



ELSEVIER

Contents lists available at ScienceDirect

## Corrosion Science

journal homepage: [www.elsevier.com/locate/corsci](http://www.elsevier.com/locate/corsci)

# Exposing the sub-surface of historical daguerreotypes and the effects of sulfur-induced corrosion



Emmanuelle A. Marquis<sup>a,\*</sup>, Yimeng Chen<sup>a</sup>, Julia Kohanek<sup>a</sup>, Yan Dong<sup>a</sup>, Silvia A. Centeno<sup>b</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

<sup>b</sup> Department of Scientific Research, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, NY 10028, USA

## ARTICLE INFO

## Article history:

Received 23 September 2014

Accepted 16 February 2015

Available online 28 February 2015

## Keywords:

A. Silver

A. Copper

B. TEM

C. Atmospheric corrosion

## ABSTRACT

Preventing the loss of image detail and resolution in historical photographs is a crucial topic, yet the properties of the image particles and mechanisms of deterioration are not fully understood. Through detailed surface and cross sectional analyzes, ungolded and gilded daguerreotypes prepared in the laboratory were analyzed before and after exposure to high sulfur-concentration environments revealing important structural consequences of the gilding process. Comparisons with the surface and sub-surface structures found on a 19th century gilded daguerreotype confirmed the slow corrosion of the underlying Ag and the accumulation of Cu and Ag sulfide particles on the surfaces of the plates.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The dramatic degradation phenomena typically observed in daguerreotypes, made by the photographic technique invented by the French chemist Louis-Jacques Mandé Daguerre in the mid-1800s, is a crucial problem for collections of historical relevance and also poses an interesting challenge from the materials science point of view. Daguerreotypes were fabricated through materials and processes that combine principles of metallurgy, surface science, and chemistry. In the 19th century, daguerreotypes were prepared by polishing a Cu plate, followed by cold-roll cladding and/or electrodeposition of a Ag layer on top. This Ag surface was then polished until a mirror-like finish was obtained, and exposed to halide vapors (iodine and/or bromine) to form light-sensitive silver halides that, when exposed to light, decomposed leading to free Ag clusters on the surface. Upon exposure to Hg vapors, Ag-rich Hg/Ag amalgam particles were formed on the Ag surface creating the daguerreotype image. After rinsing using sodium thiosulfate to remove the unreacted Ag halides, the plates were generally exposed to a gold chloride solution, a procedure called gilding [1], and subsequently dried. For pristine plates, the contrast is given by highlights and midtone areas with a high density of the Hg/Ag amalgam particles, with sizes ranging from 100 nm to 2.5 μm, and shadow areas made up of the bare polished Ag substrate with no particles or few larger particles, approximately 10–50 μm [2,3].

The issue of the fast degradation of historical daguerreotypes became particularly evident in the “Young America: The Daguerreotypes of Southworth & Hawes” exhibition, that took place between June 2005 and April 2006 [4], during which some daguerreotypes experienced a loss of image detail and resolution and a decrease in contrast when a white surface deposit appeared over their surfaces in the course of just a few weeks. The white surface deposit was identified as originating from the redeposition of Ag due to the exposure of light to the AgCl that had formed on the images during their long term storage under uncontrolled conditions in the presence of chlorine-containing contaminants [5]. Sulfur-induced degradation is one of the phenomena more commonly observed when examining 19th century daguerreotypes and it has since long been known that the presence of silver sulfide, silver oxide, and also of cuprous ions, have sensitizing effects on the photochemical properties of AgCl [6]. The challenges in addressing the questions that arise when the highly sensitive daguerreotype image particles are exposed to environmental pollutants are therefore significant. The methods and materials used for the production of daguerreotypes combined with the various environments that the materials may have been exposed to over last 150 years are essential pieces of the puzzle, the latter yet generally unknown.

Previous studies using imaging and analytical surface techniques have shed light on some details of the complex surface structures of these early photographs. Fluorescence by UV illumination revealed that tarnish might start preferably at the edges [7]. Tarnish spots with ring patterns however are also found in the middle of the plates. Scanning electron microscopy (SEM)

\* Corresponding author. Tel.: +1 (734) 764 8717.

E-mail address: [emarq@umich.edu](mailto:emarq@umich.edu) (E.A. Marquis).

and energy dispersive X-ray spectroscopy (EDS) analysis revealed the significant presence of Cu, Fe, and Cl in some locations of these tarnished areas [7]. From FTIR results, the authors speculated on the presence of a Cu cyanide compound that may have resulted from cyanide cleaners widely used in the past to clean daguerreotypes, from the electroplating of the Ag substrate, from a Au cyanide complex used in the final gilding step, or from brightening and fixing solutions used in the manufacture of the plates. Other SEM/EDS studies [8] also found large Cu rich islands on the damaged surface of an historical plate. From XRD data, Barger and White reported the presence of  $\text{Ag}_2\text{O}$ ,  $\text{AgCl}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{AgCN}$  compounds among others [1], some of these also suspected by Ravines et al. in their confocal microscopy imaging of plates that had been subjected to chemical cleaning treatments [9]. Centeno et al. [5] detected the presence of  $\text{AgCl}$  on the surface of daguerreotypes using Raman spectroscopy and associated it with the presence of redeposited Ag and the consequent severe loss of image detail. Using a combination of techniques, SEM-EDS, atomic force microscopy (AFM), X-ray fluorescence (XRF), and Raman spectroscopy, Centeno et al. also showed that  $\text{Ag}_2\text{Cl}$  crystals form on the image particles and the substrate when daguerreotype samples are exposed to a chlorine-rich environment [10].

Ravines et al. [11] distinguished three types of particles on the surface of damaged historical plates and interpreted the largest particles (>200 nm) with a smooth appearance to be the image particles, smaller ones (~50 nm) as corrosion products, and the finest ones as due to the nanocrystalline nature of the gilding layer. Barger et al. [3], as well as Swan et al. [2] and later Da Silva et al. [12], suggested that the Au is uniformly distributed all over the image, with higher levels in the bright regions (i.e. regions of high image particle density) [3]. More recently, Centeno et al. [10] demonstrated by AFM measurements that the gilding layer is conformal over all particles and substrate, with a preferential accumulation over the image particles. It is highly possible that the historical daguerreotypes for which Ravines et al. observed the presence of Au on top of the image particles only, and not on the images overall, were subjected to a past aggressive restoration treatment with an acidified thiourea solution, a cleaner widely used in the 1950s and that has been shown to partially remove the Au layer in daguerreotypes [12]. Finally, Hg, which is used in the developing step, was claimed to be present in larger amounts in the dark regions by Da Silva et al. [12], which intuitively contradicts its role in developing the Ag particles which form the daguerreotype image. Alternatively Hg was found to be less concentrated in the dark region in a different study [10]. It has also been speculated that Hg and its affinity for sulfur may lead to degradation [12].

This survey of the existing literature clearly demonstrates that the structure and degradation of daguerreotypes are still not well understood. Surface cleaning methods to remove surface tarnish involving chemicals, e.g. [13,14], laser ablation e.g. [15–17] or plasma jets, e.g. [18] have been widely used in the past despite the fact that only a few systematic studies justifying their use had been conducted. Even though aggressive treatments are not used by professional conservators nowadays, a detailed understanding of the changes induced on the surface or sub-surface structures and the long term effects are imperative to evaluate the present reactivity and long term preservation of daguerreotypes that have been treated in the past, as well as to develop safe conservation and preservation strategies.

The presence of specific corrosion products often finds its explanation in the chemistry and microstructure of the corroding material. Therefore this study investigates not only the products found on daguerreotype surfaces but also attempts to correlate these surface features and their changes in response to the environment to the microstructures underneath the surface. Two types

of daguerreotype specimens were investigated: historical plates and modern samples made in the laboratory strictly following documented 19th century methods. Modern plates were used to study the starting structure of the images, and similar samples subjected to accelerated corrosion were also examined. The corroded structures found on the modern plates were then compared to those found in a historical daguerreotype to validate the interpretations of the possible degradation phenomena.

## 2. Experimental

The historical gilded plate shown in Fig. 1a belongs to a private study collection and was selected for its high contrast regions (such as the one labeled A) and specific degradation features, including brownish and greenish tarnished regions (labeled B and C). For the laboratory samples, silvered Cu plates were prepared by the traditional clad rolling method, in which the Cu sheet has a thickness of approximately 480  $\mu\text{m}$  and the Ag layer is approximately 10  $\mu\text{m}$ . These plates were first hand polished and subsequently re-silvered by immersing them in a bath containing sodium thiosulfate and  $\text{AgCl}$ , the latter prepared by mixing  $\text{AgNO}_3$  and  $\text{NaCl}$ , and then repeatedly washed with distilled water before sensitization. The samples were sensitized with  $\text{I}_2$  for 45 s. Three different light exposures were used in order to obtain high, medium, and low image density areas in step tablets. The images were developed with Hg vapors at 70 °C for 8 min and subsequently fixed with a 3% sodium thiosulfate solution. A set of samples was gilded using a 0.1%  $\text{HAuCl}_4 \cdot \text{XH}_2\text{O}$  solution, containing 0.8% of sodium thiosulfate. The gilding solution was poured over the image and the plate was lightly heated with an alcohol lamp for approximately 3 min. A similar set of step tablets was left un-gilded.

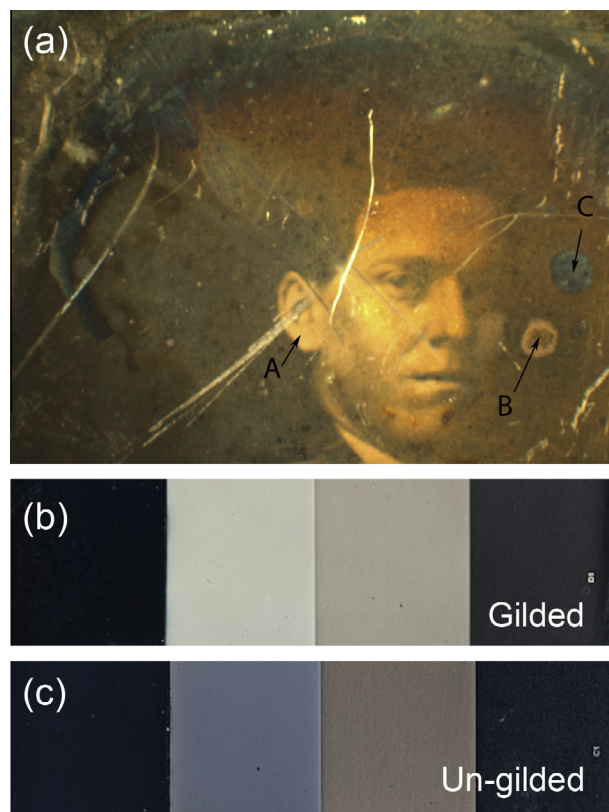


Fig. 1. Optical images of the (a) the historical 19th century daguerreotype indicating the areas selected for detailed analysis and of (b) gilded and (c) un-gilded laboratory daguerreotype samples before exposure to a sulfur environment.

Download English Version:

<https://daneshyari.com/en/article/1468660>

Download Persian Version:

<https://daneshyari.com/article/1468660>

[Daneshyari.com](https://daneshyari.com)