Article: A Summary of the National Science Foundation (SCIART) Supported Research of the Daguerreotype: George Eastman House International Museum of Photography and Film, and the University of Rochester
Author(s): Ralph Wiegandt, Nicholas Bigelow, and Brian McIntyre
Topics in Photographic Preservation, Volume 15.
Pages: 160-175
Compiler: Jessica Keister

A Summary of the National Science Foundation (SCIART) Supported Research of the Daguerreotype: George Eastman House International Museum of Photography and Film, and the University of Rochester

Ralph Wiegandt, Dr. Nicholas Bigelow, and Brian McIntyre

Presented at the 2013 AIC & ICOM-CC Photographs Conservation Joint Meeting in Wellington, New Zealand.

Abstract:

Scientific advances in the chemistry and physics of nano-scale materials, especially silver and gold, require reconsideration of our material understanding of the daguerreotype.

As molecular structures approach dimensions of several hundred nanometers and smaller, their nano-scale surface properties become increasingly dominant, which differ significantly from their bulk material properties. Research undertaken in this initiative suggests that the daguerreotype image and its degradation exhibit predominately these nano-scale physical properties. This paper presents a nanometer scale investigation of the daguerreotype and its profound conservation implications.

Micron scale and macro properties of metals have been the basis for commonly held explanations of image formation, tarnish, oxidation, and environmental deterioration. Consequently, daguerreotype restorative treatments and preservation methods, both historically and currently, appear to alter the original structure in the former, and are inadequate for preventing progressive deterioration in the latter.

Taking into account the expanding body of research on the unique physical and optical properties of silver and gold, and to a lesser extent copper and mercury, we apply this recent research to our investigation of the daguerreotype. This paper proposes new explanations for the extraordinary bio-receptivity of the daguerreotype surface, and the optical effects that occur when gold and silver nanoparticles have dimensions considerably smaller than the wavelength of the visible light spectrum.

The intent of this paper is to alert the community of photograph conservators to the reactivity of the daguerreotype's highly nano-structured surface composed of silver and gold and their unique nano properties; and to propose new preservation strategies that can halt the nearly undetectable nano-level deterioration before it advances to micro and macro stages.

Introduction:

A National Science Foundation award through the SCIART program (Chemistry and Material Science at the Interface of Science and Art), was awarded to the University of Rochester in collaboration with George Eastman House International Museum of Photography and Film in 2009. The grand conservation challenge of this award is to advance the material science understanding of this extraordinary earliest photographic medium, and to research its complex deterioration responses.

George Eastman House holds one of the world's largest and most diverse collections of daguerreotypes, associated artifacts, and archives. It serves as an international resource for the history and study of the daguerreotype. The University of Rochester is a leading research university for optics, material science, and nanotechnology. The URnanocenter provides the instrumentation and expertise necessary to research the complex physical and chemical make-up of the daguerreotype.

The daguerreotype is considered to be the first commercially successful photographic process. It was practiced widely from 1840 through 1860, primarily in Europe and America. Invented in France by Louis Daguerre in 1839, the process achieved its technical maturity within five years. The daguerreotype's intrinsic high resolution and unique image forming properties have been of continued wonder and scientific interest from its inception.

The daguerreotype is the result of the irrepressible human trait of manipulating materials to create new forms that occasionally lead to discoveries that alter the course of human history. Daguerre's discovery burst onto the scene as the first truly engineered nanoparticle substrate, and from its unlikely emergence in 1839, it has required nearly 160 years of scientific advancement to unlock its secrets. Although the nano-optical properties of colloidal gold, silver, and other metals were known to Roman glass makers, medieval stained glass artisans, and later by producers of luminescent ceramic glazes; it is the daguerreotype that manifests the multitude of physico-chemical characteristics explainable only by emergent research in 21st C. nanosciences.

The paper addresses three primary themes of this research:

I. The daguerreotype is an artifact of nanotechnology

II. A daguerreotype is archaeological. It has recorded events that have happened to it or in its close proximity since its "first light". *[The term "first light" is defined as the initiation photons that exposed and created the image, and the light reflected by which the daguerreotype was first viewed after processing. We are considering this view as the daguerreotype's original state, or original condition.]*

III. Conservators should be advancing methods to preserve and protect the residual evidence of the daguerreotype's original state at first light.

[Note: this paper will not go into an explanation of the daguerreotype process, that information is widely available from many published sources.]

How is a daguerreotype an artifact of nanotechnology? *Nano* (from the Greek for dwarf) as in nano-technology or nano-science, is the size at which surface physical properties dominate in discrete structures that have at least one dimension between one nanometer and 100nm. A nanometer is one billionth of a meter; a human hair averages 30,000 nanometers in width.

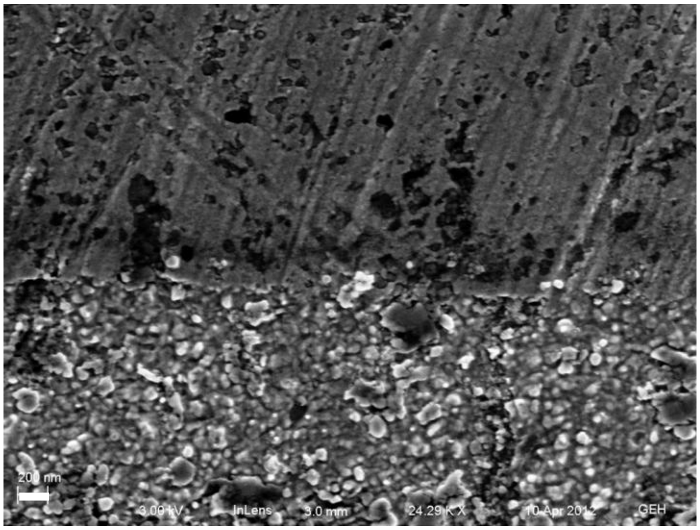

Fig. 1. SEM micrograph of a partially iodine-etched silver test coupon; scale bar is 200nm: section of a silver coupon coated with a lacquer barrier coating.

A daguerreotype becomes a nanostructured substrate by the act of sensitization. The silver halide layer that forms by oxidation when exposed to iodine, bromine, or chlorine vapors and subsequently removed (fixed) by sodium thiosulfate, creates a nano-structured surface.

Figure 1 is a scanning electron micrograph (SEM) of a silver coupon used for modern daguerreotypes: pure silver roll cladding over copper. It was roughly polished overall. The upper half was protected with a coating of lacquer prior to the sensitization and fixing steps.

1. The coupon was placed over iodine crystals in a fuming box for approximately 80 seconds to form a first order yellow-magenta interference color at grazing incidence viewing angle of silver iodide (approximately 250 nm thick). It was not exposed to light.

2. The silver iodide layer was removed in a standard photographic fixing solution of 5% sodium thiosulfate in distilled water, and immersion rinsed and dried.

3. The lacquer coating was removed by solvent.

4. The resulting SEM micrograph shows the effect of the exposure to iodine vapor that formed a layer of silver iodide, that when removed, left behind a highly granular etched silver surface structure with highly three dimensional features ranging from <10nm to 100nm.

5. Although the sample was not exposed to light and mercuralized, this simple test establishes the nanostructure of the daguerreotype. It clearly shows the vast increase in surface area caused by sensitization, and it is the starting point to propose the profound implications these nano features have on all aspects of the daguerreotype: image formation, interactions with light, and deterioration mechanisms.

At the nanoscale we begin to understand daguerreotypes very differently. The metals that constitute the daguerreotype surface: silver, mercury, and gold have physical properties that are different from those we know from their bulk material properties. The properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface becomes increasingly significant. For material dimensions larger than one micron, the percentage of atoms at the surface is insignificant in relation to the number of atoms in its bulk state. For example, gold, generally considered highly unreactive in its bulk metallic state, but as a nanoparticle its atomic properties predominate and it is highly reactive and acts as a powerful catalyst. Gold nanoparticles complex readily with sulfur compounds (thiols) and with other complexing agents, such as amines. Additionally, the optical properties of the constituent nano-metals of a daguerreotype exhibit localized surface plasmon resonance that is manifested in an exponential increase in light scattering when the frequency of incident light is resonant with oscillation of surface electrons. Other than an empirical interpretation and qualitative observation of this phenomenon, further research is required to determine the specific effects that surface plasmon resonance of silver and gold nanoparticles have on the optical qualities of a daguerreotype. It becomes important to determine how deterioration and/or deliberate interventions may alter these intrinsic visual qualities of the nanostructured gold and silver surface. This remains a yet to be characterized aspect of the daguerreotype, but one that must be considered as significant to original condition if "first light" is to be preserved, or perhaps regained in some future time through technologies yet to be invented.

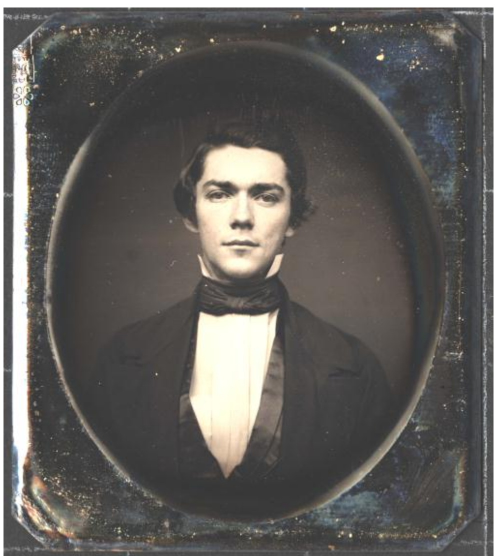

Fig. 2. 6^{th} plate (3.25" x 2.5").

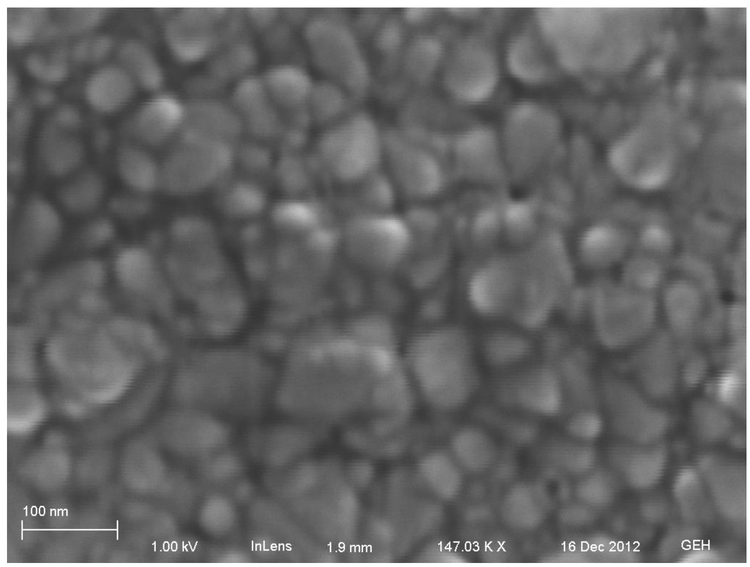

Fig. 3. SEM micrograph of the surface at 147 KX.

Figures 2 and 3 are of a daguerreotype in the Eastman House study collection that was extensively examined and analyzed by SEM. The plate is in excellent condition, and its preserver appeared to have not been opened. Figure 3 shows the surface 147,000 times magnified. This micrograph confirms the fundamental nanostructure of an historic daguerreotype, one that is both in excellent condition and demonstrates excellent mastery of process by the maker. The maker and sitter are unknown.

Biological Activity Found on the Daguerreotypes is a Function of Nanoscale Properties

The daguerreotype nanostructured surface is a fertile host for biological assembly and propagation. The constituent metals of a daguerreotype, as nano-particles, are capable of assembling organo-metallic structures and interacting with life chemistry. Current nanoscience research in the fields of bio-chemistry; bio-medicine; bio-engineering, bio-physics and others are demonstrating how the precise size, shape, and functional properties of metallic nanoparticles can lead to technological breakthroughs. Research into next generation energy sources; quantum computing; non-linear optics; nano-robotics; targeted cancer detection and treatment… and so on, creates demand for highly engineered nanoparticles –with gold and silver having particular value. Indeed, bio-generated metal nanoparticles are an efficient green pathway for controlled nanoparticle production, as well as a means to produce hybrid organo-metallic structures using biological linkages for bio-mimetic and bio-inspired assemblies of functionalized nano-metallic and nano-organic-metallic devices. This research is a literal goldmine for understanding the daguerreotype and it has been an essential resource in leading us to the reinterpretation of the daguerreotype as an artifact of nanotechnology, one that was serendipitously invented 174 years ago –long before the word *nano* came into parlance.

During those 170 plus years, many (possibly all?) daguerreotypes have served as de-facto petri dishes generating bio-metallic assemblies. The work by the Harvard group (Konkol et al 2011) was the first published experiment in harvesting such a biological sample from a daguerreotype, and successfully incubating, and identifying it as a fungus.

Working from extensive SEM imaging, energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM), our group has documented and analyzed more than 50 daguerreotypes and have visually and compositionally confirmed the presence of living, or once living organisms on every one. The astounding variety of structures that have been documented in this research and the interactivity between the daguerreotype metals and associated chemistry has given us a window into a world of bio-metallic eco-diversity. The research cited in allied fields helps provide a plausible explanation for what we have been finding, and the sheer abundance of forms and manifestations of this phenomenon appear limitless.

We are developing a research framework to explain the phenomenon by looking into some essential questions: What are the physico-chemical mechanisms? What are the rates of growth? What was the initial biochemical landscape that initiated the process? We believe answers may have intrinsic scientific value, and profound conservation implications.

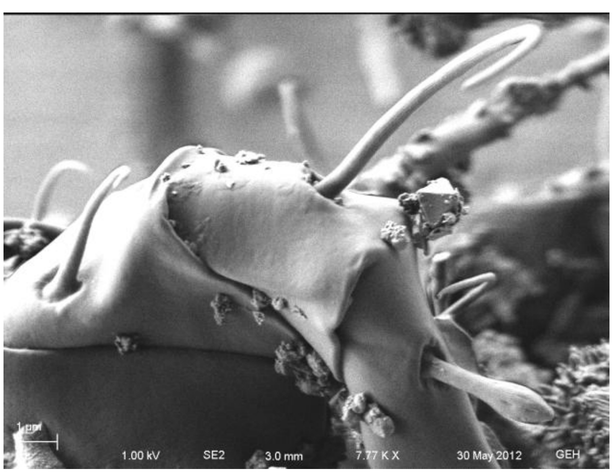

Fig. 4. SEM micrograph of a bio-metallic structure at 7.77 KX.

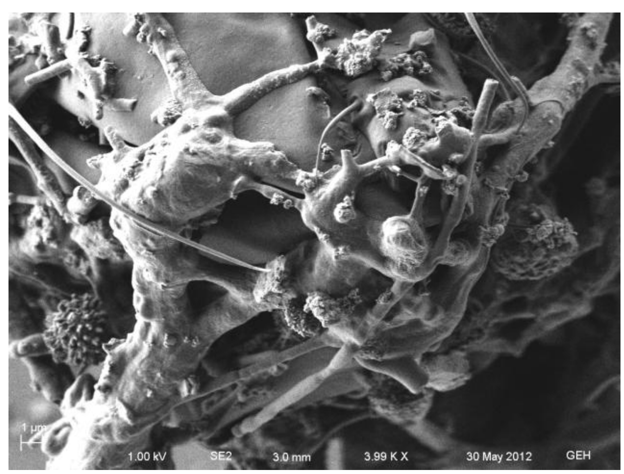

Fig. 5. SEM micrograph of a bio-metallic structure at 3.99 KX.

Figures 4 and 5 demonstrate the complexity of bio-metallic interaction that has been mediated over many years on a daguerreotype within a closed daguerreotype case. Perhaps it hosted multiple fungal, microbial, or any such broadly described biological entities. Maybe it was only a speck or two of dust, but in an adequately humid environment all the ingredients for the inception of nano-metallic biological propagation were present. This is a rather spectacular formation, but our research has catalogued a wide range of variations on this phenomenon. We propose that the complex structure in this example arises from the very specific local chemistry of the plate, the biological organism or organisms engaged, and the surrounding environmental conditions.

SEM examination provides for a visual understanding of the mechanisms by which gold and silver as nanoparticles in a plus (oxidation) state, can be reduced by biological cell contents composed of amino acids, peptides and other biological reducing chemistries. They are then mobilized to be absorbed and aggregated into or onto a biological structure.

Fig. 6. A sixth plate daguerreotype from the Eastman House study collection.

This plate was extensively examined and analyzed by SEM. While appearing to be in moderately good condition, in fact it hosts a generous variety of biological formations widely distributed across the plate.

The rectangle on the sitter's proper right arm delineates an area of biological activity that received examination.

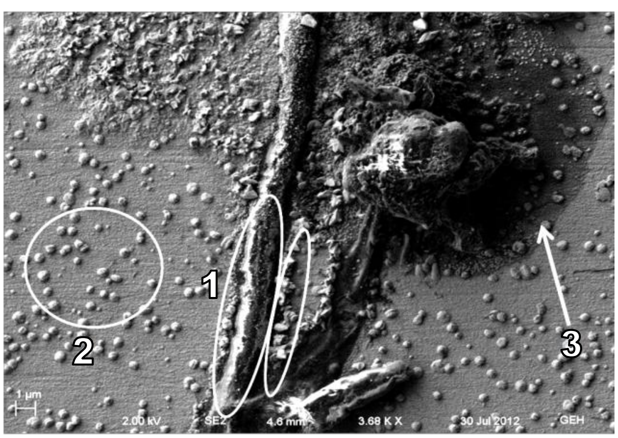

Fig. 7: SEM micrograph, feature at 3.68 KX.

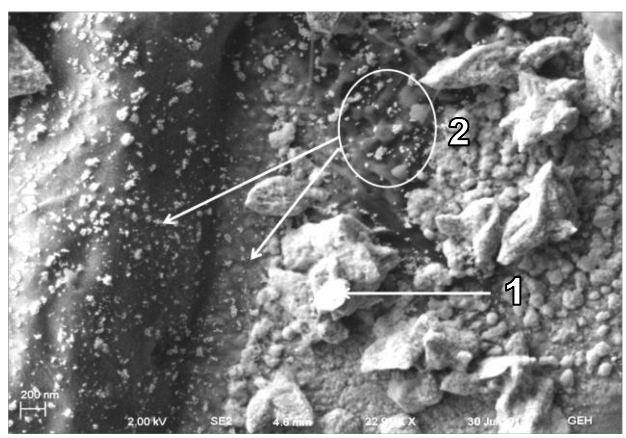

Fig. 8: SEM micrograph, feature at 22.91 KX.

Figure 7 reveals the nature of a commonly found linear carbon and oxygen rich form that we term biological fibers, or biofibers. There are many variations of these fibers found ubiquitously on daguerreotypes; most are engaged with the plate surface. Note the aggregation of particles along the main fiber [1], distinct from image particles [2]; and a surface level non-conducting film extending out from a large carbon rich mass [3].

Figure 8: At higher magnification (scale bar is 200nm), the biofiber surface is populated with nanoparticle aggregations composed of Ag and Au [2]; with similar particles emerging from the carbonaceous matrix (encircled) on the surface. The micron scale, non-uniform particles located along the fiber [2] are sulfur rich Ag crystals (confirmed by EDX analysis) that could well be formed as the moisture rich biological cell structures within the fiber reduces silver sulfide tarnish on the surrounding daguerreotype surface. The reduced silver is complexed within the extending "veil" emanating from the biofiber, and begins to aggregate with adjacent nanoparticles in the bio-matrix. The specific biochemistry and other parameters mobilize and direct the pathway of assembly on or within the biological formation. This explains the rich variation in bio-metallic formations on daguerreotypes, and helps us understand the formation of the characteristic crystalline sulfur particles that have accumulated along the edges of the biological growth, seen in detail in Figure 9 within the area labeled [2]; arrow [1] denotes the organic surface matrix that speculatively reduces the surface metals on a sub-nanometer scale and mobilizes them into the larger fiber structure. Figure 10 is the EDX spectrum of the > 1 micron angular crystals that have accumulated alongside the biofiber.

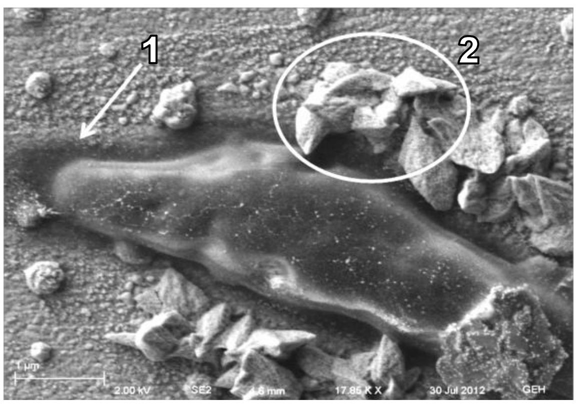

Fig. 9. SEM at 17.85 KX.

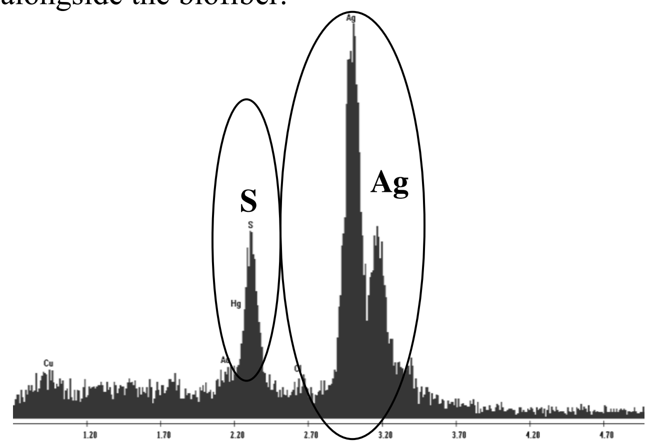

Fig. 10. EDX spectrum of crystals: predominant peaks are sulfur and silver.

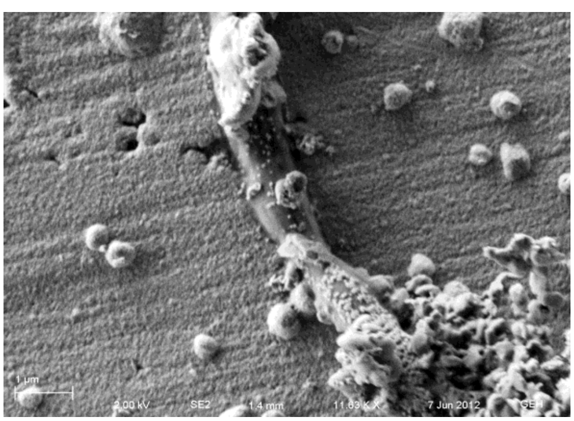

Fig. 10. Biofiber with progressive surface aggregation of Ag and Au nanoparticles.

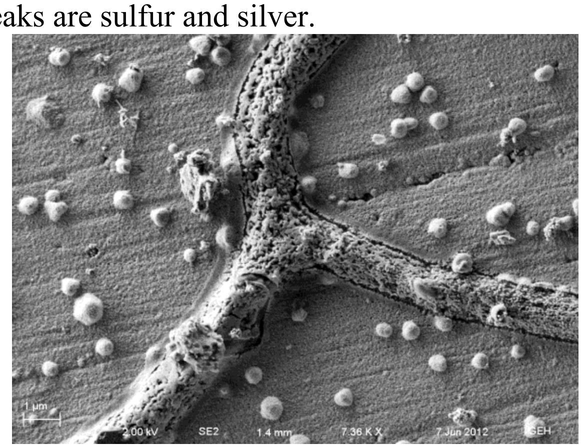

Fig. 11. Region of fiber that is nearly with encased with the aggregated nanoparticles.

The aggregation of metals on the exterior surface of this biofiber is similar to many others in our SEM examinations of daguerreotypes. We find both intracellular and extracellular metal particles; with many forming exterior clusters that appear to continue to agglomerate.

Figures 10 and 11 show Ag/Au nanoparticles fully mobilized through the biofiber, and completely covering a section in Figure 11. Note the edges of the fibers have a fully metallicized surface engagement corresponding to the organic "veil" noted in Fig. 9, indicating that the available reducing chemistry has fully reacted with the Ag/Au surface.

A review article by Rai et al (2010) lists published citations of fungal species identified for their metal nanoparticle fabrication properties.

So, why is fungus on daguerreotypes? Recent scientific publications demonstrate that fungi can systemically produce silver and gold nanoparticles when combined with solutions such as gold chloride and silver nitrate. The solution chemistry pathway is applicable to the silver and gold nano complexes that make up the daguerreotype surface. If sufficient moisture is present, ever present airborne fungal spores coming in contact with the plate will interact and mediate species specific nanoparticles composed of the daguerreotype constituent metals.

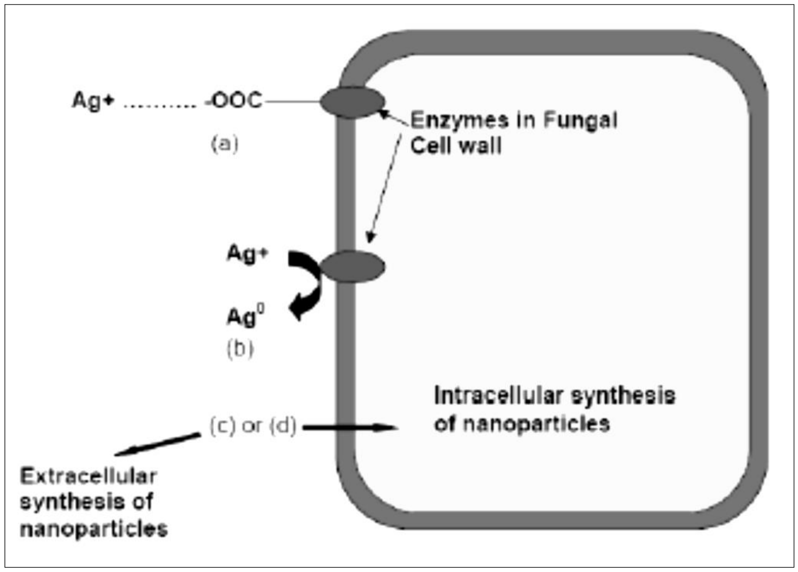

Fig. 12. Graphic from the cited review article (Rai et al 2010).

Captioned as follows: Fig. 2. Hypothetical mechanism of Nanoparticles formation in the Fungus; a. Electrostatic interaction between the metal ion and the enzyme present of the Fungal call wall; b. Reduction of the Ag^+ to Ag^0 by the enzyme; c. and d. The Ag^0 nanoparticles may be synthesized intracellularly or extracellularly.

The fungal propagation mechanisms require further research to fully explain the role each constituent plays in this complex system. SEM imaging and EDX analysis of bio-organisms demonstrate that they are found pervasively on daguerreotypes in our research –with fungi being only one possible source of biological reducing chemistry.

This graphic (Figure 12) describes a reduction pathway of silver by for nanoparticle fabrication. While recent work by the Harvard group in which fungal activity was identified and cultivated from daguerreotypes, there has not yet been a mechanistic explanation for it. An overview of current scientific literature provides plausible mechanisms to explain what our SEM imaging and analysis has revealed.

The scientific literature supports our findings and preliminary explanations for biological organisms propagating on daguerreotypes and assembling organo-metallic structures is explainable by the nanosciences. There is much more research necessary to determine the implication of these findings, assessing their risk, and developing appropriate mediation strategies.

Current Nanotechnology Research Provides New Insight into the Physicochemical Mechanism of Gilding, and Provides a New Hypothetical Model for the Surface Composition of the Gilded Daguerreotype

The reaction of the gilding solution with the silver surface of a daguerreotype has not been fully described in historic or recent research on the daguerreotype. Generally it has been considered to be a plating, or oxidation-reduction reaction, with the gold chloride being reduced and plating onto and displacing silver, and similarly displacing mercury in image particles (Barger 1990), yielding what has been reported as an accumulation of gold on the image particles (Ravines 2008).

However, current research in nanotechnology, in particular the synthesis of gold and silver nanoparticles, points toward an entirely different mechanism at play in the gilding step. Our experiments were carried out with a standard gilding solution used by daguerreotypists today, which is derived from Hippolyte Fizeau's 1840 formula (545): 0.2% gold chloride solution (aqueous) dissolved into a 5% solution of sodium thiosulfate. At this ratio, symmetrical polyhedral gold nanocrystals are formed, ranging in diameter between 10 and 20 nanometers, suspended in a colloidal solution. When the solution is heated on the plate, silver from the surface is intimately joined with the gold nanoparticles into macromolecular clusters that form a continuous gold-silver surface. This similar surface is formed over the mercury rich image particles, with mercury concentrated in the center of the image particle.

What is the basis for this hypothesis? A recent article (Zhang et al 2012) published in Nanoscale Research Letters used Fizeau's recipe to fabricate gold nanoparticles. This serendipitous research provides us with analyses that would be difficult to achieve within a conservation research laboratory.

The research group from the University of Louisville combined gold chloride and sodium thiosulfate solutions to make gold nanoparticles yielding a range of shapes and sizes by varying the solutions' molar ratios. They worked from first principles and had no knowledge of the daguerreotype, Fizeau, or Herschel's work. The UL research analyzed the solutions, quantified size, shape, and aggregation of the thiolated gold nanoparticles in solution spectroscopically, and by TEM. This highly relevant work revealed that the gold nanoparticles formed in Fizeau's classic recipe are between 10 and 25 nm in diameter, and are complexed by thiol groups that keep them from aggregating in solution.

We propose that the gold nanoparticles are well functionalized in solution by thiol bonding when they encounter the daguerreotype surface, and therefore do not participate in gold-silver displacement reactions. This is supported by TEM analysis of the spent gilding solution drawn from modern plates while in process. Neither silver nor mercury is detected in the reacted/spent solution –and would be detected if it were a displacement reaction.

Our most conclusive research on the surface structure of a daguerreotype has been achieved by SEM examination in the focused ion beam mode (FIB). This view is of a cut on the vertical axis creating cross section trench through the image forming strata. A < 10 micron cut allows the surface to be characterized and analyzed elementally in-situ by EDX. This minimally invasive technique carried out on surrogate daguerreotypes and selective historical study collection plates, reveals the physico-chemical dynamics of the gilding process on daguerreotypes. The FIB section in Figure 13 is from the daguerreotype in Figure 2, which is in excellent condition, and a very well executed daguerreotype.

Figure 13 shows a nearly continuous gold-silver layer 200nm above the underlying silver substrate. An explanation for the super layer and the corresponding sub-surface void proposes that the thiolated gold nanoparticles in the gilding solution energetically create a favorable dynamic for drawing the nano-structured halide etched silver into a discrete gold-silver super layer. Molecular clusters (yet undescribed) of the two metals fusing together, physically depletes underlying silver by the dimensional equivalent of the thickness of the super layer. This makes empirical sense because gold and silver have nearly equal metallic radii. The FIB section bisects a well formed image particle which is anchored to the silver substrate. EDX mapping shows a mercury-silver gradient that becomes increasingly mercury rich, extending radially from the center-base of the section face. At the particle surface, gold, silver, and mercury are detected. We have observed subsurface voids at the perimeter of image particles, raising the notion that similar dynamics are at play on the particle surface as on the plate surface, but we have not analyzed the precise elemental makeup.

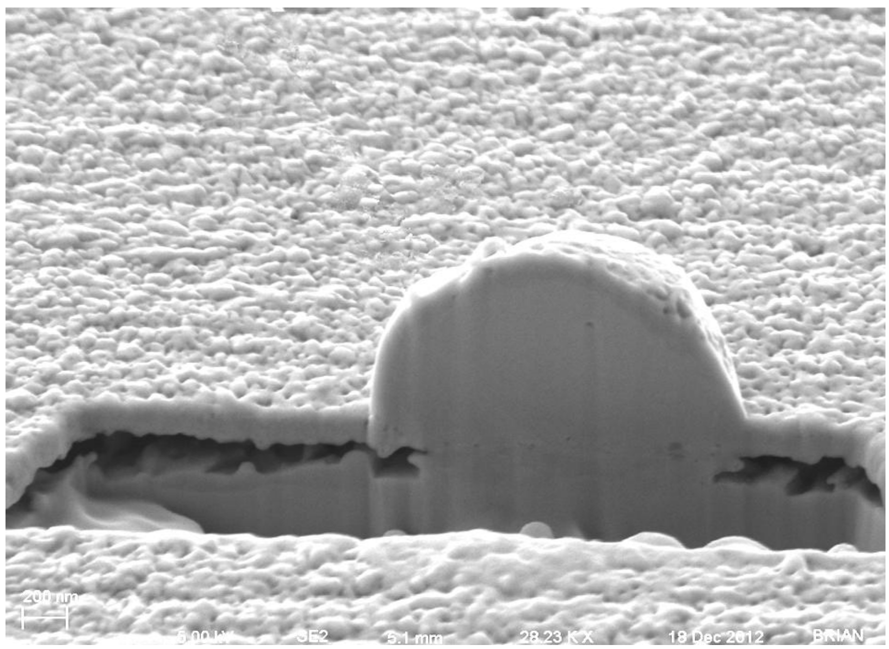

Fig. 13: FIB cross section of a gilded historic daguerreotype at 28,230 KX. Scale bar is 200nm.

To further reinforce these findings, we have conducted FIB examinations on both historic and modern ungilded daguerreotypes. We find no subsurface voids –even in association with the mercury developed image particles. On this repeated finding we are proposing that the gilding step creates subsurface voids below the surface as the heated gilding solution transports the nanostructured silver into gold-silver molecular formations. The precise molecular structures formed on the surface have yet to be characterized.

Figure 14 is an ungilded historic sixth plate (Scoville mark) from the Eastman House study collection. The associated FIB trench in Figure 15 shows no subsurface voids or disruption in the continuous silver layer –even in association with the mercury developed image particles. This FIB trench also sectioned several biological growths engaged with the surface, visible as the elongated dark forms.

Fig. 14. Sixth plate, ungilded.

Our current research shows that increasing the amount of gilding solution and lengthening the duration of the gilding process leads progressively to an extended subsurface horizontal void and formation of the super layer – which can precipitously disassociate and exfoliate from the underlying silver stratum. This phenomenon may actually be what occurs, in some instances, when exfoliation is the described condition on daguerreotypes. The assumption, prior to these experiments, has been that exfoliation on a daguerreotype occurs at a silver plating–subsurface interface and is a result of plating adhesion failure. The exfoliation due to extended or more abundant gilding is also a likely occurrence. This condition needs to be examined in greater detail by extrapolating our research results to the condition as observed on the historic daguerreotype. We believe we see this condition in some of the masterworks of Southworth & Hawes, as well as other highly accomplished daguerreotypists' work made at the technical peak of the process. Achieving the greatest optical response from the plate may result from the most gold deposition, which also creates the most extensive subsurface voids –and most tenuous surface.

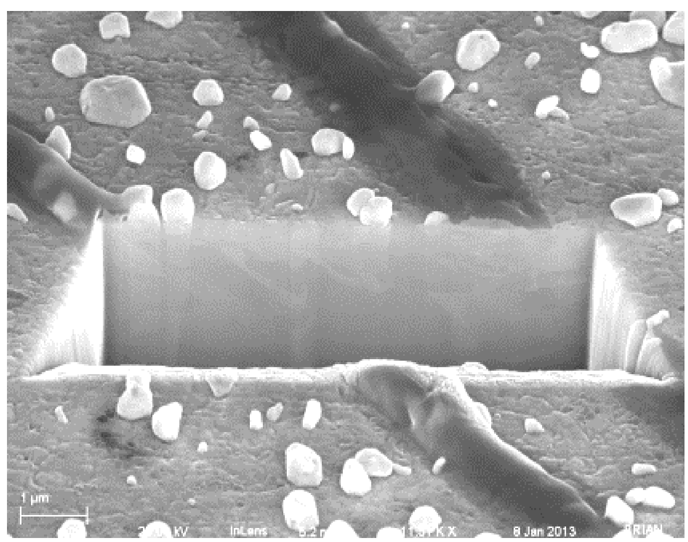

Fig. 15. FIB view of the ungilded plate, scale bar is one micron.

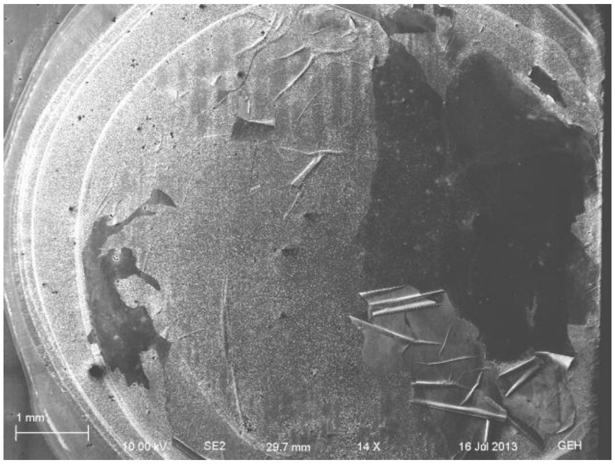

Fig. 16. SEM view of an over-gilded test region showing delamination, loss, and exfoliation on a Becquerel test sample.

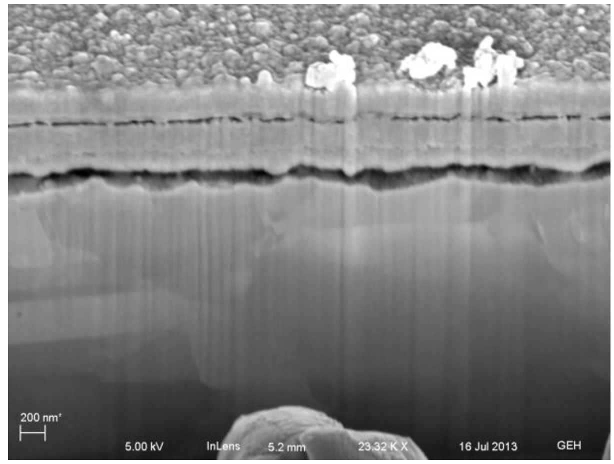

Fig. 17. FIB view of a region of intact gilding Ag-Au layer adjacent to the delaminated area.

Figures 16 and 17 are from an experiment that documented the effects of progressively adding gilding solution, in process, to the point of delamination and exfoliation. This work was carried out by Emily Thompson (Clemson University) during an NSF funded Research Undergraduate Education grant at the University of Rochester and George Eastman House. The results were startling in that there appeared to be a self-limiting thickness of the Ag-Au super layer visible in Figure 17, at which point a secondary super layer began to form. At the final stage, the entire composite structure pulled away from the base silver deformed and curled up into rolls as seen in Figure 16.

Conclusions

The presentation paper at AIC-PMG & ICOM-CC included a section on the archaeological and event history that the highly reactive surface records over time. That will not be addressed here. The primary new information coming from the NSF sponsored research on the daguerreotype through the SCIART investigation is summarized:

- We do not have a full understanding of the physico-chemical structure of the daguerreotype.
- We have yet to fully define and characterize the nature of the Ag-Au surface –which applies to the majority of daguerreotypes.
- We have yet to deduce the many avenues of deterioration by environmental agents, including light induced responses.
- Deterioration conclusively includes biological and organic interactions at the nano-scale.
- Scanning electron microscopy at 50,000X and above is necessary to study the nano-structure of the daguerreotype. It is the magnification required to detect the residual

record of an historic daguerreotype closest to its state at "first light", which should be the standard in considering treatment options.

- Research is revealing that immersion treatments that engage vigorously with the surface, irrespective of the chemical reaction or energy source, will profoundly alter the daguerreotype surface. Such treatments will inevitably move the daguerreotype to a state further removed from its "first light".

- Daguerreotypes have active surfaces in all habitable environments in which they can be viewed. Therefore there is a threshold of physico-chemical change happening at all times, unless there is a modified air environment surrounding the daguerreotype.

On the basis of this research, George Eastman House has embarked on the development of a low cost, aesthetically pleasing, archive use enclosure that is designed to hold a long-term argon atmosphere. It can be monitored from the exterior by an optical probe that senses oxygen accurate to 1/100 of a percent in air. The enclosure allows full view of the daguerreotype edge to edge, recto and verso. The enclosure can be recharged with argon through ports without disassembly.

The clear rationale for this solution, based on experience and research, is that the absence of oxygen and moisture will terminate biological activity, and prevent intermetallic or organic phase reactions that would progress in any modified or non-modified air environment, no matter how clean and ideal it may be perceived.

The application of this enclosure by George Eastman House was initiated through a National Endowment for the Arts "Save America's Treasures' grant to improve its imperiled 1,270 item Southworth & Hawes daguerreotype collection –which represents the largest holding of one daguerreotype studio, anywhere. The collection came to the Museum without any historic enclosures –the plates had been kept by the Hawes family in original plate boxes that had slots for vertical storage of the bare plates. They had been rehoused by the Museum in the 1970's in packages composed of buffered matboard, window glass, and a variety of edge binding tapes. These unique circumstances allowed for new concepts to be considered for preserving this treasure.

We acknowledge that it would be difficult to introduce a modified air environment for a typical American style cased daguerreotype. Alteration of an historical presentation is a very important ethical and value laden issue –but there is a real cost to not considering altering current practices with the least intervention and maximum gain to preserve the primary object. Much of the answer lies in engineering. Eastman House is currently researching ultra-thin, surface modified flat glass with extraordinary strength at 0.5mm thickness. Its use will permit an interior enclosure, exquisitely thin, that can reside as a low profile sealed argon enclosure within a typical daguerreotype case –with room for the original glass to be retained. Only in relatively few instances are daguerreotypes larger than their brass mats. Variations on this system can be readily adapted to the French passe-partout style housing, or any framed daguerreotype, to accommodate an interior argon preservation enclosure with minimal intervention.

The threats to the daguerreotype from nanoscale deterioration are real and ongoing, in spite of a perception that many daguerreotypes have not changed within collective memory. However there is no natural passivation for a daguerreotype, there is only less damaging and slower deterioration in both historical original cases, and current best practice archive packages.

In sum: There are emerging solutions and advanced scientific explanations that will improve the preservation prospects for the daguerreotype. Pursuing them is essential for this singular artifact of human ingenuity, artistic expression, and visual record that captured a mere twenty years of human existence –through nanotechnology.

Acknowledgements

The National Science Foundation; The Andrew W. Mellon Foundation; The Conn Center for Renewable Energy, University of Louisville; Dr. Gandong Zhang, Project Research Scientist, University of Louisville

References and Additional Reading

Anglos, D., K. Melessanaki, V. Zafiropulos, M. J. Gresalfi, and J. C. Miller. 2002. Laser induced breakdown spectroscopy for the analysis of 150-year old daguerreotypes. *Applied Spectroscopy* 56: 423-432.

Barger, S.M. and W.B. White. 1991. *The daguerreotype: Nineteenth-century technology and modern science*. Washington, D.C.: Smithsonian Institution Press.

Brodie, I. and M. Thackray. 1984. Photocharging of thin films of silver iodide and its relevance to the Daguerre photographic process. *Nature* 312 (20/27): 744-746.

Centeno, S. A. N., T. N. Meller, N. Kennedy, and M. Wypyski. 2008. The daguerreotype surface as a SERS substrate: Characterization of image deterioration in plates from the nineteenth-century studio of Southworth & Hawes. *Journal of Raman Spectroscopy* 39(7): 941-921.

Da Silva E., M. Robinson, C. Evans, A. Pejovic-Millic, and D. V. Heyd. 2010. Monitoring the photographic process, degradation and restoration of 21st century Daguerreotypes by wavelength-dispersive X-ray fluorescence spectrometry. *Journal of Analytical Atomic Spectrometry* 25(5), 654–661.

Fizeau, H. 1840. Paris letter. Academy of Sciences, August 18, 1840. *Literary Gazette; and Journal of the Belles Lettres, Arts, Sciences, etc*. (London) No. 1231 (22 August 1840): 545.

Gregory, E. A., C. S. DeRoo, and J. F. Mansfield. 2007. Characterization and restoration of 19th century Daguerreotypes by SEM, XEDS and FIB. *Microscopy and Microanalysis* 13(Suppl 2): 1422-1423.

Häkkinen, H. 2012. The gold-sulfur interface at the nanoscale. *Nature Chemistry* 4: 443-455.

Hogan, D.L., V.V. Golovlev, M.J. Gresalfi, J. A. Chaney, C.S. Feigerle, J.C. Miller, G. Romer, and P. Messier. 1999. Laser ablation mass spectroscopy of nineteenth century daguerreotypes. *Applied Spectroscopy* 53: 1161-1168.

Konkol, N. P., B. Bernier, E. Bulat, and R. Mitchell. 2011. Characterization of Filamentary Accretions on Daguerreotypes. *Journal of the American Institute for Conservation* 50(2):149-159.

Rai, M., A. Yadav, and A. Gade. 2010. Mycofabrication, mechanistic aspect and multifunctionality of metal nanoparticles –Where are we? And where should we go? In *Current Research, Technology and Education in Topics in Applied Microbiology and Microbial Biotechnology*, vol 2, ed. A. Méndez-Vilas. Microbiology Book Series. Formatex. 1343-1354.

Prathna T.C., L. Mathew, N. Chandrasekaran, A. M. Raichur, and A. Mukherjee. 2010. Biomimetic synthesis of Nanoparticles: Science, technology & applicability. In *Biomimetics Learning from Nature* ed. A. Mukherjee. http://www.intechopen.com/books/biomimetics-learning-from-nature/biomimetic-synthesis-of-nanoparticles-science-technology-amp-applicability (accessed 11/21/2013).

Ravines, P, Wiegandt, R., Hailstone, R., and G. Romer. 2008. Optical and surface metrology applied to daguerreotypes. In *Conservation Science 2007: Papers from the Conference held in Milan, Italy 24–26 May 2007*. London: Archetype Publications, 131-139.

Das, S. K. and E. Marsili. 2011. Bioinspired Metal Nanoparticle: Synthesis, Properties and Application. In *Nanomaterials* ed. Mohammed Rahman. http://www.intechopen.com/books/nanomaterials/bioinspired-metal-nanoparticle-synthesis-properties-and-application (accessed 11/21/2013).

Swan, A., C. E. Fiori, and K. F. J. Heinrich. 1979. Daguerreotypes: A study of the plates and the process. *Scanning Electron Microscopy* 1: 411-23.

Turovets, I., M. Maggen, and A. Lewis. 1998. Cleaning of daguerreotypes with an excimer laser. *Studies in Conservation* 43(2): 98-100.

Zhang, G., J. B. Jasinski, J. L. Howell, D. Patel, D. P. Stephens, and A.M. Gobins. 2012. Tunability and stability of gold nanoparticles obtained from chloroauric acid and sodium thiosulfate reaction. *Nanoscale Research Letters* 7(1):337.

Ralph Wiegandt
Senior Project Conservator
George Eastman House
Rochester, New York, USA

Dr. Nicholas Bigelow
Lee A. DuBridge Professor of Physics, Professor of Optics
University of Rochester
Rochester, New York, USA

Brian McIntyre
Senior Engineer
URNanocenter, University of Rochester
Rochester, New York, USA

Papers presented in *Topics in Photographic Preservation, Volume Fifteen* have not undergone a formal process of peer review.