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Art Meets Science

SEARCH

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Friedhard Kiekeben with Dr Paul Craig and Keith Howard

In 2003, with the kind assistance of Keith Howard, the metal salt etching processes developed by Friedhard Kiekeben were thoroughly tested by Dr Paul Craig and Dr Paul Rosenberg, both professors of chemistry at Rochester Institute of Technology (RIT). Together they wrote the following recommendation and safety assessment for The Edinburgh Etch and The Saline Sulfate Etch.

The Chemistry of Etching without Acid

Dr Paul Craig, PhD
Dr Paul Rosenberg, PhD

In the past, metal etching for the purpose of printing or art was typically done with nitric acid, which has harmful vapors and is extremely caustic. In this chemistry lab nitric acid baths are always maintained in enclosed fume hoods with separate ventilation and filtering. Such hoods are often not available in print or art studios.

The Edinburgh Etch

The Edinburgh Etch uses a mixture of ferric chloride and citrate, which circumvents the safety hazards associated with nitric acid baths. The etching of copper with ferric chloride has been well known for a number of years. However, etching is slow and results in precipitation on the surface of the copper, probably due to the accumulation of insoluble copper salts (perhaps copper hydroxide) on the surface of the copper.

If these accumulate, they interfere with the normal oxidation-reduction reaction between the Ferric (Fe3+) and the metallic copper (Cuo). In the equations shown below for this reaction in water, a positive voltage indicates an energetically favorable reaction.

The Edinburgh Etch adds one new ingredient to the ferric chloride etching bath: citric acid. Etching in this bath is much more rapid and reproducible than the original ferric chloride etch. This can be attributed to two causes:

1. The citric acid will lower the pH of the bath slightly (making it more acidic). Under these conditions, the Cu2+ is unlikely to form an insoluble salt (such as copper hydroxide - Cu(OH)2) and thus will be more soluble.
2.
3. The Cu2+ will have a tendency to form a complex with citric acid as it is released from the surface of the metal, also increasing its solubility.

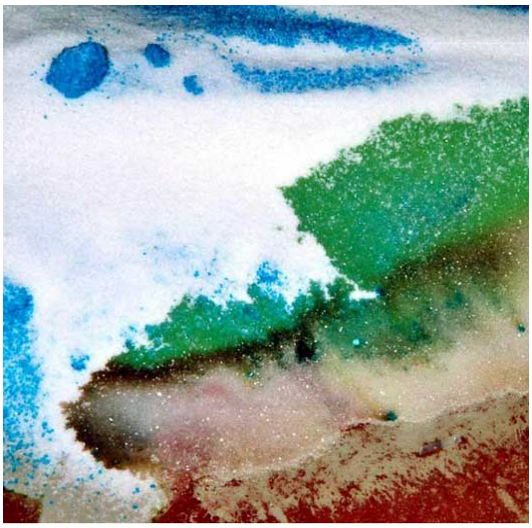
The hazards associated with the Edinburgh Etch are dramatically less than those associated with nitric acid. The solution is mildly caustic to the touch and does not emit noxious gases. In fact, the Edinburgh Etch could safely be used in an open studio or laboratory, whereas the nitric acid etch can only be safely used with a fume hood. A small amount of hydrochloric acid may be released as the copper complexes with the citric acid.

This is highly soluble in water and should not pose any serious risk of acid fumes in the lab. Nonetheless, when the Edinburgh Etch is exhausted, it is still recommended that the solution and solids be disposed of as chemical waste, rather than washing down the drain into the sanitary sewer system. High concentrations of iron and copper may interfere with normal bacterial recovery of materials in the sewer system.

The Edinburgh Etch reacts very rapidly with the copper. In our studio, we etched a clean sheet of copper (20.35 cm x 12.85 cm x 0.5 mm thick [127.56 grams including an acrylic backing]) until only the backing remained [10.50 g] in 13 hours. This was not a new etching bath - it had been in use for several months.

The Saline Sulfate Etch

The Saline Sulfate Etch is recommended for etching aluminum or zinc. Use of the Edinburgh Etch with these metals may result in the release of heat, flammable hydrogen gas and acid fumes. The reaction is comparable to the thermite reaction that is used in munitions. The reaction between iron and aluminum (or iron and zinc) is a very high energy reaction (as indicated by the much higher voltage) and should be avoided.



The Saline Sulphate Etch uses the reaction between copper and aluminum, which is quite a bit milder than the reaction between iron and aluminum, as indicated by the lower voltage. The comparable reaction for copper and zinc is also shown.

In the absence of sodium chloride, a copper etch of aluminum or zinc is characterized by high levels of insoluble copper hydroxides in the solution, which may clog the etching process, for reasons like those proposed previously for the Edinburgh Etch.

The chloride in the Saline Sulphate Etch is thought to partially prevent formation of copper hydroxide by competing with the hydroxide ion for binding to the copper. Copper chloride is much more soluble than copper hydroxide.

For the printer or artist, both these systems are mild and much safer than the traditional nitric acid bath for etching of metals, especially if proper precautions are taken when designing the reactions (e.g., no etching of aluminum with ferric chloride) and when exhausted materials are disposed of properly.

To the chemist, these are very nice systems, which are highly complex. In the chemistry lab, we usually deal with much more dilute solutions of metal ions and salts than are described here. All would bear some study from the chemistry perspective.

The real issues here are competitive equilibria. Chloro and citrate complexes of these metals are playing a major role in these systems. There is not much published information on these systems. There does not appear to be any significant or major chemical hazards associated with the chemical processes employed here, although a reaction between aluminum and iron could lead to explosive results.

Standard reduction potentials were obtained from Harris, D.C. Quantitative Chemical Analysis, 6th edition, W.H. Freeman and Company, New York, 2003.

$$3Cu^{2+} + 3e^- \rightarrow 3Cu^+ \qquad E_o' = -0.339V$$
$$Al^0 \rightarrow Al^{3+} + 3e^- \qquad E_o' = +1.677V$$
$$3Cu^{2+} + Al^0 \rightarrow 3Cu^+ + Al^{3+} \qquad \Delta E_o' = +1.338V$$

$$2Cu^{2+} + 2e^- \rightarrow 2Cu^+ \qquad E_o' = +0.161V$$
$$Zn^0 \rightarrow Zn^{2+} + 2e^- \qquad E_o' = +0.762V$$
$$2Cu^{2+} + Zn^0 \rightarrow 2Cu^+ + Zn^{2+} \qquad \Delta E_o' = +0.923V$$

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