CHAPTER I

LITERATURE SURVEY AND THEORIES OF INHIBITION
The term corrosion has been utilized to indicate a variety of phenomena by different authors. According to Evans (30), corrosion may be defined as destruction by chemical or electrochemical agencies. Speller (31) considers corrosion as, "the chemical action of certain external agencies on metal which causes their deterioration or destruction". Bengough (32) has defined two types of corrosion in brass—'complete' and 'selective'. In complete corrosion, the alloy may be attacked either generally or locally, the alloy losses copper and zinc in the same proportion as present in the alloy. In selective corrosion, only one ingredient (e.g. zinc) is lost.

Vast amount of work has been done on the corrosion of copper and its alloys under different conditions due to its extensive uses in the chemical industries handling alkalies, acids and salt solutions. Copper alloys have valuable physical and mechanical properties, long life, comparative cheapness and high scrap value. Hence, they occupy a position next to iron and steel in commercial importance.

Compared to brass, tin is quite soft metal. Among its several uses, it finds extensive use as a coating over iron for variety of purposes. Though a very useful metal, its corrosion studies has been mainly confined to as a protective coating over iron. Its behaviour as a coat on copper and brass
has not received any attention.

The literature survey is divided into three sections. The section I pertains to the corrosion of brass in various media, section II pertains to corrosion of tin and tin alloys and galvanic corrosion in various acidic media. The literature survey on corrosion inhibitors like colloids, carbohydrates and proteins for various metals and alloys is given in section III.

(I) Corrosion of brass

The corrosion of brass has been extensively studied. Tilden(33) studied the rate of oxygen in corrosion of brass. He showed that no corrosion of brass takes place provided air is excluded and that dilute solutions are more corrosive than concentrated ones as the later absorb less oxygen. Fujin(34) Bosworth(35) and Eisenbrohn(36) studied the corrosion of brasses in acetic acid in combination with various other liquids. Desai and Trivedi(37) reported that acetic acid is highly corrosive to brass. Oxygen solubility plays a significant role in corrosive action of acetic acid. The corrosion of brass in aqueous solutions of hydrochloric acid, acetic acid, phosphoric acid and other organic acids has been studied by Telati(38). He reported that the dezincification tendency is more remarkable in dilute solutions. Uhlig(39) studied the corrosion of brasses in nitric acid. He reported
a very high corrosion rate in 3.0 N nitric acid. Corrosion of copper and its alloys by common acids such as hydrochloric acid, sulphuric acid has been extensively studied(40).

The corrosion of brass (63/37) was studied in acetic acid, hydrochloric acid, nitric acid, phosphoric acid, sulphuric acid, tartaric acid and citric acid by Patel, Vora and Trivedi(41). They reported that corrosive power of 0.4 N pure acids towards brass is as follows:

\[ HCl > HNO_3 > H_2SO_4 > H_3PO_4 > Citric > Tartaric \]

Shah(42) studied the corrosion of brass in sodium hydroxide, ammonium carbonate, ammonium sulphate and sodium salts. Venator(43) found that the solution of sodium hydroxide attacks brass by dissolving only the zinc. Warsteinerber(44), while discussing the selective corrosion of brass, pointed out that in case of solutions of sodium salts, particularly sodium chloride, there is a local accumulation of sodium hydroxide, which causes local action.

According to Hudson(45) corrosion in neutral or weakly alkaline solution may be considered as a direct chemical attack. Althob(46) examined the corrosion of brass in mercurous nitrate, ammonium hydroxide and sodium hydroxide and gave a mechanism of intercrystalline and intracrystalline corrosion. Perryman and Goodwin(47) express that small
additions of titanium and zirconium to beta brass results in increased resistance of grain boundaries due to relaxation of shear stress and decreased tendency to intergranular structure.

Corrosion of brass in aqueous solutions of mango juice, lemon juice, tamarind, kokum and tomatoes has been studied by Talati (48). He reported that kokum is more corrosive than lemon, unripe mango, tamarind etc. The principal factors governing corrosion and dezincification are the inhibiting power of the colloids, nature of acids etc. In kokum, colouring matter acts as an oxidising agent contributing to the increase in corrosion.

Burns, Staffeldt and Calderon (49) have studied the corrosion of copper under sterile conditions in 1% solutions of acids that might occur in microbial environment. These acids are citric, fumaric, glutaric, itaconic, malic, maleic, oxalic and succinic. The corrosion products were metallo organic in nature as determined by infrared analysis. All the solutions turned green within 21 days.

These acids are corrosive toward copper and its alloys.

(II) Corrosion of tin-tin alloys

The surface of dry tin is normally covered with an oxide film and quickly regains it on exposure to air, if it is destroyed by reduction, solution or abrasion (50). Distilled
water and soft tap waters are not corrosive to tin. In absence of air, the corrosion rate decreases because of high hydrogen overvoltage of tin (51). The rate of corrosion of tin in acids is largely a function of oxygen concentration and the presence of metallic impurities in the tin or the acid that can concentrate on the surface and facilitate the cathodic half reaction. Under anaerobic conditions the weaker fruit acids attack tin at a very slow rate (50). The rate of attack on tin by citric, succinic, malic, malonic and acetic acids ranging from 0.5 to 0.97 mm in the order given was reported by Kohn and Sanborn (52). Oxalic acid is probably the most corrosive of the common organic acids toward tin (53). Ammonium hydroxide and sodium carbonate have little effect on tin, but a strong alkali like sodium hydroxide is corrosive even when cold and in dilute solution. Fruit juices corroded tin at a rate of 1 to 25 mm - under mildly aerated conditions at room temperature but weight losses of 12% to 35% mm have been noted for boiling lemon, tomato, red grape and apple juices (51).

Chlorine, bromine and iodine attack tin readily at room temperature, but fluorine only reacts with tin at a significant rate above 100°C (50).

According to Britton (54), the rate of corrosion of tin in alkaline media open to air is of the order of 60 mm at 30°C and about 100 mm at 70°C. In intermittent immersion, as
the cleaning of tinned-ware by alkaline detergents, the corrosion rate varies with the nature of alkali and concentration of the solution.

Ivenina and Runtikova (55) have reported, using radio-isotope techniques, that tin dissolves at the highest rate in melted cheese and very little in fresh milk.

Coatings of tin are applied on steel sheets to make tin plate, which is used for making containers particularly food cans. Tin is cathodic to iron in tin-iron couple. Iron coupled with tin greatly reduces the rate of corrosion, but the presence of tin, not in electrical contact giving rise to stannous ion, may reduce the rate even more drastically in some media (52).

Brennet (56) studied the formation of black spots on tin in NaCl, Na2SO4, and HNO3 solutions. Tin, tin rich alloys and coated metals are susceptible to form a localized corrosion known as black spotting (57). Concentrated solutions are more severe in their action than dilute solutions. Ammonium, magnesium, calcium and zinc chloride solutions behave similarly to potassium- and sodium- chloride, except that the black spots once formed, grow faster. Black spotting may be inhibited by cathodic polarisation or by reinforcement of oxide film anodically or with chromate treatment (31). Black spots can also be prevented by keeping the tin in contact with less noble metal like zinc or aluminium and possibly also by
anodic oxidation. Only those salt solutions which give no precipitate with stannous ions form black spot, chloride particularly, aids this type of attack(57).

Britton and Sherlock(58) have studied the stability constants of complex formed between Sn^{2+} and some organic acids like citric, malic, oxalic and tartaric acids. The stability constant depends on the activity of free ligand (L) complexes formed are SnL for citric, malic and tartaric acids and SnL₂ for oxalic acid. The stability constants are highest for oxalic acid. The complex stability constant is associated with differences in rates of dissolution of tin. Corrosion with reduction of cathodic depolarizers is likely to be diffusion controlled and unaffected by potential of Sn when reaction is H⁺ reduction on steel, the corrosion rate is influenced by Fe complex formation and by dissolution of Sn. These authors(59) have further studied the inhibition by stannous ions to the corrosion of mild steel and the effect of nitrate ions which promote the dissolution of tin by organic acid. The effect of nitrite is to accelerate corrosion of tin plated cans. The results can be applied to coated cans where the nitrite causes strong dissolution of Fe by pitting(60).

The rate of tin loss depends on the quality of tin plate and decreases in series: ACON > citric acid > tartaric acid.
The relatively high corrosion found in sodium chloride solution is probably caused by the contact of Fe with tin(61).

The timing of copper provides an effective barrier between copper and environment. Tin is anodic to copper and copper-tin alloys. Tin-coated copper has more corrosion resistance than uncoated copper. In Cu-Sn bronze alloys, tin is anodic and is susceptible to highly localised corrosion, especially along the contact boundary of two metals. Cu-Sn alloys show good resistance to corrosion fatigue in air, fresh water and sea-water(62).

The tartarates, sulphates, and nitrates of sodium, potassium, magnesium, and calcium are slightly corrosive towards Cu-Sn alloys. The average corrosion rate in stagnant solutions at room temperature is less than 0.0002 ipy. Copper 95% and tin 5% alloy in 2 M solution of NaCl corrodes at a rate of 0.0026 ipy at 25°C and at a rate of 0.0041 ipy at 75°C(63).

Lihi(64) has made a radiographic and metallographic investigation. He attributed the deterioration to corrosion rather than to consequences of allotropic transformation. He found that cast metal was porous, enabling the penetration of water and corrosive gases to reach the interior of the coating. The corrosion products caused swelling, blistering,
and cracking. The major corrosion products identified were CuO, Cu₂O, and basic copper carbonate.

A thorough study of the corrosion of tin and tinned copper in dilute chloride solution has been made by Britton and Michael (65).

Vadher and Vora (29) studied the corrosion rate of brass-tin couple in aqueous solutions of citric, tartaric and ascorbic acids; in this process, brass became cathode and tin became anode. A tin coating was formed over brass when the former was in close contact with the later.

Sato Shiro (66) has reported that Cu-In-Al alloys are most corrosion resistant. Increase of tin concentration increased the corrosion resistance. Corrosiveness increased with an increase of water pollution.

(III) Corrosion inhibitors

Interesting work on the inhibitory action of vegetable gums as corrosion inhibitors on copper and brass have been carried out by many workers.

Trivedi et al. (67) have studied the influence of dextrin, gelatine, gum accacia, agar agar and egg albumin on corrosion of α and α + β brasses in malic acid solution. The effect differs greatly depending on whether the added substances were cathodically or anodically absorbed to form a film on metal surface. Desai and Shah (68)
reported that gum arabic and egg albumin were equally effective inhibitors for brass in acetic, citric and malic acids, while agar agar, dextrin, gelatine and potato starch were more effective in acetic and citric acids than in malic acid.

Patel et al. (69) studied the influence of gum tragacanth, gum accacia, gelatine and dextrin as corrosion inhibitors for 63/37 brass in 0.1 - 0.5 M trichloroacetic acid solutions. They concluded that inhibitive power of these compounds was principally due to mixed polarisation. Gum accacia, gum tragacanth and gelatine were found to be excellent corrosion inhibitors, while dextrin was somewhat less effective.

Desai and others (70-72) investigated the action of some colloids on 70/30 brass in citric acid solutions. The inhibitor influenced both cathodic and anodic polarisation. Pyrogalol, tannic acid, accacia, dextrin, agar agar and gelatine were investigated as corrosion inhibitors for 63/37 brass in phosphoric acid. Gelatine was found as inhibitor for 60/40 brass in sulphuric acid but attack of corrosion increased in HCl + H2SO4 system (73). Dextrin retards the corrosion of aluminium in acidic and alkaline solutions (74-78).

Talati and Modi (79) have studied colloids as inhibitors for corrosion of aluminium in 0.1 M NaCl solution. The inhibition efficiency increased in order gelatine < dextrin < glue < agar agar < accacia < tragacanth. The efficiency
decreases with increase of NaOH concentration and increasing temperature. The inhibition was due to adsorption.

Tumeric powder was found to have maximum inhibition for $\alpha$ and $\alpha + \beta$ brasses in citric acid but not in tartaric acid (30).

Koszel (31) studied the inhibition of corrosion of aluminium by proteins and carbohydrates; galvanostatic measurements showed that inhibition by proteins, carbohydrate and amino acids was under a mixed control in hydrochloric acid solution with preponderance of cathode polarisation. In alkali solutions, inhibition was strictly under a mixed control, some compounds revealing formation of a film.

Schunkert (32) concludes from his studies of lyophilic colloids (gelatine, casein, starch, dextrin, albumin etc) that the inhibitors are absorbed on the anodic regions of the metal undergoing corrosion, retarding in consequence the transfer of metal ions into solution. It has been reported that dextrin reduces the corrosion of iron by an insignificant amount (33).

Tamin may be used as passivator for iron powder in alkaline solution (34) (e.g. potassium hydroxide solution of sp. gr. 1.2 g/ml). This substance forms stable surface compound with iron oxides.

Very little work has been done on the corrosion inhibition of tin by additives, largely because in media
where tin is used, the corrosion rate is very low. Sodium pyrophosphate is an inhibitor in acid, alkaline and neutral solutions (35). Camphor is claimed to be an effective inhibitor for the corrosion of tin in acid solutions (36). Sodium phenylacetate has been recommended as a suitable waterline corrosion inhibitor of tinned steel with bare iron edge (87). Cresol, tribenzylamine, thymol, β-napthol and diphenylamine cause a marked inhibition of anodic reaction in 0.05 N SnSO₄ + 2 N H₂SO₄ (88).
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THEORIES OF INHIBITION

The use of corrosion inhibitors has tremendously increased in the last twenty five years. 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.

Patilova, Balean and Barannik(89) classified corrosion inhibitors into the following two groups; type A inhibitors which attach to the metal surface and type B inhibitors which act by deactivating the corrosive environment. Inhibitors of type A are classified to be of three types: (i) Passivators, (ii) Inmunizers and (iii) Adsorption inhibitors. Passivators are usually inorganic oxidising 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. Inmunizers 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 solutions where the cathodic control is the discharge of hydrogen. Uhlig(90) 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 who Chappel, Poetholi and McCarthy (91) studied the effect of quinolineethiodide on cathodic and anodic polarisations of iron and steel in H sulphuric acid and concluded that inhibition was cathodic.

Mann (92) proposed a theory of cathodic inhibition by organic compounds especially amines. When a metal is introduced into an electrolyte, it becomes negatively charged. Helmholtz's 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 gets 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 attracted by the electrical forces to the cathodic area of the metal and will be held there tenaciously by adsorption in the form of a 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 area of the metal through nitrogen.

\[ \text{H-N-H} \quad \text{H-N-R} \quad \text{H-N-H} \quad \text{H-N-R} \]

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 cation ions and exist 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 polarisation at higher current densities and high negative potential.

Hackerman(23,24) modified Mann's theory by ascribing inhibition to an increase in 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(95), Maze and Haber(96) and Moor(97).

The species that are adsorbed physically by means of electrostatic or Van der Waals' forces 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.

Comparison of the properties mentioned above shows that an effective inhibiting action must normally be linked with the phenomenon of chemisorption, and examples are reported in literature, in which it 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(98,99). According to Hachu's theory the inhibition is due to ohmic resistance of inhibitor
film at the metal solution interface (4.0) or on non-specific adsorption phenomenon. These theories have been complemented and have found better definition through an analysis of the correlation 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

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 functional group which 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 (101), 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 the 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 functional atoms with respect to the chemisorption process (when the stabilities of the compounds are equal) can be taken as being in the following order (102-4):

\[
\text{Sulphur} \geq \text{Nitrogen} \geq \text{Oxygen}
\]

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 positions 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 (101, 102) 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, thials and their compounds has been made by Riggs(105) who interpreted the results on the basis of electron densities and obtained results in harmony with the theoretical assumptions.

The other structural parameters that may be mentioned include 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 area does not in general appear to be a determinative factor over the whole of the metal-inhibitor chemisorption bond, as has been shown by Podobaev(106) by comparing the results of measurements of inhibition, carried out on a series of derivatives of propargyl alcohol ($\text{HO} - \text{CH}_2 - \text{C} = \text{C}_2$), keeping the triple bond in the molecules 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 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(107). On the other hand, on studying the inhibition efficiency of homologous mercaptans, it was shown(108) that the inhibition increased on going from n-butylmercaptan to n-decylmercaptan.

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(109).

Chelation formation

Chelate formation is an important factor in explaining inhibition by organic inhibitors. 2-mercaptobenzothiazole(110), 2-benzimidazolethiol(111), benzimidazole(112), Na-DDTC(113) 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 a thin film. Kayakawa(114) showed that amongst quinoline derivatives, only substances which have OH group on 8th position inhibit corrosion by forming chelates. It was further reported(115) 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.

Inhibitory action of colloids

The colloids are known since long for their inhibitive powers (116-120). A variety of colloids are used as inhibitors with varying success. Some of them are gelatine, dextrin, agar agar and gum acacia. According to Vora et al (121) colloids, in nearly neutral media, become negatively charged when they adsorb OH ions from the solution and block the anodic areas, inhibiting corrosion. Isgaryshev and Berguenn (122) who studied the retardation of metal dissolution in sulphoric acid by gelatine, expressed the opinion that inhibition is achieved by the inhibitor removing hydrogen ion by combination with colloidal 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 dieverts and Lueg(123) and Krentzfeld(124) investigating starch, yeast
etc. The inhibitors form a continuous insulating adsorbed layer on the metal surface. Schunkert(26), from his studies on colloids, such as gelatine, casein, starch, dextrin and albumin, 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 inhibitors. It may be summed up that addition of colloids results in hydrogen overvoltage which causes inhibition. The overvoltage theory has been confirmed by many investigators who carried out experiments with various inhibitors e.g. Börner(125) with gelatine, Tilo and Kaiser(126) with gelatine and guar arabic. But the mechanism of inhibition by colloids does not find such place in literature.