

Production, characterization, and protection of artificial patinas on copper

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Copper and its alloys have found extensive use in artistic and architectural fields not only because of their notable resistance to corrosion but also due to the beautiful colours of the patina of corrosion products that are formed when they are exposed outdoors. Green roofs and façades are highly appreciated by designers and citizens. In the past, in urban environments, such green patinas could be naturally formed because of the interaction with pollutants, such as SO_x , and are typically constituted by copper hydroxide sulphates such as brochantite and antlerite. SO_x levels have been drastically reduced over the last decades and this means that we will not expect anymore the natural growth of green patinas on copper in urban environments (unless we are close to the sea, where the formation of chlorides-rich green patinas is expected). Depending on the location, artificially patinated surfaces may be nowadays a good solution to get green roofs. Artificial patinas may have quite different characteristics compared to natural ones and are often obtained by using polluting chemicals. It is therefore important to find low environmental impact procedures for their production and to obtain corrosion layers with characteristics very similar to the natural ones. In addition, it is important to understand if protective coatings would maintain their efficacy when applied on patinated surfaces. This is particularly relevant in the field of cultural heritage conservation, where they are normally applied on corroded surfaces. Continuous research is dedicated to studying and developing protective coatings, that act as barriers, preventing corrosion and simultaneously preserving the historic aspect of the surfaces. The coating also must ensure low toxicity and easy application to guarantee the safety of the restorer. In this study, a series of artificial patinas were produced and characterized. In addition, a multi-layer coating, widely used by restorers for the conservation of bronzes, and a silane-based coating have been applied on artificially patinated surfaces.

1 Introduction

Protection of metallic cultural heritage surfaces aims to preserve the object's physical integrity and aesthetic value. Metallic surfaces vary significantly in terms of the degree of corrosion and the range of corrosion products [1]. Copper and its alloys are widely used for

outdoor environments due to their excellent corrosion resistance, thanks to the patina layer that forms on the surface after the object is exposed to atmospheric conditions [2]. These patinas improve corrosion resistance [3], and their beautiful colours play an important role in visual perception and are proof of the object's age and historical journey.

During restoration processes, such corrosion layers are therefore to be preserved. Normally restorers, indeed, during conservation practices, carefully remove powdery corrosion products while maintaining the so-called „noble“ patinas. This delicate process ensures that the cultural and historical essence of the artefact remains intact. Restorers commonly apply multiple layers of INCRALAC® and microcrystalline wax to protect patinated metal artefacts [4,5]. Although effective initially, this method is prone to cracking due to the wax's short lifespan and INCRALAC®'s inability to tolerate temperature fluctuations [6]. In general, protective coatings, when applied on corroded surfaces, have limited durability and efficacy [7–9]. Here a silane-based coating that proved to be able to provide super-hydrophobicity on marble [10], was applied on artificially patinated copper. The concept of using trichloromethylsilane (TCMS) on a copper patina is to achieve better protection by using a product that can deeply penetrate the patina and that provides highly hydrophobic characteristics to the surfaces.

Developing new strategies to protect patinated surfaces is challenging due to the wide variety of metal substrates and the little literature on the protection of patinated surfaces [9,11,12]. To develop new products and strategies it is important to be able to reproduce in the laboratory the most representative natural patinas [13]. Copper initially appears salmon-pink, but with oxidation, it darkens to brown and then black, forming cuprite Cu_2O [2]. Cuprite is often seen as a preliminary stage in the patination process of copper alloys. Further reactions with atmospheric impurities in rural, urban and industrial environments lead to the formation of green patinas like brochantite $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$ [2]. Sometimes, antlerite patina $\text{Cu}_3(\text{OH})_4\text{SO}_4$ can also be detected along with the brochantite. A major com-

pound found in the outer layer of the marine environment, alongside brochantite, are copper hydroxychlorides, mainly atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ and paratacamite $\text{Cu}_3\text{Cl}_2(\text{OH})_6$, which form due to high chloride levels near the seaside [2].

In the laboratory, the same type of patina can be obtained by different methods such as, e.g., chemical methods, application of pastes, heat colouring techniques, electrochemical methods, and accelerated ageing [13,14]. Accelerated ageing methods, such as wet&dry immersion cycles and dropping tests take more time, but as discussed in previous studies [3,12,13], these patinas more closely resemble natural ones.

1.1 Objectives of this work

This work aimed to produce brochantite and copper hydroxychlorides patinas, using different methodologies to replicate natural patinas [13–15]. After full characterization of the patinas, a traditional multilayer coating (INCRALAC® plus microcrystalline wax), normally used by restorers [4,5] and a silane-based coating were applied. Only very preliminary results of the two types of coatings are here presented.

2 Materials and method

2.1 Laboratory Patinas on Copper Specimens

Chemical procedures used to create laboratory artificial patinas were carefully selected and optimized to reproduce the most common natural corrosion products.

To obtain the brochantite patina, first, a cuprite layer was produced by immersion in a boiling solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5.4 g/L) for 1 hour. Then, a wet&dry method was performed for 45 days by immersing the samples in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (8 g/L) solution for 7 hours and then drying them overnight.

For the copper hydroxychloride patina, two patination methods were used: wet&dry method and “applied paste” [13–15]. The first method resulted in the formation of a good patina in about 7 days by using a CuCl_2 solution (0.33 g/L). The “applied paste” method was designed to replicate critical conservation conditions, characterized by unstable, chlorides-rich patinas. A grounded mixture of CuCl , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and water was applied in multiple layers on the surface. All patinas were applied on copper specimens of 99.9% purity, with dimensions of 27x76 mm and 38x108 mm. Before the patination procedure, the surface of the

samples was polished with fine 800/2400 silicon carbide sandpaper and degreased with ethanol.

2.2 Protective treatments

Two different coatings were applied on copper: a traditional multi-layer and a silane-based coating.

The traditional multi-layer coating was realized by applying the first two layers of acrylic resin (INCRALAC®), followed by two layers of wax and it was applied both on brochantite and on the two types of chloride-rich patinas.

The innovative procedure of silanization by trichloromethylsilane (TCMS) was tested only on brochantite. The methodology is described in a previous work [10].

2.3 Characterisation Techniques

The patinated surfaces were characterized in terms of colour, corrosion resistance, composition and morphology. The colour was evaluated by spectrophotometry, using a Konica Minolta CM-600d spectrophotometer with a Xenon light source in the spectral range of 400 – 700 nm.

Corrosion resistance was evaluated through the evaluation of polarization resistance (R_p), which was obtained by both Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS), with a portable potentiostat Ivium Technologies CompactStat with Ivium® software 4.993 (Ivium Technologies B.V., Eindhoven, Netherlands) with a three electrodes configuration, employing the contact probe proposed by Letardi [16]. For all measurements, a commercial low mineral content water with a conductivity of around 60 $\mu\text{S}/\text{cm}$ was used as an electrolyte. In the LPR test, the potential has been varied between -10 mV and +10 mV with respect to E_{corr} with a scan rate of 10 mV/s. For EIS the following setup has been adopted: frequency range between 100 kHz and 10 mHz with ± 10 mV with respect to E_{corr} .

Optical microscopy (Leica DM6 optical microscope, equipped with LasX software) was used to characterize patina texture and surface morphology, while Fourier-Transform Infrared Spectroscopy (Thermo Nicolet iN10 MX spectrometer, operating in ATR mode) was used for the investigation of the patina composition.

Water contact angle (WCA) measurements were carried out using a Krüss DSA20E Easy Drop Goniometer.

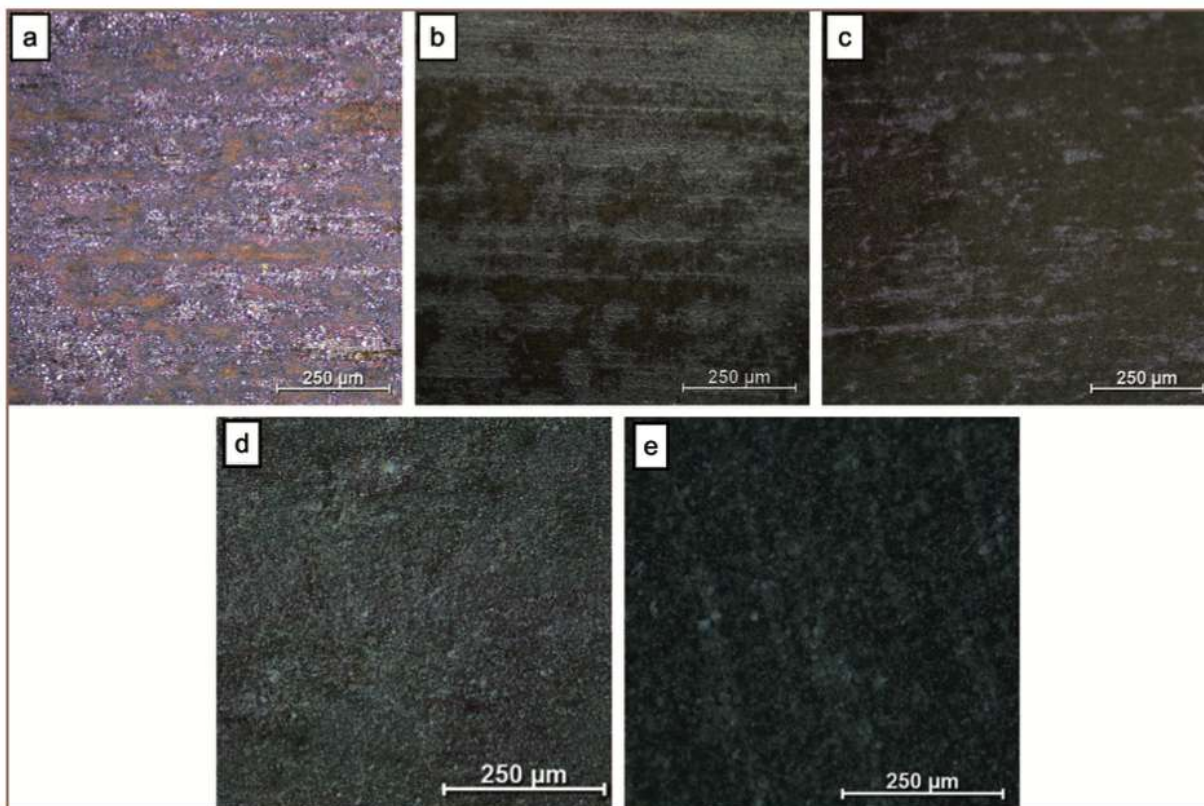


Figure 1: Optical microscope photos of brochantite patina after wet&dry cycles in sulphate solution after (a) 1, (b) 7, (c) 14 (d) 30 (e) and 45 days

3 Results and Discussion

3.1 Characterisation of brochantite patinas

Optical microscopy images of the different steps of the production of the Brochantite patina are reported in Fig. 1, showing that the resulting patina layer is already quite uniform at day 30. FTIR spectra (Fig. 2) confirmed the presence of characteristic brochantite peaks by day 7 while after boiling in sulphates and after just one day of wet&dry, only cuprite was detected. The obtained brochantite patina, after 30 days, appears to be quite compact and adherent to the metallic substrate.

R_p measurements (Fig. 3) are still ongoing and show an increasing trend over time with a value at day 14 ($R_p = 12.9 \pm 3 \Omega m^2$) that is similar to those reported in the literature for natural brochantite patinas which typically range between 2 and 20 Ωm^2 [16–18]. Hence, it can be concluded that 30 days is sufficient to form a patina with characteristics close to the natural ones.

3.2 Characterisation of chlorides-rich patinas

Results confirmed that the “applied paste” method is a quick way to produce a light green patina layer (Fig. 4, a), mainly constituted by a mixture of copper chlorides and sulphates, which represents a critical condition in terms of conservation because it is quite unstable. Ac-

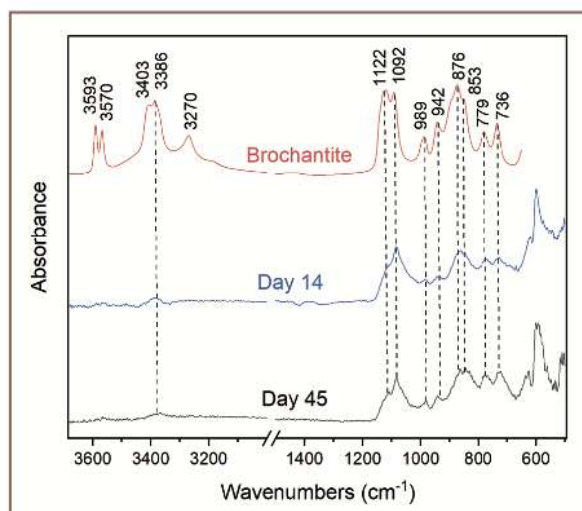


Figure 2: Representative FTIR spectra of the surface of the brochantite patina

tually, its presence over the surface accelerates corrosion ($R_p = 0.1 \pm 0.06 \Omega m^2$) with respect to bare copper ($R_p = 1.82 \pm 0.52 \Omega m^2$).

Considering the wet&dry method (Fig. 4, b-f), it can be observed that the surface of the patina of the wet&dry method is more uniform after 7 days than after 45 days. The FTIR spectra show that, initially, the paratacamite peaks dominate over atacamite peaks (Fig. 5).

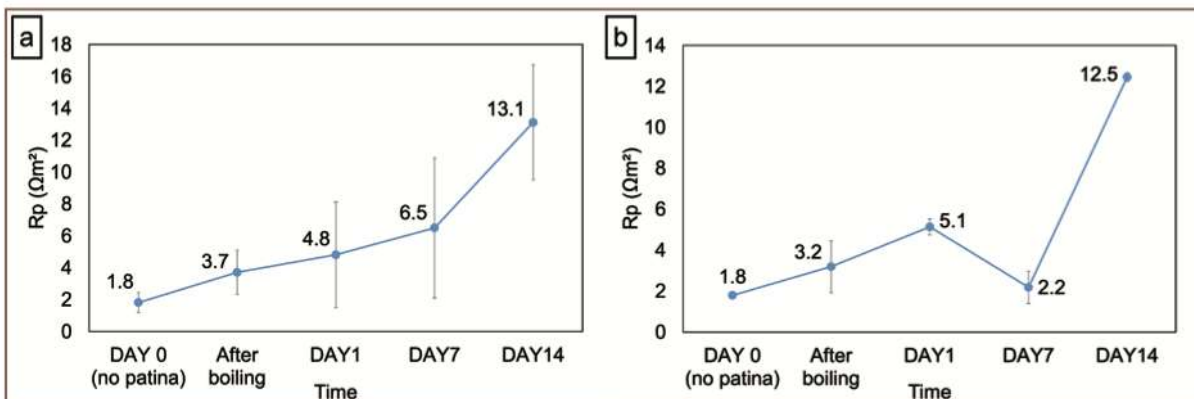


Figure 3: R_p values as a function of time during wet&dry cycles of brochantite specimens, obtained from (a) LPR and (b) EIS measurements

As time progresses, the amount of atacamite appears to increase, and both atacamite and paratacamite can eventually be detected on the surface. Electrochemical measurements show that the highest LPR and EIS values were obtained on day 7 of the wet and dry cycles ($R_p = 15.2 \pm 21.3 \Omega m^2$). Results indicate that with the wet&dry method, it is possible to obtain a much more stable patina compared with the “applied paste” method. The obtained R_p values are, indeed, similar to the ones observed in naturally occurring atacamite patinas [16].

3.3 Traditional coating, preliminary results

The treatment creates a thick layer of protection (Fig. 6), altering the original colour of the patina, and resulting in a darker shade (Fig. 7). This colour change is often appreciated as it enhances the colours of the patinas. Electrochemical measurements for chlorides-rich patina showed an increase in R_p from $0.1 \pm 0.06 \Omega m^2$ to around $7 \times 10^5 \Omega m^2$ but with a very high standard deviation ($10^6 \Omega m^2$). The electrochemical measurements on the wet&dry patinas are still ongoing. Before coating, the water contact angle (WCA) is $65 \pm 8^\circ$ on

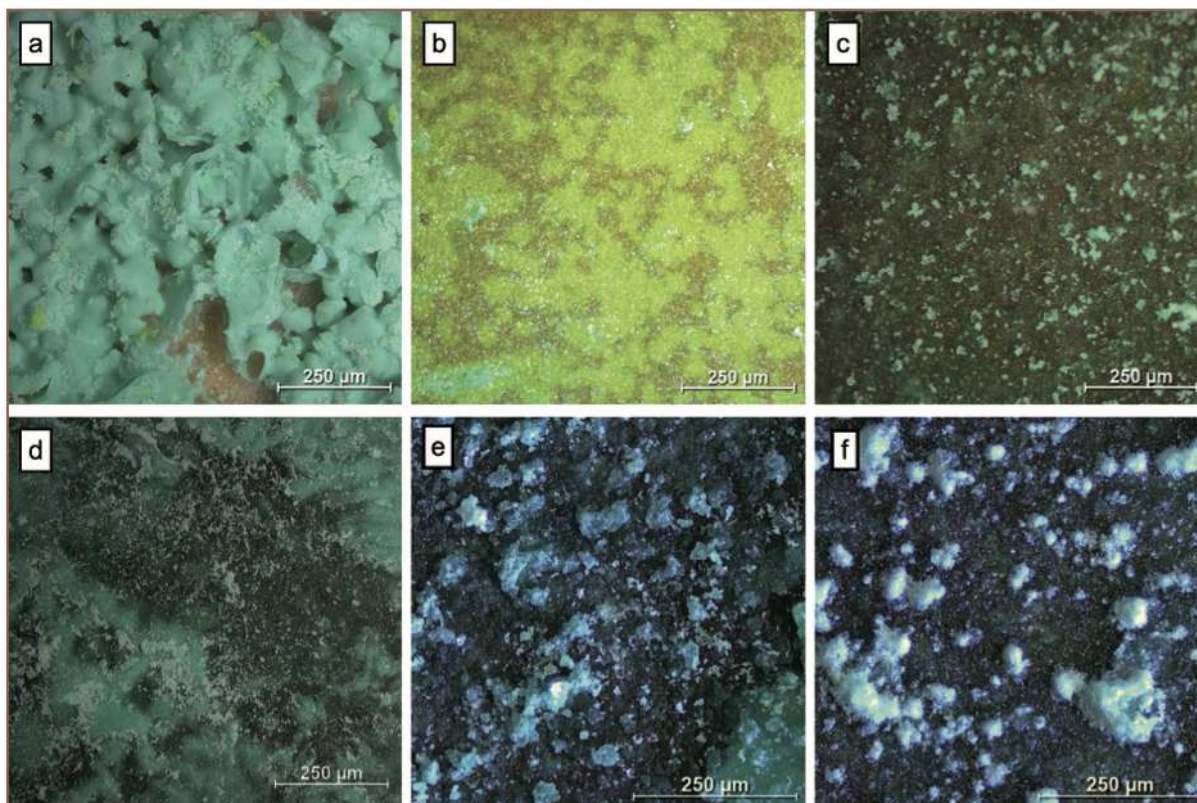


Figure 4: Optical microscope photos of copper hydroxychlorides patina, obtained by: (a) “applied paste”, and wet&dry cycle in chloride solution for (b) 1, (c) 7, (d) 14 (e) 30 (f) and 45 days

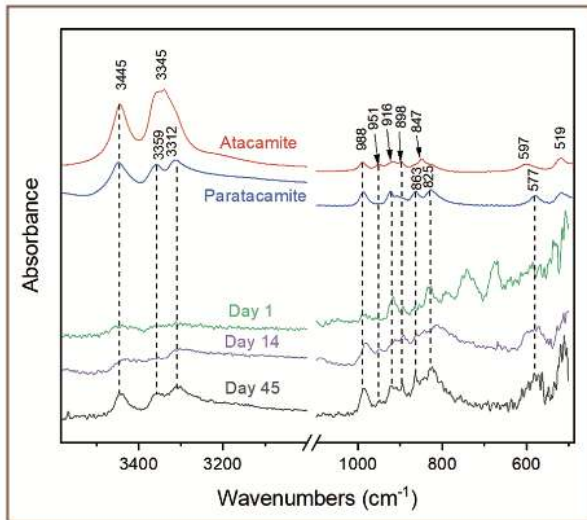


Figure 5: Representative FTIR spectra of the surface of the copper hydroxychlorides patina after wet&dry cycles

The TCMS treatment maintains the patina's original colour with minimal surface alteration (Fig. 8), with a ΔE significantly lower ($\Delta E = 3.9$), if compared with one of the traditional multi-layer coating ($\Delta E = 10.9$) (Fig. 7; Fig. 8). After the TCMS treatment, the surface looks slightly lighter and less saturated. The treatment is not visible to the naked eye.

Water contact angle measurements demonstrated that TCMS-treated surfaces became highly hydrophobic, far exceeding the hydrophobicity of the traditional wax treatment (Fig. 9).

4 Conclusions and future perspectives

The reported results confirm that it is possible to obtain patinas with characteristics very close to the natural ones through accelerated ageing (wet&dry cyc-

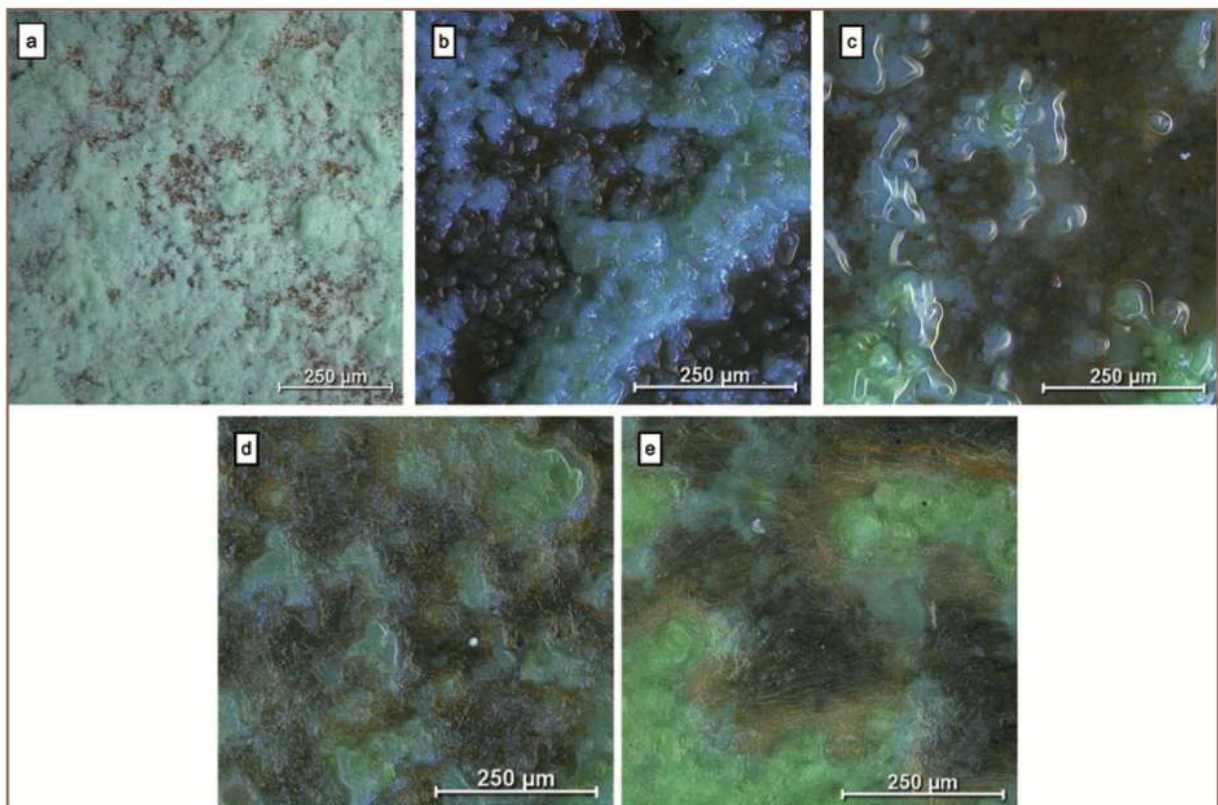


Figure 6: Optical microscope photos of "applied paste" chlorides-rich patina (a) before application of the traditional treatment and after (b) first, (c) second INCRALAC layer, (d) first, (e) and second layer of wax

brochantite and $55 \pm 3^\circ$ on "applied paste" copper hydroxychloride. After coating the WCA is very similar regardless of the underlying patina and is $104 \pm 1^\circ$.

3.4 Silane-based coating, preliminary results

Here the very preliminary, but promising, results of the application of the silane-based coatings are reported.

les). In particular, one week of wet&dry cycles seems optimal to obtain a patina constituted by a mixture of copper hydroxychlorides, mainly paratacamite and atacamite. For brochantite, a longer period of about 30 days of wet&dry cycles is required. The traditional multi-layer coating leads to a relevant change of colour and increase of polarization resistance, providing

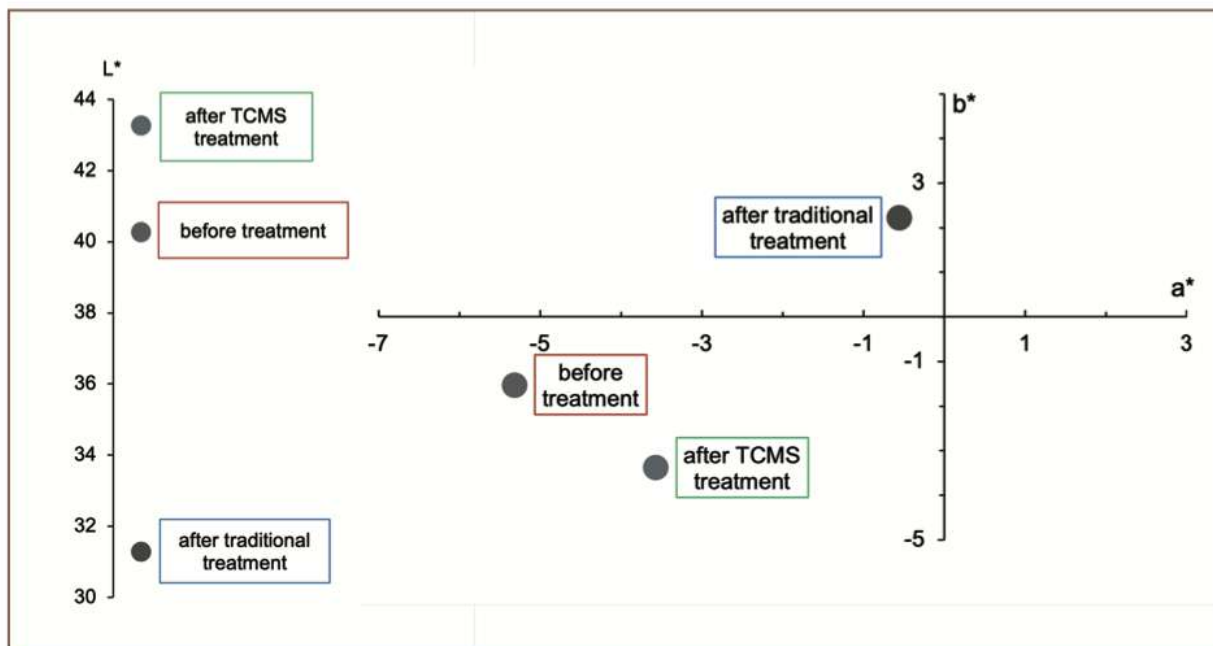


Figure 7: L*, a* and b* values of the surfaces before and after traditional and TCMS treatments on brochantite patina

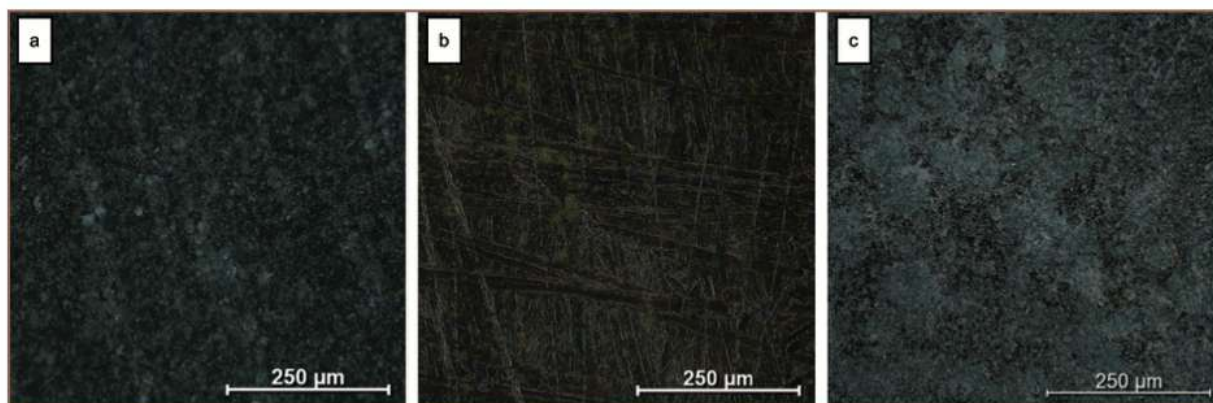


Figure 8: Optical microscope photos of (a) bare brochantite patina, (b) after application of the traditional and (c) TCMS treatment

therefore protection from corrosion. In the future, it will be necessary to verify for how long this protection is maintained after exposure outdoors. The very preliminary results on TCMS show that this treatment can provide high hydrophobic characteristics to the surfaces, with only minimal alteration of the colour. These results are very interesting and, if electrochemical measurements will confirm that it also provides protection from corrosion, different silanes (without chlorides) and various application methods (spray or brush and with less toxic solvents) will be tested in the future.

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References

- [1] Corrosion of metals and alloys – Corrosivity of atmospheres – Classification, determination and estimation, BS EN ISO 9223:2012 (2012).
- [2] T.E. Graedel, K. Nassau, J.P. Franey, Copper patinas formed in the atmosphere-I. Introduction, *Corros Sci* 27 (1987) 639–657. [https://doi.org/10.1016/0010-938X\(87\)90047-3](https://doi.org/10.1016/0010-938X(87)90047-3).
- [3] C. Chiavari, A. Colledan, A. Frignani, G. Brunoro, Corrosion evaluation of traditional and new bronzes for artistic castings, *Mater Chem Phys* 95 (2006) 252–259. <https://doi.org/10.1016/j.matchemphys.2005.06.034>.
- [4] M.T. Molina, E. Cano, B. Ramírez-Barat, Protective coatings for metallic heritage conservation: A review, *J Cult Herit* 62 (2023)

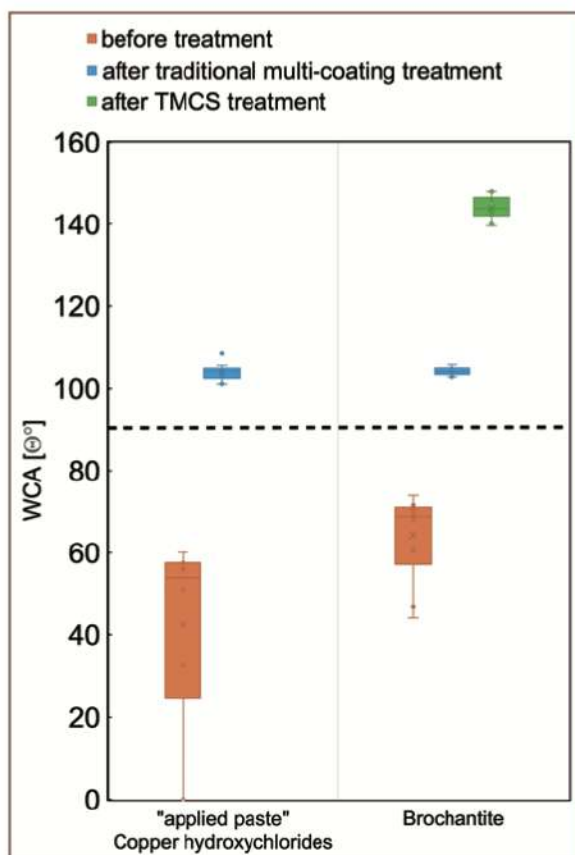


Figure 9: Water contact angle measurements on brochantite and "applied paste" copper hydroxychloride before and after traditional and TCMS treatment

- 99–113. <https://doi.org/10.1016/J.CULHER.2023.05.019>.
- [5] B. Salvadori, A. Cagnini, M. Galeotti, S. Porcinai, S. Goidanich, A. Vicenzo, C. Celi, P. Frediani, L. Rosi, M. Frediani, G. Giuntoli, L. Brambilla, R. Beltrami, S. Trasatti, Traditional and innovative protective coatings for outdoor bronze: Application and performance comparison, *J. Appl. Polym. Sci* 135 (2017) 46011. <https://doi.org/10.1002/app.46011>.
- [6] J.L. Down, The evaluation of selected poly(vinyl acetate) and acrylic adhesives: A final research update, *Studies in Conservation* 60 (2015) 33–54. <https://doi.org/10.1179/2047058414Y.0000000129>.
- [7] G. Pellis, B. Giussani, P. Letardi, T. Poli, P. Rizzi, B. Salvadori, A. Sansonetti, D. Scalarone, Improvement in the sustainability and stability of acrylic protective coatings for outdoor bronze artworks, *Polym Degrad Stab* 218 (2023) 110575. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2023.110575>.
- [8] D. Mikić, H. Curković, Protection of Patinated Bronze with Long-Chain Phosphonic Acid/Organic Coating Combined System, (2023). <https://doi.org/10.3390/ma16041660>.
- [9] G. Masi, E. Bernardi, C. Martini, I. Vassura, L. Skrlep, E. Švara Fabjan, N. Gartner, T. Kosec, C. Josse, J. Esvan, M.C. Bignozzi, L. Robbiola, C. Chiavari, An innovative multi-component fluoro-

polymer-based coating on outdoor patinated bronze for Cultural Heritage: Durability and reversibility, *J Cult Herit* 45 (2020) 122–134. <https://doi.org/10.1016/J.CULHER.2020.04.015>.

- [10] E. Pargoletti, L. Motta, V. Comite, P. Fermo, G. Cappelletti, The hydrophobicity modulation of glass and marble materials by different Si-based coatings, *Prog Org Coat* 136 (2019) 105260. <https://doi.org/10.1016/J.PORGOAT.2019.105260>.
- [11] T. Kosec, L. Škrlep, E. Švara Fabjan, A. Sever Škapin, G. Masi, E. Bernardi, C. Chiavari, C. Josse, J. Esvan, L. Robbiola, Development of multi-component fluoropolymer based coating on simulated outdoor patina on quaternary bronze, *Prog Org Coat* 131 (2019) 27–35. <https://doi.org/10.1016/J.PORGOAT.2019.01.040>.
- [12] C. Chiavari, K. Rahmouni, H. Takenouti, S. Joiret, P. Vermaut, L. Robbiola, Composition and electrochemical properties of natural patinas of outdoor bronze monuments, *Electrochim Acta* 52 (2007) 7760–7769. <https://doi.org/10.1016/J.ELECTACTA.2006.12.053>.
- [13] C. Petiti, L. Toniolo, L. Berti, S. Goidanich, Artistic and Laboratory Patinas on Copper and Bronze Surfaces, (2023). <https://doi.org/10.3390/app132111873>.
- [14] Richard Hughes, Michael Rowe, The Colouring, Bronzing and Patination of Metals, Thames and Hudson, London, 1991.
- [15] C. Petiti, Methodologies for the conservation and non-invasive study of metallic works of art, POLITECNICO DI MILANO, 2020.
- [16] P. Letardi, Laboratory and Field Tests on Patinas and Protective Coating Systems for Outdoor Bronze Monuments, in: Proceedings of the International Conference on Metals Conservation, Metal 04, Canberra, Australia, 2004: pp. 379–387.
- [17] C. Petiti, L. Toniolo, D. Gulotta, B. Mariani, S. Goidanich, Effects of cleaning procedures on the long-term corrosion behavior of bronze artifacts of the cultural heritage in outdoor environment, *Environmental Science and Pollution Research* 27 (2020) 13081–13094. <https://doi.org/10.1007/s11356-020-07814-4>.
- [18] C. Petiti, D. Gulotta, B. Mariani, L. Toniolo, S. Goidanich, Optimisation of the setup of LPR and EIS measurements for the onsite, non-invasive study of metallic artefacts, *Journal of Solid State Electrochemistry* 24 (2020) 3257–3267. <https://doi.org/10.1007/s10008-020-04822-9>.

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