Daguerreotype Research Funded by the National Science Foundation

The University of Rochester

George Eastman House International Museum of Photography and Film

Research on the gilding of daguerreotypes

The Daguerreian Society Symposium 2014 Austin, Texas

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Louis Jacques Mandé Daguerre Jean Baptiste Sabatier-Blot: daguerreotype, 1844 George Eastman House Collection



Armand Hippolyte Fizeau Chemist, physicist, inventor, visionary Literary Gazette; and Journal of the Belles Lettres, Arts, Sciences, &c. (London) No. 1231 (22 August 1840): 545. This text appears as part of a column under the header: "PARIS LETTER. Academy of Sciences, August 18, 1840."

M. Fizeau communicated a method of fixing photographic impressions obtained with the daguerreotype, by means of a chlorure of gold. The mixture employed was one gramme of chlorure of gold dissolved in half a litre of pure water (distilled), to be mixed with three grammes of hyposulphite of soda, also dissolved in half a litre of water. The two mixtures to be poured gradually together, and well stirred

The enduring mystery of brilliant minds

What transcendent ideas led M. Fizeau to prepare solutions that formed gold nanoparticles of consistent size, shape, and stability?

How small is nano?



Figure 1.1. Comparison of the size domains of naturally existing and man made systems.

Nanometer = 1 billionth of a meter

A human hair is about 40,000 nanometers wide

Silver etched by Iodine fuming



Fizeau's recipe rediscovered

Tunability and Stability of Gold Nanoparticles Obtained from Chloroauric Acid and Sodium Thiosulfate Reaction

Nanoscale Research Letters 2012, 7:337 doi:10.1186/1556-276X-7-337

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0.2% gold chloride in distilled water

OBRAK BUTLES 91/4/2012 2% Gould Chorace 10/14/2012 10/14/2012 10/14/2012 10/14/2012 Gold chloride solution mixed 1:1 with dilute sodium thiosulfate solution



Transmission Electron Microscope



University of Louisville

University of Rochester Zeiss Auriga Scanning Electron Microscope



URNanocenter Dr. Nicholas Bigelow, Director Brian McIntyre, Chief of Operations



Energy dispersive X-Ray analysis



Localized X-Ray beam; accelerating voltage 15 – 20 kilovolts; working distance > 5mm

Focused Ion Beam Milling (FIB)



Precision depth cut into the surface < 1 -5 microns Provides cross section imaging and elemental X-ray analysis

Compound FIB trench



Scale bar = 1 micron; magnification 6,240 times; viewed at 54° tilt

Energy Dispersive X-ray analysis below the surface







FIB trench at 0° tilt is nestled beneath an organic structure engaging with the daguerreotype surface; magnification is 453 times



Ungilded Plates









Southworth & Hawes



George Eastman House collection 6th plate: 1974:0193:0333



George Eastman House collection 6th plate: 1974:0193:0322







Gilded or ungilded?



- No plate maker's mark
- Faint octagonal mat mark
- Pose and clothing 1830's –early 1840's (?)
- Adhesive residues/silver loss around perimeter –perhaps an early mounting similar to Cornelius (?)
- Very weak –if at all- significant AuM EDX signal; no L line signal at 20 kV

Confirming tests to verify the hypothesis:

The Fizeau gilding recipe causes the formation of a gold-silversulfur complex by energetic mass transport of underlying silver into a discrete surface structure or "superlayer"





Ungilded Becquerel sample --no image particles Gilded Becquerel sample - with image particle

1. The progressive gilding test



This test was conducted under the NSF Research Undergraduate (REU) Program at the University of Rochester by Emily Thompson in 2013

1 and 2



1 drop of gilding solution followed by distilled water to keep the area from going to dryness during the experiment

3 and 4



3 drops gilding solution over 4 minutes followed for by distilled water for the additional 4 minutes to keep the area from going to dryness

5 and 6



7-8 drops gilding solution over 8 minutes followed by the coupon being immersed for a final rinse and air dry.The uppermost surface began to delaminate and curl up just before termination of the experiment

6: the extended gilding resulting in the superlayer delaminating and curling up



Loss of superlayers exposing subsurface Ag

Curled up superlayer – often termed exfoliation

FIB Section of Region 6



Note the full separation of superlayer 1 between the base silver layer and the Ag-Au layer above. Superlayer 2 with separation shows a possible repeat of the same phenomenon –with an increase in the Au content.

FIB – EDX analysis of ROI 6







1.20 1.60 2.00 2.40

0.40

0.80

2.80

3.20

3.60

4.00

4.40

2. Analysis of solution drawn off during gilding of a mercury developed plate (Thanks Mike!)





6 minutes Scale bar = 20 nm

8 minutes Analysis of solution at pour-off

No Ag or Hg in the solutions



























FIB-3 EDX









Ag coated grid on SEM stub



Grid square chosen for FIB analysis





Fib cuts in the 100nm Ag coated grid. The FIB beam was operated at 30kV and 2-5 pAmps @20-30 sec to cut through



92.40 nm The lower stratum is a section of the carbon grid, measuring 42.91nm



EDX of edge of FIB cut: the FIB beam may have caused the edge to deform. The EDX spectrum shows a proper proportion of Ag to Au expected in a gilded daguerreotype. The Al signal is a result of scatter —all surrounding metal is Al. The Cu signal is from the grid structure. Both the Al and Cu are to be discounted.



EDX of the sub stratum: no coating or gilding evident



EDX spectrum of top surface: lower in Au than expected



EDX of the Ag –Au surface on the webbing.

