Commun. Fac. Sci. Univ. Ank. Series B
V. 40. pp. 73-82 (1994)

EFFECT OF NO. NO AND Cl ON THE CORROSION BEHAVIOUR OF (LEAD - TIN) ALLOY IN ACID MEDIUM

GAMAL K. GOMMA

Faculty of Education, Chemistry Department, Kafr El-Sheikh, Egypt.

(Received Apr. 11, 1994; Revised Aug. 11, 1994; Accepted Oct. 18, 1994)

ABSTRACT

Corrosion of (lead-tin) alloy (34.5 % lead and 65.5 % tin) in deaerated solutions of 0.1 M oxalic, tartaric and citric acid solutions in presence and absence of NO^-_2, NO^-_3 and Cl^- ions were studied by means of potential-time, corrosion rate, corrosion current, and galvanostatic technique at the pH range 2.5-6.5 for 0.1 M of the three acids. At pH 4.5 there is a maximum negative potential at the open circuit-time curves for oxalic acid and at pH 5.5 for tartaric and citric acid solutions. From pH 2.5 to 4.5 the corrosion mechanism is anodically controlled by the reaction of Sn^{++} ion with anion of the tested acids. The open-circuit potential of the alloy in the three acids reduced in the presence of Cl^-, NO^-_3 and NO^-_2 ions. This is may be due to the attack of the oxide film by the tested anions, then followed by film repair via the insoluble complex species. Corrosion rate and corrosion current of the alloy increases as compared to the pure tin results.

INTRODUCTION

Lead-tin alloys (66 % Pb-34 % Sn) was used for making junctions between metals. Other easily fusible alloys of Pb and Sn are used in electrical fuses. Alloying tin with lead altered the rate and mechanism of corrosion of lead[1], the process of passivation probably does not involve the primary formation of a salt film on the surface of lead in the alloy. Alloys always gave intercrystalline corrosion in acid solutions[2]. During service Pb-Sn alloys suffer from corrosion. The rate of alloy corrosion decreases with increasing Sn content in the alloy[3]. This was due to the slowness of the dissolution of tin itself, since the hydrogen overpotential is higher on lead then on Sn[4]. It was found that the exchange current of Sn dissolution in sea water is less than that of lead[5]. Dissolution of (Pb-Sn) alloy is anodically controlled by Sn dissolution and not by hydrogen evolution[6]. Coupling of Pb-Sn in salt solutions enhance the corrosion of Pb and then a reversal of polarity occurs due to negative shift of the potential of the two metals[7].

The object of the present work is to study the corrosion behaviour of Pb–Sn alloy in organic acid solutions with and without Cl^-, NO_3^- and NO^-_2 anions. Polarisation was carried out galvanostatically. Rate of corrosion were determined from polarisation data.

EXPERIMENTAL

The alloy was prepared from pure grade lead and tin (BDH) as described elsewhere[8]. The required weights of lead and tin were 35.5 g and 64.5 g respectively. The alloy electrode, one cm long and 0.5 cm in diameter was used. Before each measurement the electrode surface was digressed and abraded successively with very fine emery paper and a soft cloth whereby it attained a rather smooth bright surface. It was then thoroughly washed with distilled water and rinsed with the electrolyte to be used.

The potential of the alloy electrode immersed in 0.1 M of the acid solutions was followed as a function of time by means of a manual potentiometer of the type (WPAO 0.1 % type 30, made in England) versus a saturated calomel electrode (SCE). The open circuit potential was measured at 30 °C and at different pH values ranging from 2.5 to 6.5 until a steady–state potential was attained.

0.1 M solutions of oxalic, tartaric and citric acids were prepared from the Analar reagents and double distilled water.

In order to test the effect of NO^-_3, NO^-_2 and Cl^- ions on the corrosion behaviour of the alloy in the carboxylic acid solutions, increments of concentrated solutions of $NaNO_2$, KNO_3 and KCl respectively from 10^{-4} to 10^{-1} M were added to the acid solutions. The pH values were adjusted to 4.5 by addition of NaOH solution. All solutions were deaerated by passing O^-_2 free nitrogen through the solution for at least 6h before the electrode was introduced into the cell.

The cell used for polarisation measurements was composed of two compartments separeted by a fritted glass to prevent mixing of anolyte and catholyte. The cathodic polarisation curves were obtained using a simple galvanostatic technique in absence (blank) and in presence of NO^-_3, NO^-_2 and Cl^- anions, Potential was measured using a platinum counter electrode and SCE as a reference electrode. The alloy electrodes were cathodically polarized using a constant current unite (Type LEYBOLD – Germany) with a fine Luggin capillary tube. The current was supplied and after 1 min. the potential was measured and the current was changed to a new level. All the experiments were carried at 30°C. Several runs were taken for each set of experiments.

RESULTS AND DISCUSSION

Potential–time Measurements

The open circuit potential of lead–tin alloy in deaerated 0.1 M oxalic, citric and tartaric acid solutions of the pH's 2.5–6.5 were followed as a function of time till the steady state values were attained as shown in Fig. (1–3). In all acid solutions of pH's 2.5 to 6.5 exhibit an initial rapid increasing in the negative direction i.e. decreases with the increase of the pH values from 2.5–4.5 for oxalic and from 2.5 to 5.5 for citric **and** tartaric acids then increase again at pH 5.5–6.5 during the first few minutes of immersion until the steady state potential (corrosion potential E_{corr} was reached after about 30 min). The rapid negative shift of potential with time (under open-circuit condition) may indicate the dissolution of the preimmersion oxide film[9] and or / the dissolution of tin at pores[10]. High rate of change of potential with time may indicate higher rate of dissolution[11]. The potential of alloy was also measured in presence of Cl^-, NO^-_3 and NO^-_2 at pH =4.5, it is clear that the potential of the alloy shifted to less negative poten-

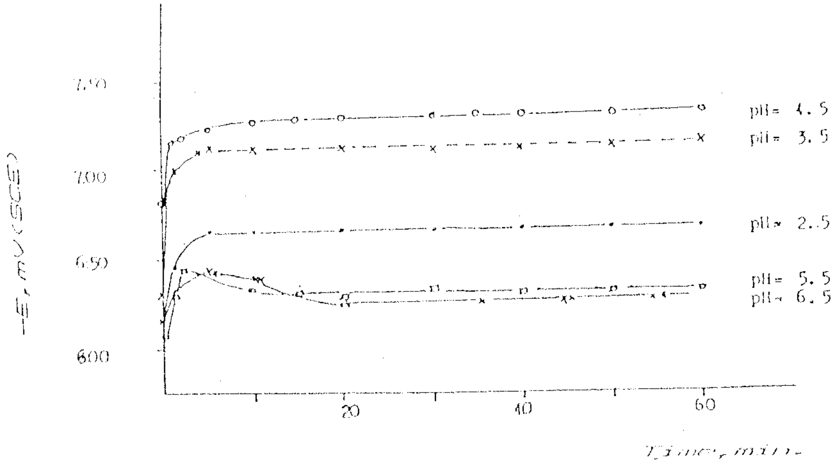

Fig. 1. Relation between potential of (lead–tin) alloy and time on 0.1 M oxalic acisd olution at different pH values.

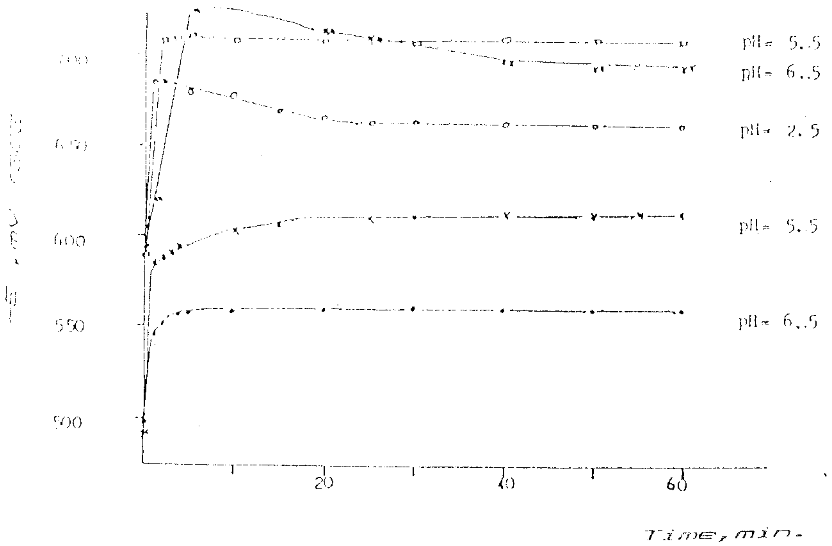

Fig. 2. Relation between potential of (lead–tin) alloy and time in 0.1 M citric acid solution at different pH values.

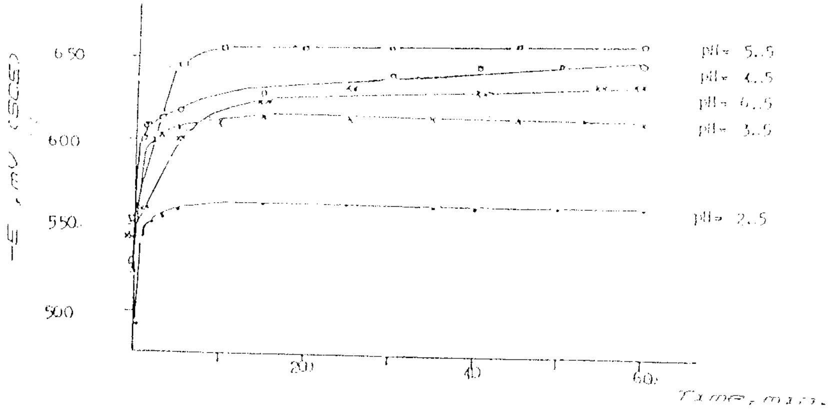

Fig. 3. Relation between potential of (lead–tin) alloy and time for 0.1 M tartaric acid solution at different pH values.

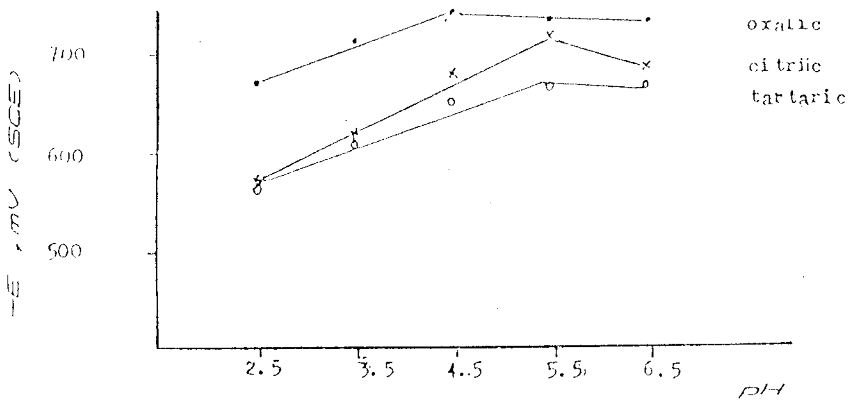

Fig. 4. Relation between potential of (lead-tin) alloy and pH values for oxalic, citric and tartaric acid.

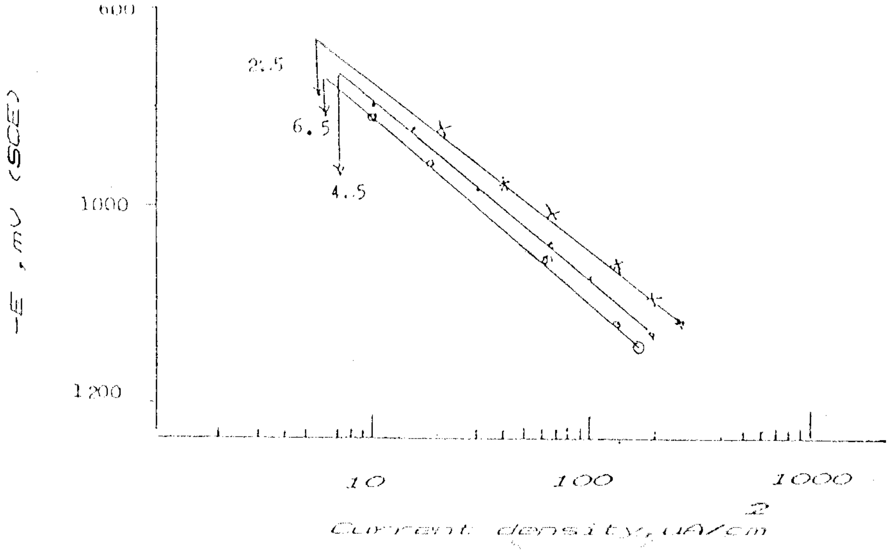

Fig. 5. Cathodic Tefal line for (lead-tin) alloy in 0.1 M oxalic acid at different pH values.

tial which may indicate healing of pre-immersion oxide film resulting in the formation of a compact oxide film[12]. It is well known that the dissolution of lead-tin alloy is anodically controlled by tin dissolution[13]. Thus the concentration of Sn (11) complex species increases with the increasing of pH values[14] From 2.5 – 4.5 the uncomplexed Sn decreases with each unit of pH change. The change of the electrode potential is due to the limitation of Sn ion concentration by complex formation (Table 1)[15], thus the corrosion mechanism in the pH range 2.5 to 4.5 is mainly controlled by complexing of Sn ions by organic ligands. The complex species will decrease with increasing pH from 4.5 to 6.5. The order of decreasing of E_{corr} of alloy in pure acid is as following tartaric $<$ citric $<$ oxalic corr which follow the same sequence of stability constants of the tin chelates.[15] The higher stability of Sn (OX) complex species (Table 1) to those of citric or tartaric will lead to an increase of the negative potential of alloy in oxalic acid than citric and tartaric (Table 2). This behaviour may be due to the formation of Sn complexes with the acids anion as a ligands as the following

Table. 1. Concentrations of Free, Complexed and Hydrolysed Tin Species in 0.1 M Oxalic, Citric and Tartaric Acid Solutions.

Acid	Concentrations (M)	pH	Free Tin Mole / L	Tin Comlexes	Sn (OH)$^+$
Oxalic	0.1	2.5	4.06×10^{-13}	1.62×10^{-7}	5.05×10^{-15}
		4.5	1.45×10^{-16}	3.59×10^{-7}	1.89×10^{-16}
		6.5	3.80×10^{-18}	5.98×10^{-8}	4.67×10^{-16}
Citric	0.1	2.5	6.08×10^{-13}	1.53×10^{-7}	7.50×10^{-13}
		4.5	4.99×10^{-14}	5.78×10^{-8}	6.16×10^{-13}
		6.5	3.60×10^{-14}	4.88×10^{-8}	4.63×10^{-12}
Tartaric	0.1	2.5	3.45×10^{-10}	8.03×10^{-8}	4.45×10^{-11}
		4.5	3.32×10^{-11}	1.09×10^{-7}	4.27×10^{-11}
		6.5	5.07×10^{-12}	4.72×10^{-8}	6.15×10^{-11}

$$\begin{array}{l} Sn \text{ —— } Sn^{++} + 2e \\ \qquad\quad\ \downarrow\uparrow \\ \qquad \text{—— } Sn^{(+2)}\ (L) \quad L\text{: complexing ligand} \end{array}$$

which will diminishing the concentration of tin ions leading to depress of the tin potential. Changing the pH to 5.5 and 6.5 leaas to change in the concentration behaviour of Sn, the potential values which may be attributed to that the pre-immersion oxide film on the alloy electrode is healed to a decrease in the anodic area. Inhibition is more at high pH values. From the results obtained in the presence of Cl^- ion

Table 2. Corrosion Potential of (Lead-tin) Alloy in Deaerated 0.1 M Carboxylic Acid Solutions in the Presence of Cl^-, NO^-_3 and NO^-_2 at pH 4.5

Anion	Concentration of Anions	Oxalic -E, mV (SCE)	Citric -E, mV (SCE)	Tartaric -E, mV (SCE)
Pure tin	0	740	685	620
Pure lead	0	537	535	540
Alloy	0	735	676	620
	1×10^{-4}	673	608	590
Cl^-	1×10^{-3}	664	597	585
(Alloy)	1×10^{-2}	668	605	585
	1×10^{-1}	662	570	535
	1×10^{-4}	705	660	648
NO^-_3	1×10^{-3}	703	657	645
(Alloy)	1×10^{-2}	701	655	645
	1×10^{-1}	699	640	643
	1×10^{-4}	687	670	621
NO^-_2	1×10^{-3}	678	664	618
(Alloy)	1×10^{-2}	670	636	603
	1×10^{-1}	660	633	600

from $10^{-4} - 10^{-1}$ M indicate that E_{corr} in all acids examined is shifted to less negative direction for each acid. This is may be attributed to the attack of oxide film by Cl^- ions which depress the potential of the alloy followed by film repair via precipitation of the insoluble complex species Sn (OH) Cl (in which the Cl^- form very sparingly soluble basic salts of the type Sn (OH) Cl). The ability of NO^-_2 ions to penetrate the oxide layer will lead to an inhibiting action via the reduction of nitrate to nitrite ions[16].

Nitrites are oxidizing inhibitors, this is because oxygen itself can exert inhibitive powers by aiding repassivation, thus NO^-_2 can easily be adsorbed on the surface and due to its ability to plug all corrosion sites. This effective coverage results in small cathodic site in contact with relatively large anodic sites, this leads to decrease in corrosion rate and corrosion potential, since small amount of oxygen is supplied to the cathodic sites thereby reducing up the cathodic reaction (reduction). In response to this, the anodic reaction (metal dissolution) decreases. Accordingly the passive potential is most probably due to the high resistance in the pores of the oxide film[17] (anodic area) which leads to a very low current density at the cathodes.

Measurements of tin in solution are tabulated in Table 1.[15]

CATHODIC POLARISATION TECHNIQUE

Values of the steady state corrosion potential (E_{corr}.) and corrosion currents (I_{corr}) (these were determined by extrapolating the cathodic Tafel lines to the steady–state open circuit corrosion potential values) and corrosion rates in deaerated corboxylic acid solutions within the pH range 2.5 – 6.5 are given in (Table 3). The data indicate that the corrosion rate increases with the increase in the pH of solution. The rate of increase d log I_{corr} / dpH (calculated directly from the slope of the d log I_{corr} vs pH plots), ranges from 0.66 for oxalic, 0.25 citric and 0.20 for tartaric acid values of d log I_{corr} / d pH for alloy are higher than the corresponding ones of pure Sn (0.34 for oxalic, 0.20 citric and 0.15 tartaric) indicating that the corrosion rate of pure tin is considerably lower than that of alloy in the carboxylic acids at the same solution pH. The increase in the corrosion rate with the increase of pH of solution is accompanied by a negative shift of potential suggesting that the corrosion of (Pb–Sn) alloy is anodically controlled and the corrosion process is dependent on the breakdown of the spontaneously formed oxide film. The destruction of such film leads to an increase in the anodic area at the expense of the cathodic area. The corrosion process for oxide covered (Pb–Sn) alloy in carboxylic acids solutions (pH 2.5–6.5) may occur in steps.

Table 3. Corrosion Potential, Corrosion Currents and Corrosion Rate For Pb–Sn Alloy in Oxalic, Citric and Tartaric Acid Solutions in Presence of Cl^-, NO^-_3 and NO^-_2 Ions.

Acid Anion	[M]	pH	-E, mV (SCE) corr. Alloy	i Tin	μA/cm² corr. Alloy	Tin	Corrosion (mg/cm²/h) Alloy	Rate x 10^{-3} Tin
Oxalic	0.1	2.5	665	612	5.5	1.4	5.72	1.45
		4.5	740	740	7.0	2.0	7.29	2.08
		6.5	725	645	6.5	1.0	6.77	1.04
+ Cl^-	0.1	4.5	662		5		5.2	
+ NO^-_3	0.1	4.5	570		6		6.25	
+ NO^-_2	0.1	4.5	635		4		4.16	
Citric	0.1	2.5	565	538	5.0	1.2	5.20	1.25
		4.5	676	720	5.5	1.6	5.72	1.66
		6.5	680	698	6.0	1.1	6.25	1.14
+ Cl^-	0.1	4.5	570		4.5		4.68	
+ NO^-_3	0.1	4.5	640		5.5		5.72	
+ NO^-_2	0.1	4.5	633		3.5		3.64	
Tartaric	0.1	2.5	565	532	4.0	0.6	4.16	0.62
		4.5	648	625	4.5	1.0	4.68	1.04
		6.5	635	615	5.0	0.4	5.20	0.41
+ Cl^-	0.1	4.5	635		3.5		3.64	
+ NO^-_3	0.1	4.5	643		4.0		4.16	
+ NO^-_2	0.1	4.5	600		3.0		3.12	

1– Adsorption of the carboxylate anions at the active anodic sites.

2– The formation of stable complexes between such anions with the tin cations in the oxide film.

3– The diffusion of such complex ions to the bulk of solution.

This may lead to the continuous thinning of the oxide layer and consequently film breakdown[18]. Lower corrosion currents I_{corr} of pure tin compared to the corresponding Pb–Sn alloy can be attributed to that the oxide film formed on tin is more compact, less porous than the corresponding oxide film formed on the alloy. This argument finds a support in the potential–time measurements where in the case of pure Sn the steady state corrosion potential are approached from less active values. The higher corrosion current I_{corr} for both pure tin and Pb–Sn alloy in oxalic acid solutions compared to those obtained in the other examined carboxylic acids at the same pH can be attributed to the higher porosity of oxide film formed in oxalic acid solution. On the other hand the higher stability of the formed soluble oxalate complexes with tin ions may lead to an increase in the corrosion current I_{corr}.

RATE OF CORROSION MEASUREMENTS

The corrosion rate of Pb–Sn alloy in 0.1 M of oxalic, tartaric and citric acid in presence and absence of Cl^-, NO^-_3 and NO^-_2 were calculated from the cathodic polarisation results. The corrosion currents I_{corr} measurements can be converted to weight–loss data.

To determine rate of corrosion based on corrosion current measurements (Table 2), we use the following equation.

$$I_{corr} = 0.96 \times (W)$$

where I_{corr}. is the corrosion current in mA / cm^2 and (W) is the corrosion rate in mg / cm^2 / h. which can be calculated over a period of hours (Table 3)[19].

CONCLUSION

1– The corrosion mechanism of lead–tin alloy is anodically controlled by the reaction of Sn ion with anion of the oxalic, citric and tartaric acids.

2– The potential of the alloy reduced in the presence of Cl^-, NO^-_3 and NO^-_2 which may be due to the attack of the oxide film by the tested anions followed by film repair via perception of insoluble complex species.

3– Corrosion rate and corrosion current of alloy increases under the tested condition as compared with pure tin.

REFERENCES

1. L.E. TITOVA, and V.A. GUSEVA., (Ural Gos Univ Im Gorkogo Sverdlovsk USSR *Zashoh, Metal*, 1968, 4, 588; *Chem. Abst.*, 1969, 70, 3376 t.
2. E. HAROL, Zahn (to Gould National Batteries, Ins.) V.S. 3, 078. 161. (Cl. 75–166 Fep. 19–1963 Appl. Apr. 3. 1958, 1 P continuation in part of U.S. 2, 841, 491 *Chem. Abstr.*, 52, 1707, 2h; *Chem. Abst.* 1963, 58, 8739.
3. N.A. FAWZY., G.H. SEDAHMED. and A.A. MOHAMED., *Surface Technology*, 1982, 15, 147.
4. J.M. WEST., "*Electrodeposition and corrosion processes*", Van Nostrand, London, 1965.
5. M.G. FONTANA. and N.D. "*Greene Corrosion Engineering*", Mc Graw Hill, New York, 1967.
6. S. ABDEL, WAHAAB., O. ABO, EL, WAFA., G.K. GOMMA. and S.M. RASHWAN, *J. Chem. Tech Biotechnol*, 1986, 36, 305.
7. G.K. GOMMA., H.Y.F. EL–BARADIE. and S.M. ABDEL WAHAAB., *Delta J. Sci.* 1986, 10, 859.
8. G.K. GOMMA. and H.Y. EL–BARADIE., *Proc.*, 1 *st Chem. Conf. Fac. of Science* Mans Univ Sept 24–25, 1986, 597.
9. A. DIPUOLA. and F.D. QUARTO., *Electrochim Acta*, 1977, 22, 36.
10. K. NİŞANCIOĞLU. and H. HOLTAN., *Corros. Sci.*, 1979, 537.
11. A.K. VIJH., *Corros Sci.*, 1972, 12, 105.
12. J.W. DIGGLE., T.C. DOWNIC. and C.W. GOULDING., *Chem. Rev.*, 1969, 65, 365.
13. V.K. GOUDA, E.N. RİZKALLA., S. ABDEL, WAHAAB and E.M. İBRAHİM., *Corros. Sci.*, 1980, 21, 1.
14. J. INCZEDY., "*Analytical Applications of Complex Equilibria*", Hor Wood, Chichester, 1967.
15. G.K. GOMMA., *B Electrochemistry*, (India) (in press) 1993.
16. S.T. HIROZAWA., "*International Conference on Corrosion Inhibitors Dallas*", 1983, paper No. 15.
17. M. COHEN., *Corrosion*, 1943, 9, 732.
18. G.C., WOOD., W.H. SATTON. and S.A. RICHARDSON., "*Localized Corrosion* NACE Houston, 1974, 526.
19. R.M. HUDSON., T.J. WARNING., *Corro. Sci.*, 1977, 17, 577.