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Original article

A comparative study of cleaning methods for tarnished silver

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ABSTRACT

Tarnishing is produced by reaction of silver with gaseous reduced sulphur compounds from atmospheric pollution. It induces the formation of Ag_2S crystals which produce a dark appearance. To remove sulphur tarnishing, different mechanical, chemical and electrochemical methods have been traditionally used. To assess the effect of different cleaning treatments on tarnished silver, coupons of pure and sterling silver (92% Ag/8% Cu) were subjected to six cycles of induced tarnishing and cleaning. The cleaning methods evaluated were mechanical (soft abrasives and rubber point mounted on a rotary tool); chemical (chelating and acid solutions) and electrochemical (potentiostatic reductions). Surface morphology, composition, weight, color and luminosity were evaluated by optical microscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy and colorimetry. The cleaning impact on tarnished silver depended on the cleaning procedure and the composition of silver. Mechanical treatments restored the original visual appearance of silver although they produced a significant mass loss and a fast re-tarnishing. Chemical cleaning methods were fast; nevertheless the surface appeared completely attacked. Electrochemical cleaning did not yield good result for sterling silver, but was an effective cleaning method for pure silver coupons.

1. Research aims

Different cleaning methods have been used for many years to remove sulphur tarnishing from silver. However, scientific studies which assess the treatment's impact on silver and the re-tarnishing rate are very scarce. Costa [1] carried out a complete bibliographic study about the cleaning procedures and their applications, although the results of these different scientific works are difficult to compare since they have not been systematically evaluated in similar conditions and materials.

The aim of this study is to quantitatively assess the efficiency, residues left on the metal and impact on the base metal of eleven mechanical, chemical and electrochemical cleaning methods to remove tarnishing on pure and sterling silver. To evaluate the effect in the long term, several cycles of tarnishing/cleaning are considered.

2. Introduction

Silver artifacts have been valuable objects since ancient times, as a symbol of status and prestige. Jewellery, cutlery, decoration objects and historical coins are the most common silver artifacts exposed in museums and private collections.

The principal alteration of silver exposed to atmospheric environment is tarnishing, which is produced by the reaction of silver surface with gaseous sulphur compounds, such as hydrogen sulphide (H_2S), carbonyl sulphide (OCS) and other organic compounds (Reaction (1) and (2)) [2,3]. The process is accelerated by the presence of humidity [1]. The tarnishing produced by sulphur dioxide was much slower than that caused by H_2S or OCS [4,5]. The result is a surface layer of silver sulphide (Ag_2S).

$$2Ag + H_2S + \tfrac{1}{2}O_2 \rightarrow Ag_2S + H_2O \quad (1)$$

$$2Ag + OCS \rightarrow Ag_2S + CO \quad (2)$$

Although it is a thin layer and the corrosion is usually mild, tarnishing has a huge visual impact, because it changes the whitish brilliant appearance characteristic of silver to a yellowish or brownish mate tone. To recover its original color and brightness several cleaning methods may be used, including mechanical, chemical

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and electrochemical procedures, with different effectiveness and surface impact.

To identify the usual silver cleaning methods applied by conservators, the bibliographic work of Costa [1] and a consultation carried out amongst metal conservation professionals working in museums and conservation institutions were considered. According to them, mechanical methods are preferred, followed by chemical ones. Other methods such as electrochemical treatments or laser are less used. The majority of professionals employed commercial products which used to be liquids, foams, pastes, waddings or cloths are usually made up of an abrasive (SiO_2, Al_2O_3, TiO_2, $CaCO_3$...) mixed with organic substances (surfactants, soaps, fatty acids...) [6,7]. The main disadvantage of commercial products is that their precise composition is unknown, and may be unexpectedly modified by the manufacturer, changing therefore their effectiveness and aggressiveness.

Pre-lim surface cleaner (Neuburg silica chalks in a water/white spirit emulsion produced by Picreator Enterprises Ltd.) and calcium carbonate are the most favored products for mechanical cleaning. Both are soft abrasives with similar hardness to silver (Mohs' Scale of silver: 2.5–4 and $CaCO_3$: 3) [2]. Previous studies confirmed that abrasives such as alumina, quartz or hematite could leave scratches on silver surface due to their higher hardness [2,6,7].

Regarding chemical methods, thiourea acid solutions (also commercially sold as "silver dip") are the most popular amongst conservators. Thiourea acts as a chelating agent, dissolving the tarnished layer according to the reaction (3) [2,8]. General solvents such as alcohol and acetone, and weak acids such as formic acid and citric acid are also used, in lesser proportion, with moderate efficiency and slow cleaning rate.

$$Ag_2S + 2H^+ + 2n\,[CS(NH_2)_2] \rightarrow 2Ag[CS(NH_2)_2]_n{}^+ + H_2S \qquad (3)$$

Electrochemical methods are scarcely used by conservators because they usually require specific equipment. In metal conservation, it is usually distinguished between "electrolytic reduction", when the source of energy is an external source (a battery, generator or potentiostat/galvanostat) and "electrochemical reduction" (or galvanic reduction) when the source of energy is the formation of a galvanic cell between the object acting as cathode and a less noble metal, usually zinc or aluminum, acting as anode [9]. Given all the variations of modern electrochemical techniques (galvanostatic, potentiostatic, potentiodynamic...) and the fact that all them have the same basis, that is, to reverse the oxidation of the metal that caused the degradation of the object, we prefer to use the generic term "electrochemical (cleaning) methods" for all of them [1]. Amongst these electrochemical methods, galvanic reduction with aluminum or zinc and an alkaline electrolyte is the most common one, although conservators declare that it leaves non-uniform results. Electrochemical methods were very popular for metal conservation for most of the XX century, but were progressively abandoned in the 1970s–1980s due to the changes in the conservation-restoration criteria [9]. However, developments in the application of electrochemical techniques in the last 20 years have made them popular again for metallic cultural heritage, as conservation treatment [10–12], for analytical purposes [13–16] or to evaluate the efficiency of other conservation-restoration treatments [9,17–19].

The ideal cleaning treatment should remove the tarnished layer without affecting the underlying silver surface. With this premise some scientific studies about the effectiveness of cleaning methods have been carried out on abrasives [6,7], thiourea-acid solutions [8], electrochemical galvanic cells [20], electrochemical reductions [21,22] and new treatments such as laser [23,24], cold plasma [25], or UV/ozone treatment [26]. However, results of different methods are difficult to compare since they have not been systematically evaluated in similar conditions and materials. To obtain a wide perspective of the impact of silver cleaning methods, a systematic comparative study of different cleaning procedures has been done to characterize their impact (cleaning efficiency, surface appearance, mass variation and color) on silver after several cycles of tarnishing and cleaning.

Table 1
Summary of eleven cleaning procedures evaluated.

Type of cleaning	Abbreviations	Description
Mechanical	MC	Calcium carbonate
	MP	Pre-lim surface cleaner
	MT	Rotary tool w/rubber point
Chemical	CD	DTPA pentasodium salt 10% w/w + Triton X-100 1.5% v/v
	CT	Thiourea 8% w/w
	CE	EDTA 10% w/w
	CA	HCOOH 10% v/v
	CP	Thiourea 8% w/w + phosphoric acid 5% v/v + Triton X-100 0.5% v/v
	CF	Thiourea 8% w/w + formic acid 5% v/v + Triton X-100 0.5% v/v
Electrochemical	EN	-1$V_{Ag\text{-}AgCl}$ – $NaNO_3$ 0.1 M
	ES	-1$V_{Ag\text{-}AgCl}$ – $Na_3H(CO_3)_2$ 0.1 M

3. Materials and methods

The evaluation of cleaning methods was carried out on pure and sterling silver coupons ($2 \times 1 \times 0.1$ cm), abraded with emery paper down to grade 2000. The original coupons were analyzed by wavelength dispersive X-ray fluorescence (WDXRF), with a Bruker S8 Tiger. Pure silver presented 99.50 wt. % of silver and 0.30 wt. % of iron and sterling silver was 92.47 wt. % of silver and 7.28 wt. % of copper. They were exposed to 6 cycles of tarnishing and cleaning, and they were characterized after each cycle and at the end of the experiment, to assess the cumulative effects of the repetitive cleaning treatments that are applied over decades to silver heritage artifacts.

Tarnishing was carried out by exposure the silver coupons to a sulphur vapor environment at 75% RH according to UNE-EN-ISO 4538 standard [27]. Upon exposure to the sulphur vapor environment, samples started to form a yellowish tarnishing after few hours that progressively darkened reaching a brownish appearance after 72 h. This degree of tarnishing was chosen for this study as representative of an advanced tarnishing level that can be found in some cases in real objects.

Cleaning methods were selected amongst the most usual ones utilized in silver conservation practice, and were applied by professional metal conservators following their customary procedures. Eleven cleaning procedures (mechanical, chemical and electrochemical) have been evaluated, both on pure and sterling silver (Table 1). Two soft abrasives and a polishing process were selected as mechanical cleaning methods. The abrasives used were calcium carbonate dispersed in distilled water (MC) and Pre-lim surface cleaner (MP), which were applied with cotton swabs until total apparent removal of tarnishing. The third mechanical method was polishing with a rubber point mounted on a rotary tool and softly abraded with Pre-lim to finish the treatment (MT).

Six chemical cleaning methods were evaluated by dipping: thiourea 8% w/w (CT); EDTA 10% w/w (CE); formic acid 10% v/v (CA); DTPA pentasodium salt 10% w/w + Triton X-100 1.5% v/v (CD); thiourea 8% w/w + phosphoric acid 5% v/v + Triton X-100 0.5% v/v (CP); and thiourea 8% w/w + formic acid 5% v/v + Triton X-100 0.5% v/v (CF), all them in distilled water [2,8,28]. Additionally EDTA 10% w/w was evaluated using cotton swabs.

The electrochemical cleaning methods were potentiostatic reductions with a Gamry Ref. 600 for 350 seconds, using $NaNO_3$