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To the Editor of
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Object: submission of paper

Dear Editor,

With respect to the object we send you the paper entitled "USING THE ETCHING TECHNIQUE TO RESTORE STAMPED MARKS: METALLURGICAL AND STATISTICAL APPROACHES" by Annalisa Fortini, Mattia Merlin, Chiara Soffritti and Gian Luca Garagnani.

The paper is original and it is not under consideration for publication elsewhere. All authors have equally and materially partecipated in the research and in the article preparation. Moreover, the authors have approved the final article.

Best regards,

Ferrara, October 24th, 2013

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USING THE ETCHING TECHNIQUE TO RESTORE STAMPED MARKS: METALLURGICAL AND STATISTICAL APPROACHES

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Abstract

Chemical etching, among several restoration techniques, is widely used in forensic laboratories for recovering obliterated serial numbers stamped on metal surfaces. The present research involved the restoration of serial numbers stamped on specifically prepared plate samples, realised in 40NiCrMo4, a low-alloy carbon steel for quenching and tempering that is actually used in the firearms industry. An alphanumeric sequence was imprinted by means of die stamping on the samples' surfaces. Microstructural characterisation was performed to study the plastically deformed region surrounding the stamped marks. To efface the imprints the samples were erased by way of a hone: controlled removals of material, up to a maximum depth of 60 µm below the marks, were carried out. Five common metallographic reagents were chosen and tested by swabbing method to assess their sensitivity and effectiveness in recovering the original serial numbers. Finally, in order to evaluate the goodness of the results, the restored characters were analysed by a systematic sampling of thirty observers to study if the positive recoveries are dependent on the operator. A descriptive statistical analysis was performed by means of McNemar and Chi-squared nonparametric tests. The obtained results revealed that Fry's reagent was the most sensitive and it was able to restore erased marks up to 60 µm under the depth of the impression. Furthermore, the reagent comprising 25 ml HNO_3 and 75 ml H_2O provided good results, recovering the major numbers of erased characters.

Keywords: serial number recovery, stamp mark, chemical etching, metallography, statistical analysis.

1. Introduction

A common problem in forensic investigations is the recovery of the original serial numbers of firearms which have been partially or completely removed to prevent their identification. Criminal intent is also to avoid the connection between the owner and the stolen weapon. While the brand name and the model can be determined from the physical characteristics, its history and the chain of ownership are related to the serial number [1]. Therefore, the recovering of obliterated numbers provides important evidence for identification purposes.

In recent years, marking-industries' efforts have been focused on the development of methods such as pin stamping, engraving and laser etching. At the moment, automotive components and firearms are being marked by laser [2]. Despite that, in most cases, firearms currently circulating in clandestine market are being still marked by die stamping. This means that the marks have been made through a steel punch, which is struck against the surface leaving the impression. Metal is compressed beyond its elastic limit and plastic deformation of the crystalline array surrounding the mark is the microscopic effect of the process. The depth to which this compressed and altered structure extends is dependent upon the material, the size and the shape of the punch, the force applied as well as the depth of the mark [1,3-8].

Criminal obliterations usually involve grinding or filing the surface until the number is no longer visible to the naked eye: criminals, in fact, take the erasure down to the full depth of the markings, believing this is enough [8]. However, even though the stamped characters are removed and seem definitively lost, the original mark can often be recovered with suitable methods [1,8,9]. In forensic practice, few experimental techniques are successfully being used to restore the obliterated serial numbers [2]. Among these, nondestructive methods, such as magnetic particle procedure, hardness testing, X-ray imaging and electron channelling contrast have been proposed. Since nondestructive restoration methods do not permanently alter the sample, these types of recovery tests are particularly attractive. A standard method, widely used before attempting other destructive techniques of restoration, is the magnetic particle procedure. A large horseshoe magnet is attached to the ferromagnetic sample, with the erased area between the poles: the specimen is then sprayed with fine magnetic particles dispersed in oil, which outline the obliterated number [8,10]. Another important nondestructive technique is hardness testing. It is well known that cold working causes hardness increase of the material, which can be used for the recovery. Thus, automatic hardness instruments, with fine resolution, allow evaluating the hardness increase in the immediate area surrounding the stamped mark, hence studying the original profile. In case of serial numbers that have been hidden with paint or body filler or by welding filler material, X-ray imaging has been successfully used: the texture topography imaging allows showing the recovery of the obliterated numbers [8]. A very interesting technique, which is in an experimental research stage, is the electron channelling contrast: by means of the scanning electron microscopy (SEM), the imaging of near-surface crystal defects is realised [8]. The contrast is due to the variation of the backscattered electron yield in deformed regions of a crystal close to a dislocation core [11-13].

However, validated destructive methods of restoration for metallic surfaces are heat treatment, ultrasonic cavitation, relief polishing, electrolytic etching and chemical etching. Among the destructive methods of restoration, in case of restoration on cast-iron substrates, a successful employed technique is the heat treatment of the stamped area. This method takes advantage of the recrystallization phenomena: heating flow causes the release of the residual tensile stresses, therefore the stored elastic energy of lower microstructure areas lifts up the upper relaxed areas, producing the arching of the original mark [8]. Moreover, an interesting method, which is applicable to all metals, is the ultrasonic cavitation. A high frequency electrical current is delivered via a piezoelectric transducer, the current is thus transformed into mechanical vibrations: if these vibrations are introduced into water then vibrational cavitation of the water will occur [1]. Hence, placing the specimen in a stream of cavitation bubbles, which take away material from the non-stamped areas, it is possible to the recovery the erased number. Another proposed recovery method, which takes advantage of the different hardness between the structural constituents of an alloy, is relief polishing. By means of hand polishing, the softer constituent is abraded at a greater rate than the harder one; therefore, the harder phase appears in bold relief revealing the original mark [2]. A metallographic method, sometimes used for the recovery of serial number, is the electropolishing process by which the specimen is made the anode and a cotton swab, soaked with the electrolytic solution, is made the cathode of the electrochemical cell: irregularities on the surface are removed by metal dissolution, caused by the applied current [8,9]. However, the optimum conditions of voltage, amperage and chemical composition of the etching solution are still under investigation by several forensic laboratories. Actually, for his simplicity and effectiveness, chemical etching is the most used method adopted to restore obliterated serial numbers on metallic substrates. It basically consists of a controlled corrosion process, made by means of a cotton wool swab soaked with a chemical reagent, that relies on the difference in etching behaviour between deformed and undeformed zones of the metallic substrate [3]. In fact, the cold worked regions are more reactive and thus the etching process lead to a local change in light reflectivity that allow revealing the character [4]. The positive recovery of the obliterated marks is strongly dependent upon the chosen reagent and its application method, in relation with the nature of the metal [5,6]. A wide number of reagents available in the open literature [1,4,6,7,9,14-16], derived from those developed by metallurgists, are suitable for serial number recovery on steels surfaces. Previous works [3,7,8,9,15,17-21] suggested that Fry's reagent and its compositional variations are widely used. Wightman and Mattew [17] remark that Fry's reagent is sold to forensic team in the UK, as an effective reagent for the recovery. Zaili et al. [18] reported that the reagent comprising 5 g $CuSO_4$, 60 ml H_2O, 30 ml NH_4OH and 60 ml HCl is the most sensitive for recover engraved marks on low carbon steels with ferrite-pearlite microstructure.

It should be pointing out that all of the previous recovery techniques could be successfully applied if, after a criminal obliteration, the metallic substrate still contains a plastic deformation due to the original presence of the marks [1,3,4,8,9,14,17,18,22,23]. All metals have a polycrystalline structure and, during the stamping operation, the grain structure of the substrate is permanently deformed. In case of die stamping, employing blunter dies generally produces plastic flow for a depth greater than V-sharper ones: the use of blunter dies by manufacturers

would be preferable, since more cold worked material would left after a criminal obliteration [4]. It is clear that the recovery is strongly dependent upon the depth of the erasure of the original mark. If the criminal obliteration has partially ground the surface leaving a small portion of the original number, the material produced by the grinding can accumulate in the cavity: this partial obliteration seems complete but cleaning the surface usually allows the examiner to recover the stamped number [8]. Whereas, in some instances, the obliteration is pushed further and the stamped impression completely disappears to the naked eye. However, the plastic deformation zone is still present and the restoration can be achieved, using the recovery techniques previously described. Finally, if obliteration goes much deeper and the plastic deformation zone is removed, then no restoration is possible. Several authors [3,4,17,23] have studied the relation between the depth of the mark and the depth to which the restoration can be achieved. In particular, Turley [3] observed that the depth of restoration increases with increasing the depth of the stamp mark.

Hence, the present study is intended to investigate the relative sensitivity and efficacy of five metallographic reagents on restoring obliterated stamp marks on low-alloy carbon steel. For this purpose, the most common metallographic techniques and microhardness testing were used to study plastically deformed region surrounding the stamped marks. The alphanumeric sequence on the sample's surfaces was erased by a hone at controlled depths beneath the bottom of the imprint. The recovery tests were performed by the swabbing method. Finally, in order to evaluate the goodness of the obtained results, a descriptive statistical analysis was performed by means of McNemar and Chi-squared nonparametric tests. These analyses were carried out to assess the operator's influence: in recovering's experimental cases the alphanumeric characters are usually imprinted and restored by the same operator. This means that, knowing the original imprinted character, the operator can be influenced during the interpretation of the results.

2. Materials and methods

Samples

The selected samples were fifty-two 40NiCrMo4 steel discs, 5 mm in diameter and 50 mm in thickness, respectively. All the samples had the same chemical composition that is reported in Table 1. They were different in terms of heat treatment: twenty-six were previously normalized and tempered, the rest of the samples were austempered.

Table 1
Chemical composition of the samples (wt.%).

C	Si	Mn	Cr	Ni	Mo	P	Fe
0.421	0.211	0.891	0.567	0.420	0.190	0.006	Bal.

In order to reproduce how firearms' serial numbers are actually realised by the firearms industries, each disc was marked with a serial number made up of a combination of seven alphanumeric characters. The sample's surfaces were manually marked; the stamping parameters are confidential. Since five reagents were to be compared, the twenty-five normalized and tempered samples and the twenty-five austempered samples were divided into five series respectively, each consisting of five samples with the same serial number. The two extra samples were used for preliminary metallographic tests.

Microstructural analyses and microhardness tests

Prior to the recovery tests, to evaluate the depth to which the plastic deformation is present, microstructural and microhardness tests were carried out. Two discs, one for each heat treatment, were transversely sectioned in correspondence of the stamp mark, in order to observe and analyse the area below the impression. Thus, the specimens were mounted in thermosetting resin and ground by using a series of silicon carbide sandpapers, from 120 grit up to 1200 grit. To reach a mirror-like finishing, they were then polished using 6 μm and 3 μm diamond paste. After the chemical etching with Nital reagent, the cross-sectional microstructures were observed by a Leica MEF4M optical microscope (OM).

Vickers microhardness profiles $HV_{0.1}$ were performed on cross sections in the area surrounding the imprint. The measurements were made starting from the bottom of the marks and going further, with steps of 40 μm, up to a depth of 400 μm.

Profilometer analyses

On the marked fifty samples, profilometer analyses were performed by means of the Hommelwerke Tester T2000. Before the erasure, one sample for each of the ten series was examined. The diamond stylus was leant on the disc to scanning the surface in correspondence to the serial number. The surface of the disc without any affection by the punching was chosen as a reference point. Hence, it was possible to identify the valleys corresponding to each character, as well as the burrs at the edge of the impressions. For each imprint of the serial number the maximum depth was collected.

Erasure of the marks

After profilometer analyses, the stamped marks were obliterated by controlled removal of material with the aid of a hone. For the five samples of each series increasing depths of erasure were considered. Hence, the first sample of each series was erased just until the mark was no longer visible to the naked eye: this depth was named "reference level". According to previous studies [3,9,17,18,19,23,24], the depth of the original marks was also determined by measuring the difference between the original thickness of the disc and the "reference level". In order to evaluate the subsequent ability of the different reagents on the recovery, increasing grades of abrasion, starting with the "reference level" and going further with steps of 15 μm, were carried out till up an erasure depth of 60 μm.

Surface finishing

As indicated by several authors [18,19,24,25], the preliminary step to the restoration technique is polishing the sample's surfaces with acetone to remove debris, dust and particles. Moreover, several authors [1,3,8,9] remarked the importance of a mirror-like finishing, achieved employing a series of successively finer silicon carbide abrasive papers. In case of manually obliteration, Wightman and Matthew [21] suggested polishing the surface as is normally carried out for metallurgical specimen preparation. However, in other studies [6,18] the polishing was avoided, especially when the depth of plastic deformation zone is not as deep as in the case of die stamping. In fact, evidences of the deformations can be removed preventing the restoration.

In the present work, in order to evaluate the influence of the surface finishing, all the sample's surfaces were cleaned with acetone. Moreover, only the first two samples of each series were also polished with fine grade P1200 and diamond paste.

Restoration tests

Several etching recipes based on empirical studies are available in open literatures [1,3-6,8,9,15,18,20]. Five reagents suitable for steels with different composition (Table 2) were chosen to be tested on 40NiCrMo4 steel, in order to compare their sensitivity. Each series of the two different heat treated discs as described above, were etched with one of the five reagents, by the swabbing method. A cotton dub, dipped with the reagent, was laid on the surface and gently rubbing in a back and forth direction. If the etching rate is almost immediate, the sample must be straight off and washed with water or acetone. Immersion of the disc was used when the reaction between the surface and the etching reagent appeared too slow. During the etching, the recovered number may appear and became straightaway very faint. Lighting represents an important feature for the restored marks [25]; each restoration was examined under a Leica MZ6 stereomicroscope.

Table 2
Etching reagents used to restore the stamped marks on the samples.

Etching Reagent	Composition	References
1	90 g $CuCl_2$ 120 ml HCl 100 ml H_2O	M.A.M. Zaili et al. [18], S.H. Yin and R. Kuppuswamy [19]
2	25 ml HNO_3 75 ml H_2O	R.S. Treptow [9]
3	5 g $CuCl_2$ 40 ml HCl 30 ml H_2O 25 ml C_2H_5OH	B.J. Heard [1], J.H. Mathews [5], J.M. Collins [14], G.F.V. Voort [16], S.H. Yin and R. Kuppuswamy [19], A. Paholke [26]
4	6 g $FeCl_3$ 93 ml H_2O	B.J. Heard [1], R.S. Treptow [9], S.H. Yin and R. Kuppuswamy [19]
5	5 g $CuSO_4$ 60 ml H_2O 30 ml NH_4OH 60 ml HCl	B.J. Heard [1], D.M. Turley [3], J.H. Mathews [5], L.C. Nickolls [6], R. Kuppuswamy and M. Senthilkumar [7], H. Katterwe [8], R.S. Treptow [9], G.F.V. Voort [16], G. Wightman and J. Matthew [17], S.H. Yin and R. Kuppuswamy [19], G. Wightman and J. Matthew [21], A. Paholke [27]

Descriptive statistical analysis

The statistical analysis was conducted comparing the three hundred and fifty images collected after erasure to the three hundred and fifty images of the recovered characters. A systematic sampling of thirty observers was chosen: fifteen men and fifteen women aged between twenty-five and fifty-five evaluated an average of twenty-five images viewed randomly, without knowing if they were from before or after recovery.

To make a more detailed analysis it was decided to establish a rating scale, made up of four levels (Table 3). The level Zero ("*Do not see any trace or shadow of the character*") corresponds to the case of any visible letters or numbers. The level One ("*Traces or shadows not uniquely attributable to a number or a letter"*) describes the presence of traces that are non identifiable. The level Two ("*Traces not uniquely identifiable but the character is much more recognizable"*) defines the presence of traces of the number or letter that is much more identifiable, compared to the level One. However, these traces are not uniquely identifiable but the possibilities are reduced

to few cases. For instance, in the image corresponding to level Two (Table 3) the character could be number "3", number "7" or letter "Z". Finally, the level Three (*"Unique identification of the character"*) describes the case of univocal identification of the character. The collected data were analysed using McNemar and Chi-squared nonparametric tests.

Table 3
Rating scale used to evaluate the images of the characters.

Level	**Description**	**Example image**
Zero	"*Do not see any trace or shadow of the character*"	
One	"*Traces or shadows not uniquely attributable to a number or a letter"*	
Two	"*Traces not uniquely identifiable but the character is much more recognizable"*	
Three	*"Unique identification of the character"*	

3. Results

Microstructural changes induced by stamping

The optical micrographs of two cross sections of the imprints are shown in Fig. 1. It is made a comparison between normalized and tempered samples and austempered samples. In the first case, it is possible to find a preferential orientation of the microstructure in the area surrounding the imprint, as reported in Fig. 1 (a). On the contrary, the austempered sample does not exhibit this altered zone, as shown in Fig. 1 (b).

Experimental observations have shown that for normalized and tempered samples the punching operation was performed after the heat treatment because of the microstructural alteration. In contrast, for austempered samples the increased hardness due to the heat treatment prevents stamping, therefore the punching was made before austempering and, consequently, any preferential orientation of the microstructure is present.

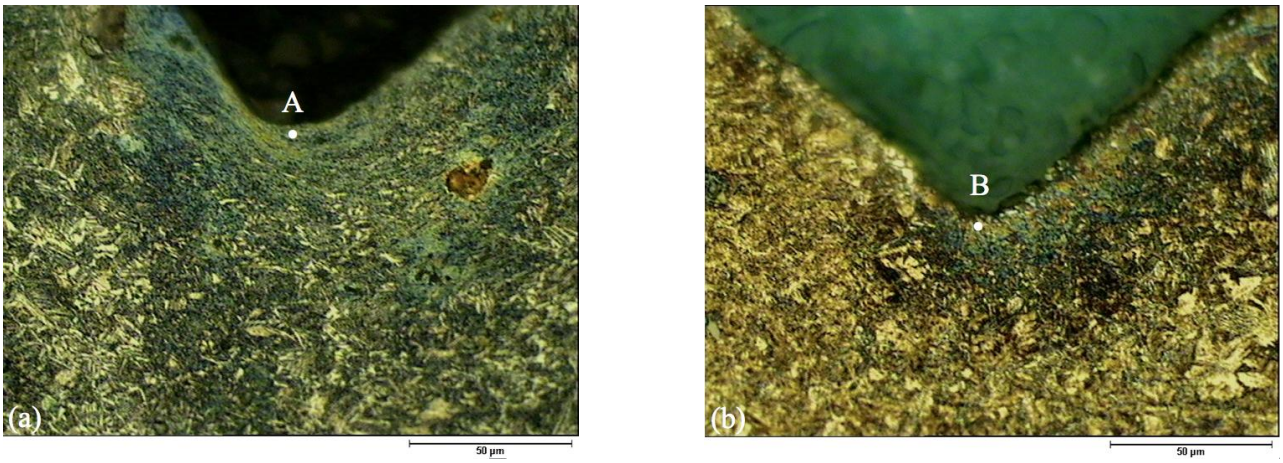

Fig. 1 Cross-sectional microstructure of an imprint after etching with Nital. (a) normalized and tempered sample. (b) austempered sample.

For better understanding this aspect, microhardness Vickers profiles in these areas were carried out and the results are shown in Fig. 2. As expected, for normalized and tempered samples it is found a decrease in hardness, moving from point "A" in Fig. 1 (a) through the sample. At a distance of 40 µm from point "A" the hardness value is $HV_{0.1}$=320 and at a distance of 400 µm from point "A" hardness decreases to $HV_{0.1}$=270. Whereas, for austempered samples a quasi-steady trend of microhardness results is observed, Fig. 2. Microhardness values are quite constant and about $HV_{0.1}$=350 from point "B" up to 400 µm through the sample.

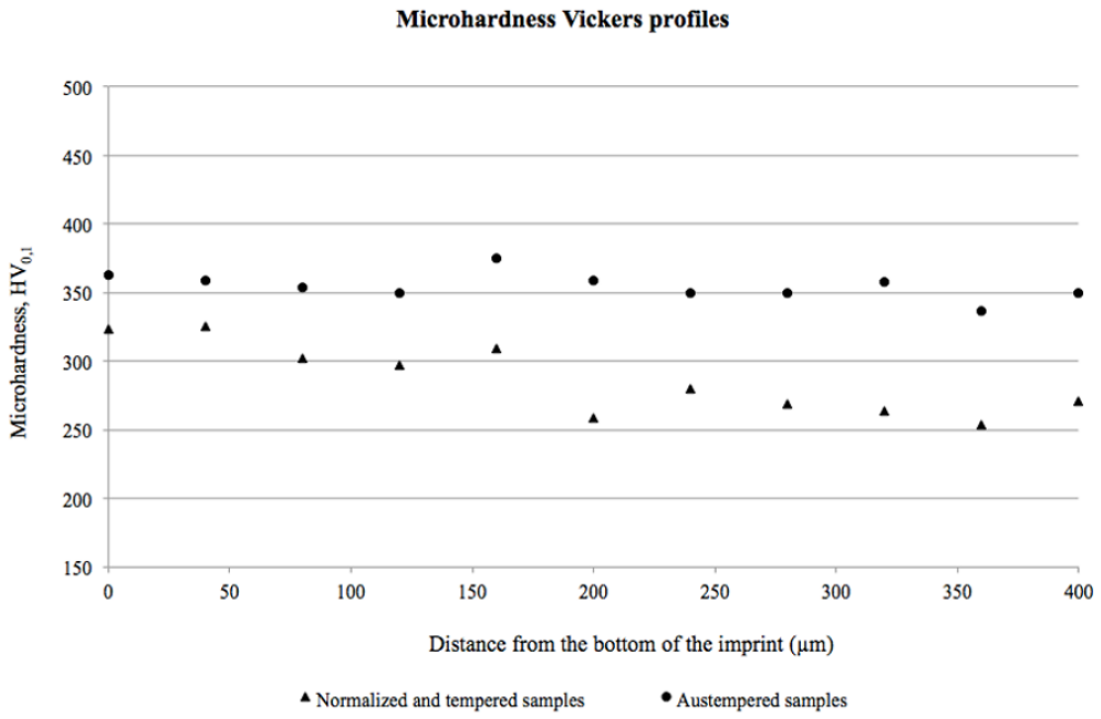

Fig. 2 Microhardness Vickers profiles for normalized and tempered samples and for austempered samples.

Depths of the stamp marks

Experimental data obtained from the profilometer analyses were evaluated by studying the maximum mark's depth for each character of the serial numbers. Considering the frequency percentages in relation with the mark's depths, which are grouped in intervals, the results show that the maximum marks' depths are between 130 and 140 µm. This outcome is in agreement with the parameters specified by the American Law Enforcement Agency "Bureau of Alcohol, Tobacco, Firearms and Explosives". Firearms' manufacturers actually follow this law and so, for identification numbers made by stamping, the mark must have a minimum depth of 80 µm [27].

During the subsequently abrasion process, the same marks considered for the profilometer analyses were also processed by a micrometer screw gauge. Mark's depths values are collected in Table 4 and these data refer to the "reference level" abrasions which were considered for the first sample of each series. The observed depths represent an average value of the entire serial number and are in accordance with the previous profilometer's results.

Table 4
Mark’s depths values for the first sample of each series.

Sample type	Serial number	Mark's depths (μm)
Normalized and tempered samples	Z32106S	140
	U32117B	130
	R83145S	120
	Z04299S	130
	Z04299F	130
Austempered samples	R32124B	130
	Z73005S	130
	V53894S	140
	Z73895S	130
	Z73895B	130

Restoration of the marks

Table 5 and 6 show a summary of the etching experiments' results for the five reagents considered. In Table 5 the ability of each reagent to achieve positive recoveries is evaluated in terms of maximum depth of erasure through which the restoration is achieved, recovery time and characteristics of the restored marks. Furthermore, Table 6 reports the number of positive recoveries at each depth of erasure depending on the heat treatment condition. The ratio between the number of restored characters and the number of erased characters, N_{RC}/N_{EC} ratio, for each reagent and for each heat treatment is also shown.

Reagent 1, commonly identified as Fry’s reagent, was able to recover characters up to 60 μm below the bottom of the mark and it is considered the most sensitive. This reagent restored fifty-two of the seventy characters considered, with a good contrast: there are not substantial differences between austempered and normalized plus tempered samples considering the N_{RC}/N_{EC} ratios (Table 6). It was observed that the application of the reagent 1 on the metal surface produced copper depositions, which were removed by gently swabbing a cotton bud soaked in reagent 2 [21]. Thus the surface become clearer accompanied with good contrast, slightly less than the surface obtained with reagent 2. Fig. 3 shows the restored marks, after erasure to a depth of 60 μm beneath the "reference level", by means of swabbing with Fry’s reagent for 15 s follow by 25 ml HNO_3 and 75 ml H_2O to remove copper depositions.

Reagent 2 was able to recover the major number of characters, since it restored fifty-seven of the seventy characters (Table 6). As reported in Table 5, this reagent recovered marks erased up to 45 μm below the bottom of the imprint. The characters were distinct and with an excellent contrast between the background and the

numbers, so that it is judge to be the most effective. The results of the recover, after swabbing for 45 s the reagent 2 on the surface's sample erased up to 45 μm beneath the "reference level", are seen in Fig. 4. Moreover, it was noticed that the developed marks were permanently visible even after a period of three months since the recovery.

As can be seen in Table 5, reagent 3 could restore characters erased up to 30 μm below the depth of the marks but with poor contrast. It was observed that the characters started to appear after the reagent was applied for several minutes: in this case the recovery took much time compared to reagent 1 and 2. Despite this high recovery time, the restored characters could be seen with great difficulty and only at certain angle with the aid of a film of alcohol on the surface's samples, to prevent surface oxidation. It was found that for normalized and tempered samples, the N_{RC}/N_{EC} ratio is much greater than for the austempered ones.

Reagents 4 and 5 were able to provide the recover of the marks only up to a maximum depth of 15 μm of erasure beneath the "reference level". Despite that, it was observed a greater number of restored characters for reagent 4 than reagent 5, which recovered just twenty-five of the seventy characters evaluated, even though the samples were etched for longer time, also up to 100 min (Tables 5 and 6). In addition, reagent 4 appeared to be more effective than reagent 5 since the contrast of the recovered characters with the background was good and remarkable, even if it was limited to slight depth of erasure. Microscopic observations demonstrated that reagent 4 did not provide positive recovery for deeper erasure even after repeated etchings. Hence, for this reagent the N_{RC}/N_{EC} ratio is 34/70.

Reagent 5 did not show good results as regards the contrast, which was good only for a few characters of the total restored ones, thus the N_{RC}/N_{EC} ratio is considerably reduced, especially for the austempered sample (Table 6).

As reported in Table 5, the use of reagent 3 and 5 required high recovery times: for this reason a cotton ball soaked with the reagent was applied on the sample's surface during the etching process.

It should be noted in Table 6 that in some cases (i.e. the two first recoveries on austempered samples etched with reagent 2 and on normalized and tempered samples etched with reagent 4) the numbers of positive recoveries are greater at higher depths of erasure. Such evidence is probably related to the specific shape of the numbers or letters that locally produces plastic deformation at different depths, in the area surrounding the stamp marks. Moreover, the number of positive recoveries at the same depth of erasure can vary considering the heat treatment conditions, because of the reactivity of the metallographic phases to the specific reagent.

Taking into account the recovery on the two samples of each series, which were polished with fine grade P1200 and diamond paste, the results showed that the N_{RC}/N_{EC} ratio is equal to 111/140. The absence of deep scratches, resulting from the abrasion, and the better contrast achieved by means of a mirror-like finishing, optimized the identification of the original marks.

Table 5
Relative sensitivity of the five metallographic reagents reported in decreasing order of sensitivity.

Chemical Composition	**Maximum depth of erasure through which the restoration is achieved**	**Recovery time**	**Characteristic of the restored marks**
Reagent 1: 90 g $CuCl_2$ 120 ml HCl 100 ml H_2O	60 µm	1-15 s	Contrast is good and the characters are identifiable up to 60 µm beneath the "reference level".
Reagent 2: 25 ml HNO_3 75 ml H_2O	45 µm	2-50 s	Contrast and sensitivity are very good up to 40 µm beneath the "reference level". The marks are reproducible.
Reagent 3: 5 g $CuCl_2$ 40 ml HCl 30 ml H_2O 25 ml C_2H_5OH	30 µm	1-45 min	Contrast is poor and the recovery take much time, the restorations are reproducible.
Reagent 4: 6 g $FeCl_3$ 93 ml H_2O	15 µm	4-900 s	Contrast and sensitivity are good; the marks are reproducible in case of slight depths of erasure.
Reagent 5: 5 g $CuSO_4$ 60 ml H_2O 30 ml NH_4OH 60 ml HCl	15 µm	5-100 min	Contrast is very poor, the characters are hardly identifiable even for those erase till 20 and 40 µm beneath the "reference level".

Table 6
Positive recoveries at each depth of erasure as a function of the heat treatment conditions.

Chemical Composition	**Heat treatment condition**	**Positive recoveries at each depth of erasure:**					**N_{RC}/N_{EC}**
		"reference level"	**15 µm**	**30 µm**	**45 µm**	**60 µm**	
Reagent 1: 90 g $CuCl_2$ 120 ml HCl 100 ml H_2O	austempered	5	5	5	4	4	23/35
	normalized and tempered	7	6	5	6	5	29/35
							Tot. 52/70
Reagent 2: 25 ml HNO_3 75 ml H_2O	austempered	6	7	7	6	2	28/35
	normalized and tempered	7	7	7	6	2	29/35
							Tot. 57/70
Reagent 3: 5 g $CuCl_2$ 40 ml HCl 30 ml H_2O 25 ml C_2H_5OH	austempered	4	3	4	2	2	15/35
	normalized and tempered	7	7	7	6	2	29/35
							Tot. 44/70
Reagent 4: 6 g $FeCl_3$ 93 ml H_2O	austempered	7	7	7	0	0	21/35
	normalized and tempered	5	6	2	0	0	13/35
							Tot. 34/70
Reagent 5: 5 g $CuSO_4$ 60 ml H_2O 30 ml NH_4OH 60 ml HCl	austempered	2	3	0	0	0	5/35
	normalized and tempered	5	5	3	1	2	16/35
							Tot. 21/70

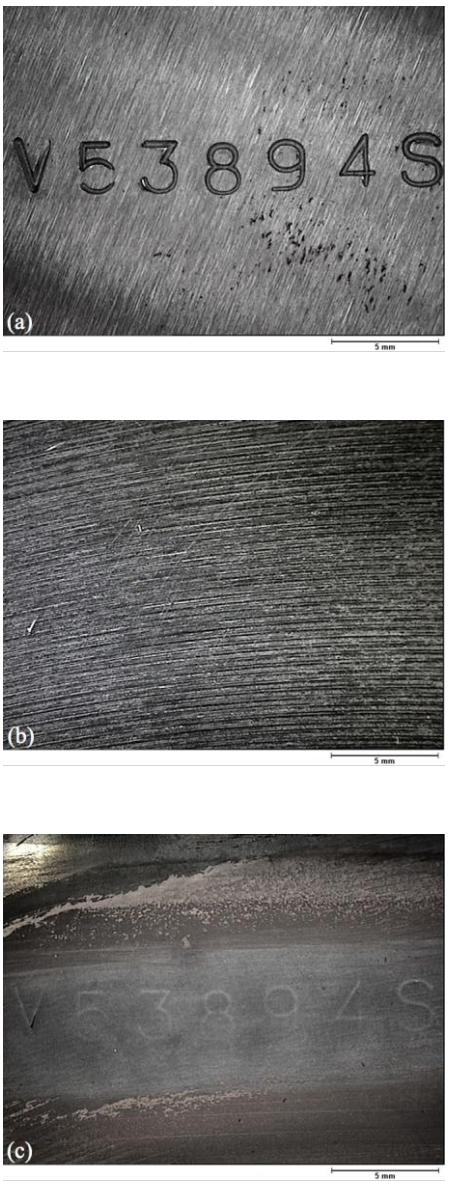

Fig. 3 Restoration of obliterated mark with reagent 1, followed by 25 ml HNO_3 and 75 ml H_2O to remove copper depositions. (a) The original stamped mark "V53894S". (b) The sample's surface after the erasure to a depth of 60 µm beneath the bottom of the imprint. (c) The recovered number after swabbing for 15 s.

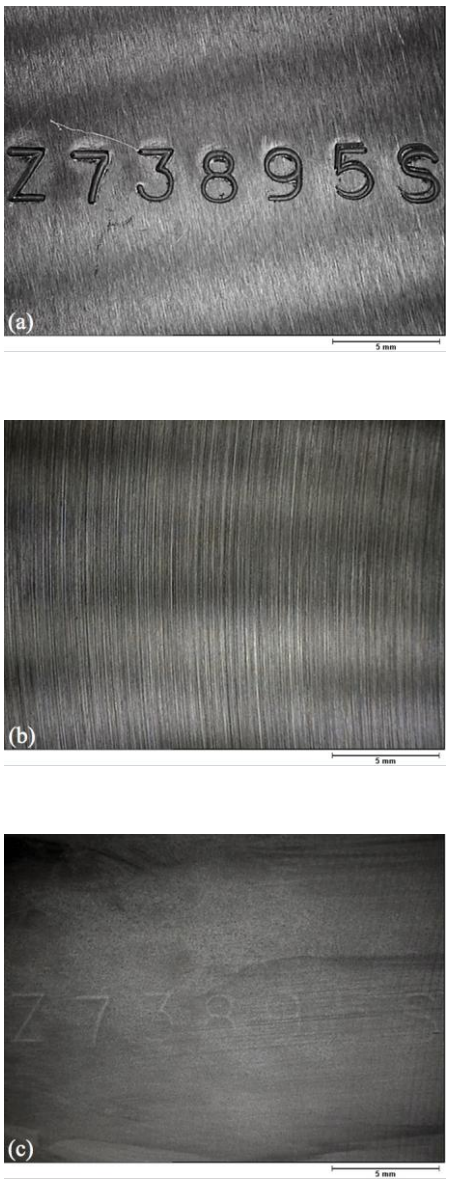

Fig. 4 Restoration of obliterated mark with reagent 2. (a) The original stamped mark "Z73895S". (b) The sample's surface after the erasure to a depth of 40 µm beneath the bottom of the imprint. (c) The recovered number after swabbing for 45 s.

Statistical testing

Fig. 5 shows the graphs of the frequency percentages for the four levels in relation with the observers' judgments. In Fig. 5 (a) are reported the observers' judgments collected after erasure of the original marks whereas in Fig. 5 (b) are reported the observers' judgments collected after the recovery with acid etching.

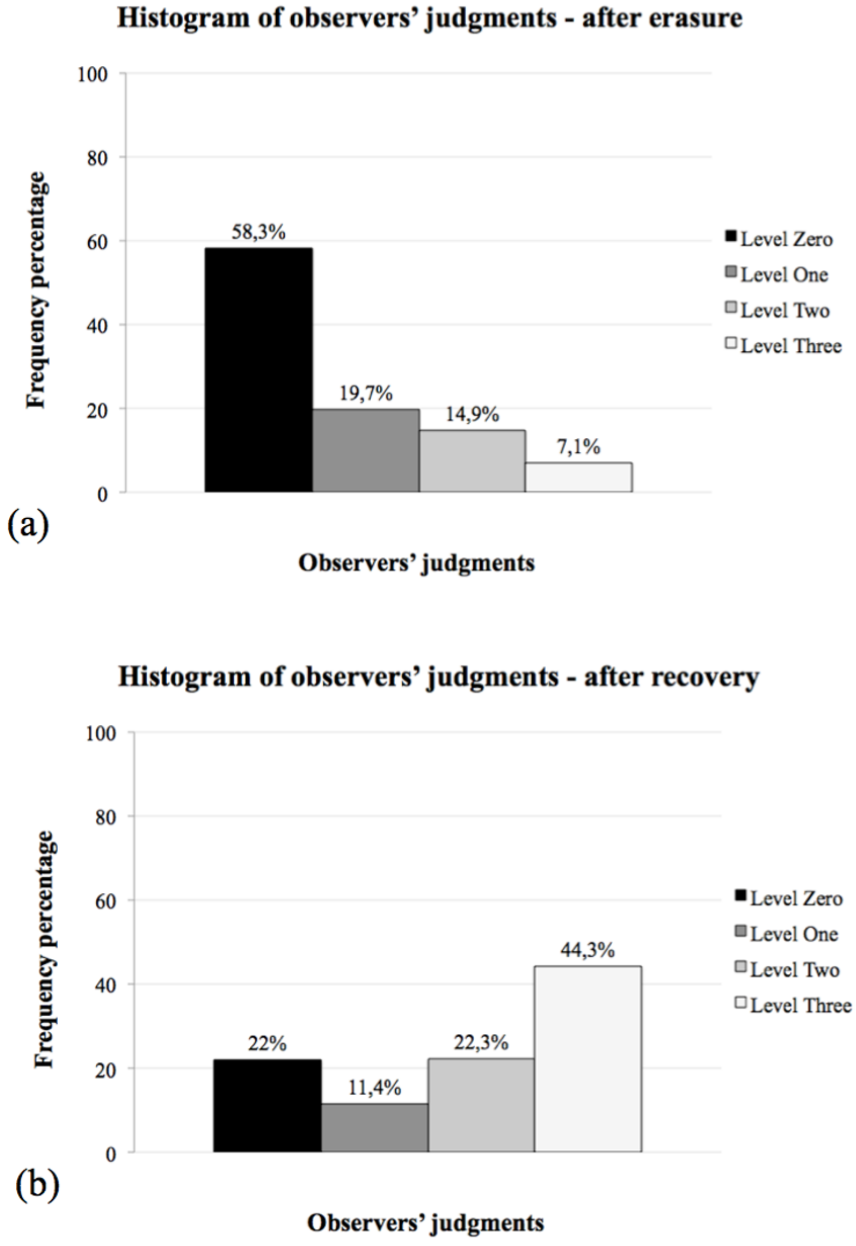

Fig. 5 Histograms of the frequency percentage for the four judgment's levels. (a) Observers' judgments collected after erasure of the original character. (b) Observers' judgments collected after recovery through acid etching.

Taking into account the frequency percentages of the observers' judgments after the erasure results show that 58.3% of the judgments is for level Zero ("*Do not see any trace or shadow of the character"*), 19.7% of judgments is related to level One ("*Traces or shadows not uniquely attributable to a number or a letter"*) and 14.9% is for level Two ("*Traces not uniquely identifiable but the character is much more recognizable"*). The latter portion corresponds to those serial number erased up to the depth of the impression, in which some characters were not completely obliterated. This has a bearing on real cases: criminal intention is to cancel the serial number just erasing tens of microns because they know that going further can be dangerous for the correct use of the weapon. The complement to 100% is given by 7.1% of evaluations corresponding to the level Three (*"Unique identification of the character"*): this portion corresponds to those characters that, despite the erasure, show traces of the original character that permit to uniquely identify them.

After recovery process by means of acid etching, as reported in Fig. 5 (b), results show that 44.3% of judgments is level Three (*"Unique identification of the character"*) and 22.3% of judgments is level Two ("*Traces not uniquely identifiable but the character is much more recognizable"*), which represent an important percentage of positive recovery. However, there are the percentages corresponding to level One and Zero, 11.4% and 22% respectively, which are related to those erased characters for which are not possible to identify the original mark.

In order to evaluate if the positive recoveries can be dependent on the sex of the operator, frequency percentages in relation with the observers' judgments were studied for women and men separately. The judgments after erasure are shown in Fig. 6 (a) whereas the judgments after recovery are shown in Fig. 6 (b).

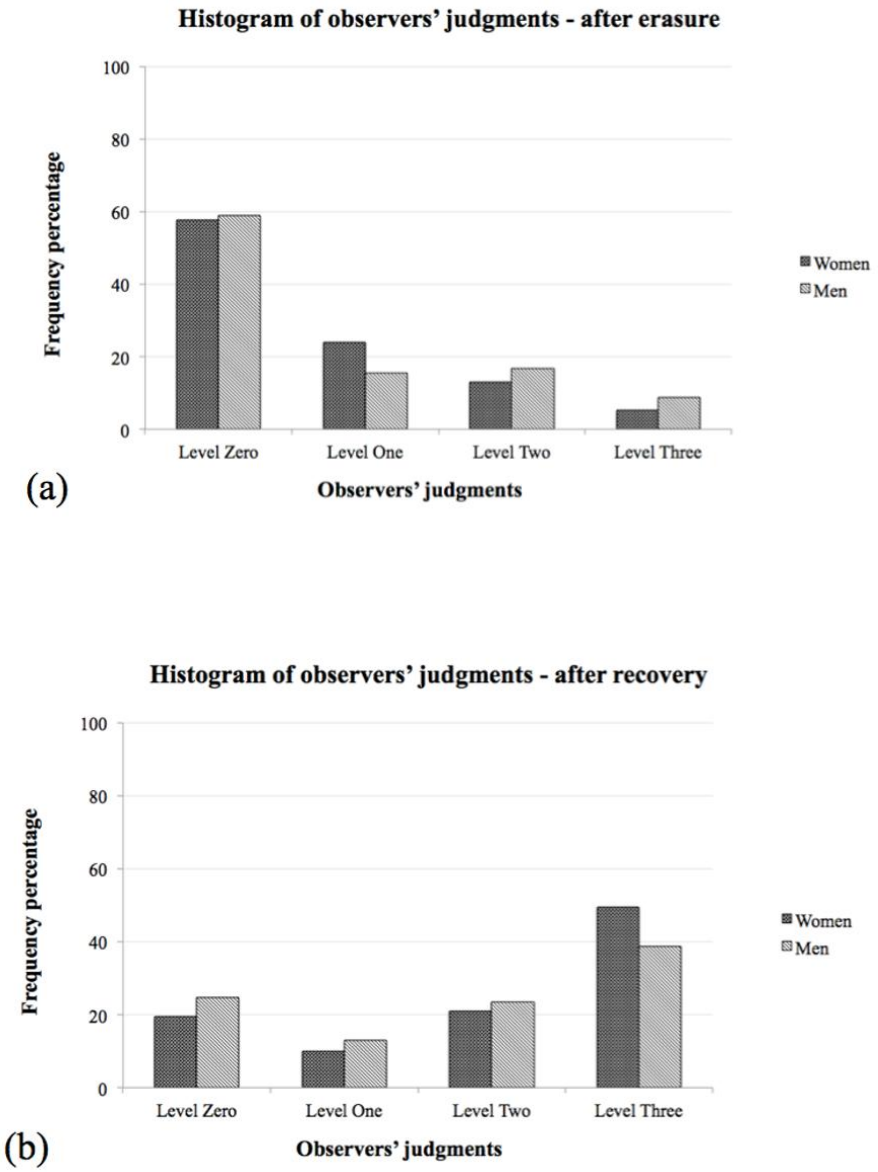

Fig. 6 Histograms of the frequency percentage for the four judgment's levels, taking into account women and men separately. (a) Observers' judgments collected after erasure of the original character. (b) Observers' judgments collected after recovery through acid etching.

Results show that both the judgments after erasure and the judgments after recovery are not significantly affected by the sex of the observers considered.

Moreover, the age of the observer has been evaluated for women and men respectively. Fig. 7 (a) and Fig 7 (b) show the histogram of women's judgments after erasure and after recovery respectively, for the three age groups considered.

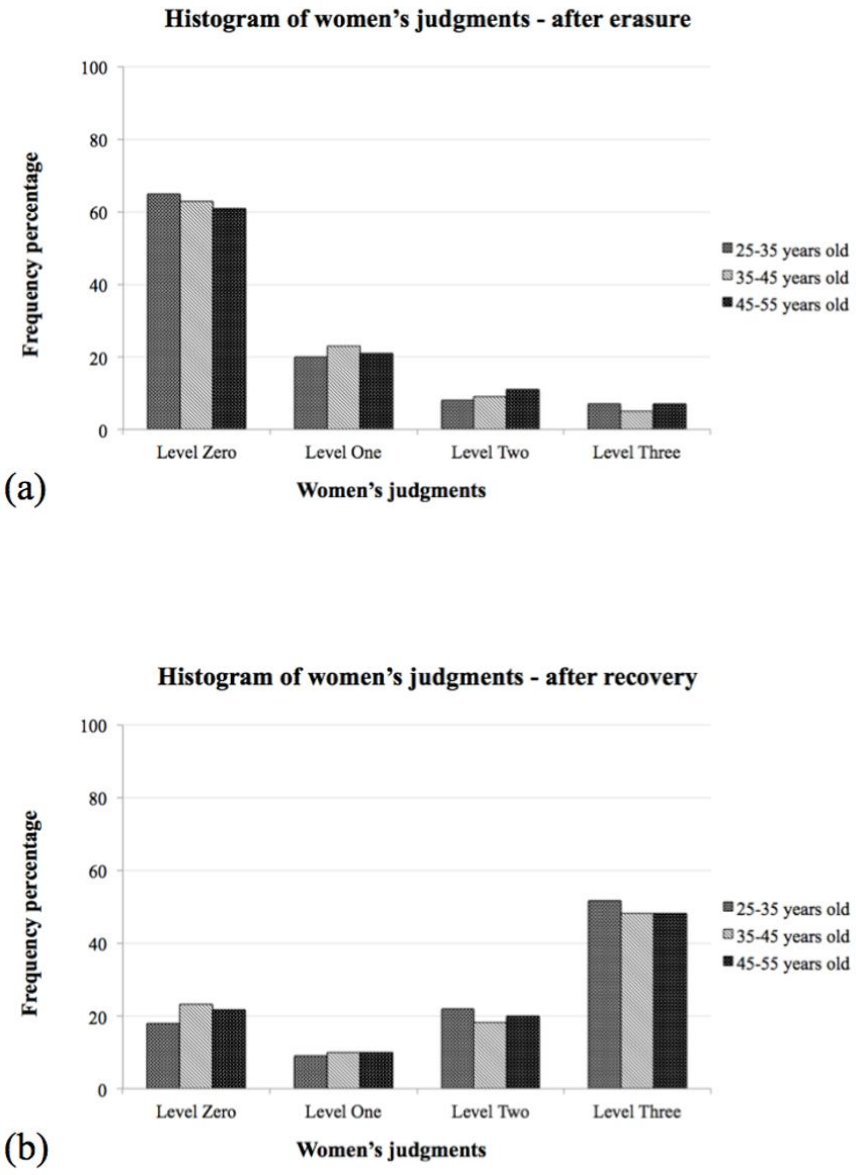

Fig. 7 Histograms of the frequency percentage for the four judgment's levels, taking into account the three age groups. (a) Women's judgments collected after erasure of the original character. (b) Women's judgments collected after recovery through acid etching.

As expected, there are no significant data corruptions with considering the different age groups of the women's chosen as observers.

Finally, in Fig. 8 (a) are reported the results for the men's judgments after erasure for the three age groups considered and in Fig. 8 (b) the results for the men's judgments after recovery.

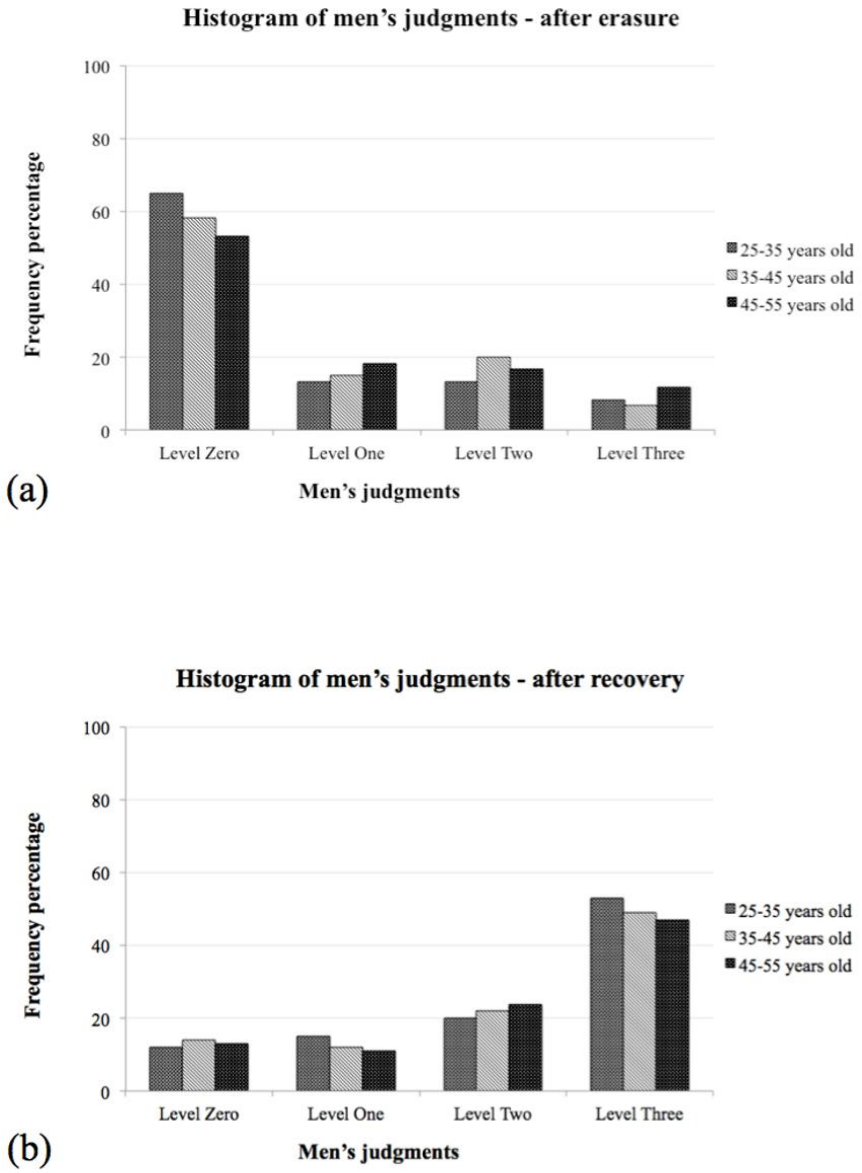

Fig. 8 Histograms of the frequency percentage for the four judgment's levels, taking into account the three age groups. (a) Men's judgments collected after erasure of the original character. (b) Men's judgments collected after recovery through acid etching.

As observed for women's judgments, also for men's judgments the different age groups considered do not affect the relative frequency percentages.

Moreover, since the judgments are an ordinal variable it is possible to consider the mode from a statistical point of view. So that, after erasure the mode is the level Zero while after recovery the mode is level Three for all the histograms taken into account.

The collected data from the observers' judgments were analysed using McNemar and Chi-squared nonparametric tests. McNemar's test allows formulating a statistical inference, without assumptions about the characteristics of the population, and it is used to assess the differences due to a certain treatment. Table 7 provides the contingency table, containing the frequencies for the considered variable. In particular, the symbol "+" means "the character is uniquely identifiable", whereas the symbol "−" means "the character is not uniquely identifiable".

Table 7 Contingency table for McNemar's test.

		After the treatment		**Row total**
		+	-	
Before the treatment	+	22	3	25
	-	133	192	325
Column total		155	195	350

Thus it is possible to formulate the null and alternative hypotheses, which are: H_0= the recovering by acid etching is not effective and H_1= the recovering by acid etching is effective.

According to the McNemar's statistic, substituting the values reported in Table 7, the Chi-square value is provided by the following equation (1):

$$X^2 = \frac{(3-133)^2}{3+133} = 124.26 \qquad (1)$$

The sampling distribution of the McNemar statistic is a Chi-square distribution with one degree of freedom. The value of the test is extremely unlikely from the distribution implied by the null hypothesis: 124.26 is greater than 6.63 which is the critical value of the Chi-square distribution with one degree of freedom and a significance level of 0.01. Hence the McNemar's test provides strong evidence to reject the null hypothesis.

Chi-squared nonparametric test is usually used to compare absolute observed data, O_j, with expected data according to a specific hypothesis, E_j. Tables 8 and 9 provide the contingency tables: Table 8 contains the absolute observed data, O_j, while Table 9 contains the expected data, E_j.

Table 8 Contingency table for Chi-squared test: absolute observed data O_j.

		After the treatment				**Row total**
		level Zero	**level One**	**level Two**	**level Three**	
Before the treatment	**level Zero**	61	38	42	73	204
	level One	10	10	22	27	69
	level Two	6	2	11	33	52
	level Three	0	0	3	22	25
	Column total	77	40	78	155	350

Table 9 Contingency table for Chi-squared test: expected data E_j.

		After the treatment			
		level Zero	**level One**	**level Two**	**level Three**
Before the treatment	**level Zero**	44.88	23.31	45.46	90.34
	level One	15.18	7.88	15.38	30.56
	level Two	11.44	5.94	11.59	23.03
	level Three	5.5	2.86	5.57	11.07

In this case the hypotheses are: H_0= the deviations, that is the differences between observed and expected data, are the result of chance and H_1= the deviations, that is the differences between observed and expected data, are the result of the acid etching treatment.

According to the Chi-squared statistic, substituting the values reported in Tables 8 and 9, the Chi-square value is provided by the following equation (2):

$$X^2 = \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{(O_{i,j} - E_{i,j})^2}{E_{i,j}} = 45.81 \qquad (2)$$

The sampling distribution of the Chi-squared statistic is a Chi-square distribution with nine degree of freedom. The value of the test is extremely unlikely from the distribution implied by the null hypothesis: 45.81 is greater than 21.67 which is the critical value of the Chi-square distribution with nine degree of freedom and a significance level of 0.01. Hence the Chi-squared test provides strong evidence to reject the null hypothesis.

4. Discussion

The possibility of carrying out a positive recovery mainly depends upon the presence of residual cold-worked regions that will be oxidized more rapidly by the reagent than the surrounding metal [22]. In the case of die stamping, it is reported that for steel the affected zone may be approximately six times as deep as the stamped marks [22].

In the present study, microstructural analyses, preformed in the region surrounding the stamp mark, reveal a residual deformation of the crystalline structure only for the normalized and tempered samples. The hardness profile from point "A" in Fig. 1 (a) through the sample is much steadier downward than the ones reported by Katterwe [8]. This can be justified considering the type of alloy: Katterwe did a microhardness profile in the area surrounding a stamp mark on X8CrNi18-8 stainless steel whereas 40NiCrMo4 steel, chosen in the present study, is not so sensitive to deformation hardening caused by punching, because of its intrinsic mechanical properties. Moreover, it should be noted that after heat treatment and plastic processing, the samples taken into account do not show marked changes of hardness because of their microstructure. In fact, it has been found the presence of a structural anisotropy related to presence of Phosphorous in the material (Table 1). Hence, it is difficult to establish how deep the plastic region under the imprint is. Conversely, for the sample subjected to austempering treatment it is accepted that the conditions, which allowed the recoveries, are due to accumulated residual stresses in the crystalline array, related to the austempering treatment. Despite that, these changes cannot be detectable with common microhardness tests.

Considering the effectiveness of the etching's reagents, it has been found that the reagent 1 is the most sensitive for the recovery on 40NiCroMo4 steels. This is in agreement with earlier works in which the authors claimed [3,8,9,19,21] that Fry's reagent was found to be very good for steels. Moreover, Treptow [9] observed that the reagent comprising 25 ml HNO_3 and 75 ml H_2O (reagent 2) reacts too rapidly on low-carbon steels while it is suitable for alloy steels. The results of the present work assess that reagent 2 is the most effective on 40NiCrMo4 steels.

Previous studies [14,19] noted that reagent comprising 6 g $FeCl_3$ and 93 ml H_2O (reagent 4) could restore marks erased only until the imprinting depth. According to these, reagent 4 has been found suitable for recovering marks only at low depths of removal under the imprint: the maximum recovery's depth was 15 μm. Zaili et al. [18] remarked that the reagent comprising 5 g $CuSO_4$, 60 ml H_2O, 30 ml NH_4OH and 60 ml HCl

(reagent 5) was more sensitive than Fry to recover erased marks, made by engraving, on low carbon steel (0.1% C). They found positive recovery for samples that were abraded up to 40 µm below the bottom of the engraving. More recently Yin and Kuppuswamy [19] reported that this reagent could restore marks on medium carbon steel (0.3% C) only up to 20 µm below the bottom of the engraving. They suggested that etching effectiveness appears to be dependent upon the carbon content but the different etching behaviour is not clearly understood [5]. The present study remarks this hypothesis since reagent 5 gives positive recovery up to 15 µm under the imprint. It was reported by Yin and Kuppuswamy [19] that the reagent 5 g $CuCl_2$, 40 ml HCl, 30 ml H_2O and 25 ml C_2H_5OH (reagent 3) could be considered effective on restoring obliterated marks like Fry's reagent. However, in this work the application of reagent 3 has roughly the same quality as Fry in terms of contrast and time for the recovery.

As regards the influence of surface finishing, the results highlight that the polishing obtained by means of acetone plus fine grade P1200 and diamond paste can improve the N_{RC}/N_{EC} ratio. The samples, which has a mirror-like finishing, provide better contrast between the restored numbers and the background: the marks appear much more distinct and recognizable. This improved surface finishing allow to a more uniform and controlled action of the acid etching. In forensic practice, emery papers are frequently used to remove scratches and gouges originate from the obliteration of the number in order to obtain a smooth finish, free from all the scratched.

Furthermore, experimental data show that there are no significant data corruptions with considering sex and age groups for both women and men chosen as observes. Statistical testing, performed by means of McNemar and Chi-squared tests, highlights the effectiveness and the goodness of the etching method employed. In particular, by means of the observer's judgments it has been proved that acid etching method's efficacy is totally independent upon the operator chosen for the analysis of the recovery's results, since unlike common experimental tests the observers were not absolutely aware of the original number as it happens for real cases of recovery. In other words, it can be stated that the observer does not affect the recovery's result achieved by acid etching.

5. Conclusions

This study has investigated the recovery of stamped marks on low-alloy carbon steel by chemical etching technique after a controlled removal of material from the surfaces of the samples. The following conclusions can be drawn:

- Reagent 2 was the most effective since it recovered the major number of characters, which were distinct and with an excellent contrast. Moreover, reagent 1 was found to be the most sensitive, since it was able to restore marks up to the maximum depth of erasure;

- Polishing obtained by means of acetone plus fine grade P1200 and diamond paste improved the N_{RC}/N_{EC} ratio and provide better contrast between the restored numbers and the background;
- Frequency percentages of the observers' judgments after the erasure show that there are no significant data corruptions with considering sex and age groups for both women and men chosen as observes;
- McNemar and Chi-squared nonparametric tests proved the effectiveness and the goodness of the acid etching on mark's restoration stamped on 40NiCrMo4 steel.

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