ETCHING ZINC PLATE WITH COPPER SULPHATE

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INTRODUCTION

There are three ways toxic materials can enter the body: by inhalation, by ingestion or through the skin.

Preventing inhalation is the most difficult as using exhausts or masks are only partly successful. Some gas, vapour or aerosol will still be left in the air you and the people around you inhale. What you do not inhale will pollute the environment.

Instead of using all kinds of equipment it is better to fight the problem at the source. Introduction of copper sulphate will 'solve' most studio related health problems, and is a true contribution to a cleaner environment.

COPPER SULPHATE

Copper sulphate ($CuSO_4$) is a salt and not an acid. Zinc is etched in a solution of copper sulphate. Aluminium is etched in a solution of copper sulphate and sodium chloride.

Etching aluminium with a mixture of copper sulphate and sodium chloride (kitchen salt) was invented by Nik Semenoff. More information about using a safer mordant for intaglio etching on aluminum and zinc can be found at Nick Semenoff's website http://homepage.usask.ca/~nis715/.

The etching of the plate is caused by the electrolytic action between the zinc and the copper ions in the bath. Zinc is removed from the plate and goes into solution as ions, which are not visible. At the same time copper ions in the solution change into copper or copper oxide, which can be seen as a sediment: a solution of copper sulphate etches zinc without producing toxic fumes.

This is contrary to etching metal with nitric acid, hydrochloric acid, Dutch Mordant, ferric chloride and Edinburgh Etch. These etching fluids produce toxic fumes and toxic aerosols, which corrode the skin, eyes, teeth and their amalgam fillings, mucous membranes, lungs, and may cause impotency. The metal equipment in a studio is corroded by the vapours, too. Etching without toxic fumes and aerosols is the main advantage of using a copper sulphate solution.

When etching aluminium or zinc with copper sulphate a minute amount of hydrogen gas is produced; more with aluminium, less with zinc. This may be observed as tiny bubbles, especially when etching open bite. The amounts of hydrogen gas produced in a printmaking studio are negligible. As such it may burn easily, but only above certain concentrations. When more than 5% of the room is filled with hydrogen gas you should take care, but the chances that this will happen in your studio are remote. Normal ventilation, always advisable in a workshop, will do.

THE ADVANTAGES OF USING COPPER SULPHATE

When etching zinc in a copper sulphate solution there is no production of harmful vapours, which is its main advantage compared to etching with mineral acids (nitric, hydrochloric etc.). The solution as such is fairly acidic and generates a minute amount of hydrogen gas during etching (see above). This amount of hydrogen gas is too small to be of any danger and will not hinder the etching of the plate. Normal ventilation will be sufficient, no exhaust system is needed and therefore overhead costs for studio set up are low. Also, because there is no production of bubbles, the bottom and sides of the grooves will have a smooth appearance. Because there are no harmful fumes it is relatively safe for children to make etchings with this mordant.

SUPPLIERS OF COPPER SULPHATE

Copper sulphate is sold as a fungicide by gardening shops, and wholesale dealers in chemical products and veterinary products, in bags of 25 kilos, by pharmacies in boxes of 250 grams, and by suppliers of artists' materials per kilo. Purity does not matter, although sometimes it is found mixed with other chemicals. Some dealers supply the sulphate as dry powder. Others have sprayed it with water to prevent dusting, which turns the powder into lumps. This makes no difference.

Always buy copper sulphate in crystals. Do not buy ready prepared solutions as their strength is not known and the solution may be adulterated with unknown chemicals.

HEALTH AND SAFETY

The powder or solution of copper sulphate irritates the eyes and the bare skin, when inhaled or ingested. Try to avoid this. If you employ the following safety measures, etching with copper sulphate will be a pleasure.

1. Wear rubber gloves in preparing the solution of copper sulphate.
2. Wear a dust mask when the copper sulphate is supplied as finely powdered crystals.
3. Scoop the copper sulphate carefully from bag or box. Do not pour, dust, or scatter around.
4. Do not prepare the solution in a strongly ventilated room, as the air currents may cause the powder to dust.
5. Wear rubber gloves when putting the plate into the bath or taking it out again.
6. If copper sulphate touches your eyes or bare skin, either as a powder or as a solution, rinse immediately with a lot of water.
7. If copper sulphate is ingested, then rinse your mouth with a lot of water and see a doctor.
8. Copper sulphate - when inhaled or ingested - is harmful to the unborn foetus. In general, it is advisable for pregnant women not to work with chemicals.
9. When etching zinc in a bath of copper sulphate, normally no exhaust system or nozzles are needed as there are no toxic fumes produced in harmful amounts. Ventilation by opening a door or window will do.
10. Use an exhaust system when large plates with large unprotected surfaces of zinc (such as with open bite or relief etch) are bitten in a strong bath for an extended period. There may be so much hydrogen gas coming from the solution sensitive skin may become irritated.
11. If you have spilled some etching fluid remove it with a wet rag while you are wearing rubber gloves. If spilled etching fluid has dried and it is white, then this is zinc sulphate. It is as irritating as copper sulphate, so take care and use rubber gloves when cleaning.
12. Clean your hands and mouth before eating, drinking or smoking.

MATERIALS, METHOD & TECHNIQUE

Requirements

Copper sulphate (intensely blue crystals), (tap) water, a plastic tray, a pair of rubber gloves, a plastic spoon, a pair of scales, a plastic jerry can, washing soda (sodium carbonate).

Preparing the Bath

Fill the tray with cold or luke-warm water. Carefully take copper sulphate from the container with a plastic spoon. Add the sulphate to the water, mix slowly, let stand, mix now and again. Dissolving takes five minutes or more, depending on the amount of sulphate. When fully dissolved the fluid has a bright blue colour and is ready for etching. Another way: take a plastic jerry can, add water, add sulphate, close, shake, let stand overnight, ready.

Proportions for Etching Zinc

The stronger the solution the faster it etches.

1. Deep etch and relief etch: 200 grams of copper sulphate to 1 litre of water (comparable to a nitric acid solution of 16-18 %).
2. Normal line etching: 100 grams of copper sulphate to 1 litre of water (comparable to a nitric acid solution of 12-13%).
3. Fine line, coarse aquatint, soft-ground: 50 grams of copper sulphate to 1 litre of water (comparable to a nitric acid solution of 7-8%).
4. Fine aquatint: 25 grams of copper sulphate to 1 litre of water (comparable to a nitric acid solution of 4-5%).

When starting with a fresh mixture, the colour of the solution will be a deep mediterranean blue with pH 3 to pH 4 (= fairly acidic) depending on the concentration. In time it will become colourless with pH 5 to pH 6 (= mildly acidic) and the fluid will act more and more slowly. Regeneration is possible twice: add the same amount of copper sulphate to the bath and, if too much water has evaporated, add a little water. Etching will be slower although the bath is blue. A freshly made bath etches best. When not in use, cover the tray with

a plate, or pour back into the plastic jerry can, to prevent evaporation and dirt falling into the bath. When pouring back through a funnel into the can you can decant or filter the sediment deposited during the etching process from the fluid. Copper sulphate solutions last less long than comparable solutions of nitric acid.

Etching zinc with copper sulphate was invented by Cedric Green and called Bordeaux Etch by him. General information on Bordeaux Etch and on electrolytic etching using copper sulphate are to be found at Cedric Green's website www.greenart.info/galvetch. Search for 'Bordeaux Etch for Zinc Plates'.

Grounds
Every type of acid resist is suited as an etching ground. Mind, however, that copper sulphate penetrates grounds faster than mineral acids. That means that wax based grounds should be thicker and more even compared to etching them with nitric acid and the like. Tiny little holes and areas that seem thin should be stopped out. The same goes for acrylic grounds which need to be dried on top of a hot plate with an exhaust overhead or in a drying cabinet with an exhaust. Cold-dried acrylic grounds break down over time with interesting results and some acrylics disappear in the bath.

Etching a Plate
Fill the tray with at least three centimetres of fluid. Prepare your plate as usual. Lower the plate in the bath and the bare zinc will turn black immediately. This black sediment is finely dispersed copper. Remove it with a soft brush or feather for regular etching and to see what is happening. Mind that this is NOT the same as the black iron sediment in ferric which sticks to the metal. Remove the sediment carefully to avoid scratching the etching ground.

Moving the plate in the bath, or moving the fluid in the bath with a feather or brush, ensures a continuous stream of fresh solution above the plate. Settling of sediment in and on top of the grooves will retard the chemical action and copper build-up may occur.

When the solution turns weak, the colour of the newly formed sediment changes from black to reddish brown. Instead of black copper particles, red copper oxides (CuO_2) are formed now, because the chemical reactions are incomplete. After prolonged etching, and not removing sediment from the plate, copper build-up seen as shiny metallic particles may form around the edges of the grooves. The copper does not adhere strongly to the plate and can be removed by brushing. Take care, because the particles are hard they may scratch the etching ground. It is better to place the plate in a fresh bath for a short while to remove them. Prevent copper build-up by feathering the plate regularly. Copper build-up may occur with prolonged etching, and especially with aquatint. For fine grained aquatints use a fresh but weak bath of sufficient depth (3 cm.).

After etching take the plate out of the bath and wash with water. If in small amounts, the deposit that goes into your sewer is not harmful to the environment. Larger studios need equipment to settle the silt. Filtering and neutralising of the rinsing water is strongly advised. Adding washing soda (sodium carbonate) to the rinsing water will neutralise the acid and metal compounds will precipitate.

Day-light Etch
The sides and bottoms of the grooves will be very smooth. The addition of citric acid (invented by Bernard van der Wielen and called Day-light Etch by him) makes an etchant which acts irregularly on the sides of the grooves, because more hydrogen gas is generated. It therefore creates wider and coarser crevices. You can add up to twice as much citric acid as copper sulphate to the etchant. For more information see the website of Nik Semenoff.

Disposal
The easiest way to dispose of the used solution - and of the rinsing water - is to pour the old, now slow mixture into a plastic bucket and leave it to stand for a few weeks. The addition of washing soda will neutralise the acid and the metal compounds will precipitate. The water will evaporate leaving a blue and white, glassy crust. Turn over the bucket in a plastic bag, tap on the bottom and the crust will break and fall into the bag. Dispose of as chemical waste. Larger printmaking studios should contact local authorities for information on disposal of their waste.
For information on disposal of the fluid waste contact the Amsterdam Printmaking Studio who have ample experience with it.

BIBLIOGRAPHY

Discussions on the use of copper sulphate can be found by searching the archives of the on-line discussion list: http://frank.mtsu.edu/~art/printmaking/wwwboard/wwwboard.html

General information on Bordeaux Etch and on electrolytic etching using copper sulphate can be found on Cedric Green's website: www.greenart.info/galvetch

General information on etching aluminium with a mixture of copper sulphate and sodium chloride (kitchen salt) can be found on Nick Semenoff's website:http://homepage.usask.ca/~nis715/

Printsafe: A Guide to Safe, Healthy & Green Printmaking.>
Tim Challis. London : Estamp, 1990.
A concise and valuable book on all health & safety aspects of printmaking. Despite the developments in safer printmaking since 1990, it is still an accurate and readable publication.

Making Art Safely: Alternative Methods & Materials in Drawings, Painting, Printmaking, Graphic Design & Photography.
Merle Spandorfer, Deborah Curtiss and Jack Snyder. New York : Van Nostrand Reinhold, 1993. Covers the whole range of artistic techniques and is very thorough.