

## Development of an etching paste

Graham Wightman and Jennifer Matthew

NOTICE: this is the author's version of a work that was accepted for publication in *Forensic Science International*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Forensic Science International*, [Vol. 180, Issue 1, (2008)]  
DOI: <http://dx.doi.org/10.1016/j.forsciint.2008.06.019>

## **Development of an Etching Paste**

**By Graham Wightman and Jennifer Matthew**

School of Contemporary Sciences,  
University of Abertay Dundee,  
Bell Street,  
Dundee.  
DD1 3HG  
Scotland  
Telephone: +44 382 308659  
Fax: +44 382 308104  
e-mail: g.wightman@abertay.ac.uk

### **Abstract**

The recovery of erased identification marks is a problem for the forensic scientist, particularly with respect to vehicles and firearms. The widely accepted procedure for steel imprints is to use Fry's reagent. The present study examined the possibility of forming a paste that may be easier to use. The paste proved to be as effective as liquid in most cases, and often gave better results. The ease of using the paste gives it distinct advantages over liquid reagent.

### **Keywords**

Erased marks, recovery, etch, restoration of stamp marks, etching paste

## **Introduction.**

In a previous paper [1] we have discussed the role of recovery of erased marks using Fry's reagent. That study extended the previous work of Turley [2]. As part of the present study it was planned to investigate more convenient reagents. A range of etches exist [3]. A recent study by Zaili et al [4] has looked at engraved rather than stamped identification marks and found that for engraved marks recovery was better using a copper sulphate/ammonium hydroxide/hydrochloric acid reagent. For stamped marks Turley [2] however has shown that Fry's reagent is effective for steel, and this is normally used by practitioners. However, a corrosive liquid is not easy to use on large items or in the field. As part of the study we therefore investigated alternative methods of applying the reagent.

Chemical etching is a specialised area, the main uses being:

- specimens for metallurgical examination
- forensic recovery of erased identification marks
- preparation of printed circuit boards
- preparation of metal surfaces for surface coating, welding, soldering

In the production of printed circuit boards a liquid in a tank is used as this gives good contact with the substrate. Similarly, for metallurgical specimens a small sample is being prepared in the laboratory and liquid reagent ensures an even contact with the metal.

For engineering applications such as welding the sample may be a complex shape (e.g. a pipe) and liquid will flow off the surface. Absorbent paper is therefore

sometimes used, or a temporary container may be improvised to try and retain the reagent. Being corrosive, any spillages naturally present a problem to the rest of the structure.

In forensic applications the item will frequently be taken to a laboratory where liquid etch may be applied. However, whilst larger items such as vehicles can be moved to indoor storage, the etching still has to be carried out in situ at the vehicle, and forensic engineers may also be dealing with structures in the field. Even items in the laboratory present problems when trying to recover erased marks. For example, the curvature of the barrel of a firearm cannot easily be treated with liquid etch

To try and circumvent some of these difficulties we examined the use of absorbent paper, and production of a paste for etching. A gel was also considered but the paste was found to be very effective.

## **Method**

Samples were prepared as previously described [1]. The metal samples used were of two types: discs of mild steel or Charpy notch test bars. Each test sample was placed on a press and a single letter die was impressed at a predetermined force. Different forces were investigated. The specimen was then abraded with a file or grinding wheel to efface the imprint. Once the imprint had been removed further filing was carried out to a pre-determined depth in order to examine recovery with different degrees of metal removal.

If the specimen had been filed manually, the damaged specimen was polished on a series of silicon carbide grits, as is normally carried out for metallurgical etching. However, when the grinding wheel was used, polishing was not necessary. Etching then took place.

The control samples were etched using Fry's reagent (90g of Copper Chloride, 120ml of concentrated Hydrochloric Acid and 100ml of water), and the liquid was placed on the surface of the specimen using a Pasteur pipette, and a Petri dish cover was placed over it to reduce evaporative loss. Periodically the specimen would be observed by tipping it to remove the liquid and adding fresh reagent if further etching was required. This continued for 9 hours, or until recovery was observed. If no mark was observed after 9 hours it was assumed that recovery was unlikely to be achieved.

To test the use of absorbent paper, a strip of general grade filter paper was used and was placed on the specimen and soaked with Fry's reagent. The same procedure was used as for the liquid (cover with petri dish and observe periodically), but the paper still tended to dry out and required regular addition of reagent.

For the test paste it was decided to use an inert solid, and alumina powder was chosen. Other powders such as silica were also considered but not tested as alumina proved to be effective. Similarly, polymeric reagents were considered for making a gel, although the high acid content was thought to be a potential problem in forming a stable gel. The success of the initial trials with alumina meant that these alternatives were not pursued. The paste was made by mixing Fry's reagent with alumina to a suitable consistency. In practice 4 grams of powder required about 3.5 mL of reagent. The paste was mixed with a glass rod and spread on the specimen. The specimen was covered and at suitable time intervals the paste was wiped off, observations made, and more paste added.

### **Observations**

On mixing the reagent and powder a blue colour fringe occurred on the liquid front. (Figure 1). This is thought to be partly due to chromatographic separation and partly

due to different coordination of the copper ions. Different ligands can cause an energy shift in the d orbitals of transition metals resulting in a spectrochemical series.  $\text{OH}^-$  produces a greater ligand field than  $\text{Cl}^-$  and results in a shift towards the blue part of the spectrum. It is possible that capillary action on the alumina is producing a short chromatographic separation of copper chloride and hydrochloric acid. This reduces the local concentration of chloride ions and copper ions can then form ligands with  $\text{OH}^-$  ions from the alumina, resulting in a blue rather than a green colour.

As the Fry's reagent was added to the alumina, the paste became thixotropic when the consistency was correct, i.e. the paste would flow whilst it was agitated with the rod, and then ceased to flow when agitation ceased. This meant that it was relatively easy to ensure the paste covered the test area but did not overflow. Once vibration with the rod ceased, the paste remained in place.

When applying the paste, if too little Fry's reagent was used when mixing the paste, it did not show thixotropic behaviour and would not flow. Uneven coverage occurred and etching was also uneven. Too much liquid resulted in a paste that flowed like the liquid reagent, and whilst this was not detrimental to the etching it did remove one of the advantages of the paste.

Once applied the paste was left and a gradual diffusion of colour from bright green to brown occurred as iron ions were leached from the specimen, giving an indication of the rate of etching as shown in Figure 3. In contrast, the liquid reagent went instantly brown.

When the specimen was to be observed, the paste was simply brushed off (e.g. with a glass rod) although care was still needed due to its corrosive nature. The metal surface remained bright, although it was often rinsed with alcohol (methanol) to remove any

remaining paste and to facilitate handling. In the case of liquid reagent the liquid was poured off and an alcohol rinse was used to remove any traces of reagent and minimise copper precipitation. However, with the liquid etch the surface of the steel often darkened due to surface oxidation.

With both the liquid and the paste reagents etching occurred, but there were some differences. On a number of occasions the paste etched more rapidly. Sometimes, too, the paste gave a wider etch mark than the liquid. This made the mark appear clearer to the naked eye but was less distinct when observed under the low power microscope.

It was found that the liquid did have an advantage in one specific case: if the stamp mark had been erased by partial infilling with filed material (burrs) then the original channel could sometimes be recovered, as seen in Figure 4(a). However, if complete removal of the indentation has occurred, the paste gives equal, and often better, recovery.

Figure 4(a) shows a letter V imprint at 40 kN force and 0.8 mm metal removed. The imprint on the left is with liquid etch and is due to removal of metal filings filling the imprint. The image on the right of the figure is from the paste. Figure 4(b) is letter S at 35 kN force and 0.8 mm of metal removed. Here there has been no in-filling and the paste image on the right is much clearer. Figure 4(c) is letter R imprinted at 25 kN with 0.8 mm of metal removed. The paste (on the right) is also much clearer after 2 hours etching.

## **Discussion**

Normally a liquid is better than a paste for carrying out a chemical reaction since there is more intimate contact and better mixing. The advantage of a paste is usually its convenience and its ability to keep the reagent in contact with the substrate. In the

present case, although the intention was to produce an etch that is easier to use, it was surprising to find it also gave better results

The apparent improvement in etching may be due to a more controlled chemical attack with the paste. Initial etching occurs at the paste/metal interface and subsequent attack requires diffusion through the paste, as indicated as the colour of the paste changes with time from green to brown. This observation coupled with the colour change noted during formation may help offer an explanation.

There are a number of potential oxidation/reduction reactions in Fry's reagent:



Combining these half cell reactions shows that metallic iron could be etched by either  $\text{H}^+$ ,  $\text{Cu}^{+2}$ , or  $\text{Fe}^{+3}$ . Based on the standard reduction potentials the order of thermodynamic favourability is:  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$ ,  $\text{Cu}^{+2}$  to  $\text{Cu}$ ,  $\text{Cu}^{+2}$  to  $\text{Cu}^+$ , and  $\text{H}^+$  to  $\text{H}_2$  and this concurs with the absence of hydrogen bubbles during reaction. However, the acid is approximately 8.5 M and the copper is 3.2 M and the Nernst correction needs to be applied. Furthermore, in the presence of high chloride concentration  $\text{Cu}^+$  is stabilised as  $\text{CuCl}_2^-$  with a formation constant of  $1 \times 10^5$ . The  $\text{CuCl}_2^-$  to  $\text{Cu}^{+2}$  ratio at equilibrium will therefore be about 0.27 compared with the very small equilibrium ratio for  $\text{Cu}^+$  to  $\text{Cu}^{+2}$ . Potentially therefore etching could occur by cupric (copper II)



ions going to cuprous (copper I). Part of the colour change observed is the formation of cuprous ions. However, the product of reaction is  $\text{Fe}^{+3}$ , and under oxidising conditions any  $\text{Fe}^{+2}$  can be further oxidised to  $\text{Fe}^{+3}$ .

In solution in the liquid, mixing is rapid and the ferric ion (Fe(III)) concentration will be dilute and the Nernst equation will inhibit ferric ions from etching iron. However, in the paste diffusion rather than liquid mixing is rate controlling, and the ferric ions will be at a higher concentration and may also be able to carry out etching (though oxygen diffusion through the paste may also be limit the Fe(III) to Fe(II) ratio). It is also possible that the iron may be only oxidised to the ferrous state rather than to the ferric state in the paste and this may account for the faster etching with the paste.

The copper(I) ions in solution will dissociate to copper metal and copper (II) ions if diluted, and this accounts for the deposition of copper on washing with water. One problem with using liquid Fry's etch can be formation of a copper deposit, whereas this is avoided with the paste.

Regarding the black coating formed with the liquid etch, it is probable that this is an oxide layer. A possible mechanism for the absence of the film with the paste is that the paste avoids air contact with the reagent and any oxygen has to diffuse through the paste

Theoretical calculations show that if all the liquid reacted it could dissolve 0.1 mm of metal (assuming 1 mL of reagent on a 3 x 1 cm sample), but this was not examined experimentally. It is therefore possible that the liquid reagent is also removing the bulk metal as well as selectively etching the strained region around the stamp mark, and is thus reducing the contrast. The paste requires diffusion through the paste and this bulk dissolution will therefore be more controlled and avoid over-etching.

## **Conclusions.**

An etching paste has been developed using alumina and Fry's reagent, Other reagents may also be used but were not tested in the present study. The paste is thixotropic, making it much easier to use, particularly with irregular shapes or on site. Coverage is good as vibration allows the paste to flow and give an even cover. Apart from cases where erasure has occurred by metal burrs filling the indentation, the paste gave as good a recovery as the liquid etch, and often it appeared to give better recovery (easier to read). A possible mechanism is proposed.

## **Acknowledgements**

The authors are grateful to the University of Abertay Dundee for the provision of facilities for this study.

## **References**

- [1] G Wightman and J Matthew 2008. *Restoration of Stamp Marks on Steel Components*. To be published, Forensic Science International.
- [2] Turley. DM. 1987. *Restoration of Stamp Marks on Steel Components by Etching and Magnetic Techniques*. Journal of Forensic Sciences Vol.32, No.3 pp640-649.
- [3] Procedure Manual , Directorate of Forensic Science, Ministry of Home Affairs, Government of India. <http://www.dfs.gov.in/downloads.htm>
- [4] A. Zaili, R. Kuppuswamy and H. Harun, Restoration of Engraved Marks On Steel Surfaces By Etching Technique, Forensic Science International, in press, published on-line 7 November 2006