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The interaction of fingermark deposits on metal surfaces and potential ways for visualisation



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ABSTRACT

The interaction of fingermark deposits on metals has been examined by a variety of techniques. Visualisation by film growth has been the main area of investigation through: thermal oxidation, anodising, peroxide solution, and the interaction with vapour of iodine and ammonium sulphide. Corrosion of the underlying metal has also been examined as an alternative means of visualisation.

Confocal microscopy was used to look at the film thickness and corrosion products around the prints. Scanning electron microscopy and energy dispersion of X-rays (SEM-EDX) examined a number of metal samples to investigate film growth and the elemental distribution. The observations suggest that differential oxidation was occurring as well as corrosion into the metal. Fingermark deposits on metals can corrode into the metal depending on the reactivity of the metal and leave a recoverable mark. However, fingermark deposits can also alter the rate of chemical reaction of the substrate metal by oxidation. In some cases organic matter can inhibit reaction, both when forming an oxide layer and when corroding the metal. However, signs of third level detail from pore contact may also be visible and the monovalent ions from salts could also influence film growth.

Whilst further work would need to be carried out to decide whether any of these techniques may have application in fingermark recovery, this study does suggest that fingermarks on metals may be recoverable after incidents such as fires or immersion in water.

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1. Introduction

Metals are widely used although often they are often coated for decorative purposes and corrosion protection. In the case of a fire scene the metallic objects may be the only artefacts remaining intact (e.g. petrol cans or car bodies). Similarly, firearms and cartridge cases as well as knife blades, metal railings, door handles and door push-plates are metallic objects that may be present at other crime scenes. Metal theft is also an increasing problem with war memorial plaques and copper cabling being added to lead roofing and silverware as targets for criminals. Historic artefacts in museums may also contain a latent record of who may have handled them. Whilst latent marks on metals may be developed by conventional techniques, it is important to understand the limits of recovery (for example, in a fire) and the potential for enhanced recovery.

Recent work by Williams et al. [1,2] and Bond [3–5] has increased the interest in this area. Williams used a scanning Kelvin microprobe to measure the potential across a surface film on

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http://dx.doi.org/10.1016/j.forsciint.2015.01.035 0379-0738/© 2015 Elsevier Ireland Ltd. All rights reserved. 100 µm spacing and interpolated data with a commercial software package. Chloride ions in eccrine deposits reduced the passive oxide thickness, allowing a map of the latent mark to be produced. Fingermarks could be identified even after heating (as in a fire) or after being painted over. In Bond's initial studies latent fingermarks were heated by propane burner to simulate the effect of a fire, and enhancement was sometimes observed. Bond then studied the effect of storage time and humidity on mark development and found the degree of development was independent of both these variables over the range of conditions examined. Electrostatic enhancement was investigated, and development occurred due to the difference in resistivity of different regions of the fingermark affecting the powder adhesion. It was hypothesised that heat destroys the organic components present in the perspiration residue and then a heat-induced reaction occurs. Bond proposed that 'under certain conditions, the current density at the anode can result in the formation of a localised large concentration of metal ions that attract negatively charged ions and, for chloride ions this leads to the formation of hydrochloric acid in an autocatalytic reaction which corrodes the metal'.

Wightman and O' Connor [6] used heat to enhance latent fingermarks on metals, and in their study an electrically heated

Tuble		
Metal	samples	used

Metal	Specification	Typical analysis	Thickness (mm)
Aluminium	BS1470 SIC (1987)	>99% Al	1.1
Brass	BS2874/CZ121M	58% Cu, 39% Zn, 3% Pb	0.8 or 0.3
Copper	BS2874/C101	99.9% Cu	0.35
Stainless steel	BS1449 pt 2304S31	17.5-19.0% Cr, 8.0-11.0% Ni	1.0
Mild steel	AISI-1008/AISI-1010	99.2-99.6% Fe, 0.3-0.6% Mn, 0.08-0.13% C	6.0 or 0.5
Tinned steel	BS 1449 Part 1 CR4	6 µm 99.98% Sn	0.3

furnace was used instead of a flame in order to give greater control over the heating conditions. However, it was identified that enhancement was occurring through differential oxidation with regions of the fingermark oxidising at different rates. This resulted in interference colours and these colour differences were enhancing contrast. In the case of stainless steel a range of colours were observed but with brass contrast occurred as shades of light and dark due to absorption of part of the spectrum by the brass. Subsequent work by Bond [7] using X-ray photoelectron and Auger electron spectroscopy has confirmed the differential oxidation mechanism.

There is forensic interest in recovering fingermarks off gun cartridges but high temperatures and abrasion in the weapon can destroy latent fingermarks and hence until recently firearms cartridge cases were not considered high priority for fingermark recovery but were examined primarily for tool marks. However, Bentsen et al. [8] studied a range of techniques on spent cartridge cases and found that some fingermarks could be recovered. Dominick et al. [9] demonstrated that latent marks could still be recovered after heating to 800 °C, although their study used glass and ceramic rather than metals as a substrate. Gashi et al. [10] have shown that temperatures during the discharge of firearms may be much lower than previously thought. In their study thermal imaging was carried out whilst a cartridge was being fired from a Browning pistol and the thermal profile at various time intervals during the firing were recorded using 8-9 µm radiation. Temperatures recorded were less than 450 K (180 °C) due to the thermal mass of the cartridge and gun and they were able to recover alleles from fingermarks on the fired cartridges. These studies therefore suggest that fingermarks may sometimes be recoverable after firearms incidents or arson cases.

A number of liquid phase techniques have been studied to enhance latent fingermarks on metals. Jasuja et al. [11] used aqueous electrolytes (primarily acid and base solutions) to enhance fingermarks on metals and concluded that secretions act as a barrier for reaction with the metal. As with differential oxidation, the technique is dependent on the reaction with the substrate, not with the deposit and the deposit is acting as an inhibiting barrier. Beresford et al. [12] used electrochromic deposition of polyaniline and poly(3,4-ethylenedioxythiophene) which deposits between ridges in fingermarks, again suggesting an inhibiting effect. By controlling the oxidation state colour contrast is achieved and enhances observation. McKenzie et al. [13] used electrochemical displacement in a molten salt as their preferred technique for reaction with the metal substrate and used copper or brass in a silver nitrate - choline chloride - urea - ethylene glycol eutectic. A displacement reaction occurs with copper replacing the more electropositive ions in the molten salt electrolyte. Other displacement reactions have also been investigated, for example the work of Migron et al. using palladium [14].

Both Cantu et al. [15] and Leben and Ramotowski [16] report on the use of gun-blue treatment of cartridge cases and the copper selenide deposit could potentially reveal latent marks. Again, reaction is occurring between the metal and the reagent to form a film, but residues from fingermarks inhibit deposition and these can be enhanced by controlled oxidation of the copper selenide film. According to McDermott [17], James has recently reported a patination process for recovering fingermarks on ammunition, although details are still to be published. A student project in Hong Kong in 2002–2003 [18] examined the possibility of electrolysis for fingermark recovery and presented good recovery of fingermarks on reactive metals, but little else seems to have been reported on electrolysis apart from recent work by Nizam et al. [19] recovering fingermarks on brass cartridge cases by electrolysis.

If it is postulated that different regions of the metal substrate can be oxidised at different rates and that the ridges of the fingermark are affecting growth of the oxide film, then control of the rate of oxidation may provide a means of improving enhancement. An alternative method for film growth on metals is the use of electrolysis or other oxidising agents such as iodine and ammonium sulphide which are known to produce interference fringes on copper [20] and may therefore present a non-thermal route to enhancement. The present study was therefore carried out in order to better understand how fingermarks affect chemical reaction of the metal substrate and to investigate other film growth methods.

2. Experimental

2.1. Oxidation: thermal enhancement

Metal discs were cut to approximately $5 \text{ cm} \times 5 \text{ cm}$ squares, and fingermarks were loaded from three donors after they had washed their hands followed by 30 min inactivity to allow eccrine sweat to predominate in the mark. Loaded discs were photographed then placed on a metal tray before being placed inside the pre-heated furnace. The heating cycle looked at the effect of varying times of heating since the amount of reaction depends on time as well as temperature. After 1 min the tray was removed, allowed to cool, photographs were taken, and the tray returned to the furnace for a further 3 min. This was repeated with 5, 7 and 9 min intervals. Three temperatures were employed for each metal, and four metals were investigated: brass, stainless steel, mild steel and copper (Table 1) and operating conditions are given in Table 2. Marks were graded on a 0–4 scale [21].

Poor enhancement occurred on 6 mm mild steel and a short series of tests was carried out on 0.5 mm sheet mild steel to investigate whether heat transfer was an issue and samples were heated at 400 °C and 600 °C for a 5 min period. Samples of each metal were also tested with different methods of support (on a metal tray or raised on a ceramic boat) in case heat transfer or air

Table 2Test conditions for metal oxidation.

Metal	Temperature (°C)	Times (min)
Brass	200, 400, 600	1, 3, 5, 7, 9
Copper	200, 400, 600	1, 3, 5, 7, 9
Stainless steel	600, 750, 900	1, 3, 5, 7, 9
Mild steel	450, 650, 850	1, 3, 5, 7, 9

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