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Corrosion and Corrosion Control of Copper by N-BTA in Storage and Atmospheric Environment by Electrochemical Technique

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Abstract

A simple modified accelerated corrosion test so called Oddy test has been devised to evaluate the corrosivity of showcase construction materials on copper and other artefacts in storage and display. This paper focuses on examining treatment of copper in situ to atmospheric environment by potentiodynamic polarization and electrochemical impedance techniques. The study confirms that nBTA coating on copper acts as mixed type of inhibitor which provides protection in accelerated corrosive environment.

Keywords: Corrosion inhibition; Copper; Electrochemical measurement

1. Introduction

In both storage and display, the processes of corrosion may threaten the stability of metal artefacts. In an enclosed area such as a display case, the concentration of slowly releasing gaseous compounds such as carbonyl sulphide or ethanoic (acetic) acid can reach to appreciable levels and accelerate deterioration of certain metal artefacts,. “Oddy test” has been used for over twenty years for testing the suitability of material for storage and display [1, 2]. The modified accelerated test assesses the impact of off-gassing on collection items being stored or displayed. The test relies on to the degree of corrosion by observing the changes in colour and appearance of the metal coupons. If the tested material visually appears more corroded or oxidized than the blank, then the material normally fails. This corrosion information is an indicator of whether the off-gas vapours from the storage materials will cause chemical degradation of an artefact in the same exhibit case or in storage. Electrochemical methods are widely applied in corrosion science, including the conservation of cultural heritage and metallic artifacts [3-10]. The use of treatments and analytical techniques is significantly constrained as the objects under investigation are unique and precious. As a consequence, all conservation/preservation methods (e.g., cleaning, coating etc.) need to be understood thoroughly (ideally before first use), and preferably to be non-invasive and reversible. It is common practice to provide protective coating on metal artifacts after remedial conservation. Now, the interest for those methods has also increased in the context of the preservation of cultural heritage especially ancient metals since they are usually treated in uncontrolled environmental conditions. Several workers have employed electrochemical impedance spectroscopy (EIS), a very sensitive, rapid and nondestructive method to evaluate the performance of coatings applied to oxidizable metals [11-15]. To illustrate the electrochemical methodology that can be used in the field of the conservation of ancient metallic artifacts we plan to study the characteristics of Benzotriazole (BTA) coating, prepared from its neutral aqueous solution, on copper metal.

BTA is known as effective corrosion inhibitors for copper and its alloys in a wide range of environments [16-20]. The addition of BTA to aqueous acidic, neutral and alkaline solution is commonly used and has significantly reduced corrosion [21, 22]. Several studies on the interaction and the characterization of copper compounds have been reported [23]. Transition metal complexes having benzotriazole as a ligand [24, 25] have also been synthesized and characterized by single-crystal diffraction studies [26, 27], found that a neutral solution of BTA (nBTA) is an excellent corrosion inhibitor for lead and have been used to prevent corrosion in ancient bronze sculpture. But characteristics of nBTA coating have not been studied so far. The aim of the present work is to investigate the inhibition effect of neutral benzotriazole coating (nBTA) on copper in storage by accelerated ageing test and atmospheric environment by potentiodynamic polarization and electrochemical impedance techniques.

2. Experimental

2.1. Material

Materials used for the study were copper (99.98% purity) substrates cut from a piece of copper plate. The substrates were polished with a series of emery papers, followed by thorough rinsing in acetone (Qualigens Fine Chemicals, India) and dried [28, 29]. All the reagents used for the study were analytical grade (AR) and doubled distilled water was used for solution preparation.

2.2. Inhibitor Preparation

Neutral BTA solution (1.0%) was prepared by adding 1.0 g of solid calcium carbonate to 100 ml of BTA solution with occasional stirring. The solution was filtered after 6 h when it attained pH 7.0.

2.3. Accelerated Ageing test

Modified accelerated “Oddy test” method is used for visual observation and weight loss measurements of copper in the absence and the presence of inhibitor [1]. The experiments were carried out in tight fitting jars in the presence and absence of inhibitor for continuously 28 days at 60 ^oC and 100% relative humidity. A 20 ml pyrex glass beaker which holds testing material i.e. ply board (Kitply industries, India) of 25 x 10 mm (0.70 g/cm^3 density) and metal coupons of 2.5 x 10 x 0.025 cm dimension folded in ‘V’ shape to an included angle of 15 to 20 degree set on the rim of the beaker (Fig. 1a).


(a) (b) (c)

Figure 1. Setup for accelerated ‘Oddy test’: **(a)** Beaker which holds ply board and metal specimen in ‘V’ shape set on the rim, **(b)** Beaker placed in the jar which contain distilled water and **(c)** Final setup which is tightly sealed with parafilm.

The beaker is placed in flint glass jar, 6 cm in diameter x 5.4 cm high, with a volume of 221 ml which contain 3 ml distilled water (Fig. 1b). This wide-mouthed jar is covered with a screw cap which is equipped with flexible inner lining of Teflon fluorocarbon resin for tight fitting. Finally, the setup was sealed externally with a ‘heat shrink’ Parafilm® M (GMBH CO., Germany) collar to achieve a tight seal and retain humidity. The set up contains uncoated copper coupons coated copper coupons (with 2% nBTA (neutral benzotriazole)) (Fig. 1c). After 28 days, the specimen was removed for visual inspection and then washed, dried and then weighed. The inhibition efficiency was calculated from the corrosion rate data using the equation:

$$(\%)IE = \frac{CR_o - CR_i}{CR_o} \times 100 \qquad (1)$$

where CR_o is weight loss value in absence of inhibitor and CR_i is the weight loss in presence of inhibitor.

2.4. Electrochemical measurements

The electrochemical studies were made using a three-electrode cell assembly at room temperature. The working electrode was a copper of above composition of 1 cm^2 area and the rest being covered by using commercially available lacquer. A platinum foil of 1 cm^2 was used as counter electrode and saturated calomel electrode as reference electrode. The working electrode was polished with different grades of emery papers, washed with water and degreased with acetone. The corrosive medium used as reference in electrochemical experiments was the ASTM D 1384-87 solution [30-32] with following composition: 148 mg/l Na_2SO_4, 138 mg/1 $NaHCO_3$ and 165 mg/1 NaCl. The 2% of nBTA solution were made in the ASTM medium and their pH was adjusted to 8. All electrochemical measurements were carried out using a Gamry Potentiostat/Galvanostat (Model G- 300) with EIS software Gamry Instruments Inc., USA. Before the electrochemical measurement, a stabilization period of 30 min was allowed, which was proved to be sufficient to attain a stable value of E_{corr}. Potentiodynamic polarization studies were carried out at a sweep rate 1.0 mVs^{-1} to study the effect of inhibitor on copper. The polarization curve for copper specimen in the test solution were recorded from -0.25 to 1.3 V. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (icorr). The inhibition efficiency was evaluated from the measured icorr values using the relationship:

$$(\%)IE = \frac{I^{o}{}_{corr} - I^{i}{}_{corr}}{I^{o}{}_{corr}} \times 100 \qquad (2)$$

where I^o_{corr} and I^i_{corr} are corrosion current value in the absence and presence of inhibitor.

The impedance studies were carried out using ac signals of 10mV amplitude for the frequency spectrum from 100 KHz to 0.01 Hz. The charge transfer resistance values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values using the following equation

$$(\%)IE = \frac{R^{i}{}_{ct} - R^{o}{}_{ct}}{I^{i}{}_{ct}} \times 100 \qquad (3)$$

where R^o_{ct} and R^i_{ct} are the charge transfer resistance in absence and presence of inhibitor, respectively.

3. Results and Discussion

3.1. Weight loss measurements

The values of corrosion rate (CR, $mmyear^{-1}$), inhibition efficiency (%IE) and weight loss ($mg\ cm^{-2}\ h^{-1}$) obtained from weight loss measurements for copper in ASTM D 1384-87 solution in the absence and presence of nBTA were summarized in Table 1. The inhibition efficiency (%IE) and corrosion rate (CR, $mmyear^{-1}$) were calculated as described previously [33]. The visual inspection revealed that the coupons without coating show slight tarnishing reveal that the plywood material causes corrosion, suitable only for temporary use. The coating of nBTA proved to be effective, retard corrosion and suitable for copper and other artefacts in storage and display.

Table 1. Weight loss parameter, inhibition efficiency, and corrosion rate of copper obtained by accelerated 'Oddy test' measurements at 60°C and 100% relative humidity for 28 days

System	Weight loss (10^{-5} gm^{-2}h^{-1})	Corrosion rate (mmpy x 10^{-3})	Inhibition efficiency (%)
Copper without coating	29.23	25.60	-
Copper with 2 % nBTA coating	1.99	1.74	93.20

Table 2. Observation of copper surface of accelerated 'Oddy test' after 28 days kept at 40 °C and 100% relative humidity

System	Visual observations
Copper without coating	Corroded and surface covered with patches of brownish spots
Copper with 2 % nBTA coating	No corrosion; bright surface

3.2. Potentiodynamic polarization measurements

In this work the effectiveness of nBTA with different immersion time 2 h, 24 h, 48 h and 72 h in ASTM D 1384-87 was determined from potentiodynamic polarization curves of the copper (Fig. 2). The values of the E_{corr}, I_{corr}, Tafel slopes β_a, β_c and polarization resistance (R_p) and inhibition efficiency (%IE) obtained from these measurements are summarized in Table 3.

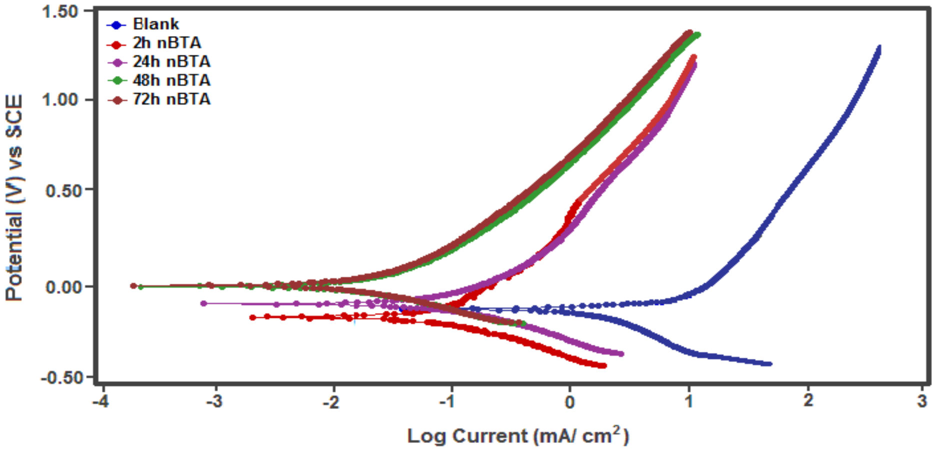


Figure 2. Potentiodynamic polarization curves for Cu in atmospheric environment inhibited with nBTA with various immersion period

Table 3. Potentiodynamic polarization parameters for copper in ASTM D1384-87 in the absence and presence of 2% nBTA at different exposure time

System	E_{corr} (mV vs SCE)	I_{corr} (mAcm^{-2})	β_a (mV/decade)	β_c (mV/decade)	IE (%)
Blank	-92.28	.847	40.2	98.1	-
2h nBTA	-141.0	.066	166.4	109.6	92.20
24h nBTA	-69.90	.051	271.6	139.6	94.01
48h nBTA	23.40	.032	408.9	226.5	96.23
72h nBTA	29.20	.031	465.3	244.1	96.30

From the corresponding polarization curves presented in Figure 2, it is implied that E_{corr} value changes slightly in the positive direction in presence of nBTA i.e., toward more noble direction, the displacements are less than 85 mV/SCE it shows that compound act as mixed type inhibitors, the behaviour reveals that the anodic suppression plays a dominant role in this process [34]. The I_{corr} value decreases significantly, %IE of neutral BTA after 2h, 24h, 48h and 72 h immersion period were found to be 92.20%, 94.01%, 96.23% and 96.30%, respectively (Fig. 2). At low concentration, the protective layer mainly restrains the cathodic activity. At higher concentration, the higher concentration the layers extend over the entire metal surface so that the anodic copper oxidation reaction is markedly inhibited [35]. The BTA [35, 36] and more likely nBTA form a protective polymeric complex at high pH and noble potential.

3.3. Electrochemical impedance measurement

Impedance measurements on Cu in ASTM D 1384-87 alone and in the presence of nBTA at different immersion time 2 h, 24 h, 48 h and 72 h were summarized in Table IV. Fig. 3a & b shows Bode plots, log |Z| vs. log f and phase vs. log f (|Z| = modules of impedance, f = frequency in Hz) of bare copper in ASTM D1384-87 solution.

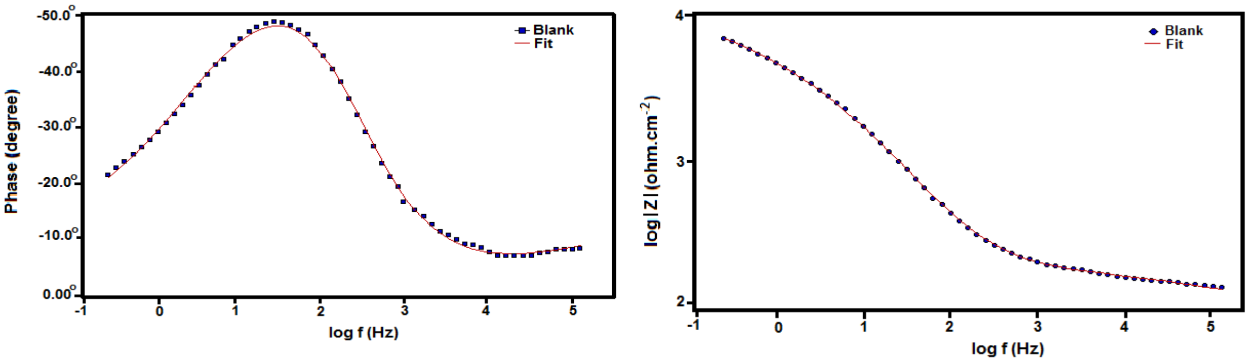


Figure 3. Bode diagrams recorded in ASTM D1384-87 solution for Cu **(a)** Bode phase plot and **(b)** Bode amplitude plot.

Table 4. Impedance parameters for Cu in ASTM D1384-87 87 in the absence and presence of 2% nBTA at different exposure time

System	R_s (Ω/cm^2)	Q_1 (F/cm)	n	R_f (Ω/cm^2)	R_{ct} (Ω /cm^2)	Q_2 (F/cm)	n	%IE
Blank	86.2	4.32. $x10^{-5}$	.740	106.6	8.9 $x10^{3}$	1.13 $x10^{-4}$	.435	-
2h nBTA	96.4	5.74 $x10^{-6}$	.803	192.5	$393x10^{3}$	1.03 $x10^{-5}$	.624	95.47
24h nBTA	132.2	1.74 $x10^{-6}$	.877	311.0	$110x10^{4}$	1.19 $x10^{-6}$	.629	98.29
48h nBTA	164.3	1.63 $x10^{-6}$	.846	215.7	$169x10^{4}$	7.37 $x10^{-6}$	.660	99.47
72h nBTA	169.2	1.59 $x10^{-6}$	.848	234.4	$228x10^{4}$	8.20 $x10^{-6}$	.687	99.60

The equivalent circuit used for the impedance study is shown in Figure 4, the symbol R_S is solution resistance, Q1 is interfacial capacitance, R_f is the resistance of the film formed on copper surface, R_{ct}, charge transfer resistance. Q_1 is composed of the membrane capacitance CPE_f and the deviation parameter n_1 and Q_2 is composed of the double layer capacitance CPE_{dl} and the deviation parameter n_2. Such a general constant phase element is described by an empirical impedance function of the type

$$Z\,(CPE)=\left[Y_o\,(j\omega)^n\right]^{-1} \qquad (4)$$

Where Y_o is the CPE constant ω is angular frequency (in rad s^{-1}), where j is imaginary number, and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [37]. Depending on the value of n, CPE can represent resistance ($n = 0$, $Y_o = R$), capacitance ($n = 1$, $Y_o = C$), inductance ($n = -1$, $Y_o = L$) or Warburg impedance ($n = 0.5$, $Y_o = W$)

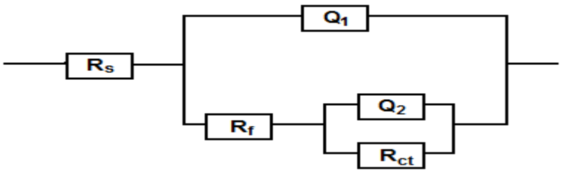


Figure 4. The equivalent circuit model used to fit the EIS experiment data.

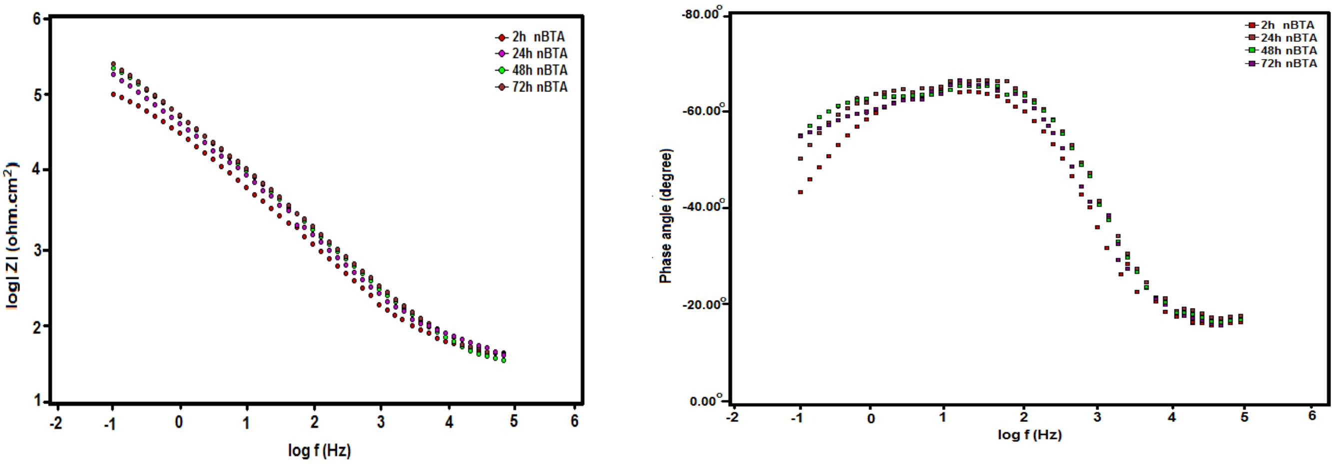


Figure 5. Bode diagrams recorded in ASTM D1384-87 with nBTA for Cu for different immersion period **(a)** Bode phase plot and **(b)** Bode amplitude plot.

The Bode plots show resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region (horizontal line and a phase angle ≈0°) at low frequencies (Fig. 5a & b).These plots show two overlapped phase maxima at intermediate and higher frequencies. Adsorption film resistance (R_f) ranged among 192.5 Ω/cm^2 (2h) and 234.4 Ω/cm^2 (72h), showing a significant improvement of the quality of the adsorbed film with increasing immersion time. The values of n_1 were found in the 0.80–0.85 interval, suggesting that the adsorbed film was relatively homogeneous. These findings showed that the inhibitor can increase the resistance of the corrosion products layer due to its incorporation into this layer as suggested by R_f values. The values of n_2 were found in the 0.60–0.68 interval, with increase in immersion time from 2h-72h which was a typical behavior for the impedance of a transport mass controlled reaction [38]. The influence of nBTA on the impedance spectra of copper with different immersion time is presented in Fig. 6, as Nyquist which is the plot of real part vs. imaginary part of impedance. Both the capacitative and low frequency resistive regions of impedance shift to higher values with the increasing immersion time of the inhibitor. The Nyquist plots (Fig. 6) shows a depressed semicircular shape; this behavior is typical for solid metal electrodes that show frequency dispersion of the impedance data. Table 4 shows that the R_{ct} value increases with increase in immersion time i.e., from 2h-72h in presence of nBTA. %IE value reaches the maximum 99.60 at 72h immersion time. Thus to prevent corrosion in copper in atmospheric environment, the charge transfer resistance has been greatly inhibited in presence of inhibitor. Compared with the blank the R_f value with the inhibitor also increases obviously which reveals that a more protective adsorption film is formed on copper surface. It is also shown in Table 4, that the Q_1 and Q_2, the constant phase element value decreases with the increase in immersion time, this can be explained by increase in the adsorption film area of inhibitor due to adsorption and thus it reduces the capacitive effect [39].

4. Mechanism of Corrosion Inhibition

The mechanism of corrosion inhibition of copper with nBTA is very much similar as BTA. Benzotriazole is one of the effective corrosion inhibitors for Cu and its alloys. It is effective in preventing copper corrosion under stationary as well as dynamic conditions. Its inhibitory effectiveness increases with time of immersion. It was shown that BTA acts as a mixed type inhibitor, but its predominant effect is on inhibition of anodic reaction. Xue and Ding [40] studied the adsorption mechanism of BTAH (benzotriazole) on Cu in pH 6. Under stationary conditions, adsorption rather than complex formation was suggested, whereas under dynamic conditions the formation of mixed Cu(I)BTA and $Cu(II)(BTA)_2$ polymeric complexes was proposed. The proposed structure of the Cu(II)(BTA)$_2$ complex is shown in Fig. 7a. The neutral BTA (nBTA) forms a polymeric chain with pairs of oxo bridges among metal centres Fig. 7b. Furthermore, the Vander waals interactions stabilizes the crystal structure with its polymeric assembly of aromatic surfaces. This might provide a protective coating on the copper surface, thus preventing corrosion.

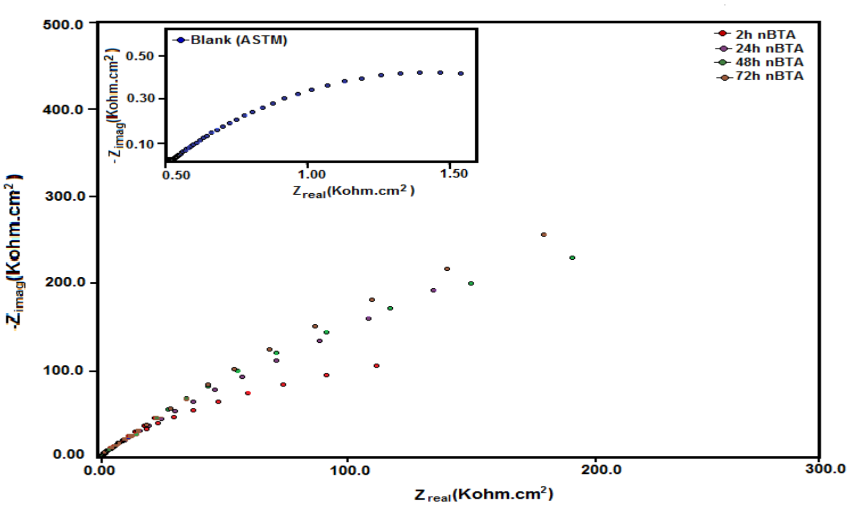
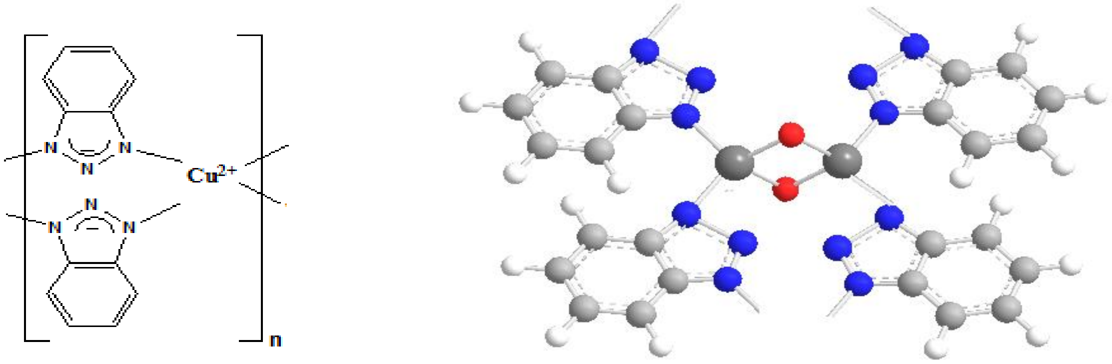


Figure 6. Nyquist impedance plot recorded in ASTM D1384-87 with nBTA for Cu for different immersion period



(a) (b)

Figure 7. (a) Cu(II)(BTA)$_2$ structure proposed by Xue and Ding (1990); **(b)** The proposed polymeric chain of nBTA with pairs of oxo-bridges between metal centres.

Conclusion

1. The modified “Oddy test” proves to be an indicator of whether the off-gas vapours from the storage materials will cause chemical degradation of an artefact in storage and display.
2. Neutral-BTA found to be more suitable as an inhibitor for copper corrosion in storage as well as in atmospheric environment.
3. Electrochemical studies reveal that the corrosion inhibition mechanism of n-BTA, is much similar to benzotriazole and n-BTA also behaves as mixed type corrosion inhibitor.

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