

SILVER TARNISHING: DO REAL CONTEXTS VALIDATE MODEL?

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The commonly accepted model to explain tarnishing identifies the reduced sulphur compounds as responsible for the formation of dark layers of silver sulphides. In lab, essays simulating the tarnishing of silver objects have been developed in two kinds of silver coupons (Ag 999‰ and Ag:Cu 925‰) conducted under a H₂S (1000 ppm) atmosphere, at 21°C ± 1 and 53% ± 2 RH, with expositions between ½ and 168h. It was possible to obtain, in a reproductive way, different dark films. The samples were analysed by XPS and the results identified sulphides, coherently with the tarnishing classic explicative model. On site, the Holly Sacrament of Eucharist Silver Altar (Porto, Portugal, build from 1632 to the 2nd ½ of 19th century) exhibits a colour palette very similar to the one obtained with the simulated environment. Based on this visual perception, the presence of silver sulphides was to be expected and specific strategies towards the reduced sulphur compounds were to be defined. The individualised corrosion products detected were identified by backscattered electrons followed by EDS analysis. The Cl, Ag, Cu, S and O peaks were identified. The semiquantitative analysis allows admitting the existence of silver chlorides, copper oxides and sulphates. Unpredictably, the black films observed didn't exhibit any evidence of individualised silver sulphides. This study seems to support those who defend dark layers' nature complexity and the need for revising the general accepted models and who argue with thermodynamic data for the most probable silver chloride formation compared to silver sulphide, since $\Delta G^0_{\text{AgCl}} = -109.8 \text{ kJ mol}^{-1}$ and $\Delta G^0_{\text{Ag}_2\text{S}} = -40.67 \text{ kJ mol}^{-1}$. Based on these preliminary results and to overcome the SEM/EDS limitations, the same two kinds of silver coupons were placed on the altar in order to monitor (at least for one year) its progressive alteration by means of XPS. The results will help to better understand the alteration process and the influences of specific real contexts. First results will be presented.