presence of a potential drop in solution or in the presence of a poorly conducting film, a feature associated with certain types of inhibitor films (e.g. inhibition of copper and copper alloys by benzotriazole) and paint films.

Passivation of Inhibitors

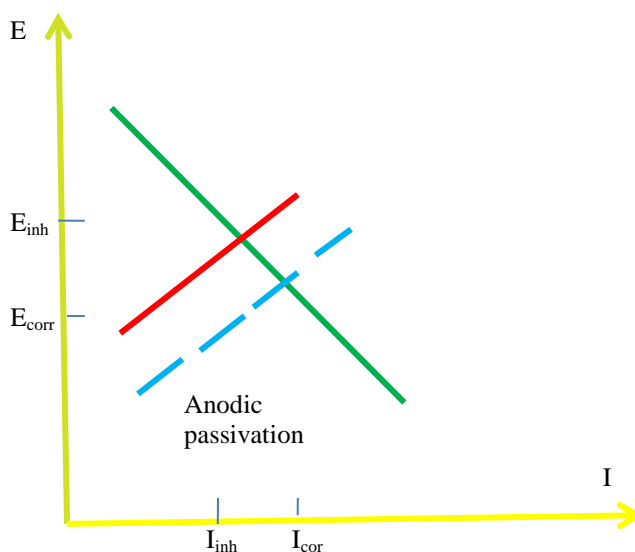
It is described as specific inhibitors. Passivating inhibitors [13] are anodic inhibitors. They cause a large potential shift in corrosion potential to make a metal passive. When they are available in sufficient concentrations, they can stifle corrosion. However they emphasis lies on their presence at a sufficient concentration, they can promote localized corrosion through being unable to inhibit the entire active anodic site and they are known as dangerous inhibitors. Cathodic inhibitors are often safe inhibitors because they do not interact directly with the anodic reaction. Nevertheless there are notable exceptions in the form of cathodic poisons which interfere with the cathodic hydrogen recombination reaction reduces general corrosion, but it can promote hydrogen blistering and embrittlement [14] due to absorption of atomic hydrogen by the metal.



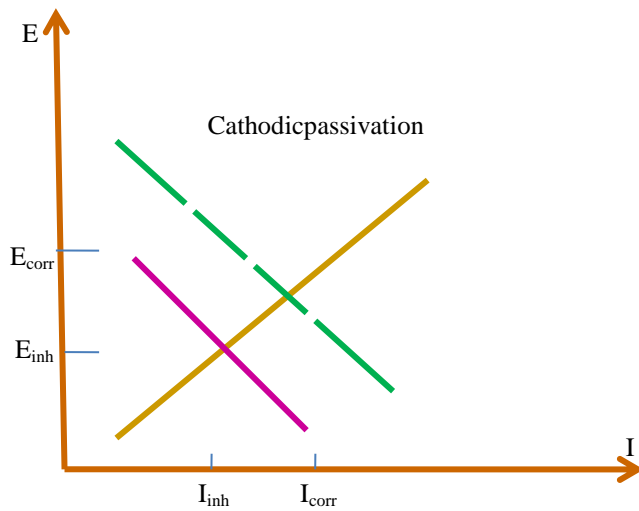
(a) Action of anodic inhibitors.



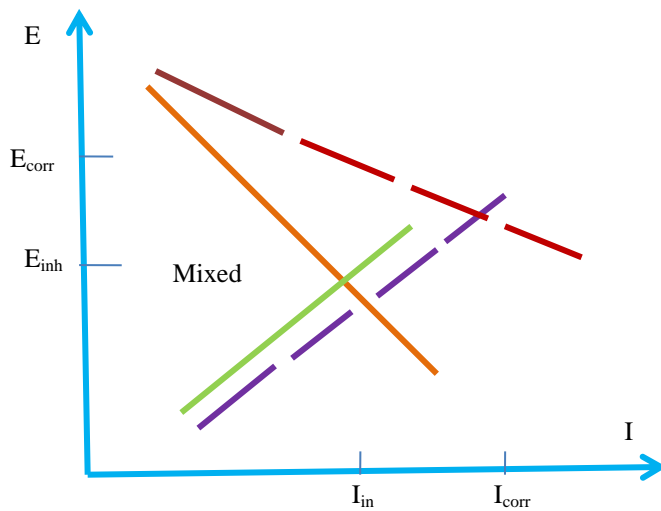
(b) Action of cathodic inhibitors.



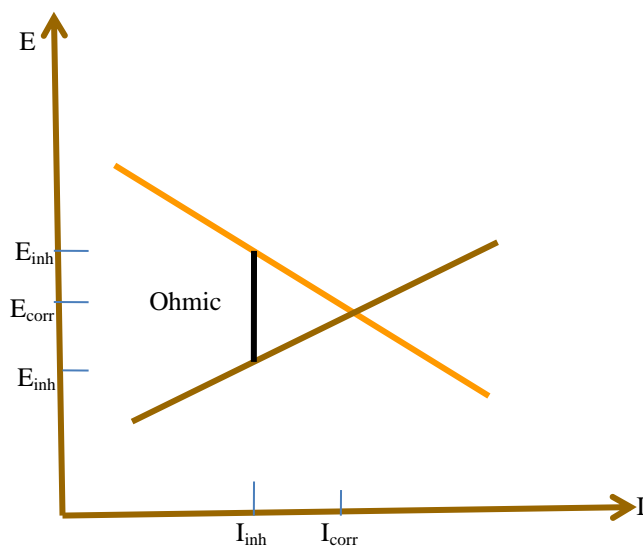
(c) Action of an inhibitor acting as an anodic passivator.



(d) Action of an inhibitor acting as a cathodic passivator.



(e) Action of an inhibitor acting as a mixed inhibitor.



(f) Action of an ohmic inhibitor.

Figure 2. (a-f) Evans polarization diagrams describing chemical inhibitor can effect corrosion inhibition.

The picture for a passivating inhibitor may be generally described as noticed in Figure 2 (a-f), where if the inhibitor is present below a critical concentration the corrosion potential can shift either in the active or passive region and unstable situation generally resulting in pitting corrosion. However, in drawing parallels with the simple picture of an anodic inhibitor in Figure 1 (a), there are some important differences. The basic criterion of inhibition resulting from an anodic shift in corrosion potential certainly applies.

The polarization diagram of Figure 2 (d) shows no basic change to be produced between the shape and position of the overall anodic polarization curve whereas the cathodic reaction changes significantly. The inhibitor is causing the potential of the corroding metal to be shifted sufficiently toward anodic site within the thermodynamically defined passive region inherent to that metal. The inhibitor oxidising action on the metal surface depends upon their concentration. Typical oxidising inhibitors are chromate and nitrite which are themselves easily reduced. They produce the effect of depolarising the cathodic reaction as is shown in Figure 3. However certainly in the case of chromate, adsorption of chromate at anodic areas also appears to play a part in the process of polarizing anodic reaction [15] and decreasing the anodic current required to move the potential into the passive region.

Certain passivating inhibitors like phosphate, silicate and molybdate, are known as non-oxidizing inhibitors. They induce passivity in the presence of oxygen. They become dangerous in insufficient concentration. The inhibitor anion forms passive oxide film, which further helping to stabilize it.

Adsorption Inhibitors

Generally, adsorption inhibitors are organic-based film-forming corrosion inhibitors [16]. The polar or charged organic molecule/ionic species are first accommodated by a physisorbed surface film which may further stabilize through chemisorption to form a donor type bond which is noticed in Figure 4.

Lewis acid and base theory is applied for the stability of the donor (adsorption) bond [17]. The Hard and Soft Acids and Bases principle where a hard acid will bond with a hard base and vice versa. The principle is exemplified in Table 2.

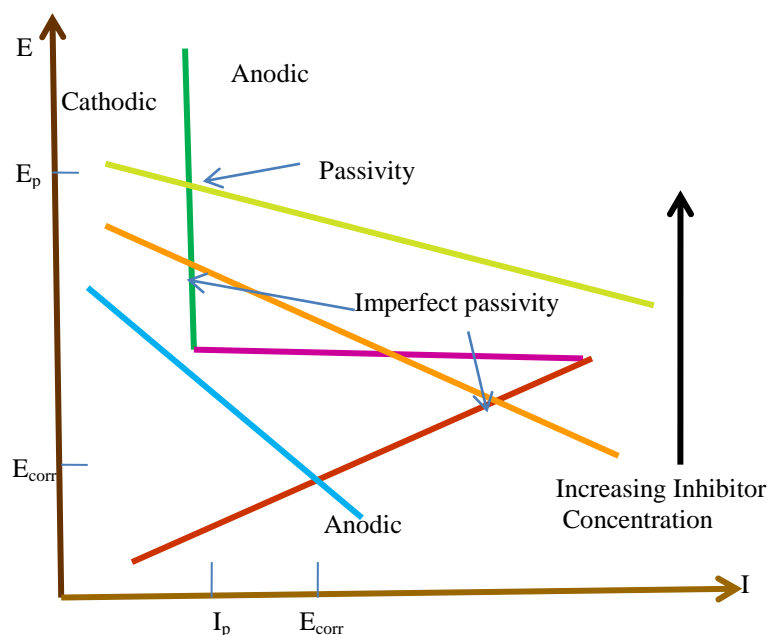


Figure 3. Evans type polarizations describing the action of a passivating anodic corrosion inhibitor.

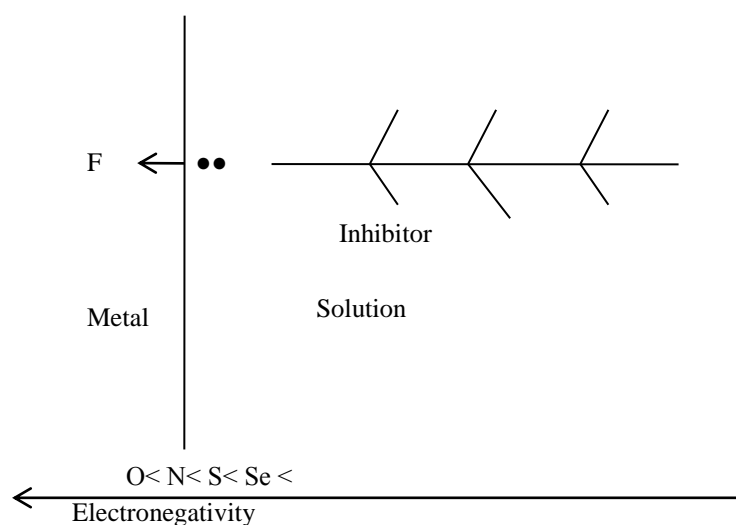


Figure 4. Schematic representation of the chemisorption process for an organic film-forming corrosion inhibitor.

Table 2. The hard and soft acid and base (HASB) principle.

Hard	Low polarisability High electronegativity
Soft	High polarisability Low electronegativity
Hard acid Iron oxide	Hard base O, N
Soft acid Active iron	Soft base S,P,Se, As

Generally, inhibitor action [18] takes place in acid solution. The corrosion of metal surface is inhibited by the cathodic and the anodic electrochemical processes of inhibitors. Inhibitor has adsorbed on the metal surface, it can affect the corrosion reactions in a number of ways: by developing a physical barrier to control diffusion of ions or molecules, by direct blocking of anodic and/or cathodic reaction sites, by interaction with intermediate corrosion reaction, by stopping the formation of electrical double layer at the metal/solution interface or by affecting the rate of electrochemical reactions taking place there.

Precipitation of Inhibitor

Metal surfaces are usually covered with oxides, hydroxides or salts present in near-neutral solutions due to they reduce corrosion of metal in this region. Here inhibitors form a protective surface film which produces a passivating action. Precipitation can inhibit corrosion; the precipitated film [19] develops a barrier to stop diffusion of oxygen to the metal surface. If the performance of inhibitor is associated with the involvement of oxygen in the overall corrosion process such inhibitors work as cathodic inhibitors. The cathodic oxygen reduction reaction tends to favour precipitation at cathodic areas of many salts. Effecting such inhibition is also known as cathodic inhibition. The most common salts in this class are insoluble hydroxides of zinc and magnesium, and carbonates of calcium and magnesium where the inhibition can be directly initiated by adjusting the bulk pH. The precipitated films cover a metal surface so that they may also exhibit some anodic protection. In the case of phosphates and silicates earlier classed as non-oxidising passivators, precipitation may well play a significant role with inhibitor action appearing to be mixed.

Corrosion Inhibitors in Practice

The review paper that follow look in more detail at specific applications of corrosion inhibitors and inhibitor testing/selection so comment here is restricted to some general observations on practice. The

range of corrosion inhibitors available is large which in itself can make selection on the basis nature of materials and environment conditions [20]. This is particularly true with regard to the ever growing range of organic based corrosion inhibitors, where small changes in inhibitor chemistry can have significant effects on performance. Inhibitor performance and thus selection will be affected by the nature of the metal and that of its surface nature and composition of the environment, temperature fluid dynamics and inhibitor concentration. The presence of dissimilar metals [21] in the same system produces crevices and other surface deposits, presence of other chemicals and toxicity regulation, and inhibitor selection becomes far from being a straightforward choice. All this serves to highlight the need to understand, and ideally accurately describe the system to be inhibited and the need to conduct laboratory studies and testing if the right inhibitor is to be finally selected and used in a cost-effective manner.

Electrochemical test methods [22] are now very much suitable in the study of corrosion inhibitors. Electrochemical studies of corrosion inhibitors have benefited enormously from the simple weight loss/exposure type test. Organic coatings can be measured by AC impedance. However, in looking at test methods no one method provides all the answers from which final inhibitor selection can be safely made. It is important to understand just what a particular test method is measuring and its limitations and the implications of this in response to possible mechanisms of inhibition. For example, work on high temperature CO₂ corrosion of carbon steel points to inhibition being achieved by retardation of the dissolution of an iron carbonate scale layer. Such an effect cannot be observed by electrochemical measurement in constant inventory autoclave tests.

Although the application of corrosion inhibitors is larger based, their principle [23] use lies in the inhibition of general corrosion. Localized corrosion is observed in many forms such problems can be solved by the successful use of a corrosion inhibitor. This may in part be associated with the corrosion cell that often results from restricting inhibitor access of particular importance to anodic inhibitors; cathodic inhibitors can have their problems like cathodic poisons which many promote cracking due to hydrogen damage. Such situations produce crevice, pitting and stress corrosion. The inhibition of stress corrosion cracking, localized corrosion and general corrosion are related to the use the inhibitors in the solution of environment. The environments which promote environment sensitive fracture are often those environments formulated to prevent general corrosion.

The application of commercial corrosion inhibitor [24] products can be formulated as specific surfactant/solvent package which work as synergism. The inhibition of mild steel by zinc-molybdated mixtures is an example of synergism which lowers the corrosion rate in the presence of both in solutions of the individual components. Inhibition is achieved as a result of the two ions combining to retard the cathodic reduction of oxygen. It is possible to produce similar effects on corrosion rate with organic film-forming corrosion inhibitors in oilfield applications. Their effects can be achieved by changing/removing the surfactant or changing the solvent package. Synergism is changing/modifying the physico-chemistry. The surfactant increases adsorption capability of the metal surface. The corrosion inhibitor species are the solvent package affects partitioning and/or dispersibility of the inhibitor available/active inhibitor concentration in solution.

Design of Corrosion Inhibitors in Oilfield

Inhibitors [25] are used to control corrosion in drilling and stimulation fluids, oil-producing wells, water injection systems, transportation and refining systems. Inhibitors are also applied externally to prevent rusting of stored tubular goods. Inhibitors are synthesized from relatively few basic materials and depend upon formation of a chemically adsorbed film, passivation of a metal surface by altering the corrosion by-product formed or forming a complex with the metal surface. Their requirements depend upon the corrosive environments and natural corrodents, the metal can be protected and equipment design parameters.

The ability of the inhibitor forming an impervious long-lasting film depends upon its chemical structure and interaction with the corrosive environment. This review paper addresses the synthesis,

formulation, testing and proper application of inhibitors based upon the requirements of particular systems in oil production and transportation. Monitoring to ensure that the inhibitor is meeting the requirements, downstream effects of the inhibitor on oil-water separation, compatibility with other treating chemical and processes, environmental considerations and effects of microbial [26] activity will also be considered.

The Requirement of Inhibitor

Before using inhibitors against corrosion, it is necessary to understand corrosive medium. The following areas and parameters and performance specifications of a particular inhibitor are required.

Top of Pipe

For a pipe since it is lying in a straight-line position, it is very difficult to inhibit. The flow velocity is less than required for turbulent velocity; liquids will not contact this area except in areas of slug or partial slug flow. In such a condition addition of a volatile inhibitor may be required.

Water Wet Area-Bottom of Pipe

In most cases free, it is observed that liquid can move along with the bottom of the pipe. It depends upon velocity and the layer of discrete layers of oil and water. At low velocities solids dropout can cause concentration cells and pits production underneath the deposits.

Turbulence Prone Areas

Areas downstream of welds, minor buckling of the line, lower area and solid deposits can increase shear stress and turbulence which may aggravate corrosion. Low spots cause slugs of liquid at intervals. Turbulence removes protective scale, aggravates abrasion and erosion if solids are present [27] and may affect inhibitor performance by removing the film. Inhibitors must be able to withstand the shear stresses.

Oil Production Systems

Tubing

Protection of production tubing requires that the inhibitor be squeezed, added continuously or have film persistency so that batch treatment is feasible. Shear stresses impose the same requirements on inhibitors to withstand velocity effects. The tubing will be wetted more completely on the low side in deviated (non-vertical) wells [28], and in low-volume production a separate layer of water on the low side may be the only corrosive area.

Down Hole Pumps

The inhibitor films have some lubricating properties [29] so it is used in pumped, wells abrasion of rods on tubing. In many wells' entry of air through the annulus so inhibitor functions requires in the presence of oxygen. Down hole centrifugal pumps are susceptible to failure due to scaling and velocity effects.

Surface Equipment

Problems occur in equipment areas such as wellheads, chokes, and vessels where velocity effects on separators and other vessels' stagnant areas, scales and solid deposits can create concentration cells. Growth of bacteria may occur in these areas.

Injection Systems

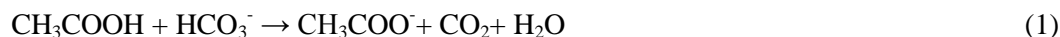
Polymers are introduced in some specific requirements in secondary recovery of water-flooding, tertiary recovery CO₂, micellar fluids. Inhibitors must have proper solubility and wetting characteristics and be able to perform in the presence of the surfactants and polymers added to the fold. A surfactant component may be required in the inhibitor to maintain injection rates in production water injection systems.

Gas/Liquid Composition and Operating Conditions

The major controlling factors for corrosion rates are the composition of the gases and liquids produced or transported and conditions of flow, temperature and pressure.

H₂S-CO₂ Contents

The acid gas content determines the type of corrosion and greatly influences the corrosion rate. Corrosion rates are directly related to the amount of CO₂ [30] dissolved in the water which determines the amount of carbonic acid and subsequent metal dissolution. If organic acids are present corrosion rate is increased by removal of bicarbonate ion and by dissolution of protective iron carbonate:



High velocity causes turbulence and increases corrosion rates. The temperature of the system, increased salinity and bicarbonate content also affect the corrosion rate and the inhibitor requirements.

Where H₂S [31] is present line failure due to penetration underneath pits can occur in a short time. The sulphide film formed may be anodic to the metal surface and afford some degree of corrosion protection. Fe-S layer is not continuous and is porous. The net result is pit formation and growth. Sulphide ion develops stress cracking and hydrogen embrittlement to consider in inhibitors for H₂S. In systems where H₂S and CO₂ both are present, the ratio of CO₂ to H₂S determines whether CO₂ or H₂S corrosion mechanisms will dominate.

Inhibitors must be Effective against H₂S and CO₂

Liquid Composition

The composition of water ranges from condensation water to high salinity formation water. Inhibitor solubility and dispersibility affect corrosion rate. Flood water gets mixed with river, pond, lake, well and sea water to produce corrosive medium. In some cases, hot water is discharged into fresh water so it develops hostile environmental.

A hydrocarbon of low molecular weight aliphatics to high molecular weight asphalt does not enhance inhibitor film formation while higher molecular weight hydrocarbons and organic compounds can help the inhibition. Paraffins and waxes form deposits and require treatment.

Temperature

The corrosion of carbon steel by CO₂ is directly dependent upon temperature. At temperatures below 60°C scale provides little corrosion protection. In the temperature range of 60 and 100°C iron carbonate will form on its surface. The scale may result in lower than predicted corrosion rates, but severe pitting can occur. At temperature above 100°C scale is formed on the surface as a thin, dense layer of iron carbonate/magnetite and affords good corrosion protection under most conditions. Temperature [32] affects the inhibitor requirements as far as stability and filming ability is concerned. No polymerization of the inhibitor can be tolerated since plugging can take place.

Pressure

Pressure has a direct effect since corrosion rates are proportional to acid gas partial pressures. It will affect inhibitor solubility since at extremely high pressures methane will act like a liquid and may remove the solvent from the inhibitor, leaving a thick residue.

Flow Parameters

The flow parameters are related to velocity, type of flow, and gas to liquid ratio. Velocity has definite effects on the ability of inhibitors to control corrosion. The type of flow determined by velocity is characterized as annular, stratified, or slug flow. Flow regimes vary in different sections of lines and tubing because of restrictions and low places; slug flow in producing wells increases

turbulence. Distribution of the inhibitor in all areas of a pipeline is related to flow velocities and the composition of the gas and liquids in the line. At annular flow velocities, the stream is homogenous, and inhibitor added continuously will contact all portions of the line equally. When flow velocities are lower, the flow is partly annular with a higher concentration of liquids in the bottom half of the pipe i.e., the film of liquids is thicker [33]. Lower flow velocities allow some free liquid to collect in the bottom of the line and slug flow predominates as the flow rate declines stratified flow predominates and the stream is a gas phase and a liquid phases. The top portion may not be regularly contacted at all with liquid except that condensed liquid form the gas. A vapour phase inhibitor or some means of a periodic batch that contacts the top of the line must be considered. In stratified flow, partitioning of the inhibitor between oil and water layers is important. Slug flow increases requirements for ability to withstand shear stress. At velocities of less than 10 m/s it is reported that very little effect on CO₂ corrosion rates will take place. At velocities of 10 to 20 m/s turbulence can cause local areas of higher attack and at velocities above 20 m/s corrosion by-products will be removed. This increases corrosion rates and could affect inhibitor filming ability.

Other Factors Affecting Corrosion Inhibitor

Other factors affecting corrosion include bacteria, scaling, mechanical or chemical treatment of lines prior to commissioning such as treatment of the pipe during storage and completion methods and treating procedures to produce corrosion. Economics of treating is important. Compatibility of the inhibitor [34] with inhibitors, oxygen scavengers, and biocides imposes special requirements.

Bacteria

Particularly sulphate reducing bacteria can increase corrosion rates and may need to be controlled with organic biocides. Organisms may be introduced during hydro-testing of lines and by contamination or producing systems from sumps and sea water flushing of vessels.

Scale

Scaling may need to be controlled to prevent pitting corrosion. The inhibitor may be a combination material which may be used separately.

Mechanical and Chemical Pre-treatment

Pipelines may require treatment to remove mill scale and deposits prior to a successful inhibitor treatment regime and will be hydro tested. Prevention of corrosion and bacterial growth [35] during testing is required.

Completion Methods and Treating Procedures

Completion methods dictate the treating procedures. If the well is flowing with a packed-off annulus it may be necessary to install a chemical string for continuous treatment. Side pocket mandrels with chemical injection valves or capillary strings require that inhibitors be stable in the annulus or the string for extended periods. If a chemical string is not feasible, batch treatments using film persistent inhibitors may be used. The inhibitor is designed to form a tough film that is not too soluble in the production stream so it will last for sufficient time between treatments. The batch may be displaced with liquids, gas, or nitrogen. Squeeze inhibitors must be designed to be stable in the formation and not cause severe emulsion problems in the formation. The adsorption characteristics must be controlled for proper feedback of inhibitor. Pumped wells can be treated by continuous addition or batching down the annulus.

Economics

Economics of inhibitor use is an important requirement and includes inhibitor costs, treating level any non-routine treating procedures, monitoring, volumes of water to be treated, and development costs for these factors.

Compatibility with other Chemicals

The inhibitor must be able to be treated in the presence of other materials such as phosphonates, polymers, bisulphites, and surface active agents and must not interfere with their functions.

Designing the Inhibitors

Test Methods and Monitoring

Proper inhibitor evaluation and development [36] depends upon selecting a test method that will examine particular requirements such as film strength or is within parameters that simulate actual field conditions. As an example of the first is the bubble test and the second is a flowing loop test. Corrosion measurements are made by weight loss, linear polarization, potentiodynamic measurement, alternating current impedance, and electrical noise. Some of the test methods used for inhibitor selection are listed below.

Static Tests

This involves placing a coupon in a corrosive environment and leaving it quiescent for a period of time. The coupon is then inspected, pitting noted, cleaned and weighed to determine weight loss and percent protection. The test can be run at different temperatures and pressures and continuous and film inhibition can be tested.

Stirred Flask (Bubble) Test

This involves the bubbling of CO₂ (or mixed gases or H₂S) through a stirred flask maintained at a specified temperature. The corrosion rate is read with electrodes immersed in the flask. Oil-water mixtures can be varied to test the partitioning of the inhibitor in the oil and water. Filming speed and the level of inhibition can be determined by LPR, AC impedance, electrochemical noise measurements and weight loss coupons.

Autoclave Test

Autoclave tests may be stirred, agitated, static, high pressures and temperatures may be obtained. These tests impose more severe conditions on the inhibitors under test and their stability under extreme conditions can be evaluated.

Rotating Cylinder or Electrode Tests

A flask containing a rotating electrode assembly can test the effect of shear stress on corrosion rates and inhibitor film strength. The shear stress can be calculated and turbulent flow in a pipeline at known hydrodynamic conditions simulated.

A cylindrical test specimen is attached to the bottom of a shaft in a standard rotating disk apparatus with a variable speed motor. A slip ring assembly is used for the electrical contact to the rotating electrode.

The effect of different shear stresses and inhibitor addition is observed and recorded. LPR (linear polarization resistance), electrical noise and AC impedance measurements may be used to measure corrosion rates. One variation of this test uses a stationary electrode and a rotating cylinder.

Flow Tests

This test simulates flow conditions found in a pipeline. The tests use weight loss coupons, electrochemical measurements and analysis of the circulating media. The fluids, acid gases, temperature and velocities can be altered as required.

The test can be modified for jet impingement studies. Jet impingement on a weight loss coupon or microelectrode assembly simulates high turbulence and mixed flow conditions. There will be a central laminar flow region, a transition zone with maximum shear stress and an outer zone where the turbulence decays proportionally to the distance from the central region.

Wheel Tests

Coupons are placed in bottles or flasks containing water and oil. The bottles are purged free of oxygen, saturated with the acid gas to be tested, sealed and installed on a rotating wheel or cylinder in a heated chamber for a specified period of time. The coupons are removed, inspected and weighed. Pitting and blistering is noted and the tendency of the inhibitor to form a stable emulsion with the oil in the test is also noted and recorded. Inhibitor can be added to the bottles or the coupons can be filmed before being put in the bottles.

Types of Chemicals and Inhibitor Mechanisms

The types of chemicals used as inhibitors are predominantly organic amines. These compounds quick form film and high resistance to wash-off, or have extremely long film persistency. Such types of inhibitors are selected to be effective against H₂S, CO₂ and organic acids [37] in particular. In some cases, resistance to oxygen contamination is important. They should exhibit at least 90% protection in the tests selected for final evaluation.

Organic amine inhibitors form a chemical bond with a metal surface. The nitrogen in the amines are cationic and bond with anionic sites on the metal surface. There is evidence to suggest that the amine forms a complex with oxides and sulphides on the metal and perhaps with the metal itself. Their mechanism is quite complicated and there is some evidence that the molecule actually re-arranges and forms a polymeric material on the surface. Some work indicated that the nitrogen acts as donor to the surface and the polymeric complex forms a strong bond to the metal. The bond is particularly strong to a sulphide layer, but amines do not bond strongly to an oxide layer. The presence of oxygen interferes with their performance: less additives are formulated in the inhibitor blend to counteract this.

The filming effect is enhanced by the presence of materials such as fatty acids and naturally occurring high molecular weight organic acids in petroleum. Addition of polybasic acids to the inhibitor formulation can cause cross-bonding of the amine layer and increase film life or persistency. Certain types of organic acids and organic compounds containing phosphorus, sulphur and other elements increase the inhibition in the presence of oxygen.

The layer of inhibitor isolates the metal from the electrolyte and stops the corrosion reaction. In continuous treatment, the film is replenished by inhibitor in solution. For batch treating, and amine or amine blend is selected that forms a long-lasting film that is replenished at intervals by another batch of inhibitor.

Raw Materials for Inhibitor

The basic raw materials [38] for preparing inhibitors are fatty acids (or synthetic long chain aliphatic acids), naphthenic acids, oxidized petroleum fractions and ammonia or organic amines. Acrylonitrile and alpha olefins are also used for synthesizing amines. Table 2 shows some of these chemicals and their reactions.

Fatty Acids

These acids range occur from low molecular weight to high molecular weight organic acids e.g., C₂ to C₁₈ carboxylic acids. The low molecular weight acids are normally used only to salt amines to achieve water solubility or dispersibility while the high molecular weight acids are used to form fatty amines. Fatty acids based on vegetable and animal fats such as tallow, coconut oil and tall oil are the most commonly used and include lauric, stearic, oleic, linoleic, and linolenic acids. Unsaturated fatty acids may be polymerized to form poly carboxylic acids.

Amines

These amines' range lies from ammonia (NH₃) to high molecular weight ethyleneamines. One manufacturing process for making ethylene amines is the reaction between ethylene dichloride and ammonia. The reaction product, ethylenediamine, can be used to make imidazoline, amido and amies.

It may be further reacted with ethylene dichloride to form diethylenetriamine and higher molecular weight ethyleneamines.

Fatty Amines

Primary fatty amines are made by reacting fatty acids with ammonia to form amides then hydrogenating to the amines. Primary amines can also be made from alpha olefins. Secondary and tertiary amines are also synthesized from alpha olefins and may be further reacted to make amides, quaternaries and the like.

Fatty Diamines

These are synthesized by reacting a primary fatty amine as described above with acrylonitrile then hydrogenating to the amine.

Fatty Amido-Amines and Imidazolines

These are manufactured by reacting selected fatty acids with polyamines such as diethylenetriamine or n-amino ethyl piperazine. Polyamines can range from two nitrogens up to 6 or more in some complex polyamines. The polyamine may contain a hydroxyl group which will impart some water solubility.

Oxyalkylated Amines

The amido-amines, primary amines and imidazolines may be reacted with ethylene oxide to make them water soluble. From one to many moles of ethylene, propylene, or butylene oxides may be added depending upon the degree of water solubility and oil-water partitioning desired. The addition of alkylene oxide to amines forms tertiary amines which may be quaternized.

Quaternaries

Quaternary ammonium salts are made from tertiary amines such as dimethyl fatty amines or oxyalkylated amines, and an organic sulphate or benzyl chloride are commonly used.

Other Amine Derivatives

Amines may be modified by adding phosphorus, sulphur, or other elements to the molecule to improve adsorption to the metal surface. They may be further reacted with epoxides, urethanes, and other cross-linking agents to build molecular weights. The amines are then blended with diamerised fatty acids, etc. to achieve cross-bonding of the molecules on the metal surface. They may be blended with low molecular weight inorganic and organic acids to make them water soluble or dispersible. Nitrite and phosphate groups may be added to achieve some surface passivation.

Formulation of Inhibitors

After proper molecules are selected or synthesized they must be formulated into a usable or "finished" product. The amines are viscous liquids or solids and must be diluted with a proper solvent. The solvent may be an aqueous blend (water, alcohol or coupling agents) for water solubility. Coupling agents include glycols, others alcohols, esters, and ketones. They are selected to form a stable solution of the amines and other additives and have the proper degree of water and brine solubility [39] or dispersibility.

Solvents

A hydrocarbon solvent will be used for oil soluble or an oil soluble water dispersible inhibitor. Aromatic solvents are preferred since they have much better solvating properties than aliphatic solvents. Pure aromatics such as xylene and toluene are rarely used because of cost, so by-product aromatic solvents form cumene and some gas oils and light cyclic compounds are used. They may contain some polycyclic materials and anthracenes, so pour point must be considered. In special instances aliphatics such as diesel will be used.

Other Additives

The formulations may contain special type of surface active agents to aid in dispersing the inhibitor, preventing emulsions and reducing the time it takes for the amine to “wet” the metal surface. They may also aid in penetrating loose deposits to the metal underneath. These may include sulphonic acids and sulphonates, oxy-alkylated materials such as amines, alkyl phenols, fatty acids and amides, amphoterics, etc. There are several products given below.

In addition to the amine, there will be materials added to increase film strength such as fatty acids. Low molecular weight organic acids and hydroxyl acids are added to achieve water solubility or dispersibility. Wetting agents may be added to help the amine contact the metal surface and penetrate loose deposits. An emulsifying surfactant/dispersant [40] may be added so that the inhibitor will form a stable dispersion in well fluids. Conversely, a demulsifier may be added to prevent formation of stable oil-water emulsions that can upset production and processing facilities. Vapour phase inhibitors include low molecular amines such as ethyl amines, diethyl amines, and triethylamines. They have low boiling points and high vapour pressures and are blended into the corrosion inhibitor formulation for a combination product [41].

Monitoring

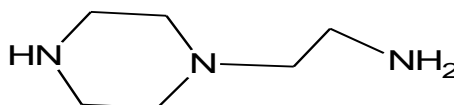
The inhibition program [42] must be monitored continuously to be sure that the desired protection is achieved. Iron counts will give a fair indication of the amount of corrosion occurring and actual iron loss can be estimated. It will not tell if pitting is occurring. Manganese analyses can be run to substantiate the iron counts. Corrosion coupons, LPR and resistance probes may be installed in the system. In pipelines an intelligent pit can be run at selected intervals to see the actual corrosion and pitting. Acoustic emission and magnetic flux devices may be used to monitor metal loss and pitting.

Table 2. Chemical Raw Materials for Inhibitor Synthesis

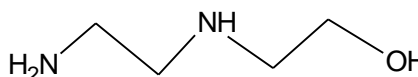
Ammonia	NH_3
Acrylonitrile Amines	$\text{CH}_2=\text{CHCN}$
Ethyleneamines:	$\text{CH}_3\text{CH}_2\text{NH}_2$
Ethylenediamine (EDA)	$\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$
Diethylenetriamine (DETA)	$\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$
Triethylenetetramine (TETA)	$\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$
Tetraethylenepentamine (TEPA)	$\text{H}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$

Condensation of the above organic compounds synthesized high molecular weight of inhibitors:

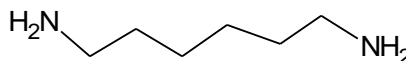
N-Aminoethylpiperazine



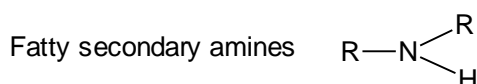
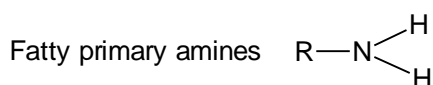
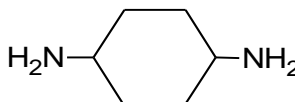
N-Aminoethylethanolamine

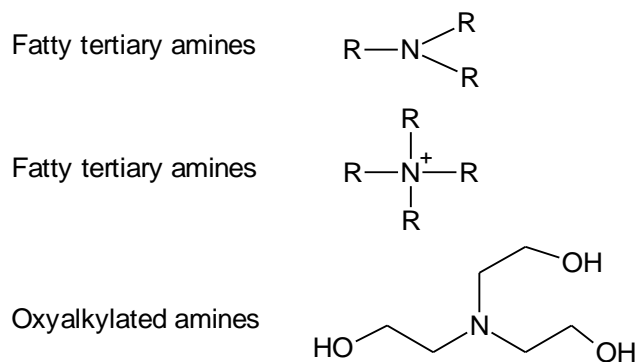
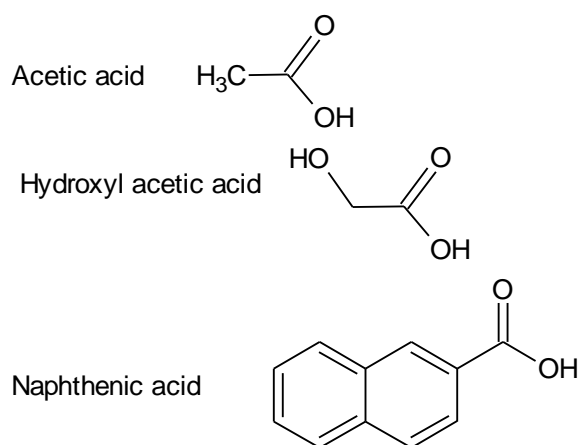


Hexamethylene diamine

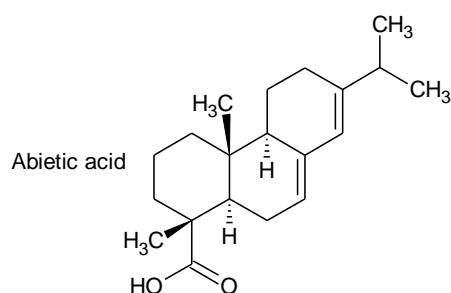
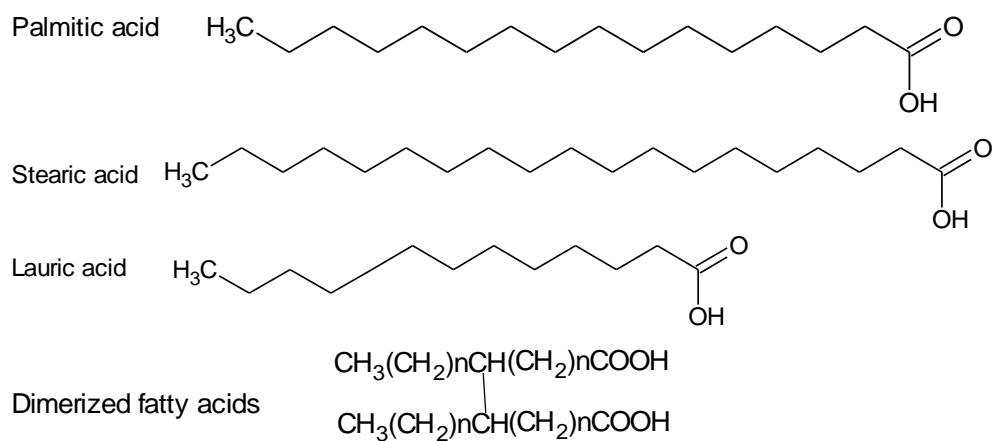


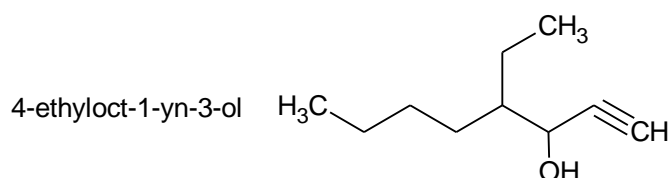
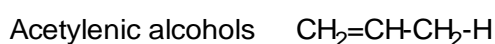
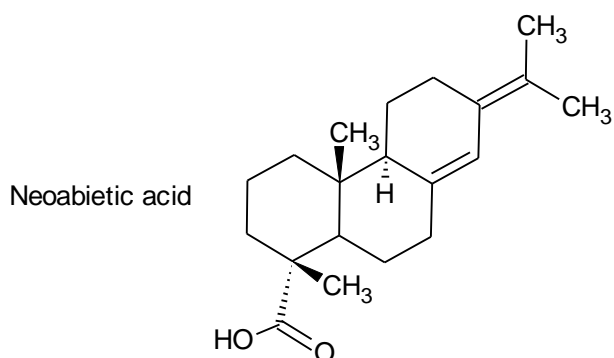
Cyclohexamethylene diamine



**Organic acids**C₁₂ to C₁₆ COOH Fatty acids

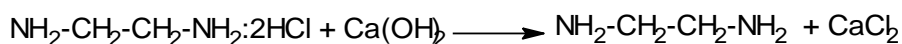
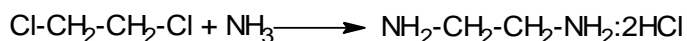
Vegetable and animal fatty acids:



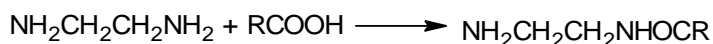


Reactions

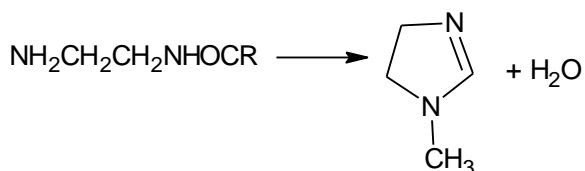
Synthesis of ethyleneamines: Ethylenamines? react with ammonia



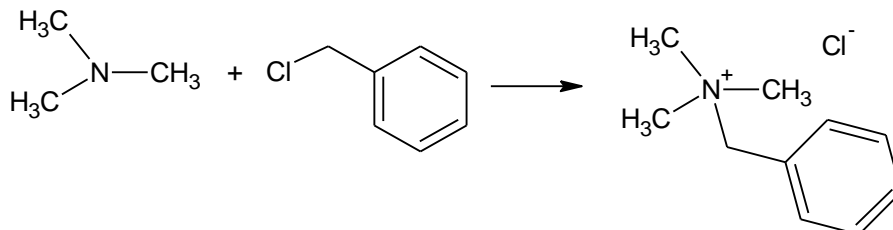
Amidization: Ethylamines react with fatty acids to form amidoamines.



Cyclization: Heating of amido-amines form imidazolines.



Quaternization: Tertiary amines react with halides or sulphates to form quaternary ammonium salts.



Epoxidation: Alpha olefins oxidize to form fatty epoxides.



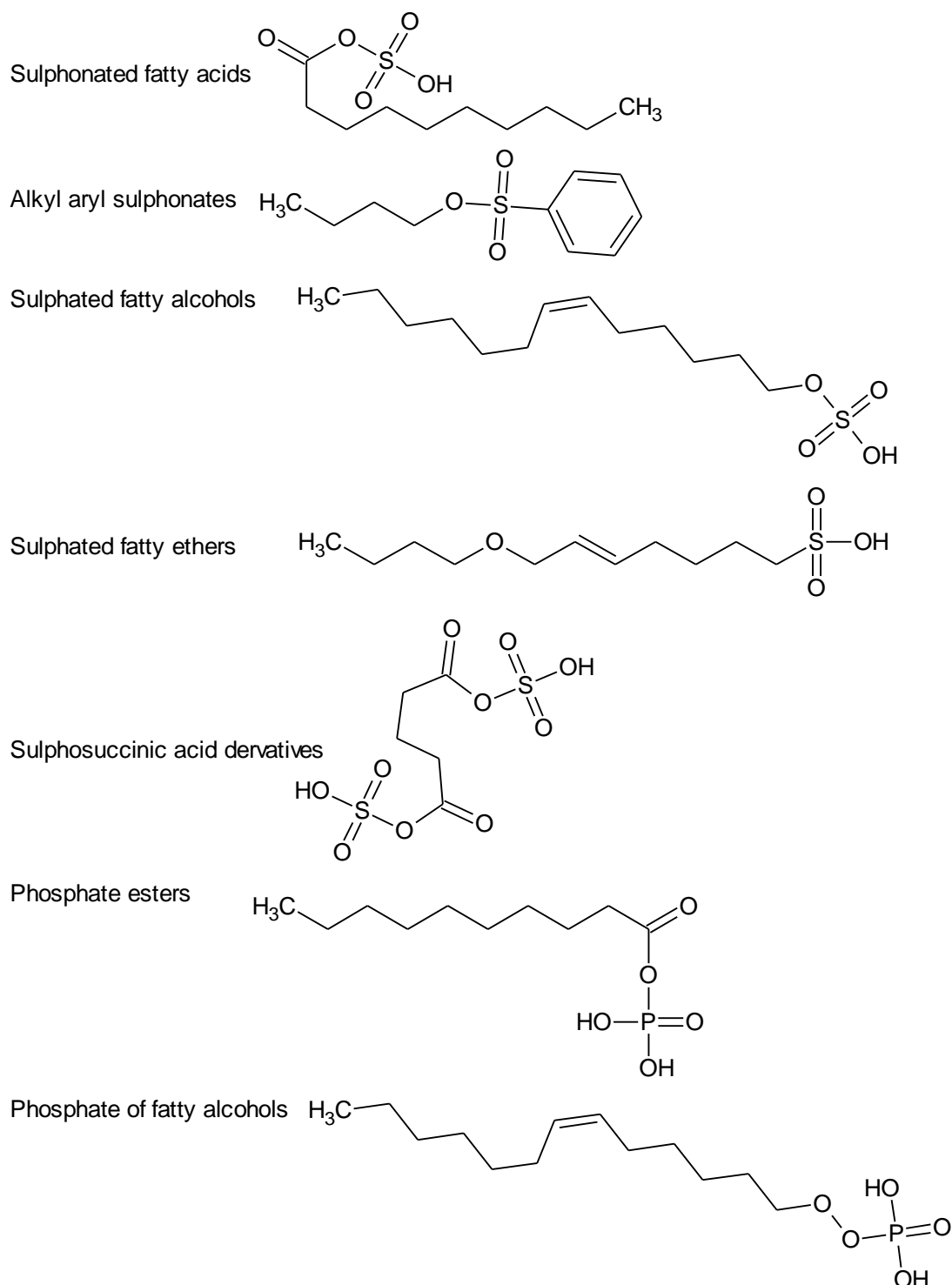
Dimerization: Polymerization of fatty acids containing double bonds by reacting with ozone form dimer and trimer carboxylic acids.

Addition of other reactive groups: Phosphorus compounds for passivation properties sulphurization of fatty acids for film strength nitrite-nitrate for passivation and oxygen resistance?

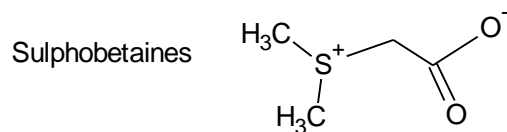
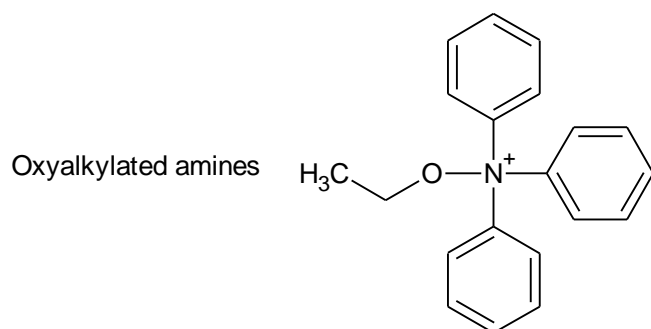
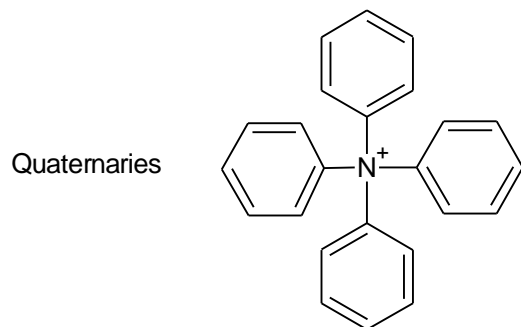
Formulation of additive corrosion inhibitors

Surfactants for wetting and dispersing

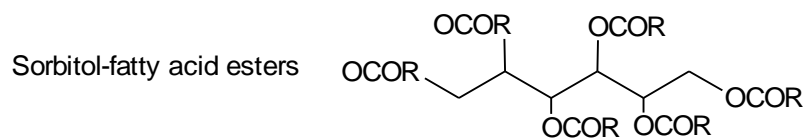
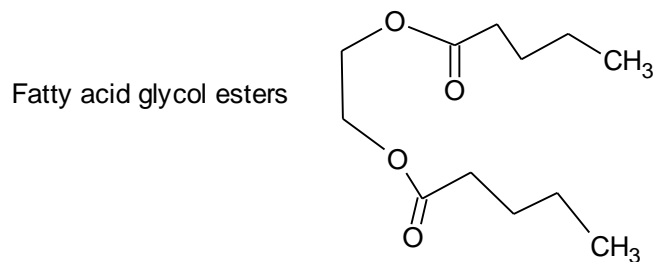
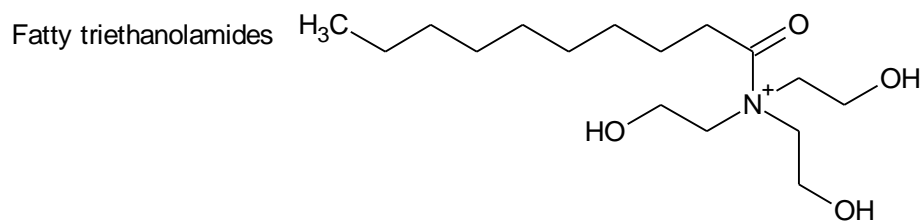
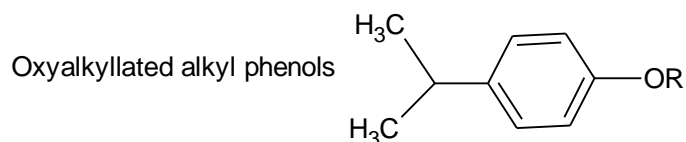
Anionics



Cationic and amphoteric:



Nonionics:



- Surfactants for emulsion prevention in Oilfield
- Propylene/ethylene oxide adducts of glycols, amines and resins
- Sulphonates in Oilfield
- Polyglycol esters, urethanes and epoxides in Oilfield
- Coupling agents for stability, solubility and pour point Oilfield
- Alcohols, Isopropanol, octanol, etc. Oilfield
- Glycol-ethylene, diethylene, etc. Oilfield
- Glycol ethers, Esters, Ketones Oilfield
- Miscellaneous Organic compounds
- Phosphonates and polyacrylates for scale control/dispersion
- Oxygen scavengers

CONCLUSIONS

In conclusion, the inhibitor must meet certain requirements for each specific application such as stability against temperature, time, and exposure to the corrosive environment. It must function at low concentrations and be easy to apply. Solubility characteristics must be designed for each application and the inhibitor must be pumpable at the system temperature. It must be compatible with other chemicals in use and must meet performance specifications. It must inhibit corrosion. It must also be compatible with the system in which it is used and not cause system upsets. It cannot be too toxic and the flash point must be within specifications. Raw materials must be readily available and not too expensive and manufacturing processes capable of control and reproducibility. It must conform to the application methods available and monitoring procedures must be straight forward and easily performed. All these parameters must be the guidance for inhibitor development. All testing and selection of materials must be based strictly on the requirements so that costs and development time are kept to a minimum.

Corrosion inhibitors have a continuing and major role to play in the cost-effective control of corrosion. Their application is broad based and extensive representing a mature technology in many areas. Basic understanding of inhibition has benefited significantly from the application of modern electrochemical techniques and theory to better describe inhibitor performance. This has helped in promoting an increasing level of sophistication in the development of commercial corrosion inhibitor products and practice. Organic-based chemical inhibitors appear to have the majority share of the market and it will be interesting to see how strongly this penetration continues.

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