Atmospheric pressure non-thermal plasma cleaning of 19th century daguerreotypes

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1. Introduction

Daguerreotypes represent the first practical form of photographs, particularly in vogue between 1840 and 1860, before becoming outdated due to the development of alternative and faster techniques. In daguerreotypes, the image results from the distribution of silver/mercury amalgam microcrystals of varying size and density on a silver-coated copper sheet.

Through years, 19th century daguerreotypes have generally suffered several corrosion phenomena, which have greatly reduced their historic and artistic value. The daguerreotype surface is typically covered by an irregular layer of tarnish, whose composition varies from piece to piece depending on its preparation procedure, conservation history and possible previous cleaning attempts. The exposure to atmospheric moisture and sulphur caused the formation of a tarnish film layer, composed by silver compounds such as silver sulphide, silver oxide and silver chloride [1-3]. Moreover, a layer of silicate particles could be found as originating from covering glass deterioration [4].

Photo-conservation requires non-invasive cleaning methods, which allow controlled removal of non-coherent corrosion products without damaging the fragile image structure and appearance before conservation procedures. Several different approaches have been applied, starting from first cleaning and restorations attempts in the 1930s. Immersion in chemical solvents (cyanide and thiourea cleaners) caused fading of images and permanent spotting due to silver loss, so that this process was discontinued in the 1970s [1]. In the early 80’s, low-pressure non-thermal plasma cleaning was proven to be able to remove tarnish, causing a visible improvement in the appearance of cleaned daguerreotype surfaces [1, 5]. Although microstructural features were generally preserved, faint white areas were observed in areas that were highly corroded, caused by micro-etching of the plate surface. Electro-cleaning with immersion in alkaline solutions was then found to be effective in cleaning without causing any observable alteration or damage to the image structure. However, when the silver electrode accidentally touched the daguerreotype, the latter was irreversibly damaged. Moreover, the procedure was not applicable to coloured plates and ungilded plates [1]. None of the cleaning methods allowed selective treatments on specific areas until laser cleaning was introduced in late 90° [4, 6]. The laser cleaning process is based on thermal ablation, relying on the different material removal thresholds for corrosion layer and silver, allowing for removal of corrosion with “no apparent damage to the image itself” [6] or “minimal removal of vital information” [7].

In the present work, an atmospheric pressure non-thermal plasma treatment was applied to clean the surface of a corroded 19th century daguerreotype by using different argon-hydrogen gas mixtures. This cleaning method allowed removal of corrosion products, without using liquid solvents or chemicals. The effectiveness of the plasma treatment on the controlled removal of tarnish products and on image quality has been evaluated through optical and microstructural analyses.
2. Materials and methods

19th Century daguerreotypes

The daguerreotype used in this study is a 19th century portrait of an unknown seated woman. The plate is about 7 cm x 8 cm (with beveled corners). Prior to experimental work, the surface showed significant surface corrosion or tarnish, darkening the photographic image (Fig. 1a).

Atmospheric non-thermal plasma treatment

An high frequency (1.1 Mhz, 6 kVpp) commercial plasma jet source (kINPen, Neoplas Tools Gmbh) [8] has been used with an electrode head for molecular gases and a flow rate of 5 l/min of an argon-hydrogen mixture (up to a 35% hydrogen content). The source was mounted on a 3 directions CNC pantograph equipped with a laser position sensing detector, with the axis of the source pointing perpendicularly to the upper surface of the daguerreotype, with a 1 mm gap distance between them. Starting from the centre of the bottom short side of the daguerreotype, the surface was treated by moving the plasma jet to the opposite side, at a constant speed of 20 cm/min on a parallel path to the long side of the sample. Several further passages were repeated by moving the starting and ending point 1 mm sideways at each repetition, till reaching the end of the sample. The treatment was performed twice.

Daguerreotype characterization

The visual observation of the daguerreotype was documented by macro-photography (Nikon D70S). The morphology of the surface was investigated on the microscopic scale by Scanning Electron Microscopy (SEM) as well as by Atomic Force Microscopy (AFM) on the sub-microscopic scale. AFM scans were carried out in contact mode, under ambient conditions, with contact forces in the range 25 nN – 30 nN, by using cantilevers with a nominal spring constant of 0.1 N/m and integrated tips with a 10 nm radius of curvature.

The identification of corrosion products on the surface of the daguerreotype was carried out by non-destructive analysis in terms of both elemental composition (SEM with Energy Dispersive Spectroscopy (EDS) microprobe) and phase composition (micro-Raman and Attenuated Total Reflection (ATR) Fourier Transform InfraRed (FT-IR) spectroscopy). Raman spectra were collected with the Ar+ laser (λ=514.5 nm), employing low laser powers (output ≤ 5 mW) to avoid sample degradation. ATR-FTIR spectra were recorded in the spectral range of 400 to 4000 cm⁻¹, resolution 4 cm⁻¹, 32 scans, using a KBr windows.

3. Results

Visual appearance

Fig 1 shows the changes in the daguerreotype visual appearance respectively after the 1st and 2nd plasma treatment of the image left half. The daguerreotype was originally covered with a bluish film as shown by the Fig. 1a. The central area clearly demonstrates an improvement in the overall visual appearance already after the 1st plasma cleaning treatment (Fig. 1b). In particular, the treated portion appears brighter and sharper. The 2nd treatment appears to supply a limited enhancement of the image quality, but most importantly demonstrates that subsequent plasma treatments at the chosen operating conditions preserve the image visual features. The improvements can be detected even more clearly by observing at higher magnification particulars of the woman’s visage (e.g. woman eye on the left side, Fig. 2) at higher magnification. Dark blue areas, mainly located near the daguerreotype borders, seems to be only marginally affected by the cleaning procedure.

Fig. 1. 19th century daguerreotype portrait: (a) untreated conditions; (b) after 1st plasma treatment (left side); (c) after 2nd plasma treatment (left side).

The improvement in image definition can be observed in the eye on the left-hand side, before and after the 1st plasma treatment (Fig. 2).

Fig. 2. Optical micrographies in white light of the figure eye on the left side in (a) untreated conditions and (b) after 1st plasma treatment.

Morphological and chemical characterization

SEM images were taken before and after plasma treatment. As shown in Fig. 3, plasma treatment do not seem to alter the surface morphology, with particular regard to features characterizing the grey levels of the
images (as the shape or number of particles of Ag-Hg amalgam). Actually, these morphological features need to be preserved in order to maintain the contrast to the image.

Fig. 3. BSE images captured on a bright (a, c) and on a dark (b, d) area before (a, b) and after (c, d) plasma treatment.

On the contrary, as reported in Table 1, the plasma treatment induced a decrease of the environmental elements C, S, Cl and O, likely due to the reduction of Ag sulphides and chlorides formed as a consequence of the interaction with the indoor atmosphere (see Raman analyses below).

Table 1. Surface composition (by large area EDS analyses) of the daguerreotype before and after conservation treatment, bright (particle) and dark (background) areas.

<table>
<thead>
<tr>
<th>Area</th>
<th>Treatment</th>
<th>Composition, % wt (bright area)</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
<th>Ag</th>
<th>Au</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>Untreated</td>
<td>2.1 2.8 0.6 0.1 85.0 9.1 0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background</td>
<td>Treated</td>
<td>0.2 1.7 - - 85.8 12.3 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle</td>
<td>Untreated</td>
<td>1.6 2.2 0.4 0.3 78.4 15.2 1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle</td>
<td>Treated</td>
<td>0.9 1.0 - - 85.4 11.6 1.1</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Raman spectroscopy was used in situ for comparing the phase composition of the surfaces before and after plasma treatments, because Raman can identify deterioration products due to the ability of the daguerreotypes’ silver surfaces to behave as SERS (Surface-enhanced Raman scattering) substrates, thus not requiring sample removal [2 Centeno08].

Fig. 4 reports Raman spectra recorded in areas with different grey levels: bright area (Fig. 4a) and dark area (Fig. 4b). After plasma treatment, two main modifications were observed in Raman spectra: firstly, the intensity of the broad band at about 240 cm⁻¹ (which can be attributed to the Ag–Cl stretch, 242 cm⁻¹ according to [2], as well as to the Ag-S stretch, 243 cm⁻¹ [9]) significantly decreases, suggesting (in agreement with EDS data in Table 1) that the plasma cleaning treatment was effective in removing the tarnish film. Secondly, the plasma treatment also reduces the baseline (which is probably related with fluorescence due to organic compounds [10]). Therefore, the cleaning treatment might have removed organic compounds on daguerreotypes’ surfaces. The presence of organic compounds might be related with the use of varnishes and coatings. However, protective coatings and varnishes were not frequently applied for protecting ungilded daguerreotypes, because the damaging optical effects from the coatings (the highlights appear less white and the black tones become dull) seemed to counterbalance the advantages [11]. The binding media used for hand-coloring, which was in use also for daguerreotypes [12], might be an alternative source of organic compounds. Even though the daguerreotype under investigation did not show visible evidence of coloring, it is not possible to exclude that traces of such a procedure might still be present on the surface, due to the bad conservation conditions of the plate.

FTIR analysis showed the presence of polydimethylsiloxane [13], which is the most common of the silicone rubbers, likely applied on the daguerreotype as hydrophobic coating. The Si-O-Si backbone shows a broad band with two maxima at 1092 and 1016 cm⁻¹. The methyl deformation band at 1261 cm⁻¹ is strong and sharp, as well as the contribution from the Si-C stretch at 798
The asymmetric CH$_3$ stretch at 2964 cm$^{-1}$ is also sharp and relatively strong. The lowering of peaks at 2964 and 1016 cm$^{-1}$ after plasma treatment is possibly related to a partial removal or structural modification of this coating. In the next steps of the work, further IR analyses will be carried out for a more detailed characterization of organic substances on the surface of this daguerreotype.

**Conclusions**

The feasibility of using atmospheric pressure non-thermal plasmas to clean the surface of a corroded 19th century daguerreotype has been demonstrated in the present work. Prior to experimental work, the surface showed significant surface corrosion or tarnish, darkening the photographic image. Overall visual appearance clearly improved already after the 1$^{st}$ plasma cleaning treatment; the treated portion being brighter and sharper. The 2$^{nd}$ treatment supplied a limited enhancement of the image quality, demonstrating that subsequent plasma treatments at the chosen operating conditions preserve the image visual features. SEM-EDS, Raman and FTIR spectroscopy analysis suggested that the treatment was effective in removing the tarnish film.

Further investigations will also involve the use of different plasma sources, able to perform large area treatments at atmospheric pressure with controlled gas composition, for the cleaning of corroded daguerreotypes and other cultural heritage applications.

**References**

5. V. Daniels, Plasma Reduction of Silver Tarnish on Daguerreotypes, Studies in Conservation, 26 (2) 1981 45-49.