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Restoration of Obliterated Stamped Marks on Aluminium Surfaces by Metallographic Etching Technique

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ABSTRACT

Serial number restoration is a frequently encountered problem in forensic science laboratories for the investigation of theft and burglary cases. These identification marks are generally introduced over metallic surfaces of different vehicle parts and firearms by various means. Chemical etching is one of the most effective and simple technique to restore obliterated, erased, over-stamped and over-engraved marks on metallic surfaces. Several significant studies on restoration of engraved markings on aluminium surfaces were previously reported. The present study attempts to find out an efficient and fast etching reagent to restore obliterated stamped marks on aluminium surfaces. Ten effective etching reagents previously reported by various researchers in their restoration studies were assessed in the present experiment. Etching reagents were individually applied on obliterated surfaces by the cotton swabbing method. The Reagent 3 (ferric chloride 25 g, conc. HCl 25 mL, distilled water 100 mL) was found out to be the most sensitive and rapid (4–6 min) for the restoration on aluminium surfaces. The study also revealed that the absence of an alkaline compound in etching reagent potentially accelerates the speed of the restoration process.

Keywords: Serial number, Aluminium, Stamped marks, Obliteration, Etching reagent, Restoration.

INTRODUCTION

Serial numbers are unique identification marks placed on engines and chassis of vehicles, firearm frames or any other metallic object[1-4]. Casting, Engraving, die stamping, pin stamping and LASER are commonly used to introduce these identification marks on the metallic surfaces[5,6]. On the contrary, perpetrators frequently obliterate or remove these marks by several mechanical means i.e., peening, punching, filing, grinding, drilling, welding over-stamping, chemical corrosion, etc. for unauthorized selling and to avoid any connection with the item1, 2, 6 - 8. Restoration of the obliterated or removed identification marks provides major leads in the identification of stolen objects[2,9]. The marking process deforms several layers underneath the actual indentation. The depth of deformation

depends on the strength of the metal, e.g., on impact, zinc deforms more than iron[10] (Fig. 1a–1c). The efficiency of restoration depends upon the depth of obliteration. Treatment of the surface with different chemicals known as macro etching is the most common restoration technique used by the researchers on metals. Macro etching is the most effective metallographic technique among all[11].

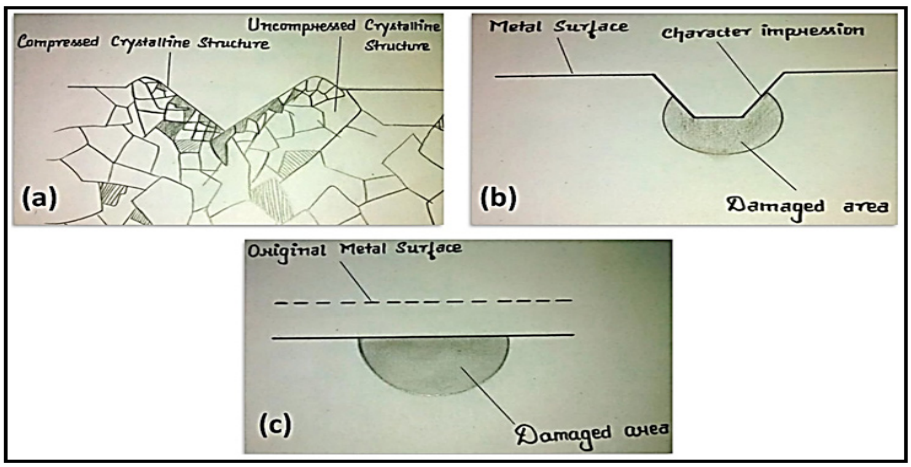

Fig. 1. Cross-section of deformed crystal structure by mechanical force

A desirable etching reagent for metallic surface always give good contrast, reproducibility and consume less time for restoration. A large number of significant studies have been performed on commonly encountered metals and their alloys. Works by Turley[12], Zaili *et al.,*[7], Wightman and Matthew[1], Yin and Kuppuswamy[13], Wahab *et al.,*[11] and Richa *et al.,*[4], showed that different composition of 'Fry's Reagent' consists of a metallic halide or salts and a strong acid is an excellent etching reagent for iron and steel surfaces. Recently Shankar *et al.,*[3] restored obliterated serial markings on copper by a combination of ferric chloride, glacial acetic acid and distilled water and Fortini *et al.,*[14] restored obliterated markings on Ni-Cr-Mo steel surface by a combination of Nitric acid and distilled water.

Aluminium and its alloys are rapidly replacing other metals in the vehicle, firearm and machinery industry in recent decades due to its strength and lightweight[2,15-16]. Different alloys (e.g. Duralumin) of aluminium also used frequently in various automobile industries[16]. Restoration on aluminium surfaces were previously performed only on obliterated engraved marks[2,9,10,15,17]. Studies by Chisum[15], Baharum *et al.,*[10], Peeler *et al.,*[17] Bong and Kuppuswamy[9] and Uli *et al.,*[2] revealed that etching reagents used for comparatively strong metals and their alloys like iron, steel, etc. are not suitable for the restoration of obliterated engraved marks on aluminium and its alloy surfaces. Few researchers recommended that an alternate application of a dilute solution of a strong acid and a strong alkali can be a good etching reagent on aluminium surfaces[2,9,10]. Present study assessed ten best etching reagents used in previous studies of restoration on different metallic surfaces to find out a fast and effective reagent for the restoration of obliterated stamped marks on aluminium surface.

Methodology

In the present study 12.1 mm thick aluminium bricks were used to restore obliterated serial numbers created by punching method. Metallographic etching or chemical etching techniques is used for the restoration in the present study. The procedure of this method has been adapted from the previous studies of restoration of obliterated engraved marks on aluminium and it alloy surfaces[2,9,10,15,17].

Sample Preparation

A stamping die was used to introduce numeric characters from 1 to 9. Each character of the die stamp covers approximately 0.3 square inch area. Finally, all the samples were obliterated by the mechanical grinding machine (Fig. 2) up to zero visibility. Samples were photographed before and after each step for permanent record and comparison.

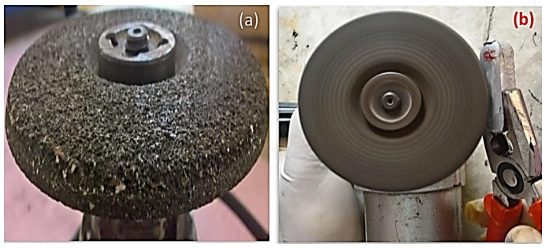

Fig. 2. Damaged area underneath the deformed crystal Layer

Preliminary Examination and Surface Preparation

Surface preparation before restoration is the compulsory step as it makes the surface uniform which in turn enhance the efficiency of the restoration. All the samples were first examined by a magnifying lens to observe any remaining visible number. Commercially available silicon carbide paper (P 60) is used to polish the grinded surface by removing scratches and other marks to give a smooth mirror-like finish for better chemical treatment. Polishing is followed by swabbing the surface with acetone to remove any dirt, grease, paint or any other loosely adherent material from the surface.

Chemical Etching

In the present work ten etching reagents Table 1 were selected from previous studies of restoration on metallic surfaces. All the selected reagents are best in their respective studies. Reagent 1, 2 and 6 were previously used on the aluminium and its alloy surfaces (Al-Zn-Mg-Cu and Al-Si). Reagents were applied on the obliterated surface by swabbing method. A cotton bud is soaked in the reagent and gently applied over the obliterated aluminium surfaces until the marks restored. Single reagents were swabbed uninterruptedly and multi-reagents were applied alternatively until the numbers restore. Since, the restored numbers were visible for a short period of time, instant photographs were captured to keep a permanent record before and after every step. The application method and composition of each reagent are summarized in the Table 1.

Table 1: Comparative effectiveness and sources of chemical etching reagents for the restoration of obliterated stamped marks on aluminium surfaces

S. No.	Etching Reagent	Composition of Reagent	Application Method	Consumed Time	Observation	Source
1	Reagent 1 (Villella's reagent)	Glycerine 30 mL Hydrofluoric acid 20 mL Nitric acid 10 mL	Continuously swabs the reagent until the numbers appear.	20–25	Both contrast and reproducibility were good and can be easily photographed.	Heard, 2008[6]
2	Reagent 2 (Hume Rothery solution)	Copper Chloride ($CuCl_2$) 200 g Hydrochloric Acid (HCl) 5 ml Distilled water 1000 mL	The solution was swabbed alternatively on the erased surface. First with Hume Rothery solution and then with distilled water.	20	The number appears in good contrast and also reproducible.	Baharum *et al.,*[6,11] 2008, Heard, 2008
3	Reagent 3	Ferric Chloride ($FeCl_3$) 25 g HCl 25 mL Distilled water 100 mL	The reagent was swabbed continuously until the numbers appear.	4–6	Good contrast, easily observed and reproducible. Can be easily photographed.	Richa *et al.,* 2012
4	Reagent 4	Solution 1 Copper Chloride 45 g HCl 100 mL Distilled water 180 mL Solution 2 15% Nitric acid	Both solutions were swabbed alternatively on the erased surface. until the numbers appear.	90	No restoration.	Wahab *et. al.,* 2012[11]
5	Reagent 5	Conc. HCl 10 mL Glacial acetic acid 25 mL	The solution was applied continuously until the numbers appear.	30	Numbers appeared in fair contrast and slightly observable and also reproducible.	Shankar *et al.,* 2014[3]
6	Reagent 6	Solution 1 10% Sodium hydroxide Solution 2 10% Nitric acid	Both the solution was swabbed alternatively on the erased surface. First with solution 1 for 3 minutes. Then solution 2 for 1 minute.	60	Both contrast and reproducibility were good and the sensitivity of numbers was also good.	Uli *et al.* 2010[2], Petterd, 2000 Bong and Kuppuswamy, 2010[9]
7	Reagent 7	Solution 1 10% Sodium hydroxide (NaOH) Solution 2 25% Nitric acid (HNO_3) (Used as highlighter for the above chemical)	Swabs with NaOH and then HNO_3	58		Technical Procedure of reagent preparation 2014[19]
8	Reagent 8	10% Sodium hydroxide Distilled water 90 mL	Continuusly swabbing over the erased surface until the numbers appear.	50	Numbers are reproducible and appeared in good contrast.	Katterwe, 2006[20]
9	Reagent 9	Nitric acid 25 mL Distilled water 75 mL		90	No restoration.	Petterd, 2000[18]
10	Reagent 10	Nitric acid 20 mL Potassium permanganet 4 g Distilled water 100 mL		90		Shankar *et al.,* 2014[3]

RESULTS

The present study is focused to find out an effective and rapid chemical reagent to restore obliterated stamped serial numbers on aluminium surfaces. Several researchers explored multiple reagents to restore obliterated serial numbers on different metallic surfaces.[10] best etching reagents from different restoration studies on aluminium and other metallic surfaces were selected for the present experiment. The experimental result shows that 7 among 10 reagents (i.e., Reagent 1: Glycerine 30 ml, Hydrofluoric acid 20 mL, Nitric acid (HNO_3) 10 mL, Reagent 2: Copper Chloride 200 g, Hydrochloric Acid 50 mL, Distilled water 1000 mL, Reagent 3: Ferric Chloride 25 g, Hydrochloric Acid 25 mL, Distilled water 100 mL, Reagent 5: Conc. Hydrochloric Acid 10 mL, Glacial acetic acid 25 mL, Reagent 6: 10% Sodium hydroxide (NaOH), 10% HNO_3, Reagent 7: 10% NaOH, 25% HNO_3 and Reagent 8: 10% NaOH, Distilled water 90 mL) successfully restored the obliterated marks. But, only three reagents i.e., Reagent 1 (Villella's reagent), Reagent 2 (Hume Rothary Solution) and Reagent 3 (Ferric Chloride 25 g, Hydrochloric Acid 25 mL, Distilled water 100 mL) showed good restoration efficiency in less time (4-25 min) Fig. 3.a-3c, 4a-4.c). Reagent 3 was the standout among all as it took the least time (4–6 min) and also produce good visibility (Fig. 5.a–5c) of restored numbers. This experiment also revealed that reagents containing alkali, took comparatively less time (4–30 min) to restore the obliterated marks than the reagents containing it (50–60 min). Table 2 shows the comparative representation of the consumed time by reagents including alkali and without alkali. Reagent 4, 9 and 10 showed no restoration on the aluminium surface.

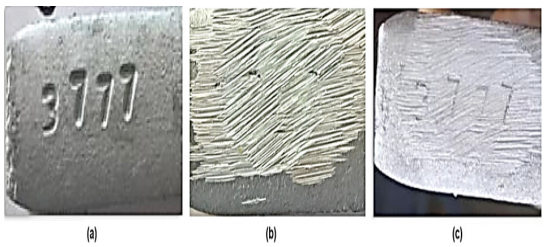

Fig. 3. Serial mark (a) pre obliteration (b) post obliteration (c) restored by Villella's Reagent

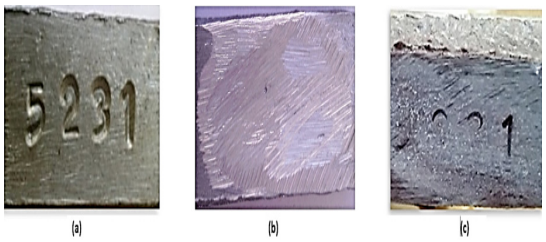

Fig. 4. Serial mark (a) pre obliteration (b) post obliteration (c) restored by Hume Rothary solution

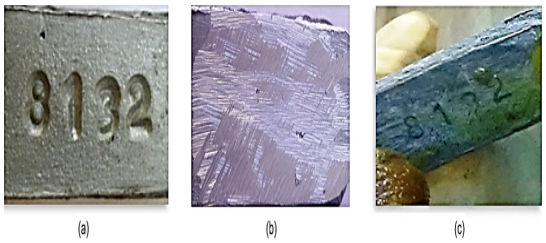

Fig. 5. Serial mark (a) pre obliteration (b) post obliteration (c) restored by Reagent 3

DISCUSSION

Richa *et al.,*[4] performed a similar experiment on steel surface by using multiple combinations of Fry's reagent and found effective results. Reagent 3 produced the best visibility in minimum time (4–6 min) with better reproducibility among all the ten reagents used. In the study by Chisum[15], a similar combination of metallic chloride (Mercuric Chloride) and a strong acid (HCl) showed good restoration on aluminium and its alloy surfaces that is similar with the results of the present study. An alternative swabbing of 60% Hydrochloric Acid (HCl) and 40% NaOH proved to be a good etching reagent for obliterated engraved marks on aluminium and its alloys in the experiments by Baharum *et al.,*[10] Bong and Kuppuswamy[9] and Peeler *et al.,*[17]. Uli *et al.,* used an alternate swabbing of 10% Nitric Acid and 10% NaOH in their study which showed good results on aluminium-silicon alloy surfaces[2]. Previous studies revealed that the effect of etching reagent on the metal surface is affected by the marking procedure. Engraved aluminium surfaces did not restore obliterated marks by the etching reagents used for strong metals because it corrodes most of the underlying shallow deformations[2,9-10]. Stamping method potentially causes greater deformation on the metal surface that make it persistent to the exposure of strong etching reagents as observed in the present study (Reagent 3). Previous studies suggested that aluminium and its alloys show gradual corrosion to the exposure of caustic solutions like an alkali[2]. NaOH

(Alkali) is present in most of the best-suited reagents previously used for aluminium and its alloys[2,9,17]. The absence of alkali probably accelerates the caustic effect on the aluminium surface that reduces the restoration time. The reagents without NaOH (i.e., Reagent 2, 3 and 5) restored the obliterated serial numbers faster than the reagents consisting NaOH. A comparison between the results of the previous and the present study on aluminium surfaces is summarized in Table 3.

Table 2: The comparative representation of the consumed time by reagents including alkali and without alkali

Reagent (Without Alkali)	Composition	Consumed Time (Min)	Reagent (Including Alkali)	Composition	Consumed Time (Min)
Reagent 1 (Villella's reagent)	Glycerine 30 mL Hydrofluoric acid 20 mL Nitric acid (HNO_3) 10 mL	20–25	Reagent 6	Solution 1 10% Sodium hydroxide Solution 2 10% Nitric acid	60
Reagent 2 (Hume Rothery solution)	Copper Chloride ($CuCl_2$) 200 g Hydrochloric Acid (HCl) 5 mL Distilled water 1000 mL	20	Reagent 7	Solution 1 10% Sodium hydroxide (NaOH) Solution 2 25% Nitric acid (HNO_3) (Used as highlighter for the above chemical)	58
Reagent 3 (Fry's Reagent)	Ferric Chloride ($FeCl_3$) 25 g HCl 25 ml Distilled water 100 mL	4–6	Reagent 8	10% Sodium hydroxide Distilled water 90 mL	50
Reagent 5	Conc. HCl 10 mL Glacial acetic acid 25 mL	30			

Table 3: Summarized table of previous and present study on aluminium surfaces

Comparative Study			
S. No.	Study	Composition of Desirable Reagent	Restoration Time (Minutes)
1	Chisum WJ, 1963	0.1M Mercuric Chloride in 0.1N Hydrochloric Acid	20
2	Baharum *et al.,* 2008	Solution 1 60% hydrochloric acid Solution 2 40% sodium hydroxide	03-60
3	Uli *et al.,* 2010	Solution 1 10% Sodium hydroxide Solution 2 10% Nitric acid	08-40
4	Bong and Kuppuswamy, 2010	(i) 10% Aqueous Phosphoric Acid (ii) Solution 1 60% hydrochloric acid Solution 2 40% sodium hydroxide	2–960 02-20
5	Present Study	Ferric Chloride 25 g Hydrochloric acid 25 mL Distilled water 100 mL	04-06

CONCLUSION

The present study is the first attempt to restore obliterated stamped serial numbers on the aluminium surface in contrast to all the previous studies on obliterated engraved markings. Among 10 chemical reagents used, reagent 3 (Ferric Chloride 25 g, HCl 25 mL and Distilled water 100 mL) produce desired results in minimum time (4-6 minute). The study also revealed that the absence of the alkaline compound potentially enhances the caustic effect to minimize the restoration time. Reagent 2, 3 and 5 including HCl showed a similar result as produced by reagent 6, 7 and 8 including NaOH. But acid-containing

reagents took lesser time to restore the obliterated numbers.

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Conflicts of Interest

The authors declare no conflict of interest.

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