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APPROACHES TO THE CONSERVATION OF DAGUERREOTYPES

Sebastian Karlsson.

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ABSTRACT

Daguerreotypes as a material are unique, While the image is created on a silver plate they cannot be treated like normal silverware nor can they be treated like other photographic material. There have been a series of attempts both historically and in more recent times which aims to develop a method for cleaning tarnish on daguerreotypes. In past decades the field of conservation has seen rapid change. Practices used in the conservation of photographs are based on the same fundaments as all conservation, the principle of minimal intervention and. a focus on stabilization of the current condition and to slow down the deterioration process. This thesis aims to investigate these different approaches and methods used in conservation of daguerreotypes. The research is conducted through the use of literary studies and case studies. The study found that the is currently no method which can be recommended for use indiscriminately while several show promise and could be justified in some cases, but more research will need to be conducted before they can be considered safe.

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Foreword

When reviewing papers for the thesis two stories have often come up, the first tells of the reaction of a widow who when the portrait of her husband is cleaned and she for the first time in years can see the face of her dead husband concludes that the cleaning process had restored the daguerreotype to its original state. The second tells of the unfortunate destruction of a portrait of Dorothy Draper which during a cleaning treatment John H. Gear in 1934 developed an unexplainable white hazy film. These two stories seem to exemplify the mixed feelings conservators have voiced regarding cleaning daguerreotypes, as they portray the polar opposites a cleaning intervention can and have result in.

For their assistance in the thesis I would like to thank Austin Nevin, Elyse Canosa, Mike Robinson, and for sharing their research Silvia Centeno and Patrick Ravines.

Index.

1. Approaches to the Conservation of Daguerreotypes

1.1 Background and problem formulation

Olmos (2009) conducted interviews with 15 photographic conservators to get indication about the current practices in the field of photographic conservation. The subject of daguerreotype cleaning was posed as a specific question. The cleaning methods discussed included dry cleaning which mostly consists of removal of loose particles and accretions using air and local mechanical cleaning using a fine brush, wet cleaning methods such as washing the plate with water, electro cleaning with and without external current and lastly plasma cleaning. Some of the interviewees expressed that the development and emergence of the profession can be evaluated and described through the practice of cleaning daguerreotypes, while some only see it as reflective of individuals professional attitudes and practice. Olmos concludes that the topic presents mixed feelings across all interviewees.

The interviewees expressed that the case for need of cleaning daguerreotypes can be certainly be made but is it seldomly warranted or conducted as risks involved are too high and the effects and the general effectiveness of intervention are not entirely understood and therefore more studies on the subject is needed.

Daguerreotypes as a material are unique, they are silver but cannot be treated like normal silverware nor can they be treated like other photographic material. Since the image is entirely reliant on the microstructure and light scattering abilities of the image forming silver amalgam particles there has been a development of several approaches unique to in the field of photographic conservation. A common sign of deterioration on daguerreotypes is the buildup of tarnish, which with time will obscure the image and formation of glass corrosion products on the inside of cover glasses.

With the development of minimal intervention there has been an increase in the need for justification of treatments in conservation. Treatments should primarily be beneficial for the object's condition and treatments such as cleaning is being reevaluated.

The thesis aims to study the material, deterioration patterns and conservation of daguerreotypes. In order to then discuss different approaches to the conservation of daguerreotypes using contemporary conservation theory.

1.2 Prior research

The Daguerreotype processes is well documented by both contemporary practitioners and modern scholars. M. Susan Barger and William B. White are two of the most prominent authors in the field, Their book *The Daguerreotype: Nineteenth-century Technology and Modern Science* is commonly cited in many of papers on the subject and has been cited as the as the most comprehensive and detailed work on the daguerreotypes by the Daguerreian society, for this reason parts of the literature study is based on their work.

Some of the study will include the original papers where many methods and treatments where first introduced. More contemporary sources will be used to investigate how the treatment methodology has developed since their introduction, and analysis of their effects on the objects.

There has to the authors knowledge not been any publication detailing the conservation ethics in the relation to daguerreotypes.

1.3 Purpose Statement

The purpose of the thesis is to investigate how conservation of daguerreotypes are currently conducted with an emphasis on cleaning methods the thesis aims to investigate which methods are currently available for cleaning daguerreotypes, and the impact they have on the object's physical properties. This information will then be weighed against a minimal intervention-based approach to discuss the impact cleaning has on authenticity of the object and its ability to convey an image, intrinsic values and meanings. Lastly how a preventive based conservation approach can limit the need for future treatments.

1.4 Framing of issues

1. Should Daguerreotypes be cleaned?
2. To which extent can a daguerreotype be cleaned while still while still preserving some patina?
3. Are any of the currently available methods suitable for cleaning daguerreotypes?
4. Can a preventive based conservation approach limit the needs for future cleaning and treatments?
5. Should daguerreotypes be re-cased?

1.5 Limitations

The work conducted in this thesis will be largely theoretical, thus evaluation of treatments will be based on the reported results as no practical investigations can be performed during the period allotted for writing of this thesis.

1.6 Method and Material

Information will be gathered through literature study.

1.7 Theoretical framework

The discussion will mainly concern the ethical considerations that has to be taken into account when working with cultural heritage objects such as daguerreotypes. All practical treatments will alter the objects in one way or another, therefore great care should be taken before a treatment can be conducted. The primary theoretical framework that will be used to discuss the ethical considerations involved in the conservation of daguerreotypes is minimal intervention. I will specifically discuss minimal intervention in the context of the interpretation proposed by Salvador Muñoz Vinas in *minimal intervention revisited* (2009).

For the methods to be considered appropriate or considered successful they will have to both achieve the aim of the treatment, to be beneficial to the objects condition and impart as little damage to the objects ability to convey its inherent meanings and values. Another ethical concept that has to be taken into account is reversibility, while hardly any intervention is entirely reversible any material added to the object should be possible to be removed without causing harm to the object.

2. Historical background

Entire chapter is based on M. Barger, W. White (2000) *The Daguerreotype: Nineteenth-century Technology and Modern Science.*

2.1 The origins of photography and the daguerreotype

Ever since the discovery of the Camera obscura and its subsequent use, the thought of capturing an image had kept inventors and artists preoccupied since the Renaissance. While the camera obscura and camera lucida was able to render a three-dimensional scene on a flat surface the only real possibility of capturing that image was for an artist to trace the image on a substrate. An early development was achieved by Albertus Magnus in the 12th century with the discovery the photosensitivity. But it would take five centuries before the first real breakthroughs could be achieved. The breakthrough came with the commercial availability of silver halides which enabled the experimentation and development of several photographical processes. The early pioneers of the medium where Joseph Nicéphore Niépce (heliography), Henry Fox Talbot (calotype) and Louis-Jacques-Mandé Daguerre (daguerreotype) often nicknamed the three fathers of photography.

Most early experiments on photography used silver halide salts and the camera obscura to capture images, the images produced by these early experiments had two main issues, there was way to fixate the image on the substrate and the image was therefore not lightfast, and the image where negative. Niépce had initially experimented using silver halides but had failed to solve any of the issues with the technique. Instead he began experimenting with different substrates. Inspired by the methods he had used as a lithographer he began to successfully produce light-sensitive plates to which he could transfer engravings. In 1826-27 Niépce, produced the oldest surviving photo with *View from the Window at Le Gras* using his technique heliography. The technique used a pewter plate (alloy containing 85% to 99% tin, antimony, copper, bismuth and sometimes silver) coated with a light-sensitive compound called asphaltum/bitumen of Judea. The bitumen exposed to the light would harden and become insoluble, the plate was then rinsed with a solvent removing the unhardened bitumen creating a photographic negative. He continued his work to try to perfect his heliography method.

Louis Daguerre was an artist who worked with building theater dioramas, and to assist him in his work he had acquired a camera obscura. It was from his experience with the camera obscura that he cultivated an interest in capturing these images on a substrate. It is unknown how much progress he had made before hearing of Niépces heliograph, but it is known that he experimented using silver salt halides on paper. Daguerre proceeded to send several letters to Niépce who after initial reluctance decided to partner up with Daguerre. In order to improve the heliography method Niépce began using polished silver-plated copper plates as these where whiter than pewter and more suitable for printing. He discovered that if he first exposed the plate using asphaltum/bitumen of Judea, developed the plate and then exposed the plate to iodine vapor the silver surface would darken. He then removed the hardened bitumen creating a positive image using his heliography technique. The first Heliography photograph required up to 8 hours of exposure time which meant that a new camera that allowed for a higher light intake was needed.

Niépce would however not live to see the fruits of his work since he died destitute of a stroke 1833. Daguerre continued the work and entered into a partnership with Nicéphore Niépces son Isidore Niépces. Daguerre continued experimenting using silver plates and discovered that he could use the iodine vapor to create a photosensitive film by itself. He called the method he developed the daguerreotype to differentiate his method from the heliography.

The daguerreotype process developed by Daguerre would start with a silver-plated copper plate which is polished to a mirror like sheen using different grit rubbing compounds. Daguerre then used Iodine fumes to sensitize the plate. The plate was placed in a specially designed plate holder to avoid direct contact during handling and protect the sensitized plate from exposure to light. The plate holder with the sensitized plate would then be placed into the camera obscura. The latent image was then developed using heated mercury fumes. The image was then fixated using a heated solution of sodium chloride.

The early daguerreotypes by Daguerre needed long exposure times they were still considerably less than the 8 hours required for *View from the Window at Le Gras.* Early daguerreotypes by Daguerre still required such extended exposure times that only stationary objects could be captured, this is demonstrated in the View of the Boulevard du Temple image which failed to capture any of the moving people except for a shoe shiner and customer (fig 1.) Some of the earliest surviving photographs by Daguerre therefore portray Landscapes and cityscapes.

With two new photographic techniques developed both the heliograph and the daguerreotype the next step for was for Daguerre and Isodore Niépces to capitalize on their inventions. Their first plan was to reveal the secret of photography in parts as a subscription-based service for 1000 francs for each subscriber (limited to 400 subscribers) or the rights could be bought outright for 200.000 franc.

Daguerre advertised the process by traveling around Paris taking Daguerreotypes with his camera, but the idea failed to materialize when neither subscribers nor any buyers emerged. Next Daguerre instead tried to target the scientific community.

The lack of ability to record their findings had long proved to be a problem in the scientific community. To be a good scientist one also had to be a good draftsman. Daguerre hoped that the daguerreotype could help scientists document what they saw and that they could convince the French state to buy the rights to the daguerreotype. This pitch caught the interest of François. Dominique Arago who was the director at the Observatory of Paris and secretary of the at the academy of science and a member of the French parliament. He hoped that the daguerreotype could be used to investigate the properties of light and that it could serve as a recording media for scientists. As a reward for the discovery Arago convinced the French state to award Daguerre and Isodore Niépces a state pension for the rest of their lives, as a part of this deal the secret of photography would be disclosed to the world as a gift from the French state.

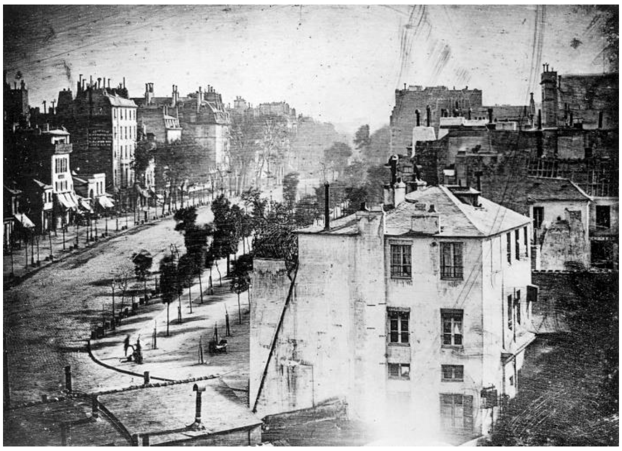

Figure 1: View of the Boulevard du Temple, Louis Daguerre 1883. The earliest reliably dated photograph of people. https://commons.wikimedia.org/wiki/File:Boulevard_du_Temple_by_Daguerre.jpg.

2.1.1 Daguerrotypomania

On August the 19th 1839 the process was disclosed at the academy of science and fine art in the Institute of France. The excitement over the news of the discovery was reported to be almost tangible and every seat in the academy was occupied and a large crowd of people had congregated in the streets outside the academy. Daguerre, Niépces and Arago where all present, in the aftermath of the disclosure of the process there was a great demand for photographic equipment. The process proved to be hard to replicate so Daguerre took to teaching and demonstrations. The process did eventually take on and during the 1839 – 1860 the daguerreotype was the primary photographic method. During these years as many as 30 million daguerreotypes where produced just in the USA. The daguerreotype was so popular that newspapers wrote about a “daguerrotypomania”.

2.2 Further development of the daguerreotype

There were a number of technical and practical issues with the daguerreotype process as presented by Daguerre. Firstly, the exposure times where too long for application in portraiture photography, secondly the silver particles which created the image could be dislodged as easily as dust making the plates very fragile and lastly the images where not colored.

Early daguerreotype exposure times ranged from 3 to 15 minutes which limited the possible application for portraiture and capturing images from life. By developing the camera optics to allow for a higher light intake the exposure times could be lowered. Improving the process chemically proved harder, originally Daguerre had used iodine to sensitize the plate. Iodine is the least light sensitive of the silver halides, so logically one should just use a more reactive halogen to lower the exposure time. It seems like this was the consensus at the time too, but in practically this proved to be hard. Elemental halogen vapor was required where needed as the bulk silver of the plate is not reactive to salt solutions unless it is dissolved. Elemental halogens where relatively recently discovered and not readily available. Chlorine was the oldest of them and the only halogen with a practical use and iodine and bromine where more recently identified at the time. None of these halogens are easy to handle nor do they exist in elemental form in nature. Bromine was the first halogen employed in the production of daguerreotypes apart from iodine since it was crystalline in room temperature chlorine followed soon after. Chlorine and bromine are more reactive which meant that the exposure time could be dramatically lowered allowing for portraiture photography.

Daguerre had recommended that the plates where protected inside a enclosed frame or glued to a cover glass. He had experimented with varnishes but found that they were not suitable as the dulled the image and with age obscured it completely, and indeed very few of these varnished daguerreotypes survive today. To solve the issue the plates where packed in a special package called the Daguerreian package. A chemical method to protect the image against mechanical wear was invented in 1840 by Hippolyte Fizeau, the method consisted of gilding the plate with a solution of gold chloride and sodium thiosulfate. The gilding made the image more mechanically stable and produced a warmer tone to the image and was universally adopted when it became publicized.

The last issue with the plates where their lack of color, this was never really truly solved. The most common method of coloring daguerreotypes where done by applying pigments to the plate. Hand coloring could be produced by painting a thin varnish and applying pigments in the still undried varnish or a binder like gum arabic, some used painted glass stencils. The most commonly used pigments where carmine, rouge, pink madder, chrome yellow, burnt sienna, ultramarine and white. While they are the most commonly used it is important to note that these are not the only pigments used daguerreotypist usually used what was available and cost effective. The pigments where usually applied by stippling using a camel hairbrush (Kozachuk et al. 2018).

Jewelry worn by the depicted persons where often painted with gold paint or could be indented to create a sparkling reflectance. Coloring of plates could also be done with electrolytic gilding, the method involved an electrolyte bath and galvanic battery which was used to selectively gild the plate using metal salts of the desired color. The plates where partially covered in a combination of gum arabic and grease to shield areas from exposure to the electrolyte, the grease was then removed, and the process was repeated for the next color.

Some hoped to be able to produce a method to capture colored images directly in the daguerreotype plate. Edmond Becquerel discovered that if a exposed daguerreotype plate was exposed to yellow light a image would appear without the use of mercury. This method of development is called the Becquerel development and is the favored method used by contemporary daguerreotypists. What is also noteworthy is that daguerreotypes produced this way are faintly colored with the same colors seen in nature. Becquerel also managed to capture the solar spectrum on a daguerreotype. Claude Felix Abel Niépces (Nicéphore Niepces’s nephew) and Levi L. Hill used the daguerreotype process to develop their own processes Heliochrome and the Hillotype both where able to capture images in color but failed to produce a commercially viable process.

3. Chemistry of the Daguerreotype

3.1 The Daguerreian Process (generalized)

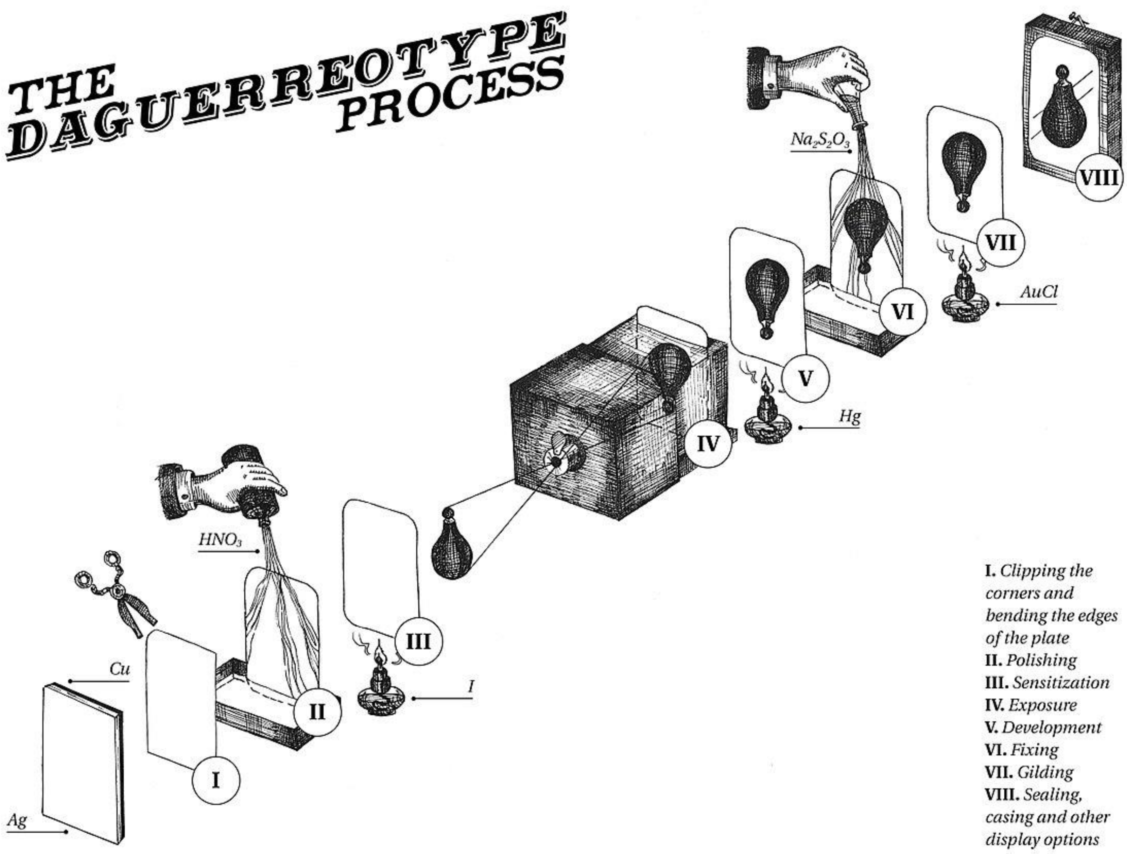

Figure 2: The Daguerreotype processes illustrated. https://commons.wikimedia.org/wiki/File:Daguerreotype_process.jpg

1. The Plate.

The first step in the Daguerreian Process is for the plate to be polished to a mirror like sheen using different rubbing compounds. The polishing is of utmost importance as the daguerreotypes are viewable through light scattering. The daguerreotype process uses silver plated copper plates, the most common plate during the Daguerreian era where made by fusing the two metal sheets in a rolling mill. These plates where called Sheffield plates (also called plating by fusion or cold roll cladding) and where mass produced in Europa and the US. During the early 1850s electroplated daguerreotype plates also appeared on the market. Electroplating is done by immersing the plate in a vat with a silver solution and using electricity to coat the plate with silver. Daguerreotypes produced using the American process used roll-clad plates that then are electroplated by the practitioner. The daguerreotype plate market became profitable and plates where produced everywhere American and French plates had the best reputation. French makes where required by law to mark their plates, these markings included a number to indicate the silver percentage and the maker while in the US only plates made in the state of Maryland had laws forcing them to mark their plates makers all over America soon adopted this to signify that their plates where every part as good as their French counterparts (Barger & White, 2000).

Plates came in different sizes and where generally 0.4 mm thick and the silver layer 10 µm thick. (Canosa, 2016)

19th-Century Image Plate Sizes:

- **Whole Plate:** 6.5 x 8.5 inches (16.5 x 21.5 cm)
- **Half Plate:** 4.25 x 5.5 inches (11 x 14 cm)
- **Quarter Plate:** 3.25 x 4.25 inches (8 x 11 cm)
- **Sixth Plate:** 2.75 x 3.25 inches (7 x 8 cm)
- **Ninth Plate:** 2 x 2.5 inches (5 x 6 cm)
- **Sixteenth Plate:** 1.375 x 1.625 inches (3.5 x 4 cm)

(https://cwfp.biz/platesizes.php)

2. Sensitization of the plate

When the plate had been prepared it was sensitized using halide fumes, this had to be carried out in a dark room to avoid accidental exposure. While Daguerre had initially used iodine other halide or combinations where soon employed, the most common where a combination of Iodine and Bromine

When these compounds react with the bulk silver they react and forms light sensitive silver halides Silver bromide (AgBr) Silver iodide (AgI) and Silver chloride (AgCl) (Canosa, 2016).

Ag^{+} (s) + X^{-} (g) → AgX (s), X^{-}= halide

The thickness of the halide layer affects the final image quality greatly the sensitization is affected by ambient conditions. By examining the interference color produced by the halide film the thickness of the layer could be judged, while Daguerre recommended a golden yellow layer of iodine later processes which used combined halides used exposure from several halides to create a thicker more reactive layer. In the most common process, the plate was first exposed to iodine then bromine and then lastly iodine again producing a steel blue interference color (Canosa, 2016).

3. Camera Exposure.

When the plate is sensitized it becomes photo-reactive and must be placed in a light-tight plate holder or placed in the daguerreotype camera (developed from the camera obscura) for exposure. The exposure time will depend on light conditions, chemicals used in the sensitization process, subject matter and ambient conditions. Common exposure times in portrait studios ranged from 20-40 seconds (Canosa 2016). When light hits the silver halide layer a photolytic decomposition reaction happens, the silver halide decomposes creating metallic silver and a halogen. (Swan et al, 1979)

Examples.

2AgBr (s) - hv → 2Ag (s) + 2Br (g)

It has been suggested that when using halogen vapor imperfections within the crystal structure are created which traps the decomposition products preventing the reformation of the silver halide thus leading to the formation of small pure silver specks. These small silver specks are what creates the latent image, areas subjected to high levels of light are denser while areas subjected to moderate are less dense creating a gradient. The silver particles creating the specks are generally spherical in shape and their sizes ranges in nanometers (Canosa, 2016).

4. Development.

The latent image formed during the exposure is developed using heated mercury fumes. The plate is placed under a vessel with mercury which is heated to 50 - 130 ^{o}C, (Canosa 2016). The mercury is deposited on the silver particles formed on the photolytic decomposition. If the plate is left to develop for too long the mercury will begin to deposit on the bulk silver and the image will be overdeveloped. The deposition of mercury on the silver particles is due to the preferential nucleation of mercury on photolytically decomposed silver particles (Swan et al 1979). The reaction between silver and mercury is instantaneous. A recent study conducted by Ravines, Nazarenko (2019) on five modern ungilded daguerreotypes using x-ray diffraction (XRD) and secondary electron microscopy (SEM) shows that the silver mercury amalgam found on daguerreotypes is Schachnerite/ζ (zeta), Ag1.1Hg0.9, mercury silver Ag0.65 Hg 0,35 and dental amalgam Ag_2Hg_3. The most predominant amalgam found is Schachnerite/ζ (zeta) which is corroborated in Barger & White's findings (2000).

In highlight areas where the density is higher the amalgam particles are homogeneous in size, particles in mid tone areas are usually somewhat larger and more irregular and particles in shadow areas are larger more irregular and agglomerated. This is due to the preferential nucleation of the mercury vapor; in areas with fewer nucleation sites (silver particles) there will be a higher concentration of available mercury and the particles formed will contain more mercury and be larger (Swan et al, 1979) (Barger & White, 2000).

The amalgam particles that are produced on the surface of the plate are light scattering, while the polished bulk silver is non-scattering. When viewed at an optimal angle the flat bulk silver appears dark while the particles on the surface scatter the light appearing white, giving the daguerreotype the appearance of a positive image, when viewed at an angle the bulk silver will instead appear white turning the daguerreotype into a negative image. (Swan et al, 1979) (Barger & White, 2000).

Figure 3: Microstructure of highlight and mid tone areas (authors image).

5. Fixation.

When mercury development has been completed the remaining halide, layer needs to be removed to stop further photolytic decomposition and formation of silver particles. If the plate is allowed to continue to develop more small silver particles will form which will make the motif appear grey. Louis Daguerre had initially used a heated sodium chloride solution to dissolve the halide layer which proved suboptimal, instead sodium thiosulfate was adopted as it had previously used by Sir John Hershel to successfully dissolve halides. In an ungilded daguerreotype the last step is to rinse the plate in distilled water (Swan et al, 1979).

6. Gilding.

Gilding was an optional (but universally adopted) step in the process carried out to further reinforce the image, produce a warmer tone and create a deeper contrast range. The standard gilding solution was prepared by adding gold (lll) chloride solution to a sodium thiosulfate solution which formed a gold (l) thiosulfate complex. The solution was then poured on to a heated daguerreotype plate causing a redox reaction reducing the gold and oxidizing and complexing the silver.

$$[Au(S_2O_3)_2]^{3-} + e^- \rightarrow Au + [Ag(S_2O_3)_2]^{3-}$$

A redox reaction is likely to occur between the gold and mercury reducing the gold and oxidizing and complexing the mercury as a mercury (ll) thiosulfate complex. The heating of the plate promoted further amalgamation of the silver and still unreacted liquid mercury which further fixed the image to the plate (Swan et al, 1979). Gilding should theoretically increase the corrosion resistance of the plate (Canosa, 2016).

3.2 The Daguerreian package

When the plate has been developed it needs to be protected, not only because of the fragility of the image but also to limit atmospheric corrosion of the plate. The finished plate was bound in a bundle called a Daguerreian package. The package contained a cover-glass, a mat or a brass spacer and the plate bound together using paper tape with a flexible brass fame called a preserver folded over the edges of the plate (Prieto, 2017). The glasses chosen for daguerreotypes vary and where chosen for their optical qualities and not for their permanence. Some research suggests that the glass was also chosen based on convenience (Barger & White, 2000).

The plate package was commonly placed in a daguerreotype case, these book like cases where ornately decorated. The cases where often made in wood and covered with leather or paper. Some cases made between 1855-65 used early thermoplastic materials these cases and are called union cases. The inside of the case was commonly lined with silk and velvet (Prieto, 2017) and sometimes stuffed with newspaper to secure the plate more tightly in the case. The housing of daguerreotypes proved invaluable in the preservation of the plate, but with time has come to pose problems, the degradation products released in the deterioration of the materials included in the cases has been proven to negatively affect the daguerreotype plates which will be discussed in chapters 4.3 and 5.6.

Figure 4: Disassembled Daguerreian package.

http://librarycompany.org/catchingashadow/section1/index.htm

4. Deterioration of Daguerreotypes

4.1 Deterioration of the image due to physical damage

One of the most common forms of damage responsible for the deterioration of the image is physical damage due to the softness of the plate and fragility of the microstructure. Barger, White (2000) suggests that the adhesion of the particles to substrate are very vulnerable to dislodging and smearing on newly created plates but that this vulnerability decreases with time. The high image quality of the daguerreotype is due to the reflectance of the highly polished surface meaning that scratches or abrasion of the plate will alter the perception of the image. Due to this reflective nature and the relative softness of silver very little force is required to noticeably scratch the plate. The softness of the plate can vary somewhat due to manufacturing processes, roll-clad plates are commonly softer due to lager grain sizes while electroplated plates as those used in American processes which had much smaller grain sizes and are therefore somewhat harder. Daguerreotype plates are somewhat pliable due to the relative thinness and ductility of the plate that is largely mediated by the daguerreotype package.

Roll-clad plates sometimes exhibit delamination of the silver from the copper surface due to flaws introduced in manufacture causing the adhesion of the two metals to be inadequate. Electroplated silver layers such as those found on American process plates can also exhibit peeling due to poor adhesion. Peeling on electroplated plates might be due to failure to clean the plate before the plating or contamination of the plating bath. This type of peeling is most often found in areas with high image particle density. (Barger & White, 2000).

4.2 Deterioration of the image due to corrosion

Like most metal objects daguerreotypes will age corrode and tarnish with time. When discussing tarnish on daguerreotypes it is often assumed that they behave in the same way as normal silverware would and that the most common corrosion product therefore found on daguerreotypes is silver sulfide. Barger & White (2000) suggests that this is not necessarily always the case, while an unprotected daguerreotype share the same environment of other silverware and can therefore be expected to tarnish as such, the vast majority of daguerreotypes are encased which means that their environment is instead the Daguerreian package, that imposes its own conditions.

The most common source of image deterioration is the formation of opaque and dull corrosion films on the surface of the plate, obscuring the image. This film is called a tarnish also commonly referred to as patina and is a thin layer of corrosion products which forms on many metals. The layer formed from tarnish is a passive layer which protects the metal from further active corrosion. Silver tarnish can exhibit a wide array of colors ranging from iridescence to browns and black with increasing buildup of the tarnish film. The color is due to interference colors which occurs as a result from the phase difference between waves. When light hits a tarnish film the reflected light wave is retarded and becomes out phase. The level of phase difference creates a modulation of color.

Silver is a metal which is highly prone to tarnish when exposed to the environment. The reaction which causes tarnish to from on silver is an electro-chemical reaction. For the reaction to be initiated an electrolyte is needed. This is created when the charged surface of the bulk silver comes into contact with air and attracts moisture from the atmosphere and becomes "wetted". The level of wetting is measured in monolayers, at 40% RH 2 monolayers can be absorbed, when the RH increases more layers will be absorbed and at 60% RH 2-4 monolayers will be formed (Canosa, 2016). Water is a universal solvent and will act a as an electrolyte, enabling the movement and exchange of electrons needed for the reaction to take place.

The next step is initiated with the addition of atmospheric pollutants such as hydrogen sulfide (H_2S), sulphur dioxide (SO_2), nitrogen dioxide (NO_2), hydrogen chloride (HCl) and ozone (O_3).When the atmospheric pollutants are dissolved in the water on the wetted surfaces a redox reaction is initiated. Silver has a high sensitivity to O_3, NH_3, H_2S and Cl^- and relatively insensitive to HCl and SO_2. (Liang, D et al, 2010). The corrosion rate is controlled by a number of factors such as wetness of the surface the number of monolayers absorbed on the surface, humidity, temperature, and the composition of the electrolyte.

At 60% RH and above the rate of corrosion rapidly increases, at lower levels of humidity the rate lowers as because the thinner layer of moisture is a less effective conductor (Canosa, 2016). The presence of strong oxidizers such as ozone, nitrate dioxide or chlorine increases the corrosion rate and formation of Ag_2S and AgCl (Wiesinger et, al 2013) (Liang, D et al, 2010).

When a examining a uncased daguerreotype two different corrosion fronts can usually be found, the first is usually found along the perimeter of the plate edge and the second from the perimeter of the brass mat. Experimental analysis carried out by Barger & White (2000) found that these corrosion fronts differ in composition from place to place and from daguerreotype to daguerreotype. The analysis carried out by Barger & White suggests that the major constituent in the corrosion front along the perimeter of the plate edge is silver sulfide, and the major constituent of the corrosion front along perimeter of the mat was silver oxide. The question whether silver oxide is a major component in the tarnish on daguerreotypes has been somewhat controversial and yet to be proven conclusively true for the majority of daguerreotypes, the mechanics involved in the formation of silver oxide are unclear and hard to replicate artificially (Canosa, 2016).

4.2.1 Sliver sulphite

Research by Barger & White (2000) suggests that if a daguerreotype has free access to a sulfate rich environment it will tarnish at a similar rate to silverware, but if contained in a Daguerreian package the barrier created will limit access to atmospheric pollutants significantly increasing the image protection against atmospheric corrosion.

While there are several Sulphur containing atmospheric pollutants such as hydrogen sulfide (H_2S), carbonyl sulfide (COS) and sulphur dioxide (SO_2) the main sulphur containing specie involved in the tarnishing of daguerreotypes is H_2S. The most commonly found sulphur containing corrosion product on daguerreotypes is acanthite (Ag2S) especially on the corrosion front along the edge of the plate. When in contact with the electrolyte the H_2S forms HS^- which reacts readily with silver ions in solution and with the silver surface which forms silver sulphite (Canosa, 2016).

COS will also cause formation of silver sulphite, when COS reacts with the electrolyte and hydrolyzed to form H_2S. SO_2 will react to form silver sulfate Ag_2SO_4 but for this reaction to be initiated the concentration needs to be three times the normal ambient concentration of SO_2. Increased humidity, concentration of H_2S, light and the presence atmospheric gases such as NO_2 and O_3 are factors known to increase the rate of corrosion. (Canosa, 2016)

Kozachuk et al. (2018) found during analysis of a plate that the primary sulphur containing compounds found on the plate where Ag_2S and SO_4^{2-}. Their findings suggested that the sulphur products where preferentially accumulated in areas of high image particle density. The analysis also found signs of interaction between sulphite and mercury in the form of HgS and $HgSO_4$.

4.2.2 Silver chloride

White hazy tarnish patches on daguerreotypes are commonly attributed to the formation of Silver chloride (Kozachuk et al., 2018). During the Young America exhibition of the Southworth & Hawes daguerreotypes a visible white hazing appeared on the plates. Out of the 165 daguerreotypes that were on display during the two hand a half year of the exhibition 25 of the plates were found to have been damaged and five of the m critically damaged (Robinson 2015). Raman spectroscopy analysis by Centeno et al. (2008) carried out on eighth daguerreotypes (two of the plates where from the Young America exhibition) and a unused daguerreotype plate concluded that the white tarnish spots found consisted of Silver chloride, redeposited silver and faint traces of substituted aromatic compounds. The deposition of the silver chloride does not correspond with image features. Silver chloride is light sensitive and will redeposit back to silver when exposed to UV light. The redeposition of the silver will further alter the appearance of plate, meaning that daguerreotypes with silver chloride corrosion are light sensitive.

Possible sources of chloride on the plate could originate from original processing as solutions of NaCl where originally used to fixating the image, and solutions of gold chloride was used in the gilding process. The chloride could also originate from past treatments as Hydrochloric acid (HCl) used during the acidification of thiourea solutions used for cleaning, or the chloride could have been introduced as an airborne particle from seawater or from organic pollutants released by industry.

In the case of the eighth daguerreotypes used in the analysis the presence substituted aromatic compounds pointed to that the likely source of chloride originated from environmental pollution by industry due to the release of many organic chloride containing compounds, something which analysis of the substituted aromatic compounds also supported. The conclusion was further reinforced since the unused daguerreotype plate showed the same results as those that had been used ruling out original processing. Though this is not universally the case. (Centeno et al., 2011)

Papers produced on daguerreotype corrosion suggested that the formation of silver chloride might be induced by near UV light and the formation of crystals which are then go through re-deposition of the silver when exposed to light. The re-deposited silver is likely the main cause for the hazing and is likely to be irreversible. Voids under the daguerreotype image structure were previously was attributed to etching from cyanide cleaners was attributed as a possible cause of the hazing due to possible trapped chlorine rich air (Robinson, Vicenzi 2015).

Robinson, Vicenzi (2015) argues that this was speculative and does not take into account other observations. The observations show that many plates do not show any inclination towards light sensitivity, the white hazing has also appeared in plates not exposed to light. Plates from the Young America exhibition have also been shown to continue developing white hazing after the plates have been stored dark. Robinson examined two plates produced at the same time and found that one was pristine, and one had developed a white hazing. The plates where created using the same method and stored together. Initial analysis of these plates was inconclusive; raman spectroscopy suggested that silver chloride was present but was unable to determine the concentration of the haze compared to the rest of the plate. Secondary electron microscopy (SEM) analysis found that the hazing consists of amorphous sub-micron particles. Energy-dispersive X-ray spectroscopy (EDX) analysis showed that the hazed areas contained five times higher chloride content than the surrounding "clean" areas the particles where characterized as likely to be AgCl.

Robinson, Vicenzi suspected that the white haze might correspond to drying traces. Robinson managed to reproduce the AgCl formation using reproductions of daguerreotypes made with the same method as Southworth & Hawes where created, the 19th century practice of drying the plates using heat from an alcohol lamp and then contaminating them with chlorine vapor. The reproduction of silver chloride on the plates where shown to be possible on plates not exposed to any light. Robinson's results contradict those of Centeno et al. showing that the cause of the white haze is not due to re-deposited silver but instead the formation of silver chloride. Analysis showed that the chlorine concentration between AgCl formed in darkness and light where the same. If the haziness was due to re deposited silver the chlorine concentration should be lower in the light exposed samples.

Robinson, Vicenzi concludes that photo-reduction of AgCl likely plays a minor role, instead a alternative photo activated reaction is likely to be responsible for the phenomenon. The work of Robinson, Vicenzi indicated that bright daylight only caused a redeposition of 7% of the AgCl. Robinson's proposes that a photochemical reaction takes place instead namely the Ostwald ripening reaction. The reaction causes an excitation of the electrons in the chemical bond raising their energy levels; this in combination with defects in the crystal lattice causes the AgCl to recrystallize and coarsen. This reaction is accelerated by light causing the formation of larger more visible crystals.

Wood can absorb halides which is then released and can contaminate daguerreotype plates. Therefore, chlorine contamination is likely to have been caused by storage and environment as suggested by Centeno et al.

4.2.3 Silver oxide

Visually thin tarnish films of silver oxide are similar to silver sulfide and can easily be mistaken for the other. Both start out as colored tarnish films and goes through a progression of interference colors with increasing thickness. Silver does not naturally oxidize from ambient conditions like other less noble metals do. Consulting a pourbaix digram shows that silver oxide is stable in highly alkaline conditions in the presence of strong oxidants (Canosa, 2016). Barger & White (2000) suggested that light is likely to play a role in the formation of silver oxide. Experimental data suggests that when Ozone is exposed to UV-light the ozone goes through a photo-disassociation reaction into atomic oxygen which reacts with the bulk silver to form Ag_2O. Experimental data suggests that in the presence of UV-light the corrosion rate of the bulk silver is proportional to the amount of ozone present in the atmosphere. The reaction of ozone and UV-light on bulk silver is to contrary to that of silver and other atmospheric pollutants as the formation of silver oxide seems to be hardly affected by the RH. (Wiesinger 2013). Under dry conditions atomic oxygen reacts with the silver, under humid conditions the oxygen is likely reacting with water to form a OH radical which then in turn reacts with silver (Liang et al 2010). As silver oxide is not formed under normal ambient conditions the extent to which silver oxide is found on daguerreotypes, whether it is a major corrosion product and how it forms remains inconclusive (Canosa, 2016).

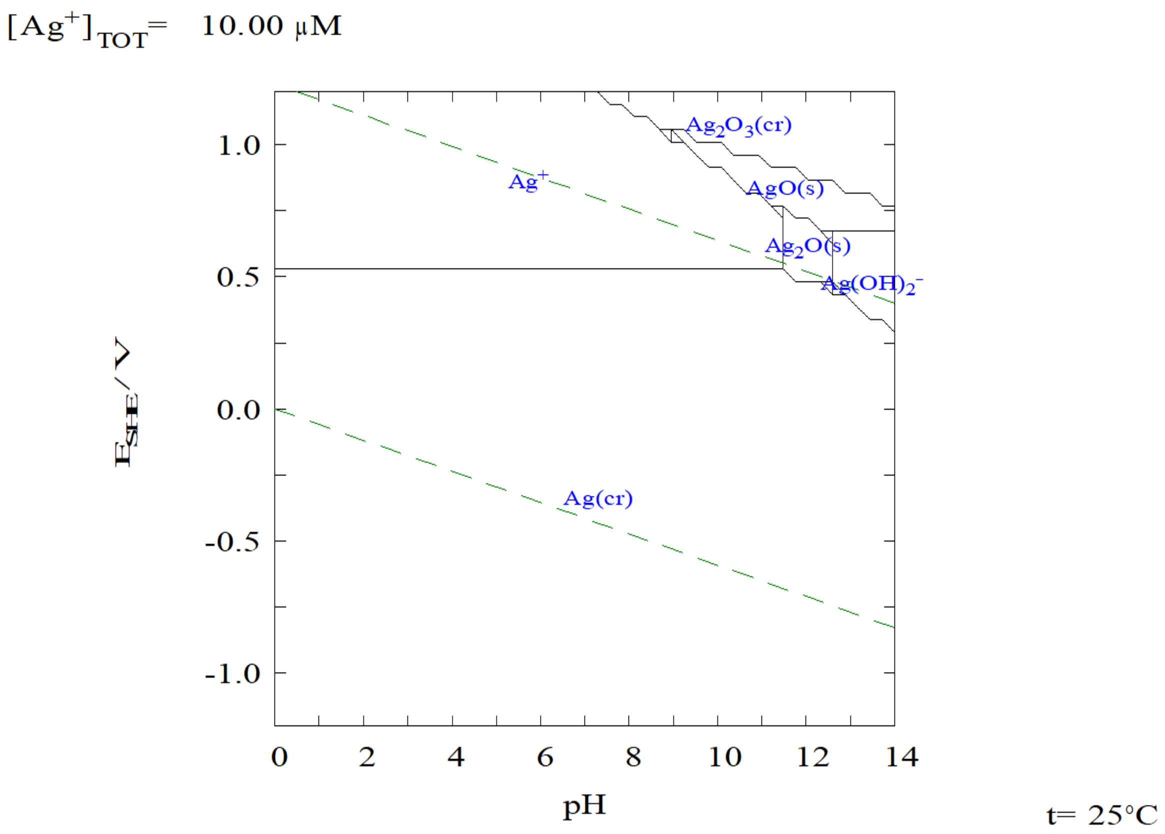

Figure 5: Pourbaix diagram showing the predominance areas of silver oxide. Made using Medusa available at https://www.kth.se/che/medusa/downloads-1.386254

4.3: Corrosion of Glass

While the Daguerreian package has managed to preserve and protect many daguerreotypes it is far from an unreactive and inert environment, it will provide an environment that protects from the most reactive corrosion processes while creating an environment which is likely to lead to corrosion in the future. In a survey conducted by the Hamburg museum it was determined that 134 of the museum's 169 daguerreotypes showed signs of corrosion, in addition to the tarnishing of silver a significant amount of the damage was attributed to glass-induced corrosion of the metal (Fischer et al. 2018). Corrosion of cover glasses is therefore a significant issue in the preservation of the daguerreotype.

Research on cover glasses has concluded that 19th century daguerreotypists chose cover glasses mainly based on their optical qualities and low price rather than their chemical stability. In the study, two hundred cover glasses where assembled and investigated. From these two hundred ten where selected for analysis. The investigation showed that the largest amount of these glasses where soda fluxed glasses the next largest where potassium fluxed and only 5% was lead glass (Barger & White, 2000).

Glass consists a silica rich mineral which forms the main body of the glass, fluxes and network modifiers which is heated to vitrification. Fluxes lower the temperature at which the glass transition phase occurs and are commonly alkaline oxides like soda (Na_2O) and potassium oxide (K_2O). The network modifies are often earth metal oxides like calcium oxide and magnesium oxide. The network modifiers reinforce the noncrystalline amorphous structure and keeps the glass from recrystallization.

The structure of glass is inhomogeneous and separated into silica rich areas and metal oxide rich areas. The higher the ionic strength of the network modifiers the more pronounced the phase separation will be. The level of phase separation is a deciding factor in a glassware's susceptibility to weathering. Other factors which affect the stability of a glassware are inherent faults in the composition of glassware, and humidity. A historic glass which is subjected to a environment with high humidity and low airflow can develop corrosion regardless of composition (Koob, 2007). The Daguerreian package is a perfect environment for this kind of corrosion to initiate because of the limited airflow and trapped humidity (Canosa, 2016).

Glass corrosion is usually initiated by with a process known as leaching, the most common leaching reaction involves the exchange of the alkaline ions (Primarily sodium) with hydrogen or hydronium ions in the structural network of glass creating a highly alkaline environment in the package. This causes the quantity of network modifiers and fluxes to lower and the quantity of silica to increase. In glasses with a high level of phase separation the porosity of the glass is increased which increases the corrosion rate. In the highly alkaline conditions, which arise inside the package hydroxyl groups forming the silica gel layer. When measuring pH on recently uncased daguerreotypes Barger & White (2000) found that the interior surfaces often ranged from between 10-14 pH. This creates a re-precipitation of the glass components and the formation of opaque layers. The continuation of this reaction will lead to dissolution of the glass structural network bonds and therefore the entire glass (Canosa, 2016)

The leached alkaline ions and glass components are dissolved by the water on the wetted surface of the glass forming droplets of the surface. This type of surface corrosion is commonly found on historical glassware created during the Daguerreian era and is referred to as weeping glass due to formation of small oily and tacky droplets on the inside of the glass. (Koob, 2007) The droplets and debris on the cover glass can deposit on the surface of the plate causing visible corrosion spots on the surface of the plate. Sharp glass particles can scratch and puncture the thin silver layer exposing the copper plate (Canosa, 2016). Analysis of tarnish found on daguerreotypes has determined cover glass corrosion can initiate large quantities of different corrosion processes but not all (Kozachuk et al., 2018).

4.4: Filamentous growths

Some daguerreotypes have filamentous growths on their surface, based on morphology these where commonly believed to be mold. Analysis by Barger & White (2000) showed no signs of either DNA or RNA. The formations where instead identified as being mainly composed of silica. At the time of their the analysis Barger & White concluded that the formation was a result of crystal formation of silica deposited on the plate due to corrosion of the glass but that the mechanisms remained unknown. More recent analysis carried out on filamentous growths by Konkol et al. (2011) found contradictory results, they found no higher concentrations of silica in the filamentous growths than the rest of the plate; instead they found that the main component was carbon and identified characteristics indicative of filamentous fungi. Whether all daguerreotypes exhibiting these filamentous growths are caused by fungi or not is conclusive. The data gathered from Konkol et al. comes from two unique case studies and might not be indicative of the composition of all types of filamentous growths found on daguerreotypes and does not necessarily invalidate the findings of Barger & White (2000).

A study on glass-induced corrosion of metals found that a commonly found corrosion product on composite objects made from copper-based alloys and glass is sodium copper formate. A part of the study focused on daguerreotypes, the study analyzed 4 uncased daguerreotypes and found sodium copper formate on three of the four plates, the corrosion was found on both the brass mat, preserver and plate itself. (Fischer et al. 2018). The presence of formats is likely originate from the degradation of organic part of the case such as the wood and paper parts.

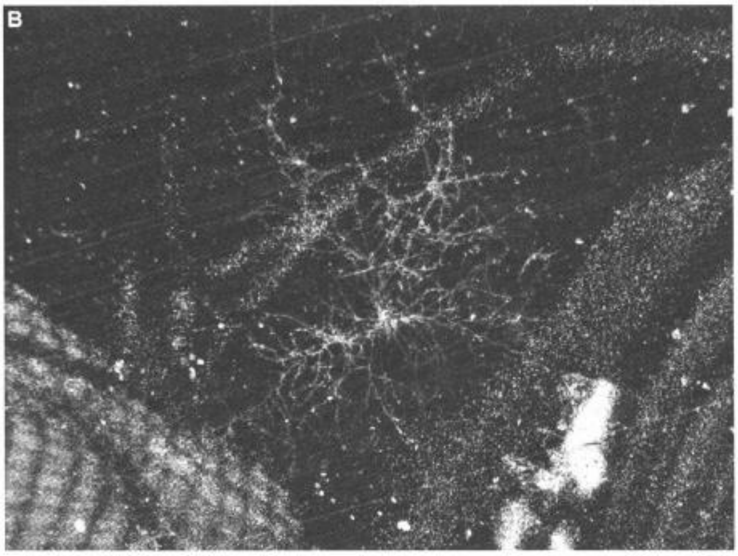

Figure 6: close up of Filamentous accreation (Konkol et al. 2011)

4.5: Copper cyanide corrosion

In 1992 a pattern was observed when examining daguerreotypes under UV light. These corrosion patterns are not always visible in normal light. Daffner et al. (1996) studied one hundred and ten daguerreotypes and found that 50 of the plates exhibited this kind of florescence. Common among the plates exhibiting this type of corrosion where plates that showed signs of over cleaning, prolonged exposure to atmospheric pollutants and general mishandling. Some plates exhibiting faint florescence where still sealed. The study could not determine conclusively the origin of the corrosion and concluded that the that type of corrosion was unique for daguerreotypes and using FTIR determined that a main component was cyanide.

Using dispersive Raman electron microscopy Shugar et al. 2017 identified peaks indicative of copper cyanide which was confirmed using SEM. The rate of the corrosion and the reactivity of the of the corrosion reaction could not be determined nor could the process which initiated the corrosion.

Figure 7: under normal illumination (left), specular illumination (center), and UVC-induced visible fluorescence (right) showing the characteristic Copper cyanide fluorescence. (Shugar et al. 2017)

5. Cleaning of Daguerreotypes

5.1 Solvent cleaners

By the mid-19th century reports began to emerge by owners of daguerreotypes of tarnishing of images. Because of the fragility of the image any mechanical abrasion would irreversibly damage the image, which meant normal silverware cleaning methods like polishing was impossible. Instead chemical solutions called silver dippers where used. The first developed techniques for cleaning daguerreotypes used a solution of potassium and cyanide (Canosa, 2016). While the cleaning of daguerreotypes using cyanide was deemed too aggressive and only to be used as a last effort by some it was commonly accepted and frequently used. The use of cyanide cleaners where so prevalent that analysis of out of two hundred plates only 2 percent showed no signs of cyanide cleaning. The use lasted to the second half of the 20th century when it was replaced by other methods (Barger & White, 2000).

Robinson (2015) suggests that the dark etching pattern Barger, White attributed to cyanide cleaners is likely void fields caused be penetration of the electron beam from the SEM used by Barge and White. Which could mean that far fewer than plates where treated using solvent cleaners than Barger, White thought.

It was believed that all tarnish on the plates where the same and that cyanide-based silver dippers acted as a solvent for Ag_2S and was nonreactive with mercury (Canosa, 2016). Instead thermodynamic data suggests that cyanide will react readily with Ag_2O, AgI, and it will react moderately with the bulk silver and is nonreactive with Ag_2S. This differing reactivity means that when the plate is cleaned using cyanide different regions are attacked at different times. The impression that the cyanide dippers removed corrosion arises from the scattering of light. The morphology of the highlight areas means that debris can easily be deposited in these areas, the cyanide would eat tunnels through the debris which altered the structure causing the debris to scatter light in a similar way to the underlaying silver particles giving an impression that corrosion has been removed (Barger & White, 2000).

Most of the cleaners used where highly unpredictable; sometimes they caused visible etching, the level of cleaning varied. Some plates where cleaned well while others saw little change and in worse cases it caused the image particles to be broken up or redeposited causing the image to disappear entirely. The likelihood of removal of image particles seems to be affected by the mercury content of the particle, gilding and age, with highlight areas exhibiting the biggest losses. The unpredictability is likely due to the different reactivity of the different products (Barger & White, 2000).

Plates cleaned using cyanide can be recognized due to etching of the grain boundaries. The etching increases the roughness of the plate thus making the plate appear less reflective and sometimes matte. Cyanide cleaners also left potentially corrosive elements on the plate which can be responsible for further corrosion. Using SEM Barger & White (2000) found that the highest concentration of silver cyanides was found on the mat edge corrosion front which would mainly consist of Ag_2O.

By mid-1950 the use of cyanide dippers fell out of favor with the introduction of thiourea based dippers. Thiourea based dippers work differently than their cyanide counterparts, the thiourea dip was based on the belief that Ag_2S will dissolve in water and ionize in minute amounts, in a ionized state it would form a complex silver-thiourea and the sulfide would form H_2S. The rate and direction of the reaction would be controlled by the pH of the solution. Using the equilibrium constants of the reactions involved the theoretical optimal pH was determined to be 1 or less. To acidify the solution strong acids such as hydrochloric acid or sulfuric acid were recommended, phosphoric acid was also adopted to avoid the formation of AgCl and Ag_2S. This reasoning assumed that all tarnish on daguerreotypes where sulphur-based and therefore did not take into the account the existence of other types of tarnish.

One effect of this was that phosphoric acid reacts readily with Ag_2O etching the plate and causing the formation of a new corrosion product silver phosphate. Daguerreotypes treated with thiourea can develop brown spots commonly nicknamed measles. Early analysis of the spots suggested that small amounts of the cleaner is trapped in crystal occlusions on the surface of the plate. It was suggested that the spots developed due to thiourea left on the plate due to inadequate rinsing of the plate after the cleaning. This was confirmed by Raman spectroscopy which identified thin thiourea films on the plate. Investigation has shown that the complexing reaction of thiourea and silver is so strong that the measle spots cannot be removed chemically (Barger & White, 2000).

Just like cyanide cleaners thiourea cleaners are also known to etch the plate cause alterations of the image structure and deposition of corrosive elements on the plate. Silver dip solutions could not be used on colored daguerreotypes as they would cause dissolution of the pigments and offer no control of the reaction. Daguerreotypes cleaned by silver dippers show a greater vulnerability to future tarnishing due to deposited reactive elements, cleaned metal surfaces are more reactive and etching of the grain boundaries increases the surface area which also increases the susceptibility. The discovery of this and the increasing value put in photographic objects during the 1970s led to an increase in the investigation of daguerreotypes (Barger & White, 2000) and led to the recommendation that cleaning of daguerreotypes should be postponed until a better solution was found. (Barger et al. 1986). In reality the use of silver dippers where still in common use by the early 1980s (Daniels, 1981).

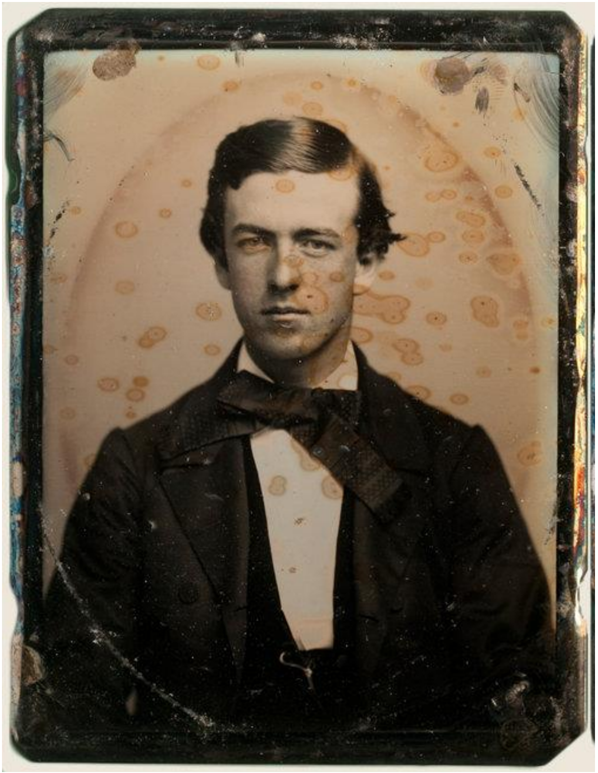

Figure 8: Daguerrean measles https://centurydarkroom.com/conservation

5.2 Sputter cleaning

In 1981 Daniels proposed a new method for cleaning daguerreotypes was plasma reduction of the tarnish. The method is commonly referred to as sputter cleaning and is refers to the use of radio frequency or direct current plasma for removal of material from a substrate. Daniels found that the method was a valuable addition and that the results where satisfying, but he recommended that the technique only be used on daguerreotypes exhibiting moderate tarnishing as the removal of more severe tarnish would leave a milky opalescence. A variation of the method was investigated by Barger, Krishnaswami, Messier in 1982 examining reactive sputtering. In reactive sputtering the gases can be tailored to only react with the material that should be removed. In physical sputtering inert gases are used to physically remove the tarnish. Their conclusion was that sputter cleaning led to a characteristic roughening of the microstructure but that the roughness was limited enough to not alter the affect optical reflectance of the plate. They determined that the technique was not optimized but showed great promise and that the results were generally less damaging than solvent cleaners. Further research based on Daniels and Barger et al. was carried out by Koch et al. in 1991 who reported findings the same type of micro abrasions.

Sputtering can be done in three different modes, plasma reduction, physical sputtering and reactive sputtering. The object is placed in a vacuum chamber and attached to a cathode, the chamber is then filled with a sputtering gas and radio frequency field is then created to create a plasma between the anode and cathode. To ensure that the right material is removed i.e. the tarnish and not the pure silver as this would cause pitting the sputtering rate must be controlled. The main methods for controlling the sputtering rate is achieved by controlling the time, distance between the target (the plate) and the substrate, gas pressure, radio frequency voltage, power and current (Barger & White, 2000).

In a reevaluation of the method in 1986 Barger et al., determined that sputtering as a method offers a high degree of control, and offers overall good results, but found that all daguerreotypes developed a white film in areas which where sputter cleaned especially in areas which were highly tarnished. Sputter cleaning also requires educated technicians and equipment. Analysis on these white films identified them as being the result of surface etching causing a visible increase in roughness of the plate (Barger et al 1986). Like solvent cleaners sputtered plates will be more chemically reactive and likely to be more prone to re-corrosion. Sputtering does however not leave any reactive compounds on the plate after cleaning such as solvent cleaners. While not as aggressive as solvent cleaners the use of sputtering cleaning should be limited but can offer a way to clean plates which should not be wetted such as hand colored plates as it provides a safe way to remove tarnishing while not harming the coloring materials.

5.3 Electrochemical cleaning

In 1986 a new method for cleaning daguerreotypes was presented by Barger et al, the basis of the method lies in elect cleaning which uses the galvanic cell to remove tarnish from the silver. A silver object is placed in a aluminum vessel which is filled with a solution serving as a electrolyte. The ensuing redox reaction causes a reduction of silver the tarnish an oxidation of the aluminum. This reaction can be controlled by applying a external current and a movable electrode, allowing for controllable corrosion removal. The method proposed used a direct current field allowing for the polarity of the silver object to be switched between anodic and cathodic cleaning. The method was named electrochemical cleaning to differentiate from the simple galvanic cleaning method. Barger suggested that the use of both and the switching between anodic and cathodic cleaning would help break up the corrosion layers and allow for easier removal of the tarnish.

The electrolyte solution proposed consisted of two parts water and one-part ammonium hydroxide, this solution works as a solvent for Ag_2O but does not work as a solvent for the pure silver or other corrosion products. The solution is maintained at 12 pH as few corrosion products are stable at this pH, the corrosion products which are stable at 12pH mostly consists of different silver oxides which fall apart from Ag_2O are unstable at normal conditions. The ammonium hydroxide will complex available silver ions and leaves no residue when washed away.

When the daguerreotype is in cathodic position the anodic electrolyte will produce a thin film of Ag_2O. when Ag_2O is formed on the corrosion surface it is very unstable in most pH concentrations. The instability is further increased due to the thinness of the film and solubility in the ammonium hydroxide. Barger et al. (1986) suggests that this instability helps to break up the thicker tarnish films, when the wand is the switched to cathodic cleaning the silver ions are reduced back to silver and the tarnish layer are detached or dissolved.

The setup used consisted of the daguerreotype, a silver wand serving as the two electrodes and a DC power supply with a toggle switch (DPDT) to switch between anodic and cathodic cleaning and a specially constructed silver plate holder. The type of wand used is not specified. The plate was then immersed in the electrolyte solution and the wand was used to locally treat areas with tarnish. Initially an aluminum wand was used which in some cases could cause pitting if the rod touched the plate and sometimes caused the silver layer to completely detach or peel away from the substrate. The aluminum would also cause wild fluctuations on the voltage output. Tests with wands made from more noble metals improved the results drastically. The best results are achieved using a silver wand, the galvanic cell is negated put the potential created by the current is still retained maintain the electrolysis. The use of a silver rod eliminates the fluctuating voltage, pitting peeling, allows for faster and a fuller cleaning. The voltage is kept between 2-5 V and the current of the cell ranged from 8-25mA. There was no real difference in results between the higher and lower voltage on the rate or effectiveness except for a few instances where an increased voltage was needed to remove some corrosion spots.

The conclusion by Barger et al. (1986) was that there is a small improvement in the microstructure of the plate due to a slight electropolishing effect improving the overall reflectance of the plate. The electropolishing reduces the roughness of the plate and therefore also the surface area resulting in an increased corrosion resistance. Electrochemical cleaning does not affect the image particles. Hand colored daguerreotypes should not be cleaned using electrochemical cleaning. Daguerreotypes colored using methods not based on the use of pigments or binders can safely be cleaned using electrochemical cleaning.

In the years since the introduction of electro-chemical cleaning further investigation of the method has been presented. Wei, et al. (2011) investigated electrochemical cleaning through the use of a potentiostat. A potentiostat can be placed between the half-cell reactions to measure the potential and current or apply a specific potential or current. Potential is defined as a measure for the potential electrical energy between two points and the current is a measure for the flow of charge between two points with different potentials. If the anodic and cathodic reactions proceed at the same rate the potentiostat would measure 0, the potential between the anode and the the cathode is called the open circuit potential which depends on the half-cell potentials.

In the method investigated by Wei, et al. (2011) the potentiostat is used to create a cathodic reaction on the plate to break up the corrosion products and reduce the silver. The cleaning should be conducted under a constant potential which is monitored using a reference electrode. The potential used is dependent on the corrosion product which is to be removed. Firstly, the potential must be determined by preforming a potentiodynamic polarization scan, typical results of the scan show that cathodic cleaning should be done with a negative current in the ranges of -1.2 to –1.5. The use of a reference electrode is imperative for monitoring a steady potential as the current will change when the corrosion products are removed.

The rate of cleaning is controlled using the cathodic current. To be able to locally clean the plate the available current needs to be directed into that era. In the electrochemical cleaning proposed by Barger et al. (1986) this can be done by using a counter electrode such as a platinum wire increasing local cleaning. Wei et al. recommends the use of platinum as it is an inert metal which will not contaminate the plate and while it is more expensive it can be reused.

The experimental methods presented Wei et al. (2011) should not be considered as necessarily the proper method but rather an attempt to determine the proper parameters and to show that the application of standard industrial methods will make electrochemical cleaning safer. The cleaning parameters where developed using artificially tarnished silver blanks before real plates where used. In initial tests ammonium hydroxide was used as an electrolyte, however it became apparent when the solution turned blue that reports of interaction between the copper and ammonium hydroxide where correct. Instead a solution of 0.1M sodium nitrate was used to avoid any reaction with the copper. A potentiodynamic polarization scan was done on the test plates to determine an ideal cathodic potential. Several potentials in the range where evaluated.

Before cleaning the plates where degreased in a ethanol bath. The copper back of the plate was sanded on the back and a copper wire was hot glued to the plate. The plates where placed vertically to ensure that removed material did not settle on the plate. The parameters for the cathodic potential used was -1.2 to -1.5 mV ESS. Cathodic potentials from -1.2 to – 1.4 was tested, -1.2 was generally slower, -1.3 and -1.4 cleaned the plates in 30 seconds while -1.2 took almost two minutes. All the sample daguerreotypes showed a faint hint of brown tarnish after cleaning (the -1.2 showed slightly more). An optimal potential was determined at -1.3 as it would offer the most control.

Wei et al. concluded that whether the results where satisfying is partially a question about aesthetics and ethics but concludes that the majority tarnish could be successfully removed and that the image has become more readable. The investigation also showed that the proposed method is safer than the original method and analysis showed no alteration in the image structure. Wei et al. notes that before the method can be responsibly used on daguerreotypes more investigation has to be conducted. Breaking up of large particles, the remaining brown film needs to be identified and closer study of the Au content needs to be conducted. Coloured daguerreotypes need to be examined as the stability of the pigments in solutions needs be determined before electrochemical cleaning can be considered.

Figure 9: Daguerreotype before and after cleaning by Wei et al. (2011).

A study by carried out by Kozachuk et al. (2019) aiming to evaluate and compare the results on electrochemically cleaned plates by using both the original method as proposed by Barger, et al. (1986) and the optimized method proposed by Wei et al. (2011). Kozachuk et al. points out that in the existing literature only localized areas have been evaluated before and after treatment which offers limited insight into any alterations done to the physical and chemical morphology of the plates. The study uses synchrotron radiation analysis (SRA) micro-x-ray florescence (μ-XRF) X-ray absorption near edge structure (XANES) to analyze how electrochemical cleaning affects the elemental distribution and chemistry on the entire surface of the plate. The plates used in the study where naturally tarnished.

Synchrotron-based x-ray analysis was chosen as it allows for micro and macro imaging before and after the electrochemical cleaning. Micro-x-ray florescence was chosen for local imaging of the tarnish products. The distribution of the tarnish products where monitored through the use of x-ray adsorption spectroscopy. The entire plates where imaged using rapid XRF. The results of the rapid scanning XRF meant that comparisons of the elemental ratios or the different areas of the image could be done before and after the cleaning. The mapping and possibility to analyze the entire plates needs to be able to fully evaluate the methods.

The results of the cleaning showed that both the Barger and Wei method showed an improvement in optical quality. The analysis showed that both methods caused both Ag and Hg to be removed or redistribute on the surface. The greatest difference was found in the highlight areas. The Ag loss was greatest in the Barger method while the losses in Hg where similar in both the Barger and Wei methods. The μ-XRF mapping allowed for a improved ability to see these larger trends resulting from the treatments. A likely reason why the losses in the highlight areas are the most prominent is due to the preferential accumulation of corrosion products in these areas. This preferential accumulation could be due to larger surface area or that there is a difference in the potential of the plate and the particles. The x-ray adsorption analysis showed that the most commonly found corrosion products where Ag_2S and AgCl and that electrochemical cleaning effectively removes both.

Lastly Kozachuk notes that each daguerreotype needs to be individually assessed before treatment, poor quality plates will still be poor quality after the treatment and plates which are in a bad condition might see the condition worsen from the treatment. Great consideration should be taken before undertaking a treatment and more work needs to be undertaken before the method can be considered safe to use. Further work should try to develop a method of cleaning the plates which do not call for immersion of the plates. Which would also allow for the cleaning of daguerreotypes which have been hand colored.

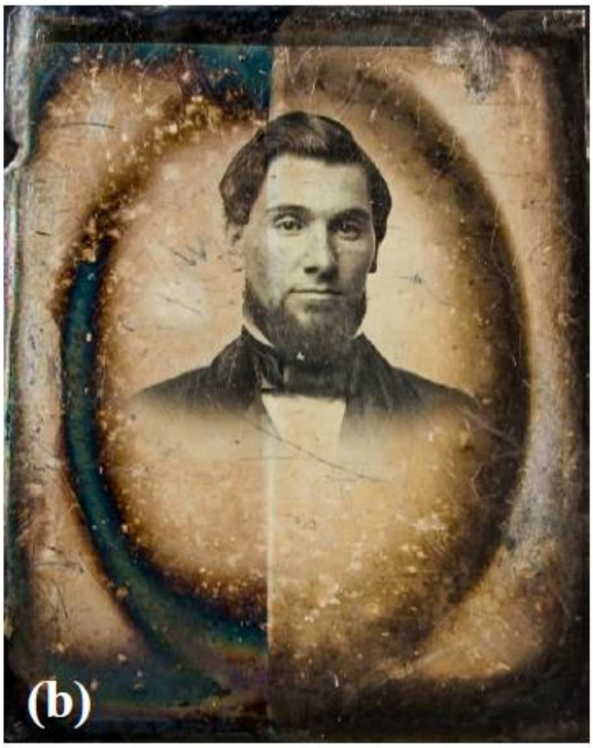

Figure: Daguerreotype partially cleaned by Canosa (2016)

A recent investigation conducted by Canosa (2016) which builds on the research conducted by Barger and Wei aimed to optimize the electrochemical cleaning method suggests that the delamination was not completely solved by switching to silver wands and that some reports suggested interaction between the copper plate and ammonium hydroxide. Canosa suggests the usage of a solution of sodium nitrate as it does not cause any deterioration on the plate. A platinum electrode wand was used to reduce the deposition of silver from the wand to plate. The use of a reference electrode is recommended to monitor that the plate is properly polarized so no accidental corrosion will occur. A constant steady cathodic voltage is recommended instead of the switching between anodic and cathodic cleaning as suggested by Barger et al. (1986) since it will ensure that no oxidation in the plate will occur.

A steady voltage of -1.3 voltage was suggested as analysis showed this to be the optimal voltage at which reduction of silver sulfide.

The perimeters set by Wei where similar to what Canosa concluded where optimal. When using the optimized cleaning method on tarnish films of Ag_2O and Ag_2S Canosa found that the tarnish was notably reduced in just 5 minutes. The rate of removal deceases as the system approaches equilibrium, full removal of tarnish is expected to require a long period of treatment. Analysis of the plates showed no alteration in the microstructure or surface deposits. The proposed method was more effective at removal of Ag_2S than Ag_2O, AgCl is likely not affected by electrochemical cleaning.

5.4 Laser Cleaning

Turovets et al. (1998) suggests that while electrochemical cleaning is has been shown to be safe there are some risks involved such as pitting caused by accidental touching of the plate with the electrode wand, that cannot be applied to colored plates, and failure of cleaning ungilded plates. The application of nanosecond Q-switched excimer laser ablation for removal of tarnish on daguerreotypes was tested. Tarnish removal by laser ablation is done by irradiation with a laser beam, the tarnish absorbs the energy of the beam, and is heated rapidly and evaporates or sublimates. Laser ablation can be done locally which means that colorized daguerreotypes can be treated in areas which are not coloured, as limited research has been done on hand colorized daguerreotypes it is unknown whether some of coloring materials can survive the laser beam.

Laser cleaning is photomechanical and hence is inert as it does not rely on the addition of any new material that can leave any material on the plate. The laser beam is highly controllable and can be focused allowing for localized treatment. Most of the laser energy is absorbed by the surface allowing for treatment of the surface without affecting the bulk. Several processes where tested some of the processes caused alterations to the image structure and some even caused the plate to melt. The presented conclusion determines that cleaning with excimer laser is superior to previously suggested techniques if the surface has not been damaged by previous treatments. The technique is also applicable to hand colored daguerreotypes if the painted areas are avoided (Turovets et al. 1998).

Laser ablation was further investigated by Golovlev et al. (2000) found that when the laser was properly optimized the ablation process using short picoseconds pulses provided a clear improvement in the overall visual appearance and found no apparent damage to the image structure. Experiments conducted using femtosecond laser by Abere et al. (2011) found no evidence of damage to image structure of the surface.

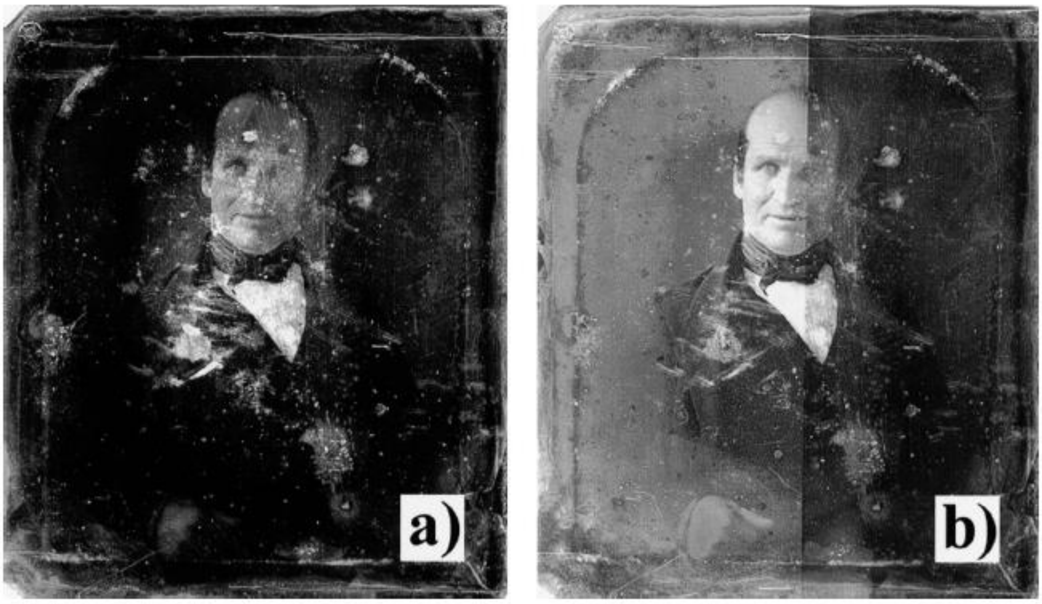

Figure 10: Partially Laser cleaned daguerreotype by Golovlev

5.5 Digital Restoration and Imaging

Recent technological advances have allowed for the possibility for imaging and digital restoration of tarnished plates. Kozachuk et al. (2018) rapid high dynamic range elemental x-ray fluorescence to image a heavily tarnished daguerreotype. The restoration was carried out on two plates, Plate A showed only faint outlines subject and details are indiscernible. Plate B is heavily tarnished along the perimeter of the image, oily residues on the surface and white fogging obscures all the image details. The images where imaged using a rapid-scanning Maia detector, that can the detect and discern specific elements in the image. This allows for imaging of the Hg and Au distribution on the plate revealing the image hidden under the tarnish. The ability to see Hg μ-XRF mapping shows that despite heavy tarnishing the Hg concentration and distribution is preserved. While electrochemical cleaning does alter the Hg distribution it is likely that the effect isn’t big enough to affect Hg μ-XRF mapping. Kozachuk et al. concludes that digital restoration of daguerreotypes using this technique allows for a non-invasive way to recover images from severely deteriorated plates that otherwise couldn't have been viewed.

Goltz, Hill (2012) used hyperspectral imaging to asses heavily tarnished daguerreotypes. The use of near infrared light can reveal the image under the plate. The hope of Goltz, Hill is that the technique could assist conservators in decision making, the use of hyperspectral imaging could show if there is a image preserved under the tarnish and how much could be recovered. The imaging could also be used for monitoring of plates during exhibitions and before and after treatments.

Figure 11: Digitally restored Daguerreotype by Kozachuk.

5.6 Preventive conservation of Daguerreotypes

Storage: When in storage the biggest threat to daguerreotypes is usually moisture more due to the potential of glass corrosion of the cover glass than the plate itself. Therefore, daguerreotypes should ideally be stored dry well below the dew point and limited temperature fluctuations. (Barger & White, 2000). General recommendations by the National Park Service (1998) suggests that daguerreotypes should be stored at 18-20 °C (65-68°F) 40-50% RH and at less than 100 Lux or 10 foot-candles.

According to Barger & White (2000) and Robinson (2015) daguerreotypes are not light sensitive, and cased daguerreotypes are automatically stored in darkness anyway. Daguerreotypes can safely be displayed under normal ambient lighting; However, the formation of silver sulfide and other atmospheric corrosion products is enhanced by light which should be taken into account. Centeno et al., (2011) however proposes that the formation and decomposition of AgCl is greatly affected by light and recommends that the exhibition of daguerreotypes should be limited. If the Oswalt ripening reaction as proposed by Robinson (2015) is correct this means that the formation of the white silver haze is accelerated by light not directly caused by it.

Robinson (2015) proposes that the white haze can easily be removed using ammonium hydroxide. NH4OH has previously been used to remove white hazing on daguerreotypes to great success. The solvent can be applied locally on colored daguerreotypes. After the treatment the plates are immersed in distilled water to thoroughly rinse the plates.

The preservation of daguerreotypes is closely linked to the integrity of their cases and the Daguerreian package. Several proposes for structural housing systems have been presented by Chen et al (2011) and Prieto et al (2017) which aims to maintain the experience of the plate while also offering support and protection. A specialized Oddy test for assessing housing materials for daguerreotype has been developed by Hodgkins et al. (2013) using silver nanofilm sensors. Barger & White (2000) recommends the use of paper tapes for resealing opened plates. Barger et al. (1986) advises against the use of buffered archival paper as mat spacers of plates and instead recommends the use of metal mats. Examination by Barger & White (2000) suggests that a majority of 19th-century cover glasses are unstable in the presence of moisture. Due to the prevalence of glass corrosion induced deterioration of the image in daguerreotypes Barger et al. (1986) recommended that cover glasses should be replaced for more modern stable glasses with similar optical properties. In a later statement Barger & White (2000) stated that the cover glasses could be viewed as being a part of the object and therefore should not necessarily be discarded, instead processes of re glazing could possibly be carried out however notes that it is a subject of some controversy. If the glass is to be considered to be a part of the object, they recommend that dry cleaning of the glass as aqueous cleaning of the glass leaves the glass vulnerable for further moisture attack. Lastly, they note that a newer glass would provide a much better protection of the plate.

5.6.1 Protective coatings on daguerreotypes

As mentioned earlier early attempts of varnishing daguerreotypes made by daguerreotypists found that the varnish diminished the contrast and depth of image the aging of the varnish commonly caused the image to disappear. It would take a futher 140 years before the subject was investigated again, Barger et al. (1984) explored several protective coatings with the intent of using coatings to limit the need of retreatment. The protective coatings tested which showed the most promise where sputter applied coatings and out of those boron nitrate gave the best results. Later investigation by Sease et al. (1997) of the use of coatings on silverware showed that instead of uniform corrosion coated silverware objects often exhibited pitting, etching, filiform corrosion, formation of silver whiskers and losses of plated silver surfaces caused by inadequate coating. In a later statement Barger & White (2000) stated that no coating had been found that could be generally recommended, as no protective coating which can be scientifically proved to protect the plate from corrosion while also not affecting the optical properties of the plate had been found. They also raise the issue of conservation ethics as the majority of coatings are irreversible and even more so on daguerreotypes than other objects. Barger et al. concludes that in some cases coatings could find applications.

5.6.2 Colored daguerreotypes

Kozachuk et al. 2018 concludes although the considerable interest in chemical composition, degradation and origin of pigments there has been little interest given to analysis of hand colored daguerreotypes. Of the work that has been conducted blues have been attributed to prussian blue and rouge tones to mars red. Kozachuk et al. conducted a study intended to characterize red pigments used on the cheeks of daguerreotypes. The study used SEM-EDX to determine the morphology and to make a estimation of the elemental composition. Raman and FTIR was used to identify the red pigment crystals and evaluate if binders where used. The study found that identification of pigments on hand colored daguerreotypes is hard due to the complex surface of the plate and low concentrations of pigment. FTIR and Raman spectra found that carmine was likely used. Identification of organic based pigments suggests that conservation procedures using solvents which could affect organic materials should be avoided on these plates.

6. Extended Case Studies

The inclusion of some case studies in the thesis is to give a context to the conservation methods discussed above.

6.1 Sterling C. McIntyre's Panoramic Views of San Francisco

The Daguerreian Annual 2013

Mike Robinson

Figure 12: Before and after Treatment.Mike Robinson, 2013 Panoramic Views of San Francisco, photograph, accessed 6 may 2020 https://centurydarkroom.com/conservation

Author: Mike Robinson

Year of publication: 2013.

Object: Panoramic Views of San Francisco

Place of origin: San Francisco

Artist: Attributed to Sterling C. McIntyre.

Dating: February of 1851

Dimensions: The object is composed of five half plates. One half plate is 11 x 14 cm (4.25 x 5.5 inches).

Description: The plates depict a panoramic view of San Francisco.

Historic context: The plates where created by Sterling C. McIntyre. In during February 1851. McIntyre was a dental surgeon and daguerreotypist who arrived in San Fransisco on November the 21st 1850. The gold rush of 1948 which led to a increase in wealth enticed many daguerreotypes to the city McIntyre being one of them. McIntyre focused heavily on landscape photography during the early years of his stay in San Francisco which led to creation of these five half plate panoramas.

Preservation related context: When the plates where acquired in 1998 by the art collector R. Isenburg the plates were sent to the George Eastman Conservation lab for evaluation, while it was there it was carefully photographed and documented.

The middle plate in frame is heavily tarnished, to such a degree that the plate tarnish has formed such a homogeneous layer that the entire plate has turned opaque. The extreme build-up of tarnish is due to more than a century of existence without a cover-glass. The four other plates are tarnished by a white veil. The seal of the Daguerreian package was broken and plates had been uncased for cleaning in the past. It is speculated by *Mike Robinson* that this was could have been done for cleaning of the cove glass and to dust the plates. When the plates where uncased, they suffered damage due to mishandling in the form of abrasion and wipes. Whether the plates had been chemically cleaned using solvents could not be determined, but *Robinson* did not suspect that had been cleaned. The tarnishing corrosion product in the white veil is believed to have been induced by a combination of fluctuations in atmospheric conditions during storage and pollutants released by the wooden frame. The conservators at George Eastman House concluded that the middle plate was too tarnished and that a possible attempt to clean the plate might result in the destruction of the plate.

Treatment methodology: The project has its beginnings in 2001 when *Robinson* being a daguerreotypist was approached by Isenberg with the proposition of recreating a copy of the original image, but in the end the project was never initiated. It was not until some years later that *Robinson* could devote time to the project. Research conducted before the treatment ruled out thiourea cleaners. *Robinson* had developed their own version of the electro cleaning method which aimed to address some of the issues they had experienced. Though experienced in the method the risk involved cleaning such a tarnished plate which in best cases might yield a dull and lifeless faint image led to the decision that the heavily tarnished should be left uncleaned. Instead it was decided that the plate would be reproduced.

Through the work of Goltz, Hill (2012). Hyperspectral Imaging of Daguerreotypes, *Robinson* was familiar with the use of near infrared hyperspectral light to reveal the underlaying image in tarnished daguerreotypes. Though a connection with Greg Hill at the Canadian Conservation Institute in Ottawa the heavily tarnished middle plate was brought in for hyperspectral imaging in 2013. Unfortunately, the plate was too tarnished, and no light could penetrate the tarnish and therefore none could be reflected back, and no imaging could be achieved.

Instead the image had to be recreated, the image had to be pieced together using a combination of an image from a Panorama owned by the George Eastman House and one plate from a panorama in the collection of the Oakland Museum. Both Institutions provided high resolution images which were combined digitally to recreate the lost image. In order to attain high resolution images to use as references the remaining four where cleaned using Electro cleaning. The white veil was removed but some of the tarnish was left along the mat edge as a patina. When the image was complete a new daguerreotype was created, as the new plate was newer it was decided that it should be patinated. The Original blackened middle plate was retained and displayed alongside the finished Panorama.

Robinson uses a method called Robinson's asymmetric electro cleaning method. While it is based on the Barger's electrochemical cleaning method it differs somewhat. Robinson's method was developed to address some of the issues they had found in the Barger method. Firstly, no wand is used as the distance between from the plate to the wand will change the distance between the electrodes resulting in changes in current density which can cause exfoliation. Also not using a wand removes the risk of contact between the plate and wand. Secondly the method uses both anodic and cathodic cleaning, but it is done at different settings and in separate solutions. When the plate is in anodic mode about a fifth of the current used when the plate is in cathodic position. The current is adjusted depending on the size of the plate and the current is never continuous, instead a pulsing current is applied by hand during the treatment. Lastly Robinson does not use ammonium hydroxide instead different solutions are used depending on currency direction, a basic solution is used for cathodic treatment and a weak acid solution is used in anodic cleaning (personal communication, 6 may, 2020).

6.2 A Glimpse from the Dawn of Photography Investigation and Stabilization of an 1839 Daguerreotype at the Peabody Essex Museum

Topics in Photographic Preservation, 16 (2015)

Elena Bulat, K. M. C., Jiuan Jiuan Chen, Katherine Eremin, Debora D. Mayer, and Phillip Prodger

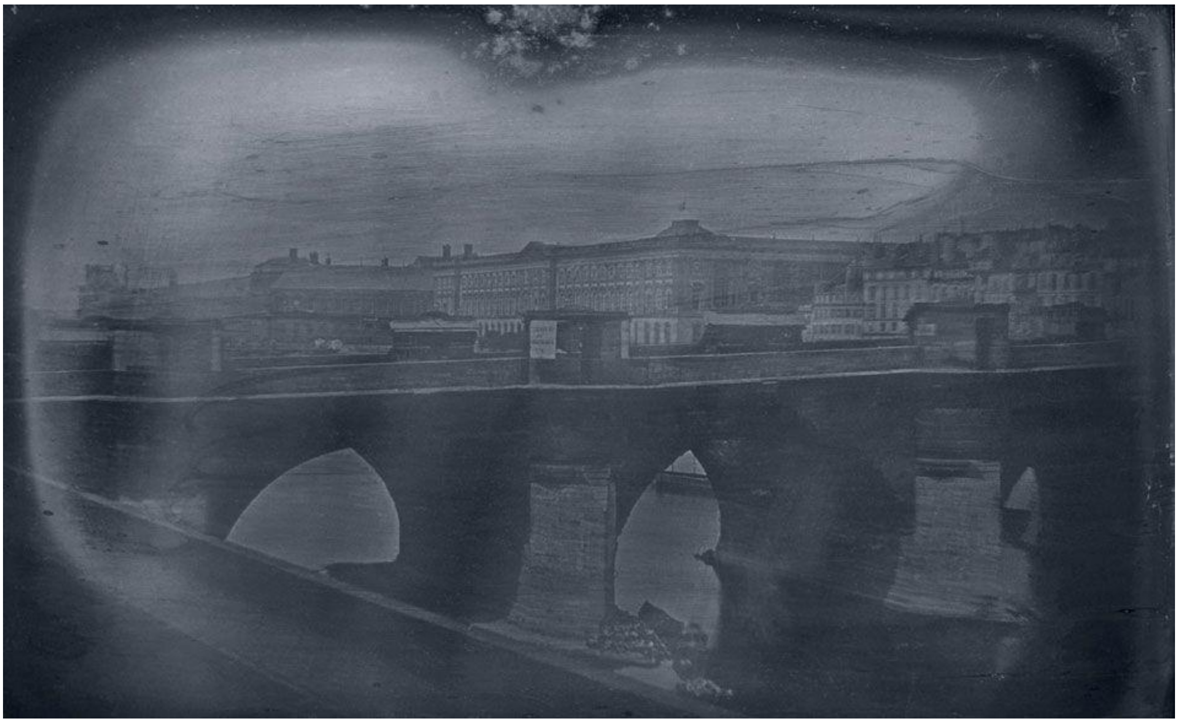

Figure 13: Peabody Essex Museum Daguerreotype of view of Paris overlooking Pont Neuf.

Authors: Elena Bulat, K. M. C., Jiuan Jiuan Chen, Katherine Eremin, Debora D. Mayer, and Phillip Prodger

Year of publishing: 2015.

Object: Peabody Essex Museum Daguerreotype

Place of origin: Paris

Artist: Attributed to Vincent Chevalier of Louis Daguerre.

Dating: 1839

Dimensions: 11,3 x 16,5 cm (a bit larger than a half plate)

Description: The plates depict a exterior a view of Paris overlooking Pont Neuf .

Historic context: Very few plates produced during the first year of the Daguerreian era survive today. A survey conducted in 1956 found that out of 32 only 10 daguerreotypes from the 1838-39 era where known to still exist, the existence of 16 others was noted but their whereabouts and status was unknown, two were listed as lost and four where destroyed during the second world war. One of these was noted to depict a view of the Pont Neuf which could possibly be the Peabody Essex Museum Daguerreotype.

The attribution to Vincent Chevalier of Louis Daguerre arises from a label of Vincent Chevaliers studio and a written pencil marking on the back of the plate dating it to 1839. The plate might also be attributed to Chevaliers assistant Pierre-Ambroise Richbourg.

Preservation related context: In 2008 the plate came to the attention of Dr Philip Prodger the curator at the Peabody Essex Museum. The plate had been donated to the museum by John Burley in the mid-19 century. The Daguerreotype was discovered in a wooden frame with a passe-partout, the plate had held in place by two pieces of adhesive which now had failed leaving the plate loose inside the frame. A conservation record from 1988 noted that the plate had been cleaned using ammonia and water to reduce grime, the cover glass was cleaned, the window mat was cleaned and adhesive residues where removed. The plate was rebound between the cover-glass and backing using filmoplast P-90 tape.

The plate had scratches along the edges, abrasions, accretions, etching and wax residues along the right edge. The tarnish front follows along the mat edge, this was determined to be due to exposure to air pollutants, humidity and acidic by products created from wood deterioration. The surface of the plate is covered in a white milky haze residue. A similar but thicker milky white residue with more consistency was found on the edge of the plate. Different corrosion stains where found on the plate some of them appeared like a white halo while others have a dark brown colour. Several residue stains are found on the surface. The top edge of the plate has a blue tarnish and a large area of etched surface and silver ex-foliation. The backside of the pate has only minor corrosion spots.

Treatment methodology: A treatment plan was developed as a collaboration between the museum administration, a curator, photograph, paper conservators, technicians and conservation scientists. The focus of the treatment approach was preventive care and documentation of the object. It was agreed that a improved housing would be a priority outcome of the treatment. The resulting treatment plan involved detailed physical examination, information gathering, Photo documentation of the plate and housing using imaging methods such as ambient light, UV and infrared red radiation and magnification. Instrumental analysis with XRF of the plate with housing and Raman spectroscopy of the was carried out on the plate. FTIR was used for identification of adhesives. Paper fibre analysis was carried out on the paper mat and other paper components of the housing unit.

The XRF showed no gold present on the surface which would be consistent with a early ungilded plate, it also showed low levels of mercury. Preliminary non-destructive Raman spectroscopy gave indications that the plate was extremely sensitive to minimal laser power which resulted in Raman spectroscopy not being pursued further. It is suggested by the authors that this sensitivity to light could likely be attributed to a lack of gilding and age. The tarnish on the corrosion front by the edge of the plate showed a considerable high sulphur content. The authors had initially suspected silver chloride to be responsible for the white hazing of the plate but XRF showed no chloride content in these areas. XRF analysis of the mounting frame and mat showed a high level of calcium, iron, copper, lead and mercury content with possible faint traces of cobalt. XRF analysis of the cover-glass revealed high levels of silicon, calcium and arsenic with traces of potassium, titanium, iron, rubidium, strontium and zirconium which corresponds to typical silica glasses from 19th to 20th century. FTIR showed that the material on the plates corners was beeswax.

UVA imaging analysis of the housing unit showed the typical florescence's of aged organic materials. UVA imagining analysis of the plate showed only speckles of dust and debris with a few small spots of florescent adhesive residue. It was noted that the plate did not show any of the green-yellow florescence typically attributed to copper cyanide. The lack of florescence is consistent with a cleaned daguerreotype. The authors found that the lack of copper corrosion on the image side meant that there is no immediate concern for the stability of the image.

Analysis of the fibres showed that the mat and backing paper contained bast fibres with possible traces of cotton. The brittleness of the fibres indicated that deterioration was the main reason for the fragility of the mat. The absence of wood fibres in the papers which was commonly in use during the second half of the 19th century supported the authors premise that the housing was original to the piece.

The paper elements of the housing where conserved by K. Carey and included removal of tapes and paper layers to access blue backing paper with the Chevalier label. The backing paper was consolidated using japan paper and wheat starch paste. The original mat was considered to be too deteriorated to be used and was replaced with a new mat. The original mat and wooden structure where rehoused and preserved separately.

The plate was surface cleaned using a manual air- blower. The historic cover-glass (which was not original) was replaced a borosilicate glass of the same thickness. The authors reasoned that borosilicate glass is optically clear and to be the most stable available glass. Filmoplast P-90 was used to reseal the Daguerreian package. The package was then placed in a secondary housing designed by J. J. Chen and constructed by M. Beeman. The design incorporated a strip of Corrosion Intercept which acts a sacrificial material which prevents atmospheric pollutants from entering the package. Lastly a storage housing was constructed by Z. Long. All materials used for housing where chosen from archival grade and ISO standard approved. However, the authors conclude that housings made from paper are not ideal. In storage the plate should be regularly monitored at least twice a year. With any signs of visual change, a photographic conservator should be contacted. The authors do not recommend that the plate should be exhibited, and if it where the case the plate has to be closely monitored. The plate should not be on exhibition for more than 3 months and due to the light sensitivity, the plate should not be kept in more than 5-7 foot candles (50 to 75 lux). The conclusion of the authors is that the knowledge of pre-1840s daguerreotypes is limited makes it difficult to predict future status of the plate. Due to the nature of the Daguerreian package some changes may be unavoidable.

6.3 Digital Analysis and Restoration of Daguerreotypes

Tang, X., Ardis, P., Messing, R., Brown, C., Nelson, R., Ravines, P., & Wiegandt, R. (2010). Proceedings of SPIE - The International Society for Optical Engineering, 7531. doi:10.1117/12.838692

Figure 14: Digitally reconstructed panorama.

Finished project https://1848.cincinnatilibrary.org/

Authors: Xiaoqing Tanga, Paul A. Ardisa;y, Ross Messinga, Christopher M. Browna, Randal C. Nelsona, Patrick Ravines, and Ralph Wiegandtb

Year of publishing: 2010.

Object: The Cincinnati Waterfront Panorama Daguerreotype.

Place of origin: Cincinnati

Artist: Charles Fontayne and William S. Porter.

Dating: September of 1848.

Dimensions: The object is composed of eight whole plates. One whole plate is 16.5 x 21.5 cm (6.5 x 8.5 inches).

Description: The Image features a panoramic view of the Cincinnati waterfront.

Historic context: The image was taken from Newport, KY ca 5 miles from the city centre. The clarity of the image is of high quality capturing many details of the city's layout and construction, including many of the landmarks and several identifiable boats. A larger scale reproduction of the panorama image is displayed in the atrium of the public library of Cincinnati. The image is often compared to a panorama of Cincinnati taken from the same place in 1990 by the photographer James Blakeway.

Preservation related context: Tang et al. reasons that while various cleaning methods have been developed to restore daguerreotypes even the gentlest of cleaning methods have been sown too cause irreversible alterations to the image and increase the potential for future corrosion. While the field is developing it is important to historically significant pieces are digitally imaged and preserved, before they are irreversibly deteriorated. Because of the unique and fragile nature of the daguerreotype digital restoration is an attractive alternative to riskier chemical and physical methods.

Treatment methodology: The imaging of the image was carried out at 16x magnification under visible light and resulted in a image of a total of 70,749,020,160 pixels. Multiple diffused light sources where used in the imaging to avoid reflection or hot spots in the captured images, however this was not completely successful as the result was not uniform in intensity or gradient. This was mediated by using large uniform areas such as a cloudless sky for computing a average intensity for the images correcting the uniformity.

The work also resulted in a automatic annotation system for polishing scratches (created during the initial steps of the daguerreotype process) and embedded dust. The annotation of dust particles is as a preliminary stage for image enhancement. A self-similarity inpainting program was used which inserts pixels from similar undamaged areas.

7. Discussion and Conclusions

Caple (2009) suggests that within the field of art conservation, the primary focus is on visual stimulation and to evoke emotion in the viewer but there are some contentions on the subject. They mean the conservators often maintain and restore the object to its perceived original status. The alteration of a work of art to its perceived original status is likely to involve some form of cleaning (Caple, 2009). The act of cleaning will alter the object, and these alterations of the object is not always desirable which has led to several controversies.

In order to make sure that actions undertaken by cultural heritage professionals safeguard the cultural heritage from harm ethics is applied to conservation. Through the professions development several theories have been influential, Lavédrine et al. (2009) concludes that in the past 30 years the field of photographic conservation has seen rapid change. Practices used in the conservation of photographs are based on the same fundaments as all conservation, the principle of minimal intervention, respecting the integrity of the object, documentation, and the compatibly and reversibility of the materials used in interventions.

Cleaning a daguerreotype will in best case increase the perceived image quality and only alter the chemical microstructure of the image forming particles minimally, while in worst cases destroy the image completely. Jedrzejewska (1976) notes that any alteration which damage the immaterial information an object can possess can be defined as harm. And that since there are no interventions which can be conducted without imparting. The cleaning of daguerreotypes can therefore easily be defined as causing harm as all the above scenarios will alter the image. Muñoz Viñas (2009) states that a conservator is permitted to carry out alterations to the object, as these alterations are expected to be in the best interest of the object's wellbeing and beneficial. Cleaning of daguerreotypes cannot generally be considered to be in the best interest of the objects wellbeing as the tarnish on daguerreotypes acts as a passive layer which protects the plate from further corrosion. Removing this layer will likely increase the plates susceptibility to corrosion, cleaning methods such as sputter cleaning have even been shown to cause micro abrasions which increases the surface area of the plate and therefore also increases susceptibility to corrosion. Removal of silver chloride should be considered an exception as the process involved is active and will likely worsen. A case could be made that a image which is considered to be in a better condition might fare better as it could be perceived as more valuable. But there are currently no cleaning methods for removal of tarnish which has been shown to beneficial to the longevity of the material itself.

Minimal intervention is often used and assumed to be universally understood by most conservators and is used by many conservators as a guideline for their treatments. According to Villers (2004) the term has been used to create the modern image of a conservation professional as impartial to their work. Further minimal intervention is often closely associated with the belief that the work of a conservator should be reversible. Villers states that both terms have led conservators to rely heavily on scientific evidence and a strong belief in objectivity. In practice minimal intervention has led to a more hands-off and preventive approach

Despite being a term which is assumed to be universally understood minimal intervention has proven to be surprisingly hard to define. Caple (2009) states that while reversibility can be scientifically tested minimal intervention cannot, as it is not a complete statement. What is the intent of the intervention? And under what context? The use of minimal intervention is often likened to common sense which is a learned bias. This has meant that the term has been used in the context to justify or condemn a wide range of treatments (Villers 2003). Muñoz Viñas (2009) concludes that the term is in fact an oxymoron. The definition of minimal is an absolute there is no room for a spectrum, minimal can only mean minimal. In turn the definition of an intervention refers to the act of intervening which is to take a decisive or intrusive role. The most minimal action possible to undertake must be to simply not do anything which in turn cannot really be defined as an intervention. Villers (2004) suggests that the meaning should be considered more of an attitude of restraint towards conservation rather than a principle.

Then if conservation practice would be based on minimal intervention cleaning would not be conducted at all as it is not compatible with the criteria's set by minimal intervention, as one of the main ideals behind minimal intervention is reversibility. But few interventions can be considered to be fully reversible, removal of materials added to objects during interventions can and ideally should be reversible, but the actions conducted during an intervention and their effects on the object is unlikely to ever be reversible. But a conservator is still expected to carry out many of these types of irreversible interventions. While some interventions might be possible to exclude for conservators working in museums but could potentially be harder for conservators working in private sectors to avoid as the customer expects them to be conducted.

Minimal intervention is therefore difficult to implement to practical work, especially cleaning of daguerreotypes as all cleaning methods alter the object and are irreversible. Villers (2004) proposes that conservation is a way to manage change, and that all treatments is an interpretation that is relative. Realising that interventions are harming and relative to contemporary interpretations is important in a post minimal intervention methodology. Muñoz Viñas (2009) proposes that minimal intervention does not actually concern the intervention itself, but it instead intends to limit the loss of the objects ability to convey its meanings. They concludes that (2009 p. 56) the ideals behind minimal intervention can be interpreted as “Conservation should enhance or preserve the preferred meanings of the object while impairing as little as possible its ability to convey any other meanings” and suggest that the term balanced meaning loss might instead be a better defined term. balanced meaning loss is a term that can be applied in practical work, as it acknowledges that while our actions are harmful their negative impact should be limited.

Lavédrine et al (2009) notes that any intervention carried out must be conducted with an understanding and respect for the cultural values, history of the material and authenticity of the object, and any intervention needs to be appropriately documented. There are not miracle treatments that can reverse time or interventions which restore photographs to their original condition. Liberally applied treatments or misguided use can compromise the objects ability to convey its historical evidences. Many chemical methods used in the past intended to revive the photographs has been proven to have permanently altered the objects in ways which can no longer be justified for object which are part of museum collections, as they carry a certain risk of damage to the object. When an intervention is carried out which aims to change the aesthetic look of an object it can never be undone, therefore treatments carried out should be done cautiously.

Lavédrine et al (2009) concludes that there are currently no “standard” interventions that can be recommended and carried out indiscriminaly on all objects and neither should there be any, as each object presents a unique case with unique challenges. Before any interventions can be carried out the object needs to be thoroughly examined, photographic processes needs to be identified and understood, causes for deterioration and extent of damage needs to be assessed. Simple interventions can easily have sudden and serious consequences. This statement reflects the results of the study which also indicate that from a technical view there is currently no cleaning method which can be generally recommended for use on daguerreotypes.

Solvent cleaners have been shown to be both ineffective and damaging to use. Sputter cleaning causes micro abrasion of the silver plate and is both logistically and practically hard to do. From a technical point of view several approaches have been found to show promise.

The currently most researched method is the electrochemical method originally proposed by Barger et al. (1986). While the method cannot be considered safe it is the most developed method and therefore likely to be safer than others if conducted correctly. Drawbacks of the method is alteration of the image structure (which will likely not be visible) and the need for immersion of the plate. If the method is used the optimized method proposed by Canosa should be used. Both proposes that electro-chemical cleaning should only be conducted at a steady cathodic potential of -1.3 voltage, with the use of sodium nitrate, a platinum electrode and the use of a reference electrode for monitoring that the plate is properly polarized so no accidental corrosion will occur. The Robison asymmetric electro cleaning should be evaluated if it was publicised or made available as the method differs on many points methodologically from that of the optimised version proposed by Canosa. The lack of a wand could likely mean that local cleaning is harder or impossible and controlling the reactions will likely require a high level of expertise.

Barger et al. (1986) suggests that electrochemical cleaning will cause the plates to be electropolished which will increase the plates corrosion resistance. The validity of the claims is somewhat uncertain as no other author found during the literature study makes this claim and no testing of the theory has been found by the author.

Initial tests on cleaning daguerreotypes using laser ablation has showed promise and could be considered if available. Laser ablation requires a more advanced setup than electro-chemical cleaning and the laser needs to be manned by skilled technicians as to avoid risk of damaging the plate. An advantage of laser ablation is that the plates do not need to be submerged.

The possibility of a digital restoration could be considered. Digitally restored images can then be used by researchers and used in exhibition purposes alongside original plates. With the use of modern daguerreotypists modern reproductions can be created to replace images that are too far gone or to fragile, but the topic of photographic reproductions and their ethical considerations are complex.

Remedial cleaning of daguerreotypes exhibiting the white haze films associated with the formation of AgCl using the method proposed by Robison, Vicenzi (2015) is likely warranted as it is a way to stabilize the object. If AgCl is allowed to remain on plates the Oswalt ripening will result in a continuation of the formation of larger and more visible AgCl crystals. Since light accelerates the process these daguerreotypes should not put not be placed on display. The cost of altering the object is likely offset by the removal of an active corrosion product and the possibility to be able to safely exhibit these pieces.

Laverdin (2009) suggests that if the tarnish does not obscure the image it is best left untouched and instead focus on taking preventive measures to limit further tarnishing. A focus on stabilization of the current condition and to slow down the deterioration process is more in line with current conservation theory. If the decision is made that a daguerreotype is to be cleaned a partial or selective cleaning should be considered. Removal of tarnish from the main focal points of the image can be conducted while corrosion fronts along the edges of the mat can be left as a patina. But it is still important to note that all available cleaning methods used in past and present will alter the chemical authenticity of the object.

The removal of the original housing or rehousing of daguerreotypes who still have their original housing is a complex question. Prieto (2017) points out that the act of looking at a daguerreotype is an intimate expedience as the image needs to be held to be viewed, therefore the case is more than just a protective system it is an integral part in how daguerreotypes are experienced. The case has held the image and protected the image to this day, and they must be preserved together. The case of the daguerreotype should be considered as integral to the object as the album is to the photographs within it. Both the daguerreotype case and the photographic album is inseparable to the object, they represent how the photograph was historically used and viewed. While the easiest thing would certainly be to re-case the photograph in a new housing unit using modern packing materials the object will have lost its context, and a treatment should not be justified by being simpler. It would be considered unethical to disassemble a composite object and store the pieces separately so why should this be the case with daguerreotypes and other cased and framed objects?

Re-casing or replacing of cover glasses is most commonly due to tarnishing by different corrosion products which causes the image to become gradually obscured due to deterioration of the cover-glass. Deteriorated cover-glasses will not only be damaging to the image structure of the plate but it will also become cloudy and opaque. Barger, White (2000) suggests that cover glasses can't be effectively cleaned as they will return to the same climate as it had before. And it is likely that the glass will re-corrode, instead it is suggested that the glasses should either be replaced or re-glazed. Koob (2004) suggests that cleaning a glass even once in its lifetime will protect the glasses for long periods of time. When working with normal glass ware objects Koob concludes that glasses should be kept with as little fluctuations in humidity as possible and with a good airflow, the humidity inside the Daguerreian package is very hard to monitor and maintain and airflow is impossible. It is unknown how well a cleaned daguerreotype glass would fare in a stable museum environment. Cover-glasses should be considered to be an integral part of the object and should not be discarded. Replacing a cover glass removes an original part from the object and while the original glass can be retained it will then suffer from the risk of disassociation. Re-glazing the cover glass could perhaps be preferable to discarding the glass but it is a major intervention.

If a objects value is not definite but a reflection of the current sociopolitical climate and of a treatment must be judged with this in mind. It is important that a conservator understands that the works are likely to be reevaluated in the future and that conservators have this in mind when conducting their work.

8. Summary

Daguerreotypes where introduced in 1939 by Louis Daguerre, the method involves the sensitization of a silver-plated copper plate by exposing the plate to halide fumes creating light sensitive silver halides. When the latent image is created the halide photochemically decomposes back to silver creating small silver specks on the surface who scatter the light making them appear lighter than the silver plate creating a image. The plate is then fixated using mercury fumes which leads to the formation of a silver amalgam on the specks, lastly the plates can be gilded using a mild solution of gold chloride which lowers the fragility of the silver particles to abrasion.

The finished plate was then bound in a bundle called a Daguerreian package of protection. The package contained a cover-glass, a mat or a brass spacer and the plate bound together using paper tape with a flexible brass fame called a preserver folded over the edges of the plate. The plate package was commonly placed in a daguerreotype case.

Daguerreotypes are vulnerable to corrosion from atmospheric pollutants and corrosion products deposited on the plate from corrosion of the cover glass. Formation of tarnish on the image causes the image on the plate to become obscured. Historically daguerreotypes where cleaned using different solvent cleaners which has been proven to be damaging to the image. A series of methods where introduced during the 80s, sputter cleaning, electrochemical cleaning and laser cleaning, in recent years the possibility to digitally image and reconstruct the images have been introduced.

The study found that the is currently no method which can be recommended for use indiscriminately while several show promise and could be justified in some cases, but more research will need to be conducted before they can be considered safe. The Daguerreian package is very hard to monitor and maintain and airflow is impossible. It is unknown how well a cleaned daguerreotype glass would fare in a stable museum environment. Cover-glasses should be considered to be an integral part of the object and should not be discarded. Replacing a cover glass removes an original part from the object and while the original glass can be retained it will then suffer from the risk of disassociation. Re-glazing the cover glass could perhaps be preferable to discarding the glass but it is a major intervention.

A objects value is not definite but a reflection of the current sociopolitical climate and of a treatment must be judged with this in mind. It is important that a conservator understands that the works are likely to be reevaluated in the future and that the practitioners have this in mind when conducting their work.

8. References

Abere, M., Murphy, R., Jackson, B., Mourou, G., Menu, M., Mansfield, J., ... & Yalisove, S. (2011). Cleaning Daguerreotypes with a Femtosecond Laser. *Microscopy and Microanalysis*, *17*(S2), 1812-1813.

Barger, M. Susan, and William B. White. (2000). *The Daguerreotype : Nineteenth-century Technology and Modern Science*. Johns Hopkins Pbk. ed. Baltimore: Johns Hopkins UP, Print.

Barger, M. S., Giri, A. P., White, W. B., & Edmondson, T. M. (1986). Cleaning Daguerreotypes. Studies in Conservation, 31(1), 15-28. doi:10.2307/1505955

Barger, M. S., Giri, A. P., White, W. B., & Edmondson, T. M. (1987). Corrigenda: Cleaning Daguerreotypes. Studies in Conservation, 32(3), 141-143. doi:10.2307/1506221

Barger, M. S., Giri, A. P., White, W. B., Ginell, W. S., & Preusser, F. (1984). Protective Surface Coatings for Daguerreotypes. Journal of the American Institute for Conservation, 24(1), 40-52. doi:10.2307/3179600

Barger, M. S., Krishnaswamy, S. V., & Messier, R. (1982). The Cleaning of Daguerreotypes: Comparison of Cleaning Methods. Journal of the American Institute for Conservation, 22(1), 13-24. doi:10.2307/3179715

Canosa, E. M. (2016). Investigation and Optimization of Electrochemical Treatment for Daguerreotypes: The University of Arizona.

Caple, C. (2009). The aims of conservation in Conservation: principles, dilemmas and uncomfortable truths. Abingdon, Oxon: Butterworth-Heinemann.

Caring For Photographs: Special Monochrome Processes (1998) National Park Service.

Centeno, Silvia & Meller, Taina & Kennedy, Nora & Wypyski, Mark. (2008). The daguerreotype surface as a SERS substrate: Characterization of image deterioration in plates from the 19th century studio of Southworth & Hawes. Journal of Raman Spectroscopy. 39. 914 - 921. 10.1002/jrs.1934.

Daffner, L. A., Kushel, D., & Messinger, J. M. (1996). Investigation of a Surface Tarnish Found on 19th-Century Daguerreotypes. Journal of the American Institute for Conservation, 35(1), 9-21. doi:10.2307/3179935

Daniels, V. (1981). Plasma Reduction of Silver Tarnish on Daguerreotypes. Studies in Conservation, 26(2), 45-49. doi:10.2307/1505867

Elena Bulat, K. M. C., Jiuan Jiuan Chen, Katherine Eremin, Debora D. Mayer, and Phillip Prodger. (2015). A Glimpse from the Dawn of Photography Investigation and Stabilization of an 1839Daguerreotype at the Peabody Essex Museum Topics in Photographic Preservation, 16, 300-312.

Fischer, A., Eggert, G., Dinnebier, R., & Runčevski, T. (2018). When Glass and Metal Corrode Together, V: Sodium Copper Formate. Studies in Conservation, 63(6), 342-355. doi:10.1080/00393630.2017.1359472

Golovlev, V. V., Gresalfi, M. J., Miller, J. C., Romer, G., & Messier, P. (2000). Laser characterization and cleaning of nineteenth century daguerreotypes. *Journal of Cultural Heritage*, *1*, S139-S144.

Goltz, D., & Hill, G. (2012). Hyperspectral imaging of daguerreotypes. *Restaurator*, *33*(1), 1-16.

Hodgkins, R., Centeno, S., Bamberger, J., Tsukada, M., & Schrott, A. (2013). Silver Nanofilm

Hodgkins, R. E., Centeno, S. A., Bamberger, J. A., Tsukada, M., & Schrott, A. (2013). Silver nanofilm sensors for assessing daguerreotype housing materials in an Oddy test setup. *E-Preservation Science*, *10*, 71-76.

Jedrzejewska, Hanna. *Ethics in conservation,* Stockholm: Kungl. konsthögskolan. Inst. För materialkunskap ; 1976

Jiuan-Juian Chen, M. B. (2011). Preservation System for Housing Bare Plate Daguerreotypes. Topics in Photographic Preservation, Volume 14.

Koob, S. P. (2007). Cleaning glass: a many-faceted issue. *Objects Specialty Group Postprints*, 60-70.

Koch, M. S., & Sjogren, A. (1991). Treatment of daguerrotypes with hydrogen plasma. In *Sauvegarde et conservation des photographies, dessins, imprimés et manuscrits. Actes des journées internationales d'études de l'ARSAG, Paris 30 sept.-4 oct. 1991.* (pp. 67-72).

Konkol, N. R., Bernier, B., Bulat, E., & Mitchell, R. (2011). Characterization of filamentous accretions on daguerreotype surfaces. *Journal of the American Institute for Conservation*, *50*(2), 149-159.

Kozachuk, M. S. & Avilés, M & Martin, R & Potts, B & Sham, T & Lagugné-Labarthet, F (2018). Imaging the Surface of a Hand-Colored 19th Century Daguerreotype. Applied Spectroscopy. 72. 000370281877376. 10.1177/0003702818773760.

Kozachuk, M. S., Sham, T. K., Martin, R. R., Nelson, A. J., & Coulthard, I. (2018). Exploring tarnished daguerreotypes with synchrotron light: XRF and μ-XANES analysis. Heritage Science, 6(1), 12. doi:10.1186/s40494-018-0171-8

Kozachuk, M.S.; Sham, T.-K.; Martin, R.R.; Nelson, A.J.; Coulthard, I.; Smieska, L.; Woll, A.R. (2019) Recovering Past Reflections: X-ray Fluorescence Imaging of Electrocleaned 19th Century Daguerreotypes. *Heritage*, *2,* 568-586.

Kozachuk, M.S., Sham, T., Martin, R.R. *et al.* (2018) Recovery of Degraded-Beyond-Recognition 19th Century Daguerreotypes with Rapid High Dynamic Range Elemental X-ray

Fluorescence Imaging of Mercury L Emission. *Sci Rep* **8,** 9565 . https://doi.org/10.1038/s41598-018-27714-5

Lavédrine, B., Gandolfo, J. P., Frizot, M., & Monod, S. (2009). *Photographs of the past: process and preservation*. Getty Publications.

Liang, D., Allen, H. C., Frankel, G. S., Chen, Z. Y., Kelly, R. G., Wu, Y., & Wyslouzil, B. E. (2010). Effects of sodium chloride particles, ozone, UV, and relative humidity on atmospheric corrosion of silver. *Journal of the electrochemical society*, *157*(4), C146-C156.

Muñoz Viñas, S. (2009). Minimal intervention in Conservation: revisited, dilemmas and uncomfortable truths. Abingdon, Oxon: Butterworth-Heinemann.

Olmos, E. A. M. (2009). *Current Status of Treatment Practices in Photograph Conservation*. Advanced Residency Program in Photograph Conservation.

Prieto, C. M. (2017). Protecting daguerreotypes: a new Structural Housing System (SHS). Journal of the Institute of Conservation, 40(3), 226-241. doi:10.1080/19455224.2017.1365743

Ravines, P., & Nazarenko, A. Y. (2019). Characterizing the Image Forming Particles of Modern Ungilded Daguerreotypes Using XRD and SEM. *Microscopy and Microanalysis*, *25*(4), 1037-1051.

Robinson, M., & Vicenzi, E. P. (2015). A twin paradox: a study of preservation and disfigurement of Southworth and Hawes daguerreotypes. *Topics Photogr. Preserv*, *16*, 1-19.

Robinson, M (2013) Sterling C. McIntyre's Panoramic Views of San Francisco: The Daguerreian Annual 2013

R. Wiesinger, I. M., Ch. Kleber, M. Schreiner,. (2013). Influence of relative humidity and ozone on atmospheric silver corrosion. Corrosion Science, 77, 69-79. doi:https://doi.org/10.1016/j.corsci.2013.07.028

Richmond, A. (2009). Conservation: Principles, Dilemmas and Uncomfortable Truths: Oxford: Routledge.

Sease, C., Selwyn, L., Zubiate, S., Bowers, D., & Atkins, D. (1997). Problems with Coated Silver: Whisker Formation and Possible Filiform Corrosion. *Studies in Conservation*, *42*(1), 1-10. doi:10.2307/1506570

Shugar, A., Lough, K., & Chen, J. J. (2017). Characterization of a Surface Tarnish Found on Daguerreotypes Revealed under Shortwave Ultraviolet Radiation. *MRS Online Proceedings Library Archive*, *1656*, 319-333.

Spencer, Madalena & Sham, Tsun-Kong & Martin, Ronald & Nelson, Andrew & Coulthard, Ian & McElhone, John. (2018). Recovery of Degraded-Beyond-Recognition 19 Century Daguerreotypes with Rapid High Dynamic Range Elemental X-ray Fluorescence Imaging of Mercury L Emission. Scientific Reports. 8. 10.1038/s41598-018-27714-5.

Swan, A., Fiori, C. E., & Heinrich, K. F. (1979). Daguerroeotypes: a study of the plates and the process. *Scanning electron microscopy*, *1*, 411-423.

Tang, X., Ardis, P., Messing, R., Brown, C., Nelson, R., Ravines, P., & Wiegandt, R. (2010). Digital Analysis and Restoration of Daguerreotypes. Proceedings of SPIE - The International Society for Optical Engineering, 7531. doi:10.1117/12.838692

Turovets, I., Maggen, M., & Lewis, A. (1998). Cleaning of Daguerreotypes with an Excimer Laser. Studies in Conservation, 43(2), 89-100. doi:10.2307/1506645

Wei, W., Gerritsen, I., & Von Waldthausen, C, (2011). Re-examining the (electro-) chemical cleaning of daguerreotypes: microscopic change vs. macroscopic perception. *Topics Photographic Preservation*, *14*, 24-40.

Villers, C. (2004). Post minimal intervention. The Conservator, 28. doi:10.1080/01410096.2004.9995197