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# Formation of Black Patina on Bronze Mirrors Caused by Multiphenol

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**Abstract**: Hot solution of hydroquinone is oxidized by air forming quinone and quinhydrone, both of which have weak oxidizeability, enabling to oxidize metals on the surface of bronze mirror samples forming black and brilliant patina. SEM and electron microprobe analysis show that Cu content is lower than that of the original alloy due to Cu loss; Sn content is higher than the original alloy in patina. This indicates that humic acid is not the substance resulting in making black patina on the bronze mirror surface, but the black patina which produced from hydroquinone solution absence of Si, Al and Mg.
**Key words**: bronze mirrors, black patina, multiphenol, metallic corrosion

As mentioned in the preceding paper[1], surface of bronze mirror samples treated by humic acid are jet-black or brown, grey and brilliant, and in the black patina layer the contents of Cu and Sn change; the presences of Si, Fe, Al and Mg being different from the original alloy are all in agreement with the results of surface investigation of unearthed black patina of bronze mirror fragments. In addition, both have four broader diffusion peaks which located near $2\theta$ angles obtained by XRDA. The main reason is due to the presence of benzoquinonyl radical or phenolhydroxyl radical in humic acid molecule, phenolhydroxyl radical can easily oxidize to benzoquinonyl radical[2,3].

Actually quinone is the simplest benzoquinone in structure and hydroquinone is the least multiphnol in term of hydroxyl radical, it is a weak organic acid with reductibility, being used as either developer for senitive film, or oxidized by contained $K_2Cr_2O_7$, $FeCl_3$ solution, even oxidized by air with hot solution containing hydroquinone forming the yellow solution containing quinone and in course acidity of solution is in certain extent enhanced.

## 1 Experimental method

A hypothetical structure of humic acid is shown in Fig. 1.

### 1.1. Sample and treatment conditions

The 02 bronze alloy samples were used, which contained Cu(69.7%), Sn(28.9%), Pb(0.9%) and Fe(0.5%). Surface were polished and cleaned up by acetone.

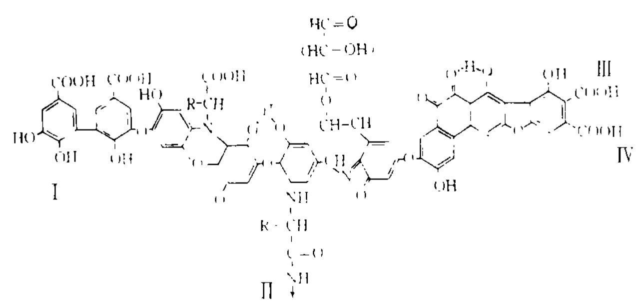
I  II III IV

**Fig.1 A hypothetical structure of humic acid**
**Ⅰ. phenolhydroxyl; Ⅱ. benzoquinonyl**
**Ⅲ. salicylic acid group; Ⅳ. o-phthalic acid group**

Two portions of analytically, pure hydroquinone (0.25 g in 100 ml $H_2O$), one portion of tannic acid (0.25 g in 100 ml $H_2O$) were used for samples treatment solution being free from acidity adjustment. Samples being cleaned up were put in containing hydroquinone and tannic acid solution respectively; the other portion of hydroquinone solution was free from bronze mirror sample. Solutions were put simultaneously in water bath at (50 ± 1) ℃, for 30 d. The solution wasn't be changed and the patina being of black brilliant surfaces were obtained, surface roughness $R_a = 0.130 \sim 0.172$ μm, after sample treatment the pH of containing quinone solution was 3.5 ~ 3.7 (pH is 6.1 prior to treatment).

### 1.2 Experimental results

(1) The element distribution in cross-section of

sample patina.

SEM measurements gave a patina thickness of 76 μm of sample 02D(alloy 02 was immersed in hydroquinone solution at (50 ± 1) ℃ for 30 d); while the thickness was 10.5 μm on sample 02H(alloy 02was immersed in humic acid solution, temperature = (88 ± 1) ℃ , pH = 6 for 50 d) and 190 μm on the unearth black patina of bronze mirror 290. The results of energy dispersive X-ray analysis for these samples are shown in Fig. 2. The composition changes showed the same tendency in these three samples, namely impoverishment of copper and enrichment of tin towards the surface, and the presence of Fe, Al and Si in the patina of 01H and 290, it has been proved that in the case of alloy 01, the sample had not contact with Fe, Al and Si bearing material except for humic acid.

(2) Electron microprobe analysis.

Surfaces were analyzed by petrographic microscope, indicating mainly three coloured portions which are black, brown yellow and white yellow. Then the elements correlated in these locations with the three kinds of colours observed under in petrographic microscope were analyzed by electron microprobe with energy dispersive X-ray analysis. The results are shown in table 1.

(3) Chemical analysis of the hydroquinone.

After drying out the blank and residue hydroquinone, take a portion for chemical analysis of Cu, Fe, Pb, Al and Si. The results are shown in table 2.

In table 2, residue solution No. 1 ~ 6 are sampled after being taken from the exchanged per 4 d successively in 24 d. Analysis results indicate that whatever in the residue solution Cu, Pb contents are higher than that of the blank solution, showing in the course of hydroquinone treatment for bronze mirror samples, CuO and PbO are soluble in hydroquinone solution being increased in acidity, Fe and Al remained unchanged prior to and after the treatment, Si content increased. On account of Si absence in the alloy sample, reason for the increase in Si content in the residue solution is probably due to the dilute acid corrosion of the glass container used in the experiment.

(4) IR analysis of hydroquinone.

IR spectrums of hydroquinone used for treatment of bronze mirror alloy No. 02 and blank are shown in Fig. 3.

Analysis results indicate that prior to or after hydroquinone treatment of bronze mirror samples are characterized by constancy of the absorption frequency, showing that the decrease in Cu content in the patina is not due to coordination of $Cu^{2+}$ ions to hydroquinonyl.

### 1.3 Treatment of the bronze mirror samples by other multiphenol

Taking 0.25 g of o-dihydroxylbenzene, resorcin and quinone respectively dissolve in 100 ml of deionized water, after putting ground bronze mirror

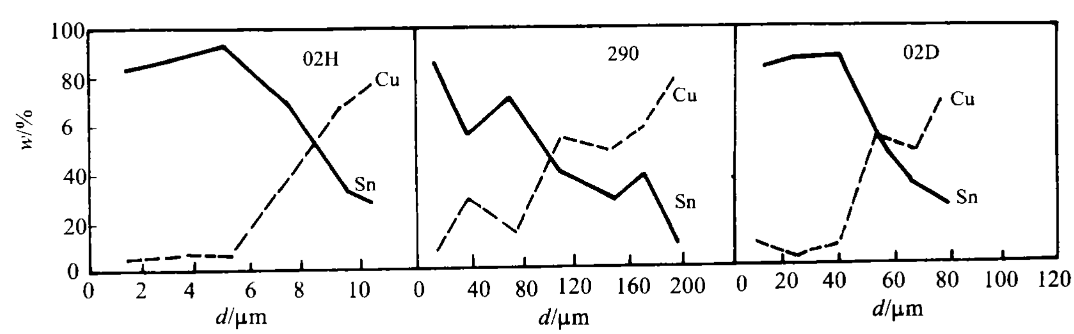



**Fig.2 Distribution of Cu and Sn in cross-section of sample patina**

**Table 1 Analytical results of the patina of sample 02D(mass fraction)** %

| Elements | Surface of sample 02D | | | Oxides | Oxide surfaces of sample 02D | | |
|---|---|---|---|---|---|---|---|
| | black | brown yellow | white yellow | | black | brown yellow | white yellow |
| Sn | 62.9 | 70.2 | 70.9 | $SnO_2$ | 79.8 | 89.1 | 90.0 |
| Cu | 13.8 | 6.7 | 7.4 | CuO | 17.1 | 8.3 | 9.3 |
| Fe | 2.4 | 2.0 | 0.6 | FeO | 3.1 | 2.6 | 0.8 |
| O | 21.0 | 21.2 | 21.1 | | | | |
| Total | 100.1 | 100.1 | 100.0 | Total | 100.0 | 100.0 | 100.1 |

**Table 2 Chemical analysis results of hydroquinone(mass fraction)** %

| | Cu | Pb | Fe | Al | Si |
|---|---|---|---|---|---|
| Blank hydrouinone | $4.5\times10^{-4}$ | $7\times10^{-4}$ | 0.02 | 0.02 | 0.037 |
| Residue of treating solution 1 | 0.19 | 0.039 | 0.02 | 0.02 | 0.085 |
| Residue of treating solution 2 | 0.15 | 0.10 | 0.02 | 0.02 | 0.14 |
| Residue of treating solution 3 | 0.16 | 0.013 | 0.02 | 0.02 | 0.096 |
| Residue of treating solution 4 | 0.09 | 0.005 | 0.02 | 0.02 | 0.13 |
| Residue of treating solution 5 | 0.28 | 0.013 | 0.02 | 0.02 | 0.30 |
| Residue of treating solution 6 | 0.15 | 0.11 | 0.02 | 0.02 | 0.15 |

samples, heated in water bath at (45 ± 1) C for

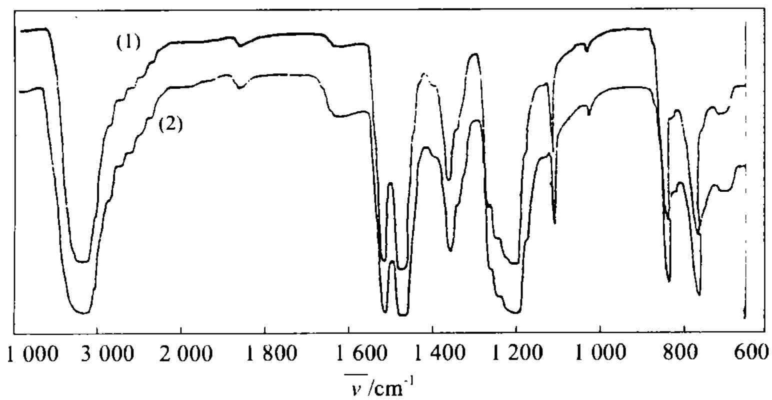



**Fig.3 The IR spectrum of hydroquinone**

**(1) hydroquinone solution heat at 50℃ for 30 d; (2) obtained from hydroquinone treating solution**

30 d, the obtained sample surfaces are all dark brown, the pH of those residue solution is of 3.5 ~ 3.7, but the original is 6.0, 6.2 and 3.7 respectively.

## 2 Discussions

### 2.1 Formation of the black patina on bronze mirror sample surfaces

It is shown in experiment that hydroquinone solution can oxidize metallic elements on the bronze mirror sample surface, forming the corresponding oxide films, colours and the surface roughness of the oxide films obtained are silimar to those of the unearthed bronze mirror fragments with black patina, and the changes of Cu and Sn content from external to the internal are all agreement with the results of the patina of unearthed bronze mirror fragments with black patina and the bronze mirror samples treated by humic acid.

### 2.2 Iron, aluminum, silicon and maguesium

On account of trace amounts of Fe, Si and Al in hydroquinone used for this experiment, in the patina of bronze mirror sample surfaces treated by hydroquinone solution, surely there are no those elements, surely there is not Mg either (Mg is not analyzed ). This had already been identified with energy dispersive X-ray analysis of SEM and EPM. As there are no Si, Al and Mg (or Fe) contents in the patina of the 02D samples treated by hydroquinone, this further identifies that the formation of black patina is due to long time reaction between humic acid in soil and the embedded bronze mirrors.

### 2.3 Copper loss and tin enrichment

Increment in the solubility of CuO due to the increase of solution acidity can be calculated by solubility product constant.

$$Cu(s) + H_2O = Cu^{2+} + 2OH^-$$

$$K = [Cu^{2+}][OH^-]^2 = 10^{-20.35}$$

The pH of the solution is 3.5, then $[OH^-]$ is $10^{10.5}$ mol/l, from the side reaction coefficent[4 ~ 6]

$$a_{Cu} = 1 + 10^{6.3}[OH^-] + 10^{10.7}[OH^-]^2 + 10^{14.2}[OH^-]^3 + 10^{16.4}[OH^-]^4$$

Where $10^{6.3}$, $10^{10.7}$, $10^{14.2}$, $10^{16.4}$ respectively are the cumulative stability constants for each stage hydroxyl coordination ion $Cu(OH)_n^{-n+2}$, substituting ionic concentration of $OH^-$ ions from the residue solution, calculate $a_{Cu} = 1$, indicating that in this case $Cu^{2+}$ ions are hardly by hydrolysis, then the solubility $s$ of CuO

$$s = K_{sp} / [OH^-]^2 = 10^{-20.35} / 10^{-21} = 10^{-0.65} \text{ mol/l}$$

in case in pure water the pH = 7, solubility of CuO can be calculated equal to $1.0 \times 10^{-7}$mol/l in comparision with both; solubility of CuO in pH = 3.5 solution remarkably increase due to the increase of solution acidity.

Quadrivalent tin ions bring about strong hydrolysis in the solution, this makes the side reaction coefficent = $10^{13}$ when solution pH = 3.5, so in this condition solubility product constant,

$$K' = K_{sp} \times a_{Sn} \times a_{OH} = 10^{-64.4} \times 10^{13} \times 1 = 10^{-51.4}$$

$$s = 10^{-51.4} / (10^{-10.54})^4 = 10^{-9.4} \text{ mol/l}$$

It indicates that in this condition, solubility of $SnO_2$ remains quite small, thereby, it does result in copper loss on the surface of the patina of the bronze mirror samples being treated by hydroquinone solution.

## 3 Conclusion

Hydroquinone reacts with bronze mirror sample surfaces, which can form the black patina on the surfaces, reaction as mentioned may include two stages, the first oxidation of metals

$$2Cu(Sn,Pb) + C_6H_4O_2 + H_2O = Cu_2O(SnO, PbO) + C_6H_4(OH)_2$$

$$Cu_2O(SnO) + C_6H_4O_2 + H_2O = 2CuO(SnO_2) + C_6H_4(OH)_2$$

the second dissolution of metallic oxides on the patina surfaces

$$CuO(PbO) + 2H^+(\text{very dilute}) = Cu^{2+}(Pb^{2+}) + H_2O$$

$SnO_2 + 4H^+$( very dilute ) practically insoluble.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# Intelligent Control Method for the Secondary Cooling of Continuous Casting


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**Abstract**: An intelligent control plan for the secondary cooling of continuous casting of slab was put forward. An off-line simulation of the system by using neural networks combined with fuzzy logic control is provided. The results show that the intelligent control system can not only control the surface temperature of the bloom of the secondary cooling but also has a good ability of self-adaptation and self-learning.



**Key words**: continuous casting, artificial neural networks, fuzzy control

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