CHAPTER I

LITERATURE SURVEY AND THEORIES OF INHIBITION
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1.1 Literature Survey

Considerable work has been done on the corrosion of copper and its alloys under variety of conditions due to its uses in the chemical industries. Despite their long life and high scrap value, copper and its alloys are invariably corroded slowly or rapidly in chemical industries by various environments.

Below is cited the fields and variety of the literature available on corrosion of copper and related metals particularly in the acid, salt solutions etc.

Wilkin et al. (16) reviewed the corrosion of copper and copper based tubing in oil refinery heat transfer equipment which included choice of alloy, control of corrosion, effect of static stress corrosion fatigue and corrosion impingement.

Diagramatic keys were presented by Heim (17) to show the performance of copper and brass in \( \text{H}_2\text{SO}_4 \), HCl, \( \text{HNO}_3 \), \( \text{H}_3\text{PO}_4 \) and NaOH. The uses of copper and copper alloys in petrochemical industry were described by Kaushal (18).

A critical review was made by Johnstone et al. (19) on copper and copper alloys tubes composition, applications,
production methods, economic aspects and types of corrosion. The polarization behaviour of copper in acidic and alkaline solution was reported by Khim and Nobe (20). The effect of various factors like electrolyte compositions, cathodic current density and temperature was reported by Bunatyan and Kitaev (21). Rowlands et al. (22) determined the corrosion rate of copper using polarisation resistance measurements. Mechanism of pitting corrosion of copper was reported by Lucey (23). Shimbor et al. (24) described corrosion of copper tubes in cane sugar industries.

An analysis was made by Albaya et al. (25) to establish a relation between current density and over potential.

The literature survey is divided in two section. The section I contains the corrosion tendency of copper in various media. The literature survey on corrosion inhibitors for copper has been presented in section II.

SECTION - I

(1) Atmospheric corrosion

The corrodibility of roofing materials like galvanised iron, aluminium, copper and zinc etc. has
been reported by Tikhmeny et al. (26).

Atmospheric corrosion of copper powder in the presence of $SO_2$ was reported (27, 28). Scholes and Jacob (29) reported the atmospheric corrosion of copper and copper alloys in marine and industrial atmosphere. They studied the nature of corrosion, change in mechanical properties etc at twenty years duration. Fiega et al. (30) reported the formation of copper hydroxide on copper plate in the ammonical atmosphere. The influence of industrial dust on corrosion in copper metallurgical plants was reported by Glowiak et al. (31). Mehta and Seshadri (32) observed at Rajkot (India) that the rate of atmospheric corrosion of copper and aluminium is considerably less than mild steel. They observed maximum corrosion rate of copper during the month of May, June, July and August.

(2) Acidic media

Copper does not normally displace hydrogen even from acid solutions and it is therefore virtually unattacked in non oxidizing conditions. However, most solutions that have to be handled contain dissolved air will cause cathodic depolarisation and enable some corrosion to take place. It is difficult therefore to lay down general recommendations for the use of copper in acid solutions. Under fairly mild conditions copper or copper alloys are successfully used for handling solution of
hydrofluoric acid (33, 34), hydrochloric acid (33, 2, 37),
sulphuric acid (2, 36, 38), phosphoric acid (33, 2, 35) and
acetic, and other fatty acids (33, 2, 36, 39, 40).

Corrosion of electrolytic copper and brass L-62
in 0.1-7 N hydrochloric acid was investigated by Dobrovolskaya
and Shafirov (41). They reported that copper corrosion rate
increased with increasing concentration <1N and then
decreased.

The corrosion of copper in nitric acid (42) depends
in a high degree on the concentration of acid and the
temperature.

Corrosion of copper in hydrochloric acid solution was
reported by Genger (43). Dissolution of copper vessel by
boiling 10-20% aqueous hydrochloric acid during the
preparation of furfural was reported by Honigs (44).
Electrochemical behaviour of copper in acid chloride solution
was investigated by Hurlen (45).

Smolyaninov and Khitrov (46) reported the corrosion
rate of electrolytic copper at 20° in 1N HCl increased
with increase in concentration of K₂Cr₂O₇. The corrosion
rate was higher in HCl + K₂Cr₂O₇ than in H₂SO₄ + K₂Cr₂O₇
because of the formation of copper complexes with chloride
ion.
Electrode potential and rate of corrosion of copper in 0.1 to 7N HCl solutions were studied in temperature range from zero to 80°(47). The dependence of corrosion rate on temperature deviated markedly from linearity for a plot of log corrosion Vs \( \frac{1}{T} \).

The kinetic of corrosion of copper in aqueous hydrochloric acid was studied at different temperatures. Reasons for the linearity of corrosion Vs time and corrosion rate Vs time curves at 20° were discussed by Smolyaninov(48).

Thermodynamic basis of some special characteristics of the corrosion behaviour of copper in 1N HCl for 20 days at 20°C was studied(49).

Effect of corrosion products on the rate of copper dissolution in hydrochloric acid solution at 7, 12, 15 and 20 days durations was examined(50).

Corrosion of copper in H₂SO₄ was reported by Jensen(51). Maja(52) studied the anomalous behaviour (anodic behaviour of copper) in 0.6 to 17N H₂SO₄ electrolytes.

Corrosion of copper with nonuniform concentration of oxidizers in the solution of H₂SO₄ was investigated(53). Copper undergoes(54) serious attack during cathodic polarisation in which hydrogen ions are reduced to H₂ on the
copper surface. This effect was found in pure copper in aerated 0.5M H₂SO₄ at 25°C by Otsuka et al. The corrosion product consists of Cu₂O possibly through an intermediate reaction product Cu-hydride.

Estimation of corrosion rate of copper in moving oxygen bubbled sulphuric acid solution by the measurement of polarisation was reported\(^{(55)}\).

The oxidation of copper at 600°C to 800°C was determined by dissolving the oxide layer in 5% H₂SO₄\(^{(56)}\).

The corrosion behaviour of nonferrous metals like Cu, Pb, Al, Zn, Cd and Sn towards alkali fluoride and alkali HF solutions was reported by Kohler\(^{(57)}\).

McCarty\(^{(58)}\) reported the corrosion of copper, Fe and Pb when suspended in water containing fluoride ions.

The complete study of corrosive effect of ClF₃ on copper was carried out with kinetic measurement\(^{(59)}\).

Weight loss corrosion test were conducted on copper wires and foils in 31% HBF₄ and in an electrolyte containing Cu(BF₄)₂, HBF₄ and H₂O \(^{(60)}\).
Nikolaev (61) reported the corrosion of copper in 2.5 - 96.6 % HF solution at room temperature for eight days duration. At 22.5% HF a noticeable film was formed.

Corrosion of copper and its alloys by acetic acid had been studied by many workers (62-68). In general, it was observed that acetic acid was mildly corrosive to copper and its alloys. Studies with halogen substituted acetic acids had also been carried out and it has been reported that these acids were more corrosive than acetic acid (69,70). It is interesting to note that trichloroacetic acid had been tried as an inhibitor of corrosion of copper in perchloric acid (71). Metals and alloys like Al, Cu, mild steel, brass, galvanized and tin plated metals were studied for their corrosion by trichloroacetates under a variety of conditions (72). Resistance of copper in acetic acid had been reported by Frolov (73).

The corrosion of Zn, Cu, Al, Fe, brass, stainless steel etc immersed in technical Olein, linoleic acid and lecithol was measured (74).

The corrosion resistance of various grades of copper in acetic acid solution was reported by Anuchin et al. (75). Johnson (76) reported the corrosion of copper and mild steel in the production of acetic acid and its
derivatives.

The corrosion of copper and stainless steel in the mixture of ethyl acetate and acetic acid was studied by Farkhadov(77).

Anuchin(78) reported that the mechanism of copper corrosion in acetic acid is not only the effect of depolarisation by oxygen. At higher concentration of acetic acid and at higher temperature, there is a better polarisation in spite of less dissolved oxygen. He assumed that in aqueous acetic acid at the cathodic surface of copper, adsorption of $\text{HOAc}^-\cdot\text{H}_2\text{O}$ takes place with the transfer of an electron from the cathode. An acetyl radical can be formed and it reacts with $\text{H}_2\text{O}$ to form AcH and a free $\text{OH}^-$ radical. Acetyl radical can react with dissolved oxygen to form a radical which in presence of AcH forms per acetic acid and a new radical. Per acetic acid is a strong oxidizer which oxidize Cu to $\text{Cu}_2\text{O}$.

(3) Alkaline media

Corrosion phenomena on Cu-ferrules in locomotive boilers are described by Perry(79). Insulated copper strips were heated in bomb type boilers containing dilute solution of sodium hydroxide.

The mechanism of anodic process during the
Electrochemical oxidation of copper in NaOH solution at 60° to 80° was reported(80).

The corrosion rate of copper in alkali was reported by Khitrov(81) and Dobrovolskaya et al.(82).

Wallbaum(83) reported that in alkaline solution copper is covered with an oxide coating which slows down the rate of corrosion but the coating is not impervious and therefore does not confer passivity.

The electrode potential polarisation characteristics and the rate of corrosion of copper plate immersed in alkaline solution was studied(84).

Electrochemical measurements with high temperature-pressure water were made by Huijbregts(85) on Fe and Cu in weak and strong alkaline solution at 250°C.

(4) Different waters

Copper, and copper alloy pipes and tubes are used in large quantities both for conveying fresh and salt waters and in condensers and heat exchangers where fresh or salt waters are used for cooling(86). Pumps, screens, valves and other ancillary equipment may also be largely constructed of copper alloys.

Corrosion problems that arise are frequently discussed under the headings (a) sea water and (b) fresh water.
There have been surveys of the problems of corrosion of condenser and heat exchanger tubes and related components in marine service and others dealing with oil refinery service (87-102).

In a stagnant condition corrosion of copper was studied in sea water and brine at room temperature for 144 hours by Nagaoka and S. Aida (103). They reported that the corrosion rate of copper linearly increased with increasing concentration of dissolved oxygen which suppressed corrosion beyond a critical concentration. They further investigated that corrosion of copper is increased with increasing dissolved oxygen in saturated salt brine and 25-30% salt slurry flowing at 1-0-3.5 m/sec at 40°C for 240 hours.

There are several distinctive types of corrosion that copper and copper alloys may suffer usually in sea water.

i. Impingement attack, ii. Dezincification of brass, and iii. Deposit attack and pitting.

Fresh waters are, in general, less corrosive towards copper than sea water and copper is widely used for distribution of cold and hot waters in domestic and industrial installations (104).

Corrosion tests of copper in pure water was studied by Matsuoka et al. (105). Yellow corrosion products were
produced by decomposition of CuO where partial pressure of oxygen was very low and water is alkaline. Red corrosion products were produced under the condition where water was slightly acidic or partial pressure of oxygen was extremely low. Black corrosion products were produced when the partial pressure of oxygen was generally high.

A critical comment was made by McCullough (106) on dissolution of copper corrosion products in deionized water at 100°F.

The corrosion of copper pipeline was studied by Howard (107). According to him ground waters of New Hampshire are aggressive on service pipes of Fe, Pb, Cu and brass.

The corrosion of Fe, Pb, Cu and Brass was studied in water by Camp (108).

Pawlik (109) reported the failures of condensers and preheaters due to corrosion of copper or copper alloys.

Corrosion of copper and copper alloys in New Zealand potable waters was reported (110).

Corrosion problems in the water steam cycles of power plants were reported (111).

The release rate of corrosion products of copper was studied by flowing deionized water at 40°C (112).
Maximum protection data were given by Myers et al. (113) for copper and its alloys for hot water with various pretreatments. According to them, copper tubing is used for potable water less than 60°, water velocity should not exceed 4 ft/sec. Solubilities of copper oxides from corrosion of copper or copper alloys in water were determined at elevated temperatures and pressures (114).

Konstantinova et al. (115) studied the corrosion of copper alloys in Caspian sea, Black sea and Pacific sea water.

The corrosion rate of copper, brass and cast iron using sea water in the return cycles of cooling systems at 40-60° was reported (116).

The corrosion characteristics of Al, Cu and Ti-based alloys in marine applications were described (117).

The corrosion resistance and failure kinetics were reported by Suprun et al. (118). According to them the relation between corrosion rate and sea water flow rate can be explained by change in the protective film properties.

The corrosion rate of copper was studied in fresh water and sea water containing reducing and nonreducing bacteria of the proteolytic and monoprotolytic types (119). Little or no corrosion occurred in the presence of living bacteria, when they die corrosion was accelerated.
Equilibrium potential-pH diagrams were presented for copper in sea water at 25° based on a critical revolution of available activity coefficient data (120).

The corrosion action of circulating sea water on copper and its alloys was reported (121). The water velocity in the tube of cooler varied from 1.5 to 2.5 M/sec. Copper showed a corrosion rate of 0.019 mm/yr. The rate of corrosion dependence was linear with the velocity.

Corrosion of copper by absolutely pure H₂O and effects of dissolved O₂ and certain ions was reported by Malvern (122).

Ives (123) reported that the film formed on copper exposed to water containing dissolved O₂ and CO₂ was predominantly of Cu₂O.

Pitting corrosion in copper water pipes caused by films of carbonaceous materials produced during manufacture was reported (124).

Electrochemical test of the susceptibility of copper to pitting corrosion in the presence of cold tap water was reported (125).

Pourbaix (126) reported the effect of chlorides on the behaviour of copper to pitting corrosion in the presence of aqueous solution by measurement of electrode potential.
The role of CuCl in pitting process of copper was studied by using electrochemical thermodynamic and kinetic methods\(^{(127)}\).

Chen\(^{(128)}\) reported that aggressive hard well water causes pitting of copper contained dissolved \(O_2\) upto 10-12 ppm, dissolved \(CO_2\) 10-12 ppm, chloride and sulphate.

It has been reported that pitting corrosion of copper tubing in tap water distribution system was associated with cracks developing in \(Cu_2O\) film or a carbonaceous film that may cover the inside of tubing\(^{(129)}\).

Pitting corrosion in copper tubes in cold water service was studied by galvanostatic method\(^{(130)}\).

Potential- pH diagram for corrosion studies for the system Cu-Cl-H\(_2\)O was reported\(^{(131)}\).

Haase\(^{(132)}\) had discussed the effect of \(O_2\), \(CO_2\), chlorides and phosphates and the formation of corrosion resistant coatings.

Sato and Sagisaka\(^{(133)}\) reviewed the effect of water properties, temperature and \(Cu^{+2}\) ion on the corrosion of copper tubes.

Knutsson et al.\(^{(134)}\) reported the relations between erosion corrosion and various operating and installation
conditions in connection with temperature, pH, oxygen content and hardness of water.

Corrosion of evaporator copper tubes in beet sugar industry has been discussed by Shimbó et al. (135) in relation to cane sugar refinery.

(5) Sodium chloride solution and miscellaneous

An electrode potential of copper in aqueous solution of various pH with and without 0.01N sodium chloride was reported (136).

Gerasimov et al. (137) studied the effect of temperature on the corrosion rate and the kinetics for electrode processes for Cu, Fe, Ni, Mg and Zn in the solutions of NaCl, NaCl + HCl, NaCl + NaOH and NaCl + KMnO₄.

Photopotential of single crystal of copper immersed in H₂O and NaCl solution was studied by Arbit and Nobe (138). They reported that in NaCl solution, Cu₂O formation was followed by the formation of cuprous halide film.

Corrosion behaviour of copper and Navel brass in 0.5M sodium chloride solution at ambient temperature was studied (139).

Electrochemical aspect for the corrosion of copper in 1-3% sodium chloride solution was studied under heat transfer condition to determine the relative contribution
of thermogalvanic and local corrosion effect(140, 141).

Corrosion fatigue of copper and α-brass was investigated in nearly aqueous electrolyte of preoxygenated solution of sodium chloride and copper sulphate(142).

The formation of Connellite \( \mathcal{L} \text{Cu}_4\text{O}(\text{OH})_{30}\text{Cl}_4\text{SO}_4\cdot7\text{H}_2\text{O} \) as a corrosion product formed during the exposure of \( \text{Cu} \) to electrolytes comprising various mixture of \( \text{NaCl} \) and \( \text{Na}_2\text{SO}_4 \) was reported using X-ray diffraction method(143).

Cathodic polarisation studies of crevices in type 304 stainless steel and copper in 0.6M \( \text{NaCl} \) solution, show that crevices with a distance to crevice opening ratio of 12000:1 can be polarised and that the pH shifted in the alkaline direction(144).

Corrosion of various metals like \( \text{Cu}, \text{Fe}, \text{Pb} \) and \( \text{Zn} \) was studied in salt solution of 0.1N \( \text{KCl} \)(145).

The corrosion rate of copper in 0.5N \( \text{KX} + 0.5 \text{N H}_2\text{SO}_4 \) (\( \text{X} = \text{Cl}, \text{Br}, \text{I} \)) was detected by weight loss method(146).

Corrosion of copper was reported by Dobrovolskaya (147) in the solution of \( \text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4, \text{KCl} \) and \( \text{K}_2\text{SO}_4 \).

Electrochemical behaviour of copper in contact with fused \( \text{NaNO}_3 - \text{KNO}_3 \) at 25\(^\circ\) was reported(148). Electrode
potential measurements and x-ray analysis indicate that film formed on the copper surface consists mainly of Cu$_2$O. Passivation of copper is induced by anodic polarization.

Copper dissolution in acidic FeCl$_3$ solution was reported by Poluboyarkseva(149).

The corrosion of copper in acidic chlorate solution was reported by Yoon(150).

The results of colorimetric study on the corrosion behaviour of Cu and Al by Br$_2$ and I$_2$ dissolved in CCl$_4$ were reported(151).

In acidic ethylene glycol solution, behaviour of copper was reported considering inter crystalline corrosion (152).

Cathodic polarization curves in 4% KCl solution for electropolished copper showed a lower corrosion rate in an air saturated solution than in hydrogen saturated solution for a surface that was electropolished and subsequently etched in a hydrogen saturated 5% H$_2$SO$_4$(153). In a hydrogen saturated KCl solution an electropolished specimen corroded slower than in mechanical polished one. The film formed during electropolishing cannot be entirely responsible for conferring passivity on the surface.
Corrosion rates were studied by Zorin et al. \cite{154} for W, Mo, Ta, Ni, Cu and various alloys in molten \(300^\circ\) and gaseous \(400^\circ-750^\circ\) \(\text{Al}_2\text{Cl}_6\) at 10 atm. for less than 1000 hrs.

Copper corrosion and its mechanism was reported by Katz \cite{155} in Na-acetate solution.

The rate of corrosion of Cu, Al and Fe in \((\text{NH}_4)_2\text{SO}_4\) solution was reported \cite{156}.

The rate of dissolution of pure copper foil was studied by Schaefer \cite{157}, either alone or in contact with Ag solder in solution of \(\text{NH}_3 + \text{NH}_4\text{Cl}\), in fresh urine and in urine collected from a urinal waste disposal system.

Reaction rates of single crystal copper and \(\alpha\)-brass surfaces exposed to solution of \(\text{Cu}(\text{NH}_3)_x(\text{OH})_2\) in \(15 \text{ M} \text{NH}_4\text{OH}\) were investigated and attempts were made to correlate film texture and composition with the mode of attack on the metal surface \cite{158}.

The corrosion of copper and its alloys in water containing 1 to 1000 ppm \(\text{NH}_3\) was studied \cite{159}. The dissolution rate of copper increased with increasing \(\text{NH}_3\) concentration and the corrosion resistance depended on the nature of the surface film.
The mechanism of corrosion of copper in aqueous NH₃ solution as a function of time and concentration was investigated (160).

The thermodynamic examination of possible anodic products of copper in the Cu-H₂O - NH₃ system, a kinetic study, was made of the behaviour of Cu and Brasses (162).

Corrosion of copper in NH₄-salt solution increased Cu + salt anion complex formation. Corrosion of copper was determined in NH₄Cl - (NH₄)₂SO₄, NH₄Cl-CuCl₂ and (NH₄)₂SO₄ - Cu₂SO₄ (161).

Geneslai (163) reported that K₂CO₃ solution produces a mixed layer of malachite and Cu₂O on copper surface.

\[ \text{Na}_2\text{Cu}(_2\text{CO}_3)_2 \cdot 3\text{H}_2\text{O} \] occurred as a corrosion product of copper in Na₂CO₃ solution according to the view of Erdos (164).

SECTION - II

(1) Acidic media

Gegner (143) recommended the use of hexametaphosphate as corrosion inhibitor for copper in hydrochloric acid solution.

Hippensteel (165) used rodine as an inhibitor for the corrosion of copper in hydrochloric acid.
The sodium salt of benzotriazole reduced the corrosion of copper in hydrochloric acid solution (166).

Honing (144) patented the use of glucose as corrosion inhibitor for copper vessel used in production of furfural in presence of hydrochloric acid.

The corrosive attack of hydrochloric acid towards copper and copper alloys is depleted by high molecular weight amino alcohol (167).

Action of thioacids towards corrosion of copper in hydrochloric acid solution was reported (168).

The effect of potassium dichromate on the corrosion and polarisation of copper in hydrochloric acid of strength 0.1-5 N at 30° had been studied by Amar and Raid (169).

Lacan et al. (170) reported the use of sodium hydrogen phosphate, stannous chloride, cobalt linolate etc., as corrosion inhibitors for copper and brass in hydrochloric acid and nitric acid solutions.

Action of K-xanthate and thiosemicarbazide has been studied for the corrosion of copper in 0.5 N hydrochloric acid solution (171).

Fujii and Kobayashi (172) investigated that ethyl mercaptan dissolved in xylene formed a film on the surface
Kobayashi (173) suggested the use of mercapto-benzo-thiazole as corrosion inhibitor for copper and brass in hydrochloric acid, sulphuric acid and phosphoric acid in the presence of oxygen. It is also reported to be effective in solution containing ferric ion.

Tseitlin (174) reported that aliphatic and aromatic aldehydes, tartaric and oxalic acids and their sodium salt glucose and maltose considerably, retard the corrosion of copper in hydrochloric acid.

The effect of benzotriazole on corrosion of copper exposed in flowing 10% H₂SO₄ was reported by Ross et al. (175).

Dobrovolskaya et al. (176) studied the action of NH₄⁺ and K⁺ on the corrosion of copper in 0.1 to 3.4 N sulphuric acid. The corrosion rate of copper decreased with increasing NH₄⁺ or K⁺ content owing to decrease solubility of oxygen and decreased rate of its diffusion to the metal surface, the effect of NH₄⁺ was the same as that of K⁺. This confirmed the view that NH₄⁺ has no specific effect on the corrosion of copper in sulphuric acid.

Levin and Solomon (177) reported that the corrosion of copper in sulphuric acid was retarded by butanal,
cyclohexanone, fatty alcohols and cyclic ketones.

The free energy of adsorption of benzotriazole by copper single crystal planes in $\text{H}_2\text{SO}_4$ was determined by S.M. Mayanna(178). The studies were related to the use of benzotriazole corrosion inhibitor for copper. The free energy was different on the various crystal planes and also dependent on surface coverage.

Ueki(179) patented that copper containing Fe oxide scale may be removed with an aqueous solution of at least one acid such as HCl, H$_2$SO$_4$, H$_3$PO$_4$ and at least one thiourea compound and at least one hydrazine compound.

(180)
Khitrov studied the effect of temperature on the corrosion resistance of copper in solutions of hydrochloric and sulphuric acid in presence and absence of inhibitors. The addition of corrosion inhibitors to the acid solutions improved the electrode potentials at all temperatures but a temperature increase shifted the stationary potentials towards more negative value as a result of decrease in the stability of the film or an increase in the metal surface free of corrosion inhibitor.
Ekonomov and Balezin (181) studied the inhibitive power of benzylamine and paraform alcohol towards the nonferrous metals in hydrochloric acid and sulphuric acid.

The influence of p-nitroaniline, aniline, butylamine and p-phenylenediamine sulphate had been studied on the anodic ionization of copper in 1N $\text{H}_2\text{SO}_4 + 0.02N \text{CuSO}_4$ and 0.99N $\text{H}_2\text{SO}_4 + 0.02N \text{CuSO}_4 + 0.01 N\text{HCl}$ by Baillot-Prompowski method (182).

A mixture containing alkali halide, heterocyclic compound such as pyridine quinoline or piperidine and glucoside such as tannin, vegetable gum had been reported as corrosion inhibitor for copper and zinc in hydrochloric acid and sulphuric acid (183).

According to Khitrov et al. (184, 185) the corrosion of copper in hydrochloric and sulphuric acids at 80°C and nitric acid at lower temperatures was prevented by waste products from synthetic rubber industry, such as foam reagent (mostly contains alcohols, butanol and hydrocarbons) heavy residues (contains amylene piperidine, hexadiene diolefins etc) and motor fuel (unpolymerised hydrocarbons).

Multicomponent diffusion coatings were obtained during Si + Al and Si + Fe diffusion coating of copper at
800 to 900°C. Corrosion resistance of diffusion coated copper samples in 10% HNO₃ and 10% HCl was presented (186).

The adsorption of thioglycolic acid on copper surface in dilute HNO₃ was studied by IR spectrometry (187).

Corrosion of copper in HNO₃ acid was prevented by the inhibitors like o-naphthylamine, benzidine, aniline, o-chloroaniline, o-phenatidine and o-toluidine (188, 189).

Furfural inhibits the corrosion of copper in HNO₃ solution (190).

The corrosion rate of copper in HNO₃ was prevented by the addition of chromic acid (191).

Putilova et al. (192) reported the use of sodium sulphite, sulphide and thiosulphate as corrosion inhibitors for copper in nitric acid. They further stated that potassium permanganate and hydrogen peroxide inhibit the corrosion at low acid concentration.

Desai and Rana (193) reported o-anisidine and quinoline as corrosion inhibitors for copper in nitric acid.

Balezin and Parfenov (194) investigated urea as corrosion inhibitor for copper in nitric acid. They reported that urea decreased the dissolution rate of copper by nitric acid.
because it decomposes the nitrous acid formed as an intermediate.

Balezin and Parfenov investigated the solution rate of copper in nitric acid in presence of tartaric acid, citric acid, formic acid, oxalic acid, glycerol and glucose (195).

The rate of corrosion of copper in nitric acid is reduced when copper specimen is rotated in the acid (196). This confirms the suggestion that nitrous acid has an accelerating effect on the reaction between copper and nitric acid, since when the specimens rotates the nitrous acid formed is removed more rapidly from the copper surface.

According to Putilova et al. (197) urea and thiourea is considerably more stable in nitric acid. Its effect on reaction between nitric acid and copper appeared to be due to decomposition of nitrous acid at the moment of its formation.

The inhibition of corrosion of copper in phosphoric acid by agar agar, tannic acid, gelatine, furfural, pyrogallol, gum acacia and dextrin was reported by Desai and Reza (198).

The corrosion resistance of Cu and copper based alloys in aqueous solutions of various inorganic and organic acids, in atmospheres containing $H_2S$, increased after
surface treatment with 2-alkylimidazole in aqueous MeOH or H₂O. The surface treatment was carried out by dipping, spraying, vapour deposition and with impregnated paper (199).

The corrosion of copper was inhibited in 0.1N chromic acid solution in pH range 1-6 (200). Experiments showed that effect of chromate on copper was to lower the chemical reactivity of the oxide film. Other experiments indicated that chromic ions formed by local electrochemical action entered the oxide lattice to form a mixed cuprous chromic oxide having a lower chemical activity than the bulk cuprous oxide.

The corrosion of copper in 0.1-72.5% perchloric acid was inhibited by addition of 0.005 part chloral hydrate, trichloracetic acid or hydrofloric acid per 100 parts of perchloric acid solution (71).

Patel and Franco (201) reported the action of 2-mercaptobenzothiazole and 2-methylbenzothiazole on the corrosion of copper in perchloric acid. Both these compounds display a tendency to form chelates with copper ions.

The inhibitory action of N-hydroxy pyridine, 2-thione, Na-DDC, thiourea and thiols towards corrosion of copper in acid medium has been reported (202). The inhibitory action was reported to be due to chelate formation with Cu²⁺ ion.
Influence of various quinones had been studied as corrosion inhibitors for copper in acidic media (203).

Prall and Shreir (204) studied the inhibitory action of benzotriazole towards copper in acidic media.

Trivedi, Soni and Bhatt (205) reported that sodium diethyldithiocarbamate acts as an excellent inhibitor for copper in buffer solution. It is decomposed below pH 5.1 with formation of carbon disulphide and diethylamine.

Popplewell and Finan (206) patented the corrosion prevention of copper by benzotriazole in weak acid.

The influence of Na-DDC towards corrosion of copper in weak acid was reported (207).

Wakoka and Yamamoto (208) observed the effect of various anions on the corrosion of copper in organic acids and found that the degree of corrosion by anions decreases in the following order: $S_2O_3^>-NO_3^>-Cl^>-SO_4^>-Cr_2O_7^->CH_3COO^->CN^>-PO_4^>OH^>-MnO_4^>-I^>-Fe(CN)_6^{3-}$

The anodic and cathodic over potentials of copper had been measured in acetic acid and acetic anhydride (209). The addition of 2-mercaptobenzothiazole which lowers the concentration of free cupric ions, produced high cathodic polarization at low current density, serving as an effective corrosion inhibitor.
Desai and Rana (210) studied the use of tannic acid and casein as inhibitors for the corrosion of copper in acetic acid. Tannic acid affords better protection to copper than casein.

An attempt has been made to evaluate the protective action of 2-benzimidazole thiol, 2-mercaptobenzothiazole and sulphathiazole towards copper in dichloroacetic acid solution (211).

Influence of some phenols on corrosion of copper in dichloroacetic acid has been reported by Patei et al. (212).

Inhibitory action of thiobenzoic acid, thiosalicylic acid and thioglycollic acid in dichloroacetic acid have been studied (213).

Thomberg and Sonla (72) reported that phosphoric acid, sodium hexameta phosphate, sodium pyrophosphate, sodium dihydrogen phosphate and ammonium and alkali salts of ortho-, meta- and pyro-phosphate retard the corrosion of copper in trichloroacetic acid solution.

Action of phenols and their thio- and aminoderivatives towards corrosion of copper in trichloro-acetic acid solution was studied (214).

Phenylthiourea, p-chlorophenylthiourea, p-nitrophenylthiourea and p-methoxyphenyl thiourea have been
investigated as corrosion inhibitors for copper in 0.1N trichloroacetic acid solution (215).

The influence of 2-mercaptothiazoline (216) and dodecylmercaptan (217) on corrosion of copper in acetic acid and chloroacetic acids have been studied by Patel et al.

The inhibitory action of 0.01-0.5% gelatine in 0.2N citric acid for 5 days duration was reported (218).

Solution containing benzotriazole was found much more effective in inhibiting the tarnishing of copper and copper alloys in the presence of citric acid (219).

Closely related compounds 2-mercaptobenzothiazole (I), 2-mercaptobenzoxazole (II) and 2-mercaptobenzimidazole were compared with respect to their use as copper corrosion inhibitors in weak acids (220).

(2) Alkaline media

Desai and Rana (221) studied about 30 substances as inhibitors for corrosion of copper in sodium hydroxide solutions. Nearly complete protection (99%) was afforded by resorcinol, naphthol, glucose, furfuraldehyde and hydrazine sulphate. The following substances retarded the corrosion to an extent of 90% or more. m-amino phenol, p-aminophenol, cyclohexanone, 8-hydroxy quinoline,
quinalzarin, hydroquinone, sodium diethyl dithiocarbamate, sodium rhodizonate, galloyamine, phloroglucinol and acriflavine. It was observed that performance of catechol, m-cresol, pyrogallol, tannin and naphthol, p-nitrophenol, salicylaldehyde, acetylacetone, acetone, cupferron, cupron, thiourea, dithioxamide, and sodium chromate was fairly satisfactory. In most of the cases, the protection afforded was due to the form of film over the metal surface.

Checkley and Mealings (222) studied $K_2Cr_2O_7$ as an inhibitor for the corrosion of copper by alkaline solution.

Radley et al. (223) reported that glucose is an efficient inhibitor for corrosion of copper in aqueous ammonium hydroxide solution, whereas non-reducing sugars and sugar alcohols are not so effective. According to them, cupric copper is reduced to cuprous copper by glucose. Cuprous is readily oxidized to cupric salt by dissolved oxygen so that the solution becomes oxygen free.

Lynes (224) reported that 1000 ppm concentration of sodium chromate inhibits the corrosion of copper in 5%
ammonium hydroxide, whereas 20000 ppm concentration is needed for 25% ammonium hydroxide.

Camp(225) reported that the corrosion of copper and its alloys on exposure to a fluid containing ammonia or ammonium compound can be eliminated by the addition of sulphur compounds such as mercaptans, carbon disulphide and hydrogen sulphide.

Copper corrosion was inhibited in the solution of NH$_4$OH and NaClO by Si$_3$N$_4$ (226).

(3) Sodium chloride and other salts:

Inhibitory action of p-thiocresol, benzimidazole thiol and sulphathiazole has been investigated for the corrosion of copper by 3% sodium chloride solution (227).

The effect of benzotriazole on the corrosion of copper in 5% NaCl solution was reported by the measurements of (1) immersion test (ii) potentiostatic polarisation (iii) AC impedance (iv) Ellipsometric measurements (228).

Anodic and cathodic polarisation curves of copper sheets immersed in neutral solutions of 0.1N NaCl solution were studied in the dark and in samples illuminated by 10$^5$ lux. The solution of NaCl was inhibited by benzotriazole and mercaptobenzotriazole. Benzotriazole inhibits by the mixed polarisation while mercaptobenzotriazole has a good effect on cathodic polarisation only (229).
Tsaitilin(174) reported that the corrosion of copper in 10% sodium chloride solution is considerably retarded by the action of aliphatic and aromatic aldehyde, tartaric and oxalic acids and their alkali salts, glucose and maltose.

Roetheli and Cox(230) studied the retardation of corrosion of copper in sodium chloride solution by sodium dichromate and observed that insufficient quantities of the retarder stimulate pitting corrosion of the metal.

Rabald (231) suggested the use of sodium dichromate for the prevention of corrosion of copper in sodium chloride solutions.

 Wormwell and Mercer(232) studied the action of several benzoates as inhibitors of the corrosion of metals in salt solutions and observed that an unusual high rate of hydrogen evolution occurred in sodium chloride solutions containing insufficient amounts of sodium benzoate.

Dugdale and Cotton(233) investigated the use of benzotriazole as an inhibitor for the corrosion of copper in 3% sodium chloride solution. According to them benzotriazole acted as a cathodic inhibitor.

The effect of stirring rate, concentration and organic surfactants chain length on corrosion of rotating cylindrical
electrode in aerated 4% NaCl solution was studied (234). Alkylamine surfactant of various chain length were added to provide an adsorbed film on the metal.

Infrared and ultraviolet visible reflection spectra of the surface films on copper treated with benzotriazole has been studied by Morito et al. (235). The surface film on copper was formed by immersing for 20 hours in 3% NaCl solution containing 0.02M benzotriazole. The thin surface film seems to be composed of a compound similar to BTa-Cu(I).

Electrochemical measurements were carried out on Cu-mild steel and Al-mild steel couples in 3% NaCl solution at 30° (236). Hexadecyl mercaptan was studied as corrosion inhibitor.

Corrosion inhibition of copper by benzimidazole was investigated by infrared and visible absorption spectroscopy and polarization measurements in 3% sodium chloride solution. They reported that inhibition is mainly due to formation of adherent protective polymer film (237).

The electrochemical behaviour of copper and brass in 3% NaCl solution containing 0.005-0.5% NaAsO₂ was studied by means of potenitio dynamic method (238).

The effect of CaO and MgO on the performance of chromatephosphate inhibitor mixture towards copper in 0.001%
NaCl solution was reported(239). Corrosion of copper was prevented by hydrazine, amines, hydroxy 1,2,3 benzotriazole etc in NaCl solution(240). The inhibitory action of benzimidazole, 2-benzimidazole thiol, 2-benzoazole thiol, sulphathiazole, 1,2,3 benzotriazole and 2-benzothiazolethiol on the corrosion of copper in aerated 0.1N NaCl solution was reported(241). Trabanelli et al.(242) reported the influence of dithioxamide, 2-aminophenol, thiourea and phenylthiourea as corrosion inhibitors in neutral media. The behaviour of benzotriazole and 2-MBT in inhibiting copper corrosion in neutral aqueous solution was reported(243).

A number of substituted benzoic acid salts in neutral aqueous solution have been tried as corrosion inhibitors for copper brass and other metals(244). The substitution of nitro, sulfo, hydroxy and amino group in benzene ring of sodium benzoate does not bring about a significant role in the inhibitive effectiveness.

Influence of pollution on corrosion of copper and its alloys in flowing salt water was reported(245). Corrosion protection of copper and copper alloys in flowing salt water was obtained with a film of Fe₂O₃ and a mixed film of MnO₂ and CuO. Thus copper surface was prevented by 0.2-0.4 gm/lit KMnO₄(246).
Loginov\(^{(247)}\) studied the inhibitor action of sodium benzoate in 3% sodium chloride and in a mixture of 3% sodium chloride and 7% sodium sulphate solution and observed that the efficiency of sodium benzoate was below that of potassium dichromate and sodium nitrite. The influence of benzotriazole as corrosion inhibitor for copper in chloride solution was reported\(^{(248)}\).

The effect on immersion of copper and other metals specimens in NaCl + Na\(_2\)SO\(_4\) solution containing benzoate, dinitrobenzoate and hexamethylenimine and its salts has been reported\(^{(249)}\).

Polarisation study for the formation of surface film on copper in air saturated NaHCO\(_3\) and NaCl solution at 25\(^\circ\)C had been made\(^{(250)}\). In 0.01 M NaHCO\(_3\), the initial oxide film is protective but it was broken down at a critical potential producing pitting. The inhibitory action of benzotriazole was reported on the corrosion of copper in NaCl, NaClO\(_4\) and HClO\(_4\) solution\(^{(251)}\).

Harrer et al. (252) patented the use of fatty acid polyamides and their alkene oxide condensation products for the prevention of corrosion of copper in acid brines and in water containing hydrogen sulphide.
Rudoi et al. (253) found that sodium oleate is an effective inhibitor for the corrosion of copper powder in 0.1N sodium sulphate, the optimum concentration is between 2 and 5x10^{-1} g/dm^2 of copper.

The behaviour of copper in 0.1N Na_2SO_4 and NaNO_3 aqueous solution was studied with respect to corrosion and corrosion inhibition by benzotriazole and 2-MBT, cathodic and anodic polarisation curves and x-ray diffraction patterns(254). Influence of K_2CrO_4, K_4Fe(CN)_6, KCNS, NaHSO_3 and Na_2S_2O_3 as inhibitors was investigated for corrosion of copper in 0.2, 0.5 and 1M NH_4Cl(255).

Kohler(256) used agar agar and gelatine as inhibitors for the corrosion of copper in ammonium chloride solutions and observed that in presence of agar agar or gelatine the corrosion of copper was greatly reduced. Tseitlin(174) studied the inhibition of corrosion of copper in ammonium chloride solutions by aliphatic aldehydes, glucose maltose etc and observed that these substances are effective inhibitors.

Desai and Rana(257) also studied agar agar and gelatine as inhibitors for the corrosion of copper in ammonium chloride solutions. The efficiency of these inhibitors ranges from 43 to 98%. A study of mechanism of
inhibitor action by potential and polarisation measurements indicated that these substances have a predominant effect on cathodic reaction. The effect of benzotriazole, 8-hydroxy quinoline and 3-mercaptopquinoline on the corrosion of copper in 1N NH₄Cl and 1N (NH₄)₂SO₄ solution was studied(258).

Langguth and Morgenthaler(259) observed that an addition of about 0.005 % of a complex inorganic cyanide such as Na₃Fe(CN)₆ inhibited the corrosion of copper by aqueous orthophosphate solutions. Addition of a sulphate to ammonium phosphate solution inhibits the corrosion of copper containers (260).

Morgenthaler(261) reported that the corrosion of copper by ammonium phosphate solutions can be effectively inhibited by an inorganic water soluble thiocyanate such as sodium, potassium or ammonium thiocyanate at pH 3-9.

Sodium phosphate was found to be a corrosion inhibitor for copper in sodium acetate solution(155). Patel and Franco(262) studied the influence of molecular structures of pyridine derivatives on corrosion of copper in 0.1M potassium persulphate solution.

An attempt was made to study the influence of molecular structures of mercaptans on corrosion of copper in 0.1M K₂S₂O₈ solution(263). Inhibitory action of m-cresol, phenyl-hydrazine and dioxane towards copper in K₂S₂O₈ solution had
been studied. Polarisation data indicate a predominant role of local cathodic areas in the protection afforded by these compounds.

Desai and Rana reported that salicylaldehyde, furfuraldehyde, and cyclohexanone were excellent inhibitors for corrosion of copper in potassium persulphate solution. The corrosion of copper in 0.002M KCl with an impressed AC of 30–50 mili amp/cm² was significantly inhibited by the addition of 0.06 to M sodium benzoate but at its higher concentration inhibition was reduced.

Different Waters

The effect of polar groups in naphthalene compounds on protective efficiency was investigated with respect to corrosion of copper and zinc in distilled water. Balezin et al. reported the mutual effect of ethylenediamine and monoethanolamine on corrosion of copper in distilled water. They concluded that with increase in concentration of amine corrosion rate increases.

Klyuchikov and Novoshinskaya reported the use of sodium adipate as corrosion inhibitor for copper, brass etc in distilled water for 2–12 months. Bogatyrova and Nagaev reported that the minimum concentration of sodium cinnamate prevents the corrosion of steel coupled with copper in distilled water and tap water.
The influence of polyphosphates as inhibitors in potable water system was reported by Hatch (271). Campbell (272) studied neutral corrosion inhibitors for copper in tap water. Addition of a sulphate to ammonium phosphate solution reduces the corrosion of copper container used for firefighting or deicing.

Longinov (247) studied the inhibitive power of sodium benzoate for copper in tap water and concluded that the efficiency of sodium benzoate is lower than that of potassium dichromate or sodium nitrate. The presence of chloride ions decreases the effectiveness of sodium benzoate.

Sanyal et al. (273) reported the inhibitive power of sodium benzoate for the galvanic corrosion of copper in tap water and concluded that the inhibitive action of benzoate depends upon the potential of metal when it comes in contact with the solution.

In a patent, Morehouse (274) stated that organosilicon compounds having an amino group joined to the silicon atom by a saturated hydrocarbon chain, not closer than the 7-carbon atom are efficient inhibitors for the corrosion of copper media containing water as solvents.

Benzoate and phenyl acetate buffer solution with pH-7 has been considered as corrosion inhibitors of steel and galvanic couples of steel with copper in water (275). The use of 1,2,3 benzotriazole as an corrosion inhibitor for copper
in water system is patented (276). Cotton (277, 278) suggested that benzotriazole form a covalent compound on copper metal surface. The sodium salt of benzotriazole reduces the corrosion of copper in neutral media (166). To retard or prevent pitting type of corrosion of water systems constructed of copper or its alloys, the surface exposed to the water are degreased pickled, and exposed to a solution of benzotriazole in iso-PrOH or H₂O followed by drying or exposed to benzotriazole vapour with condensation (279).

Liddell and Birdeye (280) patented the use of 1,2,3 benzotriazole as corrosion inhibitor for water pipe systems containing iron and copper parts. Ethyl cellulose lacquer containing a chelating agents (0.05 - 2%) can be applied as a coating to copper and copper alloys (281). Such a paint is impervious to water and oxygen.

Hormquin (282) patented the use of the mixture containing aliphatic mono or diamine, alcohol and phenols for the prevention of corrosion of copper by water. Chenick and Thompson (283) studied the influence of biguanidine derivative as corrosion inhibitors.

Morpholine has also been investigated as corrosion inhibitor for copper and brass in polymetal systems where water was the medium (284). Grover et al. (285) reported that sodium silicate and sodium dichromate inhibit corrosion of
copper by water at 40°. Deakin and Spivey (286) investigated the effectiveness of water soluble benzoatenitrite mixture at pH 6-9 towards copper in cooling water system.

Wormwell and Mercer (232) investigated that sodium benzoate completely protects copper in contact with water at room temperature; at 0.05% concentration of the inhibitor, potassium, zinc, lithium and mercury benzoate also act as corrosion inhibitors for water system.

Darrin (237) reported that Na₂Cr₂O₇ retards the corrosion of copper in various water systems. Ingold (238) reported that the rate of flow of water increases corrosion of copper and scale formation becomes more severe particularly when oxygen is present.

Hamer, Powell and Colbeck (289) studied the corrosion inhibitors for copper and brasses (60/40 and 70/30) in three different types of waters. The oil emulsion which acts as an inhibitor was made from a proprietary product comprising a mineral oil, the sodium salt of a safonated mineral oil.

Bohemlaender (290) reported that the addition of alkaline sodium borohydride solutions to the systems containing non demineralized water resist the corrosion of copper. The mixture of 200 ppm Na-hexametaphosphate, 100 ppm borax and 100 ppm Cd²⁺ ions was found effective as inhibitor for copper in flowing water system (291).
Mward and Willard noted a synergistic action of sodium metaarsenite or sodium mercaptobenzothiazole with borax for retardation of corrosion of copper in cooling water (292).

Fowe (293) studied the action of 2-MBT as corrosion inhibitor for copper and brass in cooling water system.

In recirculating aqueous media such as cooling systems, 1,2,3 benzotriazole in amount of 1-5 ppm with or without molecularly dehydrated phosphates controls the corrosion of copper or copper alloys when these metals are present together with more anodic metal like iron, zinc and aluminium (294). This compound is stable and effective in water treated with chloramine-T for slime and bacteria control.

Hoar (295) reported the treatment methods for the inhibition of corrosion in cooling water systems. He concluded that for the long lasting inhibitor action, the absorbed entity of the inhibitor and the metal should be adherent, coherent and impermeable; accordingly the best products are those which can deposit amorphous glassy layers on the metal surfaces such as sodium and calcium silicates, boro silicates and aluminosilicates.

The corrosion inhibitor in cooling tower system were first developed for steel and later on evaluated for copper (296). Some of the inhibitors are polyphosphates, chromates,
phosphate-chromate combinations, phosphate ferricyanide combinations, phosphatesilates combinations and silicates.

The inhibitive power of cyclohexylamine and morpholine for copper in condensate water has also been studied by Ristorph and Yorkgitis (297).

Sperry (298) reported cyclohexylamine and morpholine as corrosion inhibitors of the corrosion of copper in condensate waters. He further reported that cyclohexylamine was more effective due to its stability at high temperature and pressure and due to its distribution throughout the steam and water cycles.

Powell (299) studied the following inhibitors for copper condenser tubes and found them to be efficient. Straight polyphosphate, zinc polyphosphate, ferrocyanide-polyphosphates chromate-zinc/polyphosphate, and chromate-polyphosphate.

The mixture of ZnSO₄·H₂O, E.D.T.A., Octyl phosphoric ester and  N-alkyl sulphonyl glycine was recommended for the inhibition of copper corrosion in ships heat exchangers and cooling systems (300).

Zimmermann (301) studied hydrazine as corrosion inhibitor for steam generators and heat exchanger systems constructed of copper-metal.

The use of arsenic sesquioxide as corrosion inhibitor for copper construction material in refrigeration systems was patented (302).
The corrosion of copper and its alloys is inhibited by a mixture of an alkali metal salt of benzotriazole and an alkanolamide (303). The same product has been advocated as corrosion inhibitors in oil field water flood operation.

Some oxides of aliphatic tertiary alkylamines and aliphatic tertiary alkoxyl amines can be used as inhibitors for nonferrous metals in contact with water or brine (304). The action of 4-5-6-7 tetra-hydrobenzotriazole added to lubricants hydraulic glycol and other coolant mixtures to protect metals especially copper was reported (305).

Inhibitory action of benzotriazole was reported for corrosion of copper in various circulating or water glycol systems (306). The use of benzotriazole as corrosion inhibitor and theory of its mode of protection of copper in aqueous solution was reviewed (307). Cotton (308) also patented the use of 1,2,3 benzotriazole for the prevention of corrosion of copper in aqueous media.

Benzotriazole is effective in aqueous solutions and even in gaseous environment polluted with sulphur dioxide and hydrogen sulphide etc (309). Montgomery (310) patented the use of alkanolamine salts of coal acids as inhibitors for the corrosion of copper in aqueous media. Heit and Calmon (311) patented the use of sodium tetraphos-
phate as corrosion inhibitor for copper and iron in contact with the same sample of water or an aqueous solution.

The inhibitory effect of acrylonitrile on copper corrosion in sea water was reported at pH 6.8, 7.6 and 8.2. The inhibitory action was found dependent on the duration of attack and pH of the solution(312).

Data are represented by Lennox et al.(313) for 17 copper alloys and bare copper exposed at Key West in quiescent sea water for 735 days on the corrosion characteristics susceptibility to de-alloying, marine fouling characteristics electrochemical potentials and response to cathodic protection.

Fujii and Aramaki(314) reported that organic high molecular weight compounds effectively inhibit the corrosion of copper by sea water. Hoar(315) investigated the use of sodium nitrite as an corrosion inhibitor for copper in sea water. The corrosion of aluminium, brass and copper alloys in polluted seawater is prevented by ferrous sulphate treatment(316).

4-alkyl pyrocatechol had been patented as corrosion inhibitors for copper in sea water and in salt solutions(317). The side chain must be straight 4-alkyl radical of 16 to 18 carbon atoms and must be attached to the position no. 4 of the benzene nucleus. Barannik et al. (318) reported that monoethanol amine phosphate inhibits
the corrosion of copper in sea water but beyond the critical concentration, the corrosion of copper is accelerated.

The behaviour of benzimidazole, 1,2,3 benzotriazole and sulphathiazole in inhibiting copper corrosion in artificial sea water has been studied (319).

(5) Vapour phase inhibitors for copper

Kamel (320) patented the use of volatile organic amine having a vapour pressure of 7.5 to 60 mm of Hg at 20° as vapour phase inhibitor. Thus morpholine, methyl morpholine, ethylene diamine and propylene diamine alone (or mixed with another substance which can sublime) give a satisfactory performance.

The use of esters of aryl, alkyl, heterocyclic and alicyclic nitrites as vapour phase corrosion inhibitors for copper has been patented (321). Paul (322) tested several substances as vapour phase inhibitor for copper. Saverina (323) observed that pyridine, quinoline, picoline, phenol, monoethanolamine are effective vapour phase inhibitors whereas acetamide benzamide, diethylformamide are poor inhibitors.

Zawadzki (324) reported that dicyclohexylamine nitrate and cyclohexylamine carbonate are satisfactory vapour phase inhibitors for copper. Shatlov et al. (325) used monoethanolamine, monoethanolamine carbonate,
dicyclohexylamine nitrate, monoethanolamine benzoate as vapour phase inhibitors and observed that the corrosion of copper and its alloys was neither inhibited nor stimulated by these substances. Cotton (326) reported that paper impregnated with 0.5-1% benzotriazole as vapour phase inhibitor protects copper and its alloys satisfactorily.

A packing for copper is prepared by impregnating paper or plastics with a mixture of 4-methylbenzotriazole and 5-methylbenzotriazole in 4:6-7:3 ratio. The packing protects copper from corrosion in atmosphere containing \( H_2SO_3 \) or \( H_2S \) (327). Thiourea derivatives as vapour phase corrosion inhibitor have been reported by Agarwal et al. (328).

Copper and copper based alloys articles were prevented from staining and from tarnishing by the treatment of 0.1 to 10% benzotriazole (329). A dispersion of ferricyanide solution and benzotriazole derivative solution was reported for vapour phase corrosion inhibitor for copper and copper alloys (330).

The oxidation behaviour of copper immersed in benzotriazole (2-20 gm/lit) was compared with that of untreated copper in air at \( 400^\circ C \) (331). Acetylenic alcohols as volatile atmospheric corrosion inhibitors for copper were reported (32). Corrosion of copper by \( H_2S \) was inhibited by dipping the metal in aqueous solution containing \( Zn^{++} \) ion 0.25-10%; benzotriazole 0.25% \( H_2SO_4 \) 0.1-1% and
optionally diethyltriamine penta acetic acid(332).

Copper foil wrapped in vapour containing benzoazole and sealed in polyethylene bags remained unalloyed for 56 days in a humidity chamber at 95% to 100% relative humidity and 20-40°C(333).

(6) Miscellaneous

Calcott(334) reported that corrosion of copper in aqueous and alcoholic solutions is retarded by a soluble amino carboxylic acid. Elder(335) patented the use of sodium chromate, benzoic acid and hexamine for the prevention of corrosion of copper in aqueous or aqueous alcoholic systems.

Remizova(336) reported that the corrosion of copper in aqueous alcohols is retarded by 0.002M concentration of diisopropyl adipate; however, further increase in inhibitor concentration induces a decrease in its efficiency.

The introduction of sodium benzoate into aqueous solutions of ethyl alcohol prevents the corrosion of copper, but sufficient protection is achieved only in alkaline solutions(337). Copper can be protected in ethylene glycol solutions by small quantities of borax or soluble phosphates(338).

Evans(339) reported that sodium benzoate retards the corrosion of copper in cooling systems containing glycol or glycerol. Dixon(340) suggested the use of mineral
oil salts such as sodium sulphonate and pentacrythritol monooleate as inhibitors for the corrosion of copper in media containing methanol or ethylene glycol.

White and Ivacia(341) patented the use of dibasic alkali metal arsenates and alkali tetraborates as inhibitors for the corrosion of copper in aqueous glycols. Parker(342) patented the use of glycolic acid as a corrosion inhibitor in mixture of ethylenic monomers and polyesters of ethylenic dicarboxylic acids.

Squires(343) patented the use of triethanolamine phosphate and sodium mercaptobenzothiazole as corrosion inhibitors for copper in solutions containing 30 to 55% ethylene glycol.

Larbre(344) patented the use of amine type inhibitors in the presence of an organic buffer for the prevention of the corrosion of copper in polar organic media. Dicyclohexyl ammonium nitrite and triphenyl phosphate have also been patented for retardation of corrosion of copper in glycolic media(345).

Borax protects copper in antifreeze liquids containing glycols at 60-130 gms/litre concentration(346). Corrosion of copper and copper alloy article is inhibited by treating the surface with a solution containing 2-heptadecylimidazole salt(347). Aqueous solution of tellurites and selenites were found effective inhibitors
for copper alloys in aqueous coolant for internal combustion engines (348). These were found better than 2-MBT in inhibitive power particularly in coolants containing glycols and antifreeze agents.

Benzotriazole and tolyltriazole form polymeric Cu-complexes and serve as corrosion inhibitors in numerous applications. These inhibitors are used in lacquers, cooling systems, hydraulic fluids, lubricants, and petroleum base fluids both as stabilizer and corrosion inhibitor (349).

Alquist and Wasco (350) studied the action of Na$_2$Cr$_2$O$_7$ as inhibitor on corrosion of copper, brass (red and yellow) in aqueous solution of trichloroacetate. Corrosion of copper and other alloys in sodium trichloroacetate or phenyl mercuric acetate is prevented by Na-triphosphate + sodium chromate (351).

Harwood and Schulman (352) reported that a study of amine inhibitors on copper specimens indicated that adsorption at anodic spot actually may cause a decrease in solution tendency whereas adsorption at cathodic regions probably inhibits by means of diffusion, resistance, changes of overvoltage effects.

Levin and Pomosov (353) reported that corrosion of copper powder in an atmosphere of carbon dioxide saturated water can be retarded most effectively by stabilizers which hydrophobise the surface of powder particles. Benzoin,
anthranil soaps floatation reagents were studied as inhibitors.

Gysling (354) reported that the surface of copper is protected from the corrosive action of detergents and alkaline solutions by the addition of small amounts of 2-guanidinobenzimidazole. Goulb and Sylvester (355) patented the use of sodium mercaptobenzothiazole for the retardation of corrosion of copper by liquid soaps.

Roddy (356) patented the use of 2-MBT as corrosion inhibitor for copper in hydrocarbon oil. The optimum concentrations of benzotriazole in petroleum spirit (turpentine substitute) and in washing emulsion containing NH₃ 3.8% and ethanolamine oleate 3.1 weight % for corrosion protection of copper were 0.004 - 0.006 and 0.16 % respectively (357).

Chertkov et al. (358) reported that certain heterocyclic compounds in fuel reacts with copper and its alloys to form a shiny protective film on the metal surface which inhibits the corrosion of metal. These cyclic organic compounds contain in the ring one or more nitrogen atoms and sulphur which is linked to the ring through a third group or a double bond.

5-alkyl-1-H benzotriazoles inhibits the corrosion of copper and copper alloys in contacts with lubricants, hydraulic fluids, lacquers, mineral oils, polymers and glycols (359).
Triazole, benzotriazole and naphthotriazole have been studied as corrosion inhibitor for copper in acidic, neutral and alkaline solutions by Walker (360). Thiourea was reported as inhibitor for copper in mixture of CuSO₄ and H₂SO₄ solution (361). The copper surface can be prevented by immersion in a solution of 2-undecyl 4-methyl imidazole (362). Corrosion of copper or its alloys is prevented by treatment with solution containing imidazole of the general formula

![General Formula](image)

in which R is H or lower alkyl group and R' is long chain alkyl group (363).

Well and Davies (364) studied benzotriazole derivatives as the corrosion inhibitors. The corrosion of copper and its alloys is inhibited by surface coating material containing benzotriazole. Krietsch (365) studied the inhibition of metals by a mixture of 0.5-3 % triethanol ammonium phosphate and 0.1-0.2% of heterocyclic C₅ aromatic compound or 0.01-0.1% of an alkali salt of benzotriazole at pH 7.5-9 in heating and cooling systems.
THEORIES OF INHIBITION

In view of the great ranges of substances which can act as corrosion inhibitors, it is not surprising that no single mechanism has yet been suggested to explain satisfactorily the mode of action of all inhibitors.

Putilova, Balezin and Barannik (366) classified corrosion inhibitors into following groups: Type 'A' inhibitors which attach to the metal surface and Type 'B' inhibitors which act by deactivating the corrosive environments. Inhibitors of type A are classified to be of three types. (i) Passivators, (ii) Immunizers and (iii) Adsorption inhibitors.

Passivators are usually inorganic oxidizing substances such as chromates and molybdates which passivate the metal and shift the corrosion potential in the noble direction. They form protective layer on the metal surface—either of oxide or metallic salt. Immunizer do not so much reduce the corrosion rate as they only delay the onset of corrosion, after which the metal corrodes, as if uninhibited in solution. Adsorption inhibitors are used virtually in acidic solution where the cathodic control is discharge of hydrogen. Uhlig (367) has also distinguished
between passivators and adsorption inhibitors. Inhibitors of type 'B' include sulphites which deactivate the solution by combination with dissolved oxygen and therefore they retard the cathodic reaction.

A theory for the organic inhibitors was suggested by Chappel, Boetheli and McCarthy (368) who studied the effect of quinoline ethiodide on cathodic and anodic polarizations of iron and steel in N sulphuric acid and concluded that inhibition was cathodic.

Mann(369) proposed a theory of cathodic inhibition by organic compounds specially amines, when a metal is introduced into an electrolyte, it becomes negatively charged. Helmholtz double layer is formed on the surface, the positive ions of metal tending to go into solution. Hydrogen ions in the solution can replace the metal ions and ultimately get discharged as hydrogen gas. More metal ions now go into solution and the process get repeated resulting in corrosion.

If the inhibitor forms ionizable salt with the metal, there will be positive inhibitor ions which may now replace the positive metal ions of the double layer. Unlike hydrogen ion, the inhibitor ions may not be discharged but will be attached by the electrical forces to the cathodic area of the metal and will be held there
tenaciously by adsorption in the form of covering layer. Mann assumed that the salt of an amine will be ionized, the positive charge being concentrated on nitrogen. Thus the inhibitor ion is attracted to the cathodic areas of the metal through nitrogen.

\[ 
\begin{array}{c}
\text{H} - \text{N} - \text{H} \\
\text{H} - \text{N} - \text{H} \\
\text{R} - \text{N} - \text{R} \\
\text{R} - \text{N} - \text{R} \\
\text{H} - \text{N} - \text{H} \\
\text{CH}_3 \\
\end{array}
\]

It is the steric arrangement which determines whether the inhibitor ions are so packed on the metal that the hydrogen ion cannot get through. Thus the essential factors of Mann's theory is the ability of the organic inhibitor to form onium ions and existence in acid solutions as cations, so that they may be adsorbed by electrostatic attraction to the cathodic areas of the metal surface. The number, the length, and the position of aliphatic radicals on the ring of the aromatic amines are also determining factors because these all influence the symmetry of the ion with respect to nitrogen atom. The evidence for the above theory came from the studies on the cathodic polarization at higher current densities and high
nagative potential.

The cathodic adsorption theory presented by Mann has been widely accepted because inhibitive effects are observed with aliphatic amines for many metals, but there are some points unable to cover whole reaction mechanism of inhibitors only by this theory. The principal weak points of the theory are:

1. Inhibitors are not always cations in acidic media but there are cases of anions or non ions(370).

2. Inhibitors are not always adsorbed at cathode, but some results obtained from polarisation tests show that they are adsorbed at anode. Many inhibitors show both anodic and cathodic adsorption(371).

3. Temperature co-efficients of inhibitors should have negative value from cathodic adsorption theory, but measured values show cases of having negative or positive values(373).

4. Higher molecules should have bigger masking effects and bigger inhibitive effects, but there are some
lower molecules having large inhibitive effects (374).

5. Inhibitive effects increase with increasing number of active radicals. This reason should be thought due to the increase of covering area from physical adsorption theory but there are some cases in which even the amines having equal sectional area show different inhibition.

Hackerman (370, 376) modified Mann's theory by ascribing inhibition to an increase the hydrogen activation overpotential. Adsorption may be considered as a general rather than cathodic phenomenon. Adsorption is chemical in nature and leads to polarization of both anodes and cathodes. This theory is favoured by Bockris and Conway (377), Hze and Fischer (372) and Hoar (378).

The species that are adsorbed physically by means of electrostatic or van der waals force interact rapidly with the electrode but are easily removed from the surface, for example by immersion of the metal in a solution free from any inhibitors. The process of chemisorption involving charge sharing or charge transfer takes place more slowly and with high heat of adsorption. In this case the adsorption is specific for certain metals and is not completely reversible.
Comparision of the properties mentioned above shows that an effective inhibiting action must normally be linked with a phenomenon of chemisorption, and examples are reported in a literature which ranges from simple adsorption to the formation of true physical barriers.

From the results of electrochemical analysis many authors have postulated, in general terms, an action of inhibitors based on an increase in the overvoltage of the proton discharge process forming the partial cathodic reaction of the corrosion process (379, 380). According to Machu's theory the inhibition was due to ohmic resistance inhibitor film at the metal solution interface (381). These theories have been complimented and have found better definition through an analysis of the corrosion between molecular structure and inhibitor characteristics. Substantial contributions to a better comprehension of the phenomenon have been made by detailed study of the electrochemical behaviour of metallic materials in environments containing inhibitors by a deeper evaluation of the potential dependence of the adsorption phenomenon and by a better knowledge of the energy parameters involved in the interaction between inhibitors and metallic materials.
INFLUENCE OF STRUCTURAL PARAMETERS ON ADSORPTION AND INHIBITION

Below is given an account explaining the mode of inhibition as described by Trabanelli and Carassiti (8) as far as possible in their own words.

The possibility of correlating structural characteristics with the inhibitor properties of organic substances is justified by the fact that the metal inhibitor interactions are based on chemisorption. The electron density of the organic function that can be defined as the reaction centre for the establishment of the adsorption is then obviously important, since it is possible to assume a bond of Lewis acid base type (382), generally with the inhibitor as the electron donor and the metal as the electron acceptor. The strength of this bond depends on the characteristics of both the adsorbent and adsorbate.

Most organic inhibitors are compounds with at least one polar function having atoms of nitrogen, sulphur and oxygen. The polar function is regarded as the reaction centre for the establishment of the chemisorption process. In such a case, the adsorption bond strength is determined by the electron density of the atom acting as the reaction centre and by the polarizability of the function.
The effectiveness of the function atoms with respect to the adsorption process when the stabilities of the compounds are equal can be taken as being in the following sequence (383, 384, 385).

\[
\text{Sulphur} \succ \text{nitrogen} \succ \text{oxygen}
\]

The idea of electron density acquires particular importance in aromatic or heterocyclic inhibitors whose structure may be affected by the introduction of substituents in different position of the rings. The availability of electron pairs for the formation of chemisorption bonds can thus be altered by regular and systematic variations of the molecular structure.

A rational statement of the problem of the correlations between molecular structure and inhibition has been made by Hackerman (382, 383) who developed a theory of adsorption based on numerous measurements carried out in the presence of a series of secondary aliphatic amines and cyclic amines as inhibitors in an acid medium. Hackerman concluded that the greater the percentage of \( \Pi \) orbitals of the free electrons on the nitrogen atom, the more effective is the inhibiting action. An analysis of the inhibiting action of aromatic amines and thiols and their compounds has been made by Higgs (386) who interpreted the results on the basis
of electron densities and obtained results in harmony with the theoretical assumptions.

Among other structural parameters may be mentioned the molecular area of the inhibitor projected on the metallic surface, considering the various possibilities of arrangement of the organic ions or the molecules at the metal solution interface. The value of the projected molecular does not in general appear to be determinative factor over the whole of the metal inhibitor chemisorption bond, as has been shown by Podobaev (387) by comparing the results of measurements of inhibition carried out on a series of derivatives of propargyl alcohol \( \text{HO - CH}_2 - C \equiv \text{CH} \), keeping the triple bond in the molecule unchanged and substituting nitrogen containing heterocyclic nuclei in the hydroxyl group or esterifying it with fatty acids. Podobaev assumes that the surface action of propargyl alcohol is attributable to \( \pi \) conjugation between the triple bond of acetylene group which would facilitate the formation of a \( \pi \) bond with the metal.

The influence exercised by the molecular weight of the additives on inhibition can be evaluated objectively by studying the behaviour of a homologous series of organic substances chemically stable in the medium under examination. In such a case, it appears that at the same molar
concentration an increase in the length of the hydrocarbon chain of amines or imines gives an increase in the inhibition efficiency which can be attributed to the inductive effect of the methylene groups, shown in a decrease of the ionization potential of the molecules of the free base (388). On the other hand, on studying the inhibition efficiency of homologous mercaptans, it was shown (389) that the inhibition increased on going from n-butylmercaptan to n-decyl mercaptan.

Fujii and Aramaki (390) suggest that amines have a double function. They first remove water molecules normally strongly attached to the metal surface, and then occupy their places producing an inhibitive film.

CHELATE FORMATION

Chelate formation is an important factor in explaining inhibition by organic inhibitors. 2-mercapto-benzothiazole (391), 2-benzimidazolethiol, benzimidazole (392) Na-DDDC (205) etc., are efficient corrosion inhibitors for copper and its alloys in acidic media. The inhibitive power of these compounds is due to the formation of insoluble chelate with the metal ion which adheres to the metal surface in the form of thin film. Haykawa (393) showed that amongst quinoline derivatives, only substances which have OH group on 8 position inhibit corrosion by forming
chelates. They further reported that chelate bonds of organic substances are stronger than adsorption and cover the surface of metal by combining with a metal by some portions in molecule and inhibit the corrosion (394).

INHIBITORY ACTION OF COLLOIDS

Isgaryshev and Bergman (395) who studied the retardation of metal dissolution in sulphuric acid by gelatine, expressed the opinion that inhibition is achieved by the inhibitor removing hydrogen ion combination with colloid particles from which hydrogen ions are liberated slowly. This effect is due to high hydrogen overvoltage. The first adsorption theory of inhibitive action was proposed in 1923 by Sieverts and Lueg (396) and Kreutzfeld (397) investigating starch, yeast etc., as inhibitors form a continuous insulating adsorbed layer on the metal surface. Schunkert (398) from his studies of colloids such as gelatine and starch, concluded that the inhibitors are adsorbed on the anodic region of the metal. Evans considered the protection by colloids being due to screening of cathodically active centres by positively charged particles of the inhibitor. It may be summed up that addition of colloids results in hydrogen overvoltage which causes inhibition.
ELECTROCHEMICAL NATURE OF CORROSION

Metallic corrosion in electrically conducting liquid media is of an electrochemical nature. Corrosion of metals particularly in acids, usually is accelerated by the presence of impurities through the formation of local electrolytic cells. The impurities serve as cathodes of these cells; metal serves as anode and consequently suffers dissolution.

Two dissimilar metals in electrical contact and immersed in a conducting solution also form an electrolytic cell. The less noble of the two metals becomes the anode and corrodes, whereas the other metal becomes the cathode and therefore is protected.

Impurities or metallic complex, however are not essential in order for metallic corrosion to take place under electrochemical action. When a single metal or an alloy (immersed in aqueous solution) corrodes, local electrolytic cells generally operate on its surface. Some parts of the metallic surface serve as anodes and others as cathodes. The distribution of the anodic and cathodic areas depends upon such factors as the energetics of the various parts of the surface (Crystal lattice, imperfections, strains etc), the distribution of surface contaminants (layers of adsorbed substances or insoluble metal compounds),
and the environmental conditions (access of corrosive medium, air or other gases to the various parts of the surface).

As electrical current begins to flow through a local cell, the potential of the anode and the potential of the cathode (A and C respectively in Fig. 1) shift closer to each other i.e. become polarised. The anodic potential shifts toward more cathodic values and the cathodic toward more anodic values. It is believed that "polarisation results from the slowness of one or more processes occurring at the electrode during the discharge of an ion(399).

The electrochemical view of corrosion received a firm support from Evans and Hoar(400) and Brown and Mears(401) who proved that the quantity of electricity flowing through a local cell is equivalent to the amount of metallic corrosion in accordance with Faraday's laws.

The current at 'a' represents the maximum current which can flow without altering the experimental conditions at hand and corresponds to the maximum steady state corrosion theoretically possible.

The condition which decreases the slope of polarisation curve will result in accelerating corrosion and conditions which increase the slope will result in inhibition of corrosion. 'b' and 'c' represent the conditions giving higher current values due to prevention of localised corrosion respectively.
FIG. I

OPEN CIRCUIT POTENTIAL

POTENTIAL

CURRENT

POLARIZATION CURVES OF CORROSION LOCAL CELLS
the other hand, 'd' and 'e' represent decrease of current by increase in polarisation of anode and cathode respectively. Thus an increase in polarisation of anode, shifts the steady state potential towards the cathodic side and an increase in polarisation of cathode shifts the steady state potential towards anodic side. If polarisation of both increases to same extent, steady state current decreases but the potential remains same at 'f'.

**INHIBITION BY ANODIC POLARISATION**

The corrosion of a metal in an aqueous medium is due to dissolution of the metal at the anodic areas as per the following reaction:

\[ M \rightarrow M^{+x} + xe^- \]

Where M represents corroding metal, \( M^{+x} \) represents the metal ions formed during corrosion, and \( x \) represents oxidation number of the ions. The electrons released at the anode are transferred to the cathode through metallic conduction and are consumed there by cations present in the solution. The corrosion inhibitors retarding the anodic reaction cause anodic polarisation. They are termed anodic inhibitors. If the corrosion current is proportional to the anodic areas i.e., the corrosion process is anodically controlled, decrease in anodic areas
may result in decreasing corrosion current. On the other hand, if corrosion is controlled by the cathodic reaction, the corrosion current, and therefore the total amount of corrosion, is not affected by decreasing the anodic areas. In this case the same amount of corrosion must be distributed over a smaller anodic area, resulting in intensified localized attack termed 'pitting'.

The metal salts of chromates, carbonate, phosphate, silicate etc., act as anodic inhibitors. Sometimes all these inhibitors, if used in small concentration, may increase overall corrosion\(^{403}\) e.g., sodium chromate and potassium permanganate, if present in small quantities, accelerate corrosion whereas large quantities of inhibitors may act as effective inhibitors. In such cases it is likely that the inhibitor, if present in small amount, may act as cathodic depolariser and at higher concentration it may act as anodic polariser.

**INHIBITION BY CATHODIC POLARISATION**

During the corrosion of metal in acid, the cathodic reaction is

\[
2H^+ + 2e^- \rightarrow H_2
\]

In a neutral solution containing oxygen, the main cathodic reaction is the reduction of oxygen to hydroxyl ions.
\[ \frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \]

The environment favouring corrosion, substances other than hydrogen ion and oxygen may be reduced at local cathodes. Inhibitors interfering with the above reaction are called cathodic inhibitors. The cathodic areas are not attacked during corrosion, since metal itself does not participate chemically in the cathodic reactions; hence inhibition by cathodic reaction generally do not lead to a localized attack. If corrosion is controlled by cathodic inhibitors, decrease in cathodic area will results in decreasing overall corrosion. If corrosion is controlled by anodic reaction, decrease in cathodic area may result in increase of cathode current density but will not have any effect on overall corrosion.

A number of substances, on the other hand, interfere both with anodic and cathodic reactions and cause both anodic and cathodic polarisation. Gelatine, glue and other high molecular weight substances fall in this category. These inhibitors concentrate at the metal liquid interface and because of high viscosity cause decrease in diffusion rates of the corrosive substances towards the metal surface. In addition to anodic, cathodic and mixed polarisation, corrosion inhibitors may also alter the open circuit potential and thus lead to decreased corrosion.
The potential of a metal in the corrosive medium may not be of importance but change in potential occurring in the presence of inhibitors is usually significant. Shifting of the potential to more cathodic values accompanied by decrease in corrosion rate may indicate anodic polarisation. The corrosion of steel in aerated neutral or alkaline systems in the presence of an inhibitor, such as, sodium silicate, there is inhibition and potential ranges from 0.0 to 0.35 V (standard hydrogen scale(404)) while in deaerated solution, in presence of the same inhibitor, there is no inhibition, the potential remaining less cathodic. On the other hand, in the case of sodium chromate and sodium nitrite potential does not change from aerated to deaerated condition. The potential is more cathodic in the presence of the inhibitor both in aerated or deaerated condition. Potential of steel in sulphuric acid is shifted towards more cathodic value in presence of amines and other nitrogen containing compounds(378). They are termed as anodic inhibitors. On the other hand As\(^{+++}\) inhibits the corrosion of iron in sulphuric acid and shifts the potential towards more anodic value, indicating cathodic polarisation.