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Effectiveness of Corrosion Inhibitors on Bronze and Cast Iron with Prefilming Treatment

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Metallic cultural heritage are commonly with prefilming treatment of inhibitors and then exhibited or conserved in museums. In this work, we get and compare the effectiveness of different corrosion inhibitors on bare bronze and cast iron, patina bronze and rusty cast iron. The products of the patina bronze and rusty cast iron were $Cu_2(OH)_3Cl$ and γ-FeOOH or $Fe(OH)_3$ with the XRD, XPS analyses, which were the common products of cultural heritage. With immersion treatment, the inhibiting efficiency of these inhibitors on the bare bronze depends on not only the compound type, but also the concentration and corrosion medium. With the prefilming treatment, all the inhibitors used on patina bronze, bare and rusty cast iron showed low protect effect, some of them even accelerated corrosion. Results showed that the prefilming treatment can not protect the cultural heritage from the corrosion of the environment medium.

Keywords: bronze; cast iron; inhibitor; prefilming treatment

1. INTRODUCTION

Corrosion inhibitors can be a simple, effective and widely materials for the protection of metallic cultural heritage [1-5]. After the investigation of some museums, it is found that the selection and evaluation of these inhibitors are referred to the application in industry. Specimens are polished without any patina and immersed into the mixed solution of inhibitor and corrosion medium, evaluating the inhibitor effect [6-9]. There is another way called prefilming treatment, the inhibitor added to ethanol or deionized water, then applied over the surface using a brush or immersion the specimens in inhibitor solution to form an inhibitory film. Then the specimens are immersed into the corrosion medium to evaluate the inhibitor effect [10-13]. In actually, the cultural artefacts are often covered with patina or a layer of corrosion products, which may confer their aesthetics and protect substrate. To keep the original aesthetic of the artefacts, only the harmful patina was removed, but as the complex shape, carved sculpture and inscription of the artefacts, it is hard to be removed completely. So the cultural artefacts protected with inhibitors are often with mixed (harmless and harmful) patinas, then exhibited or conserved in an aggressive environments.

From investigations to inhibitors performed on bare or patina bronze [12,14-16], it is found that the mostly used inhibitors in the area of the conservation of cultural heritage in the world are 4-methyl-1-(*p*-tolyl)-imidazole(TMI), benzotriazole(BTA), 2-mercapto-5-amino-1,3,4- thiadiazole (MAT) and their derivatives. With bare bronze immersion in the simulated acidic rain solution by addition of 5×10^{-3}M MAT, 10^{-3}M MacAT, 5×10^{-3}M MmeT and 10^{-4}M MphAT， the maximum protection efficiency (>90%) are obtained [16], but BTA and its derivatives do not exert any inhibiting effect when prefilmed on bronze, then exposure to 3.5wt.% NaCl solution [12]. On patina bronze, 10^{-4}M ATA [15], 5×10^{-3}M TMI is the most effective and 10^{-2}M PMI, 10^{-3}M AMT, 10^{-2}M TMI show no protective effect in the simulated acidic rain solution [17-19]. In other investigations [20, 21], mixed inhibitor exhibit predominant advantage of removing patina, dechlorinating and inhibiting corrosion. A lot of inhibitors have been also used on the protection of cultural cast iron [22-24], such as the compound of sodium molybdate, monosodium orthophosphate, sodium chromate and tannic acid, tungstate and alkylbenzene sulfonate. From a great variety of inhibitors, selecting one at a suitable concentration to protect the precious archaeological artefacts in different aggressive environments becomes one of the most important problems for the protector. At present, the use of corrosion inhibitor actually is depended on experience, and the effectiveness of it is qualitative but no quantitative. From [13, 17, 18], the mostly used method in the laboratory evaluation were gravimetric and electrochemical technique. The aim of this work was to systematically test various inhibitors on bare and patina bronze or cast iron with prefilming treatment, and provided a basis to select an appropriate inhibitor for the protectors.

2. EXPERIMENTAL

2.1 Materials and Reagents

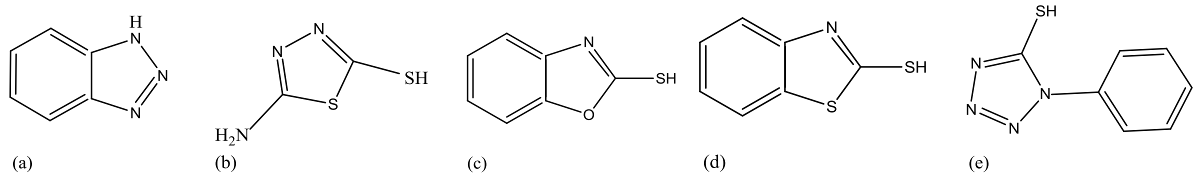

Figure 1. Molecular structure of the simple inhibitors used in this study, (a)BTA, (b)AMT, (c)MBO, (d)MBT, (e)PMTA

The bronze specimens consisted of 85.0% Cu， 14.0% Sn， 1.0% Pb and the cast iron specimens consisted of 94.3% Fe, 4.0% C，1.2% P，0.4% Mn，0.1% Si，0.02% S，which were similar to one of bronze or iron commonly used in ancient times. Each of specimens was in the dimension of 10 mm×10 mm×3 mm. Prior to measurement, the specimens were abraded with emery papers (from 300 to 800 grade), degreased with acetone, and dried in the desiccator. The corrosive medium were 0.1M NaOH, 0.05M H_2SO_4 and simulated atmosphere corrosion solution（0.028M NaCl+ 0.01M Na_2SO_4+ 0.016M $NaHCO_3$ [25].

All the inhibitors in the work were indicated in Table 1 and 2, the molecular structure of simple inhibitors were shown in Fig. 1.

2.2 Patina and rust formation

On the bronze specimens, a bright green patina was achieved by dripping the bronze surface with a solution of 0.1M HCl+2M H_2O_2 at room temperature to keep for 18h [26]. The corrosion products were examined by XRD. The model of the X-ray diffractometer was Rigaku-D/max2500PC, the target anode was Cu, the working voltage is 50kV, the angular range was 10~100˚ and the scanning velocity was 10°/min.

The cast iron specimens were immersed in 3.5% NaCl solution for 12h, the solution was neither stirred nor aerated. After the rust formation, the specimens were washed with distilled water and dried at room temperature for 12h. Then immersed and dried again, the same treatment was for three times. XPS analyses to the surface were performed using ESCALAB 250 (Thermo Fisher Scientific, USA), which with an incident mono- chromated X-ray beam from the Al target. The electron energy analyzer was operated with pass energy of 30 eV enabling high resolution of the spectra to be obtained.

2.3 Study the effectiveness of inhibitors

2.3.1 Inhibitors on bare bronze

The inhibitors B1~B5 (diluted to 10^{-2}M，10^{-3}M and 10^{-4}M) and B6~B8 (Table 1)were mixed with the corrosive medium (0.1M NaOH, 0.05M H_2SO_4 and 0.028MNaCl+0.01MNa_2SO_4 +0.016M $NaHCO_3$) respectively.

Table 1. The composition of inhibitors used in bronze

Sample	Inhibitor
B1	Benzotriazole（BTA）
B2	2- Amino -5- mercapto -1,3,4-thiadiazole（AMT）
B3	2-Mercaptobenzoxazole (MBO)
B4	2-Mercaptobenzothiazole（MBT）
B5	1-Phenyl-5-Mercaptotetrazole（PMTA）
B6	0.004% BTA+0.1% sodium benzoate +3% EDTA
B7	0.03% BTA+0.02% sodium molybdate+0.04% sodium polyphosphate
B8	1% BTA+0.1% sodium dodecylbenzene sulfonate

The bare bronze specimens were taken out after immersion 30 days in the mixed solution, removed the patina, dried at temperature of 40 ºC and weighed. As a reference, the specimens immersed in the corrosive medium without any inhibitors were also tested under the similar conditions.

2.3.2 Inhibitors on patina bronze

Prefilming treatments were carried out on the patina bronze specimens which were immersed for 6h in aqueous inhibitor solution (B1~B5 diluted to 10^{-2}M, B6~B8) in Table 1, then taken out to dry at room temperature for 6h and the same treatment for three times.

After the prefilming treatment, the specimens were immersed for 30 days in the above corrosive medium respectively, removed the patina, dried at 40 ºC and weighed. As a reference, the patinated specimens without prefilming treatment immersed in the corrosive medium were also tested under similar conditions.

2.3.3 Inhibitors on bare or rusty cast iron

Prefilming treatments were carried out on the bare or rusty cast iron specimens which were immersed for 6h in aqueous inhibitor solution in Table 2, then taken out to dry at room temperature for 6h and the same treatment for three times.

After the prefilming treatment, the specimens were immersed in the corrosive medium respectively. For a lot of bubbles generated, the specimens were taken out after 10 days immersion, removed the rust, dried at 40 ºC and weighed. As a reference, the specimens without prefilming treatment immersed in the corrosive medium were also tested under similar conditions.

Table 2. The composition of inhibitors used in cast iron

Sample	Inhibitor
C1	18% sodium benzoate +46% triethanolamine
C2	10% sodium hexametahposphate
C3	1% BTA+0.1% sodium dodecylbenzene sulfonate
C4	15% tannic acid +10% alcohol
C5	0.2% sodium tungstate +0.1% sodium dodecylbenzene sulfonate
C6	2.28% dicyclohexylamine nitrate+2.42% cyclohexylamine carbonate
C7	0.08% sodium molybdate
C8	0.01% sodium silicate

2.4 Evaluation method

The inhibiting efficiency (IE) and corrosion rate (v) were calculated according to the following equation:

$$\text{IE} = \frac{\Delta G_0 - \Delta G_1}{\Delta G_0} \times 100\% \qquad (1)$$

where ΔG_0 and ΔG_1 are the mass loss of specimens in absence and in presence of inhibitors, respectively.

$$\text{v} = \frac{C \times \Delta G}{St\rho} \qquad (2)$$

where ΔG, S, t, ρ are the mass loss, the surface area, corrosion time and density of the specimens, C is a conversion constant (C=87.6).

3. RESULTS AND DISCUSSION

3.1 Structural and morphological characterization

Fig.2 is the XRD picture showing the product formed on the patina bronze surface. It is found that green patina consist mainly of $Cu_2(OH)_3Cl$, which is called “bronze cancer”， a common patina on the bronze archaeological artefacts. Fig.3 is the XPS spectrum of the rusty surface on cast iron. From [27] the binding energy of γ-FeOOH or $Fe(OH)_3$ is 711.3 eV which is the same as the peak of Fe2p3 in Fig.3. So it can be identified that the product of rusty cast iron exist as γ-FeOOH or $Fe(OH)_3$, which is the most harmful rust on iron archaeological artefacts.

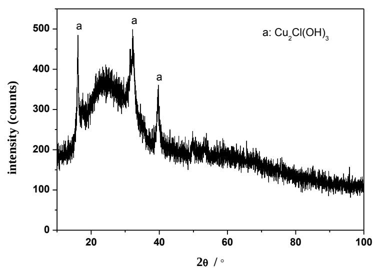

Figure 2. X-ray diffraction diagram of patina bronze surface

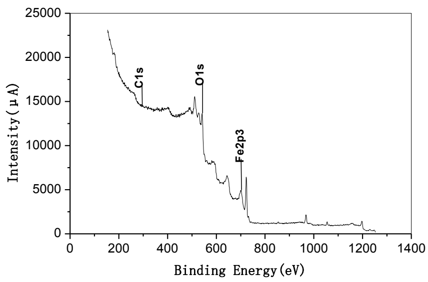

Figure 3. The XPS spectrum of the rusty surface of cast iron

3.2 Effectiveness of inhibitors on bare bronze

The corrosion rate of bare bronze without inhibitors is presented in Table 3.

The corrosion rate (*v*) of bare bronze in the corrosive medium respectively were closed to the corrosion resistance grade (0.01mm/y), which illustrated that the bare bronze without inhibitors have a good corrosion resistance. But the corrosion rate of the precious archaeological artefacts even as low as 0.01mm/y also can not be ignored. The inhibitors should be applied on the archaeological artefacts.

Table 3. The corrosion rate of bare bronze without inhibitors

Corrosion medium	v(mm/y)
0.05M H_2SO_4	0.016
0.1M NaOH	0.018
0.028MNaCl+ 0.01M Na_2SO_4+0.016M $NaHCO_3$	0.011

Table 4. The inhibiting efficiency of simple inhibitors on bare bronze (%)

	0.05M H_2SO_4			0.1M NaOH			0.028MNaCl+ 0.01M Na_2SO_4 +0.016M $NaHCO_3$		
	10^{-2}M	10^{-3}M	10^{-4}M	10^{-2}M	10^{-3}M	10^{-4}M	10^{-2}M	10^{-3}M	10^{-4}M
B1	43.65	59.67	50.00	96.43	74.63	62.80	93.97	89.91	97.95
B2	86.41	93.87	94.83	98.59	97.92	73.96	97.97	88.35	94.03
B3	98.71	94.94	94.95	98.58	86.28	94.43	87.65	93.20	84.00
B4	93.43	98.79	97.38	91.59	98.62	98.57	59.65	92.19	89.04
B5	90.77	86.96	72.60	92.87	95.87	81.52	97.98	84.09	73.91

Table 5. The inhibiting efficiency of mixed inhibitors on bare bronze (%)

	0.05M H_2SO_4	0.1M NaOH	0.028MNaCl+ 0.01M Na_2SO_4+0.016M $NaHCO_3$
B6	-50.83	15.85	-52.17
B7	51.88	70.67	95.49
B8	97.03	87.01	86.17

The inhibiting efficiency of inhibitors on bare bronze is presented in Table 4 and 5.

In 0.05M H_2SO_4 solution, AMT, MBO and MBT at the concentration of 10^{-4}M~10^{-2}M, the inhibiting efficiency of them were higher than 85%, and the maximum even approached to 99%. It proved that the three inhibitors gave a super protective effect on bare bronze in dilute sulphuric acid. The inhibiting efficiency of PMTA at the concentration of 10^{-2}M, 10^{-3}M reached 90.77%, 86.96%, and at the 10^{-4}M, it was 72.60%, which illustrated that at an appropriate concentration the PMTA could protect the bare bronze well. The inhibiting efficiency of BTA were lower than 60% at the concentration of 10^{-4}M~10^{-2}M, which showed unfavorable protection. A protective layer of Cu(I)BTA complex was formed on the bare bronze surface in the solution of pH at 4~10 [28]. Also the poor protective performances of BTA on bronze have already been documented [29].

In 0.1M NaOH, the maximum inhibiting efficiency was higher than 95% in presence of these inhibitors. In simulated atmosphere corrosion solution, except for MBT in 10^{-2}M and PMTA in 10^{-4}M, all the inhibiting efficiency was higher than 85% in this work.

0.004% BTA+0.1% sodium benzoate +3% EDTA even accelerated corrosion of bare bronze in 0.05M H_2SO_4 and in simulated atmosphere corrosion solution, it didn't have an inhibition effect on bare bronze in this work. In simulated atmosphere corrosion solution, 0.03%BTA+0.02%sodium molybdate +0.04%sodium polyphosphate gave a good inhibiting efficiency of 95.49%. The inhibiting efficiency of 1% BTA+0.1% sodium dodecylbenzene sulfonate in the three corrosion medium all were higher than 85%, which illustrated that this inhibitor compound was good enough in this work.

Therefore, the inhibiting efficiency of these inhibitors depends on not only the self compound type, but also the concentration and corrosion medium.

3.3 Effectiveness of inhibitors on patina bronze

The inhibiting efficiency of inhibitors in corrosive medium on patina bronze is presented in Table 6.

Table 6. The inhibiting efficiency of inhibitors on patina bronze (%)

	B1	B2	B3	B4	B5	B6	B7	B8
0.05M H_2SO_4	28.46	30.37	43.99	6.06	36.47	78.13	13.88	15.78
0.1M NaOH	28.33	45.32	-13.27	-114.91	5.56	23.45	61.75	14.95
0.028MNaCl+ 0.01M Na_2SO_4+0.016M $NaHCO_3$	-61.19	-49.52	5.04	-68.89	-34.80	12.57	-65.00	-83.78

The inhibiting efficiency of inhibitors all were lower than 85% (Table 6), which showed poor protection on green patina, even some of them accelerated the bronze corrosion. The same phenomenon has already been documented [12, 13]. In 0.05M H_2SO_4, 0.004% BTA+0.1% sodium benzoate+3% EDTA showed the best protection effect in these inhibitors. In 0.1M NaOH, the best protection inhibitor was 0.03% BTA+0.02% sodium molybdate +0.04% sodium polyphosphate on patina bronze. But all the inhibitors showed poor inhibiting efficiency in simulated atmosphere corrosion solution.

Compare with Table 4, 5 and 6, the inhibiting efficiency of simple inhibitors showed an apparently good protection on bare bronze than on green patina bronze. This phenomenon may be that the prefilming treatment forming a film on the surface and sealed Cl^-. As the Cl^- was the most dangerous factor to accelerate corrosion. But the mixed inhibitors could both replace the chlorine iron and inhibit the corrosion [21], so the protect effectiveness of mixed inhibitors in 0.05M H_2SO_4 and 0.1M NaOH solution were better than simple inhibitors. So the mixed inhibitor is a good selection in the practical protection on the bronze cultural heritage.

3.4 Effectiveness of inhibitors on cast iron

The inhibiting efficiency of inhibitors in different corrosive medium on bare and rusty cast iron was presented in Table 7 and 8.

Table 7. The inhibiting efficiency of inhibitors on bare cast iron (%)

	C1	C2	C3	C4	C5	C6	C7	C8
0.05M H_2SO_4	13.69	-0.31	-8.97	-2.35	-13.25	-2.13	-0.29	0.58
0.1M NaOH	29.38	-11.02	-7.61	-11.56	7.73	7.83	5.67	-21.51
0.028MNaCl+ 0.01M Na_2SO_4 +0.016M $NaHCO_3$	-0.92	-23.97	-5.43	-22.76	10.26	1.22	-13.84	-5.58

Table 8. The inhibiting efficiency of inhibitors on rusty cast iron (%)

	C1	C2	C3	C4	C5	C6	C7	C8
0.05 M H_2SO_4	20.37	10.19	27.31	34.63	31.30	52.31	42.13	44.07
0.1M NaOH	13.14	34.95	48.10	48.67	41.71	62.86	72.48	45.05
0.028MNaCl+ 0.01M Na_2SO_4 +0.016M $NaHCO_3$	72.96	28.61	48.24	40.19	26.67	36.39	43.70	27.59

The inhibiting efficiency of inhibitors on bare cast iron all were lower than 30%, some of them even accelerated corrosion (Table 7), on rusty cast iron, most of them were lower than 50% (Table 8). It showed that the inhibitors on cast iron with the prefilming treatment can not protect the iron cultural heritage from the corrosion of the environment medium. Up to now, in the actually protection, only the prefilming treatment can be used. So there is a need to explore a new way or a new inhibitor to protect the iron cultural heritage.

4. CONCLUSION

The simple inhibitors(BTA, AMT, MBO, MBT, PMTA) at the concentration of 10^{-4}M~10^{-2}M and 1% BTA+0.1% sodium dodecylbenzene sulfonate all have perfect protection effect (maximum IE> 90%) on bare bronze in 0.05M H_2SO_4(except for BTA), 0.1M NaOH and simulated atmosphere corrosion solution (0.028MNaCl+ 0.01M Na_2SO_4+0.016M $NaHCO_3$). The mixed inhibitor (0.004% BTA+0.1% sodium benzoate +3% EDTA) can not protect the bare bronze from corrosion, and even accelerated it. 0.03% BTA+ 0.02% sodium molybdate +0.04% sodium polyphosphate only in simulated atmosphere corrosion solution gave a good inhibiting efficiency of 95.49%. So the inhibiting efficiency of these inhibitors depends on not only the self compound type, but also the concentration and corrosion medium.

With the prefilming treatment, all the inhibitors used on green patina bronze or bare and rusty cast iron in this work showed poor protection, some of them even accelerated corrosion. So the prefilming treatment can not protect the cultural heritage with harmful patina from the corrosion of the environment medium and there is a need to explore a new way or a new inhibitor to protect the cultural heritage.

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