

POLYMERIC CORROSION INHIBITORS - AN OVERVIEW

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Corrosion occurs due to chemical and electrochemical reactions. Polymeric materials adsorb on the metal surface and offer inhibition to corrosion. In this overview polymeric materials employed to inhibit the corrosion of ferrous and non-ferrous materials in acidic and neutral media are presented. Polymers which act both as antiscalant and inhibitors are also discussed.

Keywords: Corrosion inhibitors, water soluble polymers, polymeric films and anti-scalants.

INTRODUCTION

Polymers are very large molecules that are formed by the combination of a number of relatively small molecules called monomers. Polymers can be made from inorganic or organic molecules. They may have different forms e.g. they may be chain like as in polyethylene or sheets like as in quartz. The synthetic polymers are long chain organic molecules whose dimensions could approach 10^5 Å as compared to simple molecules having dimensions of 10 Å. In the last two decades there has been an increase in the use of polymeric compounds as corrosion inhibitors.

In this overview, an attempt is made to discuss the role of polymeric materials to inhibit the corrosion of ferrous and non-ferrous metals in acidic and neutral media.

Corrosion of metals

The word "corrosion" comes from the Latin 'corrodere' to gnaw away. It is the gradual deterioration of a material caused by the chemical or electrochemical reaction with its environment [1]. The ancient Greek historian Herodotus (fifth century B.C.) and the ancient Roman naturalist,

Pliny the Elder (first century B.C.) mention the adoption of tin for the protection of iron from corrosion. All chemists through centuries made fertile attempts to transform base metals into noble ones latter. Early attempts to mitigate corrosion of metals were empirical and centered largely around the use of organic and metallic coatings. Inhibitors for acid corrosion of metals were known from middle ages. There were obvious measures to protect metallic structures constructed by early artisans, often at the expense of much time and very hard labour [2].

Lomonosov (1743-1756) was the first to make broad systematic experiments on the study of the action of acids on metals. In 1788 Austin noticed that water originally neutral tends to relatively recent and came quite logically after the discovery by Galvani and Volta [3] of galvanic electricity in the late eighteenth century. Hall [1] established the fact that iron does not rust in the absence of oxygen.

Davy (1826) [4] proposed an electrochemical method using sacrificial anode for the protection of copper sheathed ocean, going ships. De La Rive (1830) [5] attributed the pronounced corrosion of

impure zinc metal to the operation of short-circuited microcells on the metal surface. Faraday's research (1830-1840) established a very important relationship between chemical action and the generation of electric current [6].

Wagner [7] proposed a mixed potential theory. This theory proclaims that (i) any electrochemical reaction comprises two or more partial oxidation and reduction reactions (ii) there can be no net accumulation of electrical charges during an electrochemical reaction and (iii) the potential at the entire surface of an isolated electrode should be same.

The practical methods available for the protection of metals against corrosion are diverse. These may be divided into the following groups viz., (a) selection of metals (b) modification of metal (c) change in design (d) change in corrosive environment (e) surface coatings (f) change of the electrode potential of metal/corrosive medium. The most commonly practised methods of control is changing the environment. This is accomplished by a method known as corrosion inhibition.

Corrosion inhibitors

An inhibitor is a chemical compound that effectively reduces the corrosion rate of a metal when added in small concentration to an mildly aggressive medium or environment [8]. This acts by changing the surface or both depending on the individual system. Electrochemical corrosion involves two partial reactions, one at the anode and the another at the cathode.

On that basis, an inhibitor is defined as a chemical compound that effectively reduces the rate of either or both of these reactions. Accordingly they are classified as anodic, cathodic or mixed inhibitors. They are broadly classified as inorganic or organic, anionic and cationic inhibitors [9].

Inorganic inhibitors are usually crystalline salts as sodium chromate, sodium silicate, sodium phosphate or molybdate. In aqueous solution, they separate to form the negatively charged anions like CrO_4^{2-} , SiO_3^{2-} , PO_4^{3-} and molybdate. Only the

negative anions of these compounds are involved in reducing metallic corrosion. Therefore these are called inorganic anionic inhibitors. When zinc is used instead of sodium, the zinc cation is beneficial and the compounds may be called inorganic mixed charge inhibitors. They are used in cooling towers.

Organic anionic inhibitors such as sodium sulphonates and sodium mercapto benzotriazole are used in cooling water and antifreeze solutions. Sodium phosphonates fall into this class are used in cooling towers. Organic cationic inhibitors [10] are liquids or wax like solids.

Their active portions are generally large C-H chains or rings with positively charged amine nitrogen groups at one end. In acids and water, the terminal primary secondary and tertiary amine groups take an additional hydrogen that gives them a net positive or cationic charge. The polar amine groups are adsorbed on the metal and the hydrocarbon portion forms an oily water repellent surface film. The molecular shape (disymmetry) helps these materials act as surfactants and can stabilize emulsions of oil and water. Organic corrosion inhibitors [10-11] may function by (1) chemisorption of the molecule on a metallic surface (2) Complexing of the molecule with the metal ion which remains in a solid state (3) Neutralising the corrodent and (4) adsorbing the corrodent.

It is universally accepted that the organic molecules adsorb at the metal/solution interface. These modes of adsorption are dependent upon: (a) the chemical structure of the molecule (b) the chemical composition of the solution (c) the nature of the metal surface (d) the electrochemical potential at the metal/solution interface. There are three principal types of adsorption associated with organic inhibitors. (i) π bond orbital adsorption (ii) electrostatic adsorption and (iii) chemisorption.

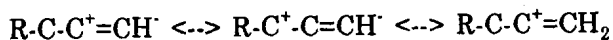
Inhibitors for ferrous materials in acidic medium**Polymer film forming inhibitors**

Organic molecules with unsaturated carbon exhibit this behaviour. The molecule with $-C\equiv C-$ bond found to be effective inhibitor. In the middle 1940's acetylenic compounds were discovered to be effective inhibitors [12]. A postulation came in 1961 which described the affinity of the triple bond of these alcohols for the metals 'd' electrons lead to the chemisorption at anodic sites with a consequent sharing of electrons. After adsorption of these species, polymerisation ensues which is responsible for the corrosion inhibition was put forward [13].

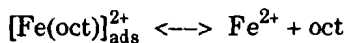
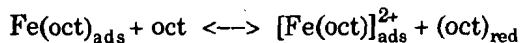
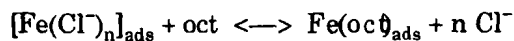
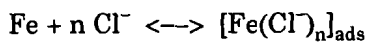
Propargyl alcohols and other alkynols were investigated in detail by IR- reflectance spectroscopy which confirmed the formation of polymers on the metal surface [14-15]. The mechanism of ethyl cyclohexanol polymerisation was studied using iron powder in 2 M H_2SO_4 , under nitrogen atmosphere [16].

From the analysis of volatile intermediates and products, the ethynol cyclohexanol was reduced on the iron and it subsequently dehydrated to form a hydrocarbon polymer. A similar mechanism was postulated for 3 butyne 2-ol. A completely different idea was suggested that the acid solution itself may interact with the acetylenic species to tautomerise or form vinylic cations which can hydrate, undergo metathesis or polymerize.

Acetylenic alcohols were investigated in detail with regard to the position of OH- and the position of the triple bond. It appears that the OH group has to be in α - position to the acetylenic function and an optimum efficiency was obtained if the acetylenic function was terminal. These two effects can be explained on the basis of tautomerism.



This formalism implies that the polarisation of the triple bond can be stabilized first by a non-classical carbonium ion and further by a α -keto-double bond configuration which is known to complex strongly with transition metal ions. It is noted that the OH group has to be located not only in α - position but on a secondary carbon atom for strong inhibition to result. This is to be expected since H^+ ions are much more optimum to form non classical carbonium ions than CH_3 groups. If the terminal proton on the triple bond is substituted with a strong electrophilic group, the polarisation of the triple bond becomes strong enough to involve the above indicated tautomerism. One can rationalise that a compound with a non-terminal triple bond experiences some steric hindrance in the formation of complexes with transition metal ions. The effect was due to steric hindrance rather than a kinetic effect concerning the intra-molecular shifts necessary for complex formation. The substituted propargyl alcohols became more effective as the alkyl chain increased. This effect most likely has to do with the nature of the "adsorbed layer" in that increasing length of the alkyl chain imparts greater hydrophobicity to the interfacial layer thus squeezing out water molecules from the interface. Alkynols have been successfully tried to inhibit corrosion of steels in acidic solutions and mechanism of inhibition was discussed [17-18]. The adsorbed alkynols first hydrogenated at the $-C\equiv C-$ to form a secondary olefinic alcohol. Oligomerisation through the terminal $-C\equiv C-$ can ensure to yield the highly branched structure. Further hydrogenation saturated some of the internal saturated $-C\equiv C-$ bonds.



The barrier film contains unreacted octynol possibly chelated with iron as well as hydrocarbon reaction product. The film is not stable without an equilibrium concentration of octynol in solution which is able to adsorb and act as the "anchor" for the hydrocarbon. The polymer product has been identified as an unsaturated oligomer of reduced octynol. 2-methyl-3 butyn-2-ol (MBO), propargyl alcohol (PA), 3-butyn-2-ol (BO) and 2-butyn-1,4- diol (BD) have been found to inhibit the corrosion of iron in hydro chloric acids [19]. PA offered more inhibition in 1.0 N acid solution while MBO offered highest inhibition. The monomeric inhibitor molecule underwent polymerisation so that a polymeric two dimensional system was formed which lightly adhered to the metal. In the case of BO and PA, the polarisation of the triple bond was stabilised first by a non-classical carbonium ion and then by a keto configuration which was known to complex with FeOH_{ads} . The terminal $-\text{C}\equiv\text{C}-$ bond did not favour π bond interaction because of steric hindrance.

The inhibition mechanism of PA was investigated for iron corrosion in 0.5 M HCl at elevated temperature using surface enhanced Raman scattering XPS and FTIR [20]. SERS spectra of PA adsorbed on an iron Fe-deposited silver electrode revealed that species derived from PA have $\text{C}=\text{C}$, $\equiv\text{CH}$, $\text{C}=\text{O}$ bonds. A high inhibitor efficiency of PA at 343 K was attributed to the coverage of the surface with a protective film of PA polymer and partly to adsorption of allyl alcohol formed by cathodic reduction of PA. Electro initiated polymerisation of PA theory was proposed. In $\text{H}_2\text{SO}_4 + \text{H}_2\text{S}$ system [21] the adsorption of H_2S and SH^- on electrode surface slowed down the formation of polymer film of PA.

The FeS produced after a long time, increased the continuity of the polymer film of PA and life.

Polymeric materials

High molecular weight organic compounds reduced the corrosion rate of metals [22-27]. Most of them were nitrogenous materials containing a fatty chain as part of their structure. Aliphatic fatty acid derivatives, imidazolines and quarternaries, esters can also be used. *m*-methyl cyclohexanol, ester of adipic acid and didecyl ester of benzyl succinic acid have good protective properties. They inhibit by adsorption. The effectiveness of corrosion inhibitors on wet steel was improved by the addition of an ester of a glycol or polyglycol e.g., ethylene glycol diacetate or tripolyene glycol monoacetate. Fatty acid esters [28] having the general formula $\text{RCOO}\cdot\text{CH}_2\text{CH}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$ where R = fatty acid hydrocarbon chain (C_{17}) and *n* is the average number of oxyethylene units present in the polyglycol and polyethylene glycol were tested as inhibitors in 0.05 N HCl solutions at 343 K. These compounds adsorbed on the surface obeying Langmuir isotherm. They offered large coverage due to the long hydrocarbon chain and by the presence of OH groups. Being hydrophilic in nature, the OH groups counter acted the effect of chain length and ensured higher solubilities.

Epoxidised fatty materials modified with aromatic amines were found very useful for mitigation of corrosion of mild steel in HCl [29]. For iron in 5 N H_2SO_4 solutions, poly vinyl pyrrolidone having a molecular weight of the order of 10,000 to 40,000 was an effective inhibitor [31]. A water soluble melamine-formaldehyde resin was developed [31] and the film formed in higher concentrations of HCl afforded lower protection. Detailed investigations carried out on polyamide epoxy systems in acid solutions revealed that the presence of an amino group, a fatty cyclic dimerised acid and an imidazoline ring in the polyamide [32] resin contributed towards good inhibitive properties. The amine cations were adsorbed on the cathodic area of the metal surface

through nitrogen atoms thereby forming a mono molecular layer over the metal surface [33-34].

Amido polyamines [35] were found to be inhibitors in 5N HCl at 333 K offering more than 95% inhibition. The polyamide resins were prepared by using dimerised vegetable oil acid and aliphatic polyamines. The amido polyamines (APA) form an ionisable salts in acid medium. The positive nitrogen centres of these compounds ensured that they could not be discharged at the cathode sites and adsorbed through the nitrogen atom. They prevented hydrogen discharge and thereby corrosion. Electrochemical studies carried out on polyacrylic acid and polyacrylamide [36] revealed that they offered 80% protection to steel in H_2SO_4 and HCl acid solutions. Methacrylonitrile- $K_2S_2O_8$ system offered inhibition by "insitu" polymerized film formation. The film formed on mild steel [37] affected both anodic and cathodic reactions in acid corrosion. Polyethoxy aniline (PEA) dissolved in ethanol act as an inhibitor for iron in 1N HCl solutions [38]. The co-existence of delocalised π electrons and the quaternary ammonium nitrogen in the polymer facilitate its strong adsorption on the iron surface. The adsorption of these polymers obey the Temkin isotherm. Polyvinyl pyrrolidone and poly ethylenimine mitigated the low carbon steel corrosion [39] in H_3PO_4 solutions. They adsorbed on the surface hindered the anodic reaction and thereby corrosion. Pectine (P), carboxy methyl cellulose (CMC), poly vinyl alcohol (PVA), poly ethylene glycol (PEG), poly acrylic acid (PAA) and sodium poly acrylate (NaPA) within the concentration range 0.02 to 0.2 gm.dm⁻³ to control the corrosion of iron in HCl, $HClO_4$ and H_2SO_4 solutions [40]. The effectiveness of polymer additives as anodic inhibitors in a corrosive medium decreased in the order $HCl = HClO_4 > H_2SO_4$. The sulphate ions competed on the surface and affected the inhibition in H_2SO_4 solutions. Polyamino-benzoquinones (PAQ) inhibited the corrosion of mild steel in 1N H_2SO_4 and 1N HCl solutions. They strongly adsorbed on the active sites and formed a protective film formed affected both anodic and cathodic reactions [41]. The

corrosion of mild steel in 1N H_2SO_4 and 1 N HCl solutions were inhibited by polyamide macrocyclic compounds. 3,4:11,12-dibenzo-2,5:10,13 tetraoxo - 1,6,9,14 - tetra azocyclohexadecane (TBOAD) acted as mixed inhibitors [42].

The use of radical polymerisation in a solution of acrylamide (AA) and oligo (oxy ethylene) methacrylate (OEGMA) for corrosion and protection of steel in highly acidic solutions. At moderately elevated temperature, OEGMA provided higher inhibition compared to AA [43]. Poly(4-vinyl pyridene poly -3-oxide ethylene) (PAVPP3OE) was investigated as inhibitor for Armco iron in H_2SO_4 . The observed 99% inhibition was due to adsorption and the adsorbed molecules obeyed Frumkin isotherm [44]. Polymers of acrylamide with specific polar end group namely thio malic acid have been synthesised, characterised and evaluated for their corrosion inhibition property for mild steel in acids. The inhibition efficiency found to depend on polyacryl amide backbone length [45].

Conducting polymers

Intrinsically conducting polymers were tried as corrosion inhibitors [46]. The conducting polymers are unprocessable due to a rigid backbone structure because of extensive delocalization of π electrons. This availability of π electrons in abundance enabled them to be good corrosion inhibitors provided these are made soluble in some common solvents and have atleast "some" solubility in acidic solutions. Polyaniline has been known for more than a century [47] polyaniline was made soluble in dimethylsulphoxide and dimethylformamide [48]. Modified polyaniline polymeric chain [38] by introducing an ethoxy group at the ortho position to the N-H bond was found to be a good inhibitor for iron in 1.0 N HCl. The co-existence of delocalised π electrons and the quaternary ammonium nitrogen facilitated its strong adsorption. The adsorbed polymer molecules obeyed Tempkin isotherm. Commercially available water soluble acetylene black II which has a structural similarity to polyaniline proved to be a

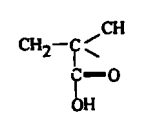
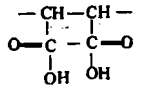
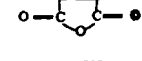
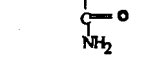
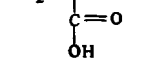
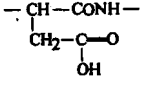
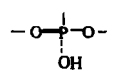
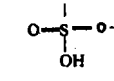
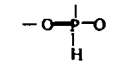
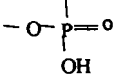
good inhibitors for iron under acidic conditions [49].

Inhibitors for non-ferrous materials in acidic medium

Silver and copper were protected by the use of spin applied conjugated polymers such as polyanilines and the addition of KI and PA offered synergistic effect [50]. The presence of iodide ions in the solutions stabilised the adsorption of PA molecules and improved the inhibition efficiency of PA. In the solutions containing propargyl alcohol there was a less possibility of polymerisation of PA. The corrosion of copper was inhibited by PMTA (1-phenyl-5-mercapto tetrazole). The polymer film was found to be superior to those formed by TTA (tetrazole), BTA (benzotriazole), HBTA (hydroxy benzotriazole), MBT(2-mercapto benzothiazole), MBI(2-mercapto benzoimidazole), IBM (imidazole) and chromates [51]. MBT inhibited copper corrosion in 0.01 M HClO₄ and ethanol [52]. The polymeric complexes involving copper ions and the ionised form of thiol offered inhibition. The effect of drag reducing polymers on the rate of flow induced corrosion of metals were studied [53]. The corrosion rate of metals was found to decrease in the presence of WSR-301. At a given polymer concentration, the maximum inhibition was found to be a decreasing function of the acid concentration and occurred between a Reynold's number of 4500 and 6000 depending on the acid concentration. 250 ppm polyox offered 23% inhibition in 0.25 M acid solutions. At elevated temperatures the copolymer of vinyl imidazole(VI) and vinyl trimethoxy silane (VTS) offered inhibition for copper corrosion [54].

The corrosion inhibition of nickel in 0.5 M H₂SO₄ solution by 2-(tri phenyl phosphoanylidene), succinic anhydride (2 TPSA), 1,4,8,11 tetra azocyclotetradecane (cylcon) and N,N'-bis (2-amino ethyl)-1,3, propane diamine were studied. The inhibition efficiency varied with chemical structure [55]. The inhibition of nickel corrosion in 1.0 N HCl and H₂SO₄ solutions by means of 3-methyl-1-butyne-3-ol (H), its halo derivatives and 1-octyn-3-ol (OCT) revealed these compounds

TABLE I: Structural units of some important polymeric scale inhibitors

| Name | Structural unit |
|------------------|---|
| Acrylic |  |
| Aspartic |  |
| Methacrylic |  |
| Maleic |  |
| Maleic anhydride |  |
| Acrylamide |  |
| Phosphoric |  |
| Sulphonic |  |
| Phosphinic |  |
| Phosphonic |  |

formed polymeric films. OCT was more efficient than H but the efficiency of the latter can be improved by replacing the H in $C\equiv CH$ by halogen, especially iodine [56].

Polymeric scale inhibitors

During water treatment in boilers, the scales formed depends on a number of parameters including the concentrations of lattice forming ions, the amounts of dissolved and suspended solids, the pH and flow properties of the solution, the rate of evaporation, the operating temperature and pressure of the system [57]. Scale facilitates the corrosion of surfaces, restricts fluid flow, reduces the quantity of heat that is transferred across the metal fluid boundary [58-59].

Naturally occurring polymers such as starch, gum tragacanth, carboxy methyl cellulose, algin tannins, lignosulphonates and gelatin were first used for scale control. They modify the crystal size and dispersants of micro crystallites [60-61]. They tend to oxidise at high temperatures and may promote the decomposition of scale to carbon. Large quantities are required to affect scale formation. Recently sub-stoichiometric amounts of synthetic water soluble low molar mass polymers or copolymers which are thermally stable and provide corrosion protection for the heat exchanger surfaces are employed [62].

Polymeric scale inhibitors may contain cationic, anionic, non ionic or ampholytic groups. The

majority of the polymers are based on acrylic or maleic acid (Table I). Low molar mass samples are found to be the most effective. It is usually necessary to use high initiator concentrations and/or radical transfer agents in the preparation of these polymers.

The pH in desalination systems is between 8 and 9 and the temperature is 451-482 K. In cooling water systems the pH is in between 6.5 and 8.5 and the temperature is 303-348 K. In boilers the pH is 10-12 and the temperature is 473-573 K at a pressure of 1380-4150KPa. The type and nature of scale formed in these systems will depend on the source of water, temperature and pH. (Table II) summarises some of the scaling components and the polymers that have been reported [63-64].

Both hydroxyl and sulphonates groups in polymer structures have the ability to prevent such gelation with calcium ions. In order to prevent gelation, effective polymers for scale inhibition must contain a certain level of these hydrophilic groups. A series of new co polymers based on these ideas were developed that are co-polymerised products of acrylic acid (AA) with 2-hydroxy-3 allyl oxy-1-propane sulphonate (HAPS) [65]. They inhibited calcium scales in the optimum molar ratio of AA/ HAPS \approx 92.5/7.5.

Sulphonated acrylate polymer (SAP), phosphino sulphonated acrylate polymer (PSAP), maleic ter

TABLE II: Scale components and inhibitors for water systems

| Scale component | Active polymeric unit |
|---------------------|---|
| Calcium carbonate | Maleic, acrylic, sulphonated styrene |
| Calcium sulphate | Methacrylic, acrylamide, meta phosphate |
| Calcium phosphate | Carboxylic-phosphonic, carboxylic sulphonic |
| Magnesium hydroxide | Maleic anhydride, vinyl sulphonate epoxy succinic |
| Calcium silicate | Acrylic-acrylamide, maleic-allyl sulphonate |
| Magnesium phosphate | Carboxylic-phosphonic |
| Iron oxides | Carboxylates |
| Silica/silicates | Maleic, acrylic, allyl polyethylene glycol, carboxylicsulphonic |

polymer (MTP) were tried as scale inhibitors [66]. MTP was proved to be an excellent CaCO_3 inhibitor. Sulphonation of an acrylate backbone provided good calcium phosphate inhibition and particulate dispersancy. The phosphino group provided enhanced inhibition properties to CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$ in SAP. The sulphonated polymers and MTP provided zinc stabilisation properties. Recently it was found that meth acrylic acid - acrylamide copolymer with thio acetic acid end group has performed well as an antiscalent [67].

Polymeric inhibitors for ferrous materials in neutral media

In cooling water systems various cationic and anionic polymers were studied. Polyethylene oxide (PEO) and polydimethyl sulphoxide (PDMS) were found to be effective inhibitors for ferrous and non ferrous materials in fresh water systems [68]. Polyethylene imine (PEI) and its derivatives, polyacrylamine (PAAM) and poly dicyano diamide derivative (PDCDA) as cationic polymers and poly maleic acid and its derivatives polyacrylic acid and its derivatives and poly acrylic acid as anionic polymers were found to be anti-scaling and corrosion inhibitors [69]. In low CaCl_2 solutions the inhibition efficiency for anionic polymers depended on number, average molecular weight, content of carboxylic group and concentration of -COOH groups. The anionic polymers were competitively adsorbed with Ca^{2+} ions on steel. To protect mild steel in 60 ppm chloride solutions [70] a new polymer based phosphonic acid was synthesised and studied. The tartrate-ethylene diamine phosphonic acid (TEDPA) found to offer inhibition in presence of zinc ions. In 3% NaCl solutions, polyaniline coated mild steel and stainless steel specimens exhibited enhanced corrosion protection [71]. A monolayer of 11-mercapto-1-undecanol adsorbed on the electrolytically reduced iron surface was modified with tetra ethoxy silane, octyl triethoxy silane and/or octa decyl triethoxy silane (TES). The two dimensional polymer film of the monolayer modified twice with TES and subsequently with C_{18} TES protected iron in aerated 0.5 M NaCl solutions [72]. Poly amino poly ether methylene phosphonate was

found to be an antiscalant and inhibitor in desalination operations [73]. The inhibiting action of 3-(trimethoxy silyl) propane thiol-1 (TMSPT) polymer film on steel corrosion in 3% NaCl solutions were studied. It acted as a passivating cathodic and anodic inhibitors. The formation of a chemisorbed methoxy silane compound which modified the surface shifted the free corrosion potentials to nobler values [74].

Polymeric inhibitors for non-ferrous materials in neutral media

3-mercapto propyl trimethoxy silane (MPS) has been used as a copper corrosion inhibitor in 0.1 M KCl solution [75]. In presence of oxygen it acted as a mixed inhibitor. The polymer film formation on the surface was confirmed by polarized grazing angle Fourier transform-infra red (FTIR) analysis. Vinyl silane modified imidazole copolymer [76] was found to be an inhibitor for copper corrosion. The free radical copolymerisation of vinyl imidazole (VI) and vinyl trimethoxy silane (VTS) was carried out in benzene at 341M K using azobis isocyanate butyionitrile as initiator. The inhibitory action of different pretreatment with meta acryloxy propyl methoxy silane (MAOS) on the corrosion of aluminum in 3.5% NaCl solutions revealed that the siloxane polymeric film formed by MAOS acted as a good corrosion inhibitor [77].

CONCLUSION

Organic compounds adsorb on the surface and interact with the surface. Some compounds form polymeric films and prevent the surface coming into contact with the corrosion environment. Polymers act both as antiscalants and inhibitors. Conducting polymers and biodegradable polymeric materials may also play vital role in future to protect materials from deterioration.

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REFERENCES

1. S N Banerjee, *An introduction to science of Corrosion and its inhibition*, Oxonian Press Pvt Ltd, New Delhi (1985)
2. Herbert H Uhlig, *Corrosion and Corrosion control-An introduction to Corrosion science and engineering*, John Wiley & Sons Inc, 2nd Ed (1971)
3. Galvani, *Meta Musculari Commentarius*, (1791)
4. H Davy, *Nicholson's J Phil Trans*, 116 (1826) 383
5. A Dela Rive, *Ann Chem Phys*, 43 (1830) 425
6. *Faraday's Diary*, Vols 1-7 (1820-1882) London G Bell and Sons
7. C Wagner and W Traud, *Z Phys Chem*, (1938) 441
8. J I Bregman, *Corrosion Inhibitors*, Macmillan, New York (1963)
9. R H Hausler, *Corrosion Chemistry*, (Ed) G R Brubaker and P B P Phillips, *ACS Symposium Series*, 89 (1979) 263
10. O L Riggs Jr and R L Every, *Corrosion*, 18 (1962) 262t
11. R H Hausler, *Proc Intl Conf on Corrosion Inhibition*, Dallas, 16 (1983), Texas 7
12. J Funhouser, *Corrosion*, 17 (1961) 283
13. I N Poutilsva, *The chemical and physical changes of inhibitors during the Corrosion process*, 2nd Eur symp on Corro Inhib, Ferrara, (1965) 139
14. G W Poling, *J Electrochem Soc*, 114 (1967) 2109
15. S A Balezein N I Podobayez, A G Voskresenky and V V Vasiliyev, *Proc 3rd Intl Congress Metal Corr*, 2 (1969) 9
16. E J Duwell, J W Todd and H C Butzke, *Corros Sci*, 4 (1964) 435
17. R F Monroe, *Acetylene derivatives as hydrochloric acid Corrosion inhibitors*, AAAS Meeting, 28 (1957)
18. W W Frenier, V R Lopp and F B Gracok, *Proc Eur Symp on Corrosion Inhib*, (6SEK), Ann Univ Ferrara, N S V 8 (1985)
19. M Jayalakshmi and V S Muralidharan, *Ind J Chem Tech*, 5 (1998) 16
20. K Aramaki and E Fujioka, *Corrosion*, 53 (1997) 319
21. L J Yan, Y F He, H C Lin and W T Wu, *Acta Phys Chim Sin*, 15 (1999) 726
22. W R Pollard and J V Lawson, *Ind Engg Chem*, 47 (1955) 2283
23. N S Benta, *Oil and Gas J*, 53 (1955) 126
24. J D Sudbury, O L Riggs and J F Leterie, *Petroleum Refiner*, 37 (1958) 83
25. C C Hubert and J A Rippetoe, *Oil and Gas J*, 51 (1953) 120
26. G C Purdy and W J Ries, *Corrosion*, 12 (1956) 17t
27. C M Blair, *Corrosion*, 12 (1951) 189
28. A A Abdel Fattah, K M Atia, F S Ahamed and M I Roushdy, *Corrosion Prevention and Control*, 6 (1986)
29. J N Putilova, S A Balezein and V P Barranik, *Metallic Corrosion Inhibitors*, Pergamon Press, New York (1960)
30. T Banerjee, *J Inst Chemists India*, 8 (1986) 87
31. A Joshi and K Srivastava, *Corrosion and its control*, 10 (1989)
32. W B Baldwin, A J Millian, D H Wheeler, H A Wittorf and C Geannopolis, *J Paint Technol*, 4 (1970) 512
33. C A Mann, B E Lauer and C T Hultin, *Ind Engg Chem*, 28 (1936) 159
34. C A Mann, B E Lauer and C T Hultin, *Ind Engg Chem*, 28 (1936) 1048
35. P K Ghosh, D K Guhasarkar and V S Gupta, *Brit Corros J*, 18 (1983) 1857
36. T Grcher, M Cvetkoska and W Schultze, *Corros Sci*, 32 (1991) 103
37. G Mengoli, M M Musiari, C Pagula and F Paolucci, *Corros Sci*, 32 (1991) 743
38. S Sathyanarayanan, S K Dhawan, D C Trivedi and K Balakrishnan, *Corros Sci*, 33 (1992) 1831
39. Y Jianguo, W Lin, V Otieno-alego and D P Schweinsberg, *Corros Sci*, 37 (1995) 975
40. A E I-Sayed, *Corrosion Prevention and Control*, 2 (1996) 27
41. S Muralidharan, K L N Phani, S Pitchumani, S Ravichandran and S V K Iyer, *J Electrochem Soc*, 142 (1995) 975
42. Mohammed Ajmel, Jaya Rawat and M A Quarai-shi, *Bull Electrochem*, 14 (1998) 199
43. M A Elmorsi, *Corros Sci*, 41 (1999) 305
44. Y Abed, Z Arrar, B Hammouti, A Aouniti, S Kertit and A Mansri, *J Chim Phys Chim Biol*, 96 (1999) 1347
45. V Karpagam, V Chandra, G P Kalaigan, P Manisankar, A Gopalan and T Vasudevan, *Bull Electrochem*, 12 (1996) 11
46. S P Sitaram, J O Stoffer and T J Okeefe, *J Coating Technol*, 69 (1997) 866
47. H Leithety, *J Chem Soc*, 15 (1962) 161
48. S K Dhawan and D C Trivedi, *J Appl Electrochem*, 22 (1992) 563
49. S Sathyanarayanan, S K Dhawan, D C Trivedi and K Balakrishnan, *Corros Sci*, 15 (1999) 109
50. V Brusia, M Angelopoulos and T Graham, *J Electrochem Soc*, 144 (1997) 436
51. X R Ye, XQ, Xin, J J Zhu and Z L Xue, *Appl Surf Sci*, 135 (1998) 307
52. J C Marconato, I O Bulhoes, M L Temperini, *Electrochim Acta*, 43 (1998) 771

53. R R Zahran and G H Sedahmed, *Mater Lett*, **35** (1998) 207
54. H Kim and I Jang, *Polymer*, **39** (1998) 4065
55. F M Mahgoub, B A Abdelnabey, M Khalifa and A Elhefnawy, *Science and Technol of Polymer*, (Ed) P N Prasad, Plenum Press, New York (1998) 175
56. A Frignani, C Monticelli and G Trabanelli, *Brit Corros J*, **33** (1998) 71
57. G F Hays, P A Thomas and B L Libutti, *Proc Engg Found Conf Pennsylvania, Eng Foundation*, New York (1982) 489
58. H Schesinger, *Z Tech Phys*, **12** (1931) 33
59. S Staub and M Paturau, *Principle of Sugar Tech*, Elsevier, New York, **3** (1963)
60. F C Welch, *J Amer Chem Soc*, (1923) 1197
61. J W Cottrell and J R Baird, in *Kirk-othemer Encyclopedia of Chemical Technol*, 3rd Ed, Grayson-Martin, Eckroth and David (Eds) John Wiley & Sons, New York, **12** (1980) 45
62. K P Fivizzani, J E Hoots and R Cloud, *Surface Reactive peptides and Polymers, Discovery and Commercialisation ACS Symp Series*, **444**, C S Sikes and A P Wheeler (Eds) *Amer Chem Soc*, Washington DC, (1992) Chapter 22
63. J W McCoy, *The Chemical Treatment of Boiler Water Chemical*, (1981)
64. A C M C Donald and J L Soos, *U S Patent 4931, 206* (1990)
65. J Imai, T Uchida, S Ano and T Tsuneki, *Materials Performance*, (1989) 41
66. Suresh Patel, *Materials Performance*, (1998) 56
67. A Alice Arul Anthony, G Paruthimal Kalaigan, A Gopalan, K Balakrishnan and T Vasudevan, *Bull Electrochem*, **15** (1999) 124
68. N A L Ahamad, R S Al Ameer and M I Ismail, *Corrosion*, **44** (1988) 750
69. I Sekine, M Sanbongi, H Hagiuda and Yuasa, *J Electrochem Soc*, **139** (1992)
70. G Gunasekaran, R Natarajan, B V AppaRao, N Palaniswamy and V S Muralidharan, *Ind J Chem Tech*, **5** (1998) 91
71. J R Santos, Jr L H C Maltoso and A J Motheo, *Electrochim Acta*, **43** (1998) 309
72. Katsuhisa Nozawa and Aramaki, *Corros Sci*, **41** (1999) 57
73. J S Gill, *Desalination*, **124** (1999) 43
74. A M Beccaria and G Poggi, *Brit Corr J*, **30** (1995) 33
75. R Tremont, H Dejesus carodona, J Garciaorozco and R J Castro, *J Appl Electrochem*, **30** (2000) 737
76. H Kim and J Jang, *Polymer Bull*, **38** (1997) 249
77. A Beccaria, G Padeletti, G Montesperelli and L Chiaruttini, *Surf Coat Technol*, **3** (1999) 240