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RE-EXAMINING THE (ELECTRO-)CHEMICAL CLEANING OF DAGUERREOTYPES: MICROSCOPIC CHANGE VS. MACROSCOPIC PERCEPTION

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Abstract

The Netherlands Institute for Cultural Heritage (ICN) is conducting a project looking at the effect of (electro-) chemical cleaning of daguerreotypes on their appearance. The objective of the project is to assist conservators in finding methods and parameters which can be "safely" used for cleaning these unique objects. The project not only includes scientific testing and surface analysis, but also considers the ethical issues of cleaning including readability, (loss of) value, and the definition of what "clean" or a "good result" is for a daguerreotype.

The results show that daguerreotypes can be electrochemically cleaned without altering the silver rich amalgam particles making up the image, or the silver plate. This is performed under cathodic polarisation at a constant potential controlled using a reference electrode, a procedure based on that which is used in industry. It is a "safer" procedure than that previously reported in the literature using alternating polarisation and no reference electrode. However, small surface changes can still be seen at a microscopic level for the current method. More work is thus required to determine if electrochemical cleaning can, in fact, be used responsibly for cleaning daguerreotypes. Work is also continuing to relate these measurements of "objective" microscopic changes to how treated daguerreotypes are actually perceived.

Introduction

The cleaning of objects of art and cultural heritage has always been a sensitive issue, beginning in recent times with the "cleaning controversy" related to the removal of varnish from paintings by the National Gallery in London in 1947. In general, the debate revolves around issues involving what cleaning chemically and physically does to the object, and how this affects what the viewer sees and how the object is interpreted. Such discussions have often been quite polemic in nature, where all parties are guilty to some extent of mixing subjective opinions with only partial or no understanding of the physical changes incurred by the cleaning process. Fear of the unknown, prejudice, a lack of communication, and a "little" knowledge create conflicts with often unsatisfactory or no results.

Within its research program, "Objects in Context", The Netherlands Institute for Cultural Heritage (ICN) is conducting a four year study entitled "Cleaning and Perception" to look at the complex issues involved in making decisions on whether or not to clean an object, and which methods may or may not be used. Case studies are being carried out related to the cleaning of paintings, photographs, and outdoor sculpture. The studies are looking at the entire process involved in the cleaning of an object, the initial discussions with clients, the scientific and art historical testing and/or research involved, and the decision making process on whether or not to clean and how. Ultimately, decisions about cleaning involve the perception of the various parties and the viewer to the issue. "Perception" is used here in the broadest sense of the word. It is not only the visual perception of the object before, during, and after cleaning, but also the perception of the situation by the different parties involved. It should be noted that the first author of this paper, as project coordinator, is playing both the role of the observer, as well as the "guilty" participant.

One of the case studies in this project is looking into issues involved in the (electro)chemical cleaning of daguerreotypes. Many questions have arisen in the past about the after effects of cleaning with, among others, thiourea and cyanide based solutions [Swan 1987; Swan 1981; Barger et al. 1986-1; Barger and White 1991]. The discussion became more intense since the introduction of electrochemical cleaning methods by Barger et al. [Barger et al. 1986-1; Barger et al. 1986-2; Barger and White 1991] in the mid 1980's.

In this paper, the electrochemical cleaning of daguerreotypes is re-examined from both a technical viewpoint as well as the viewpoint of restoration ethics and perception. The results of tests using standard techniques used in industry are reported. Recommendations and plans for further technical research combined with perception testing are given.

Introduction to electrochemical processes: corrosion vs. cleaning

Corrosion

Electrochemical processes, among them, electrochemical (or electrolytic) cleaning, have been used for decades for the cleaning of industrial and consumer products. Electrochemistry itself is the study of chemical processes where electron flow (current) is involved. Corrosion in moist and liquid environments, such as the rusting of iron and steel, is the most well-known form of an electrochemical process. The theory behind electrochemical processes can be found in many textbooks, see for example [Fontana and Green 1986; Jones 1996]. The following discussion is simplified in the hope that the non-technical reader can understand the basics behind electrochemical cleaning.

Electrochemical cleaning can be explained in a simplified manner by considering the schematic diagram in Fig. 1. In a corrosion process such as the rusting of iron, metal (iron) atoms go into solution. In order to do that, electrons come free. This is the so-called anodic reaction

$$M \rightarrow M^{n+} + ne^- \qquad (1)$$

Somewhere else on the surface, the electrons can react with ions from the liquid surroundings, such as H^+ or OH^- (water ions) in a so-called cathodic reaction such as

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

or

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (3)$$

Various combinations of the reactions 1-3 lead to the formation of a corrosion product such as rust, an oxide of iron. Note that there is a flow of electrons (current) in the metal, and ions in the solution, hence the word “electro”chemistry. The flow of electrons and ions in this case are equal, that is, the anodic and cathodic reactions have the same but opposite current. If that were not the case, the metal would spontaneously take on an electric charge, which is clearly impossible.

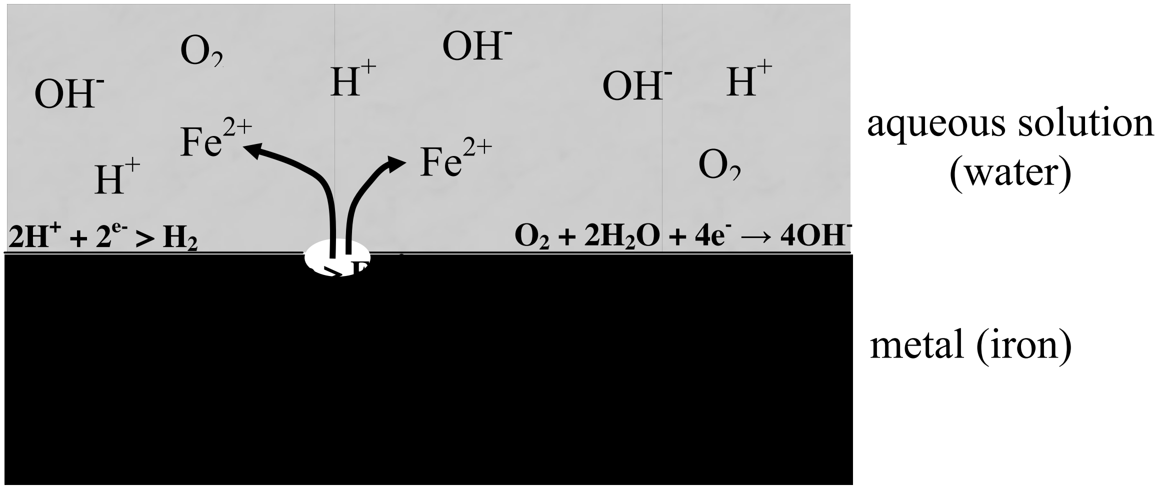


Fig. 1 - Schematic diagram of an electrochemical process, the corrosion of a metal (iron) made up of combinations of, e.g. equations 1-3.

Equipment for studying corrosion

Corrosion processes such as described above can be simulated and studied using a so-called electrochemical cell as shown in the schematic diagram in Fig. 2a. The specimen of interest (a metal such as iron) is submerged in an electrolyte along with a noble metal foil such as platinum. The iron specimen is known as the working electrode (WE), and the platinum foil is called the counter electrode (CE). The working electrode is where the anodic reactions (corrosion) takes place, e.g. eqn. 1, and the counter electrode is where the cathodic reactions take place, e.g. eqns. 2 and 3. The electrodes are connected to a potentiostat, an instrument which can measure potential (voltage) and current, or apply a given potential or current.

As described above, the anodic and cathodic reactions proceed at the same rate (current). The potentiostat will thus measure zero net current. There is a potential between the working electrode and the counter electrode, and this is known as the “open-circuit” potential. This “open-circuit” potential depends on the so-called half-cell potential of each of the two metals used for the electrodes. Tables of half-cell potentials for many pure metals and some common alloys can be found in all corrosion textbooks and handbooks, e.g. [Fontana and Green 1986;

Jones 1996]. The open-circuit potential can be measured using the potentiostat (or a simple voltmeter). For corrosion research and testing, this is measured with respect to a reference electrode (RE). There are different kinds of reference electrodes, but all have a potential related to the so-called half-cell potential of the hydrogen reaction (eqn. 2 above), which is arbitrarily defined as zero volts (V), the so-called standard hydrogen electrode (SHE).

One can influence and thus study the corrosion reaction by using the potentiostat and reference electrode. The potentiostat is used to apply a voltage (potential) between the iron working electrode and the platinum counter electrode. This is like attaching the working and counter electrodes to a battery with the + pole attached to the working electrode. A current flows, Fig. 2a, whereby electrons are drawn away from the iron analogous to Fig. 1, and it corrodes. The cathodic reaction occurs at the platinum counter electrode without affecting the platinum itself.

Note that a noble metal such as platinum is very often used as the counter electrode in electrochemical studies because it is inert. It therefore will not contaminate the electrolyte and effect the results, whether corrosion studies or electrochemical cleaning. While platinum is expensive, it is reusable, and only a small amount is necessary, for example, a small piece of foil or wire as described below in the experimental procedure.

Electrochemical (or electrolytic) cleaning

However, one can also turn the battery around and put electrons back into the metal, Fig. 2b. Cathodic reactions thus takes place on the object, the working electrode. By doing this, one can break up (reduce) the corrosion product (rust) into the metal (iron) and oxygen. Once all of the rust is reduced, nothing else happens. The pure metal (iron) that was under the rust remains unaffected. This process is what is known as electrochemical or electrolytic cleaning. In fact, this way of "turning the battery around" is also the principle behind cathodic protection, a process first used to protect seagoing ships from corrosion almost two centuries ago, and more extensively for maritime and industrial applications since the 1920's [Jones 1996]. The important point here is that <u>when the proper parameters are selected, nothing happens to the metal under the corrosion layer, or the metal being protected</u>.

It is this reduction process, which is being considered for the electrochemical cleaning of daguerreotypes as well as other silver objects. For the case of tarnish on silver, Fig. 2b, silver sulfide (Ag_2S), the sulfide is reduced according to

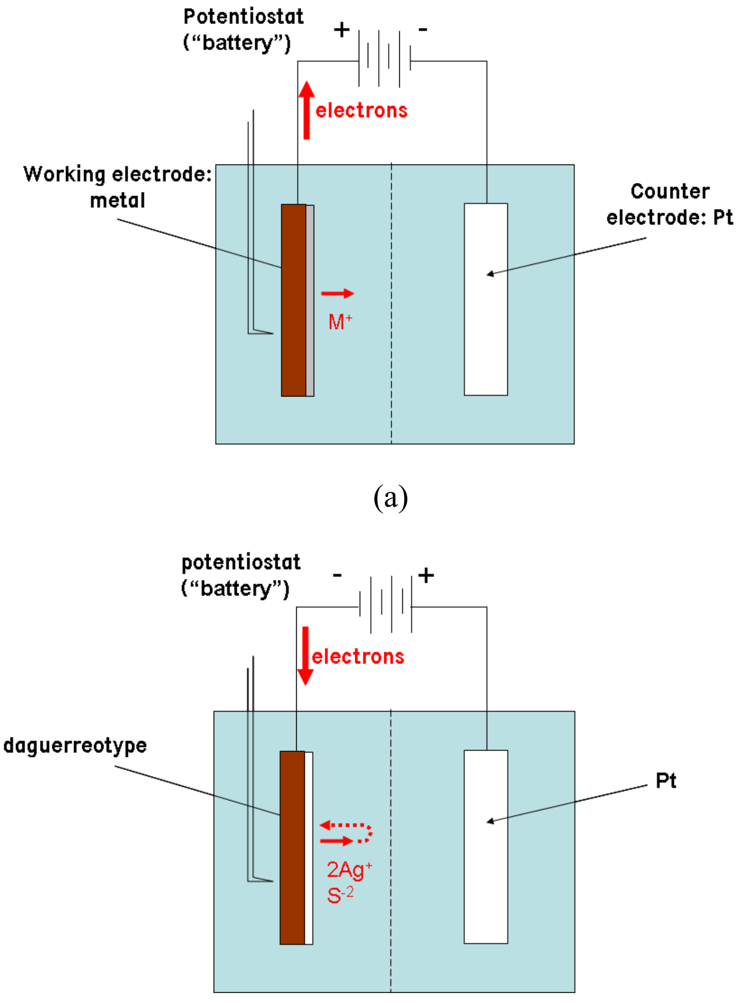
$$Ag_2S \rightarrow 2Ag^+ + S^{2-} \qquad (4)$$

The silver ions recombine with electrons to form silver,

$$Ag^+ + e^- \rightarrow Ag \qquad (5)$$

while the sulfur ions combine with H^+ ions to form hydrogen sulfide,

$$2H^+ + S^{2-} \rightarrow H_2S \qquad (6)$$



(a)

(b)

Fig. 2 - Schematic diagram of an electrochemical cell used for example, for a) studying corrosion processes, or for b) electrochemical cleaning (of daguerreotypes).

Note that the silver atoms (or iron in the case of the reduction of rust) are in solution and can redeposit on nearby surfaces such as the daguerreotype itself (dotted arrow in Fig. 2b). The hydrogen sulfide, H_2S is a gas, which causes the rotten egg smell which one notes while conducting the cleaning.

Proper potential for cleaning and the reference electrode

It is important to note that the electrochemical cleaning process should be conducted at a fixed potential measured with respect to a reference electrode. The potential necessary depends on the type of corrosion product which is to be removed. The correct potential for many combinations of simple metals and corrosion products can be determined with the use of so-called Pourbaix diagrams, diagrams which show the stability of metals and their corrosion products as a function of electrochemical potential and the pH of the solution they are in. Very often, however, as in the present case, the potential must be determined and/or optimized experimentally by performing a so-call potentiodynamic polarization scan. The potential is varied between, say + 2 V and – 2V and the current is measured. A typical result [Degrigny 1996] for tarnished silver is shown in Fig. 3. The possible range for cleaning is where the current is negative (bracket in Fig. 3), that is, with respect to the open-circuit potential.

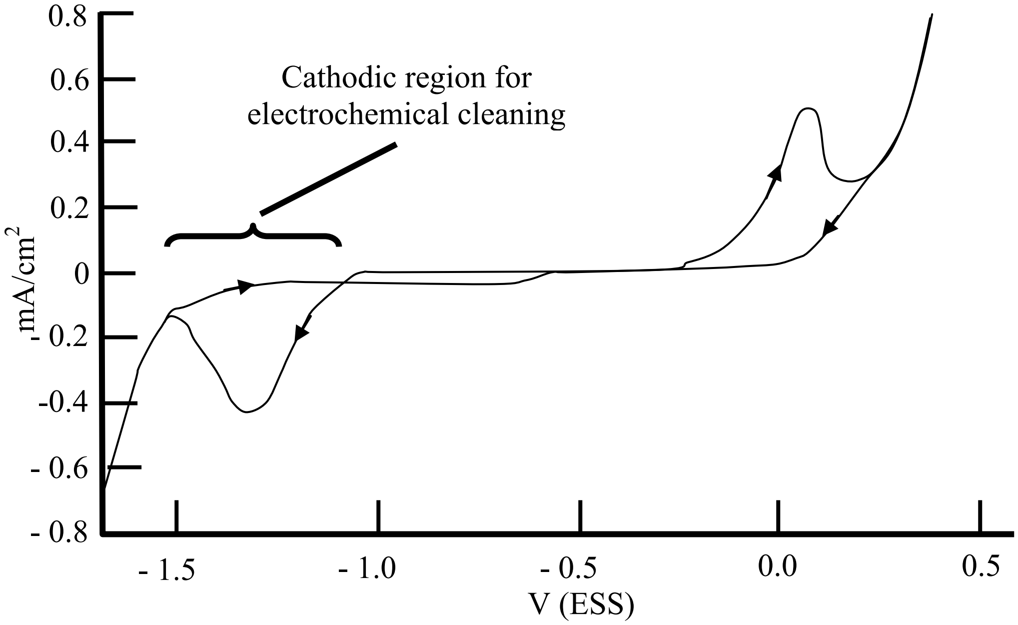


Fig. 3 - Typical potentiodynamic scan conducted on a tarnished silver specimen in 0.1 M $NaSO_4$ solution. The cathodic region of interest for electrochemical cleaning is indicated by the bracket [adapted from Degrigny 1996].

It is important that a reference electrode be used for electrochemical cleaning, because the half-cell potential of the metal to be cleaned will change as the corrosion product is removed. This means that the relative potential between the metal to be cleaned and the counter electrode that is, the open circuit potential, will change during cleaning. The reference electrode must be properly selected for the work at hand. In particular, it must not contaminate or otherwise influence the system of interest. Note that if a reference electrode is not used, there is no guarantee that the necessary potential will remain on the negative (cathodic) side of the open-circuit potential, nor that it will not drift into some other potential range and alter something on the surface of the object.

Cleaning rate

The rate of cleaning, that is, how fast the cathodic reaction proceeds, is controlled by the (cathodic) current, i. For the cleaning of daguerreotypes, this creates a problem for conservators.

The daguerreotype is the working electrode, and has a fixed size and composition. Thus, its electrical resistance, R, is fixed. If one uses a constant potential (voltage), E (or V), for cleaning, then the current is fixed according to the textbook relationship

$$i = E / R \tag{4}$$

where E is potential (voltage), and R is resistance. For cleaning purposes, this fixed current is low, and cleaning can thus take a “long” time. Moreover, one cannot easily control local cleaning.

In order to clean locally, one must thus find a way to steer the available current into a very small area, that is, increase the current *density* (current per area). (Note that electrochemical and corrosion measurements are always given in terms of current density, so that results can be easily compared and related to objects of all sizes.) This can be done, for example, by using an inert platinum wire as the counter electrode instead of platinum foil. One can then move the wire tip around the daguerreotype, thus increasing the cleaning rate locally. This is essentially what Barger et al did, although they did not use a reference electrode.

In order to monitor the cleaning process, the change in current density is measured with time, see Fig. 4. As the process continues, the current density will decrease, approaching zero, until all of the corrosion product is removed.

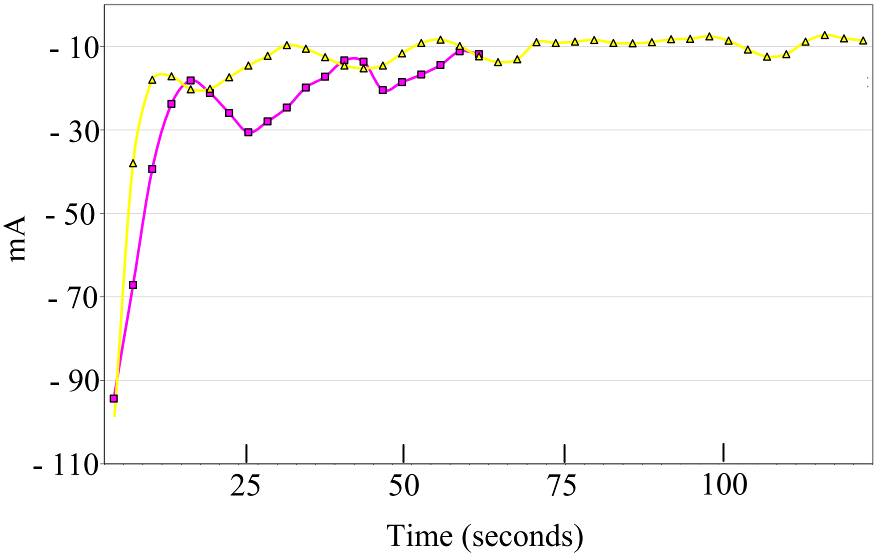


Fig. 4 - Decrease in current density with time of a daguerreotype as the tarnish is removed (note: cathodic current is negative, zero is at the top of the graph).

Choice of electrolyte

A final note in this introduction to electrochemistry is that the choice of the electrolyte is also important for optimal cleaning. The selection depends on the application. For corrosion testing, the electrolyte is the (liquid) environment in question, or some simulation thereof. For cleaning, one generally seeks a solution which is a good conductor of the small currents involved, and does not chemically attack the object. Health and safety are also important considerations.

Experimental procedure

The previous discussion of electrochemical cleaning has dealt with relatively “simple” metals such as iron. Although daguerreotypes are certainly metal objects, the situation for electrochemical cleaning is more complex. A daguerreotype is an example of a so-called mixed electrode, consisting of several metals, see Fig. 5. As is well-known, it consists of silver plated on a copper support. The physical image itself is made up of silver rich amalgam particles of varying composition dispersed on the silver. Many daguerreotypes are coated with a thin, discontinuous[*] layer of gold, and were often colored locally. A number of corrosion products can be found on historic daguerreotypes, including silver sulfide and silver oxide, copper chlorides, and copper oxides.

The work discussed in this communication involved the determination of the proper parameters for removing the silver tarnish, and to show that standard industrial methods for electrochemical cleaning are safer than those originally used for daguerreotypes reported by Barger et al. This will provide a sound basis for further discussions and research to determine whether or not one can responsibly clean such objects using electrochemical cleaning. The experimental procedure described in the following paragraphs should thus not be construed as *the* proper method for conservation work.

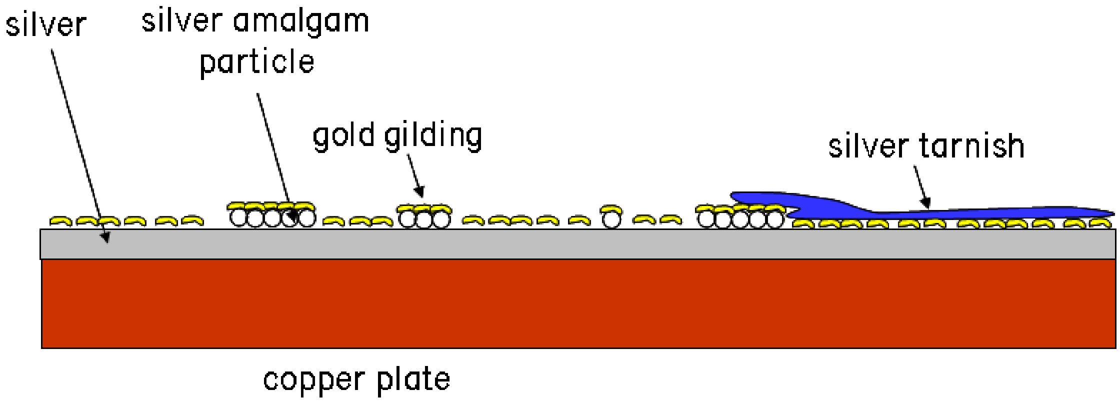


Fig. 5 - Schematic cross-section of the structure of a daguerreotype.

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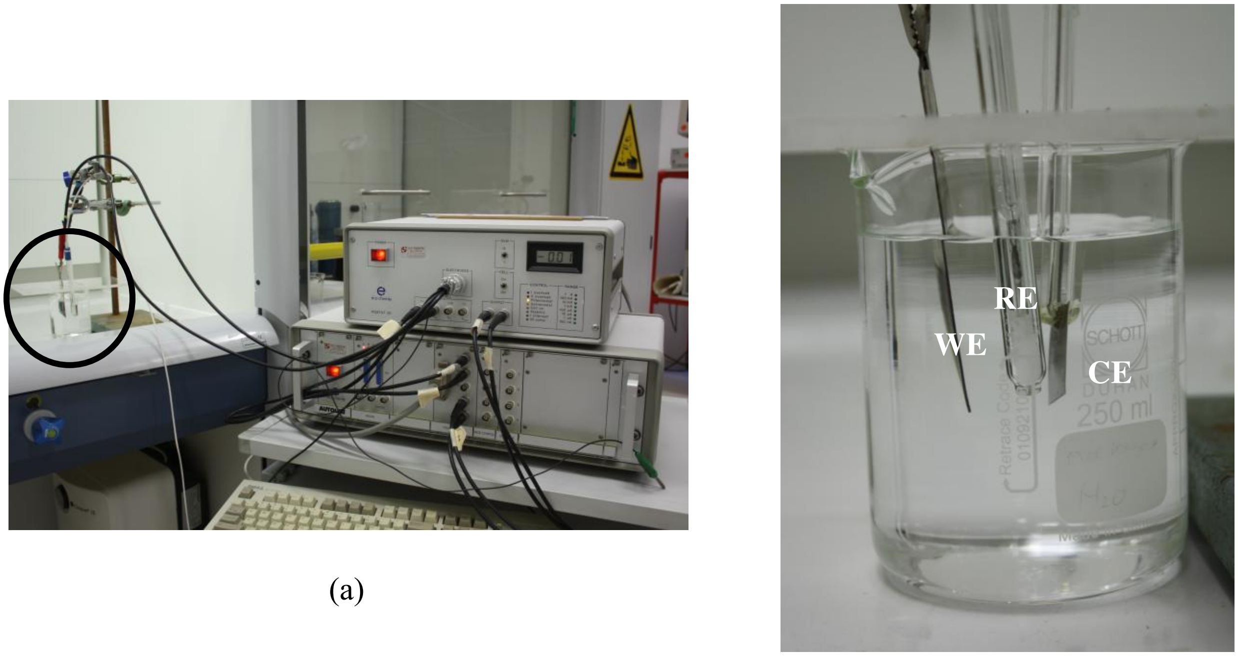
[*] It is well known in the surface science and semi-conductor literature on thin films that gold layers as thin as those found on daguerreotypes will be discontinuous.

Specimens

The cleaning parameters for removing the tarnish were determined using artificially tarnished pure silver specimens. 1 mm thick pure silver sheet was cold-rolled to a thickness of 0.5 mm, ground to 1200 grit, and lapped using Hexenvet and Langsol green polishing pastes. They were then cleaned in a soap solution, rinsed, and dried using a tissue. Specimens 75 mm x 25 mm were cut from the sheet and artificially sulfidized for approximately 14 days by placing them in desiccators with a container containing a solution of 0.08 g potassium polysulfide in 65.63 g water, and a container with a silver blackening agent.

Determination of cleaning parameters

The optimal cleaning potential was determined using an Autolab electrochemical testing system (Ecochemie, Utrecht, The Netherlands) with a PGStat 10/20 potentiostat in combination with a simple electrochemical cell, see Fig. 6a (compare with Fig. 2). The cell, Fig. 6b, was a glass beaker covered by a plastic plate through which the electrodes could be passed. The counter electrode was a piece of 0.1 mm thick platinum foil, approximately 14 x 19 mm in size. The reference electrode was a Hg/Hg_2SO_4 electrode (ESS), model REF601, from Radiometer Analytical, with a potential of 655 mV with respect to SHE (standard hydrogen electrode).



(a)

(b)

Fig. 6 - System for electrochemical cleaning.
a) Overall system with electrochemical cell (circled) and potentiostat
b) Electrochemical cell with specimen (WE), reference electrode (RE) and Pt counter electrode (CE)

Initially, ammonium hydroxide was used as the electrolyte, the same electrolyte which had been used by Barger et al. However, the electrolyte turned blue when copper plates were placed in this electrolyte for an hour, indicating that the copper support is being attacked. This agrees with observations reported during cleaning by a number of conservators interviewed by the authors. An electrolyte was found for this study which did not have this problem, a 0.1 M solution of sodium nitrate ($NaNO_3$), as suggested by Monnier [1994]. Testing was conducted at room temperature, around 20^{o} C.

In order to find the optimal (cathodic) potential for the removal of silver sulfide, a potentiodynamic scan was carried out on tarnished specimens. The resulting potential range was compared with literature values [Degrigny 1996]. Tarnished samples were then cleaned at several potentials in this range for various lengths of time. The potential for cleaning daguerreotypes was selected based on the time necessary to remove the sulfide, and visual judgment of the quality of the cleaning.

For all testing, the tarnished silver specimens were hung vertically in the electrolyte, connected to the potentiostat wires via an alligator clip such that the clip and the top of the specimen were above the solution, see again, Fig. 6b. The platinum foil counter electrode consisted of the foil, spot-welded to a piece of stainless steel wire. The wire itself was sealed in glass so that only the foil would come in contact with the solution, and the free tip could be connected to the potentiostat above the solution. The counter electrode and reference electrode were positioned approximately 2 cm from the specimens unless otherwise specified in the following discussions.

Cleaning of daguerreotypes

After determining the optimum parameters, cleaning tests were conducted on three “low-quality” American daguerreotypes purchased on www.ebay.com, see for example, Fig. 8a in the results section. For cleaning, the daguerreotypes were removed from their cases. They were then photographed on an easel using a high resolution digital camera, a Sinarback 23HR, with two Broncolor HMI F1200 flicker-free lamps set 2 meters away at a 45^{o} angle to either side. After photographing the objects, they were examined in the scanning electron microscope (SEM). Images were taken at various locations to document the distribution of silver amalgam particles making up the image. Energy dispersive spectroscopy (EDS) and X-ray fluorescence spectroscopy (XRF) were conducted to determine the chemical composition of the various features found at those locations.

In preparation for cleaning, any paper backing or tape was then removed. The plates were then degreased in an ethanol bath. A small area on the copper side was lightly sanded, and a copper wire was pressed against it and glued with a hot glue gun. Through trial and error, a good electrical connection could be made. The daguerreotypes were then connected as the working electrode to the potentiostat and then completely submerged vertically in solution. The copper wire was isolated from the solution using shrink-fit tubing and by the glue at the site of the joint on the daguerreotype. The vertical positioning was chosen to reduce the chance that any silver or other removed corrosion products would settle back onto the daguerreotypes.

It should be noted that this procedure for connecting the daguerreotypes to the potentiostat was selected for the convenience of this initial testing project. If daguerreotypes are ever again to be electrochemically cleaned, a more elegant way of making the electrical connection will need to be found.

The daguerreotypes were electrically cleaned at the chosen potential. Because the counter electrode was smaller than the daguerreotypes, it was moved around to ensure that it was close enough to provide roughly the same current density for all areas. This was thus a form of local cleaning. The cleaning procedure lasted until the tarnish was removed, and the current density dropped to a constant low value approaching zero mA, see again Fig. 4. After cleaning, the daguerreotypes were rinsed in ethanol and deionized water, re-photographed and re-examined in the SEM. In the SEM, care was taken to examine exactly the same position before and after cleaning.

Results

Cleaning parameters

The potentiodynamic scans conducted on tarnished silver specimens indicated that the possible cleaning potential lies between -1.2 and -1.5 mV ESS. This agrees with work conducted on silver specimens by Degrigney [1996], see Fig. 3. In order to find the optimal potential, cleaning tests were therefore conducted at potentials of -1.2, -1.3, and -1.4 mV (ESS) for times up to 120 seconds.

The results of these cleaning tests can be seen in Fig. 7. The initial condition of the silver specimens is shown in Fig. 7a. The sulfidized specimens, Fig. 7b had a somewhat uneven tarnish, being a predominantly thin brown film with some blue areas, as well as occasional dark blue spots where some of the silver blackening agent had accidently dripped onto a number of the specimens.

The specimens could be cleaned at all of the potentials, see Fig. 7c. The brown strips at the top of the specimens are where they were clamped and held above the electrolyte. All of the specimens do show hint of a brownish film, which was slightly more visible for the specimens cleaned at -1.2 V (ESS), specimen numbers 2.4 - 2.6 in Fig. 7c. The cleaning at -1.3 (ESS) (specimens 2.7 - 2.9) and -1.4 V (ESS) (specimens 2.1 - 2.12) was faster than at -1.2 V (ESS), with the tarnish being removed after 30 seconds as opposed to almost two minutes at -1.2 V (ESS). The current (density) for cleaning and thus the cleaning rate was higher at -1.4 V (ESS). It was thus decided to use -1.3 V (ESS) for cleaning to allow for better control of the cleaning process.

Cleaning of daguerreotypes

Photographs of one of the daguerreotypes before and after cleaning are shown in Figs. 8a and 8b respectively. The as-received daguerreotype, Fig. 8a, shows a strong blue tarnish film typical of heavily corroded daguerreotypes which has formed under and at the edges of the passe-partout (not shown). This shifts to a heavy brown film, which lightens towards the center of the image.

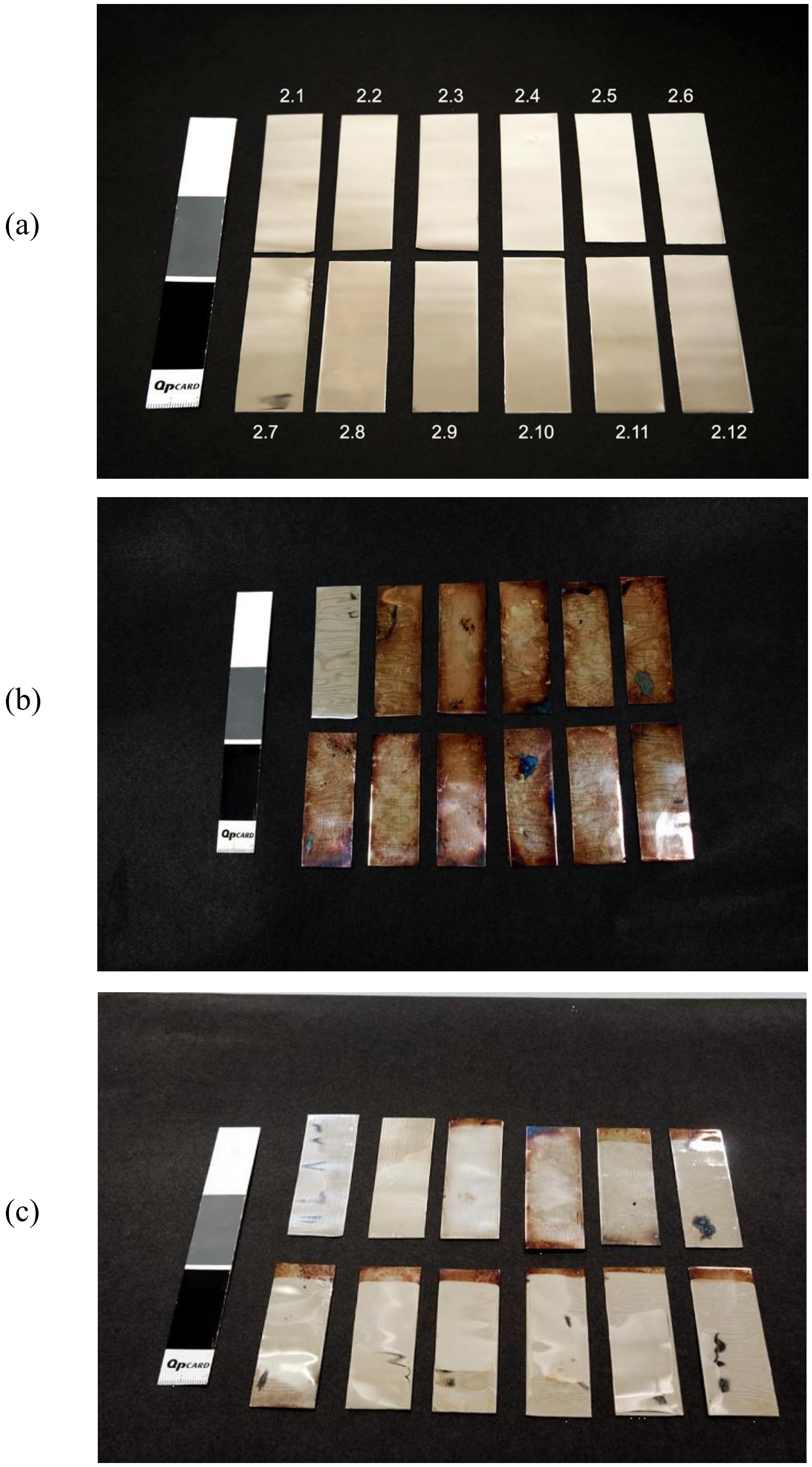


Fig. 7 - Visual comparison of silver specimens cleaned at various cathodic potentials.
a) Before artificial sulfidation
b) After artificial sulfidation

c) After electrochemical cleaning at -1.2 V (2.4-2.6), -1.3 V (2.7-2.9) and -1.4 V (2.10-2.12), all voltages ESS.

(a) (b)

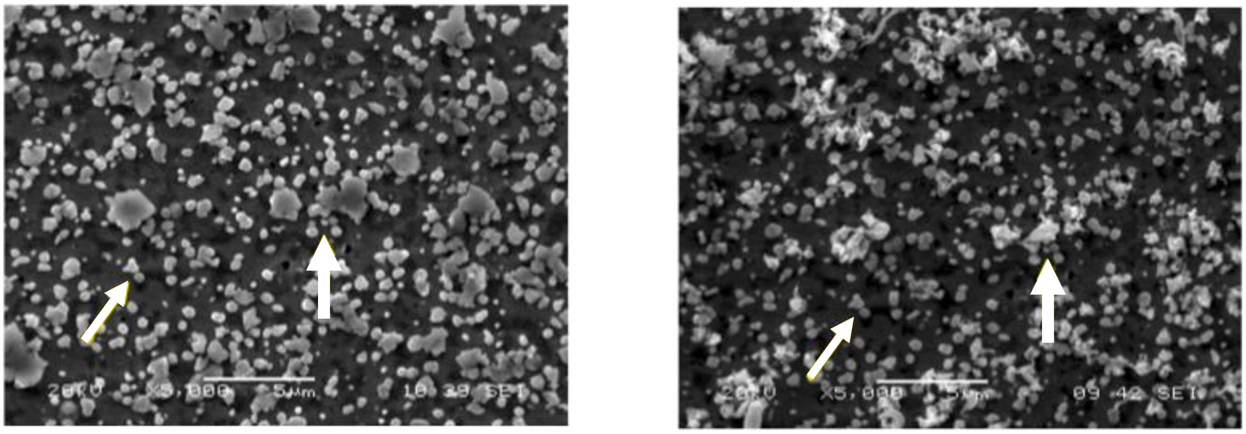
Fig. 8 - Visual comparison of a daguerreotype a) before and b) after electrochemical cleaning at -1.3 V (ESS).

The details of the woman's arms, hands, and the lower part of her dress are difficult to make out. The top of her head is also covered in the brown film.

The cleaning procedure has clearly removed the blue and brown tarnish films, see Fig. 9b. Only a hint of a brown film remains on and around the image. The pleats, folds and wrinkles in the woman's dress are now clearly visible. One can see that she wears lace gloves, and her hands rest folded in her lap. Whether or not this cleaned image is "good" or "acceptable" is an aesthetic and ethical question, a discussion of which will continue throughout the current project and beyond. However, one can certainly see that, in any case, the image is more readable.

Typical SEM micrographs taken at the same location on the daguerreotype before and after cleaning are shown in Figs. 9a and 9b respectively. A careful comparison of the two micrographs shows that all of the small image particles are still present at the same location before and after cleaning. On this scale, they do not appear to have changed in shape or size. The small arrows can be used as reference points for this comparison. However, there are several larger particles which seem to have broken up, compare the particles indicated by the larger arrows in the micrographs.

Qualitative EDS as well as XRF (X-ray fluorescence) analysis of the particles taken before cleaning showed Ag and Hg for the particles, and S and O as expected for the tarnish. Traces of Au were also found as would be expected for a gilded daguerreotype. After cleaning, EDS analysis indicates that while the small particles still contain Ag and Hg, the particles which have broken up, Fig. 10b, are primarily silver. Only a trace of S remains.



(a) (b)

Fig. 9 - SEM micrographs of image particles at the same location on the daguerreotype shown in Fig. 8 before (a) and after (b) electrochemical cleaning. The arrows are placed as reference positions, whereby the larger arrow in each micrograph indicates the location of a larger particle which appears to have broken up during electrochemical cleaning.

Discussion

The results of the experimental work conducted thus far in this project show that it is possible to electrochemically remove most, if not, all of the silver sulfide tarnish layer from daguerreotypes. With respect to the image particles and the silver plate, this method is “safer” than the original method developed by Barger et al. The method they developed is, in fact, not the way that electrochemical cleaning is normally conducted. Their use of a positive (anodic) potential to loosen a thick tarnish may make physical sense. However, by doing that, one is dissolving a thin (atomic) layer of silver under the tarnish in order to release it from the bulk plate. Whether or not such an atomic change is visible or “bad” is, however, open to question. In any case, the current experiments show that this anodic step probably was not necessary.

Furthermore Barger et al. tried to increase the current by raising the potential to +4 V, but this means that they shifted the potential out of the range for optimally removing the tarnish. The lack of use of a reference electrode means that the potential on the object actually changed from that value, and drifted with time as the tarnish and other material was removed from the object. Their use of a pen to increase the current (density) is actually correct. However, the use of a silver pen means that additional silver is going into solution and may have been deposited on the daguerreotypes, accounting for the shiny appearance they report.

For the current method, the small image particles on the daguerreotype remain unchanged, compare Figs. 9a and b, and no effect on the silver plate background was seen in the SEM. The procedure used is the standard method for cleaning used in many industries, including the electronics industry, which deals with products made up of thin films on substrates of all types. This procedure involves the use of a constant potential controlled using a reference electrode, an electrolyte which does not attack the silver or the copper plate, and an inert platinum counter electrode. Although the counter electrode used here was larger than a "pen" such as used by Barger et al, it was shown that local cleaning is possible using the parameters described.

While the method described in this paper is certainly "safer" than the Barger et al. method, there are still a number of concerns to be addressed before a final decision can be made as to whether electrochemical cleaning can be responsibly used for daguerreotypes. The breaking up of the large particles may be of concern, and work is necessary to determine what these particles are and why they are breaking up. Initial EDS measurements indicate that these may be large sulfide particles, which then break up as they are reduced. A faint brown film is also still visible on the daguerreotypes. This film still needs to be identified, and if necessary, conditions for its removal need to be found. Au was detected on the daguerreotypes, but closer study is required to determine whether or not it remains on the daguerreotypes during cleaning. It should also be noted that the method described here is only for daguerreotypes which have not been colorized. The stability of pigment layers just in solution is open to question, without even considering electrochemical cleaning.

A final question to be addressed is an ethical one. Given the high quality of current climate control technology, it is possible that a daguerreotype will probably be only be cleaned once in this manner. The question can thus be raised as to how "bad" the microscopic changes which are observed really are with respect to what one can actually be seen by the museum visitor and with the naked eye. Even though the method which Barger et al. used is not the normal way for conducting electrochemical cleaning, the daguerreotypes have been reported to be more readable and acceptable by their clients. This is a subject for further debate and perception studies, not only for daguerreotypes, but for other objects such as paintings and plastics as well [Wei 2011].

Conclusions

A study is being conducted to investigate the effect of (electro-) chemical cleaning of daguerreotypes on their appearance. The objective of the project is to assist conservators in finding methods and parameters which can be "safely" used for cleaning these unique objects. Initial work has been conducted to determine the effect of electrochemical cleaning on the surface condition and appearance of daguerreotypes, using cleaning procedures developed based on years of industrial experience.

Initial results show that the blue silver tarnish found on many daguerreotypes can be electrochemically removed in a 0.1 M $NaNO_3$ solution under cathodic polarisation conditions at a potential of -1.3 V ESS. The images were clearly more readable after the treatment. The treatment did not appear to disturb the silver amalgam image particles, or damage the silver plate itself. The procedure is based on those typically used in industry, and is a "safer" procedure than the original method reported in the literature using alternating polarisation. However, more work is required to deal with the complexity of these objects, and to deal with a number of issues including changes in large particles found in the image area, a faint brown film remaining on the specimens, the effect of electrochemical cleaning on the gilding, and how to remove other types of corrosion products in the tarnish. Further work in this project is also being conducted to relate measurements of "objective" microscopic changes with how treated daguerreotypes are perceived.

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