



## **Evaluation of the best corrosion inhibitors used with copper artifacts to protect the silver artifacts**

**Y. Salem\***

**\*Conservation Department, Faculty of Archaeology, South valley Uni.,Qena,Egypt.**

**Abstract :** The research aimed to evaluate the efficiency of three compounds from preferred corrosion inhibitors of copper artifacts to be used to protect silver artifacts. The compounds are Benzotriazole (BTA), L-methionine (Met.) and Sodium decanoate (NaC<sub>10</sub>), each inhibitor was tested with and without Nano-alumina. The evaluation of these compounds was performed using the electrochemical measurements (Potentiodynamic (pt) and Electrochemical Impedance Spectroscopy (EIS)) and accelerated corrosion test with H<sub>2</sub>S gas and water resistance test within enclosed chamber. The treated silver coupons with studied inhibitors were examined using microscopes SEM, PM and AFM to appear some important features of the formed film. The study was carried out on manufactured coupons of the silver alloy with copper. The results revealed that BTA and NaC<sub>10</sub> in presence and absence Nano-alumina have good efficiency in the protection of the silver coupons in the corrosion conditions used in the tests.

**Keywords :** the efficiency, Benzotriazole, silver artifacts, Accelerated aging and AFM.

### **Introduction**

Although silver artifacts are found in most museums and most of the ancient coins are made of silver as a main metal, Silver did not have enough studies in order to find and evaluate protective compounds to prevent silver tarnishing in the future. The studies were few in both corrosion inhibitors and protective coatings. So survey of protective compounds, either used in museums or its efficiency was studied but not used with artifacts yet, revealed that there are only two protective compounds of silver artifacts; the hexadecane-thiol [1-3] and paraloid [3-8]. In my knowledge, the hexadecane-thiol (C<sub>16</sub>H<sub>33</sub>SH) is the only corrosion inhibitor which was evaluated and presented for silver artifacts, however, almost no reference documents of its use in museums. Paraloid (72, 44) as acrylic coatings were the most evaluation from the protective coatings for silver artifacts. And most recently studies to protect the silver artifacts included the improvement of the efficiency of these two coatings by using Nano-alumina [2, 8]. Other coatings such as waxes, resins and lacquers were used in museums but currently are less used [8].

Most studies presented for the protection of metallic cultural heritage were conducted on copper and bronze artifacts that are due to the use of copper and its alloys in many modern industrial purposes. So, many non-specialist researchers in the archaeological field presented many organic inhibitors to protect Copper surfaces used for this purpose. Conservators have benefited from some these compounds and studied their

**Y. Salem /International Journal of ChemTech Research, 2018,11(08): 314-324.**

DOI= <http://dx.doi.org/10.20902/IJCTR.2018.110840>

properties and features to guarantee that they are qualified to be used with archaeological surfaces. These properties are: Visual appearance especially transparency, chemical stability, color stability, Long term efficiency, corrosion resistance, non-luster or shine and easy to apply [9]. Consequently, copper and their alloys have many corrosion inhibitors in most various copper corrosion environments in contrast to silver artifacts. Also surveys of copper protection compounds showed that there are three compounds have the highest efficiency in most previous studies. Several other studies have agreed to its efficiency in the protection of copper artefacts. These Compounds are Benzotriazole, Sodium decanoate and L-methionine. Effectiveness of each compound was tested in comparative studies, as mentioned later, with many other compounds and each one revealed the best results in these studies. As a result of high inhibit properties of these three compounds, their good results revealed in previous studies and the suitable features of archaeological object, these inhibitors can be qualified to using with other artifact metals. So, the present study aimed to evaluate their performance with and without Nano-alumina as possible tarnishing inhibitors of silver artifacts. In our knowledge, there is no study conducted on these compounds with silver artifacts.

## 2. Experimental procedure

### 2.1. Corrosion inhibitors

#### 2.1.1. Sodium decanoate $\text{CH}_3(\text{CH}_2)_8\text{COONa}$ and written as $(\text{NaC}_{10})$ .

Measurements of the polarization resistance and the corrosion potential ( $E_{\text{corr}}$ ) of this compound as corrosion inhibitor were carried out in many previous studies of three of artefacts metals family: Lead [10-12], Iron [13] and Copper [14, 15]. In all these cases gave very satisfactory results.

#### 2.1.2. Benzotriazole ( $\text{C}_6\text{H}_5\text{N}_3$ ); (BTA)

Benzotriazole is used for nearly 50 years for stabilization of copper artefacts and their alloys. Since then, it has become the most common of copper artefacts. many laboratory studies were compared BTA with some traditionally protective coatings and a new corrosion inhibitors in all these studies benzotriazole showed good efficiency as a good corrosion inhibitor and often presented the best results [16-20].

#### 2.1.3. L- methionine: (Met.)2-Amino-4-(methylthio) butanoic acid, $\text{CH}_3\text{S}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .

The efficiency of Met as good corrosion inhibitor of copper attributes to the strong banding between copper surface and the formed film. Increasing the interaction of the molecule with the metal surface is explains as result of the Nitrogen atom (heteroatoms) in met molecular which give electrons of vacant d orbitals in the atom of copper [21, 22]. Some recently laboratory studies were presented Met. as good corrosion inhibitor of copper [16] and steel [23-28] at different environments. It has important been suggested especially after comparing it with BTA and give best result but its use in museums not yet documented.

### 2.2. Preparation of The silver coupons and inhibitors solutions

Silver coupons should be similar to archaeological silver in chemical composition and thickness. The coupons were made by smelting of silver and copper in a crucible, more details in reference [16] and XRF analysis used to determine composition as in fig. (1). silver and copper in the resultant alloys was about 81% Ag, 9% Cu. About the preparation of the inhibitors solutions, 3 % Nano-alumina was suspended in acetone and ultrasonicated for 50 min, after that 15 wt. % inhibitor was added to the suspension and stirred with a magnetic stirrer. Three experimental coupons were treated with each compound by impregnation for 24 hours, then were dried in temperature room for 24 hour. Also untreated coupons were prepared. The as received suspension was applied on the silver specimen's surface by brushing [3, 5].

### 2.3. Potentiodynamic test

The electrochemical test was carried out using apparatus [potential potentiostats Galvanic (model 273 A) EG and G] with three electrode cell. Platinum was used as counter electrode, Silver Silver chloride [Ag/AgCl] as reference electrode and bronze coupons as a working electrode. Scan rate was  $5\text{ mV s}^{-1}$  and the solution of was 50 ml. All experiments were performed at temperature room [29-31]. The test carried out in the corrosive media was ASTM D1384-87 (ASTM solution) standard solution as simulation of the corrosive environment in atmospheric corrosion of the archaeological metals, solution has the following composition:  $148\text{ mg l}^{-1}\text{ Na}_2\text{SO}_4$ ,  $138\text{ mg l}^{-1}\text{ NaHCO}_3$  and  $165\text{ mg l}^{-1}\text{ NaCl}$  with tap water [12, 13, 32-33].

## 2.4. The second test electrochemical impedance spectroscopy (EIS)

Measurements were done at room temperature according to the procedure described in ASTM G-5-93 standard [13], at the OCPs by applying a 10-mV sinusoidal potential through a frequency domain from 35 kHz down to 100 mHz. The electrochemical measurements were performed using an IVIUMSTAT potentiostat-galvanostat operated under computer control. Electrochemical measurements were carried out in 0.6M NaCl electrolyte at room temperature ( $25 \pm 1$  °C), using a three-electrode electrochemical cell. Before The reference electrode that all potentials are referred was Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup> saturated calomel electrode (SCE) of  $E_0 = 240$  mV versus reference hydrogen electrode (RHE) and platinum wire was used as counter electrode. The inhibition efficiency is calculated from the EIS data using the following equation:  $I_{EIS} (\%) = [(R_p - R_0)/R_p] \times 100$  (1). Where  $R_p$  and  $R_0$  are the polarization resistances of treated and untreated coupons. [34]

## 2.5. Microscopic Examination

The following aspects can be revealed with the microscopic examination:

- The bonding rate between the inhibitor film and coupons surface.
- The shape, distribution, density, the adsorption level, coverage and thick of the products molecules.
- Some disadvantages of inhibitor layer can be appeared such as Cracks, fissures, discoloring, the porosity, hazing, peeling and blistering.
- The microscopic investigation reveals the changes of the morphological surface after treatment with protective products.

Therefore microscopic examination an effective way can be used for the evaluation of corrosion inhibitors and can be interpreted their performance. The microscopic examination was done using Scanning Electron Microscope and an Olympus BX51 polarized light microscope with an Olympus DP70 camera. The topography studies of the protected silver coupons carried out with an AFM (Model: Wet – SPM9600 (Scanning Probe microscope), over an area of 5×5μm. Silicon cantilevers with integrated pyramidal silicon nitride tips. This tip has a typical resonance frequency of 288-328 kHz and a typical force constant of 20-80 N/m. A scan rate of 1.4-1.8 Hz, The software could be given two- and three-dimensional images.

### 2.6. Accelerated aging

Accelerated aging was performed in simple chambers that could be reproduced in any conservation laboratory. Two chambers were used; one was for the exposure of H<sub>2</sub>S and the other one was for the water resistance test.

#### 2.6.1. Accelerated corrosion with H<sub>2</sub>S gas

The protected coupons will exposed to H<sub>2</sub>S gas within climate chamber as most gaseous pollutant of deterioration of silver artifacts. In our knowledge, the evaluation of corrosion inhibitors and protective coatings using this test were only presented in two previous studies [3, 4]. Although this test is closest to simulate the damage factors in the atmospheric corrosion environment. There is other accelerated deterioration factors used inside enclosed chambers such as high relative humidity and temperature (84% RH and 38 °C) [10, 11], also an acetic acid-enriched solutions [11] as simulation for acidic vapors in cabinets and the wooden boxes. In the current test, the coupons will exposed to low concentration of H<sub>2</sub>S vapors (10 ppm) for 7 days [4]. The test chamber is made of 1000 cm diameter Perspex cylinder, humidification of the air and control of humidity were done by saturated solution of NaCl, Heating of the air inside the chamber is done by a cartridge heater, The air inside the chamber is continuously mixed by a fan which was suspended from the ceiling of the chamber, The temperature and relative humidity inside the chamber are continuously measured by datalogger device [35, 36]. The details of the test and the preparation of H<sub>2</sub>S are described in reference [37].

#### 2.6.2. The water resistance test

The evaluation of the inhibitor efficiency of the water resistance inside enclosed chamber is very important especially of archaeological metals inhibitors, because the humidity is basic deterioration factor in display and storage environment of artifacts metals. The mesodology of this test described in ASTM D2247-02 and ASTM

D1735-04 [38, 39], its parameters have been modified to be a more realistic of display and storage environment [16]. In this test the inhibitors resistance of humidity will test. The coupons will exposed to high relative humidity 80% at 38 C in an enclosed chamber. Since objects in museums and historic houses are not normally exposed to relative humidity higher than this degree, Desiccator (300 mm in diameter) was used as chamber and relative humidity was obtained using a saturated solution of potassium chloride. The test period was 72 h. The samples were evaluated by visual and microscopic examination.

### 3. Results and discussion

#### 3.1. Potentiodynamic results

The results of treated and untreated coupons were compared to determine the efficiency of each compound, then the comparison among all inhibitors to select the best. The general shape of the curves revealed very close together values of all samples in absence and presence Nano-alumina Fig. [1]. The difference between highest resistance and least resistance is .105 mv and all values were limited between -.390 to -.180 mv Fig. [2]. The inhibitive performance of all inhibitors towards the silver corrosion is very good. The best results was obtained from Nano-NaC<sub>10</sub>, it recorded the corrosion potential ( $E_{corr}$ ) at (.315) mv and has the highest difference of the corrosion potential ( $E_{corr}$ ) between treated and untreated coupons. BTA was in the second rate and recorded difference of ( $E_{corr}$ ) (.290) mv. The order of the inhibitive effectiveness according to follows the sequence NaC<sub>10</sub> with Nano-alumina > BTA (290) > BTA with Nano-alumina (280) > Met. with Nano-alumina (245) > NaC<sub>10</sub> (240) > Met. (210). As shown in Figs. (3) and Table (1).

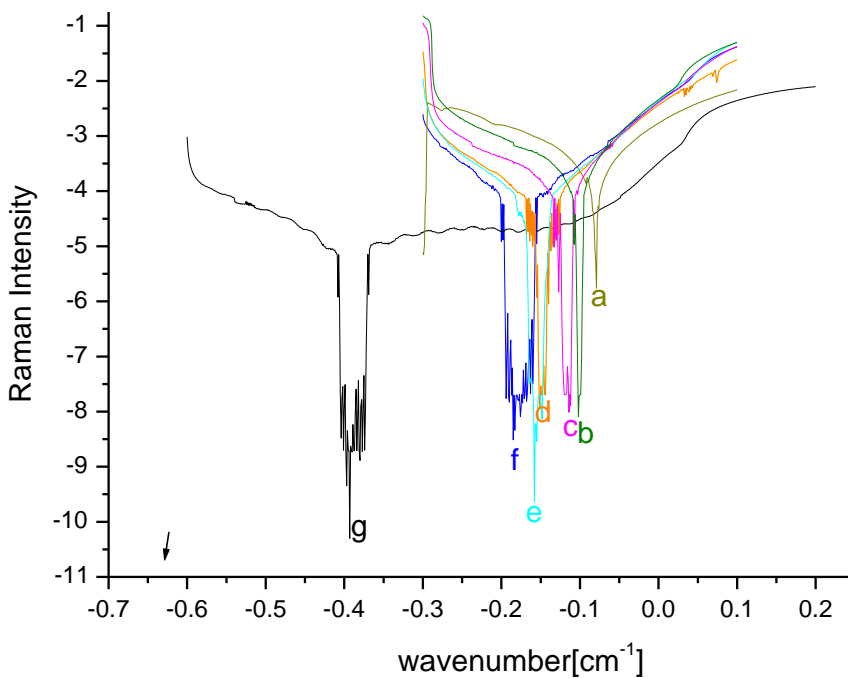
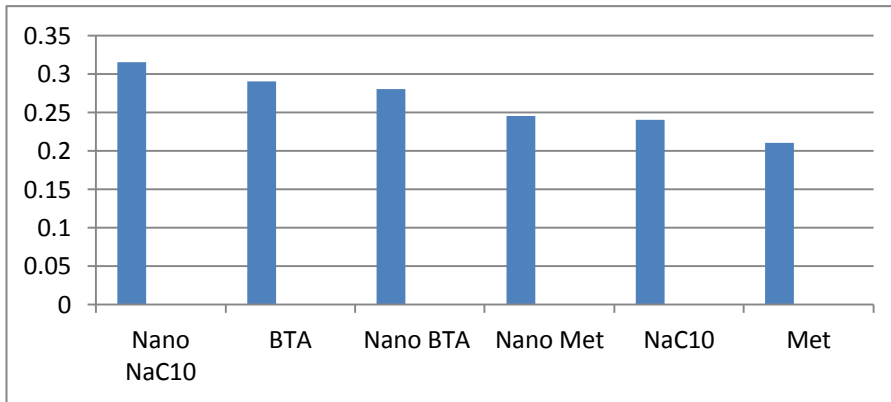


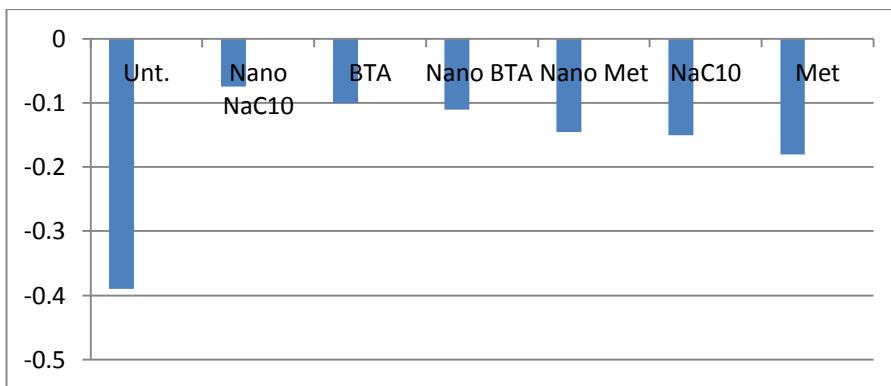
Figure 1: The potentiodynamic polarizing curves of treated and untreated Coupons: (a) NaC<sub>10</sub> + Nano-alu., (b) BTA, (c) BTA + Nano-alu., (d) Met. + Nano-alu., (e) NaC<sub>10</sub>, (f) Met., (g) untreated.

Table 2: Corrosion potential ( $E_{corr}$ ) and the difference in ( $E_{corr}$ ) of treated and untreated coupons

Coupons	Unt.	NaC <sub>10</sub> +Nano- Alu.	BTA	BTA +Nano-A lu.	Met +Nano- Alu.	NaC <sub>10</sub>	Met
the corrosion potential ( $E_{corr}$ )	-.390	-.075	-.100	-.110	-.145	-.150	<b>-.180</b>
The difference in ( $E_{corr}$ )	--	.315	.290	.280	.245	.240	<b>.210</b>



**Figure 2: The difference in corrosion potential (E<sub>corr</sub> /mv.) of treated coupons in presence and absence nano-alumina.**



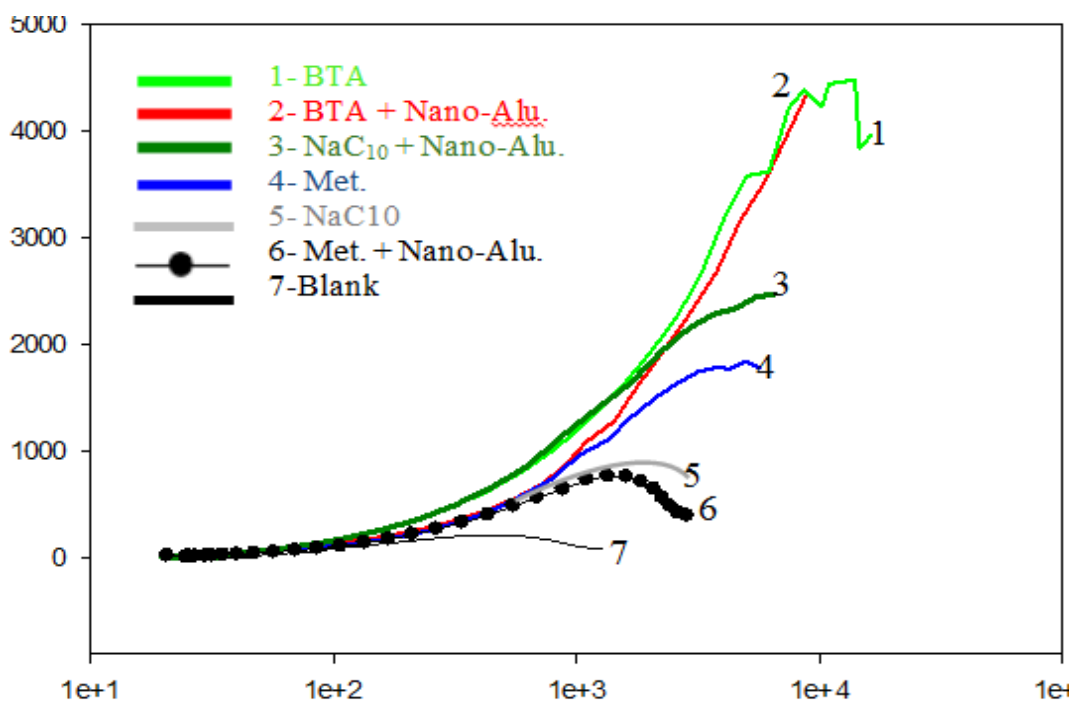
**Figure 3: Corrosion potential (E<sub>corr</sub>) of treated and untreated coupons.**

3.2. Electrochemical impedance spectroscopy (EIS)

The Bode plots of the untreated and treated coupons presented in Fig. 4, the polarization resistance values (Rp) are shown in Table 2. From this obtained data, clearly demonstrate that the corrosion rate of untreated silver is very low in 0.6 M NaCl solution. BTA without Nano-alumina shows very high resistance value and give the best result. NaC<sub>10</sub> and Met with Nano-alumina have low impedance as shown in Table (2). Clear improved in efficiency of NaC<sub>10</sub> after the addition of Nano-alumina while individually give very close value to the untreated coupons. The order of the inhibitive effectiveness follows the sequence BTA (9844) > BTA with Nano-alumina (4777) > NaC<sub>10</sub> with Nano-alumina (4662) > Met (4028) > NaC<sub>10</sub> (2628) > Met. with Nano-alumina (1839) MΩcm<sup>2</sup>.

**Table 2:**polarization resistance values (Rp) and The inhibition efficiency.

Coupons	Met	BTA	BTA	Met.	NaC <sub>10</sub>	NaC <sub>10</sub>	Blank
	+Nano- Alu.		+Nano- A lu.		+Nano- Alu.		
<b>Rp MΩcm<sup>2</sup></b>	1839	9844	4777	4028	4662	2628	823
<b>IE %</b>	55.2	91.6	82.8	79.5	82.4	68.6	--



**Figure 4:** Nyquist plot of inhibitors coupons in 0.6M NaCl solution with and without Nano-alumina.

### 3.3. Microscopic examination of treated coupons

The Microscopic examination showed that BTA and NaC<sub>10</sub> have good inhibitive features in both two phases. These aspects were clearly improved in presence Nano-alumina. BTA coupons with Nano-alumina showed a complete coverage and a dense layer as resulting of high adsorption rate as shown in AFM, SEM and PM images Figs 5a, b and 6a, b, K-n. PM reveals the formed film shape as dark layer on surface while SEM reveal a needle shape, 3D image AFM illustrated three-dimensional structures of the inhibitor particles. NaC<sub>10</sub> with Nano-alumina give very satisfactory results such as: the adsorption rate is very high, covering was complete and distribution level on surface was uniform as shown in Figs 5c, d and 6(c-f and o-r). The adsorbed molecules on surfaces of NaC<sub>10</sub> revealed as flowers shape, this shape appear in presence and absence Nano-alumina under PM and SEM. Met. in absence nano-alumina has a very low coverage and adsorption rate while with Nano-alumina a week improvement occurs but do not sufficiently covers to be protective as shown in Figs 5e, f and 6(g-j and s-v)., shape of Met. film appeared as black spots on the light silver surface in both two phases, the numbers of these spots on samples was more in absence Nano-alumina.

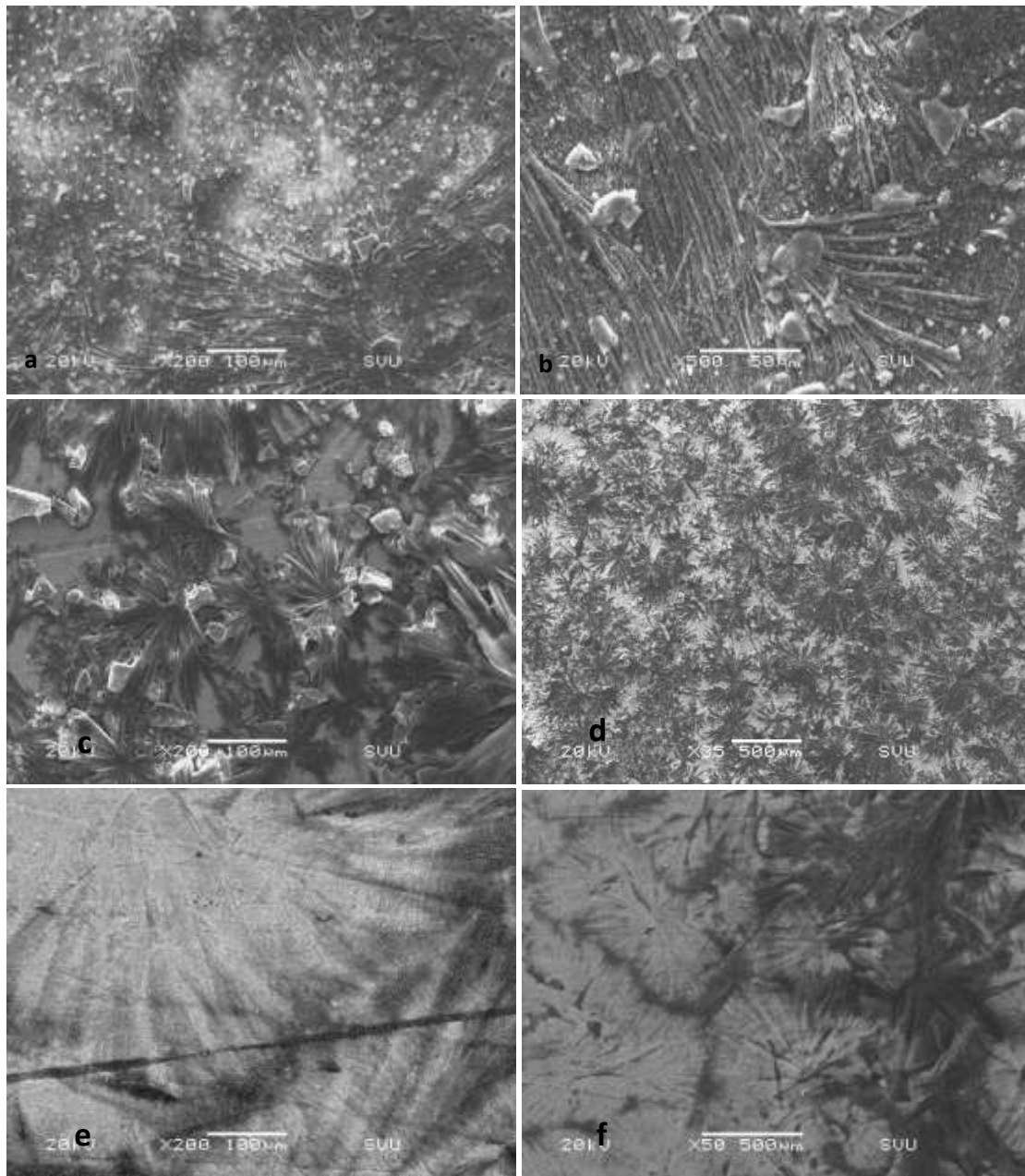
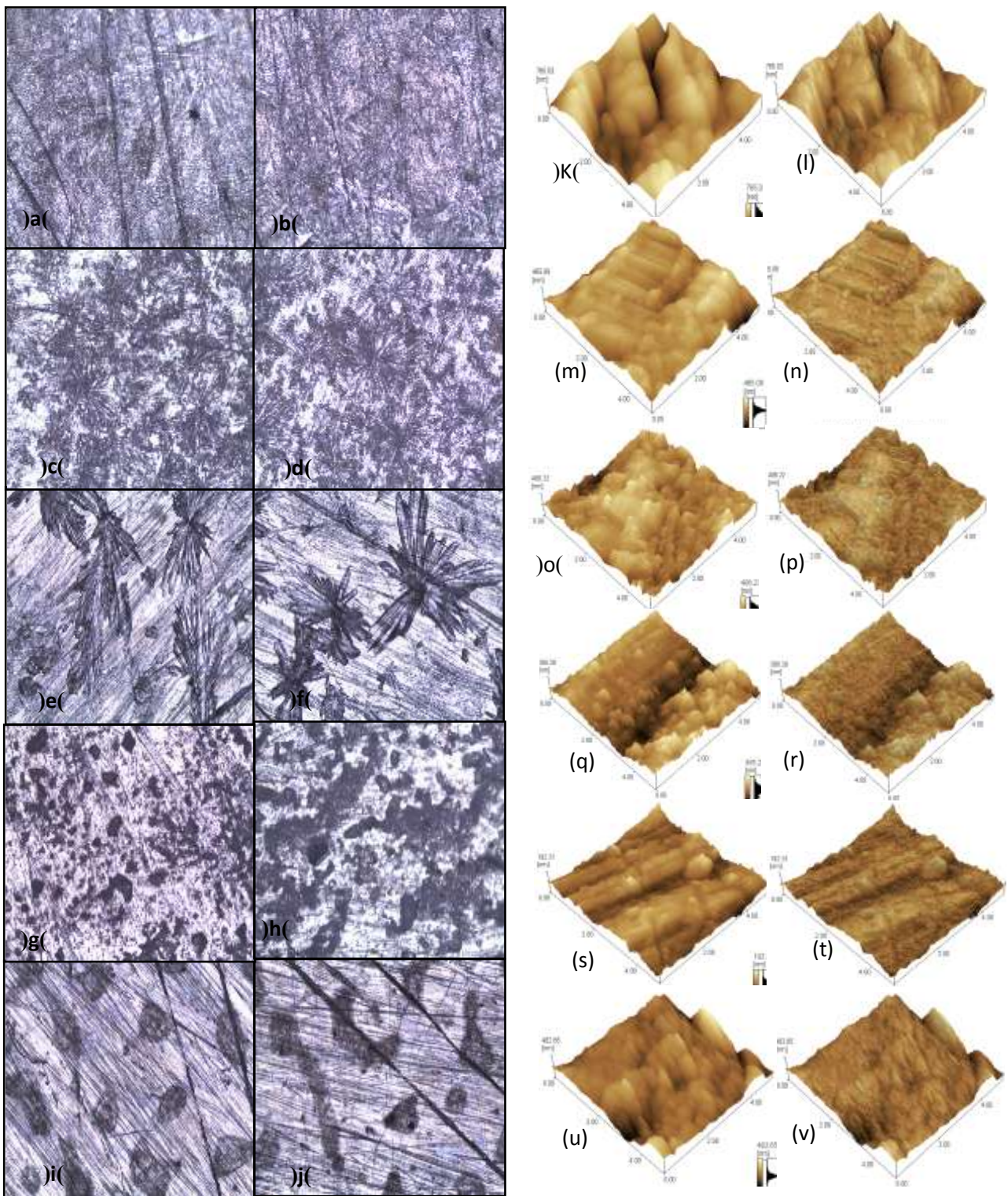


Figure 5: SEM of the three inhibitors with Nano-alumina, (a, b) BTA, (c, d) NaC10, (e, f) Met.



**Figure 6: PM and AFM topographic images for studied inhibitors. On the left PM, (a-b) Nano BTA, (c,d) NaC<sub>10</sub> + Nano-alu., (e, f) NaC<sub>10</sub>, (g, h) Met. + Nano-alu., (i, j) Met., on the right AFM, (k, l) BTA + Nano-alu., (m, n) BTA, (o, p) NaC<sub>10</sub> + Nano-alu., (q, r) NaC<sub>10</sub>, (s, t) Met. + Nano-alu., (u, v) Met..**

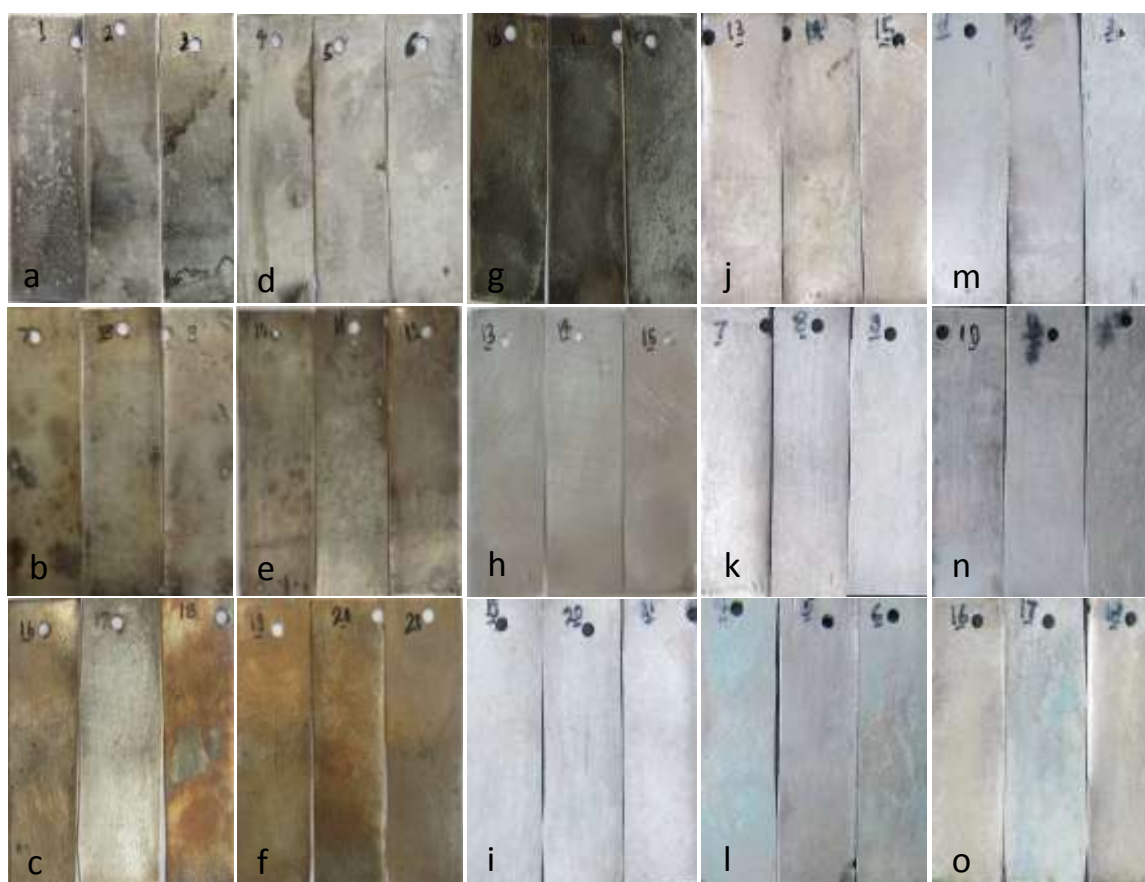


### 3.4. Accelerated Aging test

After test, inhibition properties were evaluated according to the change of the surface appearance especially the formation of black silver tarnishing. The samples were evaluated by visual examination. In H<sub>2</sub>S test, the change of surface appearance was varied as follow:

- The best result obtained from BTA with Nano-alu., resistance was very satisfactory and sufficient to prevent the reaction of H<sub>2</sub>S with surface silver, the samples showed less change in the surface appearance fig. 7d. The efficiency of BTA was less than BTA with Nano-alumina, because slight tarnishing appeared in the second coupons as in Fig. 7a.
- The coupons of Met. with and without Nano-alumina have similar appearance, the resistance was insufficient to prevent the reaction, the coupons covered with grey film and small black spots were spread to the surface as a result of the reaction, as shown in Figs. 7b, e.
- The coupons of NaC<sub>10</sub> in presence and absence Nano-alumina have medium resistance and the surface colored with yellowish color, as shown in Figs. 7c, f.
- The black silver tarnishing was clearly formed of untreated coupons, Fig. 7g.

The results of the water resistance test revealed that the coupons of silver alloy whether treated and untreated have high resistance against the influence of humidity and water. Very slight change occurred of the coupons surface, surface appearance after the test period was satisfactory of all samples as shown in Fig. 7(i-o). The coupons of BTA and NaC<sub>10</sub> in presence and absence nano-alumina revealed less change of the surface appearance after the exposure and give the best results. The Met. coupons with and without Nano-alumina showed slight change in appearance of formed film on surface from colorless to slight rate from blue.



**Figure 7:** The coupons after accelerated ageing. On the left, (a-g) the coupons of H<sub>2</sub>S test. (a) BTA, (b) Met., (c) NaC<sub>10</sub>, (d) BTA+Nano-alu., (e) NaC<sub>10</sub>+ Nano-alu., (f) Met.+ Nano-alu., (g) untreated, (h) untreated coupon before the test. On the right, (i-o) the coupons of the water resistance test, (i) untreated, (j) BTA, (k) NaC<sub>10</sub>, (l) Met., (m) BTA+Nano-alu., (n) NaC<sub>10</sub>+Nano-alu., (o) Met.+Nano-alu..

## Conclusions

The results of the different tests are very varied but the main conclusions are as follows: BTA and NaC<sub>10</sub> individually and in combination with Nano-alumina have high impedance against tarnishing of exposed silver of H<sub>2</sub>S gas, also they presented adequate protection of silver coupons against the influence of humidity and water, also revealed the high polarization resistances in .6M NaCl. So they can be presented as efficiency inhibitors of silver artifacts. Investigation of their film formed on silver surface revealed many inhibition features such as the high adsorption and good coverage which attributed to the interaction of the silver with the nitrogen atoms in their molecular. The results of tests and examinations revealed that these aspects were clearly improved in presence Nano-alumina. The evaluation results for Met. were not satisfactory whether with and without Nano-alumina to be suggested as inhibitor of silver artifacts.

### Found:

This research was financed by south valley university (Egypt).

### Materials

Inhibitor compound was obtained from Aldrich chemical Co..

### Acknowledgments

We would like to thank prof. Mai Rifai, Conservation Department, Faculty of archaeology, Cairo Uni. for all assistance and his continuous support.

## References

1. M. Evesque, M. Keddou, H. Takenouti, *Electrochimica Acta* 49 (2004) 2937-2943.
2. M.C. Bernard, E. Dauvergne, M. Evesque, M. Keddou, H. Takenouti, *Corros. Sci.* 47 (2005) 663-679.
3. V. Gouda, N. Abdel Ghany, A. Awad, J. Novakovic, P. Vassiliou, J. *Chem. Special Issue* (2009) 29-45.
4. C.L. Reedy, R.A. Corbett, D.L. Long, R.E. Tatnall, B.D. Krantz, The American Institute for Conservation of Historic & Artistic Works, Objects Specialty Group Postprints, 6 (1999) 41-69.
5. S. Grassini, E. Angelini, Y. Mao, J. Novakovic, P. Vassiliou, *Progress in Organic Coatings* 72 (2011) 131-137.
6. V. Costa, The deterioration of silver alloys and some aspects of their conservation, *Rev. Conserv.* 2 (2001) 18-34.
7. J. Novakovic, E. Georgiza, P. Vassiliou, School of Chemical Engineering, N.T.U.A., Heron Polytechniou 9, 157 80 Athens.
8. J. Novakovic, P. Vassiliou, Proceedings of the 7th European Conference "SAUVEUR", Prague, Czech Republic, 2 (2006) 863-865.
9. R.B. Faltermeier, *Stu. in Con.* 44, 2 (1999) 121-128.
10. M. Keersmaecker, K. Wael, A. Adriaens, *Progress in Organic Coatings*, 74, 1 (2012) 1-7.
11. E. Rocca, J. Steinmetz, *Corro. Sci.* 43 (2001) 891-902.
12. E. Rocca, C. Rapin, F. Mirambet, *Corro. Sci.* 46 (2004) 653-665.
13. S. Hollner, F. Mirambet, A. Texier, E. Rocca, J. Steinmetz, international conference on conservation strategies for saving indoor metallic collections with a satellite meeting on legal issues in the conservation of cultural heritage, (2007) 156.
14. A. Elia, K. De Wael, M. Dowsett, A. Adriaens, *J. Solid State Electrochem* 16 (2012) 143-148.
15. E. Rocca, G. Bertrand, C. Rapin, G.C. Labrune, *J. of Electroanalytical Chemistry* 503 (2001) 133-140.
16. A.N. Abu-Baker, I.D. MacLeod, R. Sloggett, R. Taylor, *European Scientific Journal*, 9, 33(2013) 1857-7881
17. I. B. Brostoff, Proceedings of the International Conference on Metals Conservation, ICOM-CC, James and James, (1997) 99-108.
18. J.B. Cotton, I. R., Scholes, *British Corrosion Journal* 2(1967) 1-15.
19. L.E. Merk, *Stu. in Con.* 26 (1981) 73- 76.
20. R. Rocca, F. Mirambet, *European Federation of Corrosion Publications*, 48 (2007) 307-334.

21. K. Barouni, A. Kassale, A. Albourine, O. Jbara, B. Hammouti, L. Bazzi, Amino acids as corrosion inhibitors for copper in nitric acid medium: Experimental and theoretical study, *J. Mater. Environ. Sci.* 5 (2) (2014)456-463.
22. K.F. Khaled , *Corros. Sci.* 52 (2010) 3225-3234.
23. E.E. Oguzie, Y. Lia, F.H. Wang, *J. Colloid Interface Sci.*, 310 (2007) 90 .
24. E.E. Oguzie, Y. Lia, F.H. Wang, *Electrochim. Acta.*, 52 (2007) 6988.
25. M.S. Morad, *J. Appl. Electrochem.*, 35 (2005) 889.
26. M.A. Kiani, M.F. Mousavi, S. Ghasemi, M. Shamsipur, S.H. Kazemi, *Corros. Sci.* 50 (2008) 1035.
27. O.K. Abiola, *J. Chill. Chem. Soc.* 50 (2005) 685.
28. O.K. Abiola, N.C. Oforka, E.E. Ebenso, *Bull. Electrochem.* 20 (2004) 409.
29. A. Zarrouk, B. Hammouti, A. Dafali, H. Zarrok, *Der PharmaChemica*, 4 (2011) 266-274.
30. ASTM G5-87, American Society for Testing and Materials, Philadelphia (1987).
31. D. Daloz, C. Rapin, P. Steinmetz, G. Michot, *Corrosion* 54 (1998) 440.
32. ASTM G5 – 14, Volume 03.02, Corrosion of Metals; Wear and Erosion.
33. S. Varvara, L.M. Muresan, K. Rahmouni, H. Takenouti, *Corros. Sci.* 50 (2008) 2596-2604.
34. M.M. Rifai, Z. abdelhamid, S.M. Saleh, M.M. Abdelbar, *international of journal conservation science*, 4 (2015) 611-624
35. M.N. Kim, H.S. Yu, S.E. Lee, A Small Chamber Test and Oddy Test on Medium Density Fiberboard grade (E0, E1), *Indoor Air Quality in Museums and Historic Properties*, University of East Anglia, Norwich, April 28 (2003).
36. S. Kim, J.A. Kim, J.Y. An, H.J. Kim, S.D. Kim, J.C. Park, *Indoor Air* 17 (2007) 404-415
37. Y. Salem, *Open Journal of Air Pollution*, 6 (2017) 135-148
38. ASTM 2004, Standard practice for testing water resistance of coatings using water fog apparatus. D1735–04. Philadelphia: American Society for Testing and Materials.
39. ASTM 2002, Standard practice for testing water resistance of coatings in 100% relative humidity. D2247–02. Philadelphia: American Society for Testing and Materials.
40. A.A.M. Elbeshary, M. De Keersmaecker, A. Adriaens, *Progress in Organic Coatings*, 101 (2016) 225-232.

\*\*\*\*\*