



Article: A Twin Paradox: A Study of Preservation and Disfigurement of Southworth and Hawes Daguerreotypes

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A Twin Paradox: A Study of Preservation and Disfigurement of Southworth and Hawes Daguerreotypes

Mike Robinson and Edward P. Vicenzi

Presented at the 2015 PMG Winter Meeting in Cambridge, Massachusetts.

Abstract

The Young America exhibition of Southworth and Hawes daguerreotypes in 2005 established new protocols for condition monitoring of daguerreotypes during the course of the traveling exhibit. The carefully annotated photographic records created for every image prior to exhibition provided direct evidence of spotting and hazing on the surface of a few of the daguerreotypes while on public display. In the aftermath of the Young America exhibition, the stability of daguerreotypes, once thought to be among the most enduring type of photograph, came into question. As a result of this uncertainty, curators are reticent to exhibit daguerreotypes and conservators have begun to work in collaboration with material scientists to determine the mechanism of this deterioration.

Lot Number 75 of the David Feigenbaum Collection of Southworth and Hawes daguerreotypes, sold at Sotheby's in 1999, was comprised of two nearly identical full plate daguerreotypes entitled Four Women Posed around a Table. What makes them nearly identical is that these plates were produced as a stereo pair especially for viewing in the Grand Parlor and Gallery Stereo viewer. These plates are literally twins, exposed within seconds of each other and processed one directly after the other. Yet despite their commonality, one plate developed the problematic disfiguring white haze, while the other was found in nearly pristine condition. In addition to being made at the same time with the same materials and methods, the plates have been stored in the same environment for the duration of their existence. Until now, the cause of the deterioration of one of the two plates has been speculative. This pair provided a unique opportunity to study the mechanism that produces the hazing problem associated with Southworth and Hawes daguerreotypes.

Our collaboration involving careful characterization of the full plate stereo pair, in addition to novel experimental replication methods, has uncovered a mechanism that accounts for the white haze disfigurement. For the first time, Southworth and Hawes full plate daguerreotypes have been imaged and analyzed using scanning electron microscopy and X-ray microanalysis. Morphological information within the images and chemical data obtained on the nineteenth century plates led to replication of the mechanism of deterioration using modern daguerreotypes. This new understanding allowed us to adopt a simple and successful conservation treatment to ameliorate this vexing problem. This is noteworthy because the problem has been considered untreatable given the haze has been associated with photo-reduced silver. The results of this study suggest that damage due to light sensitivity of daguerreotypes should be reconsidered.

1. Problem: Daguerreotypes Observed to Deteriorate During Exhibition

Carefully annotated photographic records created in preparation for the *Young America* exhibition and catalogue provided direct evidence of spotting and hazing on the surface of a few of the daguerreotypes while on display. This was not the first occurrence of the problem however; Southworth and Hawes scholar, Dr. Charles L. Moore noticed a full plate daguerreotype of Lola Montez forming a white haze during the Spirit of Fact exhibition in 1976. (Romer 2014) In the aftermath of the *Young America* exhibition, the stability of the daguerreotype, once thought to be among the most enduring type of photograph, came into question. As a result of this uncertainty, curators became reticent to exhibit daguerreotypes and conservators began to work in collaboration with material scientists to determine the mechanism of this hazing phenomenon.

Of the 160 daguerreotypes on view, it was reported that “25 daguerreotypes had been damaged, five of them critically” over the course of the two-and-a-half year exhibition. (Grushkin 2012, 71) This was distressing news for the organizers of the exhibition, the owners of the plates, and for all who value daguerreotypes.

2. Preliminary Study: Chlorine is Found in Deteriorated Daguerreotypes

To shed light on the issue, two plates that had formed haze during the exhibition, from the collection of the George Eastman Museum, were sent to Silvia Centeno at the Metropolitan Museum of Art for analysis, along with a group of six daguerreotypes from the Met’s own collection showing similar deterioration. The results from this analysis indicated that silver chloride was present in the affected areas, and preliminary results were first published in *Topics in Photographic Preservation*, Volume 12 2007. In that article, a pre-exhibition photograph, taken in March 2005, of a daguerreotype of a seated woman is shown next to another photograph of the same plate taken in June. The images clearly show that pre-existing faint white haze had significantly worsened in one month’s time. (Wiegandt and Meller 2007) Another daguerreotype was shown to have developed whitish rings or halos around pre-existing nuclei of undetermined contamination. At this point, the source of the chlorine on the plate was speculative; residual processing chemicals, prior conservation treatments, the environment, and housing materials were all suggested possibilities.

3. Research: The Mechanism of Deterioration Is Proposed

Centeno et al published these findings in 2008 (Centeno et al. 2008) and followed-up with a study in 2011 attempting to replicate the chlorine-induced haze. (Centeno et al. 2011) The first study posited that the formation of silver chloride on the plate was possibly due to environmental chlorine from Boston’s saline atmosphere and the mechanism for the formation of the haze and white spots was the formation of print-out silver while on display, described by the authors as “redeposited silver”. The authors conclude;

These findings have profound implications for the exhibition and preservation of the daguerreotypes due to the photosensitivity of AgCl in the ultraviolet–visible range, which can generate metallic silver that would redeposit on the surfaces of the plates. (921)

Centeno et al. made use of daguerreotype samples I prepared using 19th century materials and recipes for their 2011 follow-up study. SEM micrographs showed that these modern samples, compared to a 19th century daguerreotype, had similar image particle morphology and gilding layer microstructure, and therefore, would serve as a “suitable system[s] for mimicking the deposition of chlorides in real artworks”. (63) Modern samples were placed in a vacuum desiccator containing a saturated salt solution for three weeks. Cubic AgCl crystals formed over image particles as well as at surface defects in non-image areas, clearly indicating that the formation of silver chloride is independent of image areas on the daguerreotype (61). The study also reported that silver metal was redeposited from AgCl in seconds when struck by the electron beam of the scanning electron microscope. Extended exposure to the SEM electron beam (several minutes) formed a particle large enough at 400 nm, for EDS analysis within the SEM to determine it to be pure silver. (62) This study showed that AgCl can be reduced by the electron beam within a SEM; that museum illumination is sufficient to cause the same reaction was not rigorously addressed.

A two step scenario for the hazing has been postulated by Wiegandt; near-UV light may at first induce the formation of visible silver chloride crystals from chlorine contamination in the plate, and then museum illumination causes the re-deposition of silver from the silver chloride compounds. (Wiegandt and Meller 2007) If the haze is redeposited silver, it follows that such damage is irreversible. Wiegandt states that the only option for the long-term preservation of daguerreotypes is to enclose the plates in an inert argon gas atmosphere to prevent further degradation. (Grushkin, 2012, 73)

4. Reaction: Daguerreotypes are a Problem due to their Microstructure

If photolysis of silver chloride (redeposited silver) is the cause of the visible haze, then one would have to conclude that these plates are light sensitive. So, after these studies were published, curators and conservators began to mount daguerreotypes on walls covered with a dark curtain to block out light. This practice sends a clear message to the viewing public that all daguerreotypes are sensitive to light. Worse yet, the rigorous protocol deemed necessary to monitor changes over the term of an exhibition has resulted in the postponement of an important daguerreotype show due to the additional expenses and potential risk involved. This approach is appropriately conservative in light of the findings at this time. The issue reached the awareness of the general public when published in *The Scientific American* in 2012, and then in the *New Yorker* in 2013; both articles reporting nearly the same story...

The Case Of The Disappearing Daguerreotypes, in *The Scientific American*, December 2012
Scientists theorize that the process draws silver to the surface to form subsurface voids. In the case of Southworth and Hawes, these voids may have trapped chlorine from Boston’s salty air. Light would then re-expose the sensitive silver chloride and form a haze that mars the image. (73)

A Portrait of Immortality, Faded, in *The New Yorker*, June 2013
Bigelow, Wiegandt, and others have theorized that the Eastman House images, originally taken in Boston, trapped chlorine from the sea air in their subsurface voids. When the images

were exposed to light, the chlorine reacted with the silver plate and clouded the surface.
(Nijhuis 2013)

Grushkin's article in *The Scientific American* reproduced a FIB-SEM section of a daguerreotype with sub-surface voids. Ralph Wiegandt suggested that voids beneath the surface daguerreotype may have trapped chlorine from Boston's salty air and during exhibition reacted with light to form the haze. Sub-surface voids in the daguerreotype were first identified with FIB-SEM in late 2007. The research was conducted by Patrick Ravines, then at the George Eastman House, with assistance from the Kodak Research Laboratory personnel.

I shared my own research on modern daguerreotype samples with Ralph Wiegandt and Patrick Ravines having been apprised of this discovery.

Hi Ralph & Patrick

I now suspect the pattern found in the substrate on a SEM daguerreotype mid-tone image as due to gold toning not cyanide etching as proposed by Barger & White. See this set of SEM images of a pristine condition newly made daguerreotype.

The pattern shows up only on gold toned plates using higher than 5 kV on all three sets of images I've studied so far. Does this mean the gold is penetrating the sample, causing voids, or what? Maybe the voids that Patrick has witnessed on cross sections is actually gold?
(Robinson 2008)

SEM imaging showed these voids in the late 1980s and early 1990s, though the cause was misidentified as due to conservation intervention. In *The Daguerreotype: Nineteenth-century Technology and Modern Science*, first and second editions, Barger and White reported that "the darker pattern on the substrate ...caused by cyanide cleaning treatment" was distinct on 98 percent of the daguerreotypes they imaged in the SEM. (2000, 187) Actually, the pattern thought to be cyanide etching is the imaging of the void field below the surface of the plate due to the penetration of the electron beam. The void field lies just below the gilding layer and is roughly 200 nm thick. The electron beam penetrates the sample relative to the voltage setting with greater voltage penetrating deeper into the sample. Barger and White's SEM images were created using a 40 keV electron beam. I have made SEM images of 19th century daguerreotypes and pristine modern samples, both gilded and ungilded, for my dissertation research. The dark pattern emerges around 9 keV when gradually stepping up the electron beam voltage in 1 keV increments, and becomes increasingly more pronounced with each increment, for *gilded* daguerreotypes. Figure 1 shows a modern un-gilded daguerreotype imaged at 30 keV having no visible dark pattern (upper left), a modern gilded daguerreotype imaged at 30 keV with a visible dark pattern (upper right) and the same plate imaged at 5 keV without it (lower left). The lower right image is an SEM image from Barger's research imaged at 40 keV. (*Note: The SEM at Ryerson has a maximum electron voltage of 30 keV*).

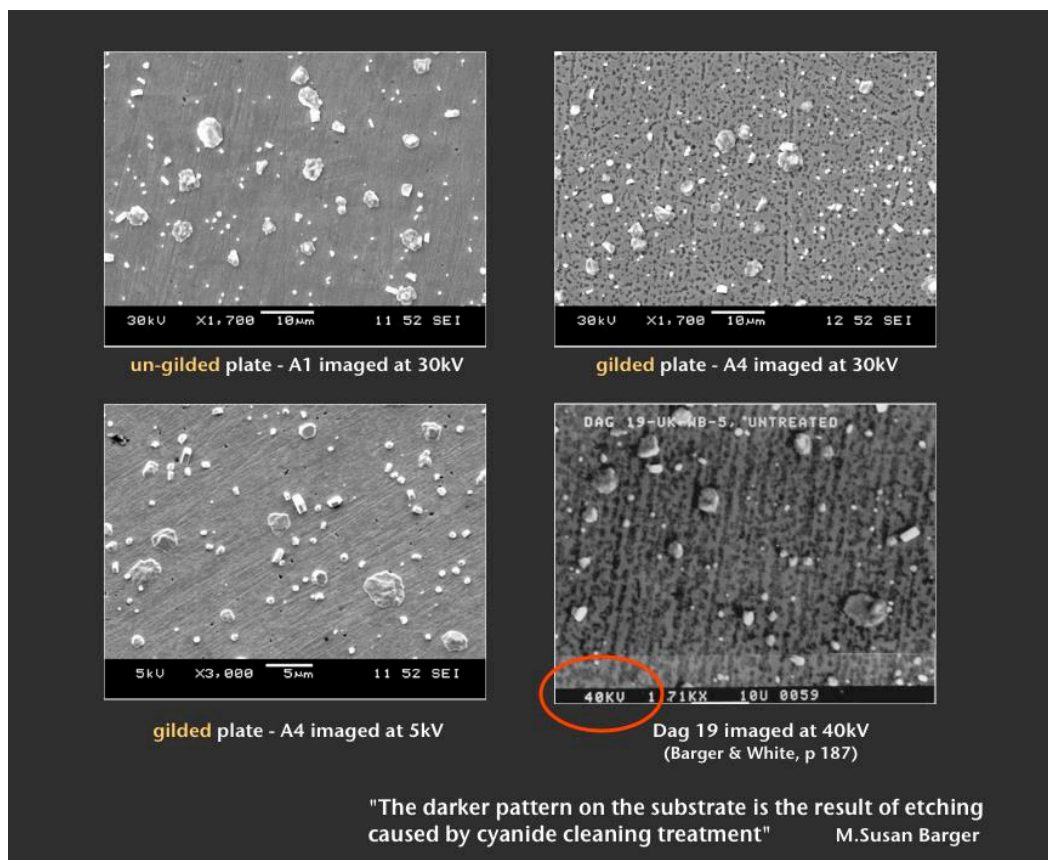


Fig. 1. Gilded and ungilded SEM images of modern daguerreotypes, courtesy of Qiang Li, Ryerson University, (lower right) 19th century daguerreotype courtesy of Susan Barger, from *The Daguerreotype: Nineteenth-century Technology and Modern Science*, 187.

Ungilded daguerreotypes do not have sub-surface voids. The dark pattern is absent, regardless of the penetration depth of the electron beam, clearly showing that the gilding process causes the sub-surface voids. Ed Vicenzi et al. (2014 a, b), using more advanced focused ion beam microscopy (FIB), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) and nano-X-ray fluorescence spectrometry (nano-XRF), was able to determine the chemical makeup and nanostructure of daguerreotype image particles, the silver substrate and voids, and the layer produced by gold toning. (Vicenzi et al., 2014a) The gilding layer covers not only the surface of the silver-mercury amalgam image particle, but also the interface between the image particle and the plate, effectively bonding the image particle to the plate surface. This diffusion-driven process explains why gilded daguerreotype image particles are far more difficult to dislodge from the plate than ungilded image particles. Vicenzi, continuing his research, found the gilding layer to be comprised of roughly two-thirds silver to one-third gold. (Vicenzi and Robinson, 2015) The high silver content of the gilding layer explains the formation of the sub-surface voids as silver atoms migrate from the plate to mix with gold in the process. Silver available in the gilding layer also accounts for the formation of silver sulfide and silver chloride deterioration. Cross section and top-down SEM imaging, with stepping electron beam penetration, show that the void field is essentially *sealed* beneath a gilding layer that is ~85 nm thick. It seems unlikely the voids serve as traps for chlorine from Boston's salt air to be later activated by museum light and form the haze on the surface. It is far more plausible that chlorine

and sulfur contaminants react with the silver available in the gilding layer *on the surface* of the daguerreotype.

5. Contrary Evidence: Is the Hazing Really Light Induced?

The suggestion that daguerreotypes are light sensitive is contrary to my experience. Nineteenth-century and modern well-sealed daguerreotypes, displayed on my north-light studio wall for over twelve years, receive continuous light exposure, and have remained unaltered. I have observed that white haze is not always induced by light exposure. There are several sixth-plate daguerreotypes from the Southworth and Hawes archive, held at the George Eastman Museum, that were received unsealed in wooden plate boxes that have rarely seen the light of day, yet are obscured by a white haze. Furthermore, a series of photographs taken between 1999 and 2013 of a whole-plate daguerreotype illustrate that hazing can continue to advance in dark storage, and is not necessarily a light induced phenomenon.

A hand tinted full-plate daguerreotype, titled *A Woman in Damask Evening Gown, Posed with a Chair*, Lot 52 in the David Feigenbaum Collection of Southworth and Hawes auction at Sotheby's New York on September 27, 1999 was purchased by collectors Michael Mattis and Judith Hochberg. The photograph taken for the auction catalogue provides a good record of the state of hazing deterioration in 1999. The presence of applied colour on this image indicates that it has not undergone any previous aqueous conservation treatment, as this tends to wash away applied colour. This plate was photographed for the *Young America* exhibition and catalogue in 2005, which clearly shows that hazing on the daguerreotype had advanced to obscure the hem of the lady's dress. Michael Mattis and Judith Hochberg, who were living in the dry climate of the American southwest at the time, assured me that the plate had not been on display during the years between the Sotheby's sale and the *Young America* exhibition. So, this change occurred while the plate was stored in a drawer, away from light. This was *not* one of the five plates reported to have changed critically during the *Young America* exhibition. Apparently the plate had remained stable, so an outgoing condition report and post-exhibition photograph was not done. If any change had occurred during the exhibition it had gone unnoticed by the curators, conservators and the owners.

However, in 2013 the plate was sent to me for consultation. I photographed the plate and it is plainly evident that further change has occurred during the interval between 2006 and 2013. Once again, the plate was kept in dark storage. In this instance, as stated, there was no noticeable change over the course of the *Young America* exhibition, however the plate had continued to deteriorate in dark storage, which contradicts the notion that the haze is due to light induced, redeposited silver. Figure 2 shows the progression of haze that occurred during dark storage from 1999 to 2005, and after exhibition to 2013.



Fig. 2. Southworth and Hawes, *A Woman in Damask Evening Gown*, whole-plate daguerreotype ca. 1850, from the collection of Michael Mattis and Judith Hochberg, courtesy of Sotheby's (*left*), courtesy of the George Eastman Museum (*center*), courtesy of the first author (*right*).

Lot Number 75 (fig. 3) in the David Feigenbaum Collection of Southworth and Hawes daguerreotypes was comprised of two, nearly identical, full-plate daguerreotypes titled *Four Women Posed around a Table*. Michael Mattis and Judith Hochberg also acquired this pair at the auction. These plates are nearly identical because they were produced as a stereo pair especially for viewing in the Grand Parlor and Gallery Stereo viewer. These plates are literally twins, exposed within seconds of each other and processed one immediately after the other. Yet, despite their commonality, one plate developed the problematic disfiguring white haze, while the other was found in nearly pristine condition.

In addition to being produced at the same time, with the same materials and methods, the plates have been stored in the same environment for their entire existence. Photographs taken in 1998, by art dealer John Cira and given to Christopher Mahoney of Sotheby's during an initial condition survey of the collection, indicate that the severely deteriorated plate had changed while in storage; either during the interval between the 1860's until the mid-1930's when the collection was transferred to Holman's Print Shop for sale, or from that point until 1999 when they were discovered in a David Feigenbaum's garage, or both.

This pair, having been made at the same time and stored together under the same environmental conditions, offered us a unique opportunity to investigate the hazing problem associated with Southworth and Hawes daguerreotypes.



Fig. 3. Southworth and Hawes, Left and right images of the full plate stereo pair, *Four Women Posed around a Table*, whole-plate daguerreotypes ca. 1853 from the collection of Michael Mattis and Judith Hochberg. Courtesy of the first author.

6. New Research: Understanding the Twin Paradox

Michael Mattis agreed to send the plates to the Metropolitan Museum of Art for non-destructive analysis. The analysis was inconclusive. Raman spectroscopy showed the presence of silver chloride but the system was unable to distinguish the relative quantities on clean versus hazed areas. (Sessa and Centeno 2013) I brought the plates to Washington, DC where Ed Vicenzi and I adapted the sample platform of the scanning electron microscope at the Museum of Natural History to safely examine, with greater precision, the full plate daguerreotypes using SEM imaging and microanalysis. The SEM images (fig. 4) of the disfigured right side stereo plate of an apparently clean mid-tone area (C7) and hazed area (E7) were distinctly different: the hazing is comprised of sub-micron amorphous particles roughly one-tenth the size of the image particles. The apparently clean area (C7) did not appear to be any different than the SEM images made from the same area on the pristine left hand stereo plate.

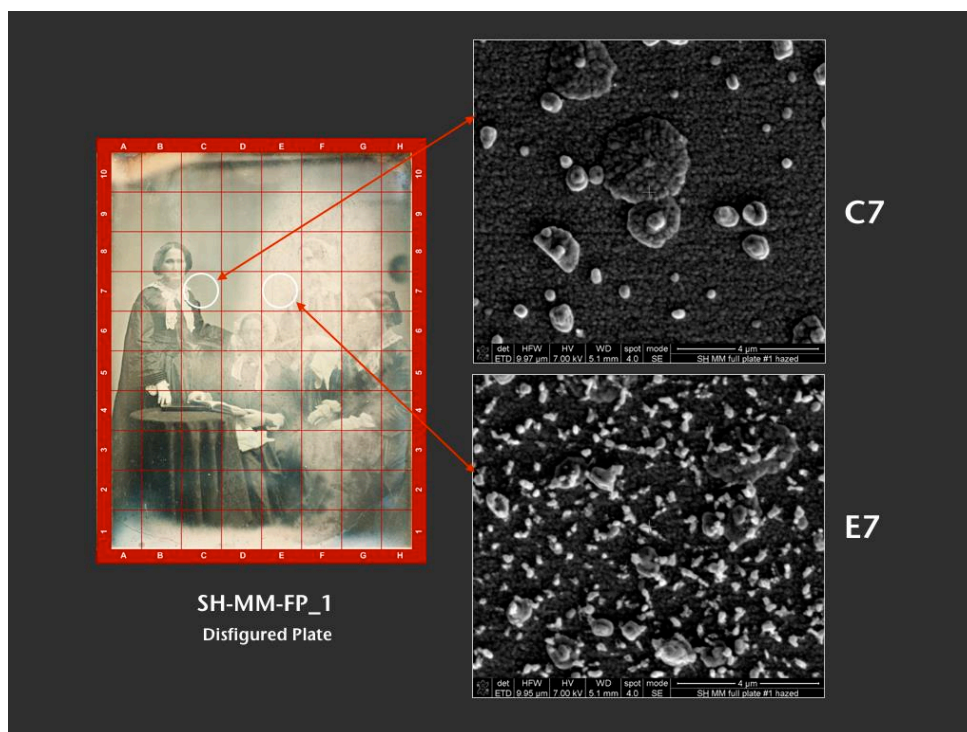


Fig. 4. Secondary electron imagery ($E_0=5$ kV) of the disfigured plate. Relatively clean area C7 (*top*), and strongly hazed area E7, of disfigured plate (*bottom*), courtesy of the authors.

Significantly, this was the first analysis of the chlorine contamination to link surface morphology to chemistry. Vicenzi, with SEM-EDX microanalysis, determined that the hazed area (E7) contained *five-times* more chlorine than the apparently clean area (C7) on the disfigured plate, and further, that the pristine plate had *zero* chlorine present. (Vicenzi and Robinson 2015) The morphology of chlorine containing particles in the SEM images reminded me of a similar microstructure I had seen on my own research samples made in 2010. In order to observe the silver halide morphology, I prepared iodized and iodio-bromized plates, unexposed and unfixed, and placed them in a scanning electron microscope. The amorphous silver-halide particles on my samples looked distinctly similar to the haze particles on the disfigured full-plate. This observation and the new SEM-EDX data led us to conclude that chlorine contamination was likely compounded as AgCl. These results confirmed the haze was due to silver chloride, but how one plate was affected and the other pristine was still a mystery at this point.

7. Revised Model: The Mechanism of Deterioration is Discovered through Replication

With the data from the 19th century stereo pair, I planned to replicate the formation of silver chloride on daguerreotypes made according to Southworth and Hawes practice. (Robinson 2005) I hoped they would serve as samples to test conservation treatment options for the historical photographs. I suspected that the tideline hazing on the disfigured plate had conformed to invisible drying traces, and wanted to see if I could replicate this patterning with chlorine contamination.

While creating the test daguerreotypes, I held them with pliers and applied heat with an alcohol lamp to replicate 19th century drying practice. I then cut the plate in two and exposed one half to chlorine vapor by suspending it for twenty minutes over two grams of calcium hypochlorite contained within a glass jar, similar to daguerreian practice when sensitizing a plate with halogen vapor. I removed the plate and observed that the light brown colour of AgCl had formed on the plate, non-uniformly, more or less intense following invisible traces left by the drying process. I quickly photographed the chlorinated plate, along side the clean half, and placed it in dark storage. (fig. 5) Two days later, I was amazed to see a pronounced white haze had formed on the chlorinated plate according to the drying pattern. I re-photographed the plate and returned it to dark storage. After two more days the haze had worsened, and the plate was even more hazed ten days later, when taken to Ryerson University in Toronto for SEM analysis.



Fig. 5. Haze progression on chlorinated modern daguerreotypes. Courtesy of the first author.

The analytical spectrum obtained from my chlorinated modern plate using the SEM at Ryerson University matched the spectrum obtained from the disfigured Southworth and Hawes full plate at the Smithsonian. The chlorinated samples mimicked the deterioration on Southworth and Hawes plates, but aged in an accelerated manner. The morphology of AgCl induced on my plates is cubic and more atomically ordered than the amorphous material found on the 19th century plate, possibly due to the rate of the crystal growth. I produced the white haze deterioration on a new plate in just two days time, while the haze on the Southworth and Hawes daguerreotypes took some decades to form. Nevertheless, the chlorination did follow invisible traces from drying the plate as suspected, similar to the disfigured half of the stereo pair of *Four Women Posed around a Table*, and the hazing advanced while in dark storage as observed with *A Woman in Damask Evening Gown, Posed with a Chair*.

The research published in 2008 and 2011 by Centeno et al, implies that the disfiguring white haze is caused by redeposited silver from light exposed silver-chloride compounds. My experiments mimicking the problem seemed to contradict this notion, as the hazing occurred while the samples were stored in the dark. However, I had to consider the possibility of light induced haze, as my samples were exposed to daylight for photo-documentation. I prepared another experiment to investigate the reaction of light exposure on a daguerreotype image contaminated with silver chloride. I masked off half of a uniformly imaged mid-tone and gilded test plate and exposed it to chlorine vapor under safelight. I then covered the plate, perpendicular to the chlorination, to completely block light on half of the plate, and placed it in my studio window for 24 hours. The light intensity averaged 50x greater than the lux during the *Young America* exhibition. I packed the sample and shipped it overnight to Ed Vicenzi, in Washington,

for SEM imaging and analysis. The un-chlorinated side of plate provided a baseline for the chemical composition and microstructure of a pristine plate. The un-exposed and the daylight exposed chlorinated samples were covered in AgCl crystals; however, the side exposed to daylight had fewer, but larger, crystals indicating a coarsening with a corresponding increase in apparent haziness. (fig. 6)

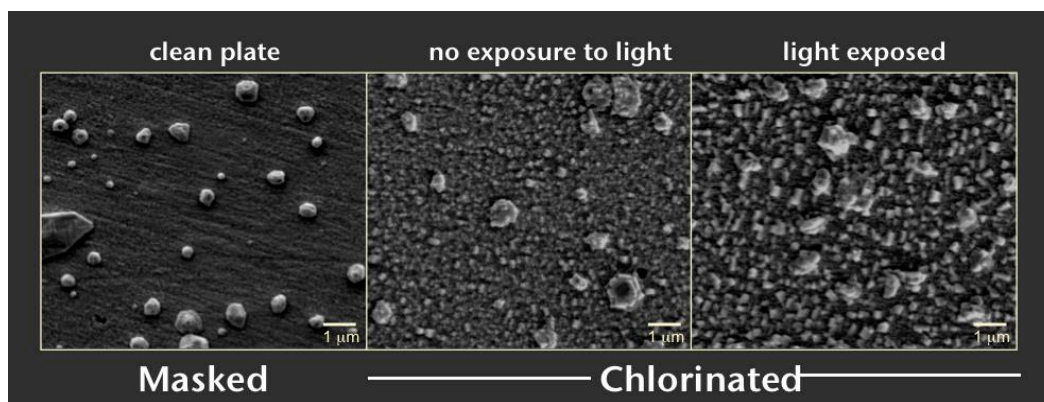


Fig. 6. SEM images of a modern daguerreotype showing clean vs AgCl formation in dark and light environments. Courtesy of Ed Vicenzi, Smithsonian Institution.

Significantly, microanalysis showed that the chlorine *counts* remained nearly the same for both the light exposed and un-exposed side. If the haziness was the result of print-out silver, as suggested by Wiegandt and Centeno, it should be expected that the chlorine counts would be *less* on the daylight exposed side of the plate. When light is incident on a halide molecule, such as silver chloride, different chemical reactions are possible. The most well known to photographers is a photolytic reaction, where high energy short-wave radiation breaks the chemical bond and prints-out silver deposits on the substrate while releasing the halogen into the atmosphere. This photolytic reaction is the foundation of the latent image in photography and the visibly darkened image in AgCl print-out photographs, such as salted paper prints. Chlorine net counts on the light exposed plate represent 93% of the chlorine kept in dark storage. These results indicate that photoreduction of AgCl to Ag plays a minor role even under the greatly enhanced light flux of the experiment. Furthermore, the micrographs show haziness is caused by larger particles that can more efficiently scatter light of all wavelengths, producing a white appearance on a daguerreotype. Print-out silver particles on an iodized daguerreotype plate are *several times* smaller and appear dark, creating a negative image, as Niépce and Daguerre understood, before mercury vapour was discovered as a means to amplify the latent image. Large mercury developed image particles also scatter light and appear brighter than the dark reflections in the polished plate.

Not previously considered is an alternative photo-activated reaction with AgCl crystals present on a daguerreotype plate. Rather than photolytic, a photochemical reaction causes the excitation of the electrons in a chemical bond raising their energy level coupled with increased lattice defects, causing the AgCl crystals to recrystallize and coarsen at a greater rate relative to unilluminated AgCl. Small particles are more entropic, having a greater surface area to mass ratio, and tend to combine with each other to form fewer but larger particles over time. This is a spontaneous process known as *Ostwald ripening*. Photographic film producers maintain the gelatine emulsion at melting temperature for extended time to promote Ostwald ripening and

produce high-speed, large grained films. A sensitized daguerreotype plate increases in photosensitivity when it is kept in the dark for an hour before exposing, perhaps due to the same spontaneous Ostwald ripening process.

The mechanism for the appearance of increased haziness or white spots is not print-out redeposited silver; it is the AgCl present on the plate that is coarsening into larger, light scattering particles, as has been demonstrated with the modern chlorine contaminated daguerreotype samples. The coarsening is accelerated by light, but it will spontaneously occur in the dark, provided there is enough AgCl present to recombine into larger particles.

8. Chlorine Source: Storage Conditions are Key

Having replicated and determined the cause for the white haze on daguerreotypes, the question remained as to the source of the chlorine on the affected 19th century daguerreotypes. Many of Southworth and Hawes' daguerreotypes, when taken from the storage boxes, have silver-sulfide tarnish that conforms to the perimeter of the opening of a brass matt and sealing tape residue on the back. This indicates that these daguerreotypes had at one time been matted and glazed, likely displayed in the studio as an exemplar of their work or a portrait of a noteworthy individual. It is plausible that the daguerreotypes were removed from display after Southworth and Hawes updated their process with collodion negatives and albumen paper prints. The bulk of the Southworth and Hawes studio archive was stored unglazed, in wooden plate boxes supplied by the plate manufacturer. Some of the whole plates were in custom made tin boxes designed to house eighteen plates per box; more if placed back-to-back in the grooves. There were no custom tin boxes made for plates smaller than whole-plate. Christopher Mahoney recorded the box type and identifier for each of the sixty-eight whole plates in the Feigenbaum sale; twenty-two plates in "Tin Box A", twenty-four in "Tin Box B" and twenty-two in "Wooden Box 6A". (Mahoney 2013) I acquired one of these tin boxes after the Feigenbaum sale and noticed on the lid in Hawes' handwriting is "Selections for Copy". This is a clue that some of Southworth and Hawes' important images were unframed for copying, then stored bare in this tin box perhaps in the late 1850's. Also written in pencil on the box side, in another hand, most likely Lewis Holman's, is "Known" and "Known Men" (which is crossed out) and "Groups XVIII" is written on the lid. Holman wrote "Hopeful" on a half plate box, and "Known" on a quarter-plate box, which shows that he used the boxes to sort and re-sort the collection for the sales catalogues "Within the Compass of a Print Shop" held in the 1930s and 1940s, and also to ship plates to prospective buyers. Mahoney recorded that the Mattis-Hochberg stereo pair was not found in the same box. The pristine plate was found in "Tin Box A" and the disfigured plate was found in "Tin Box B". Another stereo pair from the sale was Lot 19, *The Letter* and Lot 20, *The Letter, (Chair on Left Closer to the Edge of the Frame)*. Lot 19 was found in "Tin Box B" and Lot 20 was in "Wooden Box 6A". It seems illogical that stereo pairs would be separated while at the studio, so finding these pairs in separate boxes is very likely due to the sorting and re-sorting of the collection later at Holman's Print Shop. Letters from Richard Holman to collector Zelda MacKay in 1944 indicate that Holman's shipped bare plates in boxes to interested collectors and museums for consideration based on their interests. (Murata 2003, 40-1) The point of this preamble is to make clear that all Southworth and Hawes plates, smaller than whole plate size, were stored in wooden plate boxes and that whole-plates may have been kept in custom built tin or manufacturer supplied wooden boxes, based on Hawes' preference. The plates were re-positioned later by

Holman into wooden or tin boxes based on sales potential. The construction material of the storage box is germane to this investigation.

Within the ex-Matthew R. Isenburg Collection are twenty-four, unused, ninth-plates (not from the Southworth & Hawes studio) still in the original manufacturer's box. (fig. 7) The first plate in the row faced the adjacent sidewall of the box and is the most contaminated, with less deterioration on the plates behind it. All of the un-polished plates have two distinct bands of haze deterioration lengthwise where the plate had been in contact with the wooden grooves of the plate box. The centers of the plates that were behind others in the box are pristine. Ed Vicenzi and I analyzed one of these plates in Washington, DC and another plate was sent to Dusan Stulik and Art Kaplan at the Getty Conservation Center in Los Angeles, CA. The analysis of both plates showed high levels of chlorine near the edge that had been adjacent to the wooden grooves of the plate box, and no chlorine in the center of the plate.



Fig. 7. Box of unused 19th century ninth-plates (left), courtesy ACM-Toronto; 19C plate showing formation of haze on edges (right), courtesy of the author

It is clear that un-glazed daguerreotype plates in close proximity to softwood can be contaminated with chlorine. The hazing on *A Woman in Damask Evening Gown, Posed with a Chair* occurred on the sides and bottom of the plate where the metal was in direct contact with the box, while the top edge was clean due to the gap between the plate and the box lid. The disfigured stereo plate, *Four Women Posed around a Table*, was found heavily hazed in the center as well as the left, right, and bottom edge. Based on circumstantial evidence from the box of unused ninth plates, I believe that this plate may have been stored for some time in the first groove of a plate box with its silver side adjacent to the wooden side panel. This is conjecture as the plates have been shuffled during the selling process at Holman's Print Shop. The custom tin boxes also have grooved wood on two opposite sides to separate the plates; the other four sides are tinned metal. The lids are very close fitting and provide a much better seal against the atmosphere than the manufacturer's wooden boxes. Softwood may inherently contain chlorine, though there is evidence to show how wood is able to absorb halogen vapor, then transfer it to a

silver plate in close proximity. Daguerre understood this principle. In late 1839, he found a quicker way to iodize his plates. He replaced his large 4.8 liter iodizing box with a thin pine board that had absorbed iodine vapor. In placing a polished plate in close proximity to a board saturated with iodine, Daguerre found that he could achieve his desired silver-iodide coating in one-tenth the time required for his large volume box. (Arago 1839, 824)

I have shown evidence that chlorine contamination occurs when a bare daguerreotype plate is stored in close proximity to chlorine bearing wood, and that wood can be a getter for atmospheric chlorine is informed by Daguerre's use of iodine saturated softwood to sensitize his plates. The fact that all of the Southworth and Hawes whole-plates have not suffered from haze formation, and that only one of two identically prepared stereo plates was disfigured, can be explained by the material of the storage box, wood or metal, and the plates' position within the box.

9. Treatment: Conservation of the Disfigured Plates

Bright daylight conditions, unlike those used in exhibition halls, caused no more than 7% silver to re-deposit from AgCl on my samples, but it did accelerate coarsening of the silver chloride particles. This means that haze formation is restructured AgCl and therefore treatable with a suitable solvent. Silver chloride is soluble in photographic fixer, and indeed, when I dipped and edge of one of my chlorinated test samples into a 3% w/v solution of sodium thiosulfate the haze instantly cleared, however, I was reticent to treat the historic plates in sodium thiosulfate solution because it contains sulfur. Sulfur bearing solutions used for fixing and gilding daguerreotypes can become stale. These when used stale, and thiourea, can cause black specks of concentrated sulfur to form on daguerreotypes. As a cautionary side note, thiourea has been found to remove gold from a daguerreotype. (Da Silva et al. 2010, 660) Silver chloride is also soluble in ammonium hydroxide solution, (NH₄OH) and in testing, was equally effective in removing the haze from my chlorinated samples.

Ammonium hydroxide solution has been used to treat other daguerreotypes, and was particularly effective in dissolving the obscuring white haze on a trove of John Ruskin daguerreotypes. The Ruskin plates were discovered un-glazed in a wooden box separated only by thin paper on the verso; a remarkably similar storage scenario to the Southworth and Hawes archive. They too suffered from an opaque white haze that formed according to contact with the paper backing between the stacked plates. Conservator Angels Arribas poured a 10% solution of NH₄OH over the surface of the plates and the haze quickly dissolved leaving no residues behind. (Jacobson and Jacobson 2015, 348-9)

I was presented with a challenge in treating *The Woman in Damask Evening Gown, Posed with a Chair*. Pouring ammonia over the surface, or immersing the plate in a solution, was out of the question because these treatments would rinse away the flesh colored tinting on the woman's face. The best course of action was to apply the NH₄OH solution locally. I tested the treatment with my own daguerreotypes and found that I could direct a stream of ammonia solution of 2~3% strength with a squeeze bottle on a local area, and with an after-rinse of distilled water in the same fashion, no demarcation between the wetted and dry surface was visible. Figure 8 shows the pre-and post treatment results.



Fig. 8. pre-treatment (*left*); post-treatment (*right*), courtesy of the author

After treating the disfigured half of the stereo pair with NH_4OH solution, some trace hazing remained on the surface. To remove the remaining haze, while the plate was submerged in distilled water, I gently swabbed the surface with a microfiber cloth by applying only the pressure from the weight of the cloth itself. (fig. 9) I was confident with this procedure, because the plate was not hand colored, well gilded, and intact throughout. I had also tested the swabbing procedure on my own gilded daguerreotypes prior to treating the historical plate.



Fig. 9. Gently swabbing the surface with microfiber cloth, courtesy of the author
Figure 10 shows the pre-and post-treatment results for the disfigured right side of the stereo pair, *Four Women Posed around a Table*, using the treatments described.



Fig. 10. pre-treatment (*left*); post-treatment (*right*), courtesy of the author

10. Conclusion: Integrated Analysis and Synthesis Techniques Resolve the Problem

This work reviews the sequence of events that followed from the observation of hazing on a few whole plate daguerreotypes during the *Young America* exhibition in 2005. Analytical research in 2008 on a number of Southworth and Hawes daguerreotypes showed chlorine in areas of visible white disfiguring haze. The proposed mechanism for the formation of the white haze was photolytic, or redeposited silver. ($\text{AgCl} + h\nu [\text{UV-Vis}] \rightarrow \text{Ag metal}$) Concurrently with the analysis of the haze, FIB sections showed the presence of voids beneath the surface of daguerreotypes. The source for the chlorine was theorized to be saline atmosphere trapped in the sub-surface voids and activated by exposure to light.

These conclusions were speculative and did not account for other observations. Some plates hazed in the dark, some plates were unaffected, and uniquely, with a stereo pair of daguerreotypes, produced and stored under identical circumstances, one plate was heavily hazed while the other remained in pristine condition.

Analysis of the Twin Paradox pair of daguerreotypes confirmed higher levels of AgCl in the heavily hazed areas of the disfigured plate and no chlorine on the pristine plate. Synthesizing the hazing on modern daguerreotypes by exposing them to chlorine vapor has uncovered a different mechanism of deterioration than what has been previously published. This study has shown that hazing can occur in dark storage, and though accelerated by light, the mechanism of deterioration for the formation of disfiguring haze is the coarsening, otherwise known as Ostwald ripening, of the AgCl.

An explanation for the source of the chlorine contamination has been presented, based on the analysis of unused 19c plates found in their original box. The wood material of the storage boxes, as has been explained, can act as a getter for chlorine, which is then transferred to the bare

daguerreotype plate. Some of the Southworth and Hawes plates were stored in wooden boxes and some were in tightly closed tin boxes. This storage scenario explains why only some of plates were affected with the hazing phenomenon. Daguerreotypes are not inherently light sensitive, although if contaminated with chlorine they may react to light, but these chlorine-affected plates are just as likely to haze in the dark. This study has shown that the disfiguring white haze due to chlorine contamination can be removed with conservation treatment as described in the previous section.

Materials science has been used since the 1970s to explain the daguerreotype and its preservation concerns. The present study illustrates how materials scientists have, on occasion, misinterpreted the data when solely examining historical objects. Experimental replication can effectively enhance the study of historical daguerreotypes when the samples are produced with a practical knowledge of the process. The “Twin Paradox” question has been resolved through the analysis of historical daguerreotypes, in combination with the study of modern samples that replicated the disfiguring white haze.

Finally, the two conserved whole-plates, presented here, have been displayed in the exhibition, *Through the Looking Glass: Daguerreotype Masterworks from the Dawn of Photography*, along with 150 other daguerreotypes from the Mattis-Hochberg collection. The show was installed in the Frances Lehman Loeb Art Center at Vassar College from April 10 to June 15, 2015. No daguerreotypes were harmed during this exhibition.

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