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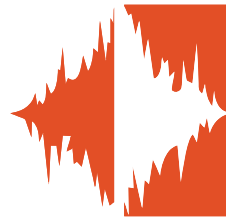
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# ATMOSPHERIC CORROSION OF PATINATED SILVERWORK: A CONSERVATION CHALLENGE

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## ABSTRACT

Patination has been frequently used by jewellers to modify the colour of silver alloys. By application of a solution of sulphur compounds, blackish or bluish surfaces can be obtained, but the intentionally produced silver-sulphur compounds are chemically similar to the atmospheric corrosion products that develop on silver alloys. The conservation of patinated silver objects, such as *Art Nouveau* jewellery, raises thus analytical challenges.

In order to define accurate conservation treatments, the patina and corroded surfaces characterisation is mandatory. In this study, sterling silver samples were patinated and subjected to corrosion by immersion in a sulphide containing solution. The identification of the chemical compounds present on the patinated sterling silver before and after corrosion was carried out by UV-visible spectrophotometry, X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectrometry. Data obtained suggest a two-stage corrosion process: a decrease of the silver compounds patina thickness caused by its dissolution, followed by the formation of corrosion products with different compositions and morphologies containing silver and copper sulphur compounds.

**Keywords:** Patination, Silverwork, Sterling Silver, Atmospheric Corrosion, Conservation

## A CORROSÃO ATMOSFÉRICA DE OBJECTOS EM PRATA COM PÁTINA: UM DESAFIO PARA A CONSERVAÇÃO E RESTAURO

## RESUMO

A aplicação de pátinas em objetos de prata, para produzir uma superfície de cor acinzentada a preta, é uma técnica de decoração frequentemente utilizada por ourives. A pátina é obtida por aplicação de uma solução, normalmente à base de compostos de enxofre, formando um revestimento constituído por compostos de prata e enxofre. Sendo estes compostos semelhantes aos produtos de corrosão atmosférica da prata, a conservação de objetos corroídos em prata com pátina levanta questões relacionadas com a incompatibilidade de tratamentos, resultantes da semelhança entre os compostos formados intencionalmente e os da corrosão atmosférica.

Para definir tratamentos de conservação específicos, é fundamental caracterizar as superfícies com pátina e com pátina corroída. Neste estudo, amostras de prata *sterling* com pátina foram corroídas por imersão numa solução contendo sulfuretos. A caracterização das superfícies com pátina antes e após corrosão foi realizada por espectrofotometria de UV-Vis, difração de raios-X e por microscopia eletrónica de varrimento com espectrometria de raios-X dispersiva em energia. Os resultados revelaram que a corrosão das amostras de prata *sterling* com pátina compreende a dissolução da pátina seguida da formação de produtos de corrosão com composições e morfologias distintas contendo sulfuretos de prata e sulfuretos de cobre.

**Palavras-Chave:** Liga de Prata, Pátina, Corrosão Atmosférica, Conservação

## 1. INTRODUCTION

Patinated silver is characterised by a blackish or bluish surface intentionally produced by an oxidiser, usually a sulphur compound [1]. This decoration technique, frequently applied on silver jewellery and ware, had a large diffusion in France in the early 20<sup>th</sup> century [2]. Inspired by the neo-gothic and neo-renaissance styles, jewellers and silversmiths applied patinas in selected areas of silver objects. Their aim was to obtain surfaces that looked like the tarnished surfaces of ancient objects. In the mid-19<sup>th</sup> century, the spread of Japonism in Europe brings to jewellery the application of patinas inspired by the Japanese *Shakudo*<sup>1</sup> and *Shibuichi*<sup>2</sup> [2]. René Lalique, one of the most representative artists of the *Art Nouveau* movement, has extensively used patinas to create colour contrasts enhancing the three-dimensional perception of his jewellery masterpieces [5].

Silver patina recipes used liver of sulphur (a potassium sulphide solution [2]) and other sulphides and polysulphides solutions [6]. Later, selenides frequently applied to blacken copper-based alloys [7], were also used in silver patination. Over time, corrosion develop on patined objects. The optical properties of their surface are modified by the formation of corrosion products with various nuances of grey, like the original patina hue. Since the atmospheric corrosion of patinated silver surfaces has a direct influence on their perception [8], because colour has a role in the material identification, the objects require an accurate conservation treatment.

The conservation of the surface effects created by the patinas is a complex task. Although the patina recipes are known, the detailed identification of the compounds formed at the objects surface is still missing. In addition, the atmospheric corrosion products (including  $\text{Ag}_2\text{S}$  and  $\text{AgCuS}$  complexes) [9] and the compounds produced by the patination processes using sulphide solutions should be similar. The missing information on the nature of the corrosion products formed, prevents the application of standard conservation treatments that could remove the patina. Due to an incorrect distinction between intentional patination and corrosion, several silver objects have in fact already lost their original decoration [2].

The present work attempts to be a first approach to the study of the atmospheric corrosion of patinated silver. Samples of sterling silver (92.5 wt% Ag; 7.5 wt% Cu) were patinated with selenide compounds and corroded by immersion in a sulphide containing solution. Data obtained by different analytical techniques for the samples before and after corrosion were compared and discussed.

## 2. METHODOLOGIES AND INSTRUMENTATION

Samples of sterling silver, the main alloy used to fabricate silver jewellery and ware, were patinated and then corroded. The samples were roughly abraded before patination [9]. The patinated samples were then corroded by immersion in a sulphide containing solution. To simplify the surface characterisation procedure, the samples were patinated with a selenide solution. Contrary to the compounds formed when using liver of sulphur, the silver-selenium compounds resulting from the use of selenide based compounds are not related to naturally occurring corrosion products [7]. Since  $\text{Ag}_2\text{Se}$  belongs to the family of silver chalcogenides  $\text{Ag}_2\text{E}$  (E = S, Se, and Te), the

compounds formed are chemically similar to sulphide compounds.

The colour, the morphology and the composition of the surfaces before and after corrosion were characterised using UV-Vis spectrophotometry (UV-Vis), scanning electron microscopy (field emission gun) with energy dispersive X-ray spectrometry (SEM-FEG-EDS) and X-ray diffraction (XRD).

### 2.1 Samples preparation

Black patina was applied on sterling silver (Ag925) samples of 1.5 cm<sup>2</sup> area and 1 mm thickness, acquired from a local jeweller supplier. The patination process was carried out by a jeweller using a commercial solution containing sodium selenite ( $\text{Na}_2\text{SeO}_3$ ). The samples were immersed in the solution during 1 minute, at room temperature, and then rinsed with water and dried. This process was repeated 6 times until a homogeneous grey-black colour surface was obtained.

The patinated samples were submitted to accelerated corrosion by immersion in a 0.1 M  $\text{Na}_2\text{S}$  aqueous solution during 120, 240 and 360 minutes.

### 2.2 Surface characterisation

The surface of the sterling silver samples was characterised before and after patination and after corrosion. Elemental analyses were carried out by XRF to verify the alloy composition and homogeneity. Data obtained showed an homogeneous silver alloy containing  $93.1 \pm 0.1$  wt% Ag and  $6.9 \pm 0.1$  wt% Cu. The optical characterisation of the patinated samples before and after corrosion was carried out by UV-Vis and the surface morphology characterised by SEM-FEG-EDS. The crystalline compounds of the patina and the corrosion products were identified by XRD.

**XRF:** The XRF was carried out with a Tornado M4 from Bruker comprising an anode of Rh with a poly-capillary lens, offering a spot size down to a 25  $\mu\text{m}$  at a working distance of 10 mm, coupled to a XFlash® silicon drift detector (SDD) technology, with a 30 mm<sup>2</sup> sensitive area and an energy resolution < 145 eV. Spectra were collected for 300 s with the X-ray tube operating at 50 kV and 300  $\mu\text{A}$ . The elemental quantification was performed using ESPRIT software.

**UV-Vis:** The UV-Vis spectrophotometry data was obtained by using a Shimadzu UV-2450PC spectrometer. The diffuse reflectance spectra were recorded with a detecting wavelength ranging from 220 to 1400 nm. Absorption data were calculated from reflectance data using Kubelka-Munk equation.

**SEM-FEG-EDS:** The surface morphology was observed with a SEM-EDS Philips XL 30 FEG equipment operated with acceleration voltage from 10 to 15 kV. Semi-quantitative elemental composition was obtained with an EDS (EDAX) system equipped with a Si(Li) detector and a 3  $\mu\text{m}$  super ultra-thin window (SUTW), allowing detection of light elements. Spectra were collected in spot mode analysis for 300 s acquisition time.

**XRD:** The analysis by XRD were obtain using a Philips Analytical X-ray diffractometer (PW 3050/60) with automatic data acquisition (X'Pert Data Collector (v2.0b) software) with a Cu  $K\alpha$  radiation ( $\lambda = 0.15406$  nm) operated at 40 kV, 30 mA. The data were collected with a step size of 0.01° and an acquisition time of 200 s deg<sup>-1</sup>. Powder diffraction files were obtained from the Pearson's Crystal Database.

<sup>1</sup>*Shakudo* is a black patinated copper-gold alloy with a percentage of gold that varies between 4 and 7% [3]. The patina is obtained by the application of *nikomi-chakushoku*, a traditional colouring treatment used in Japan in which the metal is polished to a mirror finish and then boiled in an aqueous solution containing copper carbonate, copper sulphate and potassium aluminium sulphate [4].

<sup>2</sup>*Shibuichi* is a grey patinated copper-silver alloy [3]. The grey patina is obtained by using *nikomi-chakushoku* [4].

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterisation of the patina

The patination process grey-blackened the sterling silver surfaces, keeping the metallic lustre that is characteristic of the polished metal surfaces, as shown in Fig. 1.

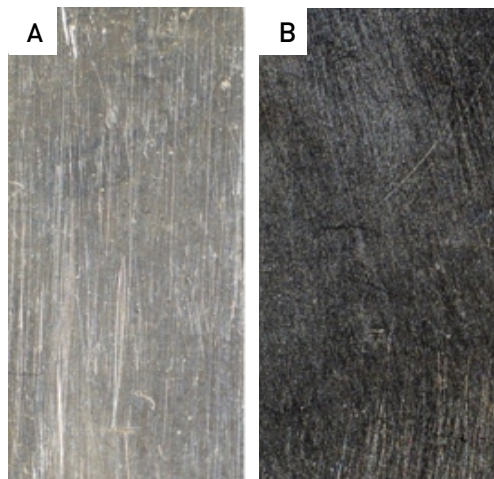


Fig. 1 - Bare (A) and patinated (B) sterling silver samples.

The UV-Vis data obtained for the bare and patinated sterling silver samples (Fig. 2) show for the latter the presence of a well-defined band at 309 nm and a broaden band between 320 and 390 nm. These bands can be attributed to the presence of  $\text{Ag}_2\text{Se}$  [10]. The presence of these bands and the shift towards lower wavelengths can be ascribed to particles with distinct shapes or sizes [11, 12].

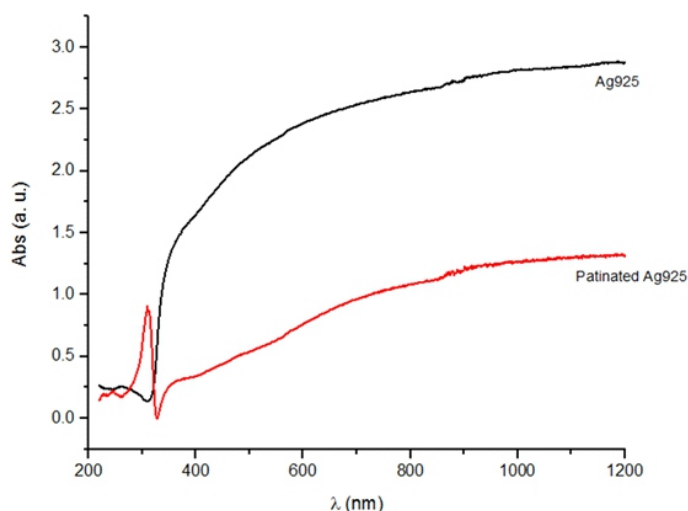


Fig. 2 - UV-Vis absorption spectra for the bare (-) and patinated (-) sterling silver samples.

The SEM secondary electron (SE) images of Fig. 3A show the bare sterling silver surface where it is possible to distinguish the grain boundaries characteristic of the metal solidification process [13]. Evenly distributed pores due to gas porosity, a casting process defect, can also be seen [14]. The surface of the patinated sterling silver is characterised by a homogeneous film composed of spherical and tubular particles present in recessed areas (Figs. 3B and 3C). The different particle shapes can be ascribed to distinct crystalline structures of  $\text{Ag}_2\text{Se}$  [12]. Data also suggest that the film is composed by overlapping layers, as shown in Fig. 3C.

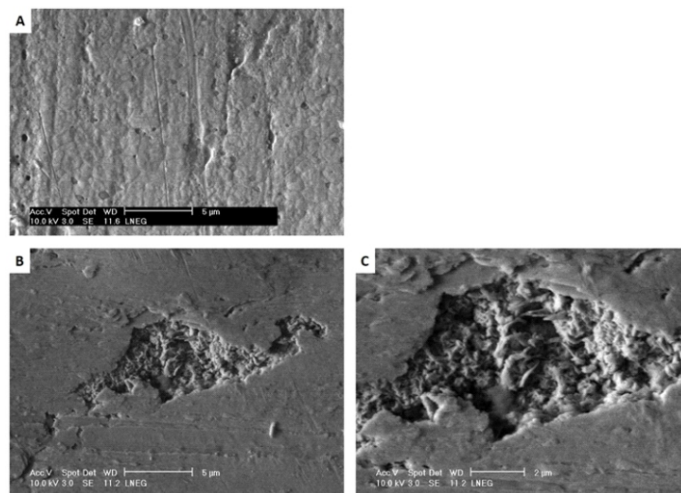


Fig. 3 - SEM-SE images of bare (A) and patinated (B and C) sterling silver surfaces. Scale bar of A and B is 5  $\mu\text{m}$  and of C is 2  $\mu\text{m}$ .

Table 1 summarises the elemental composition of the patina obtained by EDS. In this table, the Se, S, Ag and Cu contents correspond to average values of multiple measurements. The unexpected occurrence of S in the patina can be justified by its presence in the solution used for the patination process. The results obtained also suggest that tubular formations have higher Se and lower Cu contents, when compared to the spherical particles and the plane film areas.

Table 1 - Elemental composition obtained by EDS (wt%), normalised to 100%, for the bare and patinated sterling silver samples.

	Ag L-lines	Cu k-lines	Se K-lines	S L-lines
Ag925	92.7	7.3	0	0
<i>Patinated Ag925</i>				
Plane area	80.6	6.4	10.1	2.8
Spherical particles	77.7	7.2	11.8	3.3
Spherical particles (smaller size)	75.6	7.0	13.9	3.4
Tubular particles	75.7	5.2	15.6	3.5

Fig. 4 illustrates the diffractograms obtained by XRD for the bare and patinated sterling silver.  $\text{Ag}_2\text{Se}$  was identified as the main crystalline compound of the patina, confirming the UV-Vis and the SEM-EDS results. Although the presence of sulphur was identified by EDS, no S containing compound was detected by XRD. This can be justified either by the presence of small amounts of S containing compounds, agreeing with the EDS results, or by their non-crystalline structure.

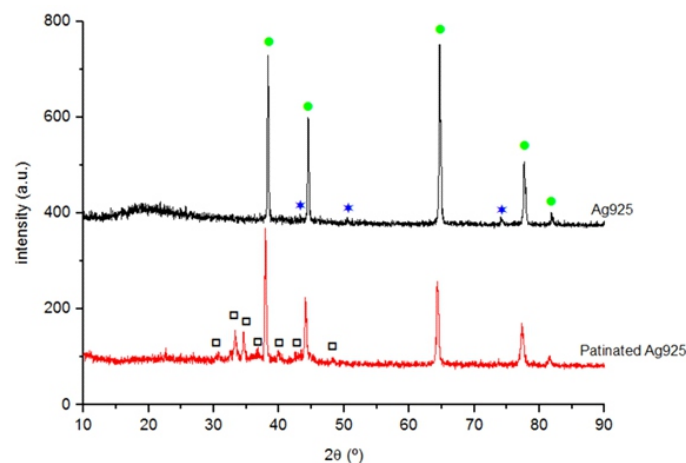
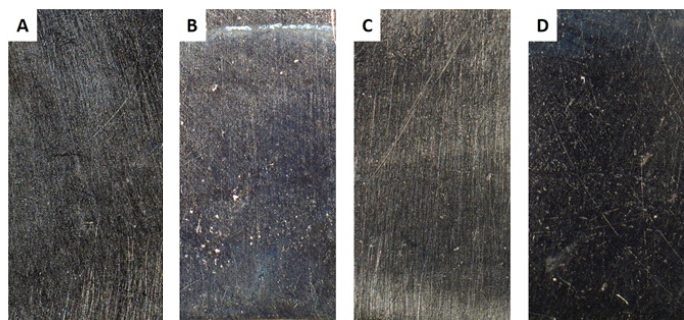


Fig. 4 - X-ray diffractograms obtained for the bare and patinated sterling silver with the identification of the Ag, Cu and  $\text{Ag}_2\text{Se}$  main diffraction peaks. ● Ag (PCD file n° 1404420); ★ Cu (PCD file n° 1412130) and □  $\text{Ag}_2\text{Se}$  (PCD file n° 310732).

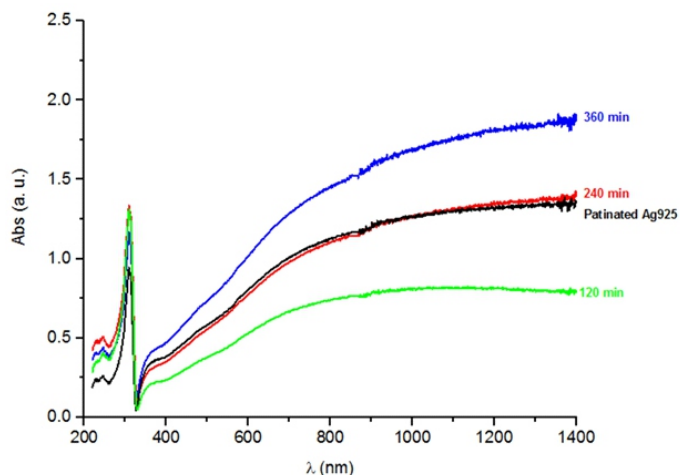
### 3.2 Characterisation of the corroded patina

Fig. 5 shows the patinated samples of sterling silver before and after corrosion. All the corroded samples have a grey-blackish colour with a dull aspect, but nuances can be perceived. The surface of the sample immersed during 360 minutes (Fig. 5D) is darker.



**Fig. 5** - Colour of the patinated sterling silver surfaces before (A) and after corrosion by immersion in a 0.1 M Na<sub>2</sub>S aqueous solution during 120 (B), 240 (C) and 360 minutes (D).

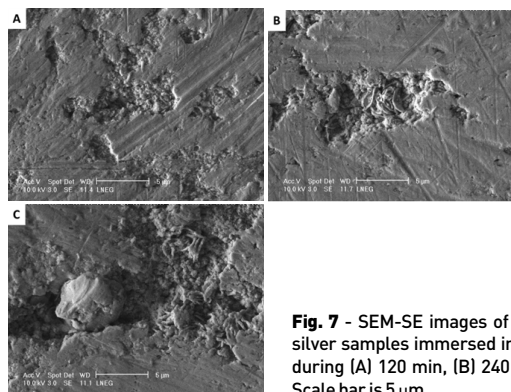
Fig. 6 compares the UV-Vis spectra of the patinated sterling silver samples before and after corrosion. The similarity of the spectra profiles does not allow to identify differences among the samples surfaces. In addition, the surface roughness can justify the differences observed for the absorption intensities.



**Fig. 6** - UV-Vis absorption spectra for the patinated sterling silver samples before and after corrosion by immersion in a 0.1 M Na<sub>2</sub>S aqueous solution during 120, 240 and 360 minutes.

The morphologies of the corroded and non-corroded surfaces observed by SEM are distinct. Fig. 7A shows a heterogeneous surface with gaps, indicating an alteration of the patina, for the sample corroded during 120 minutes. The abrasion marks become more visible for this sample. This fact suggests the patina dissolution, which induces a thickness decrease.

With the increasing of the immersion time, the samples surfaces become more homogeneous suggesting the formation of a corrosion film. On the roughest areas, nanosheets and microspheres that resemble copper sulphides morphologies can be observed (Fig. 7B and 7C) [15, 16].



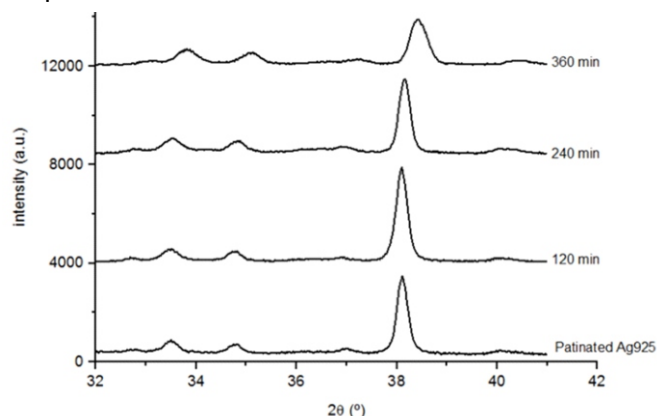
**Fig. 7** - SEM-SE images of the patinated sterling silver samples immersed in a 0.1 M Na<sub>2</sub>S solution during (A) 120 min, (B) 240 min, and (C) 360 min. Scale bar is 5 μm.

Table 2 summarises the elemental composition of the plane areas and the morphology of the particles observed on the corroded surfaces. The plane areas of both the corroded and non-corroded surfaces have similar Se and S contents, but the Cu content is lower for the corroded surfaces. The Se and S contents for the corroded samples are higher in the particles than in the plane areas.

**Table 2** - Elemental composition obtained by EDS (wt%), normalised to 100%, for the corroded patinated samples of sterling silver.

Samples		Ag L-lines	Cu k-lines	Se K-lines	S K-lines
120 min	Plane area	85.1	4.5	8.4	2.0
	Spherical particles	80.9	3.8	11.9	3.4
240 min	Plane area	86.2	2.3	9.1	2.4
	Microspheres particles	82.8	2.4	12.2	2.6
360 min	Nanosheet particles	79.4	3.7	12.9	4.0
	Plane area	82.9	3.3	10.8	3.1
360 min	Microspheres partiles	77.3	1.2	18.6	2.9
	Nanosheet particles	77.2	3.2	15.8	3.8

Fig. 8 shows the diffractograms obtained by XRD for the different corroded samples. The intensity of the Ag diffraction peak at 38.1° increases for the sample immersed 120 minutes, suggesting the patina dissolution. For higher immersion times this peak decreases, which can be related to the formation of corrosion products at the surface, increasing the corrosion film thickness. With the immersion time increase, a peak at 38.6°, which can be ascribed to the presence of Cu<sub>2</sub>S, overlaps with the Ag diffraction peak. However, the simultaneous identification of the different compounds is complex. The Ag<sub>2</sub>Se, Ag<sub>2</sub>S and Cu<sub>2</sub>S diffraction patterns are similar and the presence of broaden diffraction peaks suggests the existence of small size particles and non-crystalline compounds [17].



**Fig. 8** - X-ray diffractograms obtained for the patinated sterling silver samples corroded by immersion during 120, 240 and 360 minutes in a 0.1 M Na<sub>2</sub>S aqueous solution.

Table 3 lists the crystalline compounds identified so far, including  $\text{Ag}_2\text{S}$  and  $\text{Ag}_2\text{Se}$ . The presence of  $\text{Cu}_2\text{S}$  was identified in the samples immersed during 240 and 360 minutes. These results are in agreement with the morphologies identified by SEM. It can be suggested that the corrosion mechanism of the patinated silver comprises firstly a partial dissolution of the patina, followed by a nucleation of new compounds. In these compounds, that are distinct from those that characterise the original patina,  $\text{Cu}_2\text{S}$  is included.

**Table 3** - Elements and compounds identified by XRD on the surface of the corroded patinated samples of sterling silver.

Samples	Chemical compounds				
	Ag	Cu	$\text{Ag}_2\text{Se}$	$\text{Ag}_2\text{S}$ (?)	$\text{Cu}_2\text{S}$
<i>Patinated Ag925</i>					
<i>Corroded patinated Ag925</i>					
120 min	Ag	Cu	$\text{Ag}_2\text{Se}$	$\text{Ag}_2\text{S}$ (?)	
240 min	Ag	Cu	$\text{Ag}_2\text{Se}$	$\text{Ag}_2\text{S}$ (?)	$\text{Cu}_2\text{S}$
360 min	Ag	Cu	$\text{Ag}_2\text{Se}$	$\text{Ag}_2\text{S}$ (?)	$\text{Cu}_2\text{S}$

#### 4. CONCLUSIONS

The corrosion developed on the surface of patinated silver jewellery and ware changes the appearance of the original patina, because the corrosion products that are formed result in a layer that appears in various nuances of grey with a dull aspect. The effect created by the application of an artificial patina is then lost, altering the object appearance and, therefore, its perception. Hence, to define an accurate conservation treatment, it is necessary to fully characterize the original patina and the corroded surfaces.

Studies considering the characterisation of silver patinas and the atmospheric corrosion of patinated silverwork are scarce. In this work, sterling silver samples patinated using a selenium compound solution and then corroded by immersion in a  $\text{Na}_2\text{S}$  solution, creating a high sulphide environment, were studied.

The patina obtained has a lustred grey-blackish colour that is composed of overlapping layers of  $\text{Ag}_2\text{Se}$ , identified by SEM and XRD. The presence of  $\text{Ag}_2\text{Se}$  particles of different sizes and shapes could be characterized by UV-Vis.

After corrosion by immersion in a  $\text{Na}_2\text{S}$  solution, the corroded samples have the same colour as the non corroded ones, but the first became dull. SEM images of the surfaces show a decrease of the patina thickness caused by dissolution for the sample immersed during 120 minutes. XRD analysis confirmed the patina dissolution, because the intensity of the diffraction peak of silver at  $38.1^\circ$  decreased. For the sample with the highest immersion time (360 min), an increase of the corrosion film thickness with the formation of compounds of distinct morphologies, like nanosheets and microspheres, could be observed and ascribed to the presence of  $\text{Cu}_2\text{S}$  identified by XRD and SEM.

In conclusion, this first approach to the corrosion of patinated silver alloys suggests a corrosion process that can be divided into two stages: firstly there is a dissolution of the patina that is followed by the formation of corrosion products containing silver and copper sulphur compounds.

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