Technical Report


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Abstract: This paper examines whether electrolysis could be a useful method in the development of latent fingerprints on fired brass cartridge cases. The influence of electrolysis on galvanic metal corrosion was explored. We found that the clarity of the fingerprints was time sensitive and improved as acid concentration increased with lower duration of electrolysis.

Introduction

Fired cartridge cases are frequently recovered at shooting scenes and can be a valuable source of evidence if they can be linked to a specific firearm and to the individual who loaded the firearm. Upon being loaded and fired, a single cartridge goes through a tremendous amount of heat and pressure before being extracted from the firearm. This may obliterate the surface of cartridge cases, making fingerprints difficult to recover.

Fingerprint development techniques vary and are often dictated by the substrates and matrices. Fingerprint substrates

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Received November 18, 2010; accepted February 19, 2011
can be divided into porous (e.g., paper, wood, cardboard) or nonporous (e.g., metal) materials. Porous substrates may be treated with 1,8-diazafluoren-9-one (DFO), ninhydrin, and physical developer. Nonporous surfaces may be treated with carbon powder dusting, cyanoacrylate fuming, or vacuum metal deposition [1–3]. Most development methods enhance the moisture or organic residues that are left behind from the pores and glands of friction ridges. Techniques specifically for metal surfaces are water based (e.g., selenious acid, ammonia, silver nitrate, and palladium salts) [4–6]. These chemicals increase the contrast between the organic salt residue and the metal background.

Researchers have experimented with other procedures to find more reliable methods to reveal latent fingerprints on metal surfaces. Bouldin et al. [7] explored the chemical development of latent fingerprints on aluminum. They used the fluorescence of cadmium sulphide nanocomposites to covalently bond to the aqueous amino acid or carboxylic acid (lipid) components of the fingerprint residue. William et al. [8, 9] enhanced latent fingerprints using a scanning Kelvin microprobe (SKP). Their technique uses a wire probe to measure the solution of organic salt deposits on metal surfaces. The visual output shows the difference in electrochemical potentials between the areas that have fingerprint residue and areas that lack residue.

Recent research on the development of latent prints, specifically on fired cartridge cases, has been proposed by Bond et al. [10, 11], who demonstrated an experimental technique to accelerate reduction–oxidation (redox) reactions on brass. They proposed using temperatures of 200 °C, 400 °C, and 600 °C as a method for electrostatically charging the metal surface, followed by the application of black granular powders to enhance latent fingerprints. This technique is useful for cartridge cases found at arson scenes. Bond et al. [11] presented another fingerprint development process with the application of 1500 V of electrical potential followed by the application of conductive carbon powder. This method worked best after cartridges had been washed with detergent and rinsed with acetone. Bond theorized that inorganic salt ions in fingerprint residue accelerated the brass redox reaction. Bond’s results indicated that 5% of identifiable fingerprints were developed; therefore, further research is warranted to better understand the electrical properties of metal and friction ridge development.
This experiment further expanded on Bond’s application of potential voltage and analyzed the implications of chloride ions found in the friction ridge residue. Bastos et al. [12] suggested the use of chloride ions in solution to speed up the oxidization of copper. Hydrochloric acid (HCl) was chosen as a preferred reducing agent because chloride ions are known to accelerate the corrosive process. A potential voltage of 12 V was used in combination with different acid concentrations to enhance latent fingerprints by obtaining the ideal rate of galvanic reaction on brass.

Galvanic corrosion occurs when two or more metals are deposited into an electrolyte and one of them reduces faster than the other due to differences in electrical potential between the two metals. Metal reduction occurs when metal comes in contact with hydrogen atoms and gains electrons to create metal ions. Corrosive reduction changes both chemical and physical properties of the metal. The testing of metal properties during electrolysis is outside the scope of this research paper. In our research, electrolysis was tested to accelerate metal galvanic corrosion by reducing copper ions to enhance latent fingerprints.

Reduction of brass occurs once the fired cartridges are placed on the cathode end of the electrolysis. During the electrolysis, the hydrogen protons in the solution attack the metal surface, causing reduction [10]. The chloride ions from the hydrochloric acid act as catalysts and accelerate the reaction between metal and hydrogen [12]. The objective of this research is to study the enhancement of fingerprints using electrolysis on fired cartridge cases that have experienced high temperatures and obliterations during the firing process.

Materials and Methods

Data extracted during the experiment recorded the influence of acid concentration, time of electrolysis, and fingerprint matrix. The data was then divided into controlled and uncontrolled groups. The controlled group consisted of cartridges that were not fired. The cartridges in the uncontrolled group were subjected to the firing process. All collected data from the cartridges was entered into an Excel spreadsheet. The information from these two sets of data was analyzed using MINITAB 14 statistical software (Minitab Inc, State College, PA). The data was further exploited using a balanced analysis of variance (ANOVA) design to compare the significance of each variable using line graphs. In MINITAB 14, the response variables were
the quantitative and qualitative data, and all the other variables were used as influential variables. All combinations of influential variables were also compared using a balanced ANOVA design. Finally, the cartridge cases were examined using a Zeiss DSM 960 scanning electron microscope (Carl Zeiss Microscopy, LLC, Thornwood, NY) to explore any changes on the surface of the cartridge cases.

The quantitative analysis of fingerprints was performed using the data in Table 1, according to the gradient devised by Bandey et al. [13, 14]. The qualitative analysis of fingerprints was performed using Table 2.

A qualitative analysis chart was created for this experiment (Table 2). It includes three levels: (1) insufficient detail to eliminate or identify, (2) sufficient detail to eliminate (Level 1 detail available), and (3) sufficient detail to identify (Level 2 or Level 2 and 3 details available). It is important that both qualitative and quantitative analyses are performed in such a manner to make the repeatability of results achievable. It is also imperative to use at least two analysts to qualitatively and quantitatively analyze fingerprints [15].

<table>
<thead>
<tr>
<th>Value</th>
<th>Gradient Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No ridge development.</td>
</tr>
<tr>
<td>1</td>
<td>No continuous ridges. All ridges discontinuous or dotty.</td>
</tr>
<tr>
<td>2</td>
<td>1/3 of the impression had continuous ridges. The remainder had no development, or was dotty or smudged.</td>
</tr>
<tr>
<td>3</td>
<td>2/3 of the impression had continuous ridges. The remainder had no development, or was dotty or smudged.</td>
</tr>
<tr>
<td>4</td>
<td>The impression was fully developed and had continuous ridge detail.</td>
</tr>
</tbody>
</table>

Table 1
Gradient of quantitative fingerprint analysis.

The 9 mm caliber is a common cartridge found at shooting scenes. The .223 caliber has a larger surface area, thus, a greater probability for fingerprints to adhere. Therefore, brass cartridges for these calibers were chosen for this research. Brass is a copper and zinc alloy. Before the placement of fingerprints, the cartridges were cleaned with distilled water and air-dried. Loading the magazine. Before loading the magazine, the donor did wash and dry hands as necessary. Two different matrices were used: (1) sebaceous oil and (2) gun cleaning oil. Before each deposition, the donor was asked to rub his thumb across the forehead and down the bridge of the nose to obtain sebaceous oil as a matrix. He applied pressure on the cartridge, pushing it into the magazine to load it using the thumb and forefinger. The gun cleaning oil was applied in a similar fashion.
## Table 2

**Qualitative fingerprint analysis.**

<table>
<thead>
<tr>
<th>Value</th>
<th>Gradient Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Insufficient detail to eliminate or identify</td>
<td><img src="image1" alt="Example Image" /></td>
</tr>
<tr>
<td>2</td>
<td>Sufficient detail to eliminate</td>
<td><img src="image2" alt="Example Image" /></td>
</tr>
<tr>
<td>3</td>
<td>Sufficient detail to identify</td>
<td><img src="image3" alt="Example Image" /></td>
</tr>
</tbody>
</table>
Once the fingerprints were deposited, only the cartridges labeled uncontrolled were fired. Both the controlled and uncontrolled cartridges were processed using the electrolysis. Collected cartridges were processed within the first three hours, four days, and seven days. The long durations between testing were to mimic when real-time evidence from a crime scene is processed [16]. Performing the electrolysis in less than three hours after collection would be ideal, whereas processing four days and seven days after the collection was probably more realistic to actual time in which evidence reaches the laboratory for forensic examination. All samples were placed in the electrolytic solution that contained dilute hydrochloric acid. The two different solutions of 37% hydrochloric acid concentration in 1L of distilled water being tested were 1.0 mL and 0.01 mL (0.012 moles/L and 0.0012 moles/L, respectively) of acid, as shown in Figure 1. The cartridges were placed on the cathode (+) end to accelerate the galvanic corrosion reaction (Figure 2).

The solutions were placed in clear glass trays (Pyrex) that consisted of negative and positive electrodes. An electrical potential of 12 V was applied to the Pyrex containers through a wall unit distributor. It was important that both solutions of HCl were set at the same voltage to keep the electrical current constant. The duration of electrolysis was set for 5 minutes and 40 minutes for each HCl solution. Four cartridges from the controlled and uncontrolled groups were used in all combinations of variables. The cartridge cases were placed using brass cartridge holders on the positive end of the Pyrex glass tray. After the electrolysis was performed, the cartridges were washed with tap water and air dried. All of the results of the electrolysis were documented and all visible fingerprints were photographed.

**Results**

Figures 3 and 4 show that the 1.0 mL HCl solution in water yielded better fingerprints quantitatively and qualitatively. On the other hand, the .01 mL HCl solution in water resulted in lower visual clarity of fingerprints. Results after 5 minutes of electrolysis far surpassed results obtained after 40 minutes (Figures 3, 4). Fingerprints deposited on the uncontrolled fired group of cartridges indicated better quantitative results in comparison to the controlled group of cartridges. Controlled and uncontrolled groups were not significant on the qualitative visual analysis (Figures 3, 4). During the electrolysis, cartridge surfaces became slightly tinted in shades of white and blue (Figure 5). The best enhancement of fingerprints occurred after 5 minutes of electrolysis in 1 mL HCl solution using sebaceous oil as a matrix (Figure 6).

Journal of Forensic Identification
134 / 62 (2), 2012
Figure 1
Electrolysis apparatus.

Figure 2
View of cathodic end with a cartridge holder.
Figure 3
Quantitative data analysis output using Minitab 14.

Figure 4
Qualitative data analysis output using Minitab 14.
Figure 5
Cartridge casing showing ridge detail after 5-minute electrolysis treatment using 0.01 mL HCl.

Figure 6
Cartridge casings showing ridge detail after 5-minute electrolysis treatment using 1.0 mL HCl.
Discussion and Conclusion

This research speculated that electrolysis caused the fingerprint ridges to darken; the proposed reaction mechanism that caused this phenomenon is a galvanic corrosion between the copper–zinc alloy and the fingerprint residue. According to a simplified explanation of galvanic reaction, this phenomenon may be explained in that, initially, when the brass was immersed in the electrolyte on the cathodic end, the hydrogen protons reacted with the copper, which created free-flowing ions. Zinc did not freely ionize because it is not a noble metal [11]. The difference in electrochemical potential occurs between areas that have salt residues and areas that lack salt residues. This is due to the build up of localized chloride ions in areas that have salt residues and causes the galvanic corrosion to accelerate, creating darkening of the fingerprints and, in some cases, it causes copper to etch [11, 17]. Once the copper was reduced, it displaced and reacted with the cartridge’s surface consisting of salt deposits from the fingerprint residue. The chloride in the solution acted as a catalyst, speeding up this chemical reaction. (This is a simplified explanation of the galvanic reaction because the detailed electrochemical reaction is beyond the scope of this research paper.) A similar accelerated galvanic reaction between copper plates in salt water was reported by Bastos et al. [12]. Here are the half cell reactions of the electrolysis:

Cathodic: \( 2Cu^{2+} + 4e^- \rightarrow 2Cu \)

Anode: \( 2H_2O \rightarrow O_2^+ + 6H^+ + 6e^- \)

The readings of the scanning electron microscope suggested that the copper galvanically reacted with the salts found in the fingerprint residue, creating darkened ridges (Figure 1). The darkening of the brass was caused by the formation of copper chloride and copper oxide [12]. The whitening of the brass cartridges (Figure 4) was caused by the formation of zinc oxide [12]. Chlorine gas can be formed during this procedure, therefore, it must be performed under a fume hood with proper personal protective equipment such as appropriate filter cartridges.

The authors of this paper anticipated that the lower concentration of HCl would yield better result trends. However, throughout the experiment, this was not the result. The concentrations of hydrochloric acid were chosen at random so that low and high concentrations could be tested for better extrapolation of data. Further experiments are still needed with an increased gradient of the hydrochloric acid concentrations. Electrolysis duration times were chosen to test a low time range at 5 minutes and a
higher time range at 40 minutes, again for better extrapolation of data. The voltage was kept constant at 12 V; however, the current was measured when each batch of cartridges was put into the electrolysis. The current readings increased as the acid concentration and time of the electrolysis increased with significance to the visual output.

The clarity and the development of the fingerprints decreased over the 7-day time period. As initially predicted, fingerprints were time sensitive because the ionic salt secretions evaporated, thus reducing the amount of galvanic corrosion. The best results were achieved in less than three hours and after four days with the 1 mL HCl solution. The clarity of friction ridges will increase in cases where the quantity of organic salt from the deposition is higher. The fired group of cartridges showed better results compared to the unfired group. One possible explanation could be that the application of heat that was applied to the cartridges during the firing mechanism helped the ionic salt residue oxidize the metallic surface, creating a potential difference between the areas that had salt deposits verses areas that lacked salt deposits. The difference in the electrochemical potential was exploited further through electrolysis. Also, by placing the cartridge on the cathodic end, corrosion of the entire cartridge was slowed down by a process known as passivation [11]. However, in areas where there was an electrochemical potential, such as areas with salt deposits, a localized corrosion tended to spread into the metal instead of laterally across the surface [11]. In the controlled (unfired) group, the fingerprint residues were not able to adhere well enough to the surface because of the lack of heat and pressure applied to the cartridge before it was ejected from the firearm. Therefore, any fingerprint residues were easily obliterated by the galvanic corrosion.

A cartridge case analysis could be performed to match the firearm involved at a crime scene. Primarily the base and side wall are examined on the cartridge. On the cartridge base, the imprints of firing pin, breech face, ejector, extractor, rim, and extractor groove can be analyzed. On the cartridge side wall, the impression of magazine lip, chamber, mouth, ejection port, and barrel can be examined. It is important to keep in mind that the hydrochloric acid solution will obliterate the entire surface of the cartridge. Therefore, it is important to cover the base of the cartridge in plasticine so that a firearm examination can also be performed.
The limited scope of this research was caused by constraints in time and resources. There were many factors that should have been taken into account such as pressure distortion, internal firearm heat and pressure applied, number of catalysts, different voltages, substrates, matrices and compositions. The chemical mechanism speculated in this report needs to be further studied, tested, and verified before this method can be applied in the field. Hence, further research is suggested to extend the scope of latent fingerprint development on cartridges.

Further research is suggested to extend the scope of latent fingerprint development on cartridges. It is recommended that a wider range of catalysts, voltages, substrates, matrices, and compositions of the cartridges be analyzed.

Acknowledgment

The authors are indebted to the Toronto Police Service Forensic Identification Services Unit (FIS) for providing their facility, resources, and financial support that enabled this research to be conducted; Staff Inspector Stephen Harris, unit commander of FIS, for his continued encouragement and support of the forensic science internship program; the Emergency Task Force for allowing the use of the firearm range and providing an invaluable donation of ammunition; and the staff members who donated their time during the fingerprinting, loading, and firing exercise that were crucial to this research. We would like to especially recognize the following individuals for their intellectual contributions to this research: Dr. Mahinda Samarakoon (University of Toronto), Special Agent Robert Ramotowski (U.S. Secret Service), and Pat Wertheim (U.S. Army Criminal Investigation Laboratory).

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