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WP 21 : Corrosion of Archaeological and Historical Artefacts

This study investigates innovative non-toxic carboxylate protection treatments against corrosion of statuary bronze artefacts. Over the past decades, research has focused on conserving these objects exposed to the atmosphere with special attention on the preservation of corrosion layers (CL). Recent studies have reported the efficiency of long chain carboxylates in protecting copper patina from subsequent deterioration[1]. However, this penetration process becomes more difficult when applied by brush on site and remains a main issue. Therefore, we present a new method to address this matter. In this study, the statuary surface layer is coated with an additional silicon layer produced via the sol-gel process[2] using a dip-coating technique, with a tetra-alkoxysilane (TMOS) precursor and containing high carboxylate concentration. The carboxylic acids used display short hydrocarbon chains with 7, 8 and 10 carbons. Experiments are conducted on century old copper samples exposed to weathering interactions.

A multi-scale analytical approach is undertaken to better understand the mechanisms and physicochemical interactions between the organic treatment and the CL formed on the surface of the historical copper. The treatment‘s penetration is also investigated on samples exposed outside for one year under atmospheric condition, to measure effects of natural weathering and treatment resistivity.

In this work, we demonstrate the efficiency of silicon layer doped with short chain carboxylates as an efficient barrier layer to protect copper from corrosion. Results show that all carboxylic acids allow the formation of an organometallic complex at the surface of the CL with a surface coverage dependent on the acid. All the silicon layers doped with carboxylic acids are transparent, with a thickness up to 4 µm, and have no impact on the colour of the CL’s surfaces. Moreover, the SEM-EDS and Raman studies of the CL’s cross sections show the penetration of both the sol-gel and the carboxylic acid/copper carboxylate mix deep into the external CL of brochantite.

1. Rocca, Steinmetz, *Corros. Sci.* ***43****, 891-902 (2001)*
2. Wang, Bierwagen, *Porg. Org. Coatings* ***64****, 327-338 (2009).*