Studies in Conservation

ISSN: 0039-3630 (Print) 2047-0584 (Online) Journal homepage: www.tandfonline.com/journals/ysic20

The Cleaning of Silver Objects With a Basic Solution of Sodium Glycinate: A Study on Artificially and Naturally Tarnished Silver

João Cura D’Ars de Figueiredo Junior, Samara Santos Asevedo, Maria Luiza Seixas de Souza e Silva, Andrezza Conde Araújo & Maria Regina Emery Quites

To cite this article: João Cura D’Ars de Figueiredo Junior, Samara Santos Asevedo, Maria Luiza Seixas de Souza e Silva, Andrezza Conde Araújo & Maria Regina Emery Quites (2021) The Cleaning of Silver Objects With a Basic Solution of Sodium Glycinate: A Study on Artificially and Naturally Tarnished Silver, Studies in Conservation, 66:7, 375-383, DOI: 10.1080/00393630.2020.1859876

To link to this article: https://doi.org/10.1080/00393630.2020.1859876

Published online: 07 Jan 2021.

STUDIES IN CONSERVATION
2021, VOL. 66, NO. 7, 375–383
https://doi.org/10.1080/00393630.2020.1859876

ORIGINAL RESEARCH OR TREATMENT PAPER

The Cleaning of Silver Objects With a Basic Solution of Sodium Glycinate: A Study on Artificially and Naturally Tarnished Silver

João Cura D'Ars de Figueiredo Junior [1], Samara Santos Asevedo[1], Maria Luiza Seixas de Souza e Silva [2], Andrezza Conde Araújo[1] and Maria Regina Emery Quites[1]

[1]Department of Plastic Arts, School of Fine Arts, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil; [2]Escola de Minas, Universidade Federal de Ouro Preto, Ouro Preto, Brazil

ABSTRACT
The appearance of silver objects deteriorates due to the formation of a brown-to-black tarnish layer. Several methods are available for removing these tarnished layers, ranging from polishing through chemical cleaning to electrochemical methods. This study presents a low-cost and low-toxicity method that uses sodium glycinate to clean silver. Cleaning tests were performed on both artificially tarnished prototypes and naturally tarnished objects after characterizing them; scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) were used to characterize the artificially tarnished prototypes, and X-ray fluorescence (XRF) was used to characterize the naturally tarnished objects. The aggressiveness of the baths was analyzed by measuring the leached amount obtained through atomic absorption spectroscopy (AAS) and SEM. The procedures used for cleaning the artificially tarnished prototypes served as a guide for cleaning two naturally tarnished objects: a halo and a crown. Cleaning was guided by the presented method's characteristics as well as the object's unique characteristics and condition.

ARTICLE HISTORY
Received May 2020
Accepted November 2020

KEYWORDS
Silver cleaning; silver tarnish layers; sodium glycinate; scanning electron microscopy; X-ray fluorescence

Introduction

Artistic objects made out of silver alloys can present a tarnish caused by corrosion of the surface, resulting in a color varying from brown to black. Thus, their appearance is damaged. These tarnishes can be formed by oxides, chlorides, carbonates, sulfates, and sulfides of the constituent metals of the silver alloy. Acanthite (Ag_2S) is a major component of tarnish (Costa 2001; Vassiliou and Gouda 2013). Chlorargyrite (AgCl) is also found in moderate amounts with other components in small amounts (Vassiliou and Gouda 2013). The formation of Ag_2S requires a combination of an oxidizer, a pollutant, and an elevated relative humidity (>50%) (Costa 2001), and the most common oxidant is oxygen and the most common pollutant is H_2S.

High values of relative humidity accelerate the formation of tarnish (Costa 2001; Vassiliou and Gouda 2013). Typically, the deterioration reaction involves a silver oxidation stage forming an oxide, followed by the formation of sulfide by the reaction with H_2S.

$$4Ag + O_2 \rightarrow 2Ag_2O \quad (1)$$

$$Ag_2O + H_2S \rightarrow Ag_2S + H_2O \quad (2)$$

Another common pollutant is carbonyl sulfide (COS), which acts as a source of H_2S when reacting with H_2O (Leygraf et al. 2016).

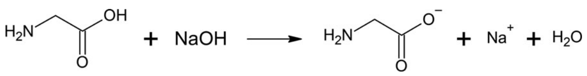
$$COS + H_2O \rightarrow H_2S + CO_2 \quad (3)$$

Conservators can remove tarnish through different cleaning methods: mechanical, chemical, electrochemical (Costa 2001), laser (Degrigny et al. 2003; Golovlev et al. 2003; Viljus and Viljus 2013; Palomar et al. 2016a), and plasma cleaning (Ioanid et al. 2011, 2013). Each of these methods has its own advantages and disadvantages, rendering their suitability dependent on the cleaning requirements. The selection of the cleaning method depends on the applied procedure, the composition of the silver alloy (Palomar et al. 2016b), and the condition of the object. Therefore, it is important to verify whether the object is fragile, whether it can withstand pressure, and whether it can be immersed and rinsed properly. Chemical cleaning methods are used when they fulfill the criteria for treatment and when the other cleaning options are not suitable, some of which have been presented in Costa (2001) dissolving the metal alloy to a minimum amount and retaining the cleaning reaction products in the solution.

To determine a compound that meets these criteria, a pro-ligand capable of forming soluble coordination compounds with the metals of the tarnish was explored. Compounds produced by the coordination of water-soluble silver amino acids were reported in

CONTACT João Cura D'Ars de Figueiredo Junior joaoc@ufmg.br Department of Plastic Arts, School of Fine Arts, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil

the literature (Nomiya and Yokoyama 2002). Furthermore, a previous study (de Figueiredo, Asevedo, and Barbosa 2014), reported results on a chemical silver-cleaning procedure involving the reaction of the corrosion products of a silver alloy (50% Ag, 50% Cu) with sodium glycinate in an alkaline medium (pH 10). Sodium glycinate is a compound that can be obtained by reacting the amino acid glycine with sodium hydroxide.



(4)

Glycinate can react with silver compounds to form the polymeric compound, silver glycinate (I), which is soluble in water (Nomiya and Yokoyama 2002; de Figueiredo, Asevedo, and Barbosa 2014). Glycinate also reacts with copper to form copper (II) glycinate, which is also soluble in water. The structural formulae of these compounds are shown in Figure 1. Water solubility is due to the complexes' ability to form hydrogen bonds. In addition to water solubility, which fulfills the criterion of keeping the cleaning reaction products within the solution, amino acids are capable of solubilizing silver and copper. They have been used in alkaline media in combination with other compounds, such as cyanide and peroxide, in the field of hydrometallurgy for extracting metals from ores of gold, silver, and copper (Oraby, Eksteen, and Tanda 2017; Tanda, Eksteen, and Oraby 2017). This indicates that amino acids are able to react with tarnish. In a previous study (de Figueiredo, Asevedo, and Barbosa 2014), alkaline solutions of amino acids were tested for cleaning artificially tarnished silver objects. Indicating its low aggressiveness toward the metallic alloy, the alkaline glycinate solution exhibited greater reactivity with the corroded species and low reactivity with the non-corroded metals. Low aggressiveness was observed while measuring the content of the leachate metals and while analyzing the surface through optical and electronic microscopy (de Figueiredo, Asevedo, and Barbosa 2014). The cause for the difference in the solution's reactivity toward corroded and non-corroded species was explained using the theory of hard and soft acid bases (HSAB) (Miessler and Tarr 2003), wherein the Ag^+ and Cu^{2+} species were attributed a hard character more similar to the amino acid ligand than the soft-character-attributed non-corroded metals. The differences in the reactivity between the bulk metals and their corrosion products are due to the alterations in free energy that are brought about through the corrosion process.

This shows that this method has properties that make it suitable for use in cleaning silver artwork, and can thus be considered an alternative to chemical cleaning using thiourea, which is commonly used in the treatment of silver objects (Palomar et al. 2016b). Thiourea is suspected to be carcinogenic; it is a reproductive toxin and is hazardous to aquatic environments. It is a long-term hazard according to the Globally Harmonized System (GHS) (National Library of Medicine). Moreover, a large amount of water is required to remove thiourea. The large water volumes needed for removal of thiourea after treatment is due to the strong affinity of the pro-ligand for both silver and copper. However, rinsing often fails to remove all residues that are responsible for uneven and blotchy retarnishing (Wharton 1989; Contreras-Vargas, Ruvalcaba-Sil, and Rodríguez-Gómez 2013; Palomar et al. 2016b; Selwyn and McKinnon 2020). In contrast, because glycinate is soluble in water, it requires less water for cleaning and it is not a toxic substance or mixture according to the GHS (Thermo Fisher Scientific, Safety Data Sheet). However, as the pH of the medium makes it reactive with skin, handling the sodium glycinate solution requires the use of gloves. Another difference between glycinate and thiourea is that the former does not cause wear on the metallic surface (de Figueiredo, Asevedo, and Barbosa 2014). Thiourea, however, causes micro roughness, thus polishing can be required after treatment (Wharton 1989).

This study builds on previous research presenting data on the behavior of silver alloys with silver content above 90%, which are the most commonly found alloys in artistic objects (Costa 2001). Artificially aged prototypes were studied to understand the behavior of glycinate during tarnish removal, its aggressiveness toward the metal alloy, and its cleaning efficiency. The behavior of glycinate on the prototypes was then used to develop procedures for cleaning naturally aged silver objects. It is important to also

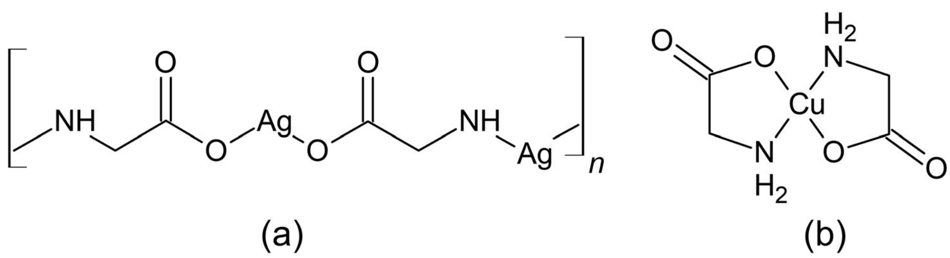


Figure 1. Coordination compounds of silver (a) and copper (b) with the ligand glycinate.

study the behavior of cleaning on naturally tarnished objects as artificial tarnish is not fully representative of natural tarnish. Therefore, the behavior of naturally aged objects during cleaning is also studied here.

Materials and methods

Artificial corrosion of prototypes and cleaning baths

Ten out-of-circulation Brazilian silver–copper alloy coins minted using silver 900 (90% Ag and 10% Cu) from the '500 Réis' series were used as prototypes for each experiment. The coins had an initial mass of 5 g. These coins were used to observe chemical reactions and changes in the details of the surface due to the cleaning. The coins were washed with distilled water and dried on a cotton cloth, polished with Massa Polir 2 – Base água – ACS, washed in ultrasound with a 1% neutral Tween 80, followed by washing with mineral white spirit, and then finally washed with ethanol.

To obtain a strongly adhered corrosion layer, the coins were artificially corroded through immersion in a 0.01-mol L^{-1} basic thiourea solution (pH = 10) for five hours. Thiourea can be used to tarnish silver because it is unstable in alkaline media and it decomposes (Equation (5)) to generate sulfide ions (de Figueiredo, Asevedo, and Barbosa 2014).

$$CS(NH_2)_2 + 2OH^- \rightleftharpoons S^{2-} + 2H_2O + CH_2N_2 \quad (5)$$

The 0.1-mol L^{-1} solution of sodium glycinate was obtained by the reaction of glycine with 0.1-mol L^{-1} NaOH dropped in the solution until pH = 10 was achieved.

The cleaning process involved immersing the coins in a 0.1-mol L^{-1} sodium glycinate solution (pH 10) for two hours. Post immersion, the coins were rubbed using a cotton swab that was soaked in distilled water until maximum tarnish was removed.

The surfaces of the coins were examined via SEM in three stages: before corrosion, corroded, and after cleaning. Images were obtained using a FEI Quanta 3D FEG scanning electron microscope coupled with a Bruker QUANTAX EDS analyzer using a voltage of 10 keV, 0° tilt angle, 35° take-off angle, 45° azimuth angle, and XFlash 5010 detector (Bruker, U.S.A.). Element quantification was performed using ESPRIT2 software (Bruker, U.S.A.).

Determination of lixiviated silver and copper

Atomic absorption spectroscopy (AAS) is an analytical technique that involves the absorption of light with specific wavelengths by free atoms in the gaseous state. This technique is used to quantitatively measure the elements in a solution sample, commonly the metallic elements in an aqueous solution, and is sensitive to small amounts in the order of parts per million (ppm). The solution with the elements to be measured is aspirated and directed to a flame at high temperatures (>2000 K), where they are heated until they are atomized. The light of specific wavelengths for each element is applied to the sample that absorbs it in proportion to the concentration of the element (Stuart 2007).

Ten coins were washed with distilled water and dried on a cotton cloth, polished with commercial polish, and subsequently subjected to ultrasound washing with a 1% neutral detergent solution. Then, the coins were washed with mineral white spirit, and finally, with ethanol. Next, the coins were weighed and immersed in 10 mL of 0.1-mol L^{-1} sodium glycinate (pH 10). After 1 h, the coins were rinsed with water that was mixed with the solution of the immersion. The final mixture was diluted to 25 mL. Ten solutions were prepared in this manner. Experiments were performed in triplicate. The percentage of copper and silver in each obtained solution was determined through AAS using a Hitachi Z-8200 spectrometer (Hitachi, Japan).

Naturally tarnished objects

Two naturally aged silver objects with a brown tarnish were studied: a silver halo of the image of Our Lady of Sorrows from the Church of São Francisco de Assis (City of Sabará, estate of Minas Gerais in Brazil) and a crown from the collection of the congregation of Nossa Senhora do Pilar (City of Ouro Preto estate of Minas Gerais in Brazil).

The silver halo is part of a polychrome wooden sculpture with leather-covered joints. The sculpture is part of the collection of the Church of São Francisco de Assis. It is thought to be manufactured in the nineteenth century. It had a light brown and discontinuous layer of patina. The silver crown was stored in a leather chest lined with calico (cotton fabric), along with other objects, for over three years. The chest was stored in a wooden cabinet. The crown had a thick continuous brown-to-black layer with residues of polishing material. In addition to the patina, it had a broken handle. It is thought to be manufactured in the eighteenth century. The leather present in the sculpture and lining material of the chest could be attributed as a source of sulfides that led to the formation of tarnish on the objects.

Characterization of the alloys of the objects

The silver alloys of the objects were characterized via nondestructive XRF spectroscopy of the surfaces. The spectra were recorded using a portable X-ray Innov – X model Alpha (Olympus, Japan) with an anode tube Ag–W, a voltage of 35 kV, a current ranging 5–30 µA, and a silicon diode detector. Calibration was performed using the fundamental parameters method with a 316 stainless steel alloy and a 50% Ag and 50% Cu silver alloy. As the surface composition differed from the bulk metal, the procedure presented in Mass and Matsen (2012b) was followed to verify alloy composition.

Cleaning procedures

The cleaning procedures used on the artificially tarnished objects served as a guide for the cleaning of the naturally tarnished objects. Artificial corrosion was observed to be different from natural corrosion; it was easier to remove, and the cleaning procedures were adapted accordingly.

Regardless of the aggressiveness of the cleaning method, unwanted removal of metal from an object always occurs, which opts for a shorter treatment time with the chemical cleaning agent. Considering this, a general cleaning protocol was established relative to the desired level of cleaning. An adequate level of cleaning is one wherein corrosion is removed to the point at which its interference with respect to the appearance is reduced. The condition and fragility of the work must be considered to ensure that cleaning does not cause further damage, such as mechanical deformation or removal of details. Furthermore, overcleaning can result in the removal of tarnish from engravings and decorations, decreasing the contrast of the work and its legibility. The protocol involved the following steps:

- Initial cleaning of the object using a soft brush to remove loosely adhered dust and dirt.
- Cleaning the object with a cotton swab soaked in 1% aqueous solution of neutral detergent Tween 80 to remove oils and other dirt from the surface, followed by a cotton swab soaked in distilled water to rinse the products.
- Cleaning the work with a cotton cloth soaked in 0.1-mol L^{-1} solution of sodium glycinate (pH 10) followed by a cotton cloth soaked in distilled water to rinse the glycinate.
- Immersion of the work or application of the 0.1-mol L^{-1} solution of sodium glycinate (pH 10) in the form of a cotton pad over the tarnish for 1 min followed by a cotton cloth soaked in distilled water to rinse the glycinate.
- Drying the work using a cotton cloth.

Notably, in step two, the tarnish can be removed, which would end the cleaning process. If the tarnish removed is considered satisfactory, the cleaning process can be terminated; otherwise, the conservator must proceed to the next step. In step four, objects with shapes that allow retention of the solution should preferably be treated using poultices and objects that have simple shapes can be immersed (Costa 2001). The dimension of the object must also be evaluated in the procedure based on the time of cleaning and retention of the solution. The immersion or application of poultices can be repeated until the required cleaning level is achieved.

Treatment of the objects

The silver halo was initially cleaned by rubbing with a cotton swab with a 1% aqueous solution of neutral detergent Tween 80, followed by rinsing with a cotton swab with distilled water; it was then dried using a dry cotton cloth. Next, the object was gently rubbed with a cotton swab soaked in a 0.1-mol L^{-1} sodium glycinate solution (pH 10) followed by rinsing with cotton swabs soaked in distilled water and then dried using a dry cotton cloth.

The cleaning of the crown began with removing dirt from the entire piece using a soft bristle brush, followed by cleaning with a cotton swab moistened with a 1% aqueous solution of neutral detergent Tween 80. This was followed by rinsing with distilled water; then, it was dried using a dry cotton cloth. The crown exhibited residues of polishing products, and certain regions had a greenish color as the copper of the alloy had preferentially corroded. These residues were removed using a cotton swab soaked in a 1% aqueous solution of trisodium citrate, followed by rinsing with a swab soaked in distilled water. The cotton swabs had to be frequently changed to avoid scratches on the surface due to polish residue in the swab.

To remove the brown tarnish, the object was gently rubbed with a cotton swab soaked in a 0.1-mol L^{-1} sodium glycinate solution (pH 10), followed by rinsing with distilled water. Then, to optimize the removal of stubborn tarnish, the crown was immersed in the sodium glycinate solution for 1 min. The crown was removed from the immersion, and while still wet, was rubbed with a cotton swab soaked in sodium glycinate solution. As the desired tarnish removal was not observed, the immersion cycle was repeated four more times, adding up to a total of 5 min of immersion. After removal, the crown was rinsed with distilled water and dried with a dry cotton cloth.

Casa do Restaurador microcrystalline wax was used to protect the objects subsequent to all treatments. It was applied as a 35% solution in white spirit with a soft brush. To make an even surface, the coating was heated with a hair dryer, and a gentle final polish was performed with a lint-free cloth.

Results and discussion

Artificially tarnished coins

Determination of lixiviated mass of silver and copper

The measure of the mass removed from the metals is indicative of the cleaning method's aggressiveness, which should aim at removing as little metal as possible. Table 1 presents the results of the amount of leached mass and its contents for the coin dipping baths in the sodium glycinate solution.

Data analysis reveals that the content of leached silver is lower than the detection limit of the equipment and is, therefore, lower than that of copper, which was detectable. This is due to the greater chemical stability of silver that can be assessed by the standard reduction potential values (Shriver et al. 2006). The standard reduction potential of silver ($Ag^+ \rightarrow Ag^0$ $E^0 = +0.80$ V) is greater than that of copper ($Cu^+ \rightarrow Cu^0$ $E^0 = +0.52$ V and $Cu^{2+} \rightarrow Cu^0$ $E^0 = +0.34$ V) (Shriver et al. 2006). After each bath, the copper content removed is relatively lower, indicating that the surface becomes richer in silver. This enrichment caused by the action of cleaning methods such as mechanical and silver dip (acid thiourea) methods have already been reported in the literature (Beck et al. 2008; Borges et al. 2017). The enrichment of silver is due to the removal of superficial layers of corrosion products richer in copper. Layers above the surface are richer in silver.

Following the immersion baths, it was observed that the added content of leached metal after 10 baths of 1 h each did not exceed 0.007% of the mass of the coins. In Palomar et al. (2016b), losses were measured in prototypes cleaned using mechanical (calcium carbonate; PRE-LIM surface cleaner; rotatory tool with rubber point) and chemical methods (DTPA pentasodium salt 10% w/w + Triton™ X-100 1.5% v/v; thiourea 8% w/w; EDTA 10% w/w; HCOOH 10% v/v; thiourea 8% w/w + phosphoric acid 5% v/v + Triton™ X-100 0.5% v/v; thiourea 8% w/w + formic acid 5% v/v + Triton™ X-100 0.5% v/v). These losses were measured after six cleaning cycles of 0.3%–1.5%.

Table 1. Average percentages of lixiviated copper and silver in solution based on the total mass of copper or silver in 90 minted alloy coin after a series of consecutive immersions in a 0.1 mol. L^{-1} sodium glycinate solution for 1 h, determined by atomic absorption spectroscopy (AAS).

Immersion number	Lixiviated mass of copper (μg)	Percentage of lixiviated copper in solution by total mass of copper in coin (%)	Lixiviated mass of silver (μg)[a]	Percentage of lixiviated silver in solution by total mass of silver in coin (%)
1	96.650	0.001933	<2.00	≅0.000025
2	52.480	0.001050	<2.00	≅0.000025
3	27.555	0.000551	<2.00	≅0.000025
4	27.735	0.000555	<2.00	≅0.000025
5	20.590	0.000412	<2.00	≅0.000025
6	18.695	0.000374	<2.00	≅0.000025
7	25.720	0.000514	<2.00	≅0.000025
8	22.850	0.000457	<2.00	≅0.000025
9	7.3950	0.000148	<2.00	≅0.000025
10	14.970	0.000299	<2.00	≅0.000025

[a]Values of lixiviated mass of silver were lower than the detection limit of equipment (2 μg). Values expressed in the table shows an estimate of maximum values observed in experiments.

Upon comparison of both results, the proposed method showed less aggressiveness toward the metallic surface.

Cleaning of artificially corroded coins

Images of one of the coins studied before artificial aging, after aging with brown tarnish, and after cleaning with 0.1-mol L^{-1} sodium glycinate solution are shown in Figure 2. After cleaning, it could be observed with the naked eye that details of the figure, as well as the text and numbers, were preserved. While there was no total removal and residues could be observed with the naked eye, the performed cleaning process effectively removed a large part of the brown tarnish. The areas where the tarnish showed darker colors, as for example, observed in the figure's neck, were the most resistant to tarnish removal and the lightest areas were easier to remove. The color of the tarnish depends on its thickness, with tarnishes less than 100-nm thick being brown and those with thicknesses exceeding 100 nm being dark in color (Homem 2013). This result suggests that the glycinate solution acts by gradually dissolving the tarnish layer, thus being more efficient with thinner layers. However, as described later, cleaning of naturally aged objects gave better results; this indicates that artificial aging produced a tarnish layer different from the natural tarnish layer, and this artificial layer was more difficult to remove. The thicker artificial tarnish layer around structural features of the image was a result of the greater stress in these areas associated with edges in the die used in the manufacturing processes and were thus more prone to corrode.

SEM-EDX analyses were performed on clean coins, after aging and after cleaning with glycinate. Table 2 lists the corresponding metal contents. In clean coins, the relative enrichment of silver is observed because the metal content, in its fineness, is 90% Ag and 10% Cu. The enrichment was accentuated by the decrease in the copper content (below 10%), which can be attributed to several causes such as the production process, corrosion, and cleaning procedures (Beck et al. 2008, 2004; Mass and Matsen 2012a; Borges et al. 2017). The initial polishing of coins for the studies performed also contributed to the enrichment of silver (Borges et al. 2017) as the superficial layers are richer in copper due to the lower stability of this metal. The elements C, Si, Mg, and Al present in these coins were attributed as impurities generated by the polishing process itself.

Coins with brown tarnish did not have elements deemed polishing residue; these were probably removed during the artificial corrosion procedure. Sulfur, not present in the clean coin, now appears, indicating the formation of sulfides on the surface. The silver content reduces owing to the increase in the Cu and O content and the introduction of S. The

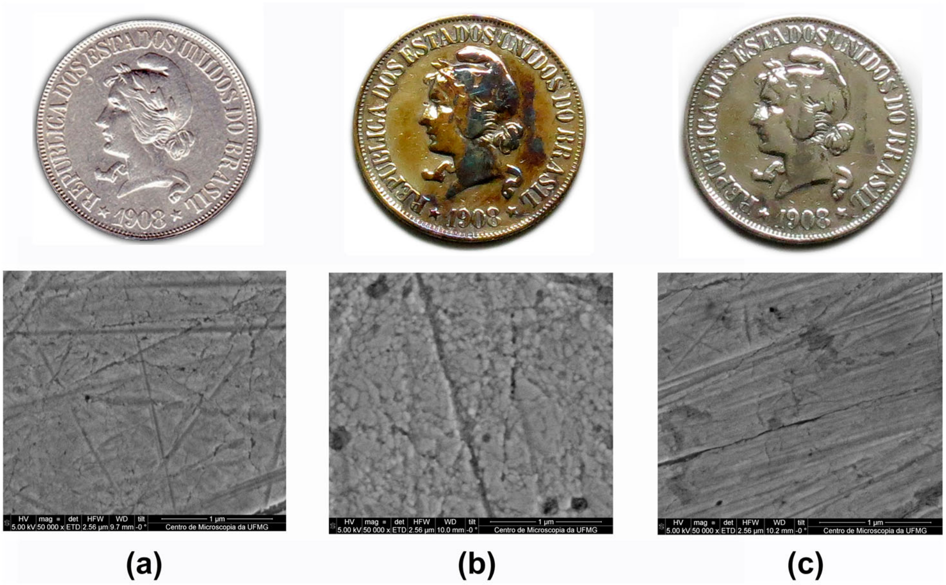


Figure 2. Coins at different stages of the corrosion and cleaning process with their respective scanning electron microscopy images (50,000× magnification). Clean coin (a), coin with brown tarnish (b), and coin after cleaning with glycinate solution (c).

increase in the copper content is due to its lower stability than silver, which favors its reaction to form corrosion products (Ortíz-Corona and Rodríguez-Gómez 2019). The increase in oxygen content indicates the formation of metal oxides.

After cleaning, the Cu, O, and S content decreased because of the removal of the corrosion products in which these compounds are combined, and by the removal of non-corroded metals. Sulfur was not completely removed, similar to other cleaning methods such as mechanical, chemical, and electrochemical methods (Palomar et al. 2016b). Another important aspect of the decrease in the Cu, O, and S content is the relative enrichment of the silver content. Both corroded and metallic silver are leached during the cleaning process; however, because of their high chemical stability, their removal is less compared to that of other elements, such as copper and lead, yielding low amounts of corroded and metallic silver after cleaning (Beck et al. 2008). Owing to the lack of detection of elements such as C and N, no evidence of significant glycinate residues was detected on the surface of the clean coin. The high solubility of glycinate complexes in water facilitates their removal.

Table 2. Average elemental compositions determined by energy dispersive spectroscopy (EDX) of coins that were clean, tarnished, and after cleaning with 0.1-mol.L^{-1} sodium glycinate solution.

Element	Clean coin (control)	Coin with brown tarnish	Coin after cleaning
Ag	90.23	72.15	89.05
Cu	4.82	12.53	5.38
O	2.65	10.05	4.13
S	–	5.27	1.44
C	1.22	–	–
Al	0.57	–	–
Mg	0.33	–	–
Si	0.18	–	–

The SEM image of the clean coin shows a pattern of scratches due to polishing. The image of the coin with the brown tarnish shows a grainy film of the corrosion products covering the scratches. In the image of the coin after cleaning, the scratch pattern can be observed again together with spots of residue from the unremoved tarnish. Corresponding to what had already been observed in the macroscopic image wherein no loss of surface details was observed, there are no characteristics of aggressiveness of the cleaning method such as cracks and localized corrosion. After the cleaning process, the coins were stored in polyethylene boxes and did not show new tarnish formation during an observation period of one year.

Cleaning naturally tarnished objects

Table 3 lists the results of the average content of the elements of the halo and crown. The values presented are average because of the variation of the content in the tarnish and that in the surface below the tarnish layer. A variation of about 0.3% silver and 0.53% copper was observed in the performed measurements.

As discussed in Mass and Matsen (2012b; Ortíz-Corona and Rodríguez-Gómez 2019), the values of surface non-destructive analyses are difficult to measure and do not correspond directly to the actual content of the objects owing to the abovementioned superficial enrichment of silver. Variables in the production of the object and in early conservation procedures, and variables considered when measuring the geometry generate difficulties in collecting accurate data. Thus, the values presented are semi-

Table 3. Average elemental compositions of naturally tarnished objects determined by X-ray fluorescence (XRF).

	Elements											
	Before cleaning						After cleaning					
Objects	Ag	Cu	Pb	Sb	Fe	Zn	Ag	Cu	Pb	Sb	Fe	Zn
Silver Halo	92.98	6.00	0.11	0.69	–	0.19	92.87	6.02	0.11	0.69	–	0.18
Silver Crown	96.17	3.57	0.09	–	0.02	0.14	96.26	3.68	0.10	–	0.02	0.14

Figure 3. Arc of the halo partially cleaned with glycinate.

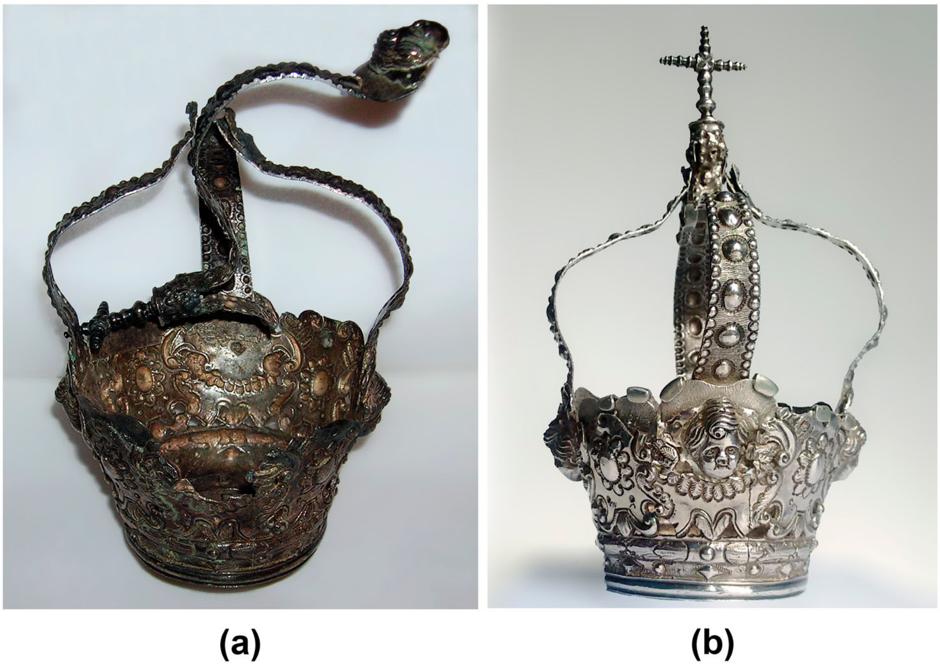


Figure 4. Cleaning of the crown. (a) The crown before cleaning with polish residue and brown tarnish. (b) The crown after removing the polishing residues with sodium citrate and the brown tarnish with sodium glycinate.

quantitative. The goal was to study the behavior of naturally aged alloys with an Ag content above 90% treated with sodium glycinate. The studied objects met the proposed objective.

The presence of elements such as Pb, Sb, Fe, and Zn were seen as impurities present in the ores from which the silver was extracted (Borges et al. 2017). Elements such as S and O, present in corrosion products were not identified owing to the technical limitations of the portable equipment.

Measurements of the elemental content after cleaning are shown in Table 3. No significant alterations in content were observed. However, these results can be attributed to the low content of the non-corroded leached metal, as presented in Table 1, as such low levels are below the detection limits of the device.

The silver halo is formed by an arch decorated with stars and had a slightly brown tarnish. The removal was adequate, exposing the silver surface of the metal. In Figure 3, the back of a section of the partially cleaned halo is shown.

The crown showed a brown tarnish darker than that observed on the silver halo. This tarnish was more difficult to remove, thereby requiring immersion in the cleaning solution. The final cleaning result of the crown is shown in Figure 4. Some small areas with black tarnish were not removed, which, at the conservator's discretion, was considered to be an adequate level of cleanliness for the exhibition of the piece.

An important result of cleaning with glycinate is that the tarnish was removed very easily, requiring little mechanical work that could have caused mechanical deformations and defects in the crystalline structure in fragile and thin parts, e.g. easily deformable crown handles.

Casa do Restaurador microcrystalline wax was used to protect the objects after all treatments. One year after cleaning, the exposed objects in the churches where they belong did not show any residual effects or change in surface. The efficacy of the microcrystalline wax is due to protection of the surface from moisture as the H_2S readily penetrates microcrystalline wax pores and defects.

Conclusions

In this study, we observed that corrosion products can be removed using 0.1-mol L^{-1} sodium glycinate solution (pH 10) from both artificially tarnished silver coins and naturally tarnished silver objects with a high silver content (90% or above). The cleaning of the artificially tarnished objects provided guidelines for the procedures applied to naturally tarnished objects. Sodium glycinate is a substance of low toxicity, cost, and aggressiveness and is an effective cleaning option.

Cleaning procedures on naturally tarnished objects started with diluted aqueous detergent solution, followed by rubbing with a cotton swab soaked in a basic glycinate solution. Tarnish could be removed from several artistic pieces in this manner. In case of inadequate cleaning, immersion baths or poultices can be used, starting with a time of 1 min, which can be adjusted as required.

Black tarnish is more resistant to glycinate. In naturally aged works a few regions were found in which this tarnish existed and, even so, after an assessment by the conservators, their total removal was deemed unnecessary. However, if necessary, this tarnish can be partially removed using other cleaning methods until the thickness allows removal by glycinate.

For future research, the potential existence of glycinate residues on the surface after cleaning must be methodologically monitored. Furthermore, the existence of residues and the performance of the proposed cleaning method against re-tarnishing must be studied. Characteristics of the new tarnish, presenting an even or blotchy appearance, must be analyzed. Analytical methods such as X-ray photoelectron spectroscopy (Palomar et al. 2016b) and electrochemical methods (Selwyn and McKinnon 2020) can provide adequate information on the same.

Finally, it is up to the conservator to assess the condition of the object and define the appropriate degree of cleaning, which will allow him or her to plan and carry out a safe treatment.

Acknowledgements

The authors would like to acknowledge the financial support from the Brazilian National Council for Scientific and Technological Development (CNPq), Pró-Reitoria de Pesquisa at Universidade Federal de Minas Gerais and the Center of Microscopy at the Universidade Federal de Minas Gerais (http://www.microscopia.ufmg.br) for providing the equipment and technical support for experiments involving electron microscopy. Furthermore, the authors would like to thank Enago (www.enago.com) for the English language review.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Brazilian National Council for Scientific and Technological Development (CNPq), Pró-Reitoria de Pesquisa at Universidade Federal de Minas Gerais and the Center of Microscopy at the Universidade Federal de Minas Gerais.

ORCID

João Cura D'Ars de Figueiredo Junior http://orcid.org/0000-0002-4901-1005
Maria Luiza Seixas de Souza e Silva http://orcid.org/0000-0003-3765-8044

References

Beck, L., E. Alloin, C. Berthier, S. Réveillon, and V. Costa. 2008. "Silver Surface Enrichment Controlled by Simultaneous RBS for Reliable PIXE Analysis of Ancient Coins." *Nuclear Instruments and Methods in Physics Research Section B* 266 (10): 2320–2324. doi:10.1016/j.nimb.2008.03.084.

Beck, L., S. Bosonnet, S. Réveillon, D. Eliot, and F. Pilon. 2004. "Silver Surface Enrichment of Silver–Copper Alloys: A Limitation for the Analysis of Ancient Silver Coins by Surface Techniques." *Nuclear Instruments and Methods in Physics Research Section B* 226 (1–2): 153–162. doi:10.1016/S0168-583X(04)00831-6.

Borges, R., L. Alves, R. J. C. Silva, M. F. Araújo, A. Candeias, V. Corregidor, P. Valério, and P. Barrulas. 2017. "Investigation of Surface Silver Enrichment in Ancient High Silver Alloys by PIXE, EDXRF, LA-ICP-MS and SEM-EDS." *Microchemical Journal* 131: 103–111. doi:10.1016/j.microc.2016.12.002.

Contreras-Vargas, J., J. L. Ruvalcaba-Sil, and F. J. Rodríguez-Gómez. 2013. "Effects of the Cleaning of Silver with Acidified Thiourea Solutions." *Conference Proceedings of Metal* 2013, September 16–20, Edinburgh, Scotland, 223–228.

Costa, V. 2001. "The Deterioration of Silver Alloys and Some Aspects of Their Conservation." *Reviews in Conservation* 2: 19–35. doi:10.1179/sic.2001.46.Supplement-1.18.

de Figueiredo, J. C. D., S. S. Asevedo, and J. H. R. Barbosa. 2014. "Removal of Brownish-Black Tarnish on Silver–Copper Alloy Objects with Sodium Glycinate." *Applied Surface Science* 317: 67–72. doi:10.1016/j.apsusc.2014.08.096.

Degrigny, C., E. Tanguy, R. Le Gall, V. Zafiropulos, and G. Marakis. 2003. "Laser Cleaning of Tarnished Silver and Copper Threads in Museum Textiles." *Journal of Cultural Heritage* 4 (1): 152–156. doi:10.1016/S1296-2074(02)01191-3.

Golovlev, V., M. Gresalfi, J. Miller, D. Anglos, K. Melesanaki, V. Zafiropulos, G. Romer, and P. Messier. 2003. "Laser Characterization and Cleaning of 19th Century Daguerreotypes II." *Journal of Cultural Heritage* 4 (1): 134–139. doi:10.1016/S1296-2074(02)01189-5.

Homem, P. C. M. D. 2013. "Corrosão Atmosférica da Prata: Monitorização e Perspectivas de Conservação Preventiva." Tese de Doutorado – Faculdade de Letras – Universidade do Porto em Museologia, Porto. https://hdl.handle.net/10216/72784.

Ioanid, E. G., A. Ioanid, B. T. Goraş, and L. Goraş. 2013. "Assessment of the Cleaning Effect of HF Cold Plasma by Statistical Processing of Photographic Image." *Measurement* 46 (8): 2569–2576. doi:10.1016/j.measurement.2013.03.020.

Ioanid, E. G., A. Ioanid, D. E. Rusu, and F. Doroftei. 2011. "Surface Investigation of Some Medieval Silver Coins Cleaned in High-Frequency Cold Plasma." *Journal of Cultural Heritage* 12 (2): 220–226. doi:10.1016/j.culher.2010.09.004.

Leygraf, C., I. O. Wallinder, J. Tidblad, and T. Graedel. 2016. "The Atmospheric Corrosion Chemistry of Silver." In *Atmospheric Corrosion*, edited by C. Leygraf, I. O. Wallinder, J. Tidblad, and T. Graedel, 337–347. John Wiley & Sons. doi:10.1002/9781118762134

Mass, J., and C. Matsen. 2012a. "Quantitative Non-Destructive Analysis of Historic Silver Alloys: X-ray Fluorescence Approaches and Challenges." In *Handheld XRF for Art and Archaeology*, edited by A. N. Shugar, and J. L. Mass, 215–248. Leuven: Leuven University Press.

Mass, J. L., and C. R. Matsen. 2012b. "Understanding Silver Hollow Wares of the Eighteenth and Nineteenth Centuries: Is There a Role for X-ray Fluorescence?" *Studies in Conservation* 57 (S1): 61–72. doi:10.1179/2047058412Y.0000000023.

Miessler, G. L., and D. A. Tarr. 2003. *Inorganic Chemistry*. Upper Saddle River: Prentice Hall.

National Library of Medicine. *Pubchem Thiourea Compound*. https://pubchem.ncbi.nlm.nih.gov/compound/thiourea#section=GHS-Classification.

Nomiya, K., and H. Yokoyama. 2002. "Syntheses, Crystal Structures and Antimicrobial Activities of Polymeric Silver(*I*) Complexes with Three Amino-Acids [Aspartic Acid(H_2asp), Glycine (Hgly) and Asparagine (Hasn)]." *Journal of the Chemical Society, Dalton Transactions* 12: 2483–2490. doi:10.1039/B200684G.

Oraby, E. A., J. J. Eksteen, and B. C. Tanda. 2017. "Gold and Copper Leaching from Gold-Copper Ores and Concentrates Using a Synergistic Lixiviant Mixture of Glycine and Cyanide." *Hydrometallurgy* 169: 339–345. doi:10.1016/j.hydromet.2017.02.019.

Ortíz-Corona, J., and F. J. Rodríguez-Gómez. 2019. "Role of Copper in Tarnishing Process of Silver Alloys in Sulfide Media." *Transactions of Nonferrous Metals Society of China* 29 (12): 2646–2657. doi:10.1016/S1003-6326(19)65171-X.

Palomar, T., M. Oujja, I. Llorente, B. Ramírez Barat, M. V. Cañamares, E. Cano, and M. Castillejo. 2016a. "Evaluation of Laser Cleaning for the Restoration of Tarnished Silver Artifacts." *Applied Surface Science* 387: 118–127. doi:10.1016/j.apsusc.2016.06.017.

Palomar, T., B. R. Ramírez Barat, E. García, and E. Cano. 2016b. "A Comparative Study of Cleaning Methods for Tarnished Silver." *Journal of Cultural Heritage* 17: 20–26. doi:10.1016/j.culher.2015.07.012.

Selwyn, L., and W. R. McKinnon. 2020. "Silver and Acid-Thiourea Silver Dips: Rinsing and Aging Monitored by Electrochemistry." *Studies in Conservation*, doi:10.1080/00393630.2020.1773056.

Shriver, D. F., P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong. 2006. *Inorganic Chemistry*. New York: W. H. Freeman and Company.

Stuart, B. H. 2007. *Analytical Techniques in Materials Conservation*. Chichester: John Wiley & Sons.

Tanda, B. C., J. J. Eksteen, and E. A. Oraby. 2017. "An Investigation into the Leaching Behavior of Copper–Oxide Minerals in Aqueous Alkaline Glycine Solutions." *Hydrometallurgy* 167: 153–162. doi:10.1016/j.hydromet.2016.11.011.

Thermo Fisher Scientific, Safety Data Sheet. *Glycine, Sodium Salt*. https://www.fishersci.ca/shop/msdsproxy?productName=AC204595000&productDescription=glycine-sodium-salt-hydrate-99-acros-organics-2.

Vassiliou, P., and V. Gouda. 2013. "Ancient Silver Artefacts: Corrosion Processes and Preservation Strategies." In *Corrosion and Conservation of Cultural Heritage Metallic Artefacts*, edited by P. Dillmann, D. Watkinson, E. Angelini, and A. Adriaens, 213–235. Cambridge: Woodhead Publishing Limited.

Viljus, A., and M. Viljus. 2013. "The Conservation of Early Post-Medieval Period Coins Found in Estonia." *Journal of Conservation and Museum Studies* 10 (2): 30–44. doi:10.5334/jcms.1021204.

Wharton, G. 1989. "The Cleaning and Lacquering of Museum Silver." *WAAC Newsletter* 11 (1): 4–5. https://cool.culturalheritage.org/waac/wn/wn11/wn11-1/wn11-103.html.