DAGUERREOTYPES: A STUDY OF THE PLATES AND THE PROCESS

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Abstract

Daguerreotypy was the first widely used photographic process. The pictures consist of silver mercury amalgam particles on a silver substrate. An explanation of the process has been developed, since this was not available in the literature. The results of a detailed electron microscope analysis of daguerreotypes in good condition indicate the plates to be about 2.4mm thick; comprised of a thin silver layer averaging 2µm thickness on a copper backing. The silver layer contained about 2 per cent copper by weight. Mercury was not found except within image particles. Gold was observed everywhere on the surface in a thin layer (0.75µm). Deteriorated daguerreotypes were also examined and the deterioration products classified. Smooth films characterized by interference colors were determined to be largely silver sulfide. Silver sulfide was additionally found as crystalline particles. Copper formed the major constituent of another type of deterioration film. Copper was also found in green accretions, often associated with the presence of sodium and calcium. Sodium and calcium were found as deterioration products of the glasses covering these plates. Our studies have shown that interdependent deterioration processes are present, involving the plate surface, the copper support, the over plate and the microclimate in the case around the plate.

Introduction

The daguerreotype process was the earliest widely used photographic process, invented by L.J.M. Daguerre and Niépce Niepce, disclosed in 1839, and in use until the early 1860's. With this invention, the civilized world had access for the first time to an optically correct, finely detailed visual record of the world, unobscured by the handmade nature of previous pictorial processes. The pictures took much less time to make than painted miniatures and were inexpensive: consequently for the first time nearly everyone could own pictures of his family. The process was regarded as a miracle of nineteenth century technological progress, whereby the sun itself was induced to become one's portraitist. Oliver Wendell Holmes called the daguerreotype "the mirror with a memory"; that mirror still provides us with thousands of images of the mid-nineteenth century: personalities known and unknown, the locales and events of the day: Emily Dickinson as a young woman, the clipper ship yards in Boston, 49'ers panning for gold in California.

That many of these plates are essential cultural artifacts and must be preserved is unquestionable. How such preservation should be accomplished is open to serious question. Like most photographs, daguerreotypes have until recently been regarded primarily as objects of popular culture; consequently a determination of their conservation requirements has been neglected. Conservation methods for daguerreotypes have not been based upon study of the objects themselves, but instead have been simple modern adaptations of the original nineteenth century packaging and cleaning techniques. Indeed, the physical structure and composition of these early photographs have never been systematically examined. The present work was undertaken to provide such a foundation, as a first step in the development of more effective conservation methods.

Since the daguerreotype process is unfamiliar and few attempts have been made to explain its mechanisms, we have found it necessary to develop an explanation of the process, insofar as possible, to provide a framework for the analysis.

The Process

The production of daguerreotypes was a complex operation; consequently numerous manuals were

published to provide detailed instruction. The following
description is based primarily upon six such manuals on daguer-
reotypy which were influential in their time, cover the entire period within which daguerreotypy
was widely practiced, represent both French and
American viewpoints, and are more accessible in reprint or translation than much of the literature.
Additions from other sources are noted.

Daguerre's original process was significantly
improved within a few years of disclosure. By the
late forties a standard process had emerged which
was used with few alterations until daguerreotypy
was supplanted by the less costly and more adaptable
collodion process. This standard process involved:

1. Obtaining appropriate plates
2. Cleaning and polishing the plate
3. Sensitizing the plate
4. Exposing the plate to light in the camera
5. Developing the plate with mercury
6. Removing the sensitive layer
7. Gilding the finished image.

The Plates

Daguerreotype plates were almost always ob-
tained ready made. They consisted of a thin silver
layer bonded to a thicker support layer of copper.
The plates came in standard sizes, all of which were
relatively small: the largest standard size, the "full
plate", measured 16.4 x 21.5 cm, by far the most
common size was the "sixth plate" which measured
7.0 x 8.0 cm. The plates were manufactured by
the Sheffield process, a cladding process in which
silver and copper sheets were brazed together, pressed
between rollers until the desired thickness was ob-
tained, annealed and cold-worked. After 1830,
electroplated daguerreotype plates are also noted
in the literature and are recommended for the greater
purity of their silver layer. In the 1850's, most
of the plates used in America were imported from
France, and the French government required plate-
makers to specify the quantity of silver in each plate.
Plates with varying thicknesses of silver were available,
but by far the commonest was the inexpensive
"No.60" plate, denoting that 1.40 of the thickness
of the plate was silver. Such plates are about 0.4
mm thick; therefore the silver layer of a "No.60" plate
should initially have been about 10 μm. However,
platemakers seem not to have always fulfilled this
requirement—the manuals are full of complaints
that plates contained far less silver than was speci-
fied.

Cleaning and Polishing the Plate

The first operation required of the daguerreot-
typist was to obtain a polished plate on the sur-
f ace of the plate. This was an important step since the
quality of the polish greatly affected the tonal range
and evenness of the final image. Daguerreotypy
is a light-scattering process; the image is formed
by varying quantities of raised, light-scattering
particles of silver-mercury amalgam on a smooth,
non-scattering silver substrate. This can be seen
in figure 1. Obviously, the smoother the substrate,
3. Sensitizing the Plate

From the time it was sensitized until the sensitive coating was removed with thiosulfate, the plate required protection from light. Standard daguerreian equipment thus included light-tight containers for sensitizing and developing, as well as plate holders with darkslides, similar to modern sheet film holders.

According to Daguerre's original directions, the polished plate was sensitized by exposing it to iodine vapor over a container of iodine crystals at room temperature. Iodine vapor reacted with the silver surface of the plate to form a layer of AgI, one of the three silver salts, along with AgBr and AgCl, commonly used as the light-sensitive component of modern silver photographic systems. The thickness of the AgI layer strongly affected the sensitivity of the plate and therefore required control in order to allow predictable exposures. Since the rate of formation of AgI is dependent on temperature and relative humidity, factors a nineteenth-century studio could not control closely, daguerreotypists monitored the thickness of the layer visually by the interference color the plate exhibited; Daguerre directed that plates should be iodized until they assumed a golden yellow color.

Poborovsky measured the thickness of AgI layers on daguerreotype plates by X-ray fluorescence and found a layer of "golden yellow with a reddish hue" to have an average thickness of about 30 nm. The color was found to be caused not only by interference, but also by scattering (and possibly by absorption). Scattering as a factor in the color of sensitized plates implies the presence of surface irregularities of an average size equal to or greater than the average thickness of the layer, and therefore implies a discontinuous, irregular layer.

Such thinly iodized plates were not very sensitive; exposures required many minutes—an exposure table appended to a reprint of Daguerre's manual in The American Repertory of Arts, Sciences and Manufactures, March, 1840, listed exposure times ranging from 3 to 70 minutes. Portraiture was consequently impractical.

By 1841 daguerreotypists had added a second sensitizing step following the initial iodide sensitization. The addition of this second sensitization shortened exposures to "a less number of seconds than it before required minutes." Exposures of 20 to 40 seconds became common in the portrait studios which quickly appeared.

Many compounds were employed for the second sensitization; as a class they were termed "accelerators" or "quicks"—all of them contained bromine, chlorine, or a combination, often with iodine, though bromine seems the most common major component. Some were simple, like bromide water; some were more complex, like "bromide of iodine" or "chlorobromide of lime"; some were proprietary and section, like the highly recommended "Hungarian Liquid." Their function was to release a small amount of bromine and/or chlorine to react with the initial silver halide layer, forming a mixed silver halide layer. The thickness of this layer was controlled either by its color or by a proportion of the time of the first sensitization.

"Accelerators" were always used with a previous iodine sensitization. The manuals indicate that chlorine or bromine used alone were ineffective as sensitizers: "By themselves (accelerators) are not photogenic, that is when employed alone they would not form with the silver a completely capable of receiving the luminous impression." This is surprising since both AgCl and AgBr have frequently been employed as the only light sensitive component of various photographic emulsions. Indeed, processes contemporaneous with daguerreotypy for producing positive paper prints employed AgCl almost exclusively. It is likely that the structure of AgCl and AgBr films formed on daguerreotype plates rendered them undevelopable.

By 1847 daguerreotypists had added a third sensitization, again over iodine crystals. Some increase in sensitivity resulted, but more important, the response of the plate to light became more even, and difficulties with indiscriminate mercury development (i.e., fog, termed the "veil of bromine" in the manuals) were avoided. Though this sensitization was always controlled by a proportion of the time of the first iodizing, the manuals are in agreement that the proper color for a triply sensitized plate was "steel blue". An extrapolation from Poborovsky's measurements of pure AgI layers indicates that the thickness of a "steel blue" layer should be about 60 nm.

The three step sensitizing procedure not only produced a much "faster" plate than Daguerre's single iodizing, but also allowed a much wider range of tonal variation between the deepest shadow and the brightest highlight. It was the standard sensitizing practice from 1847 until the obsolescence of the process.

4. Exposure

When light strikes a modern photographic emulsion of silver halide crystals it causes photolytic decomposition, producing metallic silver and halogen. If the recombination reaction can be inhibited, a large light exposure produces visible darkening of the emulsion (i.e., massive reduction of the silver, termed "printing out"); a relatively small light exposure produces specks of metallic silver on the crystals, collectively termed the "latent image", which behave as catalysts for the reduction of the silver of the crystals when a suitable reducing (developing) agent is introduced.

Latent image formation and photographic amplification systems have been extensively studied. The model systems investigated, however, have usually consisted of either silver halide crystals formed by controlled precipitation and recrystallization in aqueous gelatin solutions, or silver halide layers deposited on supports by condensation from the vapor phase. Silver halide layers formed by vapor phase halogen corrosion of silver have not been studied and probably differ significantly from both studied systems. Though the behavior of sensitized daguerreotype plates exposed to light can therefore only be considered on the simplest level, nevertheless the basic reaction is unquestionably the same: the light exposure of a sensitized plate may be regarded as forming specks of metallic silver on the silver halide surface, and as forming more specks wherever more light has struck the plate. The image is "latent" at this stage; that is, no visible change can be seen on the plate.

Even taking into account the poor light-gathering properties of camera lenses available in the first
years of photography, the singly iodized plates seem extremely inefficient. It is likely that these pure AgI layers suffered massive recombination reactions. Because AgBr and AgCl crystallize in a different structure than AgI, and because on a small amount of the chloride and bromide can be incorporated into the AgI structure, the action of bromine and chloride on an iodized plate would produce a non-uniform crystal layer with many defects. Such crystal defects have long been accepted as providing trapping sites for the products of photolysis, facilitating silver nucleation and minimizing recombination.

The optical absorption of mixed silver halide crystals is another factor in the improved sensitivity conferred by accelerators. The absorption edge of pure AgI and AgBr crystals shifts to longer wavelengths for the mixed crystals, thereby increasing the utilization of white light.

5. Mercury Development

After exposure, the specks of metallic silver constituting the latent image were amplified to visible size by treatment with mercury vapor. The plate was positioned at the top of a closed container with a crucible of mercury heated to a temperature of 50 to 90°C at the bottom. Mercury vapor condensed on the plate in accord with the light exposure—wherever the most light had struck the plate, the most droplets of mercury condensed. It was important to stop mercurizing at the right moment; if the plate were left too long, mercury would begin to condense indiscriminately on shadows as well as highlights. Thus imagewise condensation of mercury is a kinetic rate process, produced by preferential nucleation of mercury droplets on photolytic silver specks, followed by the formation of silver mercury amalgam at the nucleation sites.

Silver mercury amalgam forms readily at room temperature, to the extent that silver wool can be used as a sensitive collecting agent for mercury vapor in air pollution studies. Adequate silver for amalgam formation probably came from the plate surface; a mercury droplet might be expected to contact the plate through discontinuities in the thin halide coating. Although the initial reaction between silver and mercury is instantaneous, subsequent amalgamation takes place much more slowly due to the small solubility of silver in mercury.

The amalgam expected is the solid, body-centered cubic phase, identified in the dental literature as Ag₃Hg₃. Alloys containing less than about 0.29 weight fraction of silver (which would certainly include the condensed mercury droplets on ungilded daguerreotype plates during the first few hours after mercurizing) are partly liquid at room temperature, consisting of a mixture of solid Ag and a very dilute solution of silver in mercury. Daguerre described the liquid nature of the incompletely amalgamated particles on newly made plates: "mercury...sticks to the silver and withstands water poured on it, but cannot bear any rubbing." Indeed, an unsatisfactory image could be rubbed off and the plate repolished, but removal of an image had to be done soon after mercurizing or it became much more difficult. "For otherwise the mercury finishes by adhering to the silver."

A single daguerreotype image exhibits a wide range of amalgam particle sizes from highlights to shadows as can be seen in figures 2 and 3. The availability of mercury is apparently a controlling factor in the size of an amalgam particle; thus particles in shadow areas where there are few nucleation sites are generally much larger than particles in highlight areas where many nucleation sites are available for condensation. There is also a considerable range in mid-tone particle size from plate to plate, caused by differences in mercurizing temperature. A wide range of recommended temperatures is found in the literature. The daguerreotypist decided on a convenient and reproducible mercurizing temperature and then arrived experimentally at the optimum mercurizing time. He could mercurize "cold" for long periods, "hot" for short periods, or choose a moderate temperature-time pair. Plates developed slowly (cool) were thought to have "a much clearer and sharper outline" (i.e., better resolution), but short mercurizing times were more practical in busy studios, and also produced improved contrast. Of the winners of the 1856 Anthony Prize Pitcher Daguerrean Competition who described their working methods, all used short mercurizing times—70 seconds to 3 minutes. S.D. Humphrey, manual author and editor of one of the first photographic journals, explained the advantages; as the temperature of the mercury was increased "towards the boiling point...the vapors of mercury rise in greater abundance and collect in larger globules on cold surfaces...high temperature and short exposure (to mercury)...renders the lights of the picture more strong and clear, while the deep shades are more intense." Levi Hill, another manual author, wrote, "A long exposure (to mercury)...at a very low heat, gives the minor details of the picture exceedingly sharp: but it does not give that bold, smooth, soft, deep-toned effect which is so desirable, and so much admired."

Indeed, an examination of daguerreotype images under a microscope would seem to support this thesis: plates with generally larger amalgam particles (Humphrey's "larger globules") seem to have stronger, richer tonal contrast—more brilliant whites and deeper shadows.

6. Removing the Sensitive Layer

Immediately after mercurizing, the plate was treated to remove the silver halide layer. If this step were delayed and the plate exposed to much light before treatment, finely divided particles of metallic silver would be formed on the surface by light reduction, giving an overall gray appearance to the shadows of the finished image.

Daguerre's original solvent for the halide layer was a hot, saturated solution of sodium chloride, which cannot have been very effective in dissolving silver iodide. Even before the publication of the process in 1839 however, Daguerre learned of Sir John Herschel's application of sodium hyposulfite (photographers' "hypo" or "fixer", now called sodium thiosulfate) to dissolve silver halides from printed-out paper photographs, and "hypo" was thus incorporated into the daguerreotype process from the beginning.

Daguerreotypists used a somewhat weaker solution of sodium thiosulfate than is common today—100 g/l of the pentahydrate salt was the usual formulation. They generally poured it over the plate instead of immersing the plate; the halide layer dissolved fully in about 10 seconds. Immediately after the thiosulfate treatment the plate was thoroughly rinsed with water.
This was the last step in Daguerre's process; the plate was given a final rinse in distilled water, it was slightly warmed, and any water droplets were blown off the surface. All that remained was to seal the plate in a glassed miniature case to protect its fragile surface from scratches and tarnish formation.

7. Gilding

In 1840 the French physicist Hippolyte Fizeau announced the development of a gold treatment for finished daguerreotype images which produced such an improvement in their appearance that the process was immediately and universally adopted. In order to gild a plate, the daguerreotypist adjusted it, thoroughly rinsed after the thiosulfate treatment, on a leveling stand. Then he poured into it as much gilding solution as the plate would hold and heated the plate strongly and evenly with an alcohol lamp. After a couple of minutes the shadow areas of the picture became darker and warmer in color, whereas the "lights of the proof, which are always a little blue after the washing with the hyposulfite, become of a beautiful white." When the tonal change was complete the plate was thoroughly rinsed, dried and framed.

The standard gilding solution was prepared by adding gold (III) chloride solution to an excess of sodium thiosulfate solution, thereby forming gold (I) thiosulfate complex. When the solution was heated on a daguerreotype plate, a redox reaction with the silver surface of the plate occurred, depositing metallic gold on the plate and oxidizing and complexing silver. An analogous gold (I) thiourea complex has been found to react similarly in a modern treatment for microfilm images. The thin gold-rich surface layer which was formed caused the apparent darkening and increased warmth of the shadow tones. A redox reaction might also be expected with the liquid mercury in the image particles, depositing metallic gold (which would be incorporated into the amalgam), and oxidizing and complexing mercury as mercury (II) thiosulfate complex, probably through disproportionation. The heat involved in gilding also promoted amalgamation between excess mercury and the silver of the plate. As a result, the amalgam particles lost their liquid character, and for this reason the gilding process was often referred to as "fixing"—that is, gilding "affixed" the amalgam particles to the plate.

The amalgam particles would also have lost their spherical shapes during gilding due to amalgamation and mercury loss, taking on the flatter and more varied forms one sees now through the microscope; it is perhaps this change in geometry that is responsible for the increased whiteness and brilliance of the image upon gilding.

The amount and duration of heating during gilding required careful control. Insufficient heat failed to increase the contrast of the image and left the amalgam particles too soft to withstand brush application of dry pigments, the standard method of coloring the plates. However, too much heat caused the surface to "exfoliate, that is to say, the slight coating...detaches itself from the surface of the plate, and exposes to view the unpolished silver underneath, consequently the proof is destroyed." Such exfoliation is frequently observed around the edges of plates as detached flaps of a thin foil exposing clean silver underneath with no sign of either image or polishing marks. It occurs more frequently in shadow areas than in highlights. Exfoliation is probably caused by the difference in thermal expansion between gold and silver; gold and gold-rich alloys expand and contract much less with temperature change than pure silver does. If a gold-rich layer thick enough to behave in a coherent manner were formed on the surface of the plate, it would be expected to separate from the plate as the plate cooled. This then was the complex series of operations which produced daguerreotypes, described with such uniformity in the manuals as to suggest that significant deviations from the described process simply failed to produce acceptable images.

Analysis of the Plates

As we have seen, production methods for daguerreotypes are fairly uniform and well documented. In addition, the plates were massively produced during their time and are available from dealers in a wide range of conservation states. Consequently, we were able to bypass the difficulties of sampling museum objects by acquiring a group of plates specifically for the analysis. This allowed the analysis of a number of plates in nearly pristine condition to establish the characteristics of the undeteriorated surface. The first author has examined many daguerreotypes in the collection of the International Museum of Photography, becoming most familiar with the appearance of the frequently encountered types of deterioration. Deteriorated sample plates were selected to represent as well as possible the common conservation problems. Our sample also included one early plate acquired in France and thought to be ungilded which was generously donated by a collector, as well as two plates in deteriorated condition provided by the International Museum of Photography. Many of the plates were still in their original cases with the paper sealing tape intact, and the remainder showed no signs of ever

<table>
<thead>
<tr>
<th>Table I</th>
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<tbody>
<tr>
<td>Characteristics of the Plates in the Sample</td>
</tr>
<tr>
<td>Platemaker's Mark</td>
</tr>
<tr>
<td>No mark</td>
</tr>
<tr>
<td>&quot;double/JP/40&quot;</td>
</tr>
<tr>
<td>&quot;double/A Gaudin/40&quot;</td>
</tr>
<tr>
<td>&quot;NP&quot;</td>
</tr>
<tr>
<td>Roman bust in wreath</td>
</tr>
<tr>
<td>Casing</td>
</tr>
<tr>
<td>in original case with seal intact</td>
</tr>
<tr>
<td>in original case with seal broken</td>
</tr>
<tr>
<td>no case</td>
</tr>
<tr>
<td>Condition</td>
</tr>
<tr>
<td>pristine surface with edge tarnish</td>
</tr>
<tr>
<td>noticeable spots but most areas clear, with edge tarnish</td>
</tr>
<tr>
<td>spots and general discoloration</td>
</tr>
<tr>
<td>severe tarnishing</td>
</tr>
</tbody>
</table>

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having been “cleaned” or otherwise altered. Relevant
details regarding the sample of 15 plates which we
analyzed are tabulated in Table I. For a list of plate-
makers’ marks with some dates of production see
reference 37.

The plates were examined in a light microscope
to determine condition and to locate areas of inter-
est. Areas of interest were removed for analysis
with a punch which produced 0.64 cm diameter disks,
preserving the flatness of the samples and leaving
the image surfaces untouched. The surfaces of 40
samples were analyzed; 7 were from areas of excel-

ten condition, and 33 were from areas of deterio-
ration. Five additional samples were analyzed in
cross-section.

Characteristics of the Undeteriorated Surface

Examination of the Surface

The surface of disks from areas of excellent
condition from 7 different plates were analyzed.
Shadow areas were selected in order to obtain parti-
cles of adequate size, and to obtain large enough
areas of substrate free of particles. Analyses were
performed in a Cameca MBX* electron microprobe
equipped with three wavelength dispersive X-ray
spectrometers and an energy dispersive spectro-

ometer. Analyses were also done in a scanning elec-
tron microscope (International Scientific Inc. Super
II*) equipped with an energy dispersive spectrometer.

In the ensuing discussion the term qualitative
analysis will refer to X-ray analysis performed with
an energy dispersive detector (Lithium-drifted Sil-
icon) capable of detecting the chemical elements
sodium through uranium. The choice of this detector,
rather than wavelength dispersive spectrometers,
was dictated by the considerably greater speed with
which a qualitative analysis can be performed and
the great number of such analyses which were re-
quired.

Qualitative results consistently showed that
substrate areas contained silver as the major con-
stituent, with much smaller amounts of gold and
copper; particles contained silver as the major con-
stituent with varying quantities of mercury and gold,
as well as smaller amounts of copper.

A wide variety of forms is seen among the
shadow-area particles of different plates. Some
plates exhibit flat round particles, some have hemi-
spherical particles, some show polyhedral particles
on flat bases, some show circularly organized groups.

Typical particle shapes are shown in figures 3, 4,
and 5. Such variety is not surprising given the va-
garies of production; one might expect mercurizing
temperature, time elapsed between halide removal
and gilding, heat and duration of gilding, and many
other variables to have some effect on particle mor-

phology.

Fig. 6 shows the French plate thought to be
early and ungilded. The image consists of tones

of gray with very little contrast, the picture appears
weak, and the plate exhibits the sort of polishing

seen on daguerreotypes known to have been made
in the first few years of the process. The plate itself
is quite thick and flat, characteristic of early plates.
(The edges of later plates are usually turned back
to accommodate mounting on polishing blocks.) In
addition, the subject has the rigid, uncomfortable
look of early sitters enduring lengthy exposures.

The surface of the plate in Fig. 7 is much rougher
than those of Figs. 2-5, and polishing marks are deeper
and multidirectional. The particles have rough,
irregular shapes—clearly different from particles
on the other plates. When the plate was qualitatively
analyzed, however, gold was found both on the sur-
face of the plate and in the particles, though in much
smaller amounts than on any of the other plates.
It is evident that whether or not a plate has been
gilded cannot be visually determined.

Examination of the Cross-sections

Samples from five plates were mounted in
epoxy, cross-sectioned, polished and a 25 nm carbon
coat was applied. Polishing was difficult since the
top, image-bearing layer tended to separate from
the silver layer on all samples. Edge retention was
the major consideration in the choice of mounting
and polishing techniques.

The total thickness of each sample was mea-
sured in a light microscope using an ocular graticule.
The thickness of the silver layer was measured from
secondary electron micrographs made in the micro-
probe. Considerable local variation was found in
the thickness of the silver layers; consequently micro-
graphs were made of four randomly chosen areas
of each sample. Minimum, maximum and average
values are shown in Table II.

Differences in the thickness of the silver layer
are attributable to the daguerreotypist’s polishing
method as well as to the manufacture of the plate.
Sample 3, with the thickest silver layer, was the

*Identification of any specific instrument does not
imply recommendation or endorsement by the National
Bureau of Standards, nor does it imply that the
material or equipment identified is necessarily the
best available for the purpose.

See page 421 for figures 2-5, 7-11, 16-24.

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Table II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Platemaker's mark</th>
<th>Total Thickness (mm)</th>
<th>Thickness of Ag layer (μm)</th>
<th>min.</th>
<th>max.</th>
<th>average</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>&quot;double/A Gaudin/40&quot;</td>
<td>0.38</td>
<td>2.3</td>
<td>3.8</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>&quot;NP&quot;</td>
<td>0.39</td>
<td>2.5</td>
<td>3.8</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>no mark</td>
<td>0.40</td>
<td>6.5</td>
<td>8.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&quot;double/JP/40&quot;</td>
<td>0.39</td>
<td>5.8</td>
<td>6.9</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Roman bust in wreath</td>
<td>0.44</td>
<td>4.5</td>
<td>5.0</td>
<td>4.3</td>
<td></td>
</tr>
</tbody>
</table>

only one of the five with a silvered back, indicating electroplating.

The cross-sections were examined in the electron microscope. Secondary electron and inverted specimen current images of the cross-sections showed small pyramidal and rounded image particles of varying sizes protruding into the epoxy on the silver side of the samples (Fig. 8). The largest particles measured about 0.5 μm in the direction perpendicular to the image surface, and 2.5 μm parallel to it. Each of the sections had been cut to cross a contrast edge, thus containing a highlight and a shadow area. Only shadow particles could be measured. Highlight areas simply exhibited an irregular edge. It is possible that the smaller image particles in the highlights had been obscured or dissolved by our specimen polishing process. In both highlight and shadow areas, a layer about 0.5 μm thick, appearing brighter than the silver layer in both secondary electron and inverted specimen current modes, was evident on the image edge.

Even though small (1 μm to 10 μm diameter), gray, randomly distributed inclusions had been noticed in the copper layer of the samples, qualitative analysis of 5 inclusions from each cross section indicated only the presence of copper. Qualitative analysis of 15 randomly chosen points in the silver layer of each cross section showed that they consisted of silver with a small amount of copper. Gold and silver were observed in the thin, bright layer on the image surface of the samples. One of the cross-sections had been cut from a severely tarnished plate; qualitative analysis of the tarnished edge showed a small amount of sulfur, in addition to gold and silver.

The silver and copper layers of each cross section were quantitatively analyzed, with an accelerating potential of 20 keV, and with three wavelength dispersive spectrometers set on the silver Lα, copper Kα, and gold Mα X-ray lines, respectively. The data reduction program used was the NBS computer program FRAME B-26. The silver layers of all the samples were found to contain about 0.02 (weight fraction) of copper, with significant variation both within any sample and from sample to sample. The results are tabulated in Table III.

The gray inclusions in the copper layer were found to contain 0.89 ± 0.003 weight fraction of copper. The variation of 0.003 reflects actual differences rather than fluctuations due to counting statistics, which were sufficient to detect variations as low as 0.003. An estimate of the experimental error (accuracy) is 0.005. One inclusion from each cross section was qualitatively analyzed using a wavelength spectrometer capable of detecting boron through sodium. Oxygen was the only additional element observed. The analysis indicates that the inclusions to be cuprous oxide (cuprite).

Qualitative analysis of 25 image particles from each cross section revealed the presence of mercury, gold and silver. The dimensions of the image particles and of the gold rich layer were too small to allow quantitative microscope analysis. X-ray area scans were made of these features which qualitatively demonstrated the spatial distribution of Au, Ag, and Hg. The area scans shown in Figs. 9-11 were made using an accelerating potential of 20 keV, employing the mercury Mα, gold Mα and silver Lα X-ray lines. The area scans show that mercury is clearly limited to the particle, whereas gold is found both in the particle and in a thin layer along the surface; silver is present in the particle and throughout the layer.

In order to examine the spatial distribution of mercury, gold and silver across the image edge in more detail, X-ray line scans were made through 10 image particles and 10 regions between particles from each of the 3 cross sections. The procedure followed for each line scan was as follows: a 7.5 keV, 2 x 10^-7 A, 0.1 μm diameter electron beam was slowly moved across the image edge, starting in the mounting epoxy facing the edge and ending well within the silver layer. Three wavelength-dispersive spectrometers were set on the mercury Mα, gold Mα, and silver Lα X-ray lines, respectively. The counts from each spectrometer were recorded in a multi-channel scaler for later plotting. The 7.5 keV accelerating voltage was chosen to ensure adequate spatial resolution without sacrificing statistical requirements. To demonstrate that 7.5 keV was sufficiently low for the purposes of the analysis, a Monte Carlo electron trajectory simulation was
performed. The electron trajectory simulation is applicable to the problem of determining the electron beam-specimen interaction volume. The trajectories plotted reveal the extent of this primary interaction volume. The results of this simulation are shown in Fig. 12. Elemental carbon was chosen as an approximation to the composition and density of the mounting epoxy, the gilding layer was assumed to be pure gold, 0.3 μm thick, and the silver layer was assumed to be pure silver. No attempt was made to simulate the electron trajectories in an image particle. The trajectory of an individual electron is plotted until its energy has been reduced to zero. One hundred such trajectories are plotted in each of the three elements, carbon, gold, and silver. For gold and silver the volume of interest is the X-ray excitation volume which is slightly smaller than that of the electron interaction volume shown. As can be seen from the trajectory plots in Fig. 12, the interaction volumes are sufficiently small that an estimate of the thickness of the gilding layer, and a rough estimate of its chemical composition are possible if the actual thickness of the layer exceeds about 0.3 μm. Our estimate of the composition of gold in the gilding layer is 0.03 ± 0.006 weight fraction.

Six representative X-ray line scans are shown in Fig. 13; three are scans across image particles and three are scans across substrate areas between particles. The vertical axes are scaled to the fraction of counts observed from a pure element standard. These fractions are not adjusted for the effects of background or matrix; consequently they can be used only as a rough estimate of the weight fraction of the appropriate element. The horizontal axes are scanned in distance traversed by the electron beam, starting in the epoxy and ending in the silver layers. On the basis of the appropriate electron beam-specimen interaction volumes it is possible to estimate the thickness of the gilding layer. For line scales across the substrates of all five samples, this estimate of depth within which the substrate contains gold is 0.75±0.3 μm.

Characteristics of Deteriorated Surfaces

The surfaces of 33 samples were analyzed in the microprobe and in the scanning electron microscope. We have attempted to provide a description of the appearance of each type of deterioration in the light microscope as an aid in the assessment of the condition of plates.

1. Smooth tarnish films showing interference colors. This is by far the most frequently encoun-

tered type of deterioration. Almost all daguerreotypes that have not been recently cleaned exhibit tarnish around the edges, and it is not uncommon to see films of deep blue or purple discoloration encroaching upon even the centers of plates. This tarnish is often seen as a series of concentric interference colors following the edges of the brass window mats with which American plates were commonly encased. Color series are also observed on plates whose cover glasses have been cracked for a long time; the tarnish duplicates precisely the shape of the crack and the colors indicate that the thinnest area of tarnish lies directly under the crack. When they are examined in a microscope many small spots on daguerreotypes resolve into concentric color series rings around small centers.

Four samples exhibiting smooth, brilliantly colored tarnish were analyzed in the microprobe. Substrate areas away from image particles were selected. At an accelerating potential of 20 kV, qualitative analysis showed that silver was the major element present with small amounts of gold, copper and sulfur. In order to decrease the penetrating range of the electron beam—and increase the analytical sensitivity for the specimen surface—the accelerating potential was lowered. Fig. 14 shows energy dispersive X-ray spectra from a second order orange tarnish area at 20 kV, 10 kV and 5 kV. Many of the most visually disturbing sorts of deterioration occur in such thin layers that an accelerating potential much above 5 kV is too high for analysis of
the electron range (\(\mu m\)). We will assume that the density of the film is 7.3 (the density of \(Ag_2S\)). Since second order blue is the color beyond which we observe a constant \(5K\alpha\) to \(Ag L\alpha\) peak ratio we may assume that the analytical volume of the electron beam is totally contained in the silver sulfide layer from this point: and beyond. The thickness of second order blue would correspond, then, to a solution of the electron range equation for \(E_c = 3.35 \, keV\) (the LIII absorption edge of silver). This value is 70 nm.

These thin brightly colored tarnish films were found associated with several types of spots. Whenever encountered, their spectra showed the presence of sulfur and silver. Thin film colors and color series imply slow, even tarnishing which occurs in environments with limited access to atmospheric sulfides. Color series and film colors are seen most frequently on encased plates.

2. Highly crystalline black spots. These spots occur on moderately tarnished surfaces and are usually surrounded by concentric color rings of tarnish. Three large spots of this type were found in our sample, as well as many small ones. These spots are round, and crystal size increases toward the center. The center of a spot 0.15 mm in diameter is shown in Fig. 16. Qualitative analysis shows that these spots contain only silver and sulfur.

In areas of heavy tarnish it is not uncommon to find small black crystals situated along scratches in the plate. One of our plates showed such crystals, which were also determined to be silver sulfide.

Small round black spots surrounded with tarnish color rings are frequently seen randomly distributed over the surfaces of plates otherwise in excellent condition. Two of the plates in our sample, in optimum condition in other respects, showed such spots. A typical spot, 20 \(\mu m\) in diameter, is shown in Fig. 17. It was surrounded by rings of thin tarnish colors not visible in the secondary electron micrograph. The crystalline material's silver sulfide, and silicon and aluminum as well as silver and sulfur were found in the center. Silicon and aluminum were found in the centers of three of the six spots of this sort analyzed. Such spots on otherwise clean plates may have been formed when the image was made; thiosulfate solutions, for instance, were known to precipitate sulfur compounds; one was warned to use fresh solution and to filter the solution frequently or spots would result. Silicon and aluminum are common constituents of household and street dust; they may have acted as nucleation centers for \(Ag_2S\) crystallization or may simply have lodged in pre-existing spots.

3. Accretions of green salts. Spots of this sort are frequently observed, ranging in size from several micrometers to several millimeters in diameter. Many such spots were found on four of the plates in our sample. Qualitative analyses of these spots often showed copper peaks alone, but some spots exhibited very small peaks for sodium, potassium, calcium and/or sulfur, with copper as the main component.

The fact that it is bonded to a copper support offers the silver surface of the plate considerable cathodic protection against corrosion. However, this is useful for preservation only if the silver surface is continuous. If copper is exposed through small holes in the silver layer, oxidation of copper

See page 421 for figures 7-11, 16-24.
would be expected to occur at these sites. It is not unusual to find a shard of glass protruding from a green spot on a plate whose cover glass has been broken. If a plate, which had exhibited spots of green salts, was chemically cleaned, one often sees small pits of copper-colored metal where the spots had been. Needless to say, such spots reform readily.

4. Spots of golden crystalline material. Accretions of clear, slightly golden, crystalline material are often found associated with the green accretions above. Two of the plates in our sample showed both types of spots occurring together. In Fig. 18, the thicker, light-colored material is dark green in the light microscope; the thinner material is clear and golden as is the spot of needle-like crystals in Fig. 19. Qualitative analysis of these thin clear crystalline materials showed them to consist of copper and sodium. Spectra of other similar spots on both plates showed large amounts of copper with smaller amounts of sodium, sulfur, potassium, and calcium. In two of these spots particles of very high calcium content were found.

5. Other copper containing spots. One of the severely tarnished plates, acquired without a case, had a black corrosion layer mixed with the more usual, dark blue silver sulfide film. The black areas were found to contain large amounts of copper, sulfur and silver, sometimes with small amounts of iron. Spectra from some areas consisted of copper and sulfur alone. Qualitative analysis of several well delineated areas of highly reflective gray crystals, some of them with central regions of red crystals, showed copper alone, which was probably present as Cu₂O and CuO.

6. Thin orange and iridescent films. Rings of orange tarnish with indistinct edges and clean centers are often seen on daguerreotypes. One of our sample plates showed many such spots. Four spots were qualitatively analyzed. Three of them had small central particles consisting of copper with chloride and calcium. Immediately around each center was an iridescent pink film; spectra of this film showed copper in addition to the normal substrate composition. Small particles rich in copper, some containing traces of iron, were found in the film. Surrounding each spot was a ring of nearly clean surface--spectra taken here showed very small copper peaks accompanying otherwise normal composition. Outside this relatively clean area was a second, wider ring of orange tarnish, which was what one observed, without magnification, as the spot. This orange film contained copper. No central particle was found in the fourth ring, which also differed from the others in that silver sulfide was present along with copper, especially around the edges of the spot.

These thin copper-containing films were consistently observed to produce white luminescence under the electron beam. Small areas of similar orange films were found on four samples from three other plates. Qualitative analysis of these films showed a small amount of copper with an otherwise normal substrate composition.

7. Particles of polishing material embedded in the surface. Three of the areas of orange film noted above occurred around pieces of polishing material deeply embedded in the surface. Surface morphology indicates that the particles were probably impressed during the initial cleaning of the plate and then polished over. As can be seen in Figs. 20 and 21, the silver extends almost over the tops of some particles, and polishing marks can be seen continuing up to the edges of the silver. A large particle has been dislodged from the center of Fig. 20. Areas with such embedded particles were found widely distributed on five of the plates in the sample. Qualitative analysis, using both the energy dispersive and wavelength dispersive spectrometers, showed particles containing silicon on two plates, particles containing silicon with aluminum on two plates, and particles containing carbon on one plate. These are common constituents of polishing materials frequently mentioned in the manuals. The presence of such embedded materials and the cavities left by them, some of which evidently penetrate to the copper underlayer, carry obvious implications for conservation. Areas of embedded particles are difficult to observe in the light microscope since the particles are highly reflective and very small. Using coaxial illumination, a featureless gray spot or a structure which appears to be a small pit, the bottom of which cannot be brought into focus, is probably an embedded particle.

8. Small crystalline structures. Small colorless, hygroscopic, crystalline structures, usually circular in outline (crystallization from droplets), frequently occur on daguerreotypes, though they are difficult to observe unless the ambient humidity is low and the microscope is equipped with polarized, coaxial illumination. Such structures were found on four of the plates in our sample. Fig. 22 shows three typical forms. Spectra show the presence of either sodium or potassium and lead and sulfur, often with smaller amounts of calcium.

9. Glass decomposition. The cover glasses of most plates still in their original cases show clear signs of decomposition. The interior surface is typically covered with clear, crystalline forms which become tiny droplets of liquid at high relative humidity. Accretions (Fig. 23) from the cover glasses

**Figure Captions**

Fig. 2. Secondary electron (SE) micrograph of image particles from a highlight area.

Figs. 3, 4 & 5. SE micrographs of image particles from shadow areas.

Fig. 7. SE micrograph of shadow area of Fig. 6.

Fig. 9. Inverted specimen current image of cross-section of image particle (A), silver layer (B) and copper backing (C).

Fig. 9, 10 & 11. Magnified X-ray area scans of particle and silver layer in Fig. 8; of silver, mercury and gold respectively.

Fig. 16. SE micrograph of the center of a 0.15 mm diameter Ag₂S spot.

Fig. 17. SE micrograph of a smaller Ag₂S spot at center of tarnish color rings.

Figs. 18 & 19. SE micrographs of golden crystalline material.

Figs. 20 & 21. SE micrographs of daguerreotype surfaces showing embedded polishing material.

Fig. 22. SE micrograph of small colorless, hygroscopic, crystalline structure (small, rectangular forms are image particles).

Fig. 23. SE micrograph of glass decomposition products on interior glass surface.

Fig. 24. SE micrograph of mold formation.
of two of our plates were analyzed. In both cases, sodium and calcium were the main observed components of the leached material on the surface, with smaller amounts of aluminum, silicon, chlorine, lead, and potassium present. Several accretions were found in which calcium was the only major component. Clear areas of the glass showed X-ray emission mainly of silicon, with sodium, aluminum, chlorine, potassium, calcium and lead present in small amounts.

Glass decomposition products are hygroscopic, alkaline and strong electrolytes. There is ample evidence that they are transferred to the plate below if a cover glass shows severe crystallization, the plate often exhibits crystals with similar properties. Both of the plates which were cased with the analyzed cover glasses exhibited sodium-rich crystal structures, particles high in calcium, and multiple spots containing copper and sodium. The closest source of calcium and sodium for these plates was certainly their cover glass. The presence of a strong electrolyte on a surface which may have pits or cracks through to the copper underlayer would seem to promote copper corrosion.

10. Biological aspects. Insect carcasses are frequently observed within daguerreotype cases. Along with silver sulfide tarnish and green copper spots, mold formations are one of the most widespread and disfiguring types of deterioration found on daguerreotypes. Six of the plates in our sample exhibited mold growth on their surfaces—all were cased plates. Fig. 26 shows such a growth; this is probably a relatively recent mold—most such growths show less morphology. The central structures of such growths are often encrusted with crystalline material, and the hypnion often appear as featureless black lines on the secondary electron images. Energy dispersive X-ray spectra from the central area of the growth in Fig. 26 show silicon to be the major observable component with smaller amounts of phosphorus, potassium, sodium, sulfur, copper, aluminum and chlorine. This is typical of spectra from the mold residues we analyzed. Qualitative analyses were also performed with a wavelength spectrometer capable of detecting boron through sodium. These analyses show that carbon and oxygen are major components.

11. Several samples showing uneven, reflective surface scale were analyzed, but compositional differences between samples with surface scale and clean samples were not observed. In addition, numerous small carbonaceous particles and infrequent, discrete silver chloride particles were encountered, but were associated with no apparent pattern of deterioration.

Conclusion

Given the extraordinary difficulty of the process, we find it amazing that so many beautiful daguerreotypes were made, and that so many still remain. Daguerreotypy is the only popular photographic process to have utilized solely inorganic materials; if better methods for sealing, storage and restoration were developed for them, the useful lifetime of daguerreotypes would probably greatly exceed that of any other popular photographic process.

We have not dealt with the problem of chemical cleaning in this study, as it is of sufficient complexity to demand consideration as a separate entity.

Nevertheless, it is clear that for very precious daguerreotypes, the repeated cycle of chemical cleaning (removing Ag₂S and copper salts) followed by reconstruction of a nineteenth century paper-clay adhesive seal, followed by perhaps 75 years of gradual tarnishing, glass decomposition, copper corrosion and biological attack, is inherently unsatisfactory. Though it is undeniably essential to study cleaning processes, it seems even more important to develop methods of sealing and storing plates which avoid the necessity of future cleanings. An exploration of practical methods, usable by museum staff, for providing an impervious seal containing a dry inert atmosphere would seem a promising direction for future work.

Much of the sampling and light microscopy was conducted at the International Museum of Photography at George Eastman House in Rochester, New York. The analyses were performed at the National Bureau of Standards in Gaithersburg, Maryland.

The authors would like to acknowledge the generous help of James Coleman, Morris Dillmore, William Fink, T.H. James, Dale Newbury, C. Paffenbarger, John Small, Richard Waterstraat, and Stanley Yalkowsky.

References


25. Ibid.


31. E. Ballat, Daguerreotype et Plaques, Paris, 1850. Transl. and reprinted in Photographic and Fine Art J., Nov., 1854, p. 322. (Succeeding citations will refer to the translation.)


34. Compare with "fixing" in contemporaneous paper processes; in paper processes one "affixed" the image, or made it stable, by dissolving and removing residual silver halides, which would otherwise have darkened on exposure to light until image distinctions disappeared. Thus "fixing" referred to thiosulfate treatment of paper prints, to gold treatment of daguerreotypes.

35. Valiati, p. 332.


Discussion with Reviewers:

Geller: Would a lower accelerating voltage than 20 keV produce X-ray maps with higher spatial resolution than those in figures 9-11? Authors: Yes, a lower accelerating voltage would produce a higher resolution micrograph. Unfortunately, we were constrained by statistics. A lower voltage would have meant prohibitively long integration times - and since we required every bit of beam resolution we could get, we could not raise the probe current. Consequently, we were forced to compromise at 20 keV.

Geller: Would you comment on the use of Auger analysis for the purpose of measuring oxidation depth in the silver halide grains? Authors: Just as in modern photographic silver systems, silver halide, the light sensitive constituent of the daguerreotype plate, was dissolved and removed by treatment with thiosulfate solution (step 6 described in the paper). So, of course, no silver halide grains would be expected on a finished daguerreotype surface. We would certainly have used Auger analysis if it had been available to us.

Geller: Sublimation of iodine in the silver grains occurs when electron beam bombardment raises the temperature a few degrees. Would this have affected any of your measurements or calculations? How about the use of a LN₂ cold stage? Authors: As noted in the previous response, iodine would not be expected as a constituent of the image particles. We did, however, do a conventional "trace" determination of both substrate areas and image particles for bromine and iodine. That is to say, we used a larger electron beam and "stepped" over the appropriate X-ray lines with a wavelength spectrometer. The results were null to an estimated sensitivity of .0001 weight fraction. A cold stage was not available on our machine but certainly would have helped to prevent sublimation.

Cameron: What are some techniques for cleaning silver sulfide films? Authors: The standard method used since the 1950's has been an acid thiourea solution. Before 1950 a one percent solution of potassium cyanide was used. Further information can be found in reference 1. Reviewers: J.D. Geller and D.P. Cameron.
Additional discussion with reviewers of the paper "Clay Fabric and Related Pore Geometry of Selected Submarine Sediments..." by R.H. Bennett et al, continued from page 524.

L. Dengler: Do you know if overburden pressure might effect such swelling or adsorption?

Authors: The reduction of in situ confining stresses, including lateral and vertical (overburden) effective stress, would result in sample swelling when a core is recovered.

L. Dengler: How was clay mineral orientation determined?

Authors: Both quantitative measurements and qualitative estimates were carried out on TEM micrographs using a defined reference line and measuring the angle of a given clay particle with respect to the reference line. Clay particle orientations were measured on micrographs of sections approximately 90° to one another.

L. Dengler: I infer that orientations and void dimensions were determined primarily from two-dimensional TEM photomicrographs. What feelings do you have for the three-dimensional structure or how might it be determined?

Authors: One would need to know what particular question(s) are being addressed with regard to the determination of three-dimensional clay structures. Each question may require different approaches to a particular problem. What can be said regarding the Mississippi Delta clays is that domains exist and constitute the "building blocks" of clay fabric. The domains can form edge-to-face, edge-to-edge, and face-to-face contacts. Face-to-face contacts can form sheets in a large "shingle-type" array, and edge-to-edge contacts can form chains both of which can be structured to form high-porosity sediments.

TEM micrographs provide a plane of reference for comparing void sizes (two dimensions) relative to particle sizes. SEM micrographs provide information of an irregular fracture surface of a clay specimen with virtually no common reference plane. SEM techniques provide a broader specimen area coverage compared to TEM techniques.

W. D. Keller: Does a flat lying Paleozoic shale (not tectonically deformed) represent a statically deformed, by single vertical pressure, clay-mud deposit?

Authors: In general terms, yes, given the conditions that dewatering and densification occur in response to vertical effective stress.

W. D. Keller: Is a domain built of flocs, or vice versa?

Authors: A domain is an assemblage of face-to-face clay plates. Plates can be arranged in a "perfect stack" such as described by Sloar and Kell (1966) and by Sides and Barden (1971), or the platelets may have a slight offset to one another as described by Smalley and Cabrera (1969).

The domain is a basic particle and "building block" of clay fabric and soil structure. Thus domains can form flocs. We use the terminology of van Olphen (1963), that only edge-to-edge and edge-to-face types of particle association produce agglomerates termed "flocs." We use the term flocculation to imply a process by which two or more particles (domains or "single plates") agglomerate regardless of the particle orientations, one to another. The term "floc" denotes a fabric unit with relatively large intravoids which, conversely, is not produced by face-to-face particle association.

W. D. Keller: Isn't a "stack of plates" a face-to-face floc?

Authors: A "stack of plates" called a domain can be an original fabric unit or a rock or sediment, or it may be produced by processes of flocculation. A domain also can be produced by consolidation. The term "domain" is not used here to denote mode of origin.

References


