

Tarnishing and Milky spots on Silver

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Traditional atmospheric silver corrosion studies have so far focused primarily on sulfidation. There are however other types of corrosion that affect silver and alter its surface quality. One of them generates defects that can be found on silver-minted products in the form of whitish stains named “milky spots”. While silver surface corroded by sulfidation can be restored via simple cleaning and removal of the patina, silver with milky spots cannot be restored as the surface of the metal is severely altered by cracks and inclusions.

The objective of our study, covered here, was to further analyze the tarnishing creation as a result of sulfidation, and to understand the mechanism of formation and growth of milky spots.

Starting from old bars affected by milky spots, we investigated the origin and evolution of these defects by SEM and EDX analysis. We then looked to reproduce and speed up the formation of milky spots conducting tests combining various factors and reaction and comparing non-treated and treated Valcambi bars. Studying the mechanism of their formation and growth, we found out that it is the combination of exposure to UV light, O_3 and NaCl that generates the corrosion that leads to milky spots. This also led to the formation of additional defects: UV light and O_3 activate a process of pitting corrosion on silver and oxidizing species (O_3 or Cl_2) can enhance the formation rate of Ag_2S . In all tests, Valcambi treated bars remained intact while Valcambi non-treated bars were severely altered. Identical tests using treated and non-treated old silver coins showed similar results.

For sulfidation test, we developed an alternative non-toxic solution achieving the same results than most common but hazardous methods.

Understanding the corrosion process that leads to milky spots provides a starting point to develop solutions to prevent their formation maintaining flawless surface quality of silver products over time.