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Corrosion Prevention and Development of Inhibitors

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The use of corrosion inhibitors is one of the widely adopted methods of corrosion prevention. Research activities over a century have brought tremendous advances in the field of corrosion inhibitors. It is not practically possible to cover the entire spectrum of activity that has taken place over a century. This paper addresses the developmental activities that have taken place in very important sectors like cooling water system, Inhibitors for acid systems, inhibitors in oil and gas production and inhibitors for corrosion in concrete. The application of surface analytical techniques has revolutionized the field of inhibitors. Practically we can get information on the nature of product formed on the metal surface, the composition of the corrosion products, orientation of attachment of corrosion inhibitors etc..

Keywords : *Corrosion inhibitors, Cooling water systems, Inhibitors for acid media, Inhibitors for oil and gas production, monitoring methods, surface analytical techniques*

1. Introduction

"Rust never sleeps" says V.Ashworth quoting a popular song. Corrosion is a global problem. Corrosion is the destructive attack of metal by chemical or electrochemical reaction with its environment. Corrosion is an unavoidable evil. These are all some of the explanations offered on the phenomena of Corrosion. Corrosion assumes importance from two angles. The first one is economic importance resulting from failure of pipelines, tanks, ship hulls, machine components etc., the second one is conservation of metal resources whose availability is limited.

Modern civilization makes use of many types of materials such as metals, wood, ceramics, plastics and other polymeric materials. All these materials exhibit deterioration with time. However under practical conditions the deterioration of metallic materials alone is referred to as corrosion. Corrosion is often associated with destruction or degradation of materials because of their interaction with the environment.

Huge investments are made to extract metals from their natural ores such as sulphides, oxides and carbonates. These metals after recovery are subjected to different forms of treatments such as alloying, heat treatment, cold working, annealing, conversion into rods, wires, sheets, etc., Larger investments are made in these process rather than the process of extraction of metals from their ores.

2. Corrosion Prevention

Corrosion is a spontaneous reversion of the metals into a state in which they existed in nature. The gradual destruction by marine and industrial environments have serious consequence for the industrial world. Corrosion not only leads to wasting away of investments but also leads to leakage of products from pipelines, contamination of food products, collapse of bridges, roofs, towers, jetties etc.,

The losses caused by corrosion to the society are great and it becomes an unavoidable necessity to invest on corrosion control measures. The impact of corrosion is not very well appreciated by the public. The reason is that the natural process of corrosion is slow and its effect are not easily recognized. But the impact of corrosion on the Nation's exchequer is large.

It is always reported that the cost of corrosion can be as huge as 2-4% of the Gross National Product of any country. For India it may workout to be a staggering figure of 30,000 to 40,000 crores of rupees. The positive aspect is more than 30% of cost of corrosion could be avoided by application of existing knowledge on corrosion control. All the estimates are based on the Gross National Product.

Corrosion is a national problem affecting the national economy as a whole. There is a necessity for a national level policy to tackle this problem. Preventive maintenance is another concept to minimize the cost of maintenance due to equipment shutdown and production loss. It is a difficult task to secure continuity of production maintaining high quality at low cost of maintenance. The mechanical maintenance and technical education in mechanical maintenance must be part of corrosion prevention techniques. There must be a corrosion group in every production plant that will draw up operation programme for the corrosion prevention plan and this group will be responsible for assessment of situation, economical estimation of corrosion damages, comparison with other plants in the same field, planning of future changes in processes etc., The corrosion group will establish an information bank, the field of anticorrosion measures; materials selection, surface treatment and so on.

Recognizing the huge economic loss caused by corrosion, the following general preventive measures are adopted to control the same.

1. Use of the most economic and efficient inhibitors to control corrosion
2. Use of corrosion resistant steel in oil and gas production
3. Application of coatings and cathodic protection for protecting structures against marine conditions
4. Development of heat resistant alloys and low alloys steels to resist the atmospheric corrosion
5. Surface modification using ion implantation and laser surface alloying
6. Development of super alloys and ceramic materials to increase the efficiency of gas turbines
7. Utilization of non metallic materials in chemical industries

3. Corrosion Inhibitors

Among these methods of corrosion prevention, corrosion inhibitors play an important role in alleviating corrosion problems in industries. Corrosion inhibitors were extensively used in various applications and the operations of many industries are dependent on the successful application of corrosion inhibitors. However, chemical companies customarily hold the compositions of majority of corrosion inhibitor packages as secrecy.

In the latter period of 19th Century Marangoni and Stephanelli used extracts of glue, gelatin and bran to inhibit the corrosion of iron in acids. This is the first report available in the literature of the use of corrosion inhibitors for protection of metals. The first patent on Corrosion inhibition was filed by Baldwin, which described the usages of molasses and vegetable oils for pickling sheet steel in acids. In those days, the selection of inhibitors was based on trial and error basis. In the last 50 years extensive studies were carried out on corrosion inhibitors and theories were proposed towards the inhibitive action.

During this period, the general considerations such as double layer, inner and outer Helmhotz planes, point of zero charge, dielectric constants in the double layer, zeta potential, adsorption of inhibitor, stability of inhibitors, behaviour of inhibitor in different media were given importance.

J. L. Bregman published an excellent work on corrosion inhibitors in 1963. Over the past three decades surface analytical techniques like X-ray photoelectron spectroscopy, Auger Electron Spectroscopy, Secondary Mass Ion Spectrometry and Electron Probe Microanalysis drastically improved the field of corrosion inhibitors by way of providing useful information on the surface phenomena.

Although considerable progress was made in the chemistry of inhibitors and several thousand papers were published on inhibition, the real corrosion system possess the same type of challenges today as it was 50 years ago. The inhibitor is transported to the surface; it interacts with the metal and forms an active inhibitive species. The flow rate, temperature, solubility of inhibitor, stability and adherence determine the effectiveness of inhibitors.

In the olden days, use of corrosion inhibitors was mentioned as one of the methods to minimize corrosion and reduce corrosion costs. Although, highly corrosion resistant and exotic alloys are available in the market, economics dictate the cheaper and more commonly available materials in the industries, which are invariably susceptible to corrosion. The main aim of using corrosion inhibitor is to reduce the corrosivity of the environment to which the materials is exposed and reduce the corrosion rate and hence to minimize cost of overall industrial processes.

Corrosion inhibitors are widely used in industries. Some examples are refineries and petrochemical plants, petroleum production - primary recovery, secondary recovery, pipelines carrying petroleum products, petroleum drilling and packer fluids, potable water, cooling water, desalination system, automobile radiators, organic coatings, boiler water, microbiological corrosion control, pulp and paper mills, deicing salts, agricultural chemicals, coal slurry pipelines, refrigeration brines, reinforcing steel in concrete etc., In view of the multifarious applications cited corrosion inhibitor industry is a billion dollar one. The users of inhibitors need to possess knowledge on the chemistry and the behaviour of inhibitor, which can result in considerable savings.

Inhibitors find application in acidic, neutral and alkaline solutions. In acid medium the main applications are in the form of pickling, acid cleaning and oil well acidization. In neutral medium inhibitors are all added to potable water, cooling water, boiler water and automobile radiators. In alkaline environment, inhibitors find application in the cleaning of metals.

3.1 Inhibitors for Cooling System

Cooling systems are the heart of any industries like chemical, petrochemical, etc., Cooling towers are effective air washers and they are always saturated with oxygen. Their exposure to atmosphere ensures absorption of atmospheric pollutants like ammonia and sulphur dioxide. Micro and macro fouling enhance the severity of corrosion in cooling water systems.

3.1.1 Materials of Construction

Carbon steel is the widely chosen material of construction of heat exchangers and the distribution piping of recirculating cooling system because it is cheap. The use of copper tubes in heat exchangers is somewhat limited because they undergo impingement attack. Admiralty brass used for some times also undergoes dezinfication in spite of the addition of arsenic, antimony or phosphorous. Copper nickel alloys suffer localized corrosion. 70:30 copper alloys perform better than 90:10 copper alloys. Austenitic stainless steels are resistant to impingement attack. Water of high chloride content cannot be used on the outside of the condenser tube because pitting can initiate stress corrosion cracking at temperatures above 600C. To a lesser extent titanium metal is used as construction material in heat exchangers.

3.1.1.1 Inorganic Inhibitors

In the early 70's nitrites of about 300 to 500 ppm were used as inhibitors. Strict maintenance of pH is an essential part of the usage of nitrites. At low pH nitrites are converted to nitrous acid, which enhance the corrosion. Nitrites are oxidized to nitrates by bacteria which have no inhibitive effect. Silicates have been used for over 50 years at 500 ppm or less concentration. The ratio of SiO2 / Na2O is in the range of 2.5 - 3.0 is very effective for carbon steel. The formation of hydrated silica gel offer protection against dissolution. The protection processes are slow and need pH adjustment to 6. These are some of the drawbacks associated with the use of silicates. Sodium molybdate is very effective in the pH range of 5.5 to 8.5. It requires the presence of oxygen. Molybdates are all useful for inhibition against localized corrosion by the formation of MoO2 to film. Chromates were used as inhibitors in cooling water system for longer period. Chromates are all passivating type of inhibitors and protect ferrous and non-ferrous alloys. The usually initial concentration is 500 to 1000 ppm, which is subsequently reduced to 200 to 250 ppm. The passive film formed on iron surface consists of a layer with chromium hydroxide. Hexavalent chromium is toxic to aquatic life and causes stains on operating personnel. When used in insufficient quantities they lead to pitting type of attack.

Poly phosphates have been used as corrosion inhibitors over five decades. They are all effective against galvanic corrosion. The major drawback in their use is that they hydrolyse to their parent compound ortho phosphate. Ortho phosphate and Poly phosphate enhance the biological growth in the cooling towers as they are very good nutrients for the microorganisms. Addition of biocide is inevitable when polyphosphates are used as inhibitors.

3.1.1.2 Organo Phosphonates

Organo phosphonates are recent origin. The susceptibility of polyphosphates to hydrolysis led to the development of a stable compound like Organo phosphonates. Amino trimethylene phosphonate (ATMP) and hydroxy ethylidine diphosphonate (HEDP) are widely used in the industrial cooling systems. They are all stable towards hydrolysis. They are all very effective corrosion inhibitors as well as descaling compounds. They show synergistic inhibition with zinc salts. The desirable properties of phosphonates are : (i) control of calcium carbonate and calcium sulphate scale (ii) complexation of multivalent cations (iii) stabilization of water containing iron and manganese. They are stable beyond 1000C. All organic inhibitive system has been developed for cooling waters. This is a blend of polymers, phosphonates and corboxylic acids, which are non toxic and of low environmental impact.

3.1.1.3 Heavy Metal Zinc Combinations

Zinc polyphosphates provide protection to ferrous and nonferrous metals. Zinc increases the rate of formation of the protective film and the concentration is needed for effective protection is less than polyphosphate alone. There is an incorporation of 10 to 20% zinc in the polyphosphate layer. The effective pH range for the protection is 6.5 to 7.5. Zinc phosphates show improved inhibition compared to phosphonate alone. Very effective protection is obtained with zinc in the range of 20 - 80% and the optimum range being 30 - 60%. The mechanism of protection by zinc phosphonates is cathodic nature, while phosphonates themselves are anodic in nature. The effective pH range for the operation with zinc phosphonate is 6.5 to 9.

3.1.1.4 Non-Heavy Metal Combinations

The popular system are (i) mixture of ATMP and HEDP, (ii) Mixture of polyphosate and HEDP (iii) Mixture of polyphosate and ortho phosphate. The mixed system form complex with metal ions which serves as the protective film. They prevent the formation of calcium carbonate and calcium sulphate scale. They remove the surface deposits by acting like dispersants. Benzotrizoles are used in combinations with other mixtures to inhibit corrosion attack of copper and dispersant.

3.1.2 Chemical Fouling and its Control

Foulants also contribute to under deposit corrosion. The conventional way of scale control is controlled addition of sulphuric acid and partial softening. Complexing agents like EDTA and NTA have been used for some time. Low molecular weight polymers and naturally occurring polymers like tannin have yielded encouraging results in foulant control. These compounds have dispersing properties, threshold effect, crystal distortion and sequestration of multivalent cations.

Dispersants, sludge fluidizers, surfactants and wetting agents constitute the accepted foulant control agents. Natural dispersants such as lignins and tannins provide good results at relatively high dosages.

Tannin has better dispersion than sodium polyacrylate, sodium salt of polymaleic acid or carboxy methyl cellulose. Sodium salt of polymaleic acid has better calcium carbonate and calcium sulphate inhibition than sodium polyacrylate, tannin or carboxy methyl cellulose.

Recent developments have produced chemicals that are extremely effective. They permit much higher cycles of concentration, effective at higher temperatures and are also cost effective.

Effective crystal modifiers are polymaleic acid and sulphonated polystyrenes. They are water soluble polymers. The common range of dosage for cooling water is 0.5 - 2.0 ppm.

3.1.3 Biological Fouling and its Control

The growth of biological organisms not only leads to plugging of water passage but also causes the deterioration by under deposit corrosion. The cooling towers are ideal places for the growth of microorganisms. The availability of organic and inorganic salts along with warm sunlight moisture, oxygen provides favourable environment for their growth. Microbial growth can be curtailed by using biocides. Oxidizing biocides such as chlorine, chlorine dioxide, hypochlorite and manoperoxy sulphate etc., and non oxidizing biocides such as salts of pentachlorophenol, organosulphur compounds, organotin compounds are being used as biocides. Laboratory studies are going on to assess the biocidal action of ozone in killing bacteria by facilitating the detachment of bacterial films formed on stainless steels.

Sterilization by ultraviolet radiation of recirculating water also effective in controlling bacteria. UV radiation is an environment friendly biocontroller which also saves the cost of treatment and inhibits corrosion.

There is non combatability between inhibitors and biocides . Corrosion inhibitor need not be combatable with biocides. A good biocide may be an accelerator of corrosion. Recent studies in Central Electrochemical Research Institute, Karaikudi brought out the fact that the simultaneous addition of inhibitor and biocide at one point is ineffective. The biocide must be added before hand for controlling the bacteria. This should be followed by the inhibitor addition. There is a vast scope for further study on the combatability of inhibitors and biocides.

3.1.4 Monitoring of Cooling Systems

There are also developments in the monitoring of inhibitors in cooling water systems. The conventional ways of monitoring is based on measuring the polymer concentration using photometric methods based on absorption and turbidity. Recently a method based on fluorescence has been used for measuring corrosion inhibitor concentration in cooling water system. The polymer was tagged with fluorescent species and the polymer concentration was monitored by measuring the intensity of fluorescence. The fluorescence method has been tested in the chemical processing industries and utility power plant in USA.

3.2 Inhibitors for Acid Systems

3.2.1 Pickling

Acids find wide application in industries in the form of pickling, descaling and oil well acidization. The selection of inhibitor is based on the type of acids, temperature, flow velocity and the presence of organic, inorganic substances in the acid solutions. Hydrochloric, Sulphuric, Hydrofluoric, Citric and Formic acid are commonly employed for pickling purposes.

Hydrochloric acid is the most commonly employed acid for pickling used upto 200 gm per litre concentration at temperature 600C for a minimum period of 30 minutes and Sulphuric acid is used at 200 - 300 gm per litre at temperature upto 900C. The purpose of adding pickling inhibitor is to minimize the metal loss and to reduce the entry of hydrogen into the metal. Pickling inhibitors are all available in the form of packages containing active inhibitive substances, wetting agents, detergents and foaming agents. Literature is very much enriched with information on acid inhibitors based on different organic compounds.

Hexamethylene tetramine also known as urotropine is the commonly used inhibitor in HCl medium. This compound slowly gives rise to a volatile chloromethyl ether in reaction with HCl and this compound is carcinogenic nature. In commercial formulations nitrogen based compounds such as amines, aldoxime, ketoximes and imidazoline derivates are reported in the literature. Sulphur containing compounds such as mercaptans, thioureas and thiazoles are also used as inhibitors in HCl medium.

In the literature lot of information is available on the corrosion inhibitors for copper, brass, aluminium, zinc, nickel and titanium alloys against the attack of HCl.

Sulphur containing compounds are all effective inhibitors in sulphuric acid medium. Sulphoxides, sulphides and thioureas are used in commercial formulations of which, dibenzyl sulphoxide and dibenzyl sulphide are common. The literature is rich with inhibitive formulations for steel, copper, brass, titanium in sulphuric acid medium. Similarly references are available on the inhibitors for nitric acid, hydrofluoric acid and phosphoric acid for different metals.

3.2.2 Descaling

Scale formed in circulating water of power plant, chemical plant, steel mills, paper mills have to be removed because this affects the heat transfer efficiency of boilers, vessels, reactors, piping and other associated equipments. These scales are mainly inoroganic in nature consisting of carbonates, sulphates, phosphates, silicates of magnesium and calcium. Acids commonly employed for scale removal are hydrochloric acid, hydrofluoric acid and ammonium bifluoride mixture, sulphuric acid, sulfamic acid and citric acid. Hydrochloric acid of 5 to 15 wt.% at 800C is employed for scale removal. Hexamethylene tetramaine 33 - 37 gm per litre is commonly employed as inhibitors. When silicates scale are present hydrofluoric acids and ammoium bifluoride are added to hydrochloric acid for the removal of iron scale and silicate deposits. A rosin amine derived from Mannich base with acetophenone, acetone are effective.

The condensations of the product of diethyl and dibutyl thiourea with hexamethyline tetramine offer very good protection.

If the scale contains copper along with magnetite mixture of thiourea and Hexahydropyrimidine - 2- thione is added to HCl to achieve the dissolution of magnetite and copper.

3.2.3 Oil and Gas Well Acidization

During the process of acidization oil and gas wells to stimulate the oil and gas flow from the well, hydrochloric acid is forced under high pressure through the rock formation to produce fractures. About 10 to 15 wt. % of hydrochloric acid is usually used for this purpose and the choice of inhibitors should be stable upto 1500C to 2600C.

Arsenic was the first effective acidizing corrosion inhibitors used earlier. Organic and inorganic chemicals have replaced Arsenic corrosion inhibitors. Organic chemicals used as inhibitors today include nitrogen containing compounds, acetylenic alcohols, aldehydes, ketones, formic and derivatives, thiourea and derivatives, surfactants, oil wetting substances, alcohols, coupling agents and others.

Common inorganic chemicals include iodine, copper, tin, antimony, bismuth, mercury and their salts. Propargyl alcohol, hexynols, and decynols. The mixture of amines and acetylenic alcohols generally aids synergistic corrosion control.

Propargyl alcohol improves the performance of high temperature, when used along with cyclohexylamine, aniline and methyl aniline.

3.3 Corrosion Inhibition in Oil and Gas Wells

In oil wells the source of electrolyte is the formation containing dissolved salts in significant concentration. The other corrosive agents are CO2 and H2S. In oil fields pitting corrosion is a serious problem caused by galvanic coupling of the bare metal and film covered metal. The corrosion products consist of iron sulphide, iron carbonate, iron oxide or oxyhydroxide or combination of these formed on steel surface.

Quaternary ammonium compounds, imidazolines, pyridines were used in suitable solvents in early days. For easy transportation of the inhibitor to metal surface, the inhibitor is blended with surfactants. Nitrogen based inhibitors gave 99 % inhibition in H2S medium; 96% in CO2 atmosphere. Nitrogen, phosphorous and sulphur based inhibitors gave 90% inhibition in both H2S and CO2 atmospheres. Inhibitors are applied in batches or continuously injected into the well or periodically squeezed. The stability of inhibitors to a wide temperature range is an important property for the good performance.

Amines, imidazolines, amides, quaternary ammonium compounds in suitable solvent are used as film forming inhibitors. Films of inhibitors have lives of minutes to hours. They offer barrier type protection.

The latest concept in oil field is "GREEN" (Environmentally friendly) inhibitors for using in sensitive areas such as North Sea are less cost effective than conventional inhibitors. Environmentally acceptable inhibitors can be formulated without compromising the high level performance associated with conventional products. The future trend is to develop cost effective inhibitors based on biodegradable materials following specific protocols.

The mode of injection of inhibitor is very important, as the inhibitor has to reach the site of corrosion for effective protection. Continuous injection of the inhibitors or batch treatment in which inhibitor solution about 2 to

10% is injected in a shut in well and allowed to reach the bottom.

It is very difficult to monitor the corrosion in gas wells. Weight loss methods and iron analysis are the only available methods for monitoring corrosion of oil well. Corrosion in oil well is a fertile area of research with ample scope for future developments.

3.4 Corrosion Inhibition In Concrete

Calcium nitrite is a prominent candidate for use in concrete structures. It has been used as inhibitor for concrete in large scale and provides corrosion protection in presence of chlorides without affecting the properties of concrete. There are studies to make use of organic inhibitors as an alternative to the commonly used calcium nitrite. The organic inhibitors get adsorbed on the metal surface and form a protective film. Organic amines and esters were studied for their possible application in place of calcium nitrite. They lowered the corrosion significantly. The other inhibitors studied are mixture of glycerophosphate and nitrite showed synergistic behaviour. Polyalcohols, poly phenols and sugars have been reported as good inhibitors. The area of development of inhibitors in concrete is also a fertile area for further research.

4. Surface Analysis and Use of Modern Instrumentation

Modern surface analytical techniques give more information on the surfaces than the classic methods. The classical methods are based on the adsorption isotherms, surface roughness, photoelectric work function, ellipsometric, microscopic and reflectivity. The modern methods provide information on elemental analysis, chemical information, oxidation state, functional group, quantitative analysis etc., Fourier Transform Infrared, Laser Raman Spectroscopy and Surface Enhanced Raman Spectroscopy are important modern surface analytical techniques.

4.1 Electron Spectroscopy for Chemical Analysis

Electron spectroscopy for chemical analysis provides information on chemical bonding such as oxidation state of elements and structure of organic molecules. It detects all elements except hydrogen and helium.

4.2 Auger Electron

Auger electron spectroscopy provides information on surface segregation, corrosion grain boundary diffusion and precipitate identification.

4.3 Secondary Ion Mass Spectroscopy

Secondary ion mass spectroscopy gives depth profiling data in the case of thin film deposition on semiconductors and surface coatings for plasma analysis. SIMS is used to detect hydrogen and deuterium.

4.4 Raman Spectroscopy

Raman spectroscopy gives information on the reaction product film formed on metal surfaces. It also provides information on bonding, composition and stoichiometry of both crystalline and amorphous substances under atmospheric as well as aqueous solutions. X-ray diffraction can be applied to crystalline material. AES, ESCA and Electron Microprobe require high vacuum and cannot be employed in aqueous environment. Raman spectrum can be used to identify corrosion products in aqueous solution. Insitu corrosion detection is possible with the help of Raman spectrum. The disadvantages of Raman spectrum is low sensitivity.

4.5 Surface Enhanced Raman Scattering (SERC) Technique

Surface Enhanced Raman Scattering technique has been used to study the adsorption of benzotrizole on copper and the adsorption of pyridine on iron. This technique helps to illustrate the structure and spatial orientation of the adsorbed inhibitor.

4.6 Reflectance Fourier Transform Infrared (FTIR)

Reflectance Fourier Transform Infrared (FTIR) has been used in the development of effective inhibitors for corrosion in CO2 medium. FTIR provides information on the nature of adherence to the metal surface as well as uniformity of coverage.

Surface analytical techniques provide useful information regarding the adsorption of ions on the metal and oxides surfaces, which helps us to understand the details of the role of corrosion inhibitors. Surface analytical techniques can be classified into two types. One is exsitu, where the specimens are removed from the solution and kept in ultrahigh vacuum such as Auger electron spectroscopy (AES), X- ray photo electron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) and insitu methods such as infrared (IR), Raman and surface-enhanced Raman spectroscopy (SERS), wherein the reaction path is followed during the corrosion is in progress.

5. CECRI's Contribution to the Development of Inhibitors

Central Electrochemical Research Institute (CECRI), Karaikudi has developed inhibitors for pickling, cooling water systems and oil wells. Vapour phase inhibitor was developed for protecting steel components during transit and transport. CECRI was the first to develop an inhibited cement slurry coating for the protection steel reinforcement rods in concrete. This technology was utilized in the construction of a major road bridge connecting Indian mainland and Rameshwaram island which is facing severe marine corrosion. It has also developed low chromate formulations and non chromate formulations for industrial cooling systems. Recently it has studied the causes for corrosion and coloration during the transportation of desalinated potable water through mild steel pipelines and suggested inhibitive measures to control the corrosion taking into account the potability criteria. A number of publications on the investigation of inhibitors in different media have been published.