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Multiscale study of interactions between the corrosion product layer formed on heritage copper objects and organic protection treatments

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In the outdoor environment, bronze and copper statues undergo alterations caused by water and atmospheric pollution. This leads to physical and aesthetic modifications of the copper objects by the formation of a corrosion product layer (CPL) composed of a thin inner layer of cuprite Cu_2O (5 to 10 μm) at the metal/CPC interface and an outer and thicker layer (20 to 50 μm) consisting mainly of brochantite $\text{Cu}_4\text{SO}_4(\text{OH})_6$. To limit these effects, the restorers mainly use treatments with microcrystalline waxes but requiring frequent applications. The search for new corrosion inhibiting treatments, non-toxic, is a major issue in the field of heritage. The new treatments based on carboxylate, saturated carbonaceous long chain, in solutions (HC_{10}) have been developed, in particular on ferrous alloys, and seem promising for copper alloys. However, little information exists on the CPC/carboxylate layer interaction mechanisms.

Our work focuses on the study of the efficiency of the HC_{10} treatment by visualizing its penetration deep inside the CPL to enhance the protection effect as well as the interactions at the CPL/metal interface from micrometric to nanometric scale via a set of complementary analytical techniques mainly implemented on cross sections: μ -Raman spectroscopy for structural analyzes, EDS and electron spectroscopies, and particularly nano-Auger, for chemical investigations. This methodology will be detailed and illustrated on samples issued from the roof of the cathedral of Metz with and without HC_{10} treatment. Main result shows that CuC_{10} can precipitate at the cuprite/brochantite interface.