

# **Methods for Cleaning Brass Mats from Ambrotype and Daguerreotype Packages**

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## **Abstract**

In 2009 the Centre de conservation du Québec received a request for restoration of a composite photographic object from the collection of the Colby-Curtis Museum in Stanstead, Quebec. The object consists of twelve photographs mounted together in a wooden frame and includes daguerreotypes and ambrotypes; the brass mats of the individual photographs showed signs of corrosion. Before undertaking the restoration, three methods of corrosion removal were studied: the Rosenberg method of galvanic corrosion, local electrolysis and, lastly, localized application of an ion exchange resin, in this case Amberlite IR120 H. This article details the three methods and describes the results of the treatment method chosen using the ion exchange resin.

## **A framed composite of Ambrotypes and Daguerreotypes**

The object that initiated this study is a very rare composite arrangement of ambrotype and daguerreotype portraits mounted in a single frame. This undated object belongs to the Colby-Curtis Museum of Stanstead, Quebec and was entrusted to the Centre de conservation du Québec (CCQ) for restoration.

The object consists of a rectangular wooden frame in which are mounted twelve original photographs separated from one another by wooden fillets. There are seven collodion ambrotypes, three daguerreotypes, one carte-de-visite format albumen print and a small photogravure. The photographs were all produced in the second half of the 19<sup>th</sup>-century but the date at which they were assembled together in the current frame is not known.

Each photograph is contained in its own package which includes a brass mat, with the exception of one daguerreotype which has a gold-painted cardboard mat.

## **Deterioration of the Brass mats and Proposed Restoration Treatments**

Prior to its acquisition by the Colby-Curtis Museum, the object was likely to have been stored in an environment with conditions less than ideal for its preservation. (See Fig. 1) Additionally, only fragments of the original gummed paper sealing tapes remained. Ideally, daguerreotype and ambrotype packages have some type of peripheral seal to optimize the preservation of the photographic image inside the package. The loss of this protective feature may explain, in large part, the current condition of the object.

In ambrotype packages the brass mats are often placed outside the cover glass where they may be directly exposed to the challenges of the environment. In this case, all of them exhibit spots of corrosion distributed randomly over their surfaces.

Daguerreotype mats, on the other hand, are always placed inside the packages, behind the cover glass; this provides a degree of protection and these were generally observed to be in better condition.

### Corrosion on the Brass Mats

The spots of corrosion on the mats appeared identical – dark colored, almost black – when viewed by the naked eye. Examination using a binocular magnifier reveals differences in their color and texture; the color ranges from green to dark brown and includes intermediate reddish tones. This indicates the occurrence of several types of corrosion product.

An additional colored layer was observed on most of the mats. The appearance of this layer suggests that it is a varnish or a wax coating applied to the metallic surface.

At the outset the treatment proposed for the mats was the simplest one: following localized tests with various solvents and application tools, cleaning and degreasing of the surface. Preliminary testing showed that this straightforward approach would be unlikely to achieve satisfactory results. Specifically, solvent cleaning methods, including those using ethanol as a solvent, were not effective in removing any of the corrosion products. Tests of dry removal methods also proved unsuccessful. Mechanical removal of the corrosion products using the tip of a scalpel – even with the tool held flat against the surface – produced irreversible changes on the surface. The scratches these methods left were not necessarily visible to the naked eye but were immediately apparent under low power magnification.

The varnish layer and the adjacent patina layer – usually a layer of cuprite – appeared to be stable and we intended to leave these layers intact. It therefore seemed unlikely that we would find a corrosion removal method that involved complete immersion of the mat. At that point we decided to explore other methods for cleaning brass.

Cuprite – an oxide of copper – is the first corrosion product to form on the surface of an uncoated sheet of brass. It derives from contact between the metal and oxygen in the air and tends to form a protective layer against other forms of corrosion. This cuprite layer is considered to contain the original surface of brass objects. Generally it is preferable to maintain this surface but, in the case of certain historic objects or ones that are to be plated, it must be removed. In



Figure 1. The assembled composite photograph. © Centre de conservation du Québec. The corrosion on the brass mats is readily visible.

some cases the decision to remove or to leave intact the cuprite layer is influenced by the need to render the form of an object more readable. Cuprite is not soluble in simple aqueous solutions. The preferred removal procedure begins with mechanical methods; when the cuprite layer becomes very thin, chemical methods of removal must be employed. These methods must be carefully controlled to avoid compromising the underlying surface of the brass alloy.

### **Analysis of two Brass Mats at the Canadian Conservation Institute**

Before proceeding to develop treatment options, compositional analysis was carried out on two examples at the Canadian Conservation Institute (CCI), Ottawa. The objective here was to learn the specific composition of the brass alloy, the nature of the corrosion products and the confirmation (or correction) of our ideas concerning the coatings. Two mats were examined: a study collection mat as well as one of the mats under consideration. The analytical techniques used were scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS), Raman spectroscopy and Fourier transform infra-red spectroscopy (FTIR). (Helwig and Sirois, 2010)

The results obtained from the analysis allowed us to identify the mechanism of deterioration as de-zincification. (See further.) The corrosion products present were a copper oxalate hydrate, atacamite and clinoatacamite (a copper (II) chloride hydroxide and its polymorph), and cuprite. According to the analysts, the presence of the oxalate “suggests the action of micro-organisms on the surface or previous contact with a material containing oxalic acid.” (Helwig and Sirois, 2010, p. 4) Traces of shellac were found on the surface of the mat from the Colby-Curtis composite.

### **Cleaning Methods Examined**

Each of the cleaning methods examined were applied to a study collection mat which showed the same types of corrosion seen on the mats under consideration.

#### *1. Rosenberg method*

This technique was developed to eliminate copper chlorides. It involves the creation of a galvanic electrical cell that includes the object being treated and a sacrificial anode on which corrosion occurs. In this case, the anode is a sheet of aluminum foil and the electrolyte is glycerine. The reaction is maintained in a humidity chamber. The process causes the aluminum to oxidize while the copper is reduced and the chloride released.

In the presence of water and chlorides,  $\text{Al}^{3+}$  and  $\text{H}^+$  ions are attracted to  $\text{Cl}^-$  ions, forming soluble aluminum chlorides ( $\text{AlCl}_3$  or  $\text{AlCl}_4^-$ ). These molecules, free to interact in the water medium will form an aluminum hydroxide complex and hydrochloric acid.

The hydrochloric acid formed in this way drives the aluminum corrosion reaction forward and results in the formation of small holes on the aluminum foil. (Selwyn, 2004, p.52) The copper, now separated from the chlorides, is reduced in a more stable form (cuprite or, less frequently, tenorite). (Scott, 2002, p.367)

The various standard reduction potentials ( $E_0$ ) of the metals present partly explain this reaction. The mat is made of brass, an alloy of copper and zinc; the object is affected by chlorides ( $\text{CuCl}$  or  $\text{ZnCl}_2$ ); and the anode is aluminum.

Metal	$E_0$ (V)
$\text{Cl}_2 / 2\text{Cl}^-$	+1.34
$\text{Cu}^{2+} / \text{Cu}^0$	+0.34
$\text{Zn}^{2+} / \text{Zn}^0$	-0.76
$\text{Al}^{3+} / \text{Al}^0$	-1.56

The redox pair with the highest potential will tend to interact with the pair with the lowest potential. In this case chlorides will dissociate from the Cu-Zn alloy to react with the aluminum and thereby favour oxidation of the aluminum.

Application of this method is relatively simple. First a layer of glycerine is applied with a paint brush onto the areas that are to be treated. Then the object is wrapped in a sheet of aluminum foil ensuring that good contact is obtained between all of the elements. (See Figures 2 and 3) This combination is placed in a humidity chamber conditioned to at least 90% RH. After several hours – 24 hours in our case – the object is unwrapped to observe whether a reaction has occurred with the aluminum. Small holes in the foil will be visible where there has been anodic reaction. (See Figures 3 and 4) After removal of the residual glycerine the treated areas should be free of corrosion products<sup>1</sup> or, alternatively, covered by a layer of cuprite ( $\text{Cu}_2\text{O}$ , brown to red in colour) or tenorite ( $\text{CuO}$ , black). The process may then be repeated, if necessary. Note that the Rosenberg method softens cuprite deposits but does not eliminate them.

### 1.1 Results

This procedure was applied to the test piece over a period of ten days, at which point the chlorides had been reduced but the largest spots of corrosion remained visible while the lightly corroded areas were completely cleared.



Figure 2. Coating the mat with glycerine. © Centre de conservation du Québec.



Figure 3: Examining the result of the Rosenberg method. © Centre de Conservation du Québec



Figure 4: Corrosion on the aluminum foil. © Centre de Conservation du Québec

### 1.2 Conclusion

The Rosenberg method is quite slow and does not permit truly localized application. In this application it does not achieve the goals of the treatment. However, these results do confirm the corrosion mechanism which is at work; that is, de-zincification. This process involves the selective extraction of zinc from the brass alloy. (Selwyn, 2004, pp. 76-77) This phenomenon can often be explained by the lack of homogeneity in the mixture of the two metals at the atomic scale. At the surface this translates into an increased tendency towards corrosion in the areas rich in zinc and also produces inequalities in the surface colour of the brass: some areas will have a tone more pink than others where there is a higher proportion of copper in the alloy. The analyses carried out at CCI confirmed this corrosion-induced heterogeneity in the composition of the brass.

### 2. Local electrolysis method

This method involves the creation of a localized electrolytic cell with weak polarization. (Scott, 2002, p. 365) The operation is quite simple: the object to be treated is attached electrically to a 9 V battery so that it becomes the cathode and, on the other side contacts a weakly corrodible material such as graphite, which becomes the anode. An electrolyte deposited on the area to be treated completes the circuit. (See Fig. 5)

The solution that is usually employed as the electrolyte is sodium hydroxide but this risks harming the base metal of the mat and the shellac residues on its surface. The electrolyte selected in this case is ethylenediaminetetraacetic acid (EDTA), a chelating agent recommended for use with copper corrosion products. Shellac residues seem to be unaffected by the EDTA, particularly when it is used in low concentrations; EDTA seems therefore to present very low risks for the object under treatment.

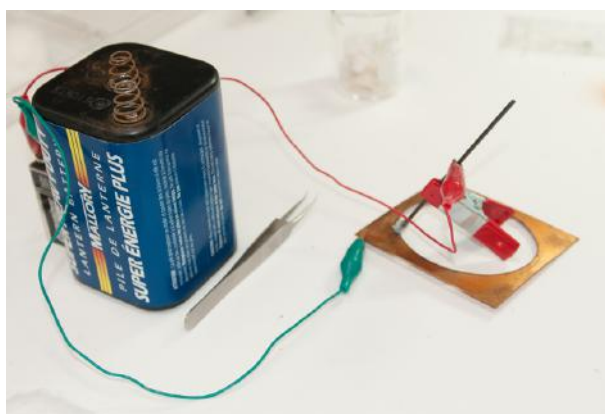


Figure 5: Reduction of oxidized spots by local electrolysis. © Centre de Conservation du Québec

In an effort to control the location of the electrolyte on the surface of the mat, the EDTA was incorporated in an aqueous gel of methyl cellulose (5% w/v). The concentration of EDTA in the gel was 5% (w/v) and the mixture was adjusted to pH 8.<sup>ii</sup> The gel is coated on a cotton swab which, in turn, is attached to the graphite electrode. This anode assembly is attached to the battery and brought into contact with the corroded area for a few seconds.

### 2.1 Results

In preliminary attempts it was noted that this method is difficult to control while working on such a small area. Typically, a ring of over-cleaned surface is formed around the target spot.

The method was modified in order to augment and better control its action by:

- reducing the voltage of the battery used to 6 V;
- reducing the concentration of the EDTA to 2% (w/v);



- further reducing the EDTA concentration to 1% (w/v);
- combining the above methods;
- reducing the size of the point of the graphite electrode.

The variations tried did not yield a success for this application. While this approach remains potentially useful, the current tests showed the action to be too powerful, too difficult to control, and globally, to achieve a satisfying result, treatment times were too long.

### 3. *Ion exchange resin method*

This method using ion exchange resins for removal of corrosion products was first used on lead objects and it was found effective in removal of chlorides and carbonates. The resins tested in earlier studies were Amberlite IR120 H and Zeo-Karb 225. (Plenderleith and Werner, 1976; Schotte and Adriaens, 2006) The resin used in this study was Amberlite IR120 H.

This resin has been used successfully to treat another copper alloy – an archaeological bronze object. (Robcis, Guilhem and Lalande, 2005) Its mode of action is simple - molecules are separated from one another by cationic substitution. The resin is an organic polymer which incorporates acidic groups. When brought into contact with metallic corrosion products the resin sequesters the oxidized metal constituents leaving the base metal free of corrosion products.

This method has the advantage of removal of the surface corrosion without the use of chemical agents. It is effective in capturing both chlorides and carbonates. Its application is simple: the resin is mixed with water and the resulting paste is applied to the area that is to be treated. Once this poultice is removed, the cleaning action stops. No further rinsing to remove residues is required.

At the time of these tests, Amberlite® IR120 H was available in the form of small beads. Since the reaction requires physical contact between the resin and the surface being treated, the application of the beads produced a pattern of round marks corresponding to the shape of the beads. In subsequent tests the resin beads were pulverized before being used. (See Fig. 6) These test produced results that met the treatment goals.

When mixed together the powdered Amberlite® and water mix becomes a translucent paste. As the water evaporates the paste whitens and cracks. Depending on the ratio resin-water it can take up to a minute to dry. The dried paste can then be easily removed with a brush. Several applications of the paste may be needed, depending on the corrosion thickness. The more water the paste contains the less action it will have. The exact ratio still has to be scientifically assessed.

The resin can also damage the varnish around the corroded spot, making it look lighter. Thus, it is important to apply it precisely on the corroded



Figure 6: The Amberlite resin is pulverized in a mortar © Centre de Conservation du Québec

areas. In our case, considering the size of the corrosion spots, the implementation is done under binocular magnification.

Two methods were tested:

1. With a masking tape: the area to treat is first masked with a self-adhesive tape<sup>iii</sup>. Little holes are then made through it with a scalpel blade at the location of each corrosion spot. The area can be treated with the Amberlite® without damaging the non-corroded areas. With this method the resin application is fast and easy, with no risk for the non-corroded areas. The resin can be applied dry on the holes before adding water with a brush, or as a paste. However it is time-consuming to cut precisely the tiny holes and there is a real risk of scratching the brass mat surface.
2. Direct application: The paste is applied with a small and rigid tool, directly on the corroded spots. Sewing needles proved to be the most appropriate one. We found that using another tool was useful. A Microbrush®<sup>iv</sup> is damped into water, then put into the resin grains thus forming the paste on the brush. The needle is then used to pick up the paste from the brush and apply it on the corroded spots. The brush works as a water source for the paste. Cotton swabs can be used too, yet the fibers tend to trap the resin grains.

The drawback of this method is the long time needed to apply the paste.

Both methods are time consuming. Nevertheless we tend to recommend the second method as there is no risk of scratching the mat surface.

The optimal dwell time of the poultice on the object was also examined. Three were tested: 2 minutes, 1 minute, and 30 seconds. The degree of cleaning obtained using the longer ones, 1 and 2 minutes, was too high and these applications risked affecting the surrounding shellac layer. The 30 second dwell time resulted in a satisfactory degree of cleaning and allowed for optimal control of the procedure. The rapidity of the process is probably due to the fact that the layers of atacamite and clinoatacamite on these objects is quite thin. A thicker accumulation of corrosion products will require longer dwell times or several repeated applications.

The Amberlite® method has numerous advantages: simple application technique, rapid action, and the ability to follow the progress of the action. The method also produces the most satisfactory visual end-point. It is however, essential to watch the process carefully since there may be a transitory evolution of hydrochloric acid at the reaction surface. On the whole, the method met the treatment goals admirably well and this was the method used to treat the mats from the Colby-Curtis photographic composite.

### **Treatment of the Brass Mats of the Composite Object from the Colby-Curtis Museum**

At the time of the treatment of the composite from the Colby-Curtis museum we had only tested the first method described above, therefore the daguerreotypes and ambrotypes were disassembled and the treatment of the mats proceeded as follows (See Figures 7 and 8):

- The areas with spots of corrosion and their surroundings were first covered with a self-adhesive transparent tape. A scalpel is used to make a small hole through the tape at the location of each corrosion spot.
- The area to be treated is covered with the ion exchange resin (Amberlite IR120 H, powdered) mixed with a bit of demineralized water. The paste is left in place for 30 seconds. This removes the corrosion products while leaving the areas protected by the adhesive tape unaffected.
- When all of the areas of corrosion have been sufficiently treated, the protective adhesive tape is removed.



Figure 7: The resin is mixed with a small quantity of demineralized water to obtain a thick paste © National Gallery of Canada



Figure 8: The thick paste is placed in contact with the corroded areas © National Gallery of Canada

### Retouching of the Cleaned Areas

The treatment using the Amberlite resin leaves the cleaned areas with a light brown color. The retouching of metal surfaces can be complex. The purpose of this treatment was not to make the cleaned areas invisible but to mitigate them so that the viewer would not be distracted from the image.

- The work was done using a binocular magnifier.
- An insulating layer is applied first; to protect the surface of a possible return of the corrosion but also for the reversibility of the retouching layer. The brass mats being often varnished, it was necessary to carry out tests to check the harmlessness of the solvent used. During this research, we used Paraloid® B72 diluted at 5% in acetone.
- For the retouching, pigments dispersed in acrylic emulsions were used. Several pigments are available on the market, with the Sepp Leaf Products® mica powders proving to be the most opaque. Various acrylic polymer emulsions from Liquitex® (gloss, semi-gloss,



matte) were used to adapt the glossiness of the medium to the one of the mat. These acrylic emulsions can be diluted in a little bit of demineralized water until the best consistency is achieved.

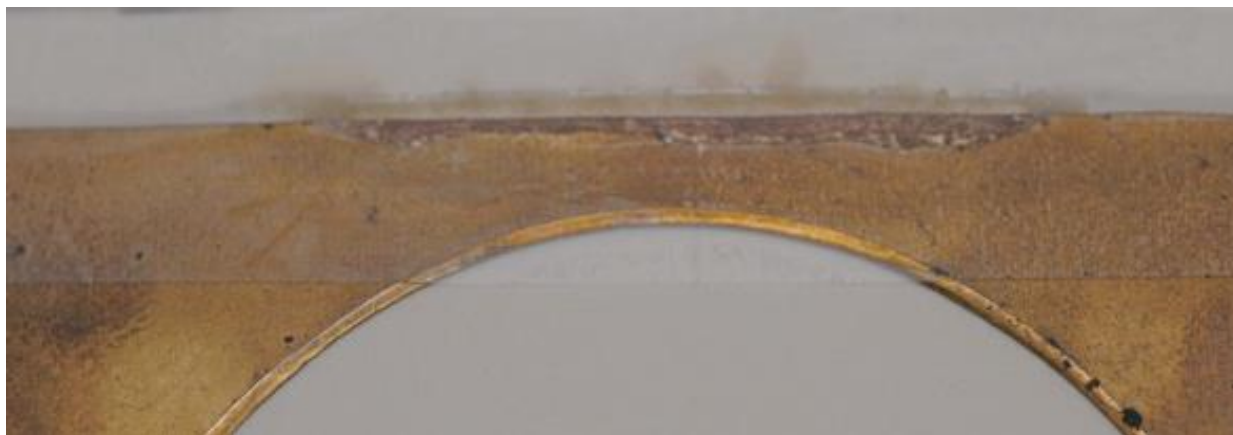


Figure 9: The adhesive tape, visible here across the top of the mat, limits the area where the resin can act.  
© Centre de Conservation du Québec

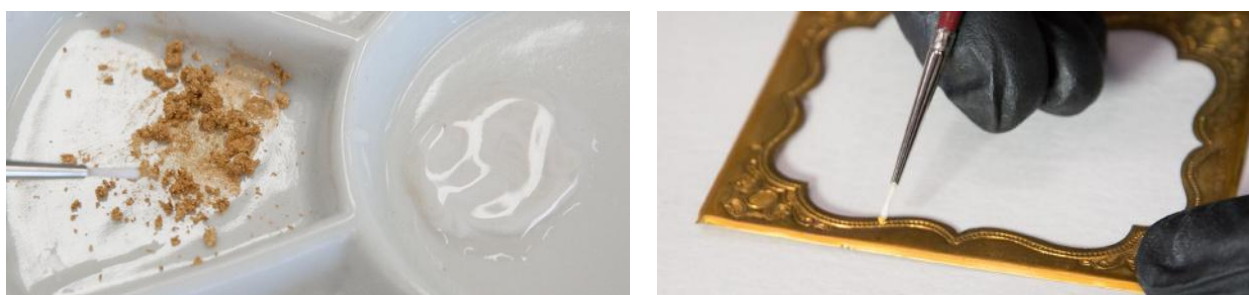


Figure 10a and 10b: Retouching using mica powders in acrylic polymer emulsion.  
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## Conclusion

Selection of the most appropriate conservation treatment techniques is made on the basis of effectiveness, rapidity, the ability to control the progress of the treatment and ease of application. Of the three methods examined here, the use of the ion exchange resin corresponded best to these criteria. This technique does, however, carry some risk in the possible formation of hydrochloric acid at the resin particle surface. Re-introduction of chlorides on the metallic surface would risk re-initiating the corrosion. Thus, it is very important to ensure complete removal of the resin paste after treatment. Both the Rosenberg method and the electrolytic method provide some advantages, but they are too difficult to safely employ over such tiny areas.

The use of ion exchange resins for this application is a promising avenue that deserves further study. Notably, the safety of the method with regards to the shellac layer and the long term stability of the treatment should be examined.



Figure 11: Mat and daguerreotype before treatment.  
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Figure 12: Mat and daguerreotype after treatment.  
© National Gallery of Canada

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<sup>i</sup> This will be the case only when the initial deposit of nantokite (CuCl) is thin.

<sup>ii</sup> The pH of the solution is adjusted with addition of sodium hydroxide.

<sup>iii</sup> It is necessary to use a low tack tape that will be easily removable without leaving adhesive residues. The tape used here was a 3M Scotch Mending Tape M81-853 (currently marketed in the USA as 3M Scotch Scrapbooking Tape).

<sup>iv</sup> From Lee Valley & Veritas®, Canada