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Extract from GREEN PRINTS by Cedric Green published by Ecotech Design, Sheffield, UK. – a handbook on new methods for non-toxic intaglio etching and metal plate printmaking, featuring the technique of Galv-Etch, a modern development of the 19th century electrolytic technique of Electro-Etching, and introducing Fractint and other new alternative methods avoiding the use of solvents and chemicals harmful to health and to the environment.

BORDEAUX ETCH FOR ZINC PLATES

- * dangers of etching zinc plates with ferric chloride
- * etching zinc plates safely with copper sulphate
- * the chemistry of Bordeaux etch
- * disposal of used Bordeaux etch

dangers of etching zinc plates with ferric chloride

Zinc plates are now very widely used by printmakers who are not concerned with trying to make huge editions, or who deep-etch plates for viscosity printing or embossing effects. Zinc is very much less expensive than copper and can be bought from building materials suppliers in large sheets, and are easy to polish. Students learning printmaking use zinc plates a great deal, and they can be bought ready polished and backed with a resistant coating.

Many printmakers believe that using ferric chloride is a completely safe acid chemical to use because it has been used in the printed circuit industry for many years. This is only partly true for copper plates, where the products of the chemical process are a deposit of cupric chloride and a solution of ferrous chloride. But ferric chloride is a strongly acidic

chemical and gloves, vapour mask and good ventilation are required (15).

But etching zinc plates in ferric chloride is a different matter altogether, and the process gives off bubbles of hydrogen gas which is explosive in air, produces a deposit of iron, which forms a crust over the etched surfaces, and the spent solution contains zinc chloride which is more toxic and corrosive than ferric chloride. The bubbles of hydrogen require removal with a feather to prevent an uneven bite and the iron crust is abrasive and the process of removing it damages the edges of the needled ground or a sensitive aquatint. When a deep bite is required over large areas of exposed metal, the chemical reaction heats the solution and gives off an extremely corrosive vapour of hydrochloric acid, carried up by the hydrogen. As any experienced printmaker knows, having to brush away bubbles and the deposit means bending over the etching tray, exposed to the vapours or gas given off, and wearing goggles, and vapour mask is uncomfortable and inhibiting. Vertical tanks are unusable in these conditions. As the solution becomes weaker ferric hydroxide is deposited and darkens it, and zinc displaces ferric ions in the solution forming the iron crust which becomes harder and harder to remove and the solution then is a mixture of unused ferric chloride and zinc chloride, which is more corrosive than the original and is very difficult to render safe for disposal.

A recent development which alleviates a little of the unpleasantness of ferric chloride is Edinburgh Etch developed by Friedhard Kiekeben, which involves adding citric acid which speeds up the bite, and dissolves some of the sediment (16). But the mixture is still a strong acid, and my personal preference is to avoid the use of all acids.(TOP)

etching zinc plates safely with copper sulphate

There is a safe way of etching zinc plates which is not electrolytic,

and
will satisfy those who want a single solution which is inexpensive and easily obtainable, and that is to use a concentrated solution of copper sulphate. I have called this Bordeaux Etch, because a copper sulphate solution is better known to vine growers, farmers and gardeners as Bordeaux mixture (Bouillie Bordelaise), very widely used as a spray against mildew. The solution is very much safer to handle than ferric chloride, and a zinc plate can be etched without the production of any bubbles of gas, although gloves should be worn to avoid skin contact. An insoluble powdery deposit of copper is produced which is very easy to remove by brushing with a feather or a soft brush in a flat tray. The other advantage is that the initially blue solution remains quite transparent, and turns gradually colourless as it is exhausted, and the progress of the etch can be very easily seen in a tray by the formation of the deposit. Nik Semenoff and L W Bader described a mordant for zinc and aluminium, similar in some respect to Bordeaux etch in an article in 'Leonardo' which was published in Spring 1998 (17)

To make up a solution follow the instructions given for mixing a concentrated solution of Copper Sulphate in the pages on preparation . I recommend a concentrated solution, but some research done at the Rietveld Academy in Holland by Ad Stijnman (20) and collaborators has found that a more diluted solution will work. Do not use readymixed commercial Bordeaux mixtures supplied by gardening shops as it is often mixed with other chemicals, and sometimes contains no copper sulphate at all !.(TOP)

the chemistry of Bordeaux etch

The effect of Bordeaux Etch with zinc is essentially an electrochemical process and the results are very similar to galv-etch. Briefly, zinc has a much higher electrode potential ($Zn^{2+} = -0.76$) than copper ($Cu^{2+} = +0.34$), and as a result it displaces copper ions from the copper sulphate

solution
(CuSO_4), and the zinc ions combine with the sulphate (SO_4) ions to form zinc sulphate (ZnSO_4). If the copper deposit remains in contact with the zinc there could be a side reaction – the metals in contact in a slightly acidic copper sulphate solution form a short-circuited galvanic cell called a zinc-copper couple – producing a very small quantity of hydrogen and thus making the solution less acidic (more alkaline). As the alkalinity builds up so that the pH goes above 7 there will be a reaction with the zinc and copper ions to give an additional precipitate of zinc and copper hydroxide. This side reaction can be exploited to create a texture over areas of open bite. But normally it is a good idea to brush away the deposit as it is formed which results in a more even bite and prolongs the life of the solution. There is usually a fine layer of black hydroxide adhering to the etched open areas which can be washed off, or comes off with the first proofs. Then the etched areas have a fine crystalline texture, similar to galv-tone, which helps to hold ink.(TOP)

disposal of bordeaux etch

Disposal can be done in two ways : filter and save the completely spent solution to use as the electrolyte for galv-etching zinc plates. If you are not doing that, or have too much, then the solution must not be put down the drain because of the zinc sulphate and the residual copper sulphate left in it. To make it safe for disposal, you can add sodium carbonate (washing soda) or sodium hydroxide to it to neutralize it, until the pH value goes up to between 7.0 and 8.0, testing it with indicator paper. Copper and zinc hydroxide will be deposited as a sludge. Allow the sludge to settle, pour off the liquid, further dilute it and then it can be poured down the drain. Collect the sludge in plastic bags and dispose of it as required by your local authority. When neutralizing it, be careful not to allow it to

become
too alkaline because the hydroxides will be redissolved. If you are
galv-etching copper plates as well as using Bordeaux etch, then keep
the
dilute copper sulphate used for that completely separate from the
concentrated Bordeaux etch solution, in well marked containers. It is
not
dangerous to use the wrong one, but a diluted copper sulphate prepared
for
galv-etch will not etch zinc satisfactorily, and a partly spent
Bordeaux
etch solution, used electrolytically for galv-etching a copper plate,
will
deposit zinc on your cathode. (TOP)

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