Long-term outdoor exposure of artificial copper patina based on brochantite

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A typical green layer of patina starts to cover copper in atmosphere condition, which is aesthetically acceptable and also provides protective properties. This work investigates stability of the artificial patina layer based on sulphates prepared from a gaseous phase during two-year exposure in atmosphere condition. XRD and SEM were employed to verify the composition and morphology of artificial patina. Colour and patina coverage were compared before and after exposure also. According to results after 1 and 2 years of exposure, it is possible to see changing of hydroxyl sulphates to more stable brochantite and filling pores in the patina layer. There is almost no colour change, however lower patina coverage is slightly evident due to precipitation and abrasive effect.

INTRODUCTION

Copper is used in architecture thanks to its resistance to atmospheric corrosion, as elements of the façade and especially the copper roof, but also in art, especially in the form of bronze alloys. With long-term exposure to weather conditions, the surface of the copper is covered with a layer, which is subsequently modified into a patina and has both aesthetic and protective properties [1-3].

Corrosion is an electrochemical process and is therefore dependent on the presence and aggressiveness of the electrolyte. Aggressiveness is affected by the composition of the atmosphere and therefore allows the corrosion rate of copper to be compared in different types of atmosphere.

- Rural atmospheres: 0.2 – 0.6 $\mu\text{m/a}$
- Urban atmospheres: 0.9 – 2.2 $\mu\text{m/a}$
- Industrial atmospheres: 1.5 – 2.5 $\mu\text{m/a}$
- Marine atmospheres: 0.7 – 1.5 $\mu\text{m/a}$

The low corrosion rate in rural areas can be explained by the higher purity of the atmosphere, which has reduced salt content and thus the conductivity of the resulting electrolyte. On the contrary, the high corrosion rate in industrial areas is caused by pollution and the

presence of sulphates, which decreased the pH of the electrolyte [1]. Sulphates may be present in acid rain at a concentration of 0.1-15 ppm, may further decrease the pH by adsorption and oxidation of SO_2 in the electrolyte, or may be present as aerosol particles [4, 5].

The patina is a heterogeneous structure and arises in several stages. In the first phase, the exposed copper begins to be coated with a dark layer of Cu_2O oxide (cuprite) approximately 5-10 μm thick, which changes the typical red colour of pure copper to brown and to black. This change takes months. Due to the action of the atmosphere, a layer containing Cu^{2+} is formed on this layer, which causes the colour change to blue-green [6]. The main phases usually found in this layer are posnjakite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}]$, brochantite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6]$, antlerite $[\text{Cu}_3(\text{SO}_4)(\text{OH})_4]$, atacamite $[\text{Cu}_2\text{Cl}(\text{OH})_3]$ and paratacamite $[\text{Cu}_2\text{Cl}(\text{OH})_3]$ depending on the environment and the composition of the surrounding atmosphere. Sulphate-based patina is typical for urban and industrial areas, while chloride-based patina, whose colour tends to be lighter and more bluish, is found in coastal areas. The thickness of this second layer is around 40-50 μm [7-12].

Due to the reduction of the content of sulphates in the air, the time of formation of sulphate-based patina is currently being extended to decades. The content of sulphates in the atmosphere of the Czech Republic is in the range of 10–100 $\mu\text{g m}^{-3}$ [13].

Carbonate-based patinas can also be found, but due to their higher solubility, they do not occur as often during atmospheric exposure and are more typical for archaeological finds [7].

The problem of artificial patinas is their low adhesion to the surface of the copper substrate, when damage occurs in the patina due to weather conditions. The reason may be its accelerated creation and the creation of weak bonds with the substrate. The artificial patina is more porous than the natural patina, so the effect of run off is easier. The abrasive effects of dust particles in the air and raindrops can also peel patina off in thin layers.

If the artificial patina differs in its composition from the natural patina, other chemical reactions take place here, which affect the colour. Therefore, it is important that the artificial patina match as much as possible with the natural patina in terms of composition and morphology, which would ensure similar mechanical resistance and similar chemical behaviour affecting the colour change [14, 15].

Various techniques are used to characterize and describe the patina in order to determine its composition (XRD), morphology (SEM) and colour (spectrophotometry). Using these techniques is possible to observe different phases and describe its development during copper exposure in a corrosive environment [6, 16-18].

In this work, these techniques were used to investigate the behaviour of artificial patina based on brochantite during a two-year exposure in atmospheric conditions.

Fig. 1. Samples installation in Ostrava – Radvanice

EXPERIMENTAL

In the exposure chamber described in the previous article, samples with artificial patina were prepared, which had different surface pretreatment [19]. Samples dimension 5×10 cm with a ground surface using a brass brush (SFx marking), samples pre-patinated in solution – 100 ml 25% NH_3 , 33 g Na_2S and 250 ml H_2O (marking RxSF) and pre-oxidized samples were tested. The first set of samples was pre-oxidized in an oven at 150 °C for 60 minutes (marking TxSF) and the second with a hot air of 500 °C for 10 minutes (marking HxSF). 4 samples were prepared from each surface treatment (2 for 1 year exposure and 2 for 2 years exposure). The prepared samples were exposed in a 30 l chamber for 14 days under predefined conditions. The temperature during the exposure was 40 °C, the volume of water in the chamber, which provides 100% humidity, was 5 l and the input dose of SO_2 was 100 ml (8.9 g m^{-3}). The condensation (16 hours) and drying phases (8 hours) were alternated during the cycle.

The obtained patina was photographically documented and described in terms of composition (XRD, X'Pert Pro, PANalytical, EA Almelo, Holland), morphology (SEM-VEGA3 LMU, TESCAN, Brno, Czech Republic), colour (spectrophotometry – CM-700d, Minolta, Tokyo, Japan) and homogeneity (image analysis – QuickPhoto Industrial, 3.2).

For long-term exposure of artificial patina in atmospheric conditions (Fig. 1) the locality Ostrava – Radvanice was chosen, where the concentration of SO_2 in the air is around $10\text{--}15 \text{ } \mu\text{g m}^{-3}$ and exceptionally in the short term it can approach the limit of $100 \text{ } \mu\text{g m}^{-3}$ [20, 21]. The first set of samples was analyzed after 1 year of exposure and the second after 2 years.

Fig. 2. Samples prior to patination A and B ground surface, C and D preoxidized in the oven

Fig. 3. Samples prior to patination A and B preoxidized with hot air, C and D prepatinated in the solution

RESULTS

Artificial patina

Figures 2 and 3 show selected samples with artificial patina, which was documented and compared with natural patina in terms of morphology, composition and colour. As follows from the literature, the natural patina is less porous than the artificial patina, which is also confirmed by observations at SEM (Figs. 4 and 5). The XRD of artificial patina confirmed that the patina consists mainly of hydroxyl sulphates and that brochantite is represented as the main component (Fig. 6). Regarding

the colour of the artificial patina, which was compared with the historical patina from the roof of Queen Anne's Summer Palace at Prague Castle, it was found that the shade of green, i.e. components a^* and b^* are close to the natural brochantite (Fig. 7), however, the resulting colour is affected by component L^* , which expresses the luminosity. Its value is lower than that of the natural patina, which explains the darker appearance of the artificial patina. The above-mentioned procedure in the exposure chamber managed to cover the surface of the copper samples with an artificial patina of approximately 74–88 % (Tab. 1).

Fig. 4. SEM image – artificial patina, surface preoxidized in the oven

Fig. 5. Natural patina

Tab. 1. Area covered with patina [%]

Set of samples	1.		2.		3.		4.	
Orientation of the exposed side of the sample	upper	lower	upper	lower	upper	lower	upper	lower
Ground surface	86	79	86	74	74	88	72	81
Preoxidized in the oven	84	73	74	73	77	80	64	89
Preoxidized with hot air	64	71	71	79	82	51	71	40
Prepatinated in the solution	77	48	96	26	52	75	56	81

Fig. 6. XRD of artificial patina with surface preoxidized in oven (sample T4SF)

Fig. 7. Reflectance spectrophotometry comparison of artificial patina with surface preoxidized in oven and natural patina

Exposure after the 1st year

After the first year of exposure, it was already possible to observe the natural darkening of pure copper, which is covered with a layer of Cu_2O oxide (Fig. 8). In Figures 9–12 is a comparison of samples with different surface pretreatment before and after the exposure. In terms of patina morphology observed by SEM (Fig. 13), it appears that the patina porosity decreases during the first year, which would suggest further growth of brochantite crystals. This would be consistent with the result of XRD analysis (Tab. 2), which shows the conversion of unstable hydroxyl sulphates to stable brochantite. However, overall it is rather possible to observe a decrease in the patina area (Tab. 3). The rate of patina loss also varies according to the orientation of the sample. On the upper side of the sample, a higher loss is noticeable, which can be caused by faster washing by precipitation and abrasive effects. A negative value on the un-

Fig. 8. Copper samples after 1 year exposure

Fig. 9. Samples of artificial patina with ground surface after 1 year exposure

derside of a set of HxSF samples preoxidized by a stream of hot air means that the patinated area has increased and thus a new patina has been formed. The colour fastness of the patina is good (Fig. 14.), but a darker appearance against the natural patina is still visible.

Fig. 10. Samples of artificial patina with surface preoxidized in the oven after 1 year exposure

Fig. 12. Samples of artificial patina with surface prepatinated in the solution after 1 year exposure

Fig. 11. Samples of artificial patina with surface preoxidized with hot air after 1 year exposure

Fig. 13. SEM of sample of artificial patina with surface preoxidized in the oven after 1 year exposure

Tab. 2. XRD analysis after the 1st year of exposure

Composition of original sample	Composition after 1. year
brochantite 70 %	brochantite 90 %
cuprite 14 %	cuprite 8 %
antlerite 2 %	copper 2 %
langite 1 %	
copper 13%	

Tab. 3. Average loss of patina area after 1st year of exposure [%]

	Orientation of the exposed side of the sample	
	upper	lower
Ground surface	13	9
Preoxidized in the oven	15	6
Preoxidized with hot air	16	-22
Prepatinated in the solution	10	4

Fig. 14. Comparison by reflectance spectrophotometry of artificial patina with surface preoxidized in the oven and natural patina

Exposure after the 2nd year

After the second year of exposure, it is possible to observe another course of darkening of the copper covered with cuprite (Fig. 15), which leads almost to blackening of the surface, as described in the literature [6]. XRD analysis showed the presence of posnjakite in this layer (Tab. 4), which is further converted to brochantite or antlerite. In Fig. 16–19 is a comparison of samples with different surface pretreatment before and after the exposure. The SEM image (Fig. 20) documents the condition of the patina and it is possible to observe the closure of the patina surface. According to the results in Tab. 5 it is clear that it is still a brochantite patina and no significant changes in composition due to weathering take place. Thus, it can be noted that the patina is relatively stable in terms of composition and colour (Fig. 21). However, the effect of weather conditions on the patina area is obvious from the results in Tab. 6, as there is a further reduction of the patinated area due to insufficient bonding with the substrate, which is a problem especially

Fig. 15. Copper samples after 2 years of exposure

for samples pre-patinated in solution. A comparison of the results of patina loss after 1 and 2 years of exposure shows an approximately uniform decrease on the underside of ground samples and samples pre-oxidized in the oven. On the contrary, on the upper side with effects of

Tab. 4. XRD of Cu samples after the 2nd year of exposure

Cu	65 %
Cuprite	30 %
Posnjakite	5 %
Brochantite	2 %

Fig. 16. Samples of artificial patina with surface preoxidized in the oven after 2 year exposure

Fig. 17. Samples of artificial patina with ground surface after 2 year exposure

run off, this process seems to slow down. This can be explained by the fact that at the same time as the patina is washed away, a natural patina can develop, as show the results in Table 4, however, the rate of new patina formation does not reach the rate of patina loss.

Fig. 18. Samples of artificial patina with surface preoxidized with hot air after 2 year exposure

Fig. 19. Samples of artificial patina with surface prepatinated in the solution after 2 year exposure

CONCLUSION

The artificial patina created from the gaseous phase in the exposure chamber is similar to the natural patina that forms in urban and industrial areas. Its main component is a stable phase of brochantite and its colour is very close to natural patina. The main disadvantage

Fig. 20. SEM of sample of artificial patina with surface pre-oxidized in the oven after 2 year exposure

Tab. 5. XRD analysis after the 2nd year

Composition of original sample	Composition after 2. year
brochantite 70 %	brochantite 70 %
cuprite 14 %	cuprite 15 %
antlerite 2 %	Cu 15 %
langite 1 %	
copper 13%

Fig. 21. Results of reflectance spectrophotometry

Tab. 6. Average loss of patina area after 2nd year of exposure [%]

	Orientation of the exposed side of the sample	
	upper	lower
Ground surface	10	19
Preoxidized in the oven	7	17
Preoxidized with hot air	15	13
Prepatinated in the solution	32	7

that affects the adhesion to the substrate is its porosity and effects of run off can occur simultaneously with abrasive effects. However, this condition has improved with the time the patina has been exposed and is probably supplemented by the formation of a natural patina. Pre-oxidation of copper helps to achieve a more even patination and, in the longer term, when done correctly, contributes to the easier formation of a natural patina.

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