

## **Comparison among the best and widely compounds used to copper artefacts protect at atmospheric environment**

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### **Abstract.**

The main objective of this subject was a comparative study of inhibition and protective properties among the best and common compounds used to Copper artefacts protect in atmospheric environment. Compounds were five of the best corrosion inhibitors: L-Methionine (Met.), L-Cystine (Cys.), Benzotriazole (BTA), 3-amino-1, 2, 4-triazole (ATA) and Sodium decanoate (NaC<sub>10</sub>) as well as two protective coatings were microcrystalline (Mic) and paraffin (Par) wax. Study carried out by electrochemical techniques including (Pt and EIS), microscopic Examination and accelerated aging in climate chamber.

Electrochemical techniques showed that BTA, NaC<sub>10</sub>, Met., ATA were the best compounds. The effectiveness of the selected compounds in potentiodynamic polarization were rated BTA > NaC<sub>10</sub>> Met. > ATA, while In (EIS) was rated Met. > BTA > NaC<sub>10</sub>> ATA. While Cys., Par. and Mic. were recorded less protection. Microscopic examination and climate chamber test were confirmed the results of electrochemical tests, the results from the different methods were in good agreement.

### **1. Introduction.**

Many of the organic compounds were presented for the protection of copper artefacts, which replaced the old coatings, the survey of these compounds showed that there five compounds were the best and high efficiency in the most presented studies and several previous studies have agreed to its efficiency in the protection of copper artefacts. compounds were L-Methionine, L-Cystine, Benzotriazole, 3-amino-1, 2, 4-triazole and Sodium decanoate, Effectiveness of each compound is tested in some studies –will said later- with many other compounds and each compound revealed the best results in these studies. The present study aims to comparison of them and determination of best these compounds, also two ancient coatings (paraffin and microcrystalline wax) were chosen of this study, the reason for choosing these coatings will be stated in Background.

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One of the evaluation and comparison methods in this study will be carried out similar test environment to deterioration environment of archaeological metals, which including to gaseous pollutants as deterioration factors, Where all the presented studies on these compounds or other did not use the gaseous pollutants as deterioration factors although the gaseous pollutants are the main factor in metallic artefacts corrosion, And most the studies carried out electrochemical tests or the weight lost and in these tests are used liquid solutions as corrosive medias, these medias are unrealistic for archaeological metals artefacts, that saved in Museum environment or outdoor environment inside display cabinets.

## **2. Background of the compounds used to study.**

### **2.1. Corrosion inhibitor.**

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

Measurements of the corrosion potential ( $E_{\text{cor}}$ ) and the polarization resistance of this compound as corrosion inhibitor was carried out in many previous studies of many metals artefacts: Lead in concentration  $0.05 \text{ mol L}^{-1}$  (25, 42, 43), Iron and copper based alloys in Con.  $0.1 - 0.05 \text{ mol L}^{-1}$ (23), Copper (17, 44) and Magnesium alloy (40). Also these studies have indicated that straight chain aliphatic monocarboxylates of general formula  $\text{CH}_3(\text{CH}_2)_n\text{-2COONa}$  with  $7 \leq n \leq 11$ , noted  $\text{NaC}_n$ , have a good inhibitor property in the case of aqueous corrosion of many metals and alloys. These compounds are non-toxic and derived from fatty acids extracted from vegetable oil. Best results of  $\text{NaC}_{10}$  solution were obtained with  $0.05 \text{ mol}$ . (15, 41, 42, 43, 44)

#### **2.1.2. L-Cysteine** (Amino-3-mercaptopropionic acid), $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ (Cys.):

L-Cysteine is an amino acid that has been investigated as corrosion Inhibitor for copper (62, 26, 7, 2) and tin (41). Zhang et al. (2005) found that cysteine inhibited the anodic dissolution of copper in acidic medium more effectively than benzotriazole. L-Cysteine is evaluated at different concentrations by potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) and weight loss measurements. The results obtained showed the effectiveness of the investigated L-Cysteine as a good inhibitor of copper in  $2\text{M HNO}_3$ . However the results presented the cysteine as an environmentally friendly replacement for benzotriazole to protect uncorroded or previously treated by reduction back to metal artefacts (61), more details are described in (2).

#### **2.1.3. 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 in protection. many laboratory studies were compared BTA with some traditionally protective coatings and a new corrosion inhibitors, in all these studies benzotriazole showed very effective as a good corrosion inhibitor and presented often the best results. (45, 14, 10, 33, 2)

Fifty museums were surveyed from Egypt, France, Greece, Italy, Jordan, Malta, Morocco, Spain, Syria, Turkey, including Czech Republic to determine the types of corrosion inhibitors and coatings used by conservators-restorers to protect indoor museum objects made either of copper, iron, silver, or gold alloys. The results found that the most popular corrosion inhibitor for copper alloy objects is benzotriazole. (4)

#### **2.1.4. 3-amino-1,2,4-triazole:** (ATA)

Two studies were presented to evaluate 3-amino-1,2,4-triazole in coupons of copper-nickel alloy (Cu-30 Ni) in corrosive solution ( $0.05 \text{ M NH}_4\text{OH}$  and  $3\% \text{ NaCl}$ ) by electrochemical evaluation and weight lost, the results were revealed that inhibitor was

good in copper alloys protect (20, 9). The ATA is the most effective at 0.1mM concentration, and the initial treatment of bronze at a higher concentration makes inhibiting effect lower. The ATA is therefore considered the most promising candidate to be applied to protect antique bronze artefacts covered with natural patina layer (39).

### **2.1.5. L- methionine: (Met.)**

2-Amino-4-(methylthio) butanoic acid,  $\text{CH}_3\text{S}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .

Some laboratory studies were presented Met. as good corrosion inhibitor of copper at different environmental. Recently study was evaluated the efficiency of eight amino acids including met. as corrosion inhibitors of copper in 1 M  $\text{HNO}_3$  by gravimetric and potentiodynamic polarization, The results obtained from two different techniques are comparable, and show that Met is the best inhibitor for the corrosion of copper. (8, 27, 34)

## **2.2. Coatings:**

### **2.2.1. Waxes of Paraffin and Microcrystalline (Par., Mic.):**

Paraffin and microcrystalline wax were used ancient to reduce the corrosion rates of metallic artefacts, first production of microcrystalline in 1925 (U.S.A) (30). In our knowledge, no laboratory studies were presented on evaluation these coatings by electrochemical tests and were replaced to other compounds without compare its efficiency with compounds currently used (18) although it has provided protection for metallic artefacts for long periods.

## **3. Experimental procedure:**

### **3.1. Preparing of compounds solutions.**

Solution 3% concentration with ethanol was prepared, excepting insoluble paraffin in ethanol that was dissolved in toluene.

### **3.2. The coupons preparation.**

Coupons of pure copper strips concentration 99.9% were used to Electrochemical tests, in climate chamber test coupons of copper 99.9% as well as coupons of ternary bronze alloy (lead bronze) (81Copper, 8 Tin, Lead 10) were used, coupons were cut (7X5 CM) (55), ternary bronze alloy should be similar for archaeological bronze alloy, which was known in ancient Egypt, concentration of ancient ternary bronze alloy was (10 tin, 10 lead, 80 copper) (37) This concentration was not commercially available and was prepared by alloying a mixture of copper (pieces from the pure copper) with tin and lead pieces. The alloy was prepared by direct addition of tin and lead to molten copper in a crucible. Composition of the bronze alloy and copper determined by EDXRF analysis as in Fig. 1. the weight percent of copper, tin and lead in the resultant alloys was about 81% Cu, 8% Sn, Pb 10. (1, 32)

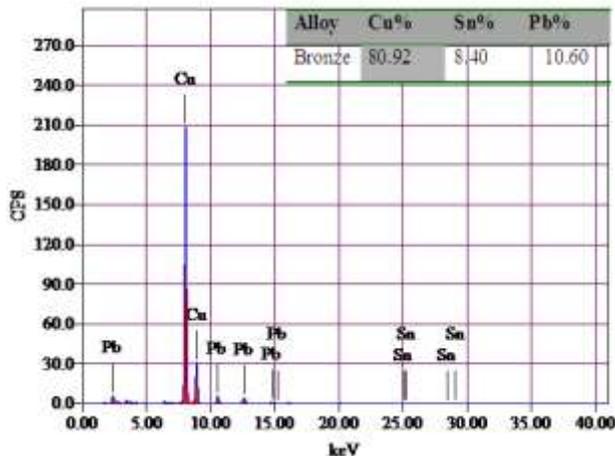


Fig. 1. XRF Spectra and elements percentage of the bronze coupons.

### 3.3. Applied of compounds solution on coupons.

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.

### 3.4. Potentiodynamic test.

#### 3.4.1. The electrochemical cell preparation. (59, 60)

The electrochemical test was carried out using apparatus [potential potentiostats Galvanic (model 273 A) EG and G] with these conditions:

- Initial potential = 0.1 V
- Final potential = 0.1 V
- Sample area = 2 CM<sup>2</sup>
- Scan rate= 5 MVS<sup>-1</sup>
- The volume of Solution = 50 ml (mix. /HCl).
- 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 [15, 6].
- All experiments were performed at temperature room.

#### 3.4.2. The corrosive medias:

The first test (Potintiodinamic) carried out in the corrosive media ASTM D1384-87 (ASTM solution) standard solution as simulation of atmospheric corrosion of the archaeological metals and their alloys, solution has the following composition: 148 mgL<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, 138 mgL<sup>-1</sup> NaHCO<sub>3</sub>, 165 mgL<sup>-1</sup> NaCl. With tap water, acidified to pH 5 by addition of dilute HCl (5, 23, 43, 57).

### 3.5. The second test Electrochemical impedance spectroscopy (EIS):

Measurements were carried out at room temperature according to the procedure described in ASTM G-5-93 standard (35) 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 obtained in 3.5% NaCl electrolyte at room temperature (25 ± 1 °C), using a three-electrode electrochemical cell. Before the measurements, the working electrode was

degreased with acetone and rinsed with distilled water. 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<sub>o</sub> = 240 mV versus reference hydrogen electrode (RHE) and Pt wire was used as counter electrode.

### 3.6. Microscopic Examination.

Examination of treated surface by corrosion inhibitor can be a strong indicator of the effectiveness of compound and the corrosion resistance. The results can be as the follows.

- Microscopic will be used to investigation the surface morphological changes of copper coupons when treated with protective compounds.
- The formation, Distribution and diffusion form of corrosion inhibitor on metal surface.
- The rate of adhesion and bonding between the formation film and coupons surface.
- The rate of adsorption of inhibitor molecules on metal surface.
- Cracks and fissures in corrosion inhibitor layer.

And therefore microscopic examination an effective way can be used in evaluation of inhibitor corrosion as shown in [Figs \(7:16\)](#). The coupons were investigated by scanning electron microscope and in some cases Polarizing microscope and stereomicroscope.

### 3.7. **Accelerated corrosion test in climate chamber.**

In this test a new approach will be used to investigate the effectiveness of compounds and comparison among them, this approach is depended on exposure experimental coupons of gaseous pollutants in climate chamber, in this test corrosion of metals artefacts and their alloy in atmosphere environment will be simulated.

In our knowledge, no studies on evaluation efficiently of corrosion inhibitors and protective coatings by exposure experimental coupons of pollutants gaseous in climate chamber were presented, Although this test closest to simulate the damage factors in the atmospheric corrosion environment.

There is a few presented studies to evaluation inside test chamber but by high relative humidity and temperature (84% RH and 38o C), as accelerated deterioration factors as well as an acetic acid-enriched solutions as simulation for acidic vapours in the wooden displays and in both cases no gaseous were used. Conditions are given in [Table 1](#).

Also some published papers were presented for investigation of corrosion effects of some organic acids vapours and gaseous pollutants of archaeological metals, Copper [Table \(1\)](#) but were used solutions liquids as sources of pollutants. In a series of earlier published papers, the influence of temperature, relative humidity (RH), air velocity and HNO<sub>3</sub> concentration on the corrosion of laboratory-exposed copper have been presented by the same authors ([46](#), [47](#), [48](#)). After surveying of more than 16 previous study of exposed to air pollution gases in artefacts metals (such as copper, bronze, silver) the procedures of this test was as shown in [Table 1](#).

Table 1 Tests procedures of previous studies were used climate chamber and curranty study.

studies	Study type	Period exposure	Tem.	R.H	Gas Con.	reference
Previous	corrosion	8-12	25 C	100-	Different con.	Silver ( <a href="#">22</a> )

	effects	week		50		Tin (49) Copper (55, 51, 54, 16, 36, 53, 11, 32) Zinc(22, 23) Lead (35, 54) Steel (48, 19)
	evaluation of corrosion inhibitors	24 h	30, 25	100, 60 %	No gaseous	23
		72	38	84	No gaseous	2
Curranty study		8-12	25 C	75- 50	ppm 500	

**3.7.1. Chamber design:**

Climate chamber designed according to ASTM as shown in Fig. (2), The chamber is made of 1000 cm diameter Perspex cylinder Humidification of the air is 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 dataloger device, Also a small chamber is manufacturing by the dimensions (30 X 30 X 30 CM) has been in mind that where all it contained large rooms achieved. (56) (ASTM D5116-97, (28, 29)



Fig. 2. Chamber used to accelerated corrosion during and before manufacturing stage, a: coupons suspended in the middle of the chamber. b, an instrument used for measuring the moisture. c, fan to mix the gas with the air inside the room, d, electric lamp to raise the temperature if necessary, e, the saturated solution to adjust the humidity.

**3.7.2. The test gaseous:**

Gases used for the test were Sulfur dioxide SO<sub>2</sub> and Chlorine Cl. Those types were the most effective and commonly in deterioration of copper artefacts. Experimental details of gaseous preparation are described in (60).

**4. Results and dissection**

### 4.1. Electrochemical measurements of coupons

The resistance Measurement of treated and untreated coupons was carried out then comparison among them to determine the efficiency of each compound, then the comparison among all compounds to select the best compound.

The compounds revealed varying degrees to corrosive resistant, the best results was obtained to BTA, it was the highest in the difference in the corrosion potential ( $E_{cor.}$ ) and recorded  $E_{cor.}$  (196) m v.  $NaC_{10}$  was in the second rate and recorded difference in  $E_{cor.}$  (185) m v, Met. had a high resistance and was in third place after BTA and  $NaC_{10}$  and recorded (170) mv, also ATA had the good resistance properties and was in fourth placed and recorded (145) m v, Mic, paraffin wax and Cys. have the least inhibition properties, its recorded difference in  $E_{cor.}$  (80, 18, 15) mv . As shown in Figs. (3, 4, 5) and Table (2).

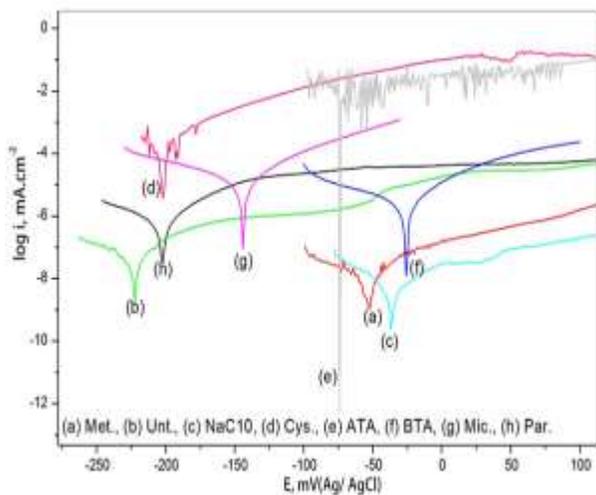


Fig. 3. The difference in  $E_{cor.}$  of treated and untreated coupons.

Table 2 the difference in the corrosion potential ( $E_{cor.}$ ) of corrosion inhibitors.

Cou.	$E_{cor.}/mV.$	The difference in $E_{cor.}$
Untreated	-220	
$NaC_{10}$	-35	185
L-Met.	-50	170
BTA	-24	196
ATA	-25	145
L-Cys.	-202	18
Par.	-205	15
Mic.	-140	80

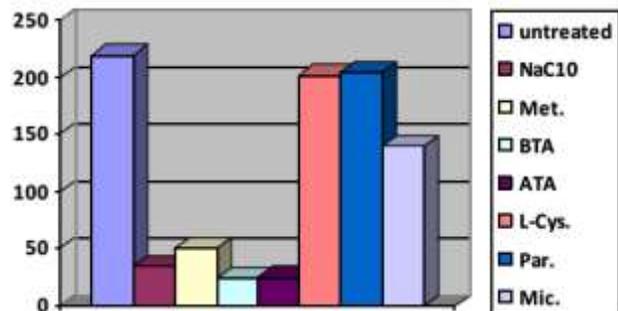


Fig. 4. Corrosion potential ( $E_{cor.}$ ) of Treated and untreated coupons.

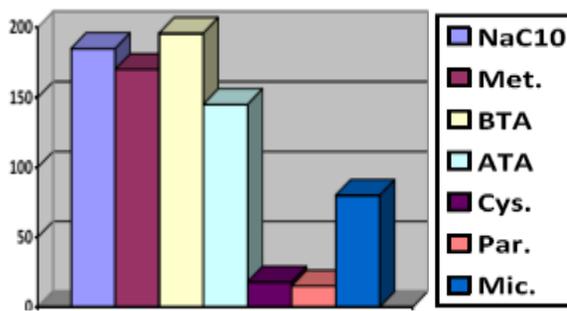


Fig. 5. The difference in corrosion potential of treated coupons.

#### 4.2. Electrochemical impedance spectroscopy (EIS)

The test (EIS) had confirmed the results of potentiodynamic test and the good inhibition properties of BTA, NaC<sub>10</sub> and L-Met., The best results of EIS were obtained of Met. ( $3.076 \times 10^4$ )  $M\Omega cm^2$ , then BTA ( $2.045 \times 10^4$ )  $M\Omega cm^2$ , then NaC<sub>10</sub> ( $1.088 \times 10^4$ ), The results also shown that Cys., Par. and Mic. have low corrosive resistance, ATA has less inhibition properties, as shown in Table (3) and Figs (6)

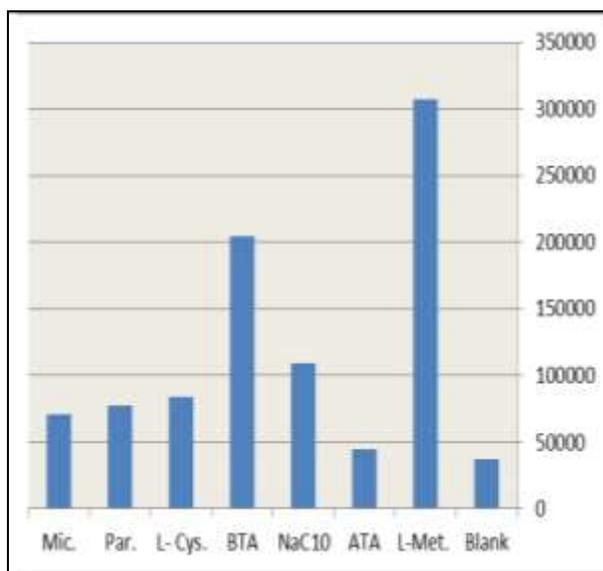


Table 2. Coupons polarisation resistance

Inhibitor	Nyquist plots $M\Omega cm^2$
Blank	$3.724 \times 10^3$
L-Met.	$3.076 \times 10^4$
ATA	$1.458 \times 10^3$
NaC <sub>10</sub>	$1.088 \times 10^4$
BTA	$2.045 \times 10^4$
L- Cys.	$8.399 \times 10^3$
Par.	$7.710 \times 10^3$
Mic.	$7.036 \times 10^3$

Fig. 6. The difference in the electrochemical impedance plots the Nyquist plots recorded for treated and untreated coupons.

#### 4.3. Microscopic examination of treated coupons

Investigation was revealed proofs and clear evidences which through can be understand and explanation cause Efficiency or inefficiency of the formation film in inhibit corrosive.

Initial SEM to untreated coupons Fig. (7) was carried, Paraffin wax coating shows good coverage of coating film on the surface, but does not have a specific form and punctuated by some cracks Fig. (8), SEM and ST of L-Cysteine revealed low deposition as adhesiveness weak Granules with surface Fig. (9, 10), L-methionine revealed the morphology of the adsorbed inhibitor film and a good coverage on surface. The formation film can be attributed to adsorption of the molecules by interaction of the copper with nitrogen, oxygen and Sulphur atoms; this forms a barrier blocking corrosion of the copper Fig. (11, 12), BTA inhibitor: Cotton [14] offered the first possible structure for Cu(II)BTA as a result of the adsorption of BTA on to any copper oxide surface. In

2011 Salem (59) presented SEM investigation of Cu(II)BTA thereby corroborating Cotton's hypothesis in structure as shown Fig. (13), In the current study Examination by Steriomicroscope of BTA revealed the adsorbed inhibitor on surface in shape a complete coverage and a dense layer Fig. (14), NaC<sub>10</sub> appears the formed film layer on the surface as dense coverage Fig. (15), ATA reveals Coverage of the adsorbed inhibitor film on the surface with the presence of cracks and holes that reduce its efficiency as corrosion inhibitor Fig. (16).

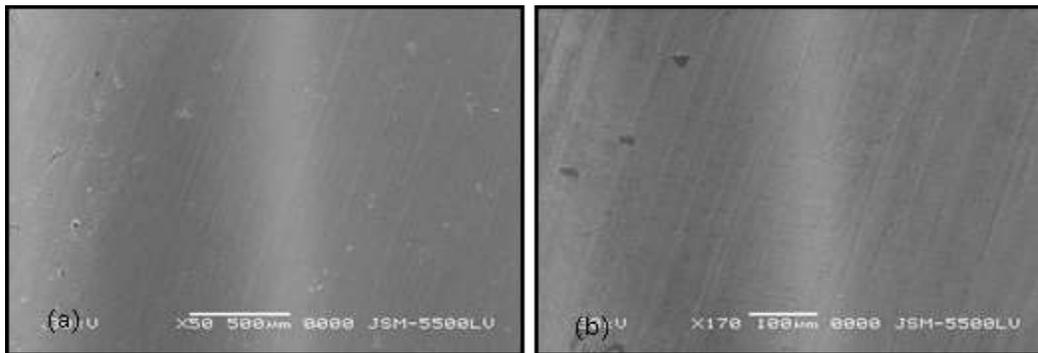


Fig. 7. SEM untreated copper coupons.

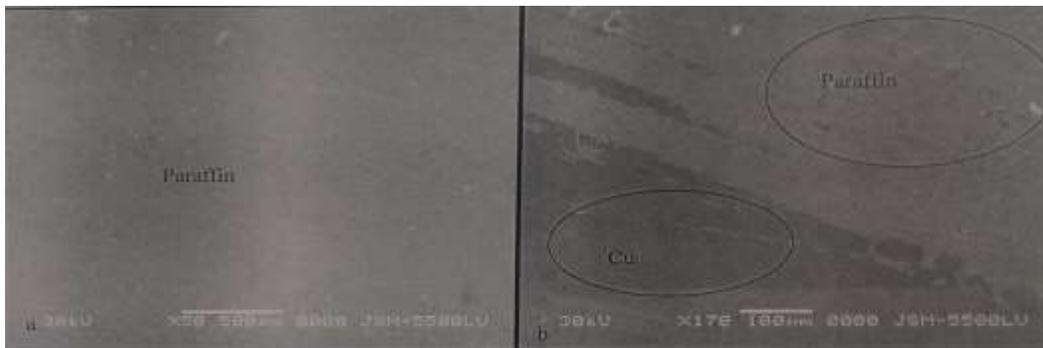


Fig. 8. SEM of Paraffin wax coating shows good coverage of coating film on the surface, but does not have a specific form and punctuated by some cracks as a result of non-deposition coating in some surface.

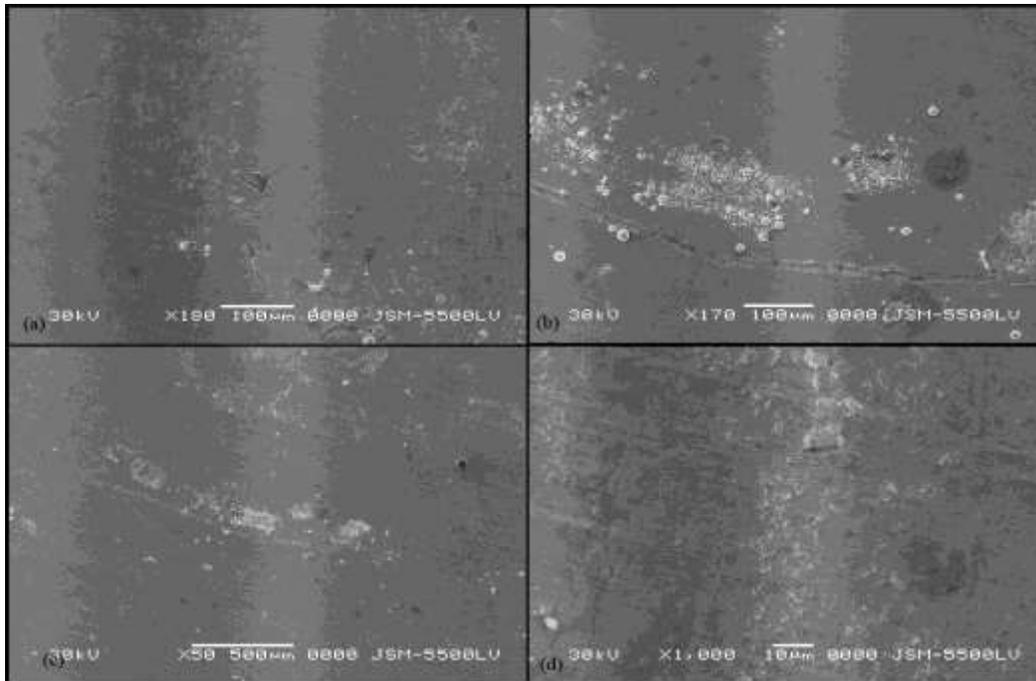


Fig. 9. SEM of L-Cysteine revealed low deposition for inhibitor on the surface as adhesiveness weak Granules with surface.

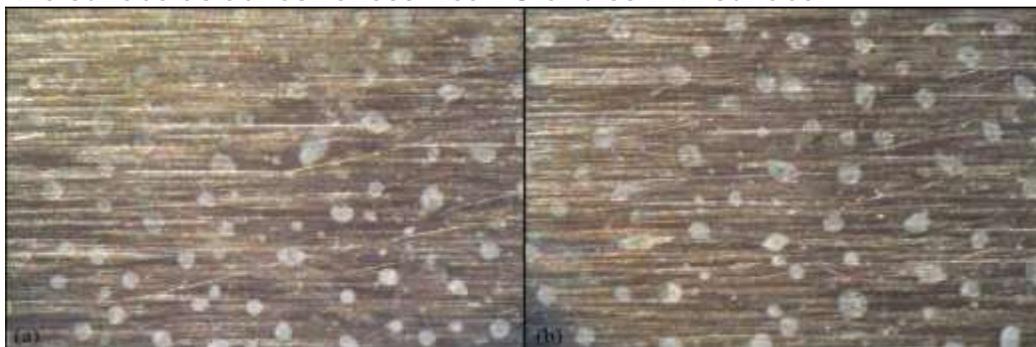


Fig. 10. Examination by Stereomicroscope x30 of L- Cys. revealed bad coverage as spaced and weak adhesion crystals with the surface.

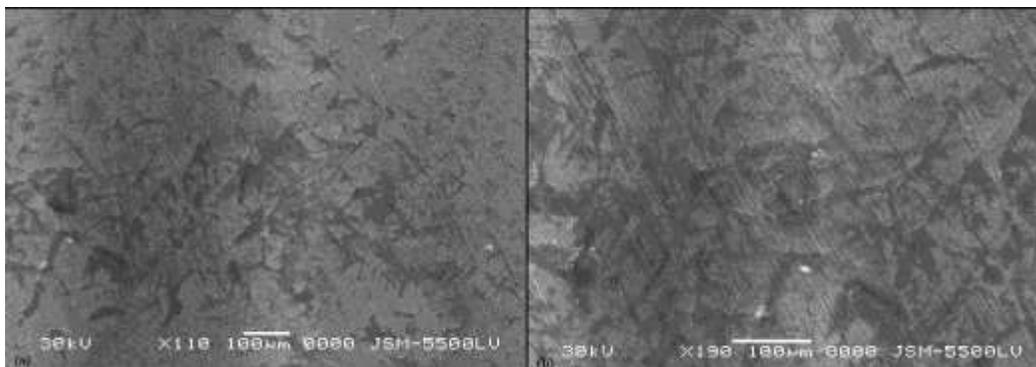


Fig. 11. SEM of treated copper coupons by L-methionine revealed the form of the adsorbed inhibitor on the surface and good coverage.

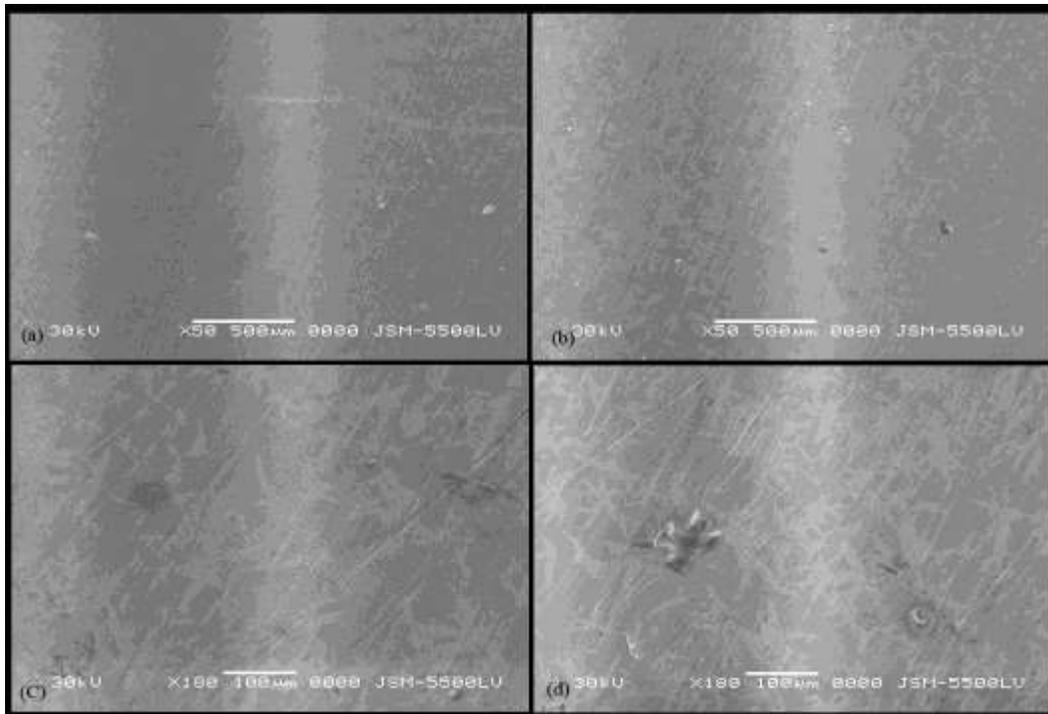


Fig. 12. SEM of treated copper coupons by L-methionine revealed the morphology of the adsorbed inhibitor film and a good coverage on surface.

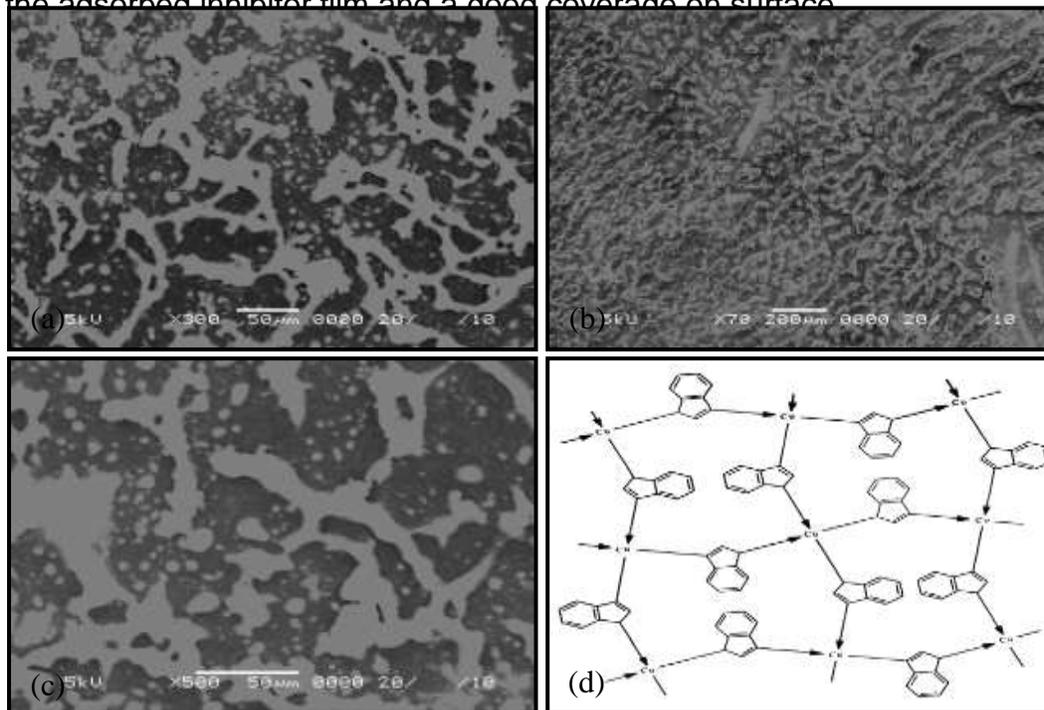


Fig. 13. A, B, C, SEM of treated coupons by BTA (after 32) shows Form of the adsorbed inhibitor on the surface and high resistance against corrosion. And agreement with Cotton's hypothesis in structure (d) (after 44)

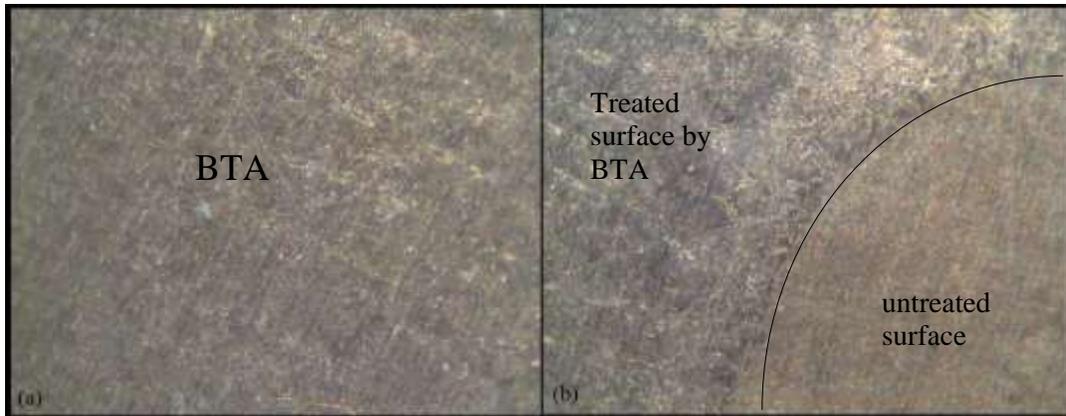


Fig. 14. Examination by Steriomicroscope 40x of BTA revealed the adsorbed inhibitor on surface in shape a complete coverage by a dense layer. And the difference between the untreated and treated surface by BTA

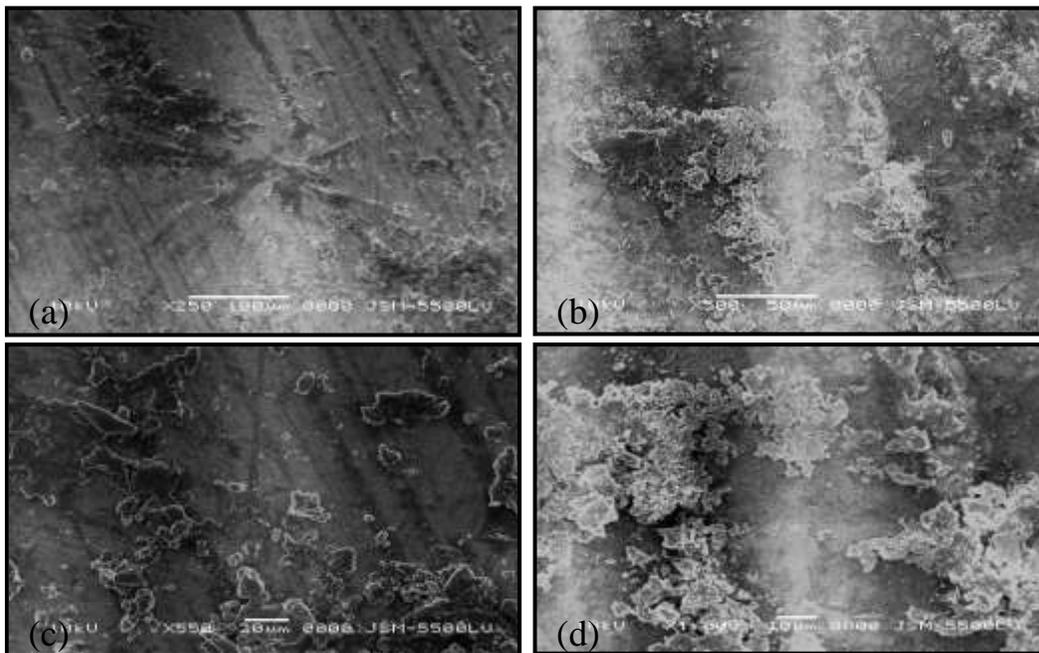


Fig. 15. SEM of NaC<sub>10</sub> appears the formed film layer on the surface as dense coverage, precipitation increases in some areas and less in others.

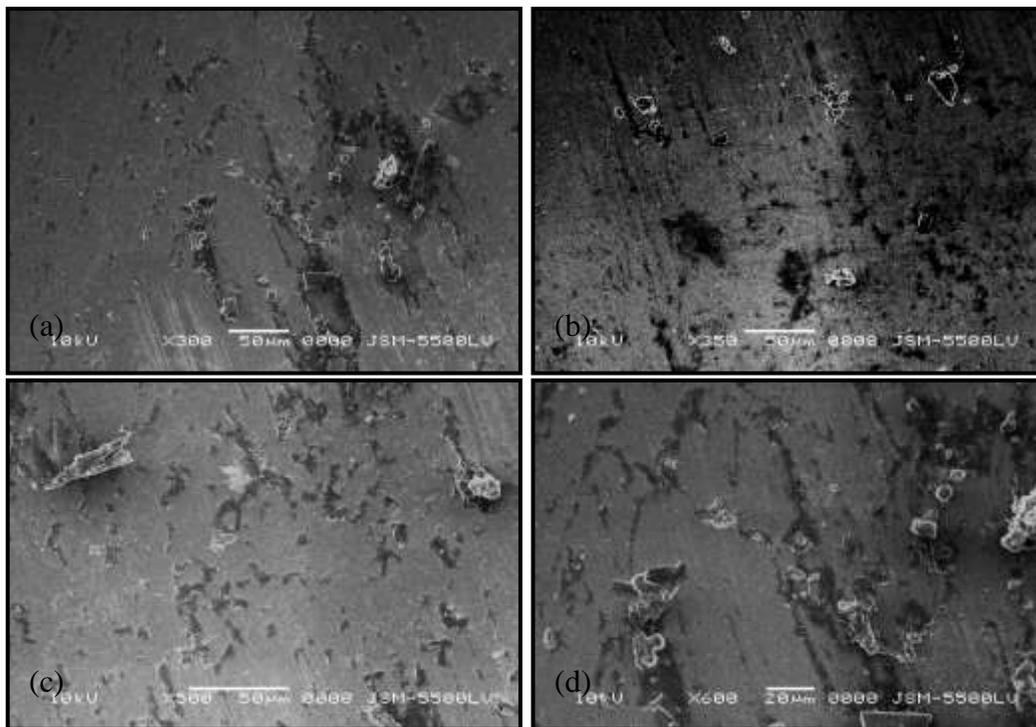


Fig. 16. SEM of ATA reveals Coverage of the adsorbed inhibitor film on the surface with the presence of cracks and holes.

#### 4.4. Exposure to gases inside a climate chamber.

Visual and microscopic examination (a microscope stereo, polarizing reflector, scanning electronic) of coupons surface after test were appeared formation of corrosion patina or not, and shows the changes on the surface of the treated coupons as shown in Fig. (17), this information is good indicator of evaluation inhibition properties and ability of corrosive resistance of compounds.

**exposure to SO<sub>2</sub> gas:** The black patina layer was appeared to bronze Coupons of SO<sub>2</sub> gas, the formation of this layer depended in inhibition properties of each compound. the results obtained confirm previous test results, BTA and NaC<sub>10</sub> was revealed the best results. Samples showed less change in the surface appearance after the test. ATA revealed a good resistance of the formation the black patina layer, L-met. and Mic. and par. were presented a low resistance and closely in three compounds where surface patina were similar, L- Cys. coupons revealed less resistance of patina layer and the surface appearance was similar with untreated coupons.

**exposure to Cl gas:** treated coupons by BTA, NaC<sub>10</sub>, L-met. and ATA were revealed a good resistance to effect chlorine gas and formation of corrosion patina, the best results and less change in the surface appearance after the test obtained BTA and NaC<sub>10</sub> then L-met. and ATA. Mic., par. and L-Cys. were less resistance of effect of chlorine.



Fig.17. Treated coupons after climate chamber test with Cl (right) and SO<sub>2</sub> (left) a- mic., b- NaC<sub>10</sub>., c- BTA., d- Cys., e- unt., f- Met., g- Par., h-ATA.

## 5. Conclusions

The following points can be drawn from the aforementioned results:

- Potentiodynamic test of selected compounds revealed varying degrees to corrosive resistant, the best results was obtained to benzotriazole, it was the highest in the difference in the corrosion potential (E<sub>cor.</sub>). effectiveness of compounds was rated as following BTA > Met. > NaC<sub>10</sub> > Amino > Cys. > Par. > Mic.
- The test (EIS) had confirmed the results of potentiodynamic test and had confirmed the good inhibition properties of BTA, sodium decanoate and L-Methionine, but it was differenced in there, effectiveness of compounds was rated as following BTA > Met. > NaC<sub>10</sub> > Amino > Cys. > Par. > Mic..
- The tests in the climatic chamber using SO<sub>2</sub>, Cl gas have confirmed The electrochemical study results, the good inhibition properties of BTA, Met., NaC<sub>10</sub>.
- Results of microscopic investigation were interpreted, expressive and agreement with electrochemical study results, investigation revealed many evidences that

prove preference (priority) of BTA and Met., the weak inhibition properties of Cys. And par. And efficiency of amino. as the aforementioned

- The obtained results from the four different tests are comparable, and show that BTA is the best inhibitor for the corrosion of copper, also L-methionine and Sodium decanoat were gave results closed to BTA, Amino, L-cysteine, Paraffin, Microcrystalline were presented the worst the results and they were in finally order. In the end, it can be classified as follows

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

**Materials:** Inhibitor compound was obtained from Aldrich chemical co..

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