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Surface Characterization of 19th Century and Modern Daguerreotypes using High-Resolution SEM

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The daguerreotype, the first commercially viable imaging process developed by Louis-Jacques-Mande Daguerre, presented to the world in Paris in 1839, gave birth to photography and began the imaging revolution (1). The daguerreotype is a single and unique image whose image particles rest on the surface of a silvered copper plate. This is in contrast to other silver-based black and white photographic processes (negative and paper print film) where silver particles are embedded in a gelatin matrix/emulsion. In this initial state of development, the daguerreotype surface image particles are highly susceptible to mechanical and physical damage. The gilding step introduced in 1840 by Armand Hippolyte Louis Fizeau (1819–1896) in 1840 (2) became an integral part of the daguerreotype process. This step affixes the image particles to the plate and enhances the image by increasing contrast by presumably 'coating' the surface with a thin gold film. Despite this initial improvement in physical image stability, tarnishing on un-gilded and gilded plates has plagued daguerreotypes since their inception. Having the surface coated with gold, a noble metal, appears not to hinder the development of tarnish with colors ranging from white and light blues to light brown-yellows to browns to dark blue blacks. To counter this disfigurement many aggressive cleaning methods were developed.

The earliest electron microscopy studies of the late 1970s and early 1980s (3-5) explain how light interacts with the daguerreotype surface to yield an image, image particle composition, estimates of gold film thickness, chemical composition of tarnish, and removal approaches. The genesis and ubiquitous nature of tarnish development on daguerreotype surfaces is not broached.

The captivating beauty of the first images recorded with light from France and the US and their problems will be presented followed by our study using state of the art analytical imaging systems applied to early photographic system. Figure 1 shows daguerreotypes from the Southworth and Hawes collection at George Eastman House in fair to good condition and with tarnish. The focus is on period 19th century and recent modern daguerreotypes using HR -SEM with magnifications ranging from 20,000 to 250,000x. This surface characterization study corroborates the metallurgical nature of the silver mercury amalgam image particles – hexagonal close packed ε (epsilon) $Ag_{11}Hg_9$ -of earlier studies (3 -4), and demonstrates the nano-textured nature of the background and image particle surface. Figure 2 shows one of the 19th c daguerreotypes of a woman from the author's collection studied under high magnification, and Figure 3 shows a modern daguerreotype of gray scales made by Irving Pobboravsky in 1995 also under high magnification. The nano-texture features of the background surface in both gilded plates provide information that potentially explains the occurrence of tarnish as corrosion in the inter-nodular regions: it appears that gold is not continuous and may only be capping silver nodules that range in size in the tens of nanometers; the narrower nodule boundary regions show tarnish cubic crystals of AgCl and/or Ag_2O inferring that a protective gold layer is not present and that silver metal is exposed to atmospheric contaminants thereby allowing tarnish to develop.

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Figure 1. Daguerreotypes from Southworth and Hawes collection at GEH. *a.* 1/6th plate daguerreotype (size: 3.25 x 2.25 inches; 8.3 x 7 cm) of an unidentified young woman wearing a checkered dress with dark tarnish on top third, ca. 1850, GEH accession number 1974:0193:0305; *b.* Quarter plate daguerreotype (size: 4.25 x 3.25 inches; 10.8 x 8.3 cm) depicting an unidentified young seated woman with bottle curl hair wearing a striped dress showing all tarnish types: the image is almost completely covered with a whitish haze, thicker in the lower half, and all borders display tarnish ranging in colors from light to dark brown to silvery blue to black, ca. 1845-50, GEH accession number 1974:0193:0409.

Figure 2. *a.* A 19th c 1/9th plate daguerreotype (size: 1.8 x 2.36 inches; 4.6 x 6.0 cm) from collection of the author of a woman wearing a white bonnet ca. 1850s with circle markers on her forehead showing areas examined before and after treatment with ammonium hydroxide solution; *b.* Image particles from her forehead before treatment at x43,000 magnification showing smaller crystallites on image particles and on background; *c.* Treatment with ammonium hydroxide solution has eradicated all small crystallites from image particles and background, also at x43,000.

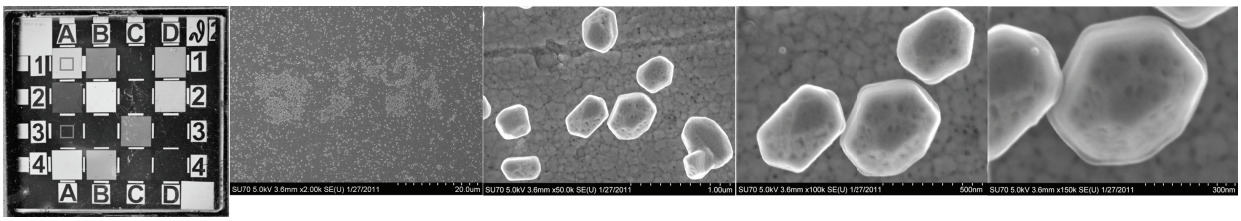

Figure 3. A modern daguerreotype of gray scales, *Theta 19*, by Irving Pobboravsky, 1995 (size: 2.24 x 2.25 in, 7 x 7 cm). Square A1 at different high magnifications ranging from x2,000 to x50,000, x100,000 and x150,000. The lowest magnification of x2000 shows a large number of image particles scattered and clustered on the surface; at x50,000 the more typical hexagonal crystals of silver mercury amalgam ($Ag_{11}Hg_9$) are observed; at x100,000 and x150,000 the hexagonal particles show stacking crystal growth patterns, what appears to be pitting on facets, and the background has a distinct nanotexture.

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