Testing of pilot 2 m³ exposure chamber for formation of brochantite based patina on copper and copper alloys – objects of practical dimensions

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Formation of natural patina on copper and copper alloys objects takes tens of years. There are solutions for patination, which are used in restorers' practice. However, these artificial patinas are usually based on nitrates, carbonates or chlorides. Patina based on brochantite is the most stable phase under atmospheric conditions. This type of patina was successfully formed in laboratory in a small exposure chamber with higher content of SO₂. This work is next step of the experiment to make this method become more practicable. It started with construction 2 m³ exposure chamber and simulation of ideal conditions for patination process. The length of drying phase, homogeneity of conditions, pH of feeding water, colour of patina, placement of samples and final appearance were observed. The chamber construction allows to achieve ideal pH value of feeding water, samples surface became dry during the ventilation and temperature during condensation was stable at 40 °C. These conditions are ideal for patination process.

INTRODUCTION

Process of patina formation on copper surface usually takes tens of years. Patina is a corrosion products layer formed on copper and copper alloys surface, with aesthetic and protective properties. These properties are valuable and a layer is desirable [1-4]. Patina has a heterogeneous structure and its composition depends on the surrounding atmosphere. The inner layer is always oxidic and it consists of cuprite (Cu₂O). In the marine atmosphere rich in chlorides, main phases formed in the outer layer are atacamite and paratacamite (Cu₂Cl(OH)₃). Patina formed in industrial atmosphere is based on sulphates and these phases are called brochantite (Cu₄SO₄(OH)₆), antlerite (Cu₃SO₄(OH)₄) and posnjakite (Cu₄SO₄(OH)₆·H₂O). Posnjakite may transform to brochantite or antlerite. Following equations describe oxidation and reduction process and formation of corrosion product [5-7].

Restorers are searching how to obtain artificial patina on copper surface of different works of art like sculptures or historic buildings roofs or facades. Even modern architects start using artificial copper patina as aesthetic element for modern buildings [7-9]. There are many ways how to obtain artificial patina. They are based on nitrates, carbonates, chlorides or sulphates [10-13]. Patina based on nitrates and carbonates is less stable in under atmospheric conditions, thus some changes in structure and appearance like stains or colour change may appear. Artificial patina based on chlorides has better properties and is also more stable, but has different colour than sulphate patina. It is lighter and more bluish and it is not recommended to combine it with elements covered with sulphate patina due to aesthetic differences [14-16].

This work is focused on patina based on sulphates and extends the knowledge from previous experiment in a small exposure chamber (30 dm³) [17]. The experiment includes observation of conditions in the exposure chamber and patination of copper sheets and bronze statue.

EXPERIMENT

According to results from previous work, an automatic pilot exposure chamber was constructed (Fig. 1) [17]. It allows temperature control (40 °C) using rod heater and sensors, drying phase using fan placed inside ventilation system of the chamber, humidity (100 % RH) and the volume of SO₂ gas (8.9–17.7 g m³) dosed at the beginning of exposure. Drying phase and presence of water film was controlled by datalogger (S3120E, COMET SYSTEM, Rožnov pod Radhoštěm, Česká republika) and special sensor for water film, which was tested in previous work [18]. Construction of chamber is made from polypropylene and stainless steel. All functions are controlled by control unit based on Raspberry Pi 4 motherboard.

At first, testing of the actual chamber was performed in order to find out if the same conditions like in the previously used smaller chamber can be reached. The tests were focused especially on the possibility of interrupting the condensation and formation of water film during drying phase, reaching the optimum pH value (glass electrode Elteca 1220) of feeding water (100 l) according to inlet dose of SO₂ and reaching homogeneous conditions in the whole volume of the chamber. Next patination parameter that was tested was a distance between samples. Samples were studied by means of reflectance spectrophotometry (CM-700d, Minolta, Tokyo, Japan) and patina surface coverage using QuickPhoto Industrial, 3.2.

Copper sheets (150 × 150 mm) were used for the tests. Possibility of using the chamber for real dimension objects was verified by patination of larger copper sheets (1000 × 500 mm) and a bronze statue. X-ray fluorescence spectroscopy (XRF, ARL 9400 XP (Thermo ARL, Switzerland) analysis was employed to verify the composition of bronze alloy. Results are given in Table 1.

Tab. 1. Composition of the bronze alloy according to the XRF analysis

Element	Cu	Sn	Pb	Zn	Ni	Sb
Weight [%]	88.7	6.9	2.6	1.4	0.3	0.1

Fig. 1. 3D model of exposure chamber

RESULTS

The previous results showed [17, 18] that the drying phase is very important in a patination cycle. Therefore this work started with testing of ventilation period after condensation. Data were recorded by datalogger inside the chamber. Interruption of condensation means that the dew point decreased under the temperature inside the chamber. This dew point drop did not take place in Figure 2, so it means that 12 hours is too short time for

the drying period. Prolongation of this period to 24 hours is shown in Figure 3. The curve for dew point evidently decreased under the temperature curve during the ventilation time and relative humidity inside the chamber decreased simultaneously. These results correspond to the results shown in Figure 4 where the temperature of feeding water decreased under the temperature inside the chamber and evaporating of water slowed down.

The surface of the objects placed in the chamber must become dry during ventilation. The sensor which was described in previous work [18] was used at this point. This sensor is sensitive to formation of water film on its surface. Voltage in electrical circuit was 11.8 V when the sensor was dry. When water film started to

Fig. 2. Record of the T/RH sensors during 12/12 h cycle

Fig. 3. Record of the T/RH sensors during 24/24 h cycle

Fig. 4. Records of the internal temperature sensors: T0 – water; T1 – chamber space, bottom; T2 – chamber space, middle; T3 – chamber space, top

form, voltage decreased according to the amount of water on its surface. This is evident from Figure 5 where it is possible to easily distinguish between condensation and the drying phase. According to Figure 5, 24 hours of ventilation is not enough for evaporating of water from sensor surface, but the sensor was placed almost horizontally in this case. The evaporation rate depends on the angle, which was very low (approx. 25°) and this made a difference between sensor surface and sample surface. Figure 6 shows setup when sensor position is closer to real inclination of samples inside the chamber (approx. 65°) and blue curve returns back close to level of dry surface during drying phase. Very slight drop of voltage in Figure 6 also proved much thinner layer of electrolyte on the more vertical surface.

Fig. 5. Record of wet-film sensor adjusted at 25° angle during 24/24 h cycle

Fig. 6. Record of wet-film sensor adjusted at 65° angle during 24/24 h cycle

Other important parameter during the patination process is corrosiveness of environment affected by inlet dose of SO₂ and consequently pH of feed water as well as surface electrolyte. Tap water was tested as the feed water at the beginning, but probably due to high buffer action of carbonates pH did not decrease. Ideal pH value of feeding solution for patination process is between 2.5–3.0. This value was reached with distilled

water (Tab. 2). Complete dissolution of SO₂ in water was possible within couple of hours as it was found in the previous work [18].

Tab. 2. Tests of inlet dose of SO₂ and type of feeding water

Type of water	SO ₂ Dose [g/m ³]	Days	pH	Sample appearance
Tap	8.9	1	8.23
Tap	17.7	3	7.5
Distilled	3 × 8.9	7	2.23
Distilled	17.7	7	2.5
Distilled	17.7	7	2.6

The determination of the ideal adjustment of the test atmosphere and cycles was followed by testing homogeneity of conditions in the whole volume of chamber. A small copper sheets (150 × 150 mm) were placed in three shelves at different levels. Five samples were placed at every level to cover the whole area. The results are given in Figure 7. The columns are average of patinated area of surface samples obtained at different levels. These results show that better conditions are in the lower half of the chamber.

Fig. 7. Test of homogeneity of conditions in entire volume of the chamber and the effect of sample position on patinated area

From the practical point of view, the distance between the samples during the patination process was tested to estimate the smallest dimensions of crevices on real objects which are suitable for patination. Bronze samples were tested as well, and they were placed between copper sheets. Figure 8 shows patinated area of the samples after exposure. Figure 9 illustrates samples placed inside the chamber after exposure.

Fig. 8. Test of distance between samples during patination and its effect on patinated area

Fig. 9. Samples placed inside the chamber after exposure

The composition of all obtained artificial patinas was verified by XRD and brochantite was confirmed as major phase in all of them. Colour of artificial patina was compared with natural patina from the roof of Queen Anne's Summer Palace at the Prague castle (Fig. 10). It showed that colour was very similar and according to L^* value was artificial patina little bit darker (natural patina $L^* = 72$, artificial patina $L^* = 61$).

Final experiment included real objects. Copper sheets were ground with a brass brushand preoxidized before the exposure according to the previous work [17]. Eight copper sheets (1000 × 500 mm) were placed in the chamber during one cycle. Figure 11 illustrates the appearance before and after exposure. The same

conditions were applied to a bronze statue. The course of patination is on Figure 12.

Fig. 10. Results of reflectance spectrophotometry, comparison of artificial patinas to natural patina

Fig. 11. Copper sheets in dimension 1000 x 500 mm before (left) and after (right) exposure

Fig. 12. Bronze statue in the original state (upper left), after brushing (upper right), after the exposure (lower left) and its detail (lower right)

CONCLUSION

Testing of pilot version of exposure chamber followed the previous works. Ideal conditions for patination process were determined and they were found reproducible. There is still room for improvement in the construction of chamber, which could lead to more homogeneous atmosphere and utilization of the entire volume of the chamber.

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