Silver Cleaning: Comparative Study of Three Commercial Polishers and Their Use on Islamic Historical Metalwork

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Abstract

Removal of tarnish is quite common for objects on museum displays. This study examines the impact of cleaning silver surfaces using three commercially available polishers: silicon rubber, cloth and foam pads. These products appear to better fulfil cleaning objectives in relation to Islamic metalwork with silver inlay, compared to methods such as pastes, as these traditionally used approaches pose risks. Investigations were conducted to analyse the nature of the three products and their impact when cleaning tarnish from silver surfaces. The

elementary compositions of these products were determined using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS). Changes of the elemental composition ratio were determined by SEM-EDS. Visual observations with different imaging techniques (microscope,

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SEM) were used to evaluate surface damage and look for residues on the silver surfaces. The results indicated that the silicon rubber was aggressive, damaging the surface, and should be used with caution and only on thicker tarnish layers. The other two products were effective only on light tarnishing. Based on the experimental results, the foam pad and silicon rubber were selected to clean the silver inlay from a 14th century brass bowl. Examination before and after treatment confirmed that the cleaning outcomes were consistent with the experimental results. The selection of polisher should depend on the type of object and the extent of tarnishing.

Keywords

Islamic metalwork, conservation of silver, silver inlay, cleaning, polishing of silver, historic silver

Introduction

The collection of Islamic metalwork at the Museum of Islamic Art (MIA) in Doha, Qatar consists mainly of copper alloys decorated with precious metal inlays, richly engraved and filled with black or red compounds (Figure 1a). Inlay decoration is rarely complete. Precious metal was habitually reused. In addition, inlays are susceptible to accidental damage due to inappropriate handling or cleaning. Degraded forms of colour

Figure 1. (1a) MIA.2013.138, Iran (Shiraz), 14th century, copper alloy based, gold and silver inlaid, black compound (1b) Details of decoration with residue of old cleaning product

compounds composed of either organic or inorganic materials are highly fragile. With mineral substances like niello or enamel, micro fractures and flaking can result in the loss of important parts. Abrasion and losses are frequent with organic substances like bitumen. Cleaning contributes significantly to the damage of these constituent elements. Often the remaining material in the decorative recesses is simply an accumulation of mixed organic deposit (La Niece, 2010).

Chemical and electrochemical methods can be employed for cleaning of silver. Yet, many conservators tend to favour mechanical methods to remove tarnish. Common mechanical treatments include commercial or homemade liquids, pastes with ingredients including abrasives (such as $CaCo₃$, $SiO₂$, $Al₂O₃$) that are applied in combination with liquid carriers (such as water, solvents, surfactants, glycerine or other chemical compounds) using different media like cotton wool or cloth (Palomar, 2015). This

process is often followed by rinsing with solvent or water to remove traces of abrasive paste. As the dispersion on the surface is facilitated by the liquid carrier, removing all residues inside the surface recess is challenging, particularly when the abrasive has a very fine size grain (Costa, 2001).

Prior to acquisition, many of the objects at MIA had undergone intensive cleaning, mostly for aesthetic purposes, resulting in recurrent surface alterations. Therefore, the corrosion and historic "patina" layers have been partially or entirely removed and the original surface, as defined by Bertholon (2000), has been damaged or destroyed. Silver has been deeply scratched and micro engravings have been abraded or have started to fade (Figure 2).

Figure 2. MIA.2013.138, silver inlaid (x40 magnification) and SEM topography

Another common cause of degradation is the mixing of the original black compound with the residue of cleaning products, dirt and old coatings that remain trapped inside the engraving. These residues can activate or accelerate selective corrosion of copper which in turn can lead to more damage (Figure 1b).

Conservation undertaken prior to displaying these objects commonly involves the removal of previous coatings, tarnish and residues of old cleaning products. The level of cleaning depends on several factors including the object condition, level of tarnishing and curatorial priorities. Silver inlay sometimes presents different levels of tarnishing that can mask micro engraving. Many objects have only localised corrosion, sometimes beneath degraded coatings. Mechanical cleaning using pastes had negative effects, mainly due to challenges with their removal, and are considered too invasive for a light, local treatment.

Compact commercial abrasives seem to offer attractive alternatives. They are ready to use; they appear to leave no residue or only large debris that can be removed mechanically or with solvents; they are easily cut into any shape to clean small areas and reach difficult embossed designs and recesses (such as inlays). With no residues obscuring the object surface, these products facilitate more precise work during cleaning without the repeated rinsing often necessitated by pastes. The results are macroscopically satisfactory, especially on light levels of tarnish. A commonly used method to examine the extent of scratching incurred is a test carried out on acrylic surfaces. A first test on Plexiglas showed that the silicon rubber produces a light frosted effect while the other two products do not (Selwyn, 1991). Only products of known composition and formula should be used on historical objects by a conservator (ibid.), although for practical reasons it is common to use commercial brands in day to day treatments. The aim of this study is to assess the efficiency of three commercial abrasives and to evaluate their impacts on artificially tarnished silver coupons.

Materials and methods

For this study, highly polished sterling silver (92.5% Ag and 7.5% Cu) was selected to prepare sixteen testing samples, each 50×50×15mm. After removing the self-adhesive protection, all coupons were carefully degreased three times in acetone using an ultrasonic bath.

Description and analysis of the tarnished samples

Different levels of tarnishing are often observed on the same silver alloy surface, with extensive tarnishing being the most severe but less frequent. Accordingly four different levels of tarnishing were selected: very light (Level A), light (Level A+), moderate (Level B), extensive (Level C). The experiment aimed to identify the best cleaning method, based on the level of tarnishing, so as to cause least damage to surfaces and micro-engravings, and without leaving any residue.

All coupons were tarnished by exposure to an ammonium sulphide atmosphere in order to produce silver sulphide/s on the surface. The elemental composition and ratio between copper (Cu) and silver (Ag) were analysed using SEM-EDS (Table 1).

Tarnished control coupon	LEVEL A: very light	LEVEL A+: light	LEVEL B: moderate	LEVEL C: extensive	Reference silver coupon
Tarnishing process	-10 ml of c.2% left for 7 min.	-10 ml of c.2% left for 14min.	-10 ml of c.2% left for 7 min. - atmosphere dispelled - 10ml of c.2% for 1hr 30mins. - atmosphere dispelled - 10ml of c.2% left for 20 hours.	-10 ml of c.2% left for 7 min. - atmosphere dispelled -10 ml 40-48% solution. left for 24hrs.	degreased in acetone using the ultrasonic bath for 3 minutes, 3 times
Cu adj %	$6.2 \ (\pm 0.17)$	7.2 (± 0.6)	$12.2 (\pm 0.41)$	$25.3 \ (\pm 13.3)$	6.9 (± 0.08)
Ag adj %	$93.8 (\pm 0.17)$	92.3 (± 0.6)	$87.8(\pm 0.41)$	$38.3 (\pm 13.3)$	93.1 (± 0.08)
Cu/Aq	$0.07 (\pm 0.0)$	$0.1 (\pm 0.01)$	$0.1 (\pm 0.01)$	$0.4 (\pm 0.2)$	$0.1 (\pm 0.00)$
Ag/Cu	15.06 (± 0.4)	$12.0 (\pm 0.9)$	7.2 (± 0.28)	$6(\pm 6.6)$	$13.5 (\pm 0.17)$

Table 1. Elemental composition of the tarnished coupon and chemical procedure for tarnishing

Macroscopically, Level A and A+ coupons had a similar homogeneous layer of thin tarnishing, the colour of which evolved between a yellowish and a reddish light grey whilst retaining, to some degree, a metallic reflectiveness. Level B and C coupons developed thicker heterogeneous corrosion layers with irregular morphology. Level B coupons were grey with local powdery corrosion product, and Level C samples were covered with extensive black tarnish with a light crystalline shine and powdery rough surface (Figure 3).

Figure 3. Tarnished sterling coupons surface: (A) very light, (A+) light, (B) moderate and (C) extensive tarnishing

Under high magnification $(x500)$ the light tarnishing Level A appeared as a thin non-homogeneous layer of silver sulphide with evident pitting. Level A+ had a similar profile with additional formation of sporadic crystals. Level B also demonstrated areas of crystal growth, evenly dispersed. The Level C surface presented a heterogeneous stratigraphy of corrosion, with different sizes of crystalline aggregates and nodules. Localised starshaped cracking was clearly visible (Figure 4). In all but the most extensive level, the general surface features of the original degreased coupons were still evident under the SEM.

Figure 4. SEM images of tarnished sterling coupons surface: (A) very light, (A+) light, (B) moderate and (C) extensive tarnishing

Upon analysis, the original elemental composition (Ag/Cu ratio) of the silver sterling coupons used in these experiments was 13.5. This was the reference used to monitor changes, although it is noted that sterling silver commonly has an Ag/Cu ratio of 12.3. The ratio of Ag/Cu increases slightly after very light tarnishing (A), but decreases at all other levels and drops to around 7 from moderate and extensive tarnishing (Table 1). The copper percentage increases significantly from 6.3 to 7.7% after very light and light tarnishing, to 12% after moderate tarnishing, 24% after extensive tarnishing in combination with the significant silver percentage drop. This enrichment of copper on the surface is consistent with other studies (Paloma, 2015).

Description and analysis of the three commercial products

Three commercial products were selected. Two of them are traditionally used by jewellers. The last one was acquired online following a recommendation made by a colleague. Some compositional information was gathered from the manufacturers and compared to data collected

during the study. The silicon blue rubber polisher EVE UNIVERSAL (BR) is made of a silicon binder with silicon carbide abrasives. The yellow polishing cloth called ASTIC-BRILLE (YC) is made of cotton fibres, impregnated in a bath solution containing abrasive and additives. The white ULTRA POLISHER PAD (WP) is described as 'thin tight-bond foam with permanently bonded micro-abrasives' (Table 2).

The FTIR and SEM-EDS results confirmed the information provided by the suppliers. BR is composed mainly of SiC and TiO₂, while YC shows more Si and Al_2O_3 , and WP presents $\mathrm{Al}_2\mathrm{O}_3$. While the abrasive is evenly distributed inside the binder for BR and WP, the particles are allocated on each cotton fibre (Figure 5). The FTIR results show some similarities in the composition between the yellow cloth and the white pad.

Figure 5. SEM images of commercial products (x500 magnification): (a) the WP, (b) the YC and (c) the BR

Testing protocol

Cleaning of the experimental coupons aimed to follow the methodology implemented during the cleaning of silver inlays on objects at MIA. In addition to the three commercial products (WP, BR, YC), calcium carbonate

 $(CaCO₃)$ dispersed in distilled water has been tested to compare solid abrasive and abrasive paste. Three levels of cleaning (LI, LII, and LIII) were selected, representing a progressive cleaning range from soft to strong and a surface result from light to high reflectiveness. To standardize the cleaning method, strokes were applied with pressure as consistent as possible, and the number of strokes recorded. The silver coupons were rotated at 45° every 10, 20 or 50 strokes to increase reproducibility. All the coupons were divided into four sections, three for the different cleaning levels and one as a control. The cleaned surfaces were rinsed with water and/or ethanol until all residues were removed macroscopically.

Experimental results

Macroscopic observations

Effectiveness of the products depended on the level of tarnishing of the silver surface. WP and YC effectively removed both light tarnishing A and A+; they were easy to control and achieved the desirable level of cleaning with a homogeneous result. No scratches were evident macroscopically. These two products were not effective at level B and C tarnishing, as a burnishing effect of the tarnishing layer was observed (Wharton et al., 1990). No residues were detected, although in the case of YC the additive perfume remained on the surface and needed additional rinsing with ethanol.

BR was effective in removing tarnishing from level A, A+ and B but less effective on the extensive tarnishing C, removing only the superficial powdery product. Difficulties were encountered in achieving the different

cleaning levels with even results. Finally, BR was too hard and caused scratches, especially at the edges of the working surface, resulting in an inhomogeneous surface. Air flow was required to remove residues.

 $\rm CaCO_{_3}$ was effective on all levels, although repeated strokes with added pressure were needed to remove the thick level C tarnishing; it was time consuming and required repeated rinsing to remove residues. Cleaning caused flaking of the corrosion layers, similar to that described by van Langh (van Langh 2004), as well as burnishing of the surface (the tarnish layer at the edges appeared shiny).

Microscopic observations

At high magnification, local spots of silver sulphide were visible on the surface. SEM imaging showed the presence and nature of dispersion of residues, and the size of their constituent particles (Table 3). For levels A and A+, all three commercial products (WP, YC and BR) leave some residual material (abrasives size 10μ), estimated at one percent coverage of the total surface. In level B and C, the WP and YC leave even more residual particles (1μ) , estimated at ten percent coverage. The consistent size and coverage of BR residues is probably due to the manufacturing process (condensation-curing of silicone with a high tear strength binder). CaCO₃ residues were estimated to be between 5 to 10 percent of coverage.

All products scratched the surface to a certain extent, depending on the tarnishing level. WP and YC give similar results in light levels of tarnishing (A, A+):

Table 3. Comparison of overall surface after cleaning (0= none, 5= more)

scratches of superficial to moderate depth, evenly distributed (Figure 6a-b). For the moderate tarnishing (B) they left a few, relatively superficial scratches, and for extensive tarnishing (C) they left none. $CaCO₃$ scratches are consistent: moderate depth with few deep scratches and dense distribution at all levels of tarnishing (Figure 6d). Finally, BR appears to scratch the surface more significantly with deeper marks, evenly distributed and with a dense network (Figure 6c).

SEM topography shows that on Level C coupons, the burnishing effect (occurring for WP and YC) flattened the tarnishing layer; the crystalline aggregates appeared diminished, while star-shaped cracks multiplied. These effects are thought to contribute to the fragility and later flaking and loss of this corrosion layer.

Effectiveness of selected products at different

Figure 6. SEM images of tarnished coupons (x200 magnification) at light tarnishing A+ and level III cleaning: (a) WP, (b) YC, (c) BR and (d) CaCO3

levels of tarnishing

Changes in surface elemental composition as well as the ratio Ag/Cu at the different levels of cleaning (LI, LII, LIII) were considered for the four products tested, and referenced against the control regions (Table 1, 4).

EDS analysis showed that all the commercial products (WP, YC, and BR) affect the surface composition with similar results for tarnishing Levels A and A+. At LI and LII cleaning levels, small differences were observed in the ratio Ag/Cu (rise of 15 -16), due to a slight increase of silver content. At LIII, the silver percentage was stable but the ratio increased considerably (average of 18). Substantial change was observed for $CaCO₃$, at all cleaning levels, with Ag/Cu rising to 22.5 due to silver increase and maximum decrease of copper at LIII (4.3%) .

Major changes in the ratio and surface composition appear at tarnishing levels B and C. For WP and YC (that do not clean effectively), we observe consistent results, close to the tarnished reference coupons. At level B, there is a decrease of silver (88 to 87%) and the Ag/Cu ratio is around 7. At level C, the copper increases and the silver falls significantly (68 to 65%), as the ratio stabilizes around a 2.1 average.

At tarnishing levels B and C, cleaning with the BR generated high standard deviation amongst alloy percentage contents (up to 6.3) and ratios (up to 5.7). The decrease of copper and increase of silver were consistent at level B, with increasing ratio Ag/Cu. At tarnishing level C, the Ag/Cu ratio rose (7.7) due to a substantial increase of silver on the surface.

 $CaCO₃$ caused the most significant changes. At level B, there is a significant increase of the Ag/Cu ratio (Control: 7.2, LI: 16.7, LII: 18.9, LIII: 20.9) linked to an

Table 4. SEM-EDS analysis for all level of cleaning (LI, LII, LIII) for the WP, BR, YC and CaCo₃; average of Copper (Cu) and silver (Ag) percentage of the alloy composition and the ratio Ag/Cu

*reference coupon: Cu adj % 6.9 (±0.08), Ag adj % 93.1 (±0.08), Ag/Cu 13.5 (±0.17).

increase of silver and decrease of copper, with a slight standard deviation. At level C, copper has almost disappeared; below one percent for LI and LII, and below three percent for LIII. When the copper was removed, the silver content is higher (97.5 to 99.5%), implying a radical rise of the Ag/Cu ratio (LI: 235) with high standard deviation.

In conclusion, the composition and ratio of the WP and the YC remain close to the percentages of the reference tarnished samples and affect the surface less during cleaning. For BR, which shows high standard deviation in almost all levels of cleaning, it is reasonable to infer that the hardness of the product as well as pressure applied during cleaning affects the surface composition of the alloy. The decrease of the Ag/Cu ratio is linked to the selective corrosion and subsequent removal of silver for all the commercial products. With $CaCO₃$, maximum changes in the composition are observed. The absence of copper could be due to enrichment of silver caused by the burnishing of surface layers.

Cleaning of silver inlay

The two silver inlays with micro engraving and black compound selected for this study were highly scratched and presented different levels of corrosion. One inlay was covered by localised areas of very light (A) and light $(A+)$ tarnishing (Figure 2). On the second one, a homogenous layer of moderate tarnishing (B) covered the surface and a local area of extensive tarnishing (C) partially overflowed the engraving (Figure 7a). A metallic surface was noticed around the spot of extensive tarnishing (C) and could have been the consequence of previous flaking (van Langh, 2004). The elemental composition of the inlay analyzed using SEM-EDS was ninety six percent silver and four percent copper. The Ag/Cu ratio was high (24.5). After considering these results, two products were employed for cleaning under a microscope: silicon rubber (BR) for the extensive (C) and moderate (B) tarnishing and white pad (WP) for light tarnishing (A, A+).

The results were consistent with the outcome of the study. The BR allowed us to remove the localised extensive tarnishing but caused new scratches (Figure 7b). While the WP showed few new marks at high magnification, it left the deep original scratches full of corrosion as before (Figure 7c). In terms of reflectivity, the surface cleaned with the WP was left with a soft lustre as a result of the burnishing.

Figure 7. Silver inlaid: (7a) before cleaning with extensive C tarnishing (hatched surface), (7b) after cleaning with BR, (7c) after cleaning with WP

Results and discussion

This study assessed the effects of three commercial products for polishing silver and confirmed that the composition of the silver alloy is affected by the polishing method used (Selwyn, 1991). The CaCO₃ paste had the greatest impact on composition by increasing the silver in surface levels after cleaning. The high level of microscopic residue that $CaCO₃$ left on the surface has been long-established (Costa 2001). Further analyses could be undertaken on the long-term effects and potential impacts on corrosion processes (Thickett, 2014). CaCO₃ was used for comparative reasons, as it is one of the most common mechanical methods used. Nevertheless, it is considered unsuitable for Islamic metalwork due to the lack of precision and resulting surface residue.

The effectiveness of the commercial products was linked to the extent of tarnishing, the achievable level of cleaning and the pressure applied. The foam (WP) and cloth (YC), as mild products, were efficient on light levels of tarnishing in terms of low residue, homogeneity of appearance, low density and minimal depth of scratches at all levels of cleaning, and low standard deviations across elemental impacts. However, these two products were inefficient on thicker tarnish layers

and their surface action could lead to the burnishing of corrosion layers and development of micro fractures. While the rubber (BR) was effective (up to Level B), a large network of profound scratches becomes apparent due to the hardness of this abrasive, as already determined in other studies (Wharton et al. 1990; Costa, 2001). However, since this product was the most malleable and permitted the greatest precision during the work, it could be exploited selectively to reduce thick tarnish layers by using low pressure, while remaining aware of the risks of physical damage.

At a light level of tarnishing, the cleaning remains easier and more controlled, with less abrasion and residual product, and causing the least surface modification. More research should be undertaken to examine and compare the long-term effect of regular polishing and irregular cleaning of thick tarnishing, along with comparisons of chemical methods. Suitable display, coatings and storage conditions must also be considered to evaluate whether it is preferable to clean more frequently, or less frequently with more extensive cleaning.

Conclusion

For the cleaning of Islamic metalwork with silver inlay, it might be preferable to clean before thick layers of tarnish develop, as this is likely to cause eventual loss of surface decoration from flaking. Cleaning must be undertaken under a microscope, reducing thick corrosion layer by layer, to recover the micro engraving and achieve a light level of cleaning. If the use of silicone rubber could be considered for local cleaning on extensive tarnishing, the pressure must be moderate to reduce surface damage. To reduce reflectivity, a mild abrasive (foam or cloth) polishing could follow. This can also help in increasing the clarity of features that are less visible on shiny surfaces. The elemental compositional changes caused by different cleaning methods must be acknowledged and professionals should be aware of the effect that common treatments like cleaning have on surfaces, as well as the analysis and interpretation of an artefact.

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Materials list

EVE®, product by Ernst Vetter GmbH, Eve Universal, light blue, item R22f. p.18, [http://www.everotary.com/fileadmin/flippingbooks/](http://www.everotary.com/fileadmin/flippingbooks/Schmuckenglisch/blaetterkatalog/index.htm) [Schmuckenglisch/blaetterkatalog/index.htm](http://www.everotary.com/fileadmin/flippingbooks/Schmuckenglisch/blaetterkatalog/index.htm)

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Jill Saunders has an MA in Principles of Conservation and an MSc in Conservation for Archaeology and Museums from the Institute of Archaeology, University College London. She is currently completing PhD research with UCL-Qatar on cleaning of non-ferrous metals. Her research incorporates public perceptions studies concerning preferences of silver tarnish levels on historic silver and cleaning levels on archaeological bronze in different contexts; materials science research into impacts of different cleaning methods on sterling silver, bronze, brass and copper coupons artificially corroded in different ways; and a professional survey into practice and attitudes about cleaning silver alloy and copper alloy objects.

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