CHANGE

CULTURAL HERITAGE ANALYSIS FOR NEW GENERATIONS

change-itn.eu

ICOM METAL France, 18 January 2021

The formation of metal soaps: model samples for painted metals degradation

Silvia Russo[1], Laura Brambilla[1], Jean Baptiste Thomas[2], and Edith Joseph[1]

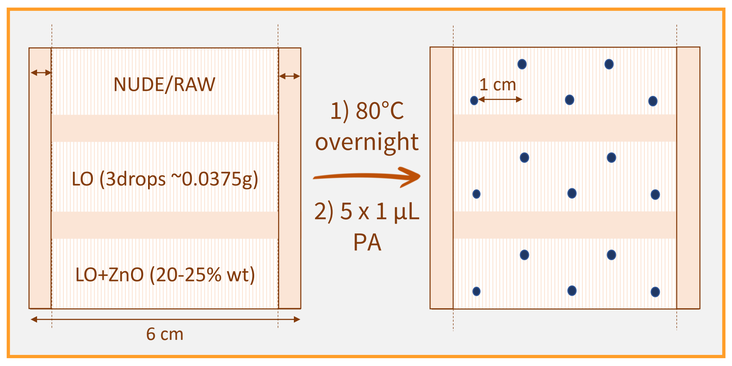
silvia.russo@he-arc.ch

INTRODUCTION

Painting on metal substrates is a widely reported practice throughout art history [1][2].
Similar degradation features have been previously identified on oil painted metal artworks with respect to paintings on canvas [3][4]. Among these, the formation of metal soaps is the focus of this work. Preliminary results of the chemically induced formation of metal soaps is presented. Particular attention is devoted here to the formation of copper carboxylates.

METHOD

- 6x6 cm copper, zinc, iron, and aluminium metal coupons (Tartaix®) undewent two different surface treatments: brushed hairline and mirror polished finishing.
- After degreasing with ethanol, each coupon was divided in three sections: untreated (Raw), coated with linseed oil (LO), and with a mixture of linseed oil and zinc oxide (LO+ZnO) using a spatula.
  Formation of Me-carboxylates was induced by adding 1µL palmitic acid (PA, ≥98%, Sigma Aldrich) in ethanol solution (0.078 M) in different areas of the surface of the coupon.



- Micro- Fourier Transform Infrared spectroscopy (µ-FTIR Thermo Scientific® Nicolet iN10 MX) for point analysis and 2D chemical imaging (every 30 minutes for 6 hours, then 24h and 48h from the addition of PA) were performed on the three sections. Reflectance-absorbance (RA) mode was preferred to increase the chances to collect signal from the interface between the metal and the coating (when <15 µ.m thickness).
- The spectra were processed using the ChemoSpec package in R: baseline and CO_2 correction, PQN normalization, and Principal Components Analysis were performed.

RESULTS

SUBSTRATE SELECTION

HISTORICAL SOURCES
«si on peint sur du cuivre, du fer (…) et qui rendent ordinairement les couches trop polies pour qu'on y-puisse peindre facilement, ce qui fait glisser les couleurs par dessus…»
Watin (1773) *L'Art du Peintre, Doreur, Vernisseur*

SURFACE FINISHING
mimicking the Old Masters' technique of scratching the surface of the metal to increase gripping of the oil paint:
BRUSHED HAIRLINE FINISHING*

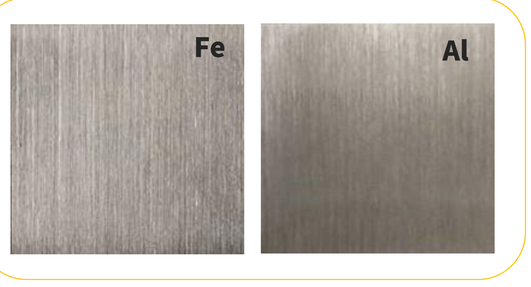
* This is a method of pressing and moving metal brushes onto material surfaces to create directional lines

YES

METAL SOAPS FORMATION

Assessed by adding 1 µL drop of PA (0.078 M) directly on the coupon (chemically catalysed degradation)

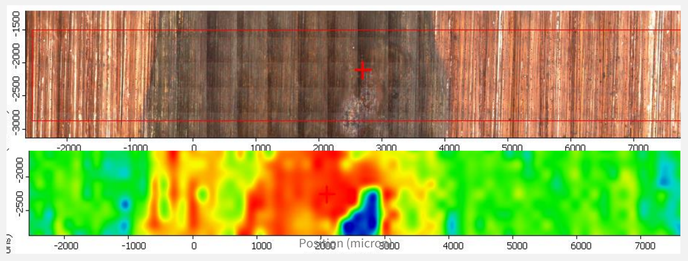
NO†



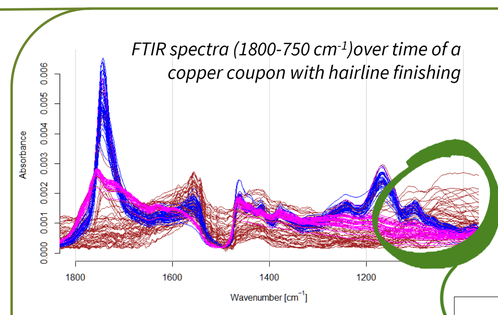
† further investigation is required

AGEING

Two series of LO and LOZnO coated copper samples were aged for two months at room temperature, 75% RH (saturated NaCl water solution), and in a laboratory oven at 80°C, 80% RH (glycerole-water emulsion), respectively. The series were periodically monitored using the µ –FTIR mapping function.

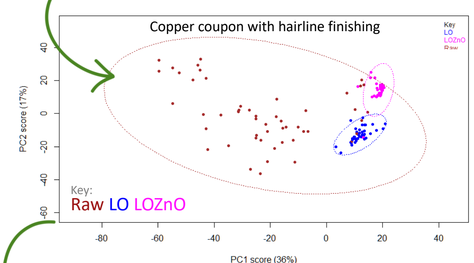


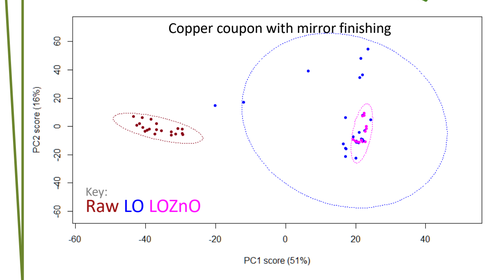
µFTIR chemical image of copper palmitate on a LO-coated copper coupon after 2 months acceletated ageing at RT and 75% RH (NaCl saturated solution in water)



The FTIR spectra collected in RA mode are affected by the hairline finishing, resulting in low reproducibility when no coating is applied (dark red line). This is well represented by the Principal Component Analysis (PCA).

Mirror finishing has been compared with the hairline finishing in terms of quality of FTIR spectra acquired in RA mode. The low reproducibility of the spectra of the bare metal results in a poor clustering when PCA is performed (dark red).





The data were auomatically autoscaled and mean centered

When mirror finishing is used, an improvement in the reproducibility of the spectra is observed for the bare metal (dark red), whereas the linseed oil coating (blue) shows great intra-group variance on the first two principal components. This is probably due to massive differences in the thickness of the coating as a consequence of the low gripping ability of the mirror finished surface, validating the appropriateness of the historical guidelines.

CONCLUSIONS AND FUTURE OUTLOOK

- A proper sample preparation is of paramount importance in the design of model samples for the study of painted metal degradation.
- Brushed hairline surface finishing that reproduces the artists' practice of scratching the metal support to increase the surface roughness and improve adhesion of the paint, allows the collection of informative FTIR spectra in reflectance mode when the coating is present. In the attempt of understanding the reactivity of different metals in presence of added free fatty acids (chemically catalysed degradation), mirror polishing the surface is recommended.
- Achieving paint layers homogeneity is of the greatest importance to obtain conclusive information on the chemical process occurring between the metal and the paint layer. With this aim, experiments on the appropriateness of plasma treatments prior to the metal coating are currently carried out. Such treatment impacts the surface tension of the metal allowing a better wettability of the surface.

Some problems in the drying process of a LO-coated coupon after plasma treatment

REFERENCES

[1] Albini, M. *et al.* (2020). *Frontiers in Chemistry* (8)289. doi: 10.3389/fchem.2020.00289
[2] Gordon, J. *et al.* (2019). In: 2019). In: *Proceedings of the Interim Meeting of the ICOM-CC Metal Working Group*, September 2019. ISBN 978-92-9012-458-0
[3] VV.AA. (2017). *Paintings on copper and other metal plates. Production, degradation and conservation issues*. ISBN : 9788416846962
[4] Casadio, F., *et al.* (2019). *Metal soaps in art. Conservation and Research*. Springer. ISBN 978-3-319-90617-1

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 813789.

[1] Haute Ecole Arc Conservation-Restauration (HE-Arc CR), HES-SO University of Applied Sciences and arts Western Switzerland, *Espace de l'Europe, 11 CH-2000 Neuchâtel (Switzerland)*
[2] Norwegian University of Science and Technology (NTNU), *Teknologiveien 22 NO-2815 Gjøvik*

haute école arc conservation - restauration
neuchâtel berne jura neuchâtel