CORROSION INHIBITORS

D. D. N. Singh
Applied Chemistry and Corrosion Division,
National Metallurgical Laboratory Jamshedpur-831007

ABSTRACT

Recent technological developments in formulations and industrial application of corrosion inhibitors have been discussed. A huge savings of materials, manpower and energy can be achieved by selecting proper inhibitor for a system.

Key words : *Corrosion inhibitors, Inhibition mechanism, Acid solutions, NML Metasave, Dross formations, Technological development.*

INTRODUCTION

The recent surveys on impact of corrosion and its related problems on the health of economy of a country, have attracted wide spread attentions of manufactures, traders and users of metals and its alloys. This is a problem that can not be completely overcomed but certainly can be reduced to a considerable extent. Various fool-proof methods such as paints, coatings, anodic and cathodic protection, alloys development and use of corrosion inhibitor are being practiced to control the problems of corrosion. Amongst all the techniques, the use of corrosion inhibitor in controlling problems related to corrosion, is an old, economical and reliable method employed by industries. Corrosion inhibitors make possible to use ordinary metallic materials of construction in very a aggressive and hostile environments where even especially designed expensive materials catastrophically fail. An added advantage in using of the inhibitors to control corrosion is that no major alternation in existing plant and machineries is required while switching over from one inhibitor to the another improved product.

Definition of corrosion Inhibitors

There are a number of definitions proposed for inhibitors but International Standard Organization define it as "A chemical substance which retards the corrosion when added to an environment in small concentration without significantly changing the concentration of any other corrosive agent." In view of this definition a chemical added to an environment to neutralize the acidic constituent or oxygen scavengers added in water to remove oxygen from the electrolytes can not be classified as the inhibitors although they help in bringing down the corrosion rate. The prerequisit that needs to be satisfied for a corrosion controlling chemical to be termed as the corrosion inhibitor is that the chemical should be adsorbed at the corroding interface either in the form of molecule or as ions (anions or cations).

Economic survey and its relevance in context to Indian economy

No systematic survey had been made for the economical impact and annual business of inhibitors' industries in India, but it is estimated that the market of inhibitors should be of hundreds of crores if taken together of their uses in all the potential sectors such as oil and gas, metal industries, power, coal, transportation, chemicals, soap and detergents, cosmetics, papers and food sectors etc. According to a survey made in USA it was estimated that the business of inhibitors in that country was to the tune of 48.6 billions US $ in 1985 which increased steadily to 74.6 billions US $ in 1989 [1]. If economical impact of these inhibitors are also considered on the basis of the money saved as result of their use, the money value should be in thousands of billions.

Corrosion inhibitors are recommended to provide temporary solution to a problem with high rate of return on investment (R.O.I). According to a theory of economics, in a system of high inflation and interest rates, a short term solution of problems is always preferred (which is the cheapest, now, today?), without regard to future costs of maintenance. This is most suited in context to the present scenerio of the economic condition of India. The use of corrosion inhibitors in solving the corrosion problems of Indian industries, should therefore, be favoured over the other techniques where huge expenditure is involved in erecting the plant and machineries using specific expensive alloys, paints and other protective coatings. Unfortunately the present scenerio is not very encouraging. The inhibitors are used in industries at a very limited scale. The main reason behind this trend is perhaps the lack of awareness, shortage of experts in industries and unorganized R&D activities in this area.

Causes of Corrosion : Formation of Electrical Double Layer

It is now well established that the corrosion of metals can take place only when an electrolyte is present in the contact of metals. These electrolytes contain charged species e.g. cations, anions, water dipoles, organic molecules, impurities etc. and they are randomly oriented under the equilibrium conditions. In metals, each point is electrically neutral. A metal consists of well ordered rigid lattice of metal cations surrounded by a cloud of free electrons. When a metal comes in contact of an electrolyte, a redistribution of charges, both at metal and solution but an eletroneutral interface is formed as illustrated from the following figure.
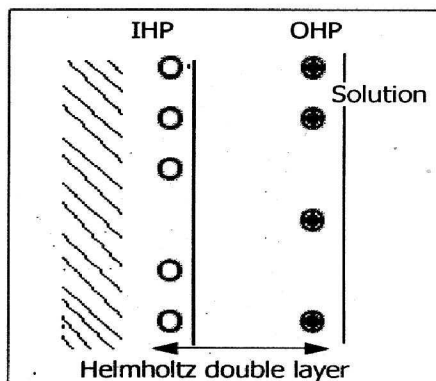

Fig. 1 *: Schematic presentation of simple double layer*

The above simple model was proposed by Helmholtz. Latter on it was proposed by Guy and Chapman that the simple model proposed by Helmholtz as described above, can not be taken as a true picture of a double layer, as disordering forces due to the thermal energy of the ions would oppose their ordering by electrostatic forces. They proposed a diffused model of the double layer where excess of the counter ions would be maximum close to the surface. Thus the double layer can be presented in to two parts, one fixed layer very close to the Helmholtz model and the other diffused layer (Fig. 2).
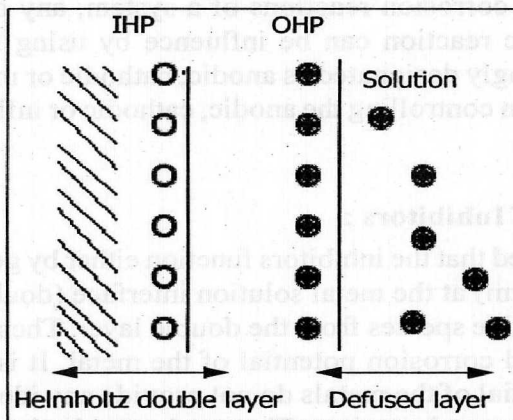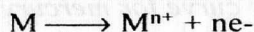

Fig. 2: Schematic presentation of Different layers

It is important to note that all charge transfer reactions such as of corrosion take place at the fixed layer only. Due to the accumulation of the opposite charges at the metal/electrolyte interface, a strong electric field in the space between the charged layers takes place. This results in the development of a potential difference. Although the potential difference is not very high (< 1.0V), the field strength (potential difference/ distance) is of the order of 10^7 V/Cm for a potential difference of 1.0 V and distance of 0.1 nm. This field is responsible for the electrons to cross the interface during the charge transfer reactions. It can be shown that by a slight change in potential at the interface, the rate of electrodic reaction can be changed to many folds[2]. The corrosion inhibitors change the potential at the interface by adsorbing themselves at the double layer as ions or dislodging the ions originally present there. Even a slight change in potential at the interface due to the action of inhibitors would change the corrosion rate significantly.
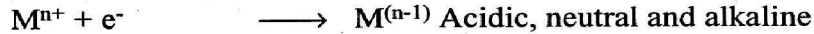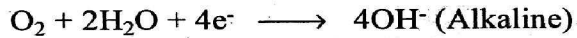
Function of Inhibitors

The corrosion of metals and alloys takes place due to the formation of minute electrochemical cells at the metal-electrolyte interface. The reactions that take place during the process of corrosion are:

    i. Anodic reaction or de-electronation reaction.

$$M \longrightarrow M^{n+} + ne^-$$

ii. **Cathodic or electronation reactions.**

$$2H^+ + 2e^- \longrightarrow H_2 + \text{ (Acidic)}$$

$$O_2 + 4H + 4e^- \longrightarrow 2H_2O \text{ (Acidic)}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \text{ (Alkaline)}$$

$$M^{n+} + e^- \longrightarrow M^{(n-1)} \text{ Acidic, neutral and alkaline}$$

In controlling the corrosion reactions of a system, any of the above reactions i.e. either anodic or cathodic reaction can be influence by using suitable inhibitors. These inhibitors can be accordingly designated as anodic, cathodic or mixed inhibitors depending on their preferential role in controlling the anodic, cathodic or influencing both the reactions respectively.

Mechanism of action of Inhibitors :

It is now established that the inhibitors function either by getting themselves adsorbed (in ionic or molecular form) at the metal solution interface (double layer) or dislodging of already adsorbed aggressive species from the double layer. These processes depend on the zero charge potential and corrosion potential of the metal. It is to be noted here that the standard electrode potential of the metals do not provide any idea about the charge present on the metals corroding in an electrolyte. These values only show the relation in which the given electrode stands to the hydrogen electrode. If two metals Mi and Mii have the same standard electrode potential, this means that both the metals are thermodynamically in equilibrium but it does not mean that they posses the same charges q_1 and q_2.

The zero charge potential of a metal can be defined as the potential of the metal at which the charge on the metal is equal to zero with respect to the solution in the absence of any surfactant. In an electrocapillary curve, the potential corresponding to maxima is taken as the zero charge potential (Fig.3).
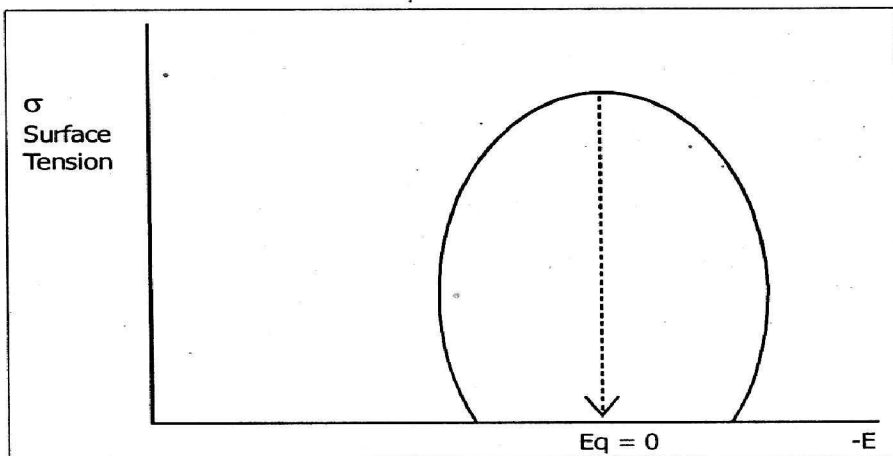

σ
Surface
Tension

$E_q = 0$ $-E$

Fig. 3: Electrocapillary curve for mercury surface

In order to understand the functioning of an inhibitor, it is important to know the ϕ potential of the metal in that particular solution.[3] The ö potential may be written as:

$$\phi = Ec - Eq = 0$$

Where ϕ= potential of the corroding metal in solution in the scale of zero charge potential

Ec = Corrosion potential and

$E_{q=0}$ = Zero charge potential of the metal.

Structure of the Double layer and type of inhibitors suitable to control the corrosion

A close relationship exists between the value and the sign of the ϕ potential and the structure of the double layer. This can be illustrated with the following figures:
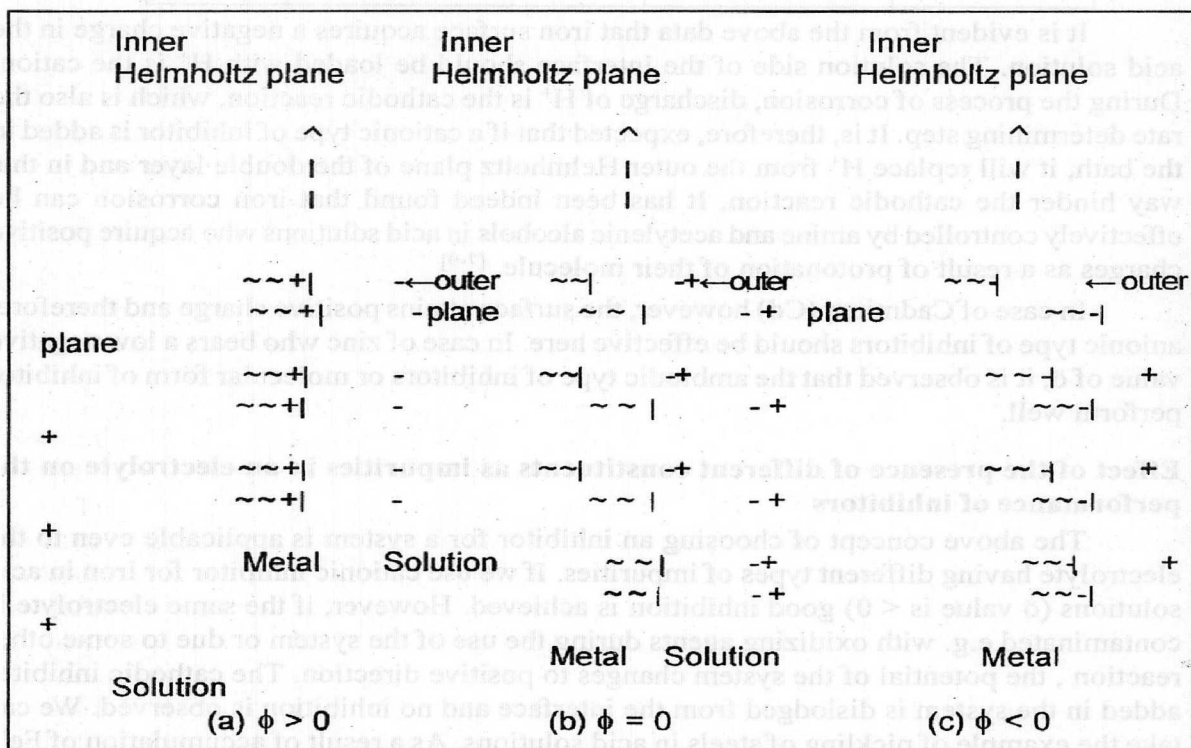
Fig.4 : Explaining the factors for selection of inhibitors

In figure (a), the ϕ potential i.e. the charge on the double layer with respect to the solution is positive. In (b), it is neutral and in (c), the value of φ negative. In first case the metal is positively charged and the solution side of the double layer is loaded with the electrolyte having their anionic group oriented towards it and therefore, an anionic inhibitor should be effective in controlling the corrosion reaction. In case (b), since no specific adsorption of the electrolyte is observed, a non ionic or molecular type of inhibitor is

expected to be effective. In case (c), where the metal is having negative charges and cationic part of the electrolyte is oriented towards the solution side of the double layer, a cationic type of inhibitor should have a strong inhibitive action towards the corrosion of the metal.

The above description can be further illustrated by taking the following examples:

Let us take the example of iron, zinc and cadmium corroding in 0.1N HCl. Their corrosion potentials (Ec), zero charge potentials ($E_{q=0}$) and corrosion potential expressed in zero charge potential scale (Eq) are as follow [4] :

Metals	Ec (SHE)	Eq = 0	Eq = Ec-Eq = 0
Fe	-0.02	-0.02	-0.30
Zn	-0.75	-0.64	-0.11
Cd	-0.75	-0.72	+0.21

It is evident from the above data that iron surface acquires a negative charge in the acid solution. The solution side of the interface should be loaded with H^+ is the cation. During the process of corrosion, discharge of H^+ is the cathodic reaction, which is also the rate determining step. It is, therefore, expected that if a cationic type of inhibitor is added in the bath, it will replace H^+ from the outer Helmholtz plane of the double layer and in this way hinder the cathodic reaction. It has been indeed found that iron corrosion can be effectively controlled by amine and acetylenic alcohols in acid solutions who acquire positive charges as a result of protonation of their molecule. [7-9]

In case of Cadmium (Cd) however, the surface attains positive charge and therefore, anionic type of inhibitors should be effective here. In case of zinc who bears a low negative value of ö, it is observed that the ambiodic type of inhibitors or molecular form of inhibitor perform well.

Effect of the presence of different constituents as impurities in an electrolyte on the performance of inhibitors

The above concept of choosing an inhibitor for a system is applicable even to the electrolyte having different types of impurities. If we use cationic inhibitor for iron in acid solutions (ö value is < 0) good inhibition is achieved. However, if the same electrolyte is contaminated e.g. with oxidizing agents during the use of the system or due to some other reaction , the potential of the system changes to positive direction. The cathodic inhibitor added in the system is dislodged from the interface and no inhibition is observed. We can take the example of pickling of steels in acid solutions. As a result of accumulation of Fe^{3+} in the bath, the corrosion potential of Fe shifts to about +0.32 V. The ϕ value, therefore, becomes +0.30- (0.02) = +0.32 V. The cationic inhibitor added in the bath will be desorbed from the interface and no inhibition will be observed. In this situation, however, an anionic inhibitor will be very much effective in controlling of corrosion[3].

Synergism in inhibitor

It is some times observed that a combination of two or more inhibitors provide a higher degree of protection than the sum of the individuals' efficiencies. This phenomenon is known as synergism in inhibition. Ionic as well as non ionic surfactants provide synergism

with inhibitors used for controlling of corrosion. The synergistic effects of inhibitors can be explained in the terms of their effects in changing the structure of the double layer. We can consider the case of acetylenic alcohols (like octynol, propargyl alcohol etc.) used as inhibitor for iron corroding in non oxidizing acidic solution. The alcohol having triple bond protonizes in the acid solution.

$$H_3C-C \equiv C-OH + H^+ \longrightarrow H_3C \equiv C-OH_2^+$$
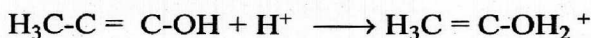
This compound has negligible effect in H_2SO_4 - Fe system in absence of suitable surfactant. In the presence of Cl^-, however, the same compound exhibits very high degree of protection. The observed degree of protection is many folds higher than the efficiencies exhibited by individual components or sum of their effects. The effects can be explained as follows:
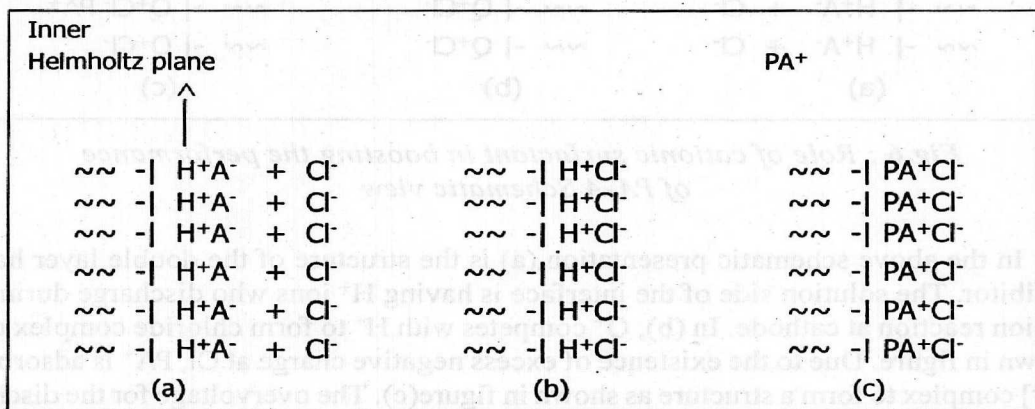
```
Inner
Helmholtz plane                                        PA+
       ^
       |
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
  ~~ -| H+A-  + Cl-      ~~ -| H+Cl-        ~~ -| PA+Cl-
        (a)                    (b)                 (c)
```

Figure 5 : *Schematic presentation of synergism in inhibition*

In the above schematic presentation, PA^+ is the protonized molecule of propargyl alcohol.

As $E\phi$ for iron corroding in acid media is negative, its surface has negative charge and the solution side of interface has positive charges (H^+layer) (figure 5). when the acid solution has no chloride present, protonized molecule of propargyl alcohol i.e PA^+ is capable of replacing H^+ from the double layer but only to a limited extent. When $Cl^-$is present in the system, the anionic part of the electrolyte(A^-), present at the interface, is replaced by Cl^- as Cl^- is more surface active and charge density at this anion is higher than any other anions (figure 5b). Due to the strong anionic charge present on chloride, PA^+ is transported to the interface to a greater extent than in the absence of chloride and its concentration at the interface is increased than in the bulk of the solution (figure 5c) resulting in an improved inhibition efficiency.

Similarly, the improved efficiencies in the presence of cationic surfactants can also be explained.

Propargyl alcohol (PA) exhibits a strong inhibition towards iron corroding in hydrochloric solutions. This is owing to the reasons as explained above. If a strong cationic surfactant such as quaternary ammonium salt (Q^+) is present along with PA^+, the inhibition

efficiency is improved to a considerable extent. The improvement in this case can be explained as follows:

Inner
Helmholtz plane

	(a)		(b)		(c)

$$\sim\sim \ -|\ H^+A^- \ +\ Cl^- \qquad\qquad \sim\sim\ -|\ Q^+Cl^- \qquad\qquad\qquad \sim\sim\ -|\ Q^+Cl^-\ PA^+$$
$$\sim\sim \ -|\ H^+A^- \ +\ Cl^-\ [Q+] \quad \sim\sim\ -|\ Q^+Cl^-\ [PA+] \quad \sim\sim\ -|\ Q^+Cl^-\ PA^+$$
$$\sim\sim \ -|\ H^+A^- \ +\ Cl^- \qquad\qquad \sim\sim\ -|\ Q^+Cl^- \qquad\qquad\qquad \sim\sim\ -|\ Q^+Cl^-\ PA^+$$
$$\sim\sim \ -|\ H^+A^- \ +\ Cl^- \qquad\qquad \sim\sim\ -|\ Q^+Cl^- \qquad\qquad\qquad \sim\sim\ -|\ Q^+Cl^-\ PA^+$$
$$\sim\sim \ -|\ H^+A^- \ +\ Cl^- \qquad\qquad \sim\sim\ -|\ Q^+Cl^- \qquad\qquad\qquad \sim\sim\ -|\ Q^+Cl^-\ PA^+$$
$$\sim\sim \ -|\ H^+A^- \ +\ Cl^- \qquad\qquad \sim\sim\ -|\ Q^+Cl^- \qquad\qquad\qquad \sim\sim\ -|\ Q^+Cl^-$$
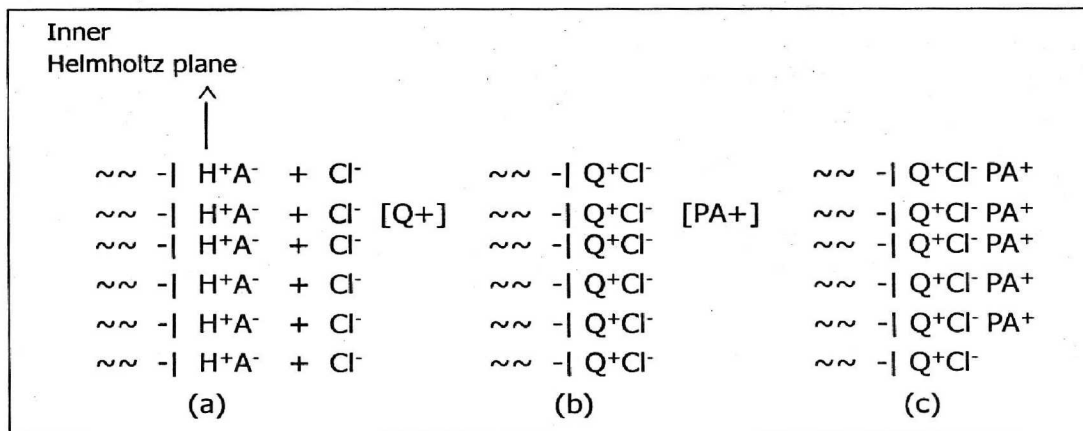
(a) (b) (c)

Fig.6 : *Role of cationic surfactant in boosting the performance of PA-A Schematic view*

In the above schematic presentation,(a) is the structure of the double layer having no inhibitor. The solution side of the interface is having H^+ ions who discharge during the corrosion reaction at cathode. In (b), Q^+ competes with H^+ to form chloride complex of Q^+ as shown in figure. Due to the existence of excess negative charge at Cl, PA^+ is adsorbed at $[Q^+Cl^-]$ complex to form a structure as shown in figure(c). The overvoltage for the discharge of complex at (c) is quite high compared to H^+ and therefore, strong inhibition is observed.

Techniques Employed to study the inhibition mechanisms

The above principles help one in selection of proper inhibitors to a system. Various types of techniques have been developed to understand the mechanism of action of inhibitors for corroding interface. Some of common techniques commonly employed are:

1. Electrochemical Techniques: Cathodic and anodic polarization, polarization resistance, impedance studies, potential -time plots, order of reaction rates at fixed current, fixed potentials, pH, ionic species etc.

2. Eletrocapillary Curves: The nature and the role of inhibitors are studied on electrocapillary curves of mercury metal amalgam interface. The observed zero charge potential provides a clue about the functioning of inhibitors.

3. Surface analysis: Energy dispersive analysis of X-rays (EDAX), X-ray photoelectron spectroscopy (XPS earlier name was ESCA i.e. Electron spectroscopy for chemical analysis), Augur electron spectroscopy (AES), etc. provide strong clues about the film formed on the surface of metals.

4. Analysis of corrosion products: Techniques such as Infra red spectroscopy, X-ray diffraction studies etc are used.

Testing of Inhibitors

The merits on which a user decides to use an inhibitor in an application are as follows:

- The use of inhibitor should be economically viable and technically feasible.
- The inhibitors should not adversely affect the further processing of the liquid.
- The efficacy of the inhibitors should not be adversely affected with rise in temperature or concentration of the electrolyte
- Accumulation of corrosion products should have no deteriorating effect on the efficacy of the inhibitors.
- The diffusion of hydrogen in the material in contact with the electrolyte should be minimal.
- The inhibitor should be environmentally friendly and biodegradable

The above tests are performed first at laboratory scale and if found acceptable then only a plant scale evaluation is performed.

Plant scale testing

The following tests at the plant scale are performed.

- Metal loss of coupons exposed insitue of the plant conditions.
- Pitting of surface.
- Hydrogen absorption.
- Productivity.
- Quality improvement in the finished products.
- Pollution control.

Selection of Proper Inhibitors for a system

Potential use of inhibitors in various sectors are shown in figure 7. Depending upon the applications, a proper designing of an inhibitor is necessary. Some criteria are described below for recommending/developing of suitable inhibitor for a system.

Pipelines carrying crude and condensate

Special type of steels of moderate ultimate tensile strength are used as construction materials for pipe lines. Since the corrosion takes place generally due to the accumulation of condensate which is normally acidic in nature, at 6 O' clock position of the pipe
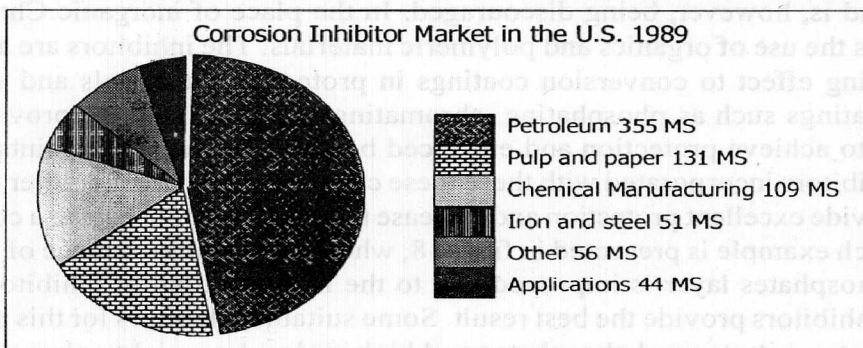

Corrosion Inhibitor Market in the U.S. 1989

- Petroleum 355 MS
- Pulp and paper 131 MS
- Chemical Manufacturing 109 MS
- Iron and steel 51 MS
- Other 56 MS
- Applications 44 MS

Fig. 7 : Potential uses of inhibitors

Care should be taken not to select an inhibitor, which inhibits cathodic reaction of corrosion i.e. the re-combination of adsorbed hydrogen at the interface. This will increase thew fugacity of hydrogen and encourage hydrogen-assisted cracking/embrittlement. The best solution is the use of high molecular weight fatty amines who polarize anodic as well as the cathodic, both the reaction, [5,8] and is able to retain the strength of pipeline materials to a considerable extent.

Acidization during oil well drilling

To increase the flow of oil and gas which are entrapped in calcerious rocks, HCl is fed in to the bore holes of oil and gases. Due to high pressure, the temperature inside the bores is very high. This results in severe corrosion of steels. To control the corrosion of drill bits and bore tubes, inhibitors are added in the boreholes. Film forming inhibitors such as acetylenic alcohols mixed with copper iodide and certain non- ionic surfactants are poured into the boreholes to achieve protection of bore tubes and drill bits. These inhibitors not only protect the components from uniform and pitting attack but also from hydrogen attack

Vapour phase corrosion inhibitors

Some parts and components of equipments are required to be protected from corrosion during their transport and storage. Here, volatile inhibitors are used in closed system. These inhibitors vaporize in molecular form and due to their strong tendency of adsorption towards metals, they form a dense layer of monomolecular thickness of some examples of these inhibitors are Dicyclohexyl ammonium nitrite (DICHAN), Dicyclohexyl ammonium chromate(DICHAC), Benzotrizole, Tolyltriazole etc. While designing these structures of the inhibitors, care should be taken that the vapour pressure of the compound should neither be high nor very low. A detail review on this subject has been given elsewhere.

Inhibitors in paints coatings/ surface conversion coatings

Inhibitors are impregnated with paints and coatings to protect metals in situation when cracks and fissures develop in coatings. These inhibitors block the exposed surface and protect the materials effectively. Earlier, it was a common practice to employ chromium based compounds for this purpose. With the growing awareness on pollution , the use of such compound is, however, being discouraged. In the place of inorganic Chromate, the present trend is the use of organics and polymeric materials. The inhibitors are also used to provide boosting effect to conversion coatings in protecting the metals and alloys. The conversion coatings such as phosphating, chromating and anodizing are provided on the metal surface to achieve protection and enhanced bonding between the paints and metal substraite. Inhibitors incorporated with these these coatings both during or after the coating formation, provide excellent protection and increase the life of components to a considerable extent. One such example is presented in figure 8, where corrosion resistance of galvanized surface and phosphates layer is improved due to the incorporation of inhibitors[3]. Strong film forming inhibitors provide the best result. Some suitable inhibitors for this purpose are organic chromates, nitrates and phosphates and high molecular weight polymeric material having active adsorption centres such as N,S, O, As, Sb, Se etc.

Inhibitors for boilers

Presence of oxygen and ionic species in boilers feed water are the main culprit in causing corrosion of water side of boilers. Above the temperature of 200°C, a spontaneous formation of magnetite (Fe_3O_4) take place. This layer is very protective under the conditions of boiler water . The role of inhibitors in boilers is to minimize the dissolved oxygen content in water. Normally hydrazine hydrate and sodium sulphite are added in boilers water to scavenge oxygen. These chemicals some times complicate the corrosion process and cause severe corrosion to the walls of tubes. The recent trend is, therefore, to use all –polymer based products based compositions whether able to disperse the boiler contaminants and effectively complex the hardness and keep them in soluble form[14].

Inhibitors for concrete corrosion

An idea concrete mixture (comprising of cement, sand, gravels and water) free of chloride ions provides an excellent protection to the re-inforcement steel surface. This is due to the alkaline nature of concrete, which helps in the formation of protective oxide layer on the surface. The concrete becomes highly corrosive due to the chloride ions present either as an inherent part of the cement such as the use of calcium chloride as accelerator, or ingress from the extraneous sources such as use of water containing high degree of salinity or sand or exposure to brine water. The structure fail catastrophically due to the deteriorating effect of the chloride on re-inforced bars. To prevent this, corrosion inhibitors are added in the concrete mixture or alternatively bars are pre- treated with suitable inhibitors prior to putting them in the concrete mixture. The later techniques is more economical effective for practical applications. It was suggested that the proper treatment of bar with a nitrite solution should provide good protection to the steel surface. A number of patents had appeared on this aspect and most of them incorporated the salts of metal nitrites. It is, however, observed that these salts do not provide longer life and deterioration starts after some time. The recent trend is the use of multi component inhibitors such as nitrites- glycine-hydrate, nitrite-amines-hydrogine-water soluble polymers etc.[15] These components of the inhibitor play specific roles and protect the metals effectively for longer period of time.

Pickling of Metals

During hot rolling of metal and alloys, they acquire oxide layers on their surface. This oxide has to be removed before they are painted, galvanized, tinned, aluminized, cold drawn or phosphated. Different techniques such as sand blasting, shot blasting or acid pickling are recommended to remove the oxide scale from the surface. Due to economical and other commercial reasons, acid pickling is more preferred by industries over the other techniques. Once oxide of the surface is removed due to the reaction of acid with oxides, the virgin metal comes in contact of the acid and an unwanted dissolution of the metal takes place. This causes a huge loss of metal and acid and also results in air pollution due to the evolution of acid mists. Corrosion inhibitors are successfully used to prevent this unwanted losses. Different types of inhibitors are used for ferrous and non- ferrous metals.

Non –ferrous Metal

Inhibitors such as thioureas, triazoles, amine etc. are employed during the pickling of Al, Brasses, Copper, Ti and its alloys. Their commercial applications are, however,

limited compared to the ferrous metals. Same studies pertaining to the corrosion inhibition of different grades of aluminium in acid media are presented in references 17-34.

Ferrous Metals

Owing to the great economical impact of these inhibitors, a detail mechanism about the oxide dissolution and functioning of inhibitors will be described here.

Composition and structure of scale on steel's surface

When mild steel is subjected to high temperature oxidation during hot rolling (570°C to 800°C), it develops a thick and adherent layered structure that consists of a layer of wustite (FeO) of ~ 80%adjacent to the metal, a layer of magnetite (Fe_3O_4) of ~18% and an outer layer of hematite (Fe_2O_3) of up to 2%[35,36]. Changes in production practices can affect this composition.[36]

If the material is allowed to cool rapidly, the wustite, which is metastable below 570°C, does not disproportionate into magnetite and iron, and the proportion of wustite increases in the scale[35]. Since wustite is more readily soluble in acidic solutions than the other oxides of iron (Fe_3O_4 and Fe_2O_3), many investigators have tried to exploit this observation in developing a wustite —ich scale to achieve more amenable conditions for pickling [36]. If hot —rolled material is cooled in air, half or more of the wustite decomposes into magnetite and iron, thus making the acid pickling step difficult[37].

Dissolution of scale in Acid Solutions

Since the expansion modulus of magnetite is higher (2.0) than that of wustite (1.83 to 1.65), high compressive stresses develop in the scale that results in shear strains and delamination of scale[37]. The cavities are formed first in the magnetite, which develops a potential in the range of 0.7 V vs a normal hydrogen electrode (NHE) to 0.6 V_{NHE} in solutions of pH =39. These cavities allow the wustite to come into contact with the acid solution, and rapid dissolution of the wustite takes place along with magnetite. The electrode potential is reported to decrease and remain in the range of 0.6 V $_{NHE}$ to 0.45 V_{NHE} [37].

This is known as the first pickling period and characterizes the dissolution of isolated oxide phases.

Wustite also contains cavities. The acid solution penetrates through these cavities and reaches the base metal surface. An electrochemical cell is formed in which the steel (base metal) behaves as the anode and the magnetite and wustite behave as soluble cathodes (due to reductive dissolution)[40]. Magnetite acts as a cathodic depolizer, whereas hematite suffers from negligible dissolution and has little effect on the cathodic process. Magnetite is dissolved partially during the cathodic dissolution of wustite and magnetite by:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$FeO + 2H^+ + 2e^- \longrightarrow Fe + H_2O$$

$$Fe_3O_4 + 8H^+ + 8e^- \longrightarrow 3Fe + 4H_2O$$
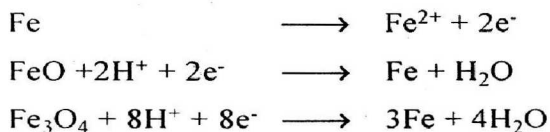
Since the wustite is removed by the acid, the contact between the magnetite and metal is lost, and the scale is delaminated due to hydrogen evolution at the base metal surface. Thus, the metal surface becomes totally free of oxides and the base metal comes in contact of acid.

Inhibitor for Acid pickling of steels

Metals and alloys posses different types of electrical double in contact of different acids. For examples, iron surface which bears a zero charge potential of the order of -0.33 to $-0.02V$ (nhe) 314 corrodes at $-0.25V$ in $1NH_2SO_4$ which means that it acquires a negative charge on the solution side of the interface surface. Cathodic inhibitors are therefore, considered to be good inhibitor for the this system. Iron in contact with HCl, acquires a negative charge owing to chemisorption of Cl^- on the surface, and hence, a cationic inhibitor is considered to the good inhibitor for this system. These thumb rules should be kept in mind while attempting to develop a pickling inhibitor for a system. The performance of these inhibitors can be further improved by providing synergistic effect by the use of the other surface active species with the inhibitors. For pickling operations, normally four types of acids are employed. These include: a) Hydrochloric acid b) Sulphuric acid c) Phosphoric acid and d) Mixed acids.

Expect few inhibitors which are ambiodic in nature, most of them are effective for a particular acid but ineffective or exhibit poor inhibition toward the others.

Inhibitor for Hydrochloric acid

As discussed above, ferrous metals in contact of hydrochloric acid solutions acquire negative charges at the interface. It is therefore, expected that cationic inhibitors should perform satisfactorily for this system. It has been established by us that the cationic inhibitors such as acetylenic alcohols, hexamine, high molecular weight polymerized amines, amino amine, quaternary ammonium salts etc. who provide cationic species in the solution, afford good protection toward steel in HCl solution.[41,42,9-11] Synergism in inhibition efficiencies has been noted when compounds who provide anionic species in acid solutions are incorporated in the cathodic inhibitors. These ions, when present alone in acid solutions, some time accelerate the attack. Their effect, however, is reversed when added in the solution in the presence of cathodic inhibitors. The mechanism for this behaviour has been discussed elsewhere[41].

Inhibitors for Sulphuric acid

Electrical double layer of steel in contact with H_2SO_4 solutions acquire negative charge. It is therefore, expected that those inhibitors who can furnish cationic species in the solution, should provide good inhibition toward the metal dissolution. We have synthesized and tested a number of inhibitors based on sulphur compounds for dissolution of steels in sulphuric acid solution[43,44]. These S based compounds such as Thioureas, sulphoxides, thiocynates etc. furnish S^{2-}, HS^- and CNS^- species in the solution and provide excellent protection toward the metal with Cationic species, when added in small quantity provide synergistic effect toward the inhibition effeciency. Anionic species also boost up the efficacy

of these inhibitors. This is due to the co-adsorption of anionic species with the inhibitors who release anionic surface active species, Chlorides, Sulphides, etc are such species who can be incorporated with anionic inhibitors to boost up their performance.

Inhibitors for Phosphoric Acid

It is extremely difficult to develop an effective inhibitor for steel/ H_3PO_4 system[45]. The main reason behind this is that, $H_2PO_4^-$ ion is highly surface active and adsorbs at the interface more quickly and preferentially than any of the known inhibitors. This combines with Fe^{2+} and forms insoluble phosphate at the surface who hinders the adsorption of the inhibitors. We had evaluated a number of common inhibitors such as thioureas, thiocynates, sulphides, chlorides, amines, quaternary ammonium salts, acetylinic alcohols etc. and have concluded that non of these inhibitors provide satisfactory protection to the metal exposed to H_3PO_4[46]. These inhibitors on the other hand, depending upon the nature of ionic species released in acid solutions, provide excellent protection toward the metal in hydrochloric and sulphuric acid solutions. The measurements of zeta potential values at the interface of iron powder in acid solutions provided the clue for this behaviour. It can be seen from the table II that the value of zeta potential in H_3PO_4 solution is highly negative compared to HCl and H_2SO_4. Addition of anionic and cationic inhibitors (e.g. ammonium thiocyanate and tetrahydropyrimidine respectively) shift the potential of iron in contact of H_3PO_4, in positive directions. This indicated that the proper inhibitor for this system should be a judicious selection of mixture of anionic and cationic surfactants. We have indeed observed that a combination of tetra hydropyrimidine(THP,cationic),tetra benzyl ammonium chloride (TB,Acationic) and ammonium Thiocyanate (ATC,anionic) provides protection to the system to an order of >98% or above[46].

Table 2 : Zeta potential values of iron powder in contact of different acids[46].

Sl.	System	Zeta potential values (mv)		
		0.01N H_3PO_4	0.01N HCl	0.01N H_2SO_4
A.	Blank	-24.5	-14.7	-18.5
B.	A + 0.1 % THP	+7.1	-9.1	-10.4
C.	A + 0.1 % ATC	-13.8	-20.4	-21.6
D.	A + 0.1% TBA	+37.0	-4.8	+3.2

Inhibitors for Mixed Acids

Universal type of Inhibitors: Sometimes mixed acid system is recommended for use as pickling medium. For such system, universal type of inhibitor is required for protecting the steel from corrosion. In this situation, the nature of the double layer depends upon the ratio of acids present in the bath. It is generally observed that an ambiodic type of inhibitor (i.e. which contains anionic as well as cationic active centres for adsorption) is more effective for such system. NML Metasave[45](a trade name) has been established as an effective inhibitor for HCl. H_2SO_4 and also for the mixture of the acids.

REFERENCES

1) *Frost & Sullivan Line, USA, Report No. A-1998*

2) *J. Om. Bocksis and A.K.N. Reddy, Vol.2 Modern Electrochemistry (Plenum Press)*

3) *L.I. Antropov, Kinetics of electrode processes and null points of metals. CSIR, New Delhi. (1960)*

4) *L.I. Antropov, J. Ind. Chem 500 35(1958) 309.*

5) *Singh DDN & Chatterjee P., Corrosion Prev. & Control 37(1990) 37.*

6) *Singh DDN & Chatterjee P. J. Electrochemical Soc. (India) 38 (1989) 277.*

7) *Singh DDN, Chaterjee P and Paty B. B., proceedings of Asia Corrosion 88. Singapore (1988).*

8) *Singh DDN & Chatterjee P. Anti Corrosion Meth & Mat. 38 (1991) 4.*

9) *Singh DDN & Dey A.K., Corrosion, 49 (1993) 594.*

10) *Singh DDN, Pati BB, and Chatterjee P, Corrosion 46 (1990) 354.*

11) *Singh DDN & Pati BB, Corrosion 48 (1992) 442.*

12) *Singh DDN and Banerjee M.K., Anti Corrosion Meth. & Mat., 31 (1984) 4.*

13) *Singh DDN, Dey A K, Dalal a k, Bhatia B S and Topp O.L., NML Internet Report No. 05793249*

14) *Pierce CC and Graham DA, Corrosion review 8(1989) 239.*

15) *Rosenberg AM and Gaidis JM, US Patent no.4, 365,999 (1982).*

16) *Fujita T and Kashima T, US Patent no. 4, 365, 999(1982).*

17) *Singh DDN, J. Electrochem. Soc. 132 (1985) 378.*

18) *Singh DDN, & Banerjee MK, Corrosion 42 (1986) 156.*

19) *Singh DDN, & Banerjee MK and Nag PS, NML Techn. Journal 24(1982) 31*

20) *Singh DDN, Chaudhary RS, and Agrawal CV, Ind. J. Tech. 18 (1980).*

21) *Singh DDN, Chaudhary RS Yadav PNS , and Agrawal CV J. Electrochem. Soc. 29 (1980) 125*

22) *Singh DDN, Chaudhary RS and Agrawal CV J. Electrochem Soc. 129*

23) *Singh DDN, Chaudhary RS and Agrawal CV Corrosion Prev. & Control 29(1982)4*

24) *Singh DDN, Chaudhary RS and Agrawal CV J. Applied Electrochem 11(1981)671*

25) *Singh DDN, Chaudhary RS Singh MM and Agrawal CV Electrochem. Acta 26(1981)1056*

26) *Singh DDN, Chaudhary RS Singh MM and Agrawal Appl.Electrochem. 10 (1980)587*

27) *Singh DDN, Chaudhary RS and Agrawal CV British Corrosion J. 14(1989)235*

28) *Singh PNY,Singh DDN, Chaudhary RS and Agrawal CV Ind. J. Tech. 19(1981)461*

29) Singh DDN, Chaudhary RS and Agrawal CV Ind. J. Techn 18(1980)392

30) Singh DDN, Chaudhary RSand Agrawal CV J. Electrochem Soc. (India)28 (1979)241

31) Singh DDN, Chaudhary RSand Agrawal CV J. Electrochem Soc. (India)27 (1978)91

32) Singh DDN, Chaudhary RSand Agrawal CV J. Electrochem Soc. (India)28 (1979)169

33) Singh DDN, and Dey AK, NML Techn. J. 35(1993)6

34) Singh DDN, and Dey AK, NML Techn. J. 35(1993)36

35) Bernar JM, Oxidation of Metals (Moscow, Russia, Metallurgia) (1968) 174

36) Lipkin Y.N. Devyatkina TS and LI Gol'sdshtein, Technika (1980).

37) Oshe EK, Zimina TY and Fokim MN , Zashch Met. 23(1987)3

38) Wei F./I., SEASIQ 19(1990) 20.

39) Pdobaev Ni, Prot. Met. 23(1987)683

40) Pdobaev Ni, and Sheheglova MN, Zashch Met. 8(1972)25.

41) Singh DDN, Singh T.B. and Gaur B, Corrosion science 37(1995)1005

42) Singh TB, Dey AK, Gaur B, and Singh DDN, Anti Corrosion Meth. & Materials, 42 (1995)19

43) Singh DDN, and Gaur B, Corrosion 51 (1995)593

44) Gaur B, Singh TB, and Singh DDN, Corrosion 52 (1996) 154

45) Gorsheneva, V.F., Goricher IG and Kluchnikov NG, Zasheh, Met. 23(1985)40

46) Singh DDN and Singh VK, (unpublished work).

47) Singh DDN and Mukherjee KP, Indian Patent No. 170765 (1987)