

# Formation of Black Patina on Bronze Mirrors Caused by Humic Acid

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**Abstract:** The formation of black patina caused by soil humic acid under different conditions has been studied, and the black, grey and brown shiny surfaces prepared in laboratory have been analysed. The formation of tin-rich shiny black surface on mirrors was the product of the soil corrosion of the bronze mirrors. It is formed by reaction between the alloy and the humic acid in soil, and leaching of copper and lead oxides through a long period of time when the mirrors were buried under the ground. A dense corrosion-resistant layer on the bronze mirrors consisted predominantly of stannic oxide.

**Key words:** bronze mirrors, black patina, humic acid, soil corrosion

Bronze mirrors with black patina on the black and shiny surface are embedded in the soil for more than a thousand years. It was corroded only  $10^{-4}$  mm in depth per year. The black patina is known to the antiquarians as "Hei-qi-gu" or black lacquer antique, a name appeared in Chinese literature in about 960 ~ 1279 A.D.. In the past 70 years a great deal of investigations have been carried out both at home and abroad on the special surface of the patina. Except the black shiny surface, the following information has been obtained: higher tin content and less copper content exist in the black patina than that in original alloys. However, there are also impurities such as Fe, Al and Si, which are absent in the original alloy and there are some metallic oxides such as  $\text{SnO}_2$  or  $\text{SiO}_2$  in the black patina. There are mainly two points of view accounting for the formation of black patina: (1) Collins<sup>[1,2]</sup> and Gettens<sup>[3,4]</sup> suggested in their earlier studies that the patina was the result of corrosion. (2) Chase and Franklin<sup>[5]</sup> studied its chemical composition, they showed that there was enrichment of tin oxide in patina with a small amount of other elements such as Si and Fe. Some Chinese scholars<sup>[6,7]</sup> suggested that the high tin content on the patina surface is due to artificial tinning by coating or corrosion by ferric chloride. It is widely known among Chinese antiquarians that the black patina is more frequently found on bronzes, particularly mirrors, embedded in certain geographical regions and that it is more commonly associated with wet or cultivated soil. Shan-Chun

Liang summarizing the unearthening of bronze mirrors said that, there are a lot of water pits in South China and the water quality is of acidity, "Hei-qi-gu" is abundant. Substances which cause corrosion of the bronze mirrors surface in soil include dissolved oxygen,  $\text{MnO}_2$ , ferric oxide and humic acid. The composition and structure of humic acid vary with soil, generally regarded as a reducing agent in soil, relative to some other constituents such as the  $\text{MnO}_2$ . As humic acid structure contains benzoquinonyl radicals, redox potential  $E_h$  is about 0.7 V in water<sup>[8]</sup>, theoretically, humic acid can oxidize Cu, Sn and Pb in the bronze mirror surface, forming the corresponding metallic oxides or aqueous metallic ions. In addition, humic acid contains also salicylic acid radical and o-phthalic acid radical which can make selective coordination with a lot of metallic ions such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , etc. in solution, thereby resulting in dissolution of metallic oxides and oxidized mineral related<sup>[9]</sup>.

## 1 Experimental method

### 1.1 Preparation of humic acid and bronze mirror samples

Humic acid is the most typical constituent product when humus is extracted from soil with alkali and then acid. Sodium humate from Beijing region was used as a raw material for preparation of humic acid. Its average molecular weight was 2857<sup>[10]</sup>, and the redox potential ( $E_h$ ) was measured to be about 0.65 V<sup>[8]</sup>.

Samples simulating bronze mirror named alloy 01 or 02 were prepared by melting of electrolytic Cu(70%), Sn(25%), Pb(5%) with or without some Fe. The samples numbered 290, 649, 643 and 223 are the unearthed black patina bronze mirror fragments from periods 618 ~ 907 A.D. and 475 ~ 221 B.C.. The effect of tin content of the alloy was studied with samples taken from ancient bronzes of different composition. Before immersion tests the sample surfaces were ground with 1000 mesh emery paper and mechanically polished.

### 1.2 Corrosion study

Polished bronze samples (roughness =  $0.015 \sim 0.04 \mu\text{m}$ ) were immersed in pH =  $4 \sim 10$  humic acid solution (1 g in 100 ml  $\text{H}_2\text{O}$ ), the temperature was kept at  $(85 \pm 1)^\circ\text{C}$  for 50 d.

### 1.3 Composition and structure of the patina

The distribution of Cu, Sn, Fe, Al and Si in the cross-sections of patina sample was measured with energy dispersive X-ray analysis of SEM. The colour of patina surfaces were observed by petrographic microscope, then the regions of different colours were analyzed by electron microprobe to detect the composition. The humic acid was analyzed by atomic absorption spectrometer and infrared spectrophotometer. In order to observe the crystalline structure X-ray diffraction analysis and electron diffraction analysis were carried out on the sample of patina<sup>[11]</sup>.

## 2 Experimental results

Under the same conditions better patina can be obtained if the amount of tin is about 25%, as sample 290 the original patina was completely or partially removed by polishing, the sample had been immersed in humic acid solution, the better black patina named 290H was obtained. The qual-

ity of patina decreased in the case of the tin content lower than 20%. It was identified by experiment that black, grey or brown patina is attainable when pH is  $5.5 \sim 6$  in humic acid solution (table 1), in case higher or lower this value better patina is unattainable. The pH value of solution decreased about  $0.5 \sim 1$  per 4 d in humic acid solution immersed the sample. The rate of sample weight loss was higher at the initial stage and slowed down with the immersing time of the patina increased (Fig. 1), simultaneously the pH of the solution decreased. The presence of Fe, Al and Si in the patina of 290 and 01H (alloy 01 was immersed in humic acid solution at  $(88 \pm 1)^\circ\text{C}$  and pH = 6 for 50 d). It has been proved that in the case of alloy 01, the sample had not contacted with Fe, Al and Si bearing material except humic acid.

The internal reflection colours of the sample 02H and 290 surfaces were observed by a petrographic microscope. Sample 290 has black colour as its prominent colour and has some black-green and orange colour in addition; sample 02H showed a yellowish-green colour over most of the surface and some black and yellow colour in the same areas. Then the elements relating with the three kinds of colours observed in those locations under the petrographic microscope were analyzed by electron microprobe with energy dispersive X-ray analysis. The results are listed in table 2.

Atomic absorption spectrometric and infrared spectrophotometric analyses were carried out on the original or blank and residue of humic acid. Chemical analysis results are listed in table 3.

The spectra of the humic acid used for immersing bronze mirror samples and the original humic acid are shown in Fig. 2. By comparison the spectra show the two absorption peaks at  $\tilde{\nu} = 1720 \text{ cm}^{-1}$  and  $\tilde{\nu} = 1230 \text{ cm}^{-1}$  disappeared, while two bands at  $\tilde{\nu} = 1600 \text{ cm}^{-1}$  and  $\tilde{\nu} = 1386 \text{ cm}^{-1}$

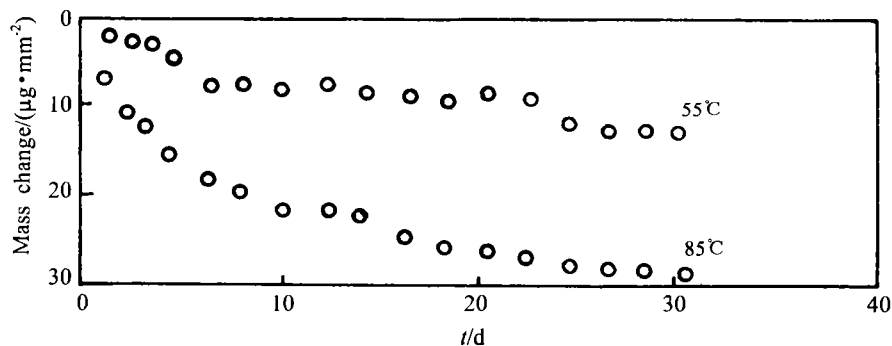


Fig.1 Relationship between sample mass changes with treating times

**Table 1 Influence of pH of humic acid solution on the formation of sample patina (85 °C)**

| Sample No.         | pH of solution | Duration/d | Surface appearance     | Roughness / $\mu\text{m}$ |
|--------------------|----------------|------------|------------------------|---------------------------|
| 1                  | 4              | 9          | copper, rough          |                           |
| 2                  | 5              | 9          | black brown, rough     |                           |
| 3                  | 5.5            | 51         | black, lustre          |                           |
| 4                  | 6              | 51         | dark grey, lustre      | 0.159~0.238               |
| 5                  | 7              | 51         | grey, lustre           |                           |
| 6                  | 8              | 51         | grey, lustre           |                           |
| 7                  | 9              | 51         | dark yellow, no lustre |                           |
| 8                  | 10             | 51         | yellow, no lustre      |                           |
| 9(290 fragment A)  | 6              | 50         | jet-black, lustre      |                           |
| 10(290 fragment B) | 6              | 7          | jet-black, lustre      |                           |

**Table 2 Analytical results of different colored portions by electron microprobe analysis %**

| Composition                    | Surface of sample 290 |        |                | Surface of sample 02H |        |              |
|--------------------------------|-----------------------|--------|----------------|-----------------------|--------|--------------|
|                                | black                 | orange | blackish green | black                 | yellow | yellow green |
| Elements                       |                       |        |                |                       |        |              |
| Sn                             | 43.9                  | 54.6   | 45.8           | 21.0                  | 59.8   | 62.6         |
| Cu                             | 29.0                  | 4.8    | 24.2           | 56.3                  | 9.0    | 8.1          |
| Fe                             | 1.2                   | 4.9    | 1.3            | 0.5                   | 1.0    | 1.5          |
| Si                             | 0.9                   | 3.6    | 1.9            | 0.2                   | 2.3    | 1.5          |
| Al                             | 0.1                   | 1.4    | -              | 0.2                   | 3.3    | 2.6          |
| Mg                             | 0.9                   | 1.6    | 1.1            | 0.9                   | 0.2    | 0.2          |
| Pb                             | 2.8                   | 5.0    | 3.8            |                       |        |              |
| O                              | 21.3                  | 24.1   | 21.9           | 20.9                  | 24.4   | 23.5         |
| total                          | 100.1                 | 100.0  | 100.0          | 100.0                 | 100.0  | 100.0        |
| Oxides                         |                       |        |                |                       |        |              |
| SnO <sub>2</sub>               | 55.7                  | 69.3   | 58.1           | 26.7                  | 76.0   | 79.6         |
| CuO                            | 36.3                  | 6.0    | 30.3           | 70.5                  | 11.3   | 10.2         |
| FeO                            | 1.5                   | 6.3    | 1.7            | 0.6                   | 1.2    | 2.0          |
| SiO <sub>2</sub>               | 1.9                   | 7.7    | 4.1            | 0.3                   | 4.9    | 3.2          |
| Al <sub>2</sub> O <sub>3</sub> | 0.2                   | 2.7    | -              | 0.3                   | 6.2    | 4.9          |
| MgO                            | 1.5                   | 2.7    | 1.7            | 1.6                   | 0.4    | 0.3          |
| PbO                            | 3.0                   | 5.4    | 4.1            |                       |        |              |
| total                          | 100.1                 | 100.1  | 100.0          | 100.0                 | 100.0  | 100.2        |

**Table 3 Chemical analysis results of humic acid (mass fraction) %**

|                                      | Cu    | Sn     | Pb   | Fe    | Mg    |
|--------------------------------------|-------|--------|------|-------|-------|
| Blank humic acid                     | 0.020 | ≤0.001 | 0.19 | 0.120 | 0.068 |
| Residue of treating solution 1       | 0.330 | ≤0.001 | 0.19 | 0.100 | 0.039 |
| Residue of treating solution 2       | 0.130 | ≤0.001 | 0.16 | 0.094 | 0.032 |
| Residue of treating solution 3       | 0.048 | ≤0.001 | 0.16 | 0.110 | 0.029 |
| Residue of treating solution 4       | 0.021 | ≤0.001 | 0.20 | 0.120 | 0.018 |
| Residue of treating solution 5       | 0.061 | ≤0.001 | 0.14 | 0.120 | 0.046 |
| Residue of treating solution 5(55°C) | 0.025 | ≤0.001 | 0.13 | 0.077 | 0.019 |

strengthened in spectrum 2. Spectrum 2 is in accordance with Cu-humate<sup>[10]</sup>.

### 3 Discussion

#### 3.1 Formation of the black patina on bronze mirrors

Gettens<sup>[3]</sup> suggested that bronze mirror embed-

ded in soil caused Cu and Sn on the mirror surface oxidized due to the reaction of air or of oxygen in underground water and in mineral. But the redox potential of copper, tin and lead in forming CuO, SnO<sub>2</sub>, and PbO at solution pH = 6 are 0.199, - 0.362 and - 0.112 V respectively. The humic acid solution at pH = 6 is about 0.4 V. It

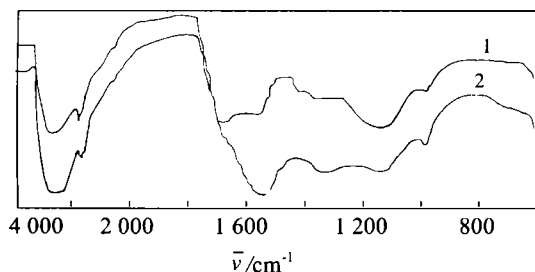


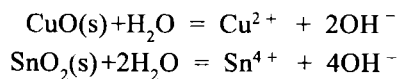
Fig.2 The IR spectra of humic acid

- (1) humic acid solution heated for 96 h at 85°C  
 (2) obtained from humic acid treating solution

shows that the humic acid can easily oxidize copper, tin and lead to  $\text{Cu}_2\text{O}$ ,  $\text{SnO}$  and  $\text{PbO}$ , and to  $\text{CuO}$ ,  $\text{SnO}_2$  also, but not  $\text{Cu}^{2+}$ ,  $\text{Sn}^{4+}$  and  $\text{Pb}^{2+}$  ions if there is enough humic acid. So  $\text{CuO}$ ,  $\text{SnO}_2$  and  $\text{PbO}$  are the main constituents of patina.

### 3.2 Copper loss and tin enrichment in patina

Gettens<sup>[3]</sup> also suggested that copper on the bronze mirror surface being buried in the soil were oxidized to be copper ions, then carried away by carbonic acid-bearing water. In this paper, it is identified experimentally that cupric oxide on the bronze mirror surface is dissolved in the humic acid solution due to the formation of chelates by humate ions as the ligand, while tin oxides don't form stable chelates with humate ions, thereby resulting in copper loss and tin enrichment in the patina. As it is known, the solubility product constants of  $\text{CuO}$  and  $\text{SnO}_2$  in pure water are  $10^{-23.5}$  and  $10^{-64.4}$  respectively<sup>[13]</sup>, and their dissolution in pure water can be expressed by the following two reactions:



By these equations the solubilities of  $\text{CuO}$  and  $\text{SnO}_2$  in pure water can be calculated to  $1.07 \times 10^{-7}$  mol/l and  $1.6 \times 10^{-15}$  mol/l, and the solubility is  $4.5 \times 10^{-5}$  mol/l for  $\text{CuO}$  in pH = 6 solution. Because humic acid can form a chelate with  $\text{Cu}^{2+}$  ions, it can be shown by calculation that in this solution the solubility of  $\text{CuO}$  may increase to be 0.5 mol/l as the humic acid has  $\text{p}K_{a1} = 3.2$ ,  $\text{p}K_{a2} = 4.9$  and if  $\log \beta_2$  is about 9.0.  $\text{SnO}_2$  does not react with humic acid and in a pH = 6 solution its solubility is  $4 \times 10^{-11}$  mol/l. This is the reason why copper is lost and tin is enriched in the patina.

On the other hand, when the bronze mirror sample is immersed in humic acid solution, copper is partially lost from the patina which makes the sample mass and the pH value of solution decreased.

### 3.3 Silicon, aluminium, iron and magnesium in patina

In this study as well as those studied by Chase and Franklin<sup>[3]</sup>, and He Tangkun<sup>[4]</sup> showed that the unearthed mirror fragment and the surface of bronze mirror samples immersed in humic acid solution contained little Fe, Si, Al and Mg in the patina. These elements did not exist in the original alloy. Analyses (Table 3) showed that the humic acid contained some Si, Fe, Al and Mg, during immersion in humic acid solution the Fe, Al and Mg humate reacted with the bronze mirror sample surfaces, at the same time copper was lost and Fe, Al and Mg deposited in the patina. Furthermore, silicate which was absorbed by humic acid might form insoluble  $\text{SiO}_2$  in the patina through hydrolysis and dehydration.

### 3.4 Factors influencing formation of black patina

(1) Humic acid, tin content and the solution pH.

In the same conditions grey or brown patina was obtained in different sources of humic acid, and better patina can be obtained in case the amount of tin is about 25%. It is also identified by experiment that the brown, grey or black patina are attainable when pH is 5.5 ~ 6.0 in solution.

(2) The colour of patina.

The black patina is attained when the solution pH is 5.5, because in a definite range of solution pH with a same ionic strength, the stability constant of Cu-humate is greater at pH = 6 than that at pH = 5, when the solution pH = 5.5 small amount of  $\text{CuO}$  are dissolved out, sample surface is black. Black patina are also obtained in case of polishing off the patina on the surface of unearthed mirror fragment also, with the same humic acid at the solution pH = 6, it is probably due to trace element influence.

(3) Anion in solution.

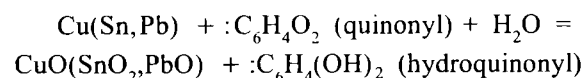
Chlorine ions can lengthen the time for patina growth, however, better quality is obtained. In the presence of sulfate radical, carbonate radical or sili-

cate radical ions, growth of the patina accelerated, however, brightness of the patina decreased.

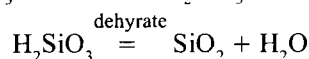
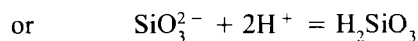
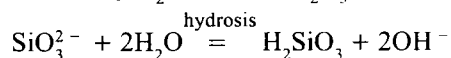
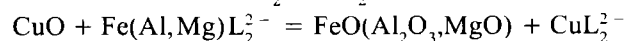
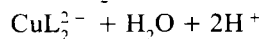
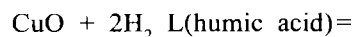
## 4 Conclusions

The formation of the black patina on some ancient Chinese bronze mirrors by humic acid or humus in wet aciditic soil may include two stages.

the first



the second



First the patina was formed on the sample surfaces, then the further oxidation of the metal by humic acid must proceed through the patina. In this case the oxidation of bronze mirror samples was controlled by diffusion of oxygen ions inward and  $\text{Cu}^{2+}$  ions outward. Both processes are very slow. So a thick patina film needs a very long time for its formation. In addition, on account of relatively enrichment of  $\text{SnO}_2$  in the patina and

$\text{SnO}_2$  in the microcrystal, the resistance of the unearthed mirrors to the external environment corrosion is enhanced.

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