Avakening to reality

Available online at www.elixirpublishers.com (Elixir International Journal)

## Corrosion

Elixir Corrosion 69 (2014) 22941-22946



## Protective effect of N-[(benzylidene hydrazino)-propyl]- benzotriazole and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole for the control of corrosion of Cu-Ni (90/10) alloy in Sea water

K. Chadrasekaran<sup>1</sup>, A.C.Jayasree<sup>2</sup>, Bangaru Sudarsan Alwar<sup>3</sup> and R.Ravichandran<sup>1,\*</sup> <sup>1</sup>Department of Chemistry, Dr.Ambedkar Government Arts College (Autonomous), Chennai – 600 039, India. <sup>2</sup>Research and Development Centre, Bharathiar University, Coimbatore – 641 046, India. <sup>3</sup>Department of Chemistry, D.G. Vaishnav College (Autonomous), Chennai – 600 106, India.

## ARTICLE INFO

Article history: Received: 28 February 2014; Received in revised form: 20 March 2014; Accepted: 3 April 2014;

## Keywords

Copper –nickel alloy, Benzotriazole, Sea water, Polarization, EIS, Scanning electron microscopy.

## ABSTRACT

The effect of novel corrosion inhibitors, new class of substituted benzotriazoles namely N-[(benzylidene hydrazino)-propyl]- benzotriazole(BPBT) and N-[(4-oxo-2-phenyl-1,3thiazolidineimino)-propyl]-benzotriazole (OPBT) were synthesised and their inhibition behaviour on Cu-Ni alloy in natural sea water were investigated by the weight-loss method, potentiodynamic polarisation and electrochemical impedance studies. Polarization measurements showed that the organic compounds investigated are mixed type inhibitors, inhibiting the corrosion of Cu-Ni alloy by blocking the active sites of the metal surface. They decrease the anodic reaction rate more strongly than the cathodic reaction rate and render the open circuit potential of Cu-Ni alloy more positive in natural sea water. Changes in the impedance parameters (charge transfer resistance (R<sub>ct</sub>) and double layer capacitance (C<sub>dl</sub>)) are related to adsorption of organic inhibitors on the metal surface, leading to the formation of a protective film. Solution analysis revealed the decrease in dissolution of both copper and nickel in the presence of benzotriazole derivatives. The morphology of the Cu-Ni alloy after corrosion in the presence and absence of the benzotriazole derivatives was examined using scanning electron microscopy (SEM). All studies clearly show that the substituted benzotriazoles inhibits the corrosion of Cu-Ni alloy in natural seawater and the value of inhibition efficiency increases with increasing concentration of inhibitors.

## © 2014 Elixir All rights reserved.

## Introduction

Copper-nickel alloys are extensively used in marine applications because of their good electrical and thermal conductivities, corrosion resistance, and ease of fabrication of the equipment [1]. The 90/10 copper-nickel alloy is a material of selection for condensers and heat exchangers, where seawater is used as a coolant and in desalination plants [2, 3]. This alloy is resistant to stress corrosion cracking by ammonia and sulphide ions [4] and has good resistance to biofouling due to the release of copper ions [5]. This alloy is also resistant to pitting and crevice corrosion in quiet seawater [6]. The corrosion resistance of this alloy is related to the performance of the passive film, which is mainly composed of Cu<sub>2</sub>O [7]. Azoles have been widely used as corrosion inhibitors in several environments (8, 9). Among the azole compounds, the remarkable efficiency of benzotriazole (BTA) as a corrosion inhibitor for copper alloys in aqueous environment has been well established for several decades. Fenelon and Breslin [10] studied the formation of BTA surface films on Copper, Cu-Zn alloy and Zn in chloride solution. Otieno-Alego et al. [11] studied the electrochemical SERS study of the effect of 1-[N,N-bisand (hydroxyethyl)amionomethyl]benzotriazole (BTLY) on the acid corrosion and dezincification of 60-40 brass. Huynh et al. [12] investigated the action of octyl esters of 4 and 5-carboxy benzotriazole for copper corrosion in sulphate solutions and attained 98% IE when compared to benzotriazole. Zhang et al. [13] investigated the protective action of bis-(1benzotriazolymethylene)-2,5-thiadizoly)-disulphide on copper in chloride media and concluded that the inhibitors effectively

Tele: 91-44-25523716/25523715 E-mail address: varmaravi2003@yahoo.com

© 2014 Elixir All rights reserved

control corrosion. Al Kharafi et al. [14] analyzed the kinetics of interaction of BTA with the surface of copper in 3.5% NaCl. Ravichandran et al.[15] investigated the effect of N-[1-(benzotriazol-1-yl) methyl] aniline (BTMA) and 1hydroxy methyl benzotriazole (HBTA) on corrosion of brass in neutral aqueous NaCl solution. Although there is an extensive literature on the corrosion properties of triazoles such as imidazole and benzotriazole on steel and copper, there remains little information on the effect of various functional groups in the BTA derivatives on the corrosion of cupro-nickel alloy. Based on this, the inhibitors have been considered and synthesized according to the previous report. In the present investigation, it is proposed to study corrosion protection of cupro- nickel alloy in natural seawater with two BTA N-[(benzylidene hydrazino)-propyl]derivatives namely benzotriazole(BPBT) and N-[(4-oxo-2-phenyl-1,3thiazolidineimino)-propyl]-benzotriazole(OPBT). Weight-loss method and electrochemical studies such as polarization and impedance spectroscopic techniques were used to assess the inhibition efficiencies of the above compounds. Solution analysis was carried out to find out the concentration of Cu and Ni leached out from the cupro- nickel alloy using ICP-AES. The morphology of the cupro-nickel surface was analyzed using JOEL<sup>R</sup> JSM 35C SEM.

## Materials and Methods Materials

The composition of Cu-Ni (90/10) alloy used in the present study is given in Table 1. The cupronickel alloy specimens were

taken from the same Cu-Ni (90/10) alloy sheet. The natural sea water is collected near National Thermal Power Station (NTPC), Ennore, Chennai, India. The chemical composition of the seawater is analyzed by analytical technique, whose composition is given in Table 2. The pH of the seawater is 6.8. The inhibitors N-[(benzylidene hydrazino)-propyl]benzotriazole (BPBT) and N-[(4-oxo-2-phenyl-1,3thiazolidineimino)-propyl]-benzotriazole(OPBT) were synthesized according to the reported procedures [16] and their structures are shown in the scheme 1.

## Synthesis of N-[(benzylidene hydrazino)-propyl]benzotriazole(BPBT)

A mixture of N-(hydrazino propyl)-benzotriazole (2g, 0.01 mol) and benzaldehyde (1.11g, 0.01 mol) in methanol (20 mL) in the presence of a catalytic amount of glacial acetic acid was refluxed for 5.3 hrs. The solvent was removed under reduced pressure to and the resulting crude product was purified by passing it through a chromatographic column packed with silica gel using chloroform: methanol (8:2 v/v) as eluant. Resulting purified product was recrystallized by chloroform to give compound.

# Synthesis of N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole(OPBT).

A mixture of compound N-[(benzylidene hydrazino)benzotriazole(BPBT) propyl]-(1g, 0.003 mol) and SHCH<sub>2</sub>COOH(0.331g, 0.003 mol) in methanol (20 mL) containing a pinch of anhy. ZnCl<sub>2</sub> was first stirred for about 2 hours followed by refluxing on a steam bath for about 6 hrs. The recation mixture was cooled and excess of solvent was evaporated under reduced pressure. The solid crude product was purified by passing it through a chromatographic column packed with silica gel using chloroform: methonal (8:2v/v) as eluant and again purified by recrystallisation from ethanol to give compound N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]benzotriazole.

## Scheme 1. Structure of BTA derivatives



N-[(benzylidene hydrazino)-propyl]- benzotriazole (BPPT)



N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]benzotriazole(OPBT)

#### Methods

For the weight-loss method, the cupro-nickel specimens (4 cm x 2.5 cm x 0.2 cm) were abraded with silicon carbide papers (120-1200grit), thoroughly washed with distilled water, degreased with acetone, rinsed with distilled water, dried and

weighed. The specimens were immersed in 300 ml of natural sea water, with and without inhibitors at  $30^{\circ}$ C for 45 days.

For electrochemical studies, the working electrode with an area of  $1 \text{ cm}^2$  was embedded in epoxy resin in a Teflon holder. The electrode was abraded mechanically with silicon carbide papers from 120 to 1200 grit followed by polishing with 5 µm diamond paste. The electrode was thoroughly washed with double distilled water, degreased in acetone for 15 minutes using ultrasonic vibration, rinsed with distilled water and dried. The cell assembly consisted of cupro-nickel as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge.

Polarization studies were carried out using a Vibrant potentiostat/ galvanostat model No. VSM/CS/30 at a scan rate of 1mV/s.. The working electrode was immersed in natural sea water (open atmosphere) and allowed to stabilize for 30 minutes [33]. In each case a potential of -1500 mV was then applied for 15 minutes to reduce oxides. The cathodic and anodic polarization curves for cupro-nickel specimen in the test solution with and without inhibitors were recorded between -500 to 500 mV at a scan rate of 1 mV/s. The inhibition efficiencies of the compounds were determined from corrosion current density using the Tafel extrapolation method. A.C. impedance measurements were conducted at room temperature using an AUTOLAB with Frequency Response Analyzer (FRA), which included a Potentiostatic model "Autolab PGSTAT 12". An ac sinusoid of +10 mV was applied at the corrosion potential ( $E_{corr}$ ). The frequency range of 100 kHz to 1mHz was employed. All potentials are reported Vs SCE.

During the anodic polarization, metal dissolution takes place releasing considerable amounts of metal ions from the material. Hence, the solutions were analyzed to determine the leaching characteristics of the cupro-nickel alloy. The solution left after polarization measurement was analyzed for copper and nickel by inductively coupled argon plasma-atomic emission spectroscopy (ICP-AES). Solutions containing the optimum concentration of the inhibitor were chosen and a blank was also analyzed for comparision purposes. The morphology of the cupro-nickel surface after polarization measurements was analyzed using JOEL<sup>R</sup> JSM 35C SEM.

## **Results and Discussion**

## Weight-loss method

The corrosion rates and inhibition efficiencies of cupronickel alloy with different concentrations of BBT and OBT in natural sea water at room temperature ( $30^{\circ}$ C) are given in Tables 3. The corrosion rate (CR) and percentage inhibition efficiency (IE %) were calculated using the following equation [17].

$$CR (mm yr^{-1}) = \frac{D x A x T}{D x A x T}$$

$$IE\% = \frac{CR_{(bl)} - CR_{(inh)}}{CR_{(bl)}} \times 100$$

where W is the weight-loss, D is the density, T is the immersion time, A is the area of the specimen and  $CR_{(inh)}$  and  $CR_{(bl)}$  are the corrosion rate of cupro-nickel alloy in the presence and absence of inhibitors respectively. The inhibition efficiency increases with increase in concentration of the inhibitors. The maximum IE% of each compound was achieved at  $10^{-2}$  M. The optimum of concentration of the inhibitors was  $10^{-2}$  M and OPBT was superior to BPBT.

The inhibition of corrosion by these compounds can be attributed to their adsorption on the metal surface because of the following interactions.

- the interaction between the  $\pi$ -electrons of the benzotriazole ring and the positively charged metal surface, and

- the interaction between the lone pair of electrons of the atoms of nitrogen and the positively charged metal surface.

Inhibition of corrosion of cupro-nickel alloy in natural sea water can be explained in the following way. The adsorption of benzotriazole derivatives on the surface of cupro-nickel alloy leads to the formation of a protective layer of Cu(I) chloridecomplex on the surface of alloy. Actually the formation of a benzotriazole film starts with the chemisorption of the inhibitor molecule on to the slightly oxidized areas of the copper surface. The adsorption of benzotriazole molecules on the oxidized parts of the copper surface was found to occur much faster than on bare metal zones. The film formed in this way has a limited hydrophobic action, which succeeds in protecting alloy in the corroding medium by blocking main reaction centres on the metal surface.

Based on the results, both BPBT and OPBT showed better inhibition efficiencies, due to the presence of heteroatom such as N, O, S and  $\pi$  electrons on aromatic nuclei. When compared to BPBT, OPBT showed highest inhibition efficiency, which may be due to the presence of S atom and high molecular weight and possessed by the OPBT molecule. The higher inhibition efficiency of the organic compounds are due to the basis of donor-acceptor interactions between the  $\pi$  electrons of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions.

## **Polarization studies**

The cathodic and anodic polarization curves of cupro-nickel alloy in natural sea water containing optimum concentration of BPBT and OPBT are shown in Figure 1. It is evident that in the presence of inhibitor, the cathodic and anodic curves were shifted towards noble direction and the shift was found to be dependent on inhibitor concentration. Tables 4 illustrate the corresponding electrochemical parameters. The  $E_{corr}$  values were marginally shifted in the presence of BPBT and OPBT, which clearly indicated that the inhibitors control both cathodic and anodic reactions and thus act as mixed type inhibitors. The current density also decreased with increasing concentrations of the inhibitors. The corrosion rates and inhibition efficiencies [18] were calculated from polarization curves using the following equation.

$$CR = \frac{3.27 \times 10^{-3} \times I_{corr} \times EW}{D}$$

Where CR is the corrosion rate (mmpy), D is the density (g cm<sup>3</sup>), EW is the equivalent weight of the specimen, IE is the inhibition efficiency and I<sub>corr (inh)</sub> and I<sub>corr</sub> are corrosion current density in the presence and absence of inhibitors respectively.

The values of cathodic Tafel slope (b<sub>c</sub>) and anodic Tafel slope (b<sub>a</sub>) of benzotriazole derivatives are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both the reactions. The inhibition efficiency of BPBT and OPBT in natural sea water attained a maximum value at  $10^{-2}$  M. The values of inhibition efficiency increase with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in the solution with the optimum concentration of inhibitor. The corrosion rate of cupro-nickel alloy natural sea water was found to be 7.185 x  $10^{-2}$  mmpy and it was minimized by adding the inhibitors to a lower value of 0.43

x  $10^{-2}$  mmpy and 0.219 x  $10^{-2}$  mmpy due to the adsorption of BPBT and OPBT on the metal surface respectively.

A comparison of the values of inhibition efficiency obtained by weight loss measurements and polarization studies bring out clearly the fact that there is a fairly good agreement between these values. It is also found that the compounds function more effectively on the corrosion inhibition of cupro-nickel alloy in natural sea water.



*Fig. 1.* Polarization curves of cupro-nickel alloy in natural sea water containing optimum concentrations of BPBT and OPBT

## A.C. Impedance studies

The corrosion behaviour of cupro-nickel alloy in natural sea water in the presence of benzotriazole derivatives was investigated by EIS method at room temperature. Nyquist plots of cupro-nickel alloy in inhibited and uninhibited sea water containing optimum concentrations of BPBT and OPBT after immersion of 72 hrs is shown in Figure 2. The percent inhibition efficiency (IE %) of corrosion of cupro-nickel alloy was calculated as follows [19]:

I.E % = 
$$\frac{(R_{ct})^{-1} - R_{ct(inh)})^{-1}}{(R_{ct})^{-1}} \times 100$$

where, R<sub>ct(inh)</sub> and R<sub>ct</sub> are the charge-transfer resistance values with and without inhibitors respectively. IE% attained 97.21 after 72 hrs immersions with optimum concentration of OPBT, which was comparatively higher than that of BPBT in natural sea water. This behaviour was attributed to more surface coverage of OPBT on the cupro-nickel alloy surface from sea water. The inhibition efficiency values determined using the polarization curves were lower than those determined by EIS experiments, this difference was probably due the shorter immersion time in the case of the polarization measurements. Impedance parameters derived from these investigations are given in Table 5. In the presence of optimum concentration of inhibitors, R<sub>ct</sub> values increased, whereas C<sub>dl</sub> values tended to decrease. The term (C<sub>dl</sub>) is voltage dependant and in aqueous media this capacitance is typically a few tens of microfarads per square centimeter, and the measured value can be used to estimate the effective area of a corroding electrode. The decrease in C<sub>dl</sub> values was caused by adsorption of benzotriazole derivatives on the metal surface. The tendency to decrease in C<sub>dl</sub>, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the benzotriazole derivatives function by adsorption at the metal-solution interface [20].

Table 1. Chemical composition of Cu/Ni (90/10) (in wt.%)								
Alloy	Cu	Ni	Fe	Mn	Pb	Al	Other trace elements	
Composition	89.23	9.663	0.682	0.267	0.0594	0.0435	0.0551	

sition	89.23	9.663	0.682	0.267	0.0594	0.0435	0.0551

Table 2. Composition of natural sea wat
---

Species	Concentration (mg/ lit)		
Dissolved oxygen	0.62		
Chloride	29,974		
Sulphate	543		
Bicarbonate	76		
Phosphate	0.59		
Silicate	4.52		
Nitrate	0.623		
Nitrite	0.04		

## Table 3. Inhibition efficiency at different concentrations of PBBT and OPBT of cupro-nickel alloy in natural sea water

Inhibitor concentration	Corrosion rate x 10 <sup>-2</sup>	Inhibition efficiency
(M)	(mmpy)	(70)
Blank	7.694	-
BPBT		
10-5	3.521	54.24
10-4	2.384	69.01
10-3	1.192	84.51
10 <sup>-2</sup>	0.788	89.76
OPBT		
10-5	3.122	59.03
10-4	1.716	77.70
$10^{-3}$	0.898	88.33
10 <sup>-2</sup>	0.453	94.11

### Table 4. Electrochemical parameters and inhibition efficiency for corrosion of cupro-nickel alloy in natural sea water containing different concentrations of benzotriazole derivatives

Inhibitor Concentration	E <sub>corr</sub>	ba	b <sub>c</sub>	Icorr	Corrosion Rate	Inhibition Efficiency
( <b>M</b> )	(mV vs. SCE)	/mV (dec) <sup>-1</sup>	/mV (dec) <sup>-1</sup>	/µA cm <sup>-2</sup>	/ mmpyx 10 <sup>-2</sup>	/ %
9.67	-273	69	-121	6.23	7.185	-
BPBT						
10 <sup>-5</sup>	-251	93	-98	2.76	3.183	55.70
10-4	-237	113	-73	1.74	2.007	72.07
10-3	-216	128	-52	0.73	0.841	88.28
10 <sup>-2</sup>	-205	142	-45	0.43	0.496	93.09
OPBT						
10-5	-242	98	-93	2.43	2.802	60.99
10 <sup>-4</sup>	-228	118	-65	1.26	1.453	79.78
10-3	-207	132	-46	0.55	0.634	91.71
10-2	-198	156	-34	0.19	0.219	96.95

Table 5. Impedance measurements and inhibition efficiency of cupro-nickel alloy in natural sea water containing optimum concentrations of BPBT and OPBT after 72 hrs immersion

Inhibitors	$R_{ct} \ge 10^4 (ohm \ cm^2)$	$C_{dl}$ (µ Fcm <sup>-2</sup> )	Inhibition efficiency (%)
Blank	0.96	33.64	-
BTPH	21.93	0.096	95.62
BTAP	34.46	0.074	97.21

Table 6. Effect of optimum concentrations of PBBT and OPBT on the Denickelification of cupro-nickel alloy in natural sea water

	Solution	analysis		Percent inhibition		
Inhibitors	Cu Ni		Denickelification factor (n)	Cu	Ni	
	(ppm)	(ppm)		(%)	(%)	
Blank	0.946	12.36	117.71	-	-	
BPBT	0.085	0.926	87.44	91.00	93.36	
OPBT	0.051	0.34	60.06	94.61	97.24	

The change in  $R_{ct}$  and  $C_{dl}$  values was caused by the gradual replacement of water molecules by the chloride ions of the sea water and adsorption of the substituted BTA molecules on the metal surface, reducing the extent of dissolution [21]



Fig.2. Nyquist diagram of cupro-nickel alloy in natural sea water containing optimum concentration of BPBT and OPBT after immersion of 72 hours

## Accelerated leaching studies (ICP-AES)

n

The results of solution analysis and the corresponding denickelification factor (n) in the presence and absence of benzotriazole derivatives at their optimum concentration level in natural sea water for cupro-nickel alloy are given in Table 6. The denickelification factor (n) was calculated using the relation.

$$= \frac{(Ni/Cu)_{sol}}{(Ni/Cu)_{allov}}$$

Where, the ratio  $(Ni/Cu)_{sol}$  is determined from solution analysis and  $(Ni/Cu)_{alloy}$  is the ratio of weight-percent in the alloy.

From the table, it can be observed that both copper and nickel were present in the solution whereas in the presence of inhibitors, which are able to minimize the dissolution of both copper and nickel. The data recorded in tables illustrate that the percent inhibition efficiency against the dissolution of nickel was correspondingly high as compared to the dissolution of copper. This indicates the excellent inhibition efficiency of inhibitors to prevent the denickelification of cupro-nickel alloy in natural sea water, which is also reflected in the values of denickelification factor. Among the inhibitors studied, OPBT shows highest inhibition efficiency in the dissolution of cupronickel alloy in natural sea water. The percent inhibition efficiency against the dissolution of Ni was correspondingly high i.e. 97.24% can be achieved in the presence of OPBT containing natural sea water for cupro-nickel alloy, indicating that the preferential dissolution of nickel was almost completely minimized.

## Scanning Electron Microscopy

SEM investigations were carried out to verify whether the studied inhibitors, BPBT and OPBT are adsorbed on the alloy surface. The SEM micrograph for cupro-nickel alloy surface in the absence and presence of optimum concentration of benzotriazole derivatives are shown in Figure 3(a,b and c). The micrographs of the surface after polarization experiment are analyzed. The alloy surface in the absence of inhibitors was found to be severely affected in seawater (Fig. 3a). The metallic surface seems to be not affected by corrosion in the presence of

BPBT and OPBT inhibitor molecules (Fig. 3 b and c). At the optimum concentration of the inhibitors, the surface is covered by a thin film of inhibitor which effectively controls the dissolution of the alloy. A comparison of SEM micrographs obtained in the absence and in the presence of the BPBT and OPBT molecules reveals a significant inhibiting effect of these compounds.



(c)

(3) SEM images of Cu/Ni (90/10) alloy in the absence (a) and the presence of BPBT (b) and OPBT (c)

#### Conclusions

1. Both BPBT and OPBT show good inhibition efficiency in natural sea water. The %IE of OPBT was higher than that of BPBT.

2. The polarization studies indicated that the inhibitor considerably shifts the corrosion potential to less negative values and greatly decreases the corrosion current density. These studies give valuable information regarding Cu-Ni (90/10) alloy in the absence and presence of BTA derivatives, which is proved to be a mixed inhibitor, predominantly anodic in nature.

3. Electrochemical impedance spectroscopy shows that  $R_{ct}$  values increase, while  $C_{dl}$  values decrease in the presence of BPBT and OPBT.

4. Solution analysis reveals that the BPBT and OPBT excellently prevent the denickelification of cupro nickel alloy in natural sea water.

5. SEM studies confirm the presence of protective BTA film on the alloy surface.

#### References

[1] R. W. Cahn, P. Hassen, and E. J. Kramer, *Materials Science* and *Technology*, *A comprehensive Treatment, Structure and* 

Properties of Non-Ferrous Alloys, vol. 8, VCH, New York, NY, USA, 1996.

[2] E. G. West, *Copper and Its Alloys*, Ellis Horwood Ltd., Halsted Press, New York, NY, USA, 1982.

[3] B. Todd and P. A. Lovett, "Marine engineering practice: selecting materials for seawater systems," Tech. Rep., Institute of Marine Engineers, London, UK, 1976.

[4] C. A. Powell, "Marine applications of copper-nickel alloys, section 1: copper-nickel alloys-resistance to corrosion and biofouling," Tech. Rep., Copper Development Association, Potters Bar, UK, 1998.

[5] F. Mansfeld and B. J. Little, *Electrochimica Acta*, 1992, 37,2291.

[6] C. Kato, B. G. Ateya, J. E. Castle, and H. W. Pickering, *Journal of the Electrochemical Society*, 1980, 127,1890.

[7] R. F. North and M. J. Pryor, Corros. Sci, 1970, 10, 297.

[8] P.R.P. Rodrigues, A.H.P. De-Andrade and S.M.L. Agostinho Br. Corros J., 1998, 33, 211.

[9] R.F.V. Villamil, Corio P., J.C. Rubim and S.M.L. Agostinho J. Electroanal. Chem., 1999,472, 112.

[10] A.M. Fenelon and C.B. J. Breslin Appl. Electrochem., 2001, 31, 509.

[11] V. Otieno-Alego, G.A. Hope, T. Notoya and D.P. Schweinsberg (1996), Corros. Sci. 1996, 38, 213.

[12] N. Huynh, S.E. Bottle, T. Notoya and D.P. Schweinsberg, 2000. 42, 259.

[13] D. Zhang, L. Gao and G. Zhou, Appl. Surf. Sci., 2004, 225, 287.

[14] F.M. Al-Kharafi and B.G. Ateya, J. Electrochem. Soc., 2002, 149, 206.

[15] R. Ravichandran, S. Nanjundan and N. Rajendran, Appl. Surf. Sci., 2004, 236, 241.

[16] Adesh Dubey, S.K. Srivastava and S.D. Srivastava. Analele UniversităŃii din Bucuresti – Chimie (serie nouă), 02, 115.

[17] M. G. Fontana, "Corrosion Engineering," 3rd Edition, McGraw-Hill Book Company, New York, 1987.

[18] B. Ramesh Babu and R. Holz, British Corr. J, 2000, 35, 204.

[19] SSA. El-Rehim, and MAM.Ibrahim, J. Appl. Electrochem. 1999, 29, 593.

[20] R. Ravichandran, S.Nanjundan, N. Rajendran, J. Appl. Electrochem. 2004, 34,1171.

[21] S.Muralidharan, J. Electrochem. Soc. 1995, 142, 1478.

### Acknowledgement:

The authors wish to thank UGC, New Delhi for financial support.