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Restoration of Obliterated Stamped Marks on Cast Iron Surfaces by Etching Techniques

Dissertation submitted in partial fulfillment for the Degree of Bachelor of Science in Forensic Science

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ABSTRACT

Restoration of erased obliterated marks on cast iron surface by chemical etching is very difficult. Hence, a series of experiments were conducted to identify a sensitive and efficacious reagent that could recover obliterated stamped numbers on this surface. One cast iron (3.29%C) car engine block was purchased and cut into several small pieces. Some numerical characters were stamped on their surfaces using Instron Table Mounted Universal Testing Machine at 8kN. The stamped numbers were then removed by filing until no longer visible. Eight metallographic of which most contained copper compounds were chosen for restoration. The restoration was done by swabbing and immersion techniques. The results have shown that among eight etching reagents a modified Fry's reagent consisting of 45 gram cupric chloride, 100mL hydrochloric acid, and 180mL water gave excellent contrast and sensitivity of the recovered numbers. This reagent also successfully recovered the marks obliterated by centre punching/peening and over stamping.

INTRODUCTION

Vehicle theft has become a serious problem over the past many years. Based on the statistics from Royal Malaysia Police, the number of stolen vehicles in Malaysia has increased every year. In the year 2005, 66,927 vehicles were reported stolen, and this value increased to 85,058 cases in 2007. Increase of about 27% in two years period only shows how serious the vehicle theft is in Malaysia. When these stolen vehicles are recovered, it is part of forensic science laboratory's work to reveal the true identity of the vehicles that may identify the owner.

Vehicles contain several kinds of identification marks in the form of serial numbers such as plate number, chassis number and engine number. Serial numbers are important as they provide an easy method to distinguish and also to establishing the ownership of the items. Serial numbers consist of individual or combination of numerals, letters or symbols. When vehicles are stolen, their serial numbers usually are obliterated to hide the true identity of the vehicles. In addition a new serial number will be given so that it can be used like normal legal vehicles. Chassis and engine numbers are the most important identification marks on the vehicles because they are quite difficult to be removed and if there is any obliteration to them, there is a possibility to restore their original numbers.

Types of Markings and Serial Numbering

Serial numbers are applied in a variety of ways, depending upon the substrate to be marked and the environment under which the number will be used in (Petterd, 2000).

Important serial numbering methods used in the automotive industry include the following (Collins, 1999; Katterwe, 2006): Die stamping, stylus/pin marking, roll marking, type wheel marking and engraving. While die stamped marks are found commonly on the chassis and engine of cars, both old and new, stylus pin marking is used for marking VIN (Vehicle Identification Number). Laser marking is also used for marking serial numbers in vehicles.

Methods of Obliteration of Identification Marks

Method of obliteration generally falls into the following six categories (Heard, 1997; Petterd, 2000; Katterwe, 2006):

a) Filing and Grinding

It is done by simply removing the numbers by hand filing or grinding with a speed carborundum grinding wheel. This is often followed by polishing and then over stamping with a new number.

b) Over-stamping

This is done by simply stamping a new number over the old. For numbers with curved surface (e.g.2, 3, 5,6,8,9 and 0) the 8 stamp is the most chosen. For number with straight surface (e.g.1 and 7) the stamp 4 is the obvious choice. Serial numbers with a preponderance of "8" and "4" should be treated with suspicion.

c) **Centre Punching**

This technique is done by fully obliterating the numbered surface with a pointed punch in order to hide or distort the whole numbered surface.

d) **Drilling**

In this technique, the numbers and the surrounding metal will be completely removed using a drill. The hole left is usually filled up with lead solder or weld material or other filler in order to hide the distortion left.

e) **Welding**

This is done by heating the surface until the metals flow with either an oxy-acetylene or an arc-welder.

f) **Peening**

This merely involves the hammering of the surface with a round punch to completely hide the number.

Of all the six techniques, only grinding and welding permanently remove all recoverable traces of the original numbers. With drilling, unless it is very superficial, the altered crystalline structure will be removed and so will any recoverable traces of the numbers.

Theory Behind Serial Number Restoration

The atoms within metals have a three dimensionally periodic (crystalline) arrangement within local regions and are called grains by metallurgists. Upon application of a force, the metal first becomes elastically strained and would return to its initial shape. However, when force exceeds the elastic limit of the metal, one part of the grain moves relative to the other part. This is called dislocation which causes plastic deformation to occur. The number stamped onto a metal consists of visible indentation, a plastically deformed region surrounding and defining the indentation, and an elastically strained region bordering the plastic region. Elastically deformed region is constrained from relaxing to its original condition by adjacent plastic region. The amount of plastic flow and depth of plastic region depend upon the shape of the die. Blunter dies produce greater plastic flow and better depth of plastic region than v-shaped dies. The number can still be recovered if just incomplete obliteration takes place where part of number visible is removed, here the plastic deformation will still be present. However, the number cannot be recovered if completely obliterated, where the indentation and all plastically deformed metal is removed. Elastically deformed region is no longer been constrained by plastic region and now relaxes back to the original condition (Polk and Giessen, 1975).

In plastic deformation area, the hardness, tensile strength and yield point increase, while the malleability and ductibility decrease. Besides that, the position of the metal in plastic deformation area in electromotive series is raised, which results in a lowering of resistance to chemical oxidation. Significant from these phenomena is that the area of the obliterated marks which have been affected by stamping process will be removed by etching solution more rapidly than the surrounding metal.

Serial Number Restoration Techniques

The surface must be prepared, before any restoration method is applied. The preparation method consists of a series of steps during which material is removed mechanically from the sample surface by means of successively finer abrasives. Finer grades of waterproof abrasive papers are used to gradually smooth out the surface until a mirror like "metallographic" finish occurs (Voort, 1984; Katterwe, 2006).

There are many methods used to restore erased numbers in metals and these methods are divided into destructive and nondestructive. The most important procedures include the following (Katterwe, 2006).

a) Chemical etching

Chemical etching is a major method used to recover obliterated serial number in metal substrates. For recovering obliterated numbers, the method relies on the phenomenon that the rate of reaction of the applied chemicals with the substrate differs between the damaged and undamaged areas and therefore is attacked selectively or at least at a different rate. This method creates a visible contrast between the damaged and undamaged region of the substrate. This contrast is the result of differential reflection or scattering of light from damaged area compared with the undamaged area after chemical etching (Thornton and Cashman, 1976). The chemicals used depend on the composition of the substrate and they can be applied in two ways: by wiping them across the surface of the substrate with a cotton swab or by forming a frame of modeling clay around the area and then pour the etching solution (immersion).

b) Electrolytic etching

This technique is a modification of the standard chemical etching technique. It involves the addition of an electric current in the etching process. In this process, the metal to be etched is used as the anode in an electrolytic bath of some etching solution. The cathode consists of a wire, which holds a cotton swab kept wet with the solution. The metal surface is gently swabbed with the wet cotton swab like standard chemical etching technique.

c) Heat treatment

This technique is very successful when applied to restoring obliterated serial numbers on cast-iron substrates. In this method, heat is applied directly to the obliterated area until the metal turn into a light cherry red color. This results in the release of the residual tensile stresses and allows the deformed area to bulge above the surroundings. After heating, the area is lightly rubbed with abrasive paper, which removes any soot or oxide layer from the raised characters, showing good contrast to the dark surroundings.

d) Ultrasonic cavitation

This is an erosive wear mechanism involving hydrodynamic processes. The substrate is placed into the water bath and the bubbles which are generated by hydrodynamic process are of high energy. These bubbles have a capability to destroy metal surfaces where damaged areas are the main sites to destroy compared to undamaged areas which result in the restoration of obliterated numbers.

REVIEW OF LITERATURE

There are a lot of studies that have been addressed to the problem of obliterated serial numbers on different metal surfaces. All these studies have been done to understand the principles, theory and methods to successfully restore the obliterated serial numbers.

Many researchers discussed metallurgical background of metals, theory and mechanism behind number restoration by chemical etching (Polk and Giessen, 1975; Thornton and Cashman, 1976; Heard, 1997; Petterd, 2000; Katterwe, 2006).

Etching technique is frequently used for microscopic and macroscopic examination for quality control, failure analysis and research studies of metal. Extensive information on the technique and metallographic reagent in the restoration of obliterated on metal surfaces is available in literature (Nickolls, 1956; Jackson, 1962; Metal Progress, 1974; Thornton and Cashman, 1976; Cunliffe & Piazaa, 1980; Voort, 1984; Polk & Giessen, 1989; Maxwell, 1993; Heard, 1997; Petterd, 2000; Katterwe, 2006; Hogan et al, 2006; M. Azlan et al, 2007; Siaw and Kuppuswamy, 2009). However the choice of the reagent and its application on the surface are both dependent on the nature of metal. A wide variety of chemical etching reagent for iron and steel and common nonferrous metal and alloys are available in literature (Nickolls, 1956; Jackson, 1962; Metal Progress, 1974; Cunliffe and Piazza, 1980; Voort, 1984; Polk and Giessen, 1989; Heard, 1997; Petterd, 2000; Katterwe, 2006). Detailed etching procedures and time of etching are also compiled there in. Composition of the alloy will strongly enhance the choice of a particular reagent. Etching techniques for obliteration marks for iron and steel have been described in forensic literature more than any other metal because of the greater use of these in the automobile engine and chassis and also firearms.

Fry originally published a method for revealing strain lines in iron and steel (Voort, 1984). There were many variations of Fry's reagent and his most popular composition was 90 g cupric chloride, 120 ml hydrochloric acid and 100 ml water, which was adopted by the forensic community to restore the obliterated marks on the chassis and engine of motor vehicles and frames of firearms. Following Fry's method, many obliterated serial numbers were restored (Thornton and Cashman, 1976; Polk and Giessien, 1989; Heard, 1997; Petterd, 2000; Katterwe, 2006; Nickolls, 1956). This reagent contained considerable hydrochloric acid. Hydrochloric acid keeps free copper from depositing on the sample during etching. In original Fry's method, the obliterated sample was first polished, and then immersed in the reagent for 1-3 minutes. After that etching was continued by rubbing with a cloth moistened in the solution and covered with $CuCl_2$ for 2-20 minutes. The surface was washed with alcohol and dried periodically for inspection. Various studies have confirmed that Fry's reagent was an effective etch for recovering erased marks on steel and iron surfaces.

Cast steel does not respond well to treatment by chemical etching (Nickolls, 1956). Cast iron and steel are the most difficult to develop (Jackson, 1962). Etching has been found to be very limited in its application to cast iron engine number restorations (Maxwell, 1993). Maxwell (1993) proposed heat treatment using oxyacetylene flame in restoration of cast iron engine number. The heat treatment utilized the fact that various phases present in polycrystalline metal displayed different behavior when subjected to heat.

The oxyacetylene equipment used to perform recoveries was costly to purchase and maintain. Hence Hogan et al. (2005) used MAPP (methyl-acetylene-propadiene) gas (which was made by combining 44% methyl-acetyl-propadiene and 56% liquefied petroleum gas) to restore obliterated serial marks on a vehicle engine block. This gas was used instead of oxyacetylene in direct heat treatment technique because it was light weight and was not costly. The result showed that MAPP gas gave results as good as oxyacetylene.

Wightman and Matthew (2008) studied the application of Fry's reagent to recover erased marks from steel and they confirmed that Fry's reagent was an effective etch for recovering erased identification marks in steel. However, they noted that Fry's reagent became less reactive and the time required to restoring the marks increased after 4 weeks of storage from 95 to 115 minutes. Recovery also became difficult when low applied force (less than 20kN) was used to form the imprint.

Azlan et al. (2007) investigated whether metallographic reagents used in the restoration of stamped marks could be applied to recover engraved marks on low carbon (0.1%C) steel surfaces, where the deformation zones were low. They conducted experiments by mechanically engraving alphanumeric characters on several low carbon steel (0.1%C) plates using a computer controlled engraving machine "Gravograph". The markings were later erased from the above steel plates by removing the metal in stages of 0.01 mm through 0.04 mm below the bottom of the engraving. Eight metallographic reagents were tested on each one of the above erased plates using swabbing technique. The results had shown that while most of the reagents were able to restore marks up to certain levels of erasure, the reagent comprising 5 g copper sulphate, 60 ml water, 30 ml concentrated ammonium hydroxide and

60 ml concentrated hydrochloric acid restored marks erased to a depth of 0.04 mm below the engraving depth, thus presenting itself to be the most sensitive reagent. The above reagent was also able to decipher successfully the original engraved marks that had been erased and engraved with a new number, or obliterated by centre punching.

In a more recent study, Siaw and Kuppuswamy (2009) investigated the most sensitive chemical etching reagents for medium carbon (0.31%C) steel. The carbon steel surfaces were engraved with some alphanumeric characters using ''Gravograph'' and erasing them to several depths below the bottom of their engraving depth. Seven metallographic reagents of which most of them were copper containing compounds were chosen for etching. The erased plates were etched with every one of these etchants using swabbing method. The results have revealed that Fry's reagent comprising cupric chloride 90 g, hydrochloric acid 120 mL and water 100 mL provided the necessary contrast and was concluded to be the most sensitive.

From the literature survey, it can be concluded that Fry's reagent was an effective etching reagent for iron and steel. However this reagent was not very effective for cast iron. Cast iron and steel are of same in their composition except that cast iron contains higher carbon content, between 2-6% C. Further the work of M. Azlan *et al.* (2007) and also Siaw and Kuppuswamy (2009) demonstrated that, low and medium carbon steel surfaces required different composition of Fry's reagent. Most of the automotive companies use cast iron for their engines, so it is considered desirable to use cast iron engine as a sample in this project. Hence the purpose of this study was to find the suitable reagents and methods for restoration of obliterated markings on high carbon steel surfaces.

OBJECTIVE OF THE STUDY

1. To identify the most sensitive and effective metallographic reagent, among the several ones used for steel surfaces, that can restore erased engraved marks on cast iron surfaces.

MATERIALS AND METHODS

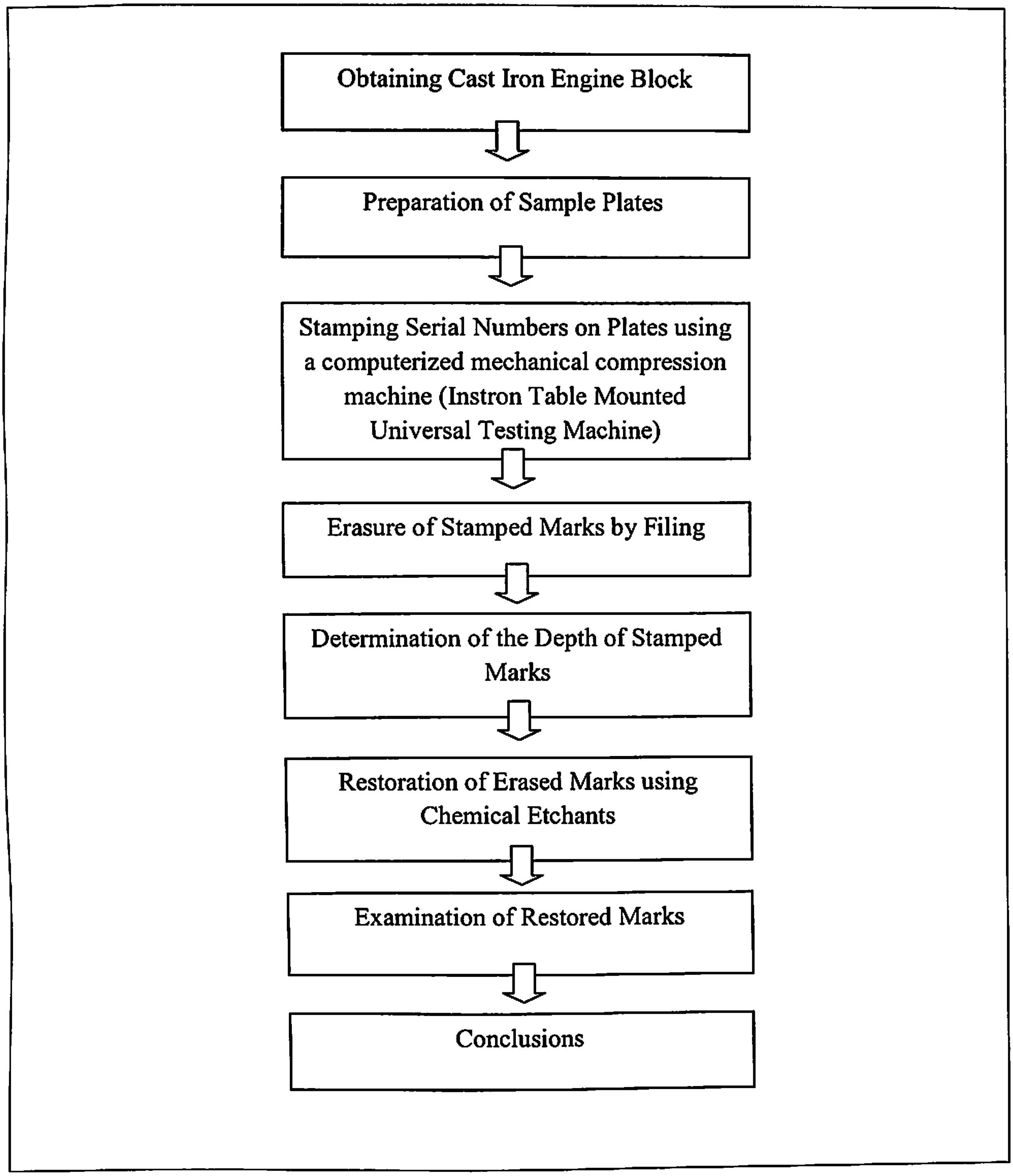

Chart 1: Flow chart showing the plan of work

Metal Samples

One cast iron engine block of Proton Saga car was purchased for this work. The engine block was cut into several small plates which were approximately about the same in size. The surface of the plate was polished with grinding machine to remove rust caused by oxidation of the iron and also to give a smooth surface. After polishing, the engine block was cleaned and cleared from grease, oil and other foreign particles using detergent and acetone.

Figure 1: Original rusty cast iron plate

A sample of the engine metal was sent to professional laboratory in India for analysis and it was found that it was containing 3.29% carbon content. Besides that, a sample of this engine was also analyzed in the School of Mechanical Engineering, Engineering Campus, USM, Penang for measurement of its hardness by using Hardness Testing Machine. Their hardness value was found to be 213.6 Hardness Vickers (HV).

Figure 2: Hardness Testing Machine used for testing hardness of cast iron sample.

(School of Mechanical Engineering, Engineering Campus, USM, Penang)

Stamping Plates

The cast iron plates that had been cut from the car engine were used as the sample plates. A large number of these plates were then stamped with numerical characters "18" number punch by using a computerized mechanical compression machine Instron Table Mounted Universal Testing Machine, model 3367. The Hunter brand number punch size 7mm was used. Their hardness value was 592.6 HV. The number punch was compressed three times onto each plate by using 8kN load. The characters "18" were chosen, as they contained both straight and curved surfaces. The plates were then labelled appropriately with specific marks for easy identification, since each of plate would be treated with a different etching reagent.

Figure 3: Instron Table Mounted Universal Testing Machine used for stamping numbers on cast iron sample. (School of Mechanical Engineering, Engineering Campus, USM, Penang)

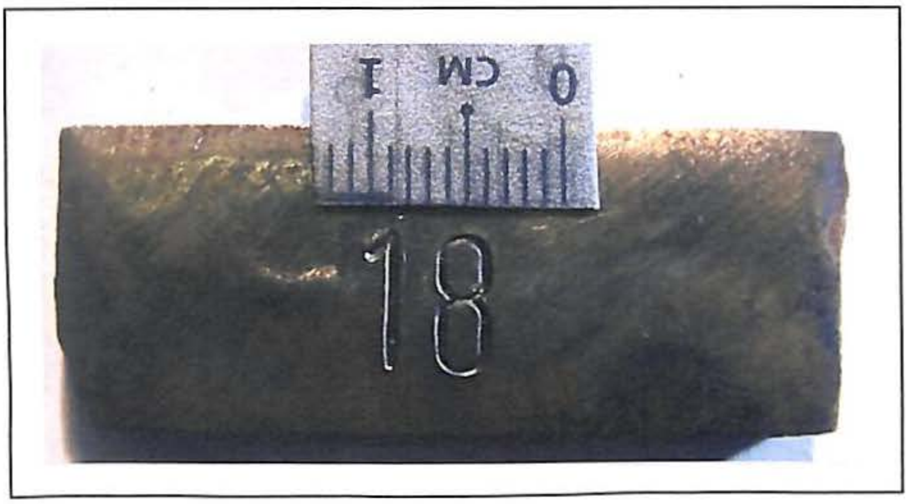

Figure 4: A cast iron plate stamping with numeric characters "18" using Instron Table Mounted Universal Testing Machine

Obliteration of Stamping Marks

a) Obliteration by Erasure

Before erasing the stamped numbers, each individual plate's surface was treated with acetone to remove any debris and the initial thickness of the individual plate was measured using micrometer screw gauge. The numbers stamped on the plates were then removed by using hand filing followed by polishing using silicon carbide abrasive papers of different grades to give the surface a mirror finish. Three different grades of abrasive papers were used: coarse grade (P60), medium grade (P120) and fine grade (P320). The coarse grade was first used after hand filing, and then followed by medium grade and fine grade abrasive paper.

Removal of the marks was continued until the visible stamping marks were no longer visible. Then the plate thickness was measured again using micrometer screw gauge. The difference of initial thickness and thickness after erasure was the depth of the stamping. The depth of stamping was found to vary between 0.2mm and 0.3mm.

The erasure process was the most challenging part to do. First, it was time and energy consumed because the cast iron was a very hard metal. It took 30 to 60 minutes to erase the stamped numbers and to give it a mirror-like finish on each individual plate. Second, each stamped marks on the individual plate must be erased evenly and carefully so that the indentation marks were obliterated to the same level. This was important because uneven and too deep obliteration would also remove the plastically deformed region that could fail the restoration of obliterated stamped marks. There were 30 erased plates prepared for the etching experiments.

b) **Obliteration by Over-stamping**

The stamped marks "18" were erased by hand filing until they were no longer visible. A new number "26" was over-stamped in the erased area.

c) **Obliteration by Centre Punching**

The original stamped marks "18" were obliterated by hammering the surface of the plate using a centre punch until the marks were totally obliterated, and could not be deciphered visually.

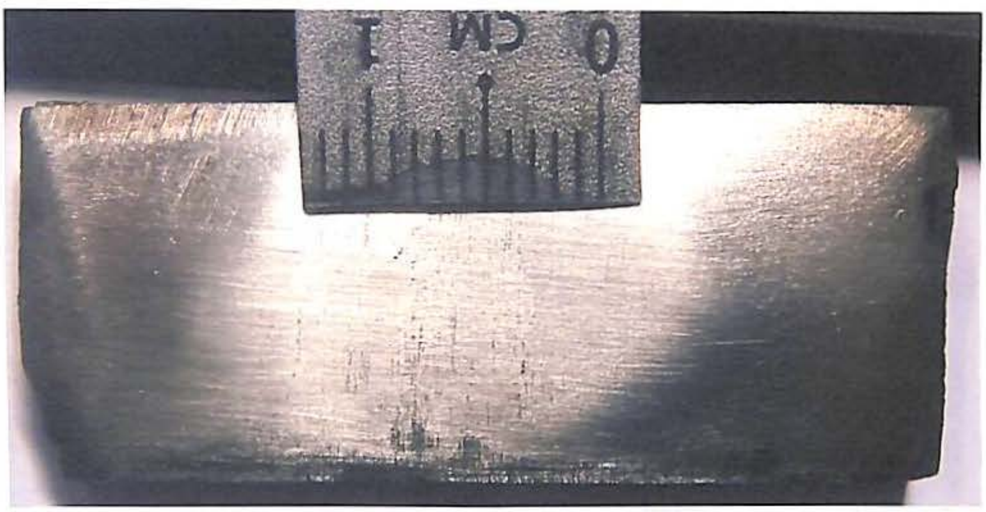

Figure 5: The cast iron plate after erasure of the stamped numbers.

Selection of Etching Reagents

The following metallographic reagents recommended by several workers in the past for restoration of obliterated stamped marks were chosen (Table 1). These reagents were prepared to recover obliterated stamped marks on cast iron (3.29% carbon) plates in an attempt to study the effectiveness and sensitivity of each solution.

Etching Reagent	Composition	Source
Etching reagent 1	a) Copper sulphate 5g, Conc. hydrochloric acid 60mL, Water 60mL, Conc. ammonium hydroxide 30mL. b) 15% Nitric acid.	Cunliffe and Piazza,1980; M.Azlan *et al.*,2007
Etching reagent 2	a) Ferric chloride 5g, Hydrochloric acid 50mL, Water 100mL b) 15% Nitric acid.	Petterd, 2000; Katterwe, 2006
Etching reagent 3	5% Potassium dichromate in 10% sulphuric acid (See Appendix 2)	Nickolls,1956; Jackson,1962
Etching reagent 4 (Fry's reagent)	a) Cupric chloride 5g, Hydrochloric acid 40mL, Water 30mL, Ethanol 25mL. b) 15% Nitric acid.	Metal Progress, 1974; Voort, 1984; Polk and Giessen, 1989; Heard, 1997; Petterd, 2000
Etching reagent 5 (Fry's reagent)	Cupric chloride 45g, Hydrochloric acid 180mL, Water 100mL.	Metal Progress, 1974; Voort, 1984
Etching reagent 6 (Fry's reagent)	a) Cupric chloride 90g, Hydrochloric acid 120mL, Water 100mL. b) 15% Nitric acid.	Nickolls, 1956; Metal Progress, 1974; Voort, 1984; Heard, 1997; Petterd, 2000; Katterwe, 2006

Table 1: Etching reagents used to restore obliterated stamped marks and their sources

Etching Reagent	**Composition**	**Recommended by**
Etching reagent 7 (Fry's reagent)	a) Cupric chloride 12.9g, Hydrochloric acid 80mL, Water 60mL, Ethanol 50mL b) 15% Nitric acid.	Jackson, 1962; Warlow, 2004
Etching reagent 8 (modified etching reagent 5)	Cupric chloride 45g, Hydrochloric acid 100mL, Water 180mL	Proposed reagent

Table 1: Continued

Restoration Procedures

Prior to restoration process by etching, the cast iron plate was cleaned with acetone to remove any dust, debris, grease and other particles. The swabbing technique was applied for all reagents except for the etching reagent 3 where immersion technique was also done.

In the swabbing technique, a cotton bud was dipped into etching reagent and swabbed onto the plate surface where stamped marks were removed. Care was taken that the etching reagent was swabbed on the entire erased surface evenly, constantly with a gentle movement and with the same force all the time. This ensured that entire surface was etched evenly and at the same level of reaction. This would help in good and full recovery of erased numbers. First the sample surface was cleaned with acetone, followed by swabbing with etching reagent for 1 minute, then cleaned again with acetone and lastly swabbing with 15% nitric acid for 1 minute. These steps of etching were repeated until the obliterated numbers restored.

For etching reagent 3, immersion technique was also used (Jackson, 1962; Nickolls, 1956). The plate surface was first swabbed for 10 minutes. Then plasticine wall was built on the plate surface around the obliterated marks and the etching reagent was poured using syringe. For every 30 minutes the etching reagent was removed and the surface was observed. This was done for about 3 hours.

Etching experiments were conducted in an environment, where proper ventilation was available. Also there should be sufficient amount of lighting to view the faintly recovered marks. There were several criteria needed to be considered in determining the effectiveness and sensitivity of the metallographic etching reagents. These criteria were the clarity and appearance of the recovered numbers and the time consumed from the first time the etching reagent was swabbed until the numbers were clearly visualized. So the clarity and appearance of the recovered number was carefully observed all the time during etching process until it gave the most clear visualized restored numbers. However, certain etching reagents did not work for restoration of erased numbers. So certain time limit was decided for the swabbing process to be carried out. The time limit was one hour. Any etching reagent that could not restore erased numbers in one hour was considered as not effective.

In the initial stage of restoration the numbers appeared very faintly and later disappeared. A magnifier (X2) helped in observing the strain lines of the number during initial development of the numbers. The plate was also to be observed from different angles because this gave different light reflectivity and enhanced the appearance of the numbers. The etching process was stopped at this time, and the clarity, appearance and time consumed were recorded. The swabbing was continued until the number appeared clearly. The time consumed was recorded and photographs of the restored numbers were taken. Then the plate surface was cleaned with acetone and preserved by applying a thin layer of grease to prevent rusting of the surface.

For restoring the marks obliterated by over-engraving and centre punching, the most sensitive reagent identified from the restoration of erased marks was used. It was applied either by swabbing or immersion method.

RESULTS

The results provided by each etching reagent are described individually below.

a) Etching reagent 1

This etching reagent consisted of two solutions. Solution 1 consisted of 5g copper sulphate, 60mL conc. hydrochloric acid, 60mL water, and 30mL conc. ammonium hydroxide and solution 2 was 15% nitric acid. These two solutions were applied alternately and acetone was applied in between these two solutions. No number restoration was successful using this etching reagent. After 15 minutes of etching, the plate surface became pitted and turned to red/brown colour. Further etching for 1 hour did not reveal any number, but the pitting became worse. No number was recovered.

b) Etching reagent 2

This solution contained 5 gram ferric chloride, 50mL hydrochloric acid and 100mL water. This etching reagent was applied for 10-20 seconds and then acetone was applied to wash the plate surface before any number restored was observed. This cycles were continued until the erased marks were retrieved. After 14 minutes of etching, a very faint number was seen from certain angles but was unable to be photographed. The surface also became pitted. The pitting became worse after 20 minutes of etching and caused no number recovery.