Quantitative evaluation of the effect of electrochemical cleaning of silver artefacts

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GENERALITAT



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MINISTERIO DE ECONOMÍA Y COMPETITIVIE

To quantify the effect of electrochemical cleaning treatments on silver, and to compare it with chemical and mechanical treatments



Pure silver (99.95%) coupons (1x1 cm) abraded with emery paper down to grade 2000

Electrochemical cleaning (EC) Potentiostatic reduction with a Gamry Ref

Potentiostatic reduction with a Gamry Ref 600, $-1V_{Ag-AgCl_{,,}}$ 2120 sec, using NaNO₃ 0.1M as electrolyte.

Mechanical cleaning (MC)

Pre-lim[®] surface cleaner (Picreator Enterprises Ltd.) applied with cotton swabs and removed with deionized water/ethanol 50% v/v.

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3 min. immersion in a 0.001% Na₂S solution

Tarnishing



Chemical cleaning (CC)

1 h immersion in a solution of 10% DTPA pentasodium salt $C_{14}H_{18}N_3Na_5O_{10}.xH_2O$ + 1.5% v/v Triton X-100 .

How much silver is removed in each cycle?

5 x



This figure shows the mass loss of each coupon after the different cleaning cycles. It can be observed that MC eliminates silver in each cycle, producing a significant damage to the base metal. EC and CC do not produce measurable mass loss of the metal

How is the surface texture modified by tarnishing and cleaning?





Are residues left on the silver?



SEM of MC coupons present spots on the surface. EDX analyses show the presence of C and Si, attributable to the composition of the cleaning compound (chalk in water-white spirit emulsion)



Further information?

Contact details?



How much sulphur is left on the surface?



S2p X-ray photoelectron
spectroscopy (XPS) spectra show
that EC is the treatment leaving less
sulphur compounds on the surface.
MC is not able to completely remove
S from the surface. CC is completely
ineffective, leaving S levels
comparable to the tarnished sample



Atomic force microscopy (AFM) shows on the original coupon scratches from the preparation. Tarnishing produces a fine-grained texture over these scratches. CC and EC preserve the texture of the tarnished coupon. MC polishes the surface, eliminating the features of the original coupon.

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Discussion and preliminary conclusions

The three cleaning methods studied present a very different efficiency for removing sulphur tarnishing, as well as different impact on the base metal. MC is efficient in removing tarnishing, even though some remaining S can be detected by XPS. However, it produces a significant mass loss of the silver, alteration of the surface texture, and may leave some residues on the metal. CC, in the conditions used in this study, is very mild and does not eliminate tarnishing. It does not produce damage on the base metal and perhaps might be considered for cleaning mildly tarnished silver. Finally, potentiostatic EC has demonstrated a good efficiency for removing sulphides without damaging the base metal. Surface texture is not altered and no sulphide is left on the surface.

This poster presents work in progress and further studies will be carried out to evaluate other treatments and address questions such as the resistance of silver to re-tarnishing after cleaning. Comments and suggestions are welcome!