An Optimized Nontoxic Electrolytic Etching Procedure for Fine Art Printmaking

KATHARINA BOSSMANN, JOSE COVARRUBIAS, ASANKA S. YAPA, BENJAMIN INGLE, STEFAN H. BOSSMANN AND JASON SCUILLA

In their National Endowment for the Arts-funded project the authors sought to provide artists with an innovative method for creative expression using electrolytic etching techniques long used in the electronics and biotech industries. Using scientific methods, the electrolytic etching process was improved and then compared side by side with copper etched in ferric chloride after analysis with an AFM. The optimized electrolytic etching method proved to be superior to classical acid etching in intaglio printing.

Fine art etching has always confronted toxicity problems inherent to the practice. The use of nitric acid and other etchants to etch metal etching plates (Dutch mordant, for example: nine parts of water saturated with potassium chlorate to one part of hydrochloric acid), solvents to remove resists in the etching process, the resists themselves and the printing inks all present hazardous conditions for the printmaker. In an effort to change some of these issues, we have been experimenting with various processes to make printmaking safer for printmakers and better for the environment. Using ferric chloride to etch copper has been a step in the right direction, but by using electrolytic etching methods used in the IT and commercial plating industries, we can create fine art–worthy prints using chemicals that can be more easily disposed. Printmakers who have made notable contributions to the medium of electrolytic etching over the past 30 years include Nik Semenoff (Canada) [1]; Cedric Green, Robert Adam and Carol Robertson (U.K.) [2–4]; Alfonso Crujera (Spain) [5–7]; Henrik Bøegh (Denmark) [8]; and Merion Behr, Regina Held and Ray Maseman (U.S.A.) [9,10].

Building on their developments, Jason Scuilla, a master printer and printmaking professor at Kansas State University, worked on creating an electrolytic etching process that would stand up to the rigors of a traditional etching artist practice with plates and resulting prints. Once the process had been realized, questions started coming from the printmaking community about how it could work in a university studio setting; how it actually worked; and whether this was truly a process that could replicate all the various processes—line, aquatint, open bite, etc.—used in printmaking. To answer these questions definitively, Scuilla sought a collaboration with chemistry professor Stefan Bossmann, an expert in biomaterials. This collaboration was further strengthened by an Artworks Grant from National Endowment for the Arts, "Transforming Printmaking through Chemical Innovation." We performed experiments to find a range of marks and lines to create a library useful for the artist and then looked at the etched lines under an atomic force microscope to compare them scientifically with etched lines made using ferric chloride.

As can be seen in Fig. 1, the range of lines, crosshatching, stippling and other marks is definitely comparable to traditional etching to the naked eye.

DAMMAR RESIN/BEESWAX RESIN (DC SAFE GROUND) ON CUSO₄

In order for the etching ground to withstand the rigors of the electroetching process, we needed to find something more stable than the traditional grounds that had been in use in our studios. We had tried Charbonnel hard ball ground, asphaltum in naphtha in various ratios, Graphic Chemical liquid hard ground and Lamour soft ground. They all resulted in extensive foul biting or flaking or broke down around line work, causing creep bite and reduction in line sharpness. To overcome these shortcomings, we needed to develop a new

© ISAST https://doi.org/10.1162/leon_a.02000

LEONARDO, Vol. 54, No. 4, pp. 000–000, 2021 427
custom-mixed intaglio hard ground. We refer to this type of ground as DC (direct current) safe ground.

Based on the physicochemical properties of dammar resin and beeswax, and the fact that both are relatively nontoxic and commonly used in the process of encaustic wax work, the combination of both waxes appeared to be suitable for creating the optimal ground for electroetching purposes [11]. Dammar resin is obtained from the Dipterocarpaceae family of trees in Asia. It is mainly a triterpenoid resin, composed of numerous triterpenes and their oxidation products, such as dammarane, oleanane and their corresponding acids [12]. It has a relatively high melting point (T > 180°C), but it can be dissolved in organic solvents and other waxes with lower melting points, such as beeswax (T > 62°C). For the purpose of forming strongly adhesive layers on copper surfaces, the content of the polymeric fraction of the hydrophobic polymer polyocadinenine is very important [13]. Beeswax is a natural wax produced by honeybees. Its main components are oleate esters of long-chain alcohols (30–32 carbons), as well as palmitate and palmitoleate. For the purpose of electrolytic etching, we determined the optimal combination of beeswax and dammar resin to be three parts beeswax to two parts resin. This was melted together in a pot and then poured into silicone forms for easy use and left to harden at room temperature for at least 24 hours. To use the DC safe ground, one puts a cleaned copper plate on a heated surface of 43 ± 1°C. The ground is then put on the copper plate by stroking the cakes of mixed wax/resin in overlapping stripes across the plate quickly and smoothly. During application, the printmaker should feel slight resistance as the ground adheres to the plate. If the grounding feels comparable to a crayon drawing, it is too cool. If the ground liquifies upon application, it is too hot. For the printmaker who prefers a thicker ground, they can leave the grounded plate on the hot plate for an extra five minutes to allow the DC safe ground to even out. If a very thin, even ground is preferred, one can use a chamois leather dauber to even out and thin the ground on the plate: First, heat the dauber on the hot plate to ensure any prior wax is melted. Then, starting in the top left corner of the plate, daub in very soft taps horizontally across the plate. Continue to daub across the plate in slightly overlapping horizontal bands until the entire plate has a smooth, even coating.

Once cooled to room temperature, the printmaker will take the ground plate to a well-ventilated area and "smoke" using tapers or a beeswax candle.

We purchased copper plates from Atlas Metals. We obtained R&F damar resin and U.S. pharmaceutical-grade beeswax from Dick Blick Art Supplies [14].

**ELECTROLYTIC ETCHING SETUP**

We built the electrolytic etching baths used in our experiments using a 21-cup Rubbermaid Premium Modular Food Storage Container (product number 1840746). Two holes were drilled into each short side to support the copper rods at exactly 1.9 cm apart. Twelve-inch 3/16 diameter multipurpose 110 copper rods (McMaster-Carr product number 8966k3) were inserted in the holes, creating the support for the copper wire cloth grid and the “to-be-etched” plate. We cut 'copper wire cloth' (4 × 4 mesh size .203 in opening size [McMaster-Carr product number 9224t47]) to 9 × 8 inches and then bent with a one-inch overhang, used to hang on one of the copper rods, making the grid 8 × 8 inches (see Fig. 2b). We attached the negative wire from the power supply to the copper rod with the copper grid hanging from it. The positive wire is then attached to the copper rod that will have the etching plate hanging from it. We cut and then bent with a one-inch overhang, used to hang on one of the copper rods, making the grid 8 × 8 inches (see Fig. 2b). We attached the negative wire from the power supply to the copper rod with the copper grid hanging from it. The positive wire is then attached to the copper rod that will have the etching plate hanging from it. We used seven identical power supplies (type Volteq DC Power Supply HY1503d) and the corresponding electrolytic etching baths to perform the described electro-etching experiments (see Fig. 2a). We chose this power supply because it permits the constant setting of
the voltage throughout the electro-etching process (for up to 60 minutes and beyond). Due to the fact that the kinetics of electrolytic etching processes are driven by the electric field strength per unit of length (V/m), and lines and other features are only found on the frontside of the copper plate, the backside does not have to be protected during electrolytic etching processes.

**LINEAR OPTIMIZATION OF ELECTROLYTIC ETCHING CONDITIONS**

The first step in our investigation of electrochemical conditions for the intaglio printmaking process consisted of optimizing the concentration of copper sulfate at constant voltage (1.5 V). We decided not to try any additives to copper sulfate, because we wanted to elucidate the maximum performance of this electrolytic etching system first. The optimum conditions were then used as a center point of a Doehlert matrix, which is a straightforward optimal experimental design methodology (OEDM). The use of OEDM has the advantage of obtaining significant results with a minimum of required experiments.

In Table 1, we summarize the experimental conditions of the first round of electrolytic etching experiments.

We chose bath number six as the best concentration for a consistent, unbroken, clean line. This was determined by visual plate inspection using a loupe magnifying glass and the results of the printed plate (see Fig. 3) and a vote by eight evaluators.

**TABLE 1**

<table>
<thead>
<tr>
<th>Bath #</th>
<th>CuSO₄ × 7 H₂O g/L</th>
<th>Time/Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>125</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>2</td>
<td>115</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>3</td>
<td>105</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>1 5 10 20 30 60</td>
</tr>
<tr>
<td>7</td>
<td>65</td>
<td>1 5 10 20 30 60</td>
</tr>
</tbody>
</table>

All experiments were conducted at 1.5 volts. Voltage was kept constant for the duration of the entire experiment.

**Fig. 2.** (a) Electrolytic etching baths and power supplies. (b) Close-up view of the experimental electrolytic etching tank without aqueous copper sulfate. (© Katharina Bossmann)

**Fig. 3.** The hand-printed plates from the experiments in Bath #6 (75 g/l copper sulfate in bidistilled H₂O) that evaluators determined to be the best etched plates of our first round of bath experiments. We were able to produce a full range of marks, cross hatches, curvy lines and stippling with unbroken, clean lines when printed. (© Katharina Bossmann)
Fig. 4. (a) Atomic force microscope line image of a line formed in a copper plate with adhesive DC safe ground after smoking procedure and 60 min. electrolytic etching using 75 g/L CuSO₄ × 7H₂O in bidest. H₂O and 1.5 V at 20 ± 0.5 °C. (b) Calculated surface view of the same area. (© Stefan H. Bossmann)

Fig. 5. (a) Atomic force microscope line image of a copper plate with adhesive DC safe ground after smoking procedure and etched in ferric chloride [22]. (b) Calculated surface view of the same area. (© Stefan H. Bossmann)

Fig. 6. (a) Atomic force microscope line image of a copper plate with adhesive DC safe ground after smoking procedure and ferric etching [23]. (b) Calculated surface view of the same area. (© Stefan H. Bossmann)
undergraduate and three graduate students of fine arts in the printmaking program at Kansas State University, together with Scuilla, their printmaking professor.

OPTIMAL EXPERIMENTAL DESIGN METHODOLOGY (OEDM)
The optimization of the electrolytic etching process aimed at creating clean, unbroken, sharp lines in electrochemical conditions that can be easily maintained in the printmaking studio. We determined the effects of two main process variables (U1) on line quality (experimental response Y): (1) concentration of copper sulfate (U1, grams per liter bidistilled H2O) and (2) constant voltage during electrolysis (U2, V). OEDM was used for designing an experimental matrix able to provide meaningful results with a minimum of experiments required [15,16]. The OEDM methodology is explained in detail in the online supplemental materials.

ATOMIC FORCE MICROSCOPY
An atomic force microscope (AFM) can look at the actual etches into the copper so as to compare the two different etching methods. We hoped that being able to measure the etched lines and also visually see the etches would allow us to determine whether the electrolytic etching process could be proven comparable to conventional processes. Our AFM images were taken by a Nanoscope AFM image system (Digital Instruments) utilizing TESP-

AFM probes in tapping mode. The spring constant of the tip was 50 N/m and the frequency was 350 kHz. The set point, P gain and I gain were set at 1.2, 0.6 and 0.5, respectively. The images were gathered with 256×256-pixel resolution at a scan rate of 1.969 Hz. The imaging window was 10 μm × 10 μm. The images were then analyzed by Bruker's Nanoscope software [17]. We have imaged a region in which a distinct line was formed by either electrolytic or ferric etching in order to observe the resulting topologies. Figure 4 shows a line generated by electrolytic etching: The etches are sharp and steeply descending, whereas the bottom of the etched line is flat. A second similar AFM image can be seen in the online supplemental materials.

Ferric etching produces a completely different geometry of etched lines than electrolytic etching, as shown in Figs 5 and 6. In Fig. 5, the chemical etching process generated very smooth troughs instead of sharp trenches. Furthermore, chemical etching appears to be incomplete, as indicated by regions of copper that have not been removed. These observed differences in topology can be then attributed to the differences in line clarity and printing contrast.

DISCUSSION
In the 1980s, N. Krishna Reddy showed printmakers what was thought to be what etching through various methods looked like: nitric acid (1:5 water) was thought to undercut the surface; Dutch mordant (HCl + KClO3 1:9 in water) was thought to create a smooth “V” etched into the surface; and ferric chloride (concentrated 1:5 water) was thought to create smooth straight perpendicular cliffs, creating a box shape with a flat bottom surface [18]. This was what one sees by inspection with a magnifying glass. We obviously saw more jagged and sloped ridges when observed through the AFM. This advanced microscopic process has shown that actually etching with ferric chloride does not produce the straight wall as originally thought. Electrolytic etching does produce the almost 90°-angled canyon formerly attributed to a ferric etched line. This is a better etched line for printmakers because it is harder to overwipe the plate.

Our hypothesis for the electrochemical reasons for the observed deviations in line formation is this: Electrolytic etching proceeds according to the following chemical formula (Cu2+: water-soluble copper cation; e−: electron; the standard electrochemical potential of this reaction is + 0.34 V) [19]. This means that at V > + 0.34V, copper will readily dissolve as Cu2+. These conditions are met throughout the entire experimental domain.

Cu → Cu2+ + 2e−

As indicated by the quadratic response equation, the etching increases linearly with increasing voltage. It also increases, albeit less strongly, with rising copper concentration, indicating the following thermal etching reaction:

Cu + Cu2+ → 2Cu+

The standard electrochemical potential for this reaction is comparable to that of copper dissolution to copper(II) [20]. The efficacy of this reaction increases with copper(II) concentration. Note that electrolytic etching is performed in the presence of air. Therefore, copper(I) will be oxidized to copper(II) in aqueous solution. The only quadratic term of relevance is the product of copper(II) in solution and applied voltage. It is noteworthy that there is a negative dependence of the copper dissolution kinetics from this quadratic term. Since voltage is a positive driver of copper dissolution, copper(II) must be responsible for the observed negative pre-sign of the quadratic term. A physicochemical interpretation of this behavior is that the dissolution of copper as copper(II) has to be achieved against the ionic strength of the copper(II) that is already in solution. Finally, the observed sharp and steeply descending line features are formed, because the effective voltage is a function of geometry [21]. The effective voltage is much higher at copper regions that are exposed. Therefore, electrolytic etching proceeds faster there than at smooth surfaces.

Ferric etching proceeds according to the following equation:

Cu + 2Fe3+ → Cu2+ + 2Fe2+

The ratio of two iron(III) cations that are required to dissolve one atom of copper makes diffusion processes very important. Therefore, the diffusion conditions during ferric etching create shallow jagged “valleys” instead of deep, straight lines. The lack of diffusional transport is most likely also responsible for the observed regions that are virtually untouched by ferric etching.

Bossmann et al., An Optimized Nontoxic Electrolyte Etching Procedure for Fine Art Printmaking

431
CONCLUSION

Plates etched using electrolytic techniques, combined with a DC formulated resist and calculated etching solutions, can equal and surpass traditional acids. The reduction of hazardous fumes and materials allow for this technique to be practiced in academic and home-based studios that lack access to ventilation and waste disposal. Together, this combination has the potential to make a global impact on the practice of fine art etching. The team involved in this research project serves as an example of groundbreaking interdisciplinary collaboration between science, technology and fine art. Print media grows and evolves through the practice and collaborative nature of the printmaking studio. Once experienced, the potential for further traditional and experimental electrolytic etching development will appeal to the greater print community. We will continue to invite a consortium of nationally recognized printmakers, emerging artists and commercial master printers to our labs to work with the scientists and student researchers involved in this project. This will continue to expand our knowledge of what functions well and further facilitate technology transfer to other studios.

Acknowledgments

The authors gratefully acknowledge NEA Grant #17-4100-7006, “Transforming Printmaking through Chemical Innovation,” and the support of the Departments of Chemistry and Art at Kansas State University.

References and Notes

3 www.greenart.info/galvetch.
13 Vahur et al. [12].
20 Larson et al. [19].
22 Procedure ferric chloride—the anhydrous ferric chloride, ordered from Takach Press (42 Baume) diluted 1:1 with water, plate was etched for 60 mins in a vertical tank at 21.2 ± 1 °C: www.shop.takahpress.com/Ferric-Chloride-p/ferric-chloride.htm.
23 See Ref. 22.

KATHARINA BOSSMANN is a Master of Fine Arts candidate at Kansas State University.

JOSE COVARRUBIAS is a graduate student of chemistry at Kansas State University.

ASANKA S. YAPA is a postdoctoral researcher of chemistry at Kansas State University.

STEFAN H. BOSSMANN is University Distinguished Professor of Chemistry at Kansas State University.

JASON SCUILLA is Full Professor of Art and a master printmaker at Kansas State University.