TREATMENT AND CONSERVATION OF TWO METALLIC DAGGERS, KNEW KINGDOM , SINAI , EGYPT

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ABSTRACT

Two metallic daggers were found during recent excavations at tell-Habwa , North Sinai , Egypt . They belong to pharaonic period , knew kingdom . They had severe corrosion products . The two objects were studied by x- ray diffraction XRD , atomic absorption (AAS) , examined by metallographic and scanning electron microscopes to identify the types of corrosion product minerals , and to determine the constituting metals and the degree of their deterioration . XRD data showed that the corrosion products constitute of cuprite , atacamite , and paratacamite , whereas AAS analysis declared that .

the two daggers composed of bronze alloys .Microscopic examination reveals that the two daggers were nearly completely transformed to corrosion products . The objects were treated by electrochemical reduction method , followed by electrical one . Experimental accelerated corrosion tests were carried out on six inhibitors for determination their efficancy on brorze manufactured samples . The obtained results showed that paraloid B-82 and benzotriazole were the best inhibitors for conservation of the two archaeological daggers .

Kewords :TellHabwa ,bronze objects, consevation

1.INTRODUCTION

Sinai peninsula was famous in ancient Egypt , not only due to the abundance of copper , gold mines , and turquoise , but also to the existence of the oldest military road which is called by Horus road in

ancient Egypt (1-4) . This road was extended through north of Sinai till Palastine and Syria . Several archaeological discoveries as temples, fortresses , citadels , and military tools were found along this road belong to the pharaonic period till the Islamic one .The two metallic daggers , the subject of this research were found among these discoveries . They were found in Tell Habwa, north of Sinai at 1993 by expedition of Egyptian mission . They were encrusted with heavy green corrosion pnoduct layers (see fig . 1)

The aim of the present work is to identify the corrosion products of the two daggers as well as their constituting metals in order to carry out scientific treatment and conservation. For this purpose , an experimental accelerated corrosion study was done on six inhibitors to select the best ones for their conservation .

2.MATERALS and METHODS

The two archaeological metallic daggers had a heavy crust of green corrosion products .The dimensions of the daggers are: dagger A : 24cm length , 3.5cm width , about 1.5cm thickness, whereas dagger B : 22.5cm (l) , 3.5cm (w) , and 1-1.5cm (th) .

The two daggers were examinad by metallogaphic and scanning electron Miorscopes .

Corrosion products were analysed by x-ray diffraction method (XRD) , and the metallic portion was detected by atomic absorption analysis (AAS) .

According to the obtained results , the two daggers were treated with electrochemical reduction method , and electrical reduction one .

Six inhibitors were studied representing four different families : Acrylic , triazole , polystyrene , and silicone resins . They are paraloid (B66-B72-B82) , benzotriazole , polystyrene, ethyl silicate . They were subjected to experimental accelerated corrosion tests to detemine their efficiency, to apply the best ones in the protection and conservation of the daggers .The polarization test was carried out for this evaluation using apparatus model

Meinsberg potentiostal Galranostet ps6 . A simple electric cell has three electrodes was used, sample , graphite , and reference electrode (calomel) . The three electrodes were putted in 3% NaCl as an electrolyte .

3.RESULTS

3.1 Metallographic Examination (ME)

Examinatian of the two daggers before treatment declared that the daggers were nearly completely transformed to corrosion pnoducts . Cuprite red color represents the core of the body , which encrusted by green corrosion products , as shown in fig . 2 . Metallographic photomicrographs of the daggers after treatment shows the elongation of the metallic grains in the direction of hammering . this is in addition to the appearance of deterioration spots dispersed on the metal surface , as shown in fig . 3 .

3.2 Scanning Electron Microscopic Examination (SEM)

SEM examination of the daggers (cross section) showed their alteration to corrosion produdts.This confirmed the results obtained by metallographic examination as shown in fig. 4.

3.3 X-Ray Diffraction Analysis (XRD)

X-ray diffraction patterns of the corrosion products of the daggers (fig . 5) declared that they consist essentially of cuprite Cu_2 O ASTM card No 5-0667 , atacamite $Cu_2(OH)_3Cl$,card No . 2-0146 , and paratacamite $Cu_2(OH)_3Cl$, card No .
15-0649 .

3.4 Atomic Absorption Analysis (AAS)

AAS analysis of the two daggers declared that they consist of bronze alloys . Dagger A : Cu : 91. 23 %, Sn : 4.89% , Pb 0.38% , Zn : 1.17% ,

Fe : 0.53% , Ag : Nil , As : Nil,Sb: Nil. Dagger B : Cu : 86 .92% , Sn : 10.97% Pb 0.05% , Zn 0.32% , Fe : 0.326%

3.5 Accelerate Corrosion Tests

Bronze strips (90 %Cu , 10%Sn) were prepared . three samples for each test . The strips were immersed in cupric chloride solution for 24 hours to form artificial patina of nantokite . Then they were putted in distilled water for 1/2 hour , dried in ethyl alcohol at 50c then at 105c for 30 minutes , cool in a dessicator , finally weighed till 0.001mg . The inhibitors were applied on these strips leaving strips without inhibitors as blanks .These bronze strips were exposed to deterioration agents (40c , 95% Rh) for 24 hours, the color of the untreated samples changed to dark green , whereas there was no color change with respect to acrylic polymers and benzotriazole . On the other hand , there was a break in the polymer layer in case of polystyrene and ethylsilicate . Evaluation of inhibitors was determined by carrying out the polarization test , the polarization curves are given in fig . 6 . The results showed that paraloid B-82 gives the highest inhibition degree 99.85% , followed by paraloid B-66 , 99.38% , then paraloid B-82 mixed with 5% Benzotriazole 99.34% . The next was Benzotriazole 99.30% , followed by paraloid B-72 99.03% and finally polystyrene 77.78% , (see figs 7,8 and Table -1)

3.6 Treatment and Conservation

Electrochemical reduction method was used firstly to regain some of the metallic body of the dagger A , then electrical reduction method was applied . On the another hand , the dagger B was treated by using electrical reduction method only .The electrochemical reduction method was applied by creating a simple auto- electrochemical cell using zinc powder as negatively elecrtic pole , whereas the copper of the dagger is a positively elecrtic pole in a 2% diluted sulphuric acid as an electrolyte . As a result of the difference in electrical potentiality between copper and zinc , the electrochemical reactions initiated , led to the reduction of

corrosion products to the copper metal . After one week , the dagger was lifted from the cell . The dirties on its surface were removed using 1.5% of sulphuric acid solution , and new zinc powder & strips were used . The cell was remained for two months . The treatment process was continued by using electrical reduction method. In case of dagger B electrical reduction method was only used.In the latter method , the dagger was connected to the negative pole (cathode) of the electric cell , and the stainless steel pole was used as anode. The two poles were mounted in a plastic basin containing 2% H_2SO_4 solution with an external electric current 3 volt . The cell was persisted for 2 weeks about (5-6 hours per day) .The sum of the treatment hours are 70 hour . The corrosion products were reduced to copper metal. The two daggers were cleaned by normal water, then distilled one , dried , then isolated with paraloid B-82 dissolved 3% toluene (see fig . 9)

4.DISCUSSION

From the obtained results , it was found that one of the metallic daggers was nearly completely transformed to corrosion products , whereas the another one was still had some of its metallic core . X- ray diffraction data showed that the composition of the corrosion product encrustations is cuprite , atacamite ,and paratacamite . The latter compounds are basic copper chloride and are very dangerous as corrosion products (5,6) . The sandy soil whereas the two daggers were excavated played an important role in their severe corrosion . This soil is a porous one changed from subsaturation to saturation with water , had different salt ions , specially , the dangerous chlorine ion (7-9). This circulation of saline water in the soil had a serious effect on the daggers , which led to the formation of the bronze disease chloride components (10,11). Metallographic examination and atomic absorption analysis declared that the daggers consist of bronze alloys had avery low percentage of lead . This lead content may came from the used copper ores during extraction . The intended high percentage of lead in bronze alloy may protect it from

severe corrosion .The elongation of the bronze grains revealed the use of the hammering method in the Manufacture of the daggers . This played a negative role in their deterioration due to the existed strain inside the metallic structure .

The application of electrochemical reduction method on the dagger A was very urgent to regain some of its metallic core (13) , so electrical reduction method could be carried out .With respect to dagger B which had some metallic core , electrical reduction method only was applied . The conservation of the daggers was very necessary (14-17) to prevent further corrosion in the future . So , the accelerated corrosion tests were very important to evaluate the six selected inhibitors against corrosion . The polarization tests declared the success of paraloid B-82 and benzotriazole as separate inhibitors and also as a mixture , and the fail of polystyrene and wacker OH . This success is due to the coherent bonds formed with copper compounds , whereas in case of polystyrene and wacker OH , the bonds were ruptured during artificial corrosion processes , led to the formation of cracks , and extension of the corrosion process .

5.CONCLUSIONS

Electrical reduction method is very useful in treatment of the bronze objects which had chloride corrosion products and still had a metallic core. In case of nearly complete transformation of the metallic core into corrosion products , it is advisable to apply firstly electrochemical reduction method to regain some of the metal , then followed by the electrical reduction one .Paraloid B-82 and benzotriazole inhibitors proved their stability and durability against accelerating corrosion tests, not only as separate ones , but also as a mixture of both .

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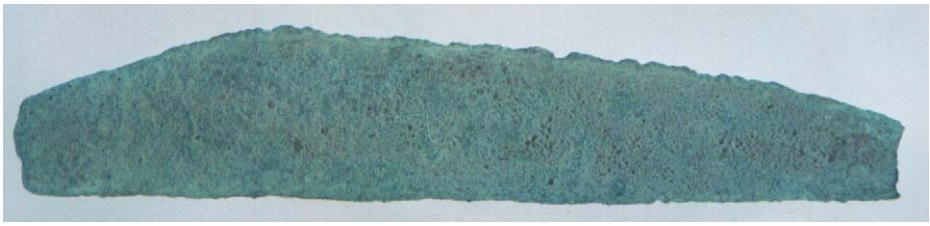
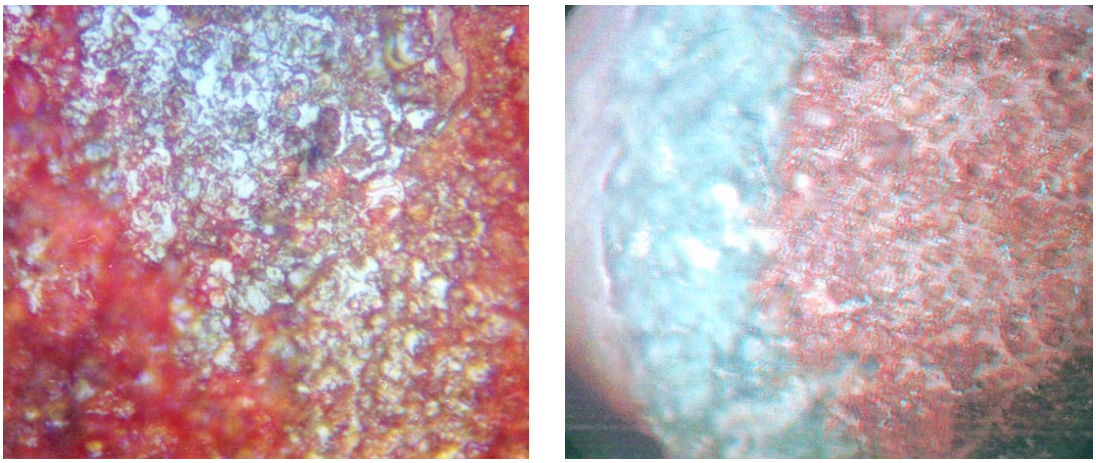
A



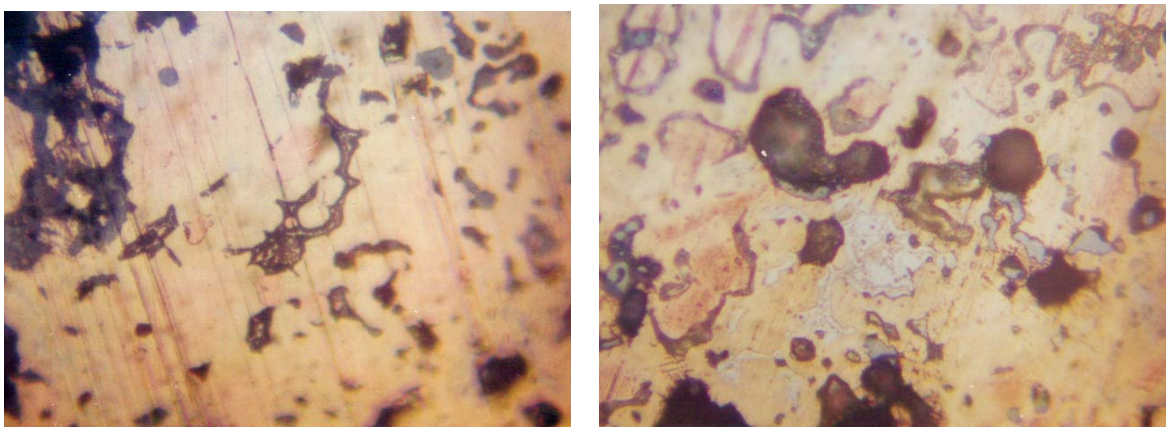
B

Fig. 1- Photos of the two metallic daggers with thick green corrosion products.



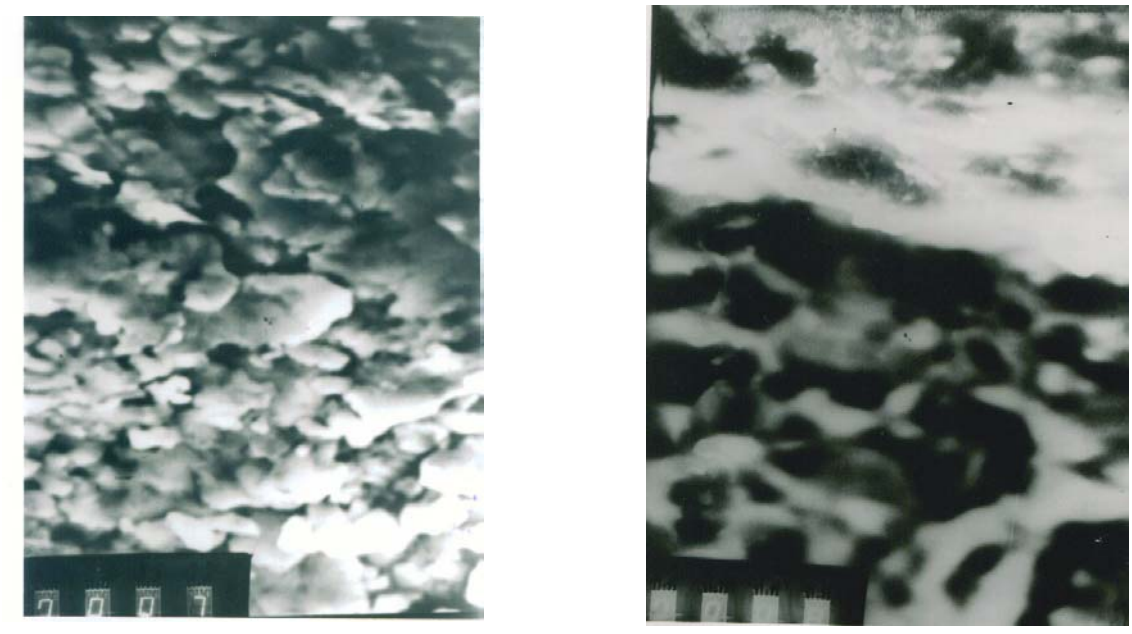
A B

Fig. 2- Metallographic photomicrograph of the daggers before treatments.



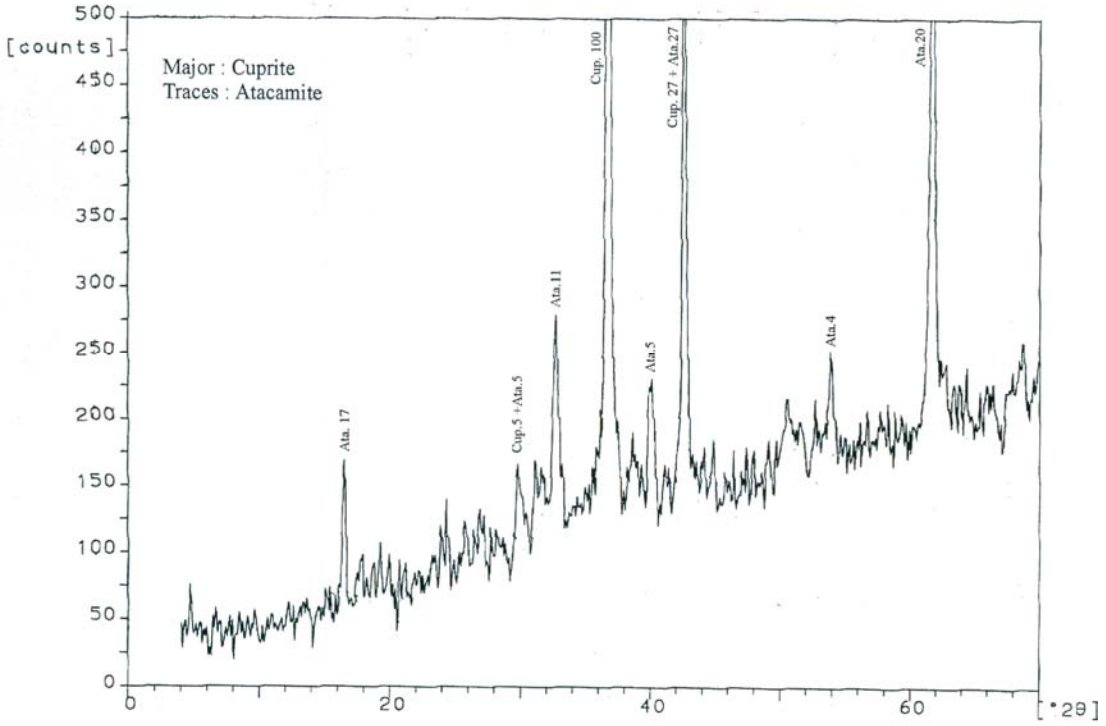
A (650 X) **B (200 X)**

Fig.3– Metallographic photomicrographs of the daggers after treatment.

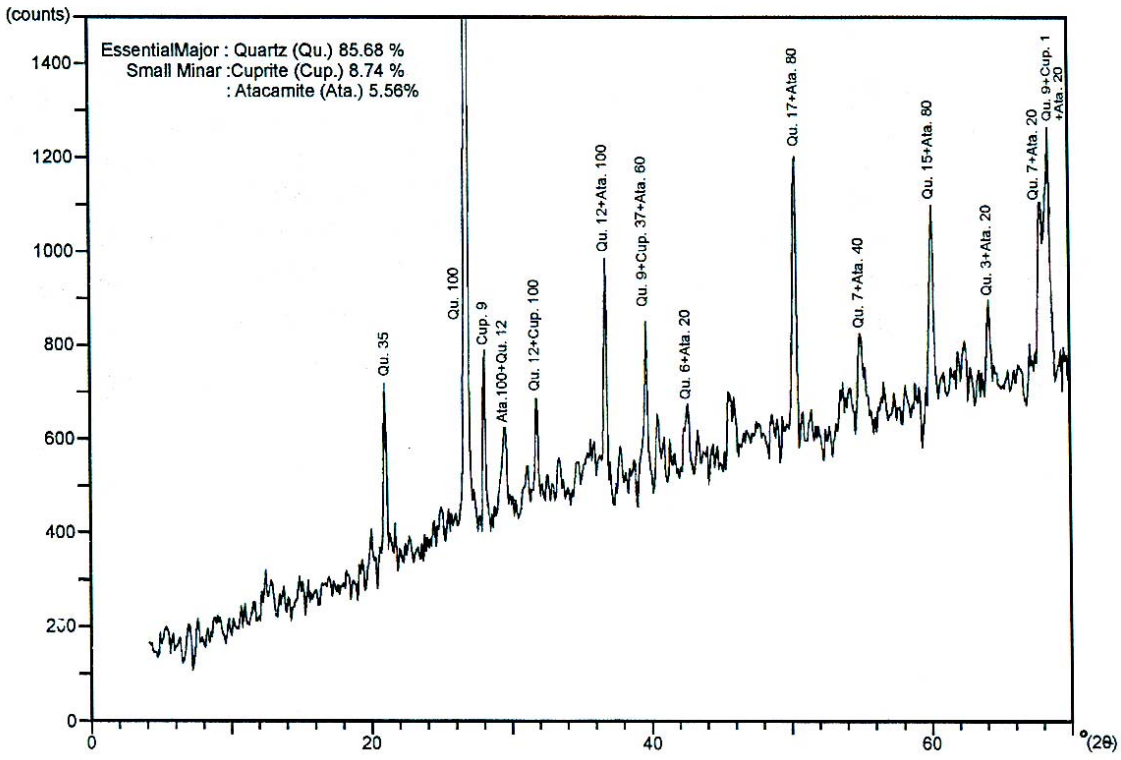


A (3000 X) **B (1600 X)**

Fig.4– SEM photomicrographs examination of the daggers



(A)



(B)

Fig.5- X-ray diffraction patterns of the corrosion products of the daggers.

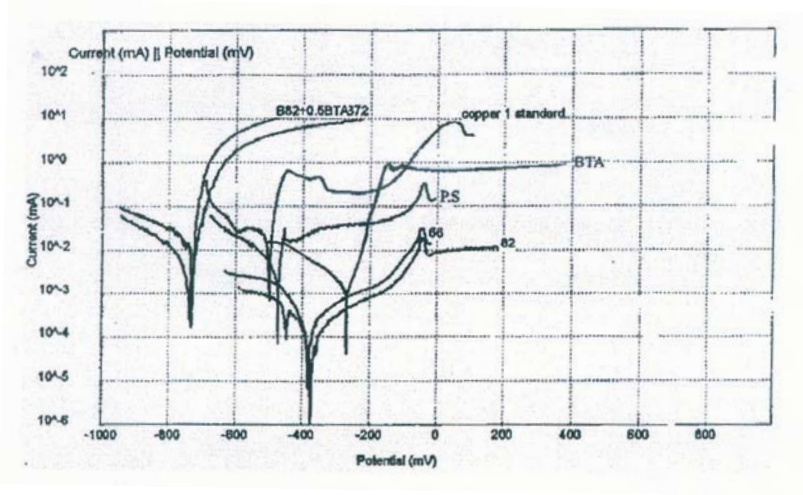


Fig.6- The polarization curves of the untreated and treated bronze samples with selected inhibitors.

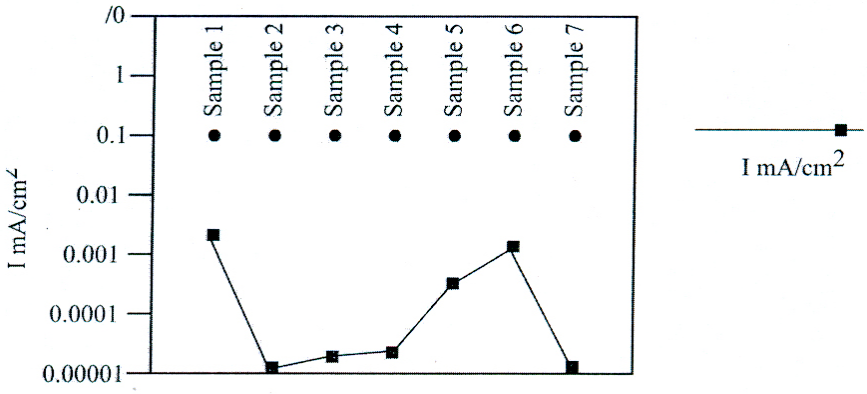


Fig.7- Declares the change in the density of corrosion current of the tested samples.

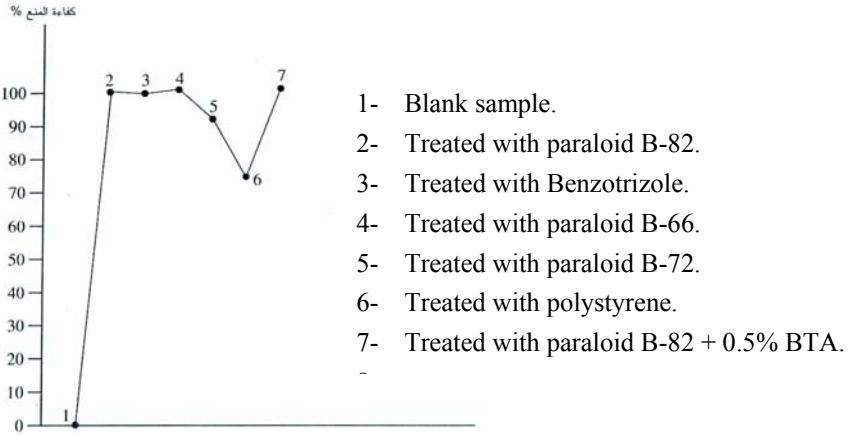


Fig.8- shows the efficiency of the applied Inhibitors through electrochemical measurements (polarization test).

(A)

(B)

Fig.9 (A, B)- Photos of the two daggers after treatment and conservation.

Table(1) shows the average of corrosion current density, the corrosion rate (m m / year), and efficiency of Inhibition.

Samples	ICorr.(A m) Cm^2	Corr. Rate (m m/ year)	Inhibition
1-Untreated	0.007668	0.088923	0.00
2- treated with paraloid B-82	0.000011	0.000125	99.85 %
3- treated with Benzotiazole	0.000027	0.000616	99.30 %
4- treated with paraloid B- 66	0.000032	0.000372	99.58 %
5- treated with paraloid B- 72	0.000686	0.007956	91.05 %
6- treated with polystyrene	0.002010	0.023311	73.78 %
7- treated with paraloid B-82 to + 0.5% BTA	0.000025	0.000584	99.34 %