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Abstract:

From 1979 – 1984 there was extensive research into the materials characterization of the daguerreotype process at the Materials Research Laboratory at The Pennsylvania State University. This paper is a brief overview of the work done there.

In the fall of 1977, I left Rochester, New York, where I had completed two years of non-degree graduate work in photographic science, to begin studies for my doctorate at the Materials Research Laboratory (MRL) of The Pennsylvania State University. In 1979, after the completion of my comprehensive examinations, I began working exclusively on the materials analysis of the daguerreotype and that work continued until the fall of 1984 when I left to become the Mellon Fellow in Preservation Science at the Library of Congress Research and Testing Laboratory. There was some additional work that was done later, but most was of the daguerreotype research

was completed before I left. My daguerreotype study at the Materials Research Laboratory resulted in part in my doctoral dissertation, a large group of scientific and technical papers, and finally, the book, *The Daguerreotype: Nineteenth Century Technology and Modern Science* (1st ed. Smithsonian Press, 1991). A complete listing is given at the end of this paper.

The research that I did at the MRL was the first application of the principals of materials science to the study of any photographic process, and outside of the field of metallurgy, one of the first applications of materials science to study art materials in general. It remains the largest and most extensive materials analysis of any photographic material. The aim of my work was to understand what a daguerreotype is, what gives rise to its characteristic optical properties, and based on my findings to define what properties of a daguerreotype must be maintained when a daguerreotype is cleaned, preserved, or treated in some way. Work done after the completion of my dissertation in 1982 was concerned with understanding corrosion mechanisms that affect daguerreotypes, devising an effective method to remove tarnish and corrosion from daguerreotype surfaces, and finally, understanding image formation in daguerreotypes.

The MRL at Penn State is the second oldest materials lab in the United States. It was very well known for pioneering research in materials characterization and in devising the instruments for such characterizations, as well as for fundamental work in semiconductors, crystal growth, nanotechnology, cement, and for mapping the SiOx phase diagrams. It was also a place that was particularly interested in the relationship of art and science and so, the daguerreotype project was welcomed and stimulated a good deal of interest. Being in MRL, meant that I had easy access to the most advanced materials characterization tools and expertise. For instance, I had three scanning electron microscopes ten feet down the hall from my office and for several years made almost daily use of those instruments. MRL allowed me to take a significantly different view of daguerreotypes – to view them as materials, rather than viewing them through the established photographic model.

**Samples**

The research done at MRL was done with a very large and varied sample set that included about 130 garden-variety daguerreotypes gather from a variety of sources, geographic locations, and ages; 20 gilded and 20 ungilded daguerreotype step tablets made by Irving Pobboravsky and additional step tablets later made by me, on daguerreotypes plates manufactured in the lab; daguerreotypes loaned by collectors for analysis; and finally, some of the earliest American daguerreotypes including the oldest, extant American daguerreotype, “View of Central High School” by Joseph Saxton and about two thirds of the, then known, Robert Cornelius daguerreotypes. This widely varied sample set of daguerreotypes made it possible to move beyond the realm of speculation to develop a quantitative understanding of the properties of daguerreotypes and the daguerreotype process.

**Analysis Techniques Employed**

The analytical techniques used to characterize daguerreotypes and daguerreotype corrosion products were: scanning electron microscopy, energy dispersive x-ray spectroscopy, Computer Evaluation of Scanning Electron Microscopic Images (CESEMI), diffuse reflectance
spectroscopy, infrared spectroscopy, Fourier transform infrared spectroscopy, goniophotometry, profilometry, x-ray diffraction, Gandolfi x-ray diffraction, atomic emission spectroscopy, Auger electron spectroscopy, Raman spectroscopy, transmission electron microscopy, optical microscopy, optical spectroscopy, and optical densitometry.

**Image Structure and Chemistry**

The long held myth about daguerreotypes is that the image is a static silver amalgam that causes the image to be forever mushy and fragile. My work at MRL showed in a quantitative way that neither of these beliefs is true.

In order to determine the structure and chemistry of daguerreotype images, I used one of the first scanning electron microscopes designed to analyze and count particles on surfaces using a process then called, Computer Evaluation of Scanning Electron Microscopic Images (CESEMI). I used this instrument to analyze hundreds of thousands of daguerreotype image particles on many different daguerreotypes to determine the chemistry of each particle as well as its size and particle to particle spacing. These results led to the conclusion that daguerreotypes are made up of almost pure silver crystals on a silver surface (the daguerreotype plate) whose size and particle to particle spacing are the same size as the wave-to-wave measurement of the visible light. In other words, daguerreotype image particles are generally between 400 and 700 nanometers in diameter and height, as well as in their spacing from each other. The whitest highlights of a daguerreotype have approximately 200,000 particles/mm² and images areas that are midtones have proportionately fewer image particles of approximately the same size and chemistry with slightly larger average particle to particle spacing. Shadow areas have approximately 10 particles/mm² and those particles tend to be very large and poorly formed – I called them shadow particle agglomerates.

The agglomerates are visible to the naked eye and appear as bright spots in shadow areas. It is interesting to note that several cross sections of daguerreotype image particles have been published in the past and based on my image particle measurements, these all appear to be cross sections of shadow particle agglomerates rather than more typical image particles found in highlight or midtone image areas.

Shadow particles agglomerates usually have some measurable amount of mercury, however, the vast majority of daguerreotype image particles are silver (compare 200,000 silver particles per square millimeter to ten particles per square millimeter). Daguerreotype images are formed in mercury vapor (see section on image formation below) and image particles start out as a silver-mercury solid solution or an amalgam thus, the freshly-made image is somewhat mushy. Think of when the dentist makes a silver amalgam filling to fill a dental cavity. The amalgam is initially plastic so that it can be molded to the cavity, but in a matter of hours the amalgam begins a process call “hardening” which continues over time until the dental filling is firm and with sufficient aging a filling can even become embrittled. The freshly made daguerreian image is analogous to the dental filling and the small amount of mercury present in most image particles is lost over time due age hardening (for ungilded plates) or during the gilding process. The image particles are dynamic and continue forming either until the plate has been gilded or the age hardening has been completed – a process that takes about a year. The agglomerates retain some
mercury that is neither lost during gilding nor during the process of age hardening. However, in
general daguerreotype image particles do not retain mercury and ultimately, it is misleading to
refer to the image as an amalgam.

In addition to looking at the microstructure of the daguerreotype image, I did make some
measurements of the nanostructure of the image; however, these analyses added nothing of
significance to the overall materials characterization of the daguerreotype except to confirm what
had already been determined through the study of the microstructure.

Along with the particle counting and chemical analysis, I measured the optical properties of
daguerreotypes using diffuse reflectance spectroscopy. While this technique is more often used
for chemical analysis, it is also used to characterize surfaces to understand microstructure.
Diffuse reflectance curves for daguerreotypes are bell shaped curves centered over the visible
spectrum. These curves indicate that the dominant optical feature of daguerreotypes is light
scatter in the highlights and high reflectance in the shadow areas. It also happens that the diffuse
reflectance spectra match the distribution curves of image particle sizes and particle to particle
spacing. The reflectance spectra of the daguerreotype surface predict the daguerreian
microstructure and visa versa.

The Physical Model for the daguerreotype that I devised from particle counts and analysis and
diffuse reflectance spectra ties image appearance to image structure and provides a framework
for understanding what daguerreotype characteristics need to be controlled in order to preserve
daguerreian images. The surprising result is that maintaining the image microstructure, i.e.
particle size and spacing is far more important than maintaining the specific chemistry of the
image. The Physical Model also indicates that small changes in particle size and spacing can
equal large changes in the appearance of a daguerreotype. Therefore, a cleaner that etches or
alters the daguerreotype plate surface, causes changes in image particle size or spacing, or leaves
films on the daguerreotype surface will produce undesirable changes in the appearance of a
daguerreotype. The specific chemistry of a daguerreotype is of minor importance in the
preservation of a daguerreotype.

Gilding

The first of the only two changes made to the daguerreotype process after it was introduced in
1839, was the adoption of gilding. Gilding is a process where a weak solution of gold chloride
and hypo is placed on a daguerreotype plate after washing the developed image in hypo, and the
plate is heated. There is a persistent idea that gilding causes a gold layer to be put down on the
daguerreotype plate. Again, this idea is not borne out by analysis. Gilding does two things: gold
replaces mercury in image particles making them 1) larger (gold atoms are somewhat larger than
mercury atoms) and 2) more mechanically robust. Gilded daguerreotypes have whiter highlights
than ungilded daguerreotypes because the slight enlargement of the image particles shifts the
image scattering curve to make it more directly centered over the visible spectrum with a
maximum at 550 nm if the daguerreotypist has developed skill in making daguerreotypes. The
bell shaped scattering curve for the diffuse reflectance spectra of a gilded daguerreotype matches
what is called the luminosity curve of human vision – that is where human vision is most
sensitive.
Unless gilding is overdone or the gilding solution too saturated, there is no layer of gold laid down on the daguerreotype surface. First, there is not sufficient gold in the gilding solution to make a gold layer. Secondly, gold is aurophobic i.e. gold atoms tend to form small, isolated clumps rather than form continuous films; it takes many, many atomic layers of gold to form a continuous film. There are also some people who refer to the process of gilding as gold toning implying that this process is the same as gold toning in conventional photographic processes. While gold toning in conventional photographic processes is derived from the gilding process in daguerreotypes, the two processes are not the same.

**Daguerreotype Corrosion**

Once image structure and appearance were understood, I turned to understanding how daguerreotypes age. Using a wide variety of materials characterization techniques, I discovered that the corrosion process for daguerreotypes is far more complicated than had been previously thought. Daguerreotypes did not act like silverware – corrosion films were composed of a variety of silver oxides, combined with thin films left from using cleaning solutions containing cyanide or thiourea cleaning. The most surprising results were my discovery of the role of glass corrosion in the deterioration of daguerreotypes which results in very odd silicate corrosion products on the daguerreian surface, including products once identified visually identified as mold and fungus. Using a multitude of characterization tools, I was able to show that these odd silicates seen in the daguerreotype package as well as those materials previously identified as “fungus” or “mold” on glass lenses were not living organisms: they could not be cultured and had no DNA or RNA. I was the first person to identify and report on the relation between glass corrosion and deterioration of both daguerreotypes and photographs on glass supports.

**Daguerreotype Preservation**

The ultimate aim of my research was to determine better ways to preserve daguerreotypes, which covered two general subjects: daguerreotype cleaning and the daguerreotype package. The prevailing thought when I began to work on daguerreotypes was that the efficacy of a daguerreotype cleaner could be determined by assessing the amount of mercury found in spent cleaning solutions. Thus, a “good” cleaner would have little or no mercury present. The work on image structure and chemistry showed that this clearly would not be a profitable pursuit because there is almost no mercury in the daguerreotype image.

At MRL we investigated both the traditional ways of cleaning daguerreotypes (cyanide and thiourea solutions) to measure their effects on plates and we looked at new ways to cleaning, including using high vacuum sputtering and electrocleaning. We rejected sputtering because it required high vacuum equipment and it was very difficult to control – part of controlling the process meant doing counter-intuitive things like adding hydrogen sulfide gas to the sputtering chamber to poison cleaned surfaces to prevent etching of bare silver. Vincent Daniels at the British Museum reported on this process and ultimately came to the same conclusion as we did. We also briefly looked at laser cleaning, but it was clear that, at that time, it would be very difficult to control lasers sufficiently to have practical cleaning method for daguerreotypes.
Above all, I wanted to find a cleaning method that was easily adoptable by conservators and that would produce reliable results, while assuring that the daguerreotype image structure was not affected by process and that no cleaning residues would be left on the plate surface to initiate corrosion in the future. Ajay Giri and I tried electrocleaning, a well known and much used process for many metals, after abandoning sputter cleaning. It looked very promising, but I felt I needed a conservator to test this process in the field. I wanted to work with someone who would follow our instructions, who would give a fair analysis of the work, and who would be a good partner in the development of the cleaning process.

Tom Edmondson became my tester after he made a brief stop at MRL while returning from a trip to the West. We showed Tom what equipment and chemicals he would need, gave him instructions and sample daguerreotypes that had been cut in half to use for testing and sent him home. Tom went back to Connecticut where he was living at the time, put together an electrocleaning rig and began working. He eventually came back to MRL so that we could examine what he had done and compare cleaned daguerreotypes with the untreated portions that had been left at the lab. Before we announced the electro cleaning method at the PMG Winter meeting in Philadelphia, we had had cleaned and analyzed over 100 daguerreotypes. We had done sufficient testing so we no longer consider the method as experimental.

The Daguerreotype Package

Even 30 years ago, there were many people working designing the ultimate daguerreotype package. The traditional method used to seal daguerreotypes was made up of the daguerreotype plate, a mat, glazing and a tape to hold the whole thing together. This package has both positive and negative effects on the daguerreotype. The package protects the daguerreotype from scratches and physical damage. The tape helps to slow down corrosion and helps to keep water vapor from entering the package, however it is difficult completely seal a daguerreotype.

In more recent times, various sealing methods were introduced for daguerreotypes ranging from complicated packages constructed out of archival mat board and various tapes to elaborate treasure box enclosures that allowed the viewer to remove layer by layer of the package and finally, view the bare daguerreotype plate. Brass mats were removed because some people thought that the metal mats initiated corrosion.

In my examination of the daguerreotype package, I analyzed corrosion films and the locations of corrosion films. There are two corrosion fronts on daguerreotypes: 1) at the plate edge and 2) the interior edge of the mat. It turns out that these are both active corrosion areas because of the geometry of the daguerreotype package. Using tape as a seal slows down corrosion and it turns out the style of taping is also a factor. A continuous tape seal is better than a seal made up of several short pieces of tape. The geometry of this protective package also drives glass corrosion on the interior of the daguerreian package because it is impossible to have an impermeable package that has no openings. Water vapor enters the daguerreotype package through the tape and becomes trapped on the interior of the daguerreian package. Under the right conditions, even the smallest amount of water vapor will initiate corrosion of the inside of an unstable cover glass. Since it is impossible to completely seal a daguerreotype, I feel that the parts of daguerreotype seals should be viewed as ephemeral and that they should be unhesitatingly changed as needed.
In addition to looking at the daguerreotype package, the Getty Conservation Institute was investigating protective coatings for objects. The thought was that protective coatings could be used to prevent corrosion and allow objects to be treated once and coated. About 1982, I was asked me to submit daguerreotypes to be coated with Parylene. We also looked at several sputtered coatings for daguerreotypes. All of these coatings were interesting; however, none of them were appropriate for daguerreotype preservation because they all of these films altered the daguerreotype’s characteristic optical properties.

**Image Formation in Daguerreotypes**

One of the final things I looked at was how the daguerreian image is formed. Previous to my work, the general assumption about image formation in daguerreotypes was that mercury acted like a photographic developer in that it caused the reduction of silver halide at latent images sites to form the image. When I began looking at image formation, this conventional photographic model was my guide.

I quickly had to dismiss the conventional photographic model because it was clear that mercury was not a reducing agent for silver salts. Further, from practical experience, it was clear that there is very little mercury is consumed when a daguerreotype is made. A daguerreotypist might use the same mercury in his mercury bath for many years with no significant loss. Also, the specific silver halides used in the daguerreotype process are not the same as in conventional photographic processes. In a daguerreotype silver is corroded in halogen vapor to form a silver halide layer rather than having discreet crystals of silver halide formed from solution dispersed in some sort of carrier as would be the case for conventional photographic processes.

My work showed that daguerreotype image formation is an example of chemical vapor deposition in which silver crystals are grown in a vapor phase mercury solvent. This crystal growth process takes some skill to learn and I was able to show that it is possible to identify a novice daguerreotypist because there are image structures that are characteristic of incomplete or transitional phases during crystal growth in mercury vapor; once a practitioner has matured these structures are rarely observed in his work. My experimental observations were verified when I was able to examine the Robert Cornelius set of daguerreotypes. I was able to use microstructure to sequence Cornelius’ daguerreotypes according to when they had been made and also to identify when he began to use bromine as an addition to his sensitizing process. The addition of bromine to the sensitizing procedure is the second of the two changes made to the daguerreotype process and its adoption made possible portrait photography by reducing exposures to well under a minute.

There was quite a bit published from the work done at MRL. The following is a complete listing.

*Books*


Dissertation

Papers in Refereed Journals

Papers in Conference Proceedings

**Papers in Other Professional Journals**


**Papers in Edited Monographs**


**Published Abstracts**


**Articles about Barger's Work**


**Television Programs about Barger's Work**


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