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Visualization of Latent Fingerprint Corrosion of Metallic Surfaces

ABSTRACT: Chemical reactions between latent fingerprints and a variety of metal surfaces are investigated by heating the metal up to temperatures of ~600°C after deposition of the fingerprint. Ionic salts present in the fingerprint residue corrode the metal surface to produce an image of the fingerprint that is both durable and resistant to cleaning of the metal. The degree of fingerprint enhancement appears independent of the elapsed time between deposition and heating but is very dependent on both the composition of the metal and the level of salt secretion by the fingerprint donor. Results are presented that show practical applications for the enhancement to fingerprints deposited in arson crime scenes, contaminated by spray painting, or deposited on brass cartridge cases prior to discharge. The corrosion of the metal surface is further exploited by the demonstration of a novel technique for fingerprint enhancement based on the electrostatic charging of the metal and then the preferential adherence of a metallic powder to the corroded part of the metal surface.

KEYWORDS: forensic science, latent fingerprint, print visualization, metal surface

Where latent fingerprints are deposited on metal surfaces, common enhancement techniques include powdering, vacuum metal deposition, and various chemical treatments such as cyanoacrylate fuming, dyeing, and immersion in small particle suspensions (1–3). The technique selected depends on the history of the item being treated, for example, whether it has been exposed to elevated temperatures, wetted, etc. (4).

Recent workers have looked to extend the range of techniques available for enhancing latent fingerprints, particularly when deposited on metal surfaces. Bouldin et al. (5) described the chemical development of latent fingerprints on aluminum by the fluorescence of cadmium sulphide nanocomposites bonded to either the aqueous amino acid or carboxylic acid (lipid) components of the residue, a strategy that is seemingly independent of whether the item had been wetted.

Bersellini et al. (6) proposed a novel process involving the electropolymerization of pyrrole (an aromatic compound) on metal surfaces containing a lipid rich fingerprint, the fingerprint acting as an insulator to the electrochemical process. Bersellini et al. stated that their technique was particularly applicable to firearms, especially unfired weapons made of Ergal (a hard aluminum alloy, also known as Al 7075). The development of fingerprints on both fired and unfired cartridge cases has also been considered by other workers in terms of redox etching techniques (7,8), aqueous development techniques (9), and metal vapor deposition (10).

Most recently, Williams et al. (11,12) have demonstrated fingerprint visualization using a Scanning Kelvin Microprobe. This technique is based on a measurement of the potential difference arising between a wire probe and a metal surface due to differences in their respective work functions. The magnitude of this potential difference is affected by electrolytes present in solution on the surface of the metal, which, in the case of fingerprints, are ionic salts such as sodium chloride (NaCl) present in the fingerprint residue. Ionic adsorption and redox corrosion reactions at the metal surface produce the observed variations in potential difference across the metal surface. By measuring this variation in potential, an image of the fingerprint was visualized in terms of potential difference. The usefulness of this technique was demonstrated further by successfully visualizing an image of fingerprint residue after heating the metal substrate to 600°C (11), covering the metal surface with layers of smoke (12), and spray painting the metal surface with a clear cellulose lacquer (11). In all cases, the reaction between the ionic salts in the fingerprint residue and the metal surface enabled the Kelvin probe to successfully image the fingerprint. By modifying their apparatus, Williams et al. also demonstrated the scanning Kelvin probe technique on non-planar metal objects (such as cartridge cases). As discussed above, fingerprint visualization on spent cartridge cases has attracted considerable attention for many years, not least because of the problems it has presented in terms of heat damage to the residue caused during the firing process (13).

In this paper, we expand further Williams et al.'s recent results and consider in more detail the action of heat on fingerprints deposited on a variety of metal surfaces. We consider this in terms of the likely chemical processes taking place at the fingerprint metal interface and how this might be affected by the variation in the composition of fingerprint residue between individuals. These results are then used to demonstrate the visualization of fingerprints from metal surfaces that have been:

(i) Subject to both elevated temperatures and smoke or soot contamination as might be experienced in an arson crime scene (14).

(ii) Spray painted with an acrylic derived primer followed by a cellulose derived topcoat.

(iii) Subject to elevated temperatures as might be experienced on a cartridge case during firing.

The redox corrosion reactions between the metal surface and ionic salts present in the fingerprint residue are then exploited to demonstrate the initial results of a novel technique for enhancing fingerprints. This technique applies an electrostatic charge to the metal object and then preferential adherence of a metallic powder to the corroded part of the surface is used to visualize the fingerprint.

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Experimental Details

Materials

Samples of 1 mm thick brass, 68% copper and 32% zinc by weight, copper, steel (DC01), and aluminum were obtained from Nobles Engineering, Northampton, UK and cut into 50 mm diameter disks. Prior to any fingerprint deposition, all samples were washed in warm water containing a few drops of a commercial detergent (containing both anionic and nonionic surfactants). Following this, all samples were washed in distilled water, acetone, and then again in distilled water. Finally, each sample was dried with a paper towel. Fingerprints were deposited by pressing a finger onto the metal surface. All fingerprint donors washed their hands with soap and water 20 min prior to depositing fingerprints and no artificial stimulation of sweat was employed such as placing the hand in a plastic bag (10) or wearing a latex glove prior to deposition (15). To evenly distribute sweat, donors rubbed their hands together prior to deposition.

Methods

All samples were heated by placing the metal over a propane gas burner with the fingerprint deposit not directly in contact with the flame. A K-type thermocouple probe was placed on the metal adjacent to the fingerprint residue and the temperature of the metal recorded by means of a digital thermometer. The temperature of the metal samples was raised steadily with heating times of up to a few minutes. After the required temperature had been reached, samples were allowed to cool naturally in air.

Results and Discussion

Heating Fingerprint Residue Deposited on Brass

In order to examine any effects arising from the time interval between depositing a fingerprint on a metal surface and heating it, fingerprints were deposited on brass from 40 different donors and then left for time intervals of <5 min, 24 h, or 7 days prior to heating. As other workers have taken crime scene fingerprints to be *c*. 1-day-old when recovered (16) these time intervals seemed a reasonable span of what might be encountered at crime scenes. Samples were heated to 200°C, 400°C, and 600°C, encompassing the range of heating used by Williams et al. (11).

Each donor provided nine fingerprints in total, one in each of the above three time and temperature categories and used a different finger for each deposition. This produced a total of 360 depositions.

The results of the heating showed a great deal of variation in the amount of fingerprint ridge detail disclosed and produced a range of ridge detail from none at all to full development. Figure 1 shows typical full development for the three temperature categories where the heating was carried out <5 min after the print was deposited. It can be seen from Fig. 1 that the heating has produced clear full development of the ridges. An attempt was then made to powder the fingerprints by the application of a black granular powder applied by means of a squirrel hair brush (17), the results being shown in Fig. 2.

Figure 2 shows that, while the powder has adhered to the fingerprint ridges, little has been gained by way of improved clarity of the ridge detail.

It is interesting to note that, despite being heated to up to 600°C, it was still possible for powder to adhere to the residue. The metal disks shown in Figs. 1 and 2 were then washed in a solution of warm water containing a few drops of the commercial detergent used to initially clean the disks. The disks were rubbed vigorously with a nonabrasive cloth to remove all traces of the black powder and any fingerprint residue that might remain. Figure 3 shows the same brass disks after this process and it can be seen that, while the black powder has been removed, the impression of the fingerprint in the metal is impervious to this type of cleaning.

On samples where some, but not a full, development of ridge detail was obtained the disclosed pattern of ridges ranged from a few discrete dots, to a pattern of dots with a few continuous ridges, Fig. 4 showing a typical example.

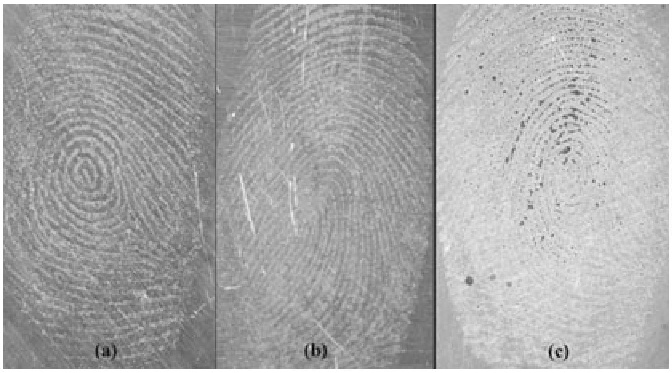

FIG. 1—*Typical full ridge detail development for fingerprints deposited on brass and heated to (a) 200°C, (b) 400°C, and (c) 600°C < 5 min after the prints were deposited.*

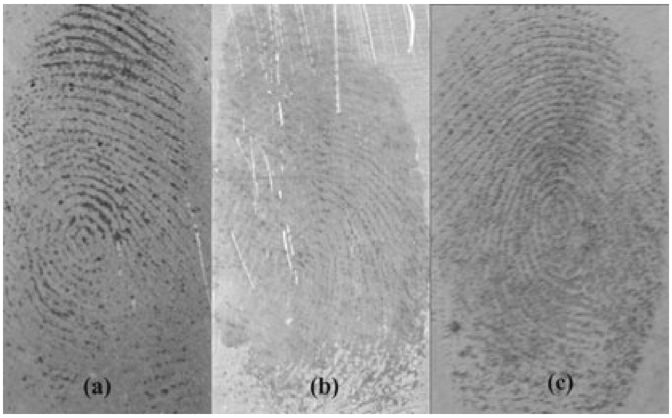

FIG. 2—*Fingerprint impressions shown in Fig. 1 after the application of black granular powder.*

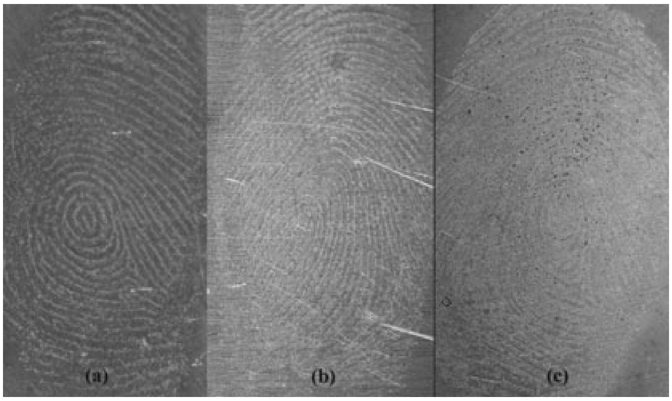

FIG. 3—*Fingerprint impressions shown in Fig. 1 after washing.*

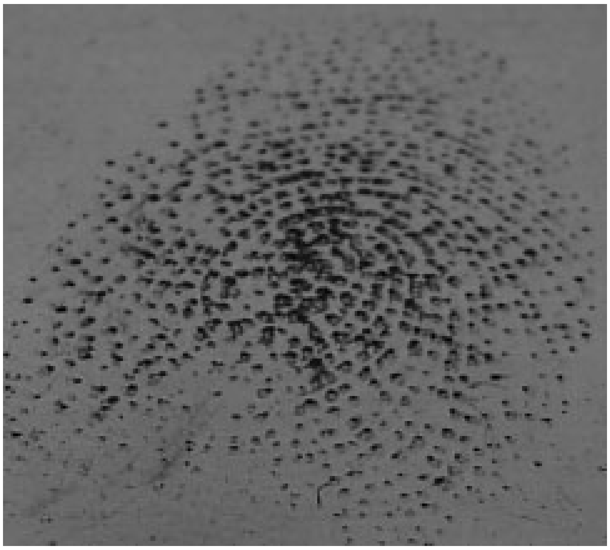

FIG. 4—*Typical partial ridge detail development for fingerprints deposited on brass and heated to 400°C <5 min after the prints were deposited.*

Such a pattern of development shown in Fig. 4 is consistent with that described by Thomas (18), who observed eccrine rich fingerprint deposits taking the form of independent circular droplets with (often) NaCl crystals being visible in the regions corresponding to the pores in the papillary ridges of the fingers. A similar observation made during these experiments is shown in Fig. 5 as a scanning electron micrograph image. Figure 5*a* shows what appear to be droplets on the metal surface, which in Fig. 5*b* have the appearance of a dried, cracked film. X-ray fluorescence of the droplets revealed the presence of chlorine.

The variation in the degree of ridge detail development between donors can be explained in terms of variations in the amount of salt being secreted by different donors (19). An association between chloride salt secretion and metal corrosion because of fingerprint deposition has been known for many years (20) as chemically aggressive chloride ions will combine readily with metals to form metal salts (21), the reaction being accelerated by elevated temperatures (22).

At room temperature the reaction is initiated through the coupling of two primary corrosion reactions: an anodic (oxidation) reaction

$$M \rightarrow M^{Z+} + Ze^- \qquad (1)$$

in which M represents a metal, and a cathodic (reduction) reaction

$$2e^- + H_2O + 1/2O_2 \rightarrow 2OH^- \qquad (2)$$

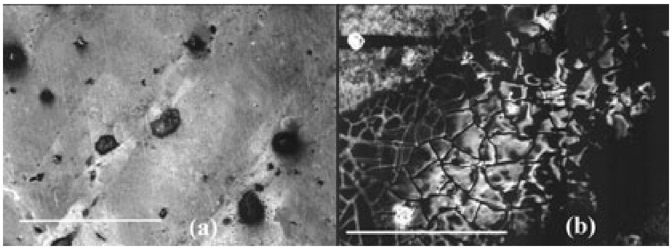

FIG. 5—*Scanning electron micrograph of untreated fingerprint residue on brass showing (a) droplets of residue (white bar = 600 µm) and (b) close up of droplet (white bar = 50 µm).*

These produce the reaction

$$M + H_2O + 1/2O_2 \rightarrow M(OH)_2 \qquad (3)$$

which cathodically protects the metal from further corrosion by slowing down the anodic reaction, a process known as passivation (22).

Electrons liberated in Eq. (1) travel to the cathode through the conducting metal M, as illustrated in Fig. 6.

Under certain conditions, the current density at the anode can result in the formation of a localized large concentration of metal ions that attract negatively charged ions and, for chloride ions, leads to the formation of hydrochloric acid in an autocatalytic reaction

$$M^{Z+} + ZCl^- + ZH_2O \rightarrow M(OH)_Z + Z(H^+ + Cl^-) \qquad (4)$$

In this localized area, the pH of the solution decreases and the concentration of the Cl^- ion increases. This can lead to what is termed pitting corrosion (22), which is a form of localized corrosion that tends to spread down into the metal rather than laterally across its surface and creates a pit in the metal. The lack of lateral spreading is a result of the passivation of the surface away from the pit.

The formation of a localized large concentration of metal ions is favored by the growing anodic pit occupying a small area relative to the cathode as this smaller area produces an anode current density much greater than the cathode current density (22).

Pitting corrosion can be initiated when the open circuit potential of a mixed electrode undergoing corrosion (known as the corrosion potential) exceeds a critical level known as the critical pitting potential (E_b). The value of E_b has been shown to decrease linearly as the logarithm of anion concentration (such as Cl^-) increases (22). Similarly, E_b has been shown to decrease as the temperature of the metal increases (22).

The effect observed in Fig. 4 is consistent with pitting corrosion at points where the chloride ions were deposited from papillary ridge pores. The development of full ridge detail as shown in Fig. 1 is indicative of the joining up of the discrete pools of chloride ion rich eccrine sweat to form continuous lines coincident with the contact points between the fingerprint ridges and the metal surface. Thomas and Reynoldson (23) demonstrated that eccrine rich fingerprints tend to produce continuous lines of deposit and these may act as a carrier to distribute the chloride salts throughout the contact points. Figure 7 shows a scanning electron micrograph of an eccrine rich fingerprint deposited on brass prior to any treatment and which demonstrates this continuous line of deposit.

Fingerprint deposits left for either 24 h or 7 days prior to heating produced similar results to those described above with Fig. 8 showing typical examples of full ridge development from samples left for 7 days.

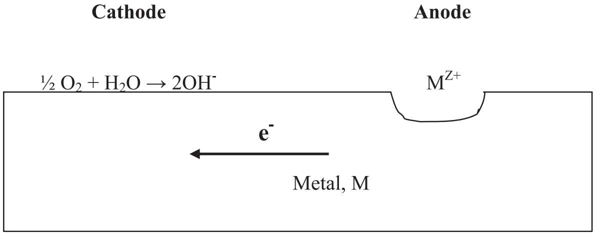

FIG. 6—*Diagrammatic representation of electron flow through a conductor undergoing electrochemical corrosion.*

Given the variation in the degree of ridge detail disclosed by the heating of fingerprints from the 40 donors, each of the 360 fingerprints deposited were graded based on the quality of ridge detail. For this, the grading system devised by Bandey (24) was used and this is reproduced in Table 1.

Each of the 360 prints (which were all taken at the same time) was graded according to the above and the results shown plotted in Fig. 9. Encouragingly, the majority of the 360 fingerprints donated (53%) produced either a grade 3 or grade 4 which, in terms of crime scene fingerprints, would make them suitable for identification.

It is also interesting to note that, amongst the 40 donors, 27 deposited fingerprints where different fingers produced different grades, the differences being up or down by one grade. This suggests that the level of salt secreted by a given individual at a given time may well vary between fingers. This is an important consideration for workers reporting techniques where success relies on the salt content of the fingerprint residue such as the Scanning Kelvin Microprobe discussed above and also micro-X-ray fluorescence, reported recently by Worley et al. (15).

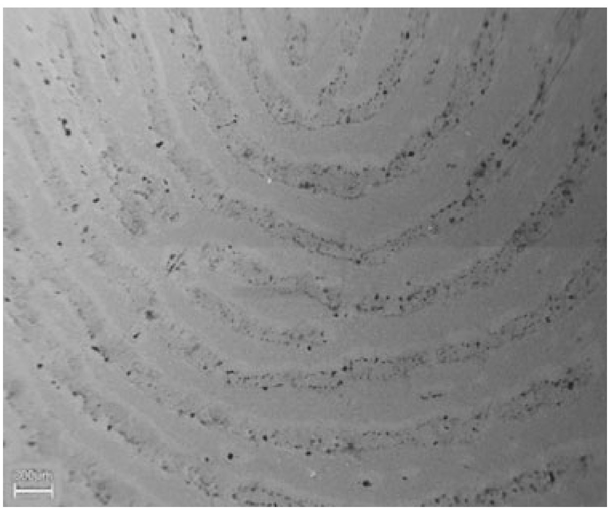

FIG. 7—*Scanning electron micrograph of untreated fingerprint residue on brass showing continuous lines of deposition (white bar = 300 μm).*

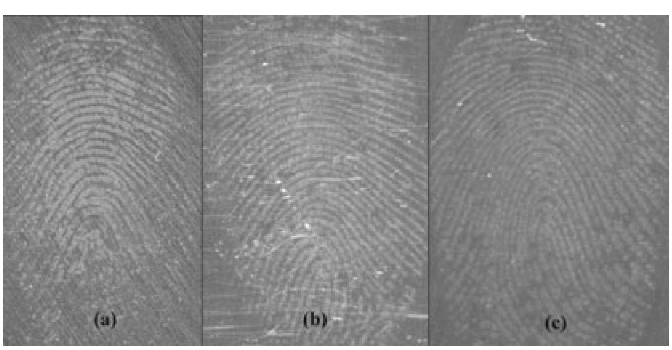

FIG. 8—*Typical full ridge detail development for fingerprints deposited on brass and heated to (a) 200°C, (b) 400°C, and (c) 600°C 7 days after the prints were deposited.*

TABLE 1—*Grading system for determining the quality of ridge detail for enhanced fingerprints devised by Bandey (24).*

Grade	Comments
0	No development
1	No continuous ridges. All discontinuous or dotty
2	One-third of mark continuous ridges (rest no development, dotty)
3	Two-thirds of mark continuous ridges (rest no development, dotty)
4	Full development. Whole mark continuous ridges

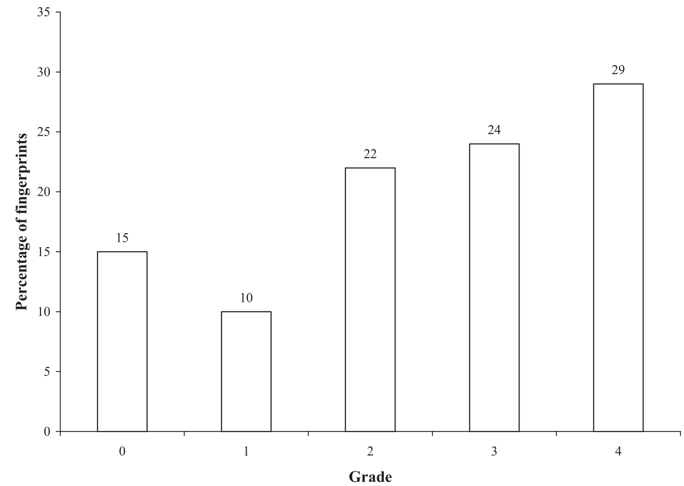

FIG. 9—*Grading of 360 fingerprints deposited on brass disks by 40 donors.*

From the above, the ability to enhance fingerprints appears to be independent of the time interval between deposition and heating, which would support an explanation that the corrosion is determined primarily by the presence of a chemically aggressive element such as chlorine.

A further demonstration of this effect was undertaken by cutting brass disks into two equal semi-circular disks, placing two halves back together to make a circular disk and then depositing a fingerprint on the disk such that part of the deposition lay on each of the two half-disks. Such a technique to separate fingerprint residue on metal surfaces has been employed previously by other workers (5). One semi-circular disk from each deposition was heated to 400°C *c*. 5 h after deposition and the other semi-circular disk placed in a desiccator. The desiccator was used to observe any effect on fingerprint visualization that removing the water content from the fingerprint residue might have. Fingerprint deposits were taken from the same 40 donors (one fingerprint deposit from each donor) with each semi-circular disk containing approximately half of the deposit. The semi-circular disks placed in the desiccator were left for varying periods of between 48 h and 7 days and then also heated to 400°C. As was found in the above experiments, the degree of fingerprint ridge detail development varied amongst the 40 donors. However, the degree of development between the two halves of each deposition did not vary irrespective of the length of time a sample was left in the desiccator. Figure 10 shows examples of typical full development. Thus, as described above, the ability to enhance the fingerprint by means of heat-induced corrosion can occur with the fingerprint residue in an anhydrous state. The anhydrous development of fingerprint ridge detail is considered further later in this paper.

A simulation of the effect of fingerprint residue deposited on metal in an arson crime scene was then undertaken by placing brass disks into a controlled fire. As demonstrated above, and also as reported by Williams et al. (11), the fire should act as a heat source for the required redox reaction. Fresh fingerprint deposits were taken from each of the 40 donors (one fingerprint on a brass

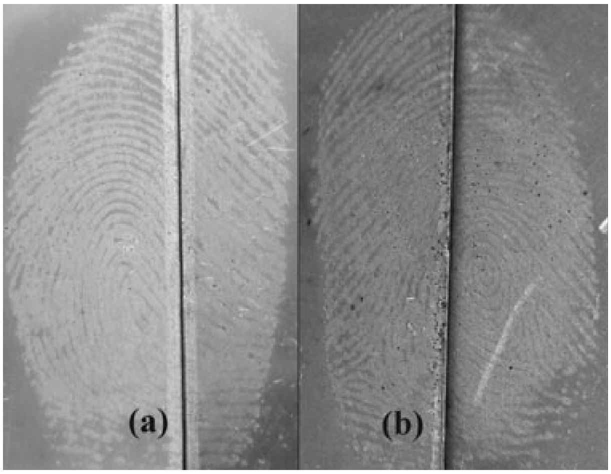

FIG. 10—*Typical full ridge detail development for fingerprints deposited on brass and heated to 400°C. Right-hand side of both (a) and (b) heated* c. *5 h after deposition. Left-hand side of (a) heated after 48 h in desiccator and (b) after 7 days in desiccator.*

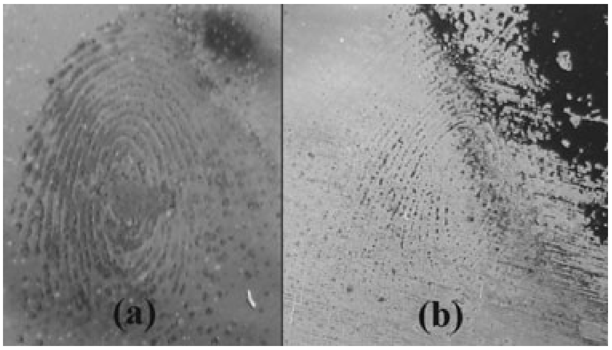

FIG. 11—*Typical ridge detail development for fingerprints deposited on brass and heated in a controlled fire. (a) was positioned around the edge of the fire and (b) positioned within the fire.*

disk from each donor) and these were placed into a controlled fire *c.* 24 h after being deposited. The fire was prepared by soaking a cloth in paraffin (to produce a smoky fire) with wood and plastic placed on top of the cloth. Some brass disks were positioned around the edge of the fire (not directly in contact with the burning material) while others were placed within the burning material. The fire itself was contained within a cast iron stove and, after lighting, the air supply to the stove was restricted to produce a reducing atmosphere as might be experienced in an arson crime scene (14). The air temperature inside the stove was measured by means of a K-type thermocouple probe and, at its peak, reached a temperature of 390°C. The fire burnt for several hours and was left to cool naturally. Upon removal from the fire, all the brass disks were covered in a layer of soot, which completely obliterated any fingerprint detail and this was removed by washing the disks in warm water containing a few drops of commercial detergent. The disks were rubbed vigorously with a non-abrasive cloth to remove all traces of soot. Those disks that had been in contact with the burning material also had a black deposit, possibly wood tar, which was removed by vigorous rubbing with a glass fiber pencil.[1] As might be expected, the brass disks displayed a range of ridge detail as has been discussed above. Figure 11 shows typical examples of ridge development with Fig. 11*a* showing ridge development for a disk positioned around the edge of the fire and Fig. 11*b* a disk positioned within the fire. The black area visible in the top right of Fig. 11*b* is part of the black (tar) deposit not yet removed and which is still covering part of the fingerprint ridge detail.

Two recent studies have highlighted the difficulties of recovering fingerprints from a range of objects present in a fire scene (25,26). Bleay et al. (25), in particular, investigated fingerprint recovery on a range of surfaces exposed to fire, including metal, where they found marks can become "baked" onto metal surfaces. While considering a visual examination as a means of detecting these "baked on" fingerprints, Bleay et al. concluded:

It is expected that above 200°C most of the organic components of the latent marks will have been destroyed, leaving only the inorganic salts. If the surface has not been wet, these salts will be present to react with superglue.

We have demonstrated that these inorganic salts can themselves react with the metal substrate producing an image of the fingerprint that survives both high temperatures and vigorous post-fire cleaning to remove soot and other fire-related deposits. Indeed, contrary to Bleay et al.'s observation that fingerprints are more likely to survive if the item has not been exposed to temperatures >300°C, for brass substrates, a high temperature can increase the redox reaction and thus preserve an image of the fingerprint beneath fire deposits.

The effect of covering fingerprint residue with a layer of paint was then considered by taking a further series of fingerprint deposits on brass disks from the same 40 donors (one deposit from each donor). These 40 samples were left for a period of *c.* 5 h and then spray painted with a commercially available acrylic derived metal primer followed by a cellulose derived topcoat, following the manufacturer's instructions, to a thickness that covered the disk. The disks were allowed to dry for the recommended period and then heated to a temperature of 400°C. As the paint finish was only good up to temperatures of ~120°C, the applied heat had the effect of removing most of the paint finish back to the bare metal and, after being left to cool in air, the disks were subject to the usual vigorous washing in warm water containing a few drops of commercial detergent. Any residual paint deposits were removed by rubbing the metal surface with a glass fiber pencil. Again, the degree of fingerprint ridge detail development varied amongst the 40 donors with a typical example of full ridge development being shown in Fig. 12. It can be seen that the paint has not inhibited the redox reaction, which is also impervious to the post-heat cleaning of the disk to reveal the developed fingerprint.

Finally, in this section, we consider a further practical application of this technique, namely, the enhancement of fingerprints deposited on cartridge cases prior to being fired. For these experiments, 40 brass 9 mm pistol cartridges were washed in distilled water followed by a wash in acetone and finally another wash in distilled water prior to drying with a paper towel. Each cartridge was handled by one of the 40 donors in order to leave one or more fingerprints on the cartridges. The cartridges were then loaded into magazines, which were inserted into a pistol and discharged. When fired, each cartridge was automatically ejected from the magazine. The 40 spent cartridges were collected, heated to 400°C and then left to cool in air. Unlike the above results, the quality of developed fingerprints did not follow the pattern shown in Fig. 9. Out of 40 cartridge cases, only two displayed any sign of continuous ridges and these were

[1]A glass fiber pencil is used for accurate abrading of a surface and has a propelling pencil action to expose more or less of the glass fibers—the shorter the fibers showing, the more abrasive the action.

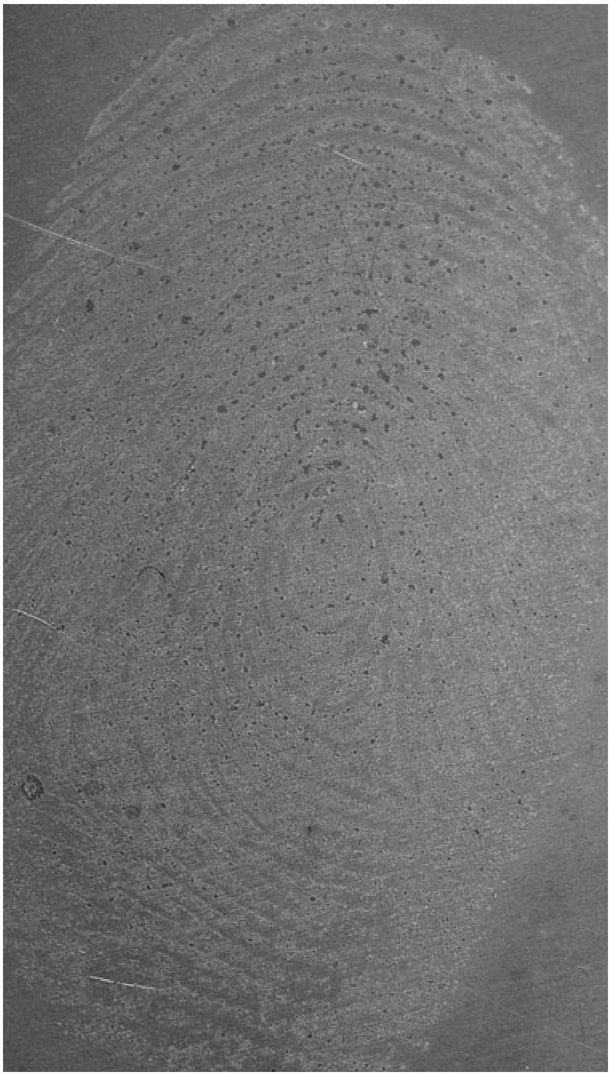

FIG. 12—*Typical full ridge detail development for fingerprints deposited on brass, spray painted and then heated to 400°C.*

graded at three using the Table 1 grading score. The majority of cartridges (32) showed no sign of developed fingerprints. The reason for this difference between the cartridge cases and the brass disks used above is thought to be associated with the physical contact experienced by the cartridges during loading and ejection from the magazine, which would tend to obliterate fingerprint deposits. Also, the relatively small surface area for contact between the cartridge and finger (relative to the planar surface of the brass disk) means that a smaller area of fingerprint residue is initially deposited. The difficulties of developing fingerprints on spent cartridge cases (where the fingerprint has been deposited prior to the cartridge being discharged) are well documented (10). Figure 13 shows the developed fingerprint ridge detail on a spent cartridge case, which appears faint when compared with the results shown above on planar brass disks. The development of fingerprint ridge detail on spent cartridge cases is considered again later in this paper.

Heating Fingerprint Residue Deposited on Copper, Steel, and Aluminum

The range of experiments described in the above section on planar brass disks were then repeated for planar disks of copper, steel (DC01), and aluminum.

FIG. 13—*Ridge detail development for fingerprint deposited on brass 9 mm pistol cartridge prior to discharge. Cartridge case heated to 400°C post-discharge and then washed in warm water containing a few drops of commercial detergent.*

In general, the development of fingerprint ridge detail on copper was similar to that observed on brass, a notable difference being that, at temperatures >~400°C, the copper disks were subject to oxide flaking (27). Figure 14*a* and 14*b* show typical ridge detail development for copper disks heated to 200°C and 400°C, respectively, 7 days after deposition. Figure 14*c* shows the effect of oxide flaking when the disk is heated to 600°C, although the outline of the area of fingerprint deposit is still visible. Figure 14*d* shows that by quenching the copper disk in water immediately after heating to 600°C, the oxide flaking can be inhibited and ridge detail developed.

Fingerprint development on steel produced different results to brass and copper in that the development appeared to be dependent on temperature with higher temperatures producing more development. Figure 15 shows typical fingerprint ridge development on steel disks heated to 200°C, 400°C, and 600°C, respectively. Also, unlike brass and copper, more samples failed to produce high quality grades (3 or 4), the distribution for 360 depositions (all taken at the same time from 40 donors) being shown in Fig. 16.

From Fig. 16, the majority of grades were 2 or less demonstrating the reduced effect that heating had on the redox corrosion reaction on steel. In all cases, on the steel disks the developed fingerprints had a blue/black appearance, which contrasted well with the steel substrate. The fingerprint residue is thought to have undergone a chemical process similar to bluing, a passivation process in which steel is partially protected against rust and is named after the blue/black appearance of the resulting protective film (28). In

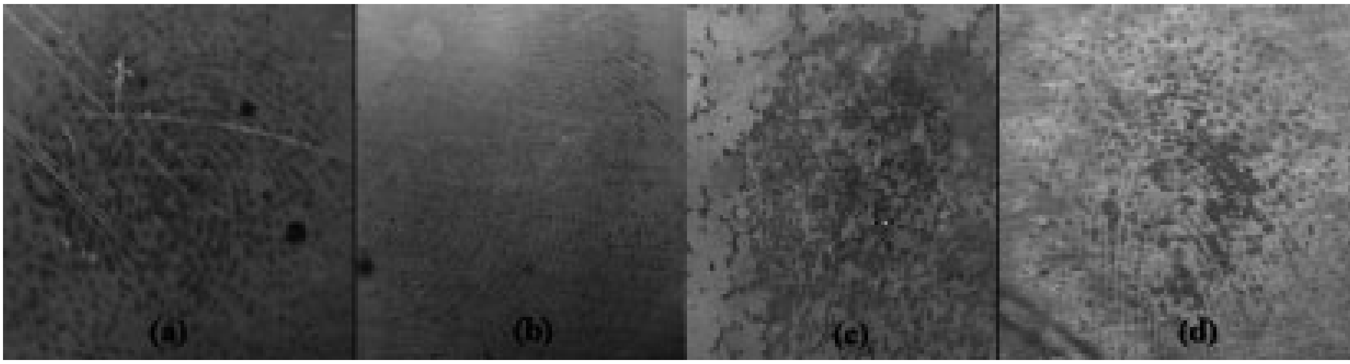

FIG. 14—*Ridge detail development for fingerprints deposited on copper and heated to (a) 200°C, (b) 400°C, (c) 600°C showing oxide flaking and (d) 600°C followed by immediate quenching in water.*

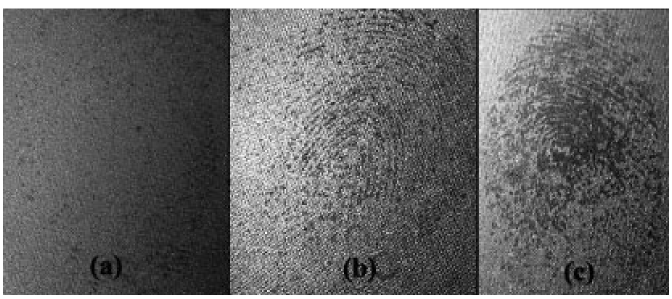

FIG. 15—*Ridge detail development for fingerprints deposited on steel and heated to (a) 200°C, (b) 400°C, (c) 600°C.*

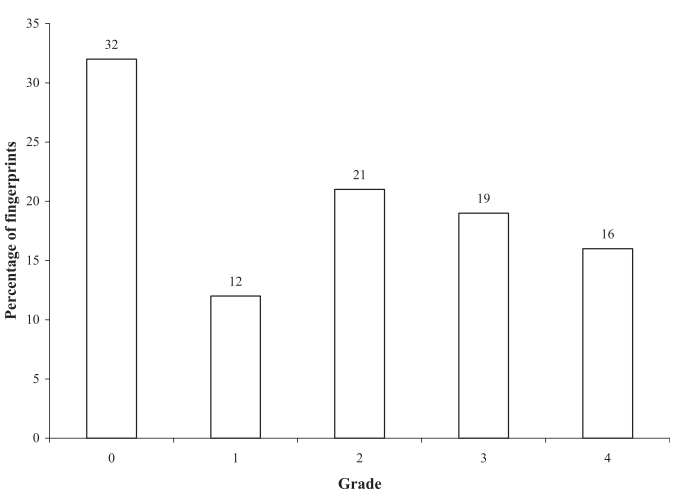

FIG. 16—*Grading of 360 fingerprints deposited on steel disks by 40 donors.*

bluing, the blue/black appearance results from an oxidizing chemical reaction with iron on the surface of the steel forming black iron oxide (Fe_3O_4). Fe_3O_4 occupies the same volume as normal iron and therefore does not exhibit oxide flaking as would be expected with red iron oxide (Fe_2O_3). Bluing can be performed as a "hot" process and is achieved by applying a solution of salts to steel and heating (28), not unlike the process being undertaken here with fingerprint residue.

None of the aluminum disks produced any discernible fingerprint ridge development and samples could not be heated to >~400°C as the planar aluminum disks began to buckle. The lack of any ridge detail development is thought to be a consequence of the ease with which aluminum naturally forms a passivating oxide layer in moist air (22). Steel can also easily autopassivate and this could well explain why the ridge detail development was less successful on steel than on brass or copper as the latter two are more electronegative (than either steel or aluminum) and hence less likely to form a passive layer that inhibits the redox corrosion reaction with the fingerprint residue.

Ambient Temperature Corrosion of Fingerprint Residue on Brass and Copper

During the experiments with fingerprint residue deposited on brass and copper disks, it was noted that some deposits caused a reaction with the metal substrate at room temperature without any heat being applied. To investigate this, a further series of fingerprint deposits were taken on brass disks from the same 40 donors (one deposit from each donor). These 40 samples were left at room temperature in air for a period of 10 days. After this time, the visible corrosion was assessed for each disk and graded according to Table 1. The results, in Fig. 17, showed that the overwhelming majority of samples failed to produce a high quality grade (3 or 4) although the percentage of samples that produced no development (grade 0) was approximately the same as for samples heated.

All 40 samples were then heated to 400°C and the degree of ridge detail development re-assessed. As might be expected, there was a shift towards higher grades for most samples, the exception being those with, initially, grade 0 (no development). After heating, the distribution of grades appeared relatively similar to Fig. 9. Figure 18*a* shows a typical sample 10 days after deposition with Fig. 18*b* showing the same sample after heating. The increase in the number of continuous lines of ridges after heating can be clearly seen.

Despite the visualization having the same appearance for fingerprints either left in air or heated, the chemical process is thought to differ. While heating the metal as described above clearly produces a heat-induced redox reaction with the metal substrate (22), leaving the fingerprint deposit at room temperature in moist air produces the redox reaction described earlier.

To test this, further samples were taken from the 40 donors with each fingerprint being deposited on the semi-circular disks described in a previous section. Forty deposits were made on brass semi-circular disks and 40 on copper semi-circular disks. One half of each disk was left at room temperature in air and the other placed in a desiccator for 10 days. After this time, as might now be expected, the semi-circular disks left in air showed a typical distribution of fingerprint ridge quality as described above. None of

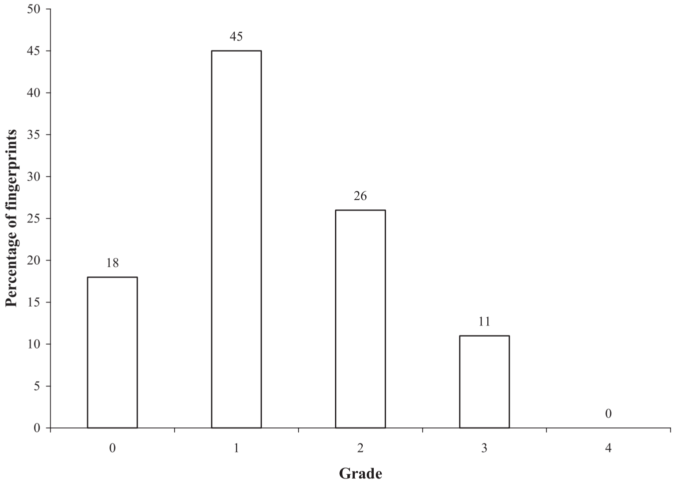

FIG. 17—*Grading of 40 fingerprints deposited on brass disks by 40 donors.*

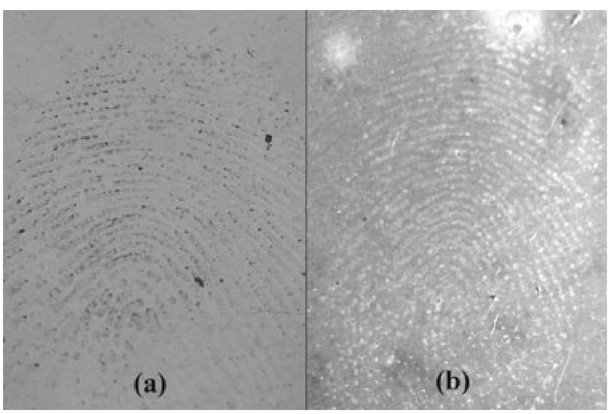

FIG. 18—*Ridge detail development for a fingerprint deposited on brass and (a) left for 10 days in air and (b) after heating to 400°C.*

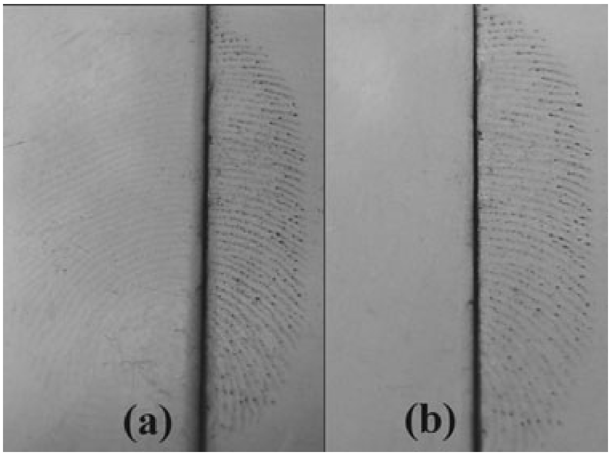

FIG. 19—*Ridge detail development for a fingerprint deposited on brass, 10 days after deposition. The left-hand side of (a) shows the portion of the deposit placed in the desiccator and the right-hand side of (a) the portion left at room temperature in air. Image (b) shows (a) after washing.*

the semi-circular disks placed in the desiccator showed any sign of corrosion with Fig. 19*a* showing a typical sample for brass in which the left-hand side of the fingerprint has been kept in the desiccator and the right-hand side in air. The faint fingerprint image visible on the left-hand semi-circle is the residue itself rather than any corrosion caused by the residue. To illustrate this, all samples were then washed in the usual solution of warm water containing a few drops of commercial detergent and vigorously rubbed. Figure 19*b* shows the same fingerprint after washing and it can be seen that, while the right-hand side of the fingerprint is unchanged, the left-hand side no longer presents a visible fingerprint.

Electrostatic Enhancement of Fingerprint Residue on Metal Surfaces

The clear indication that corrosion of brass and copper by fingerprint residue can occur at room temperature to a sufficient degree to enable fingerprints to be identified led us to consider how this phenomenon might be exploited further.

In this section, we describe initial results from a novel technique to enhance fingerprint ridge detail that is present on the surface of a metal substrate through the redox reactions discussed and demonstrated above. The technique involves applying an electric potential (typically 2.5 kV) to the metal and then introducing a black conducting powder with a grain size of ~10 μm to the metal. The introduction of the powder to the metal was achieved by using Cascade Developer supplied by Foster and Freeman, Evesham, UK, which comprises ~400 μm spherical beads that can be coated with the conducting powder. By rolling the spherical beads back and forth across the charged metal surface, the conducting powder was found to preferentially adhere to the areas of corrosion on the metal thus enabling the fingerprint to be visualized.

The necessary electric potential was generated by constructing a high voltage unit, based around a Brandenburg 3590 series high voltage module. The finished unit enabled the generation of a continuously variable potential from 0-2.5 kV. A mechanical support was constructed to hold the 50 mm metal disks such that, when placed flat on the support, the disks were in electrical contact with the high voltage output and able to be tilted about an axis parallel with the flat surface of the disk. The Cascade Developer was introduced to the support a few centimeters away from the metal disk and the support tilted to enable the Developer to roll back and forth across the metal, as illustrated in Fig. 20.

Fresh fingerprint deposits on brass disks were taken from each of the 40 donors, two fingerprints from each donor on separate disks. All the disks were left at room temperature, in air, for 5 days and then all samples were washed in distilled water followed by a wash in acetone and finally another wash in distilled water. This washing regime was to remove as much of the remaining fingerprint residue as possible. One sample from each donor was subject to a conventional treatment, which comprised submersion in a solution of a small particle reagent (a suspension of fine molybdenum disulphide particles), as this was deemed the most suitable treatment given the washing regime (2,29). The remaining sample from each donor was subject to the electrostatic treatment described above with a typical potential of 2.5 kV. Conventional enhancement produced no additional fingerprint ridge detail over and above that visible through redox reaction on any of the 40 samples whereas 14 of the 40 produced some degree of additional fingerprint enhancement with the electrostatic technique. It was found that if a disk already displayed a grade 3 visualization of the fingerprint (through redox reaction) then the electrostatic technique did not significantly improve the visualization. However, where the degree of visualization was grade 1 or 2, the electrostatic technique improved the visualization. Figure 21 shows a typical example with

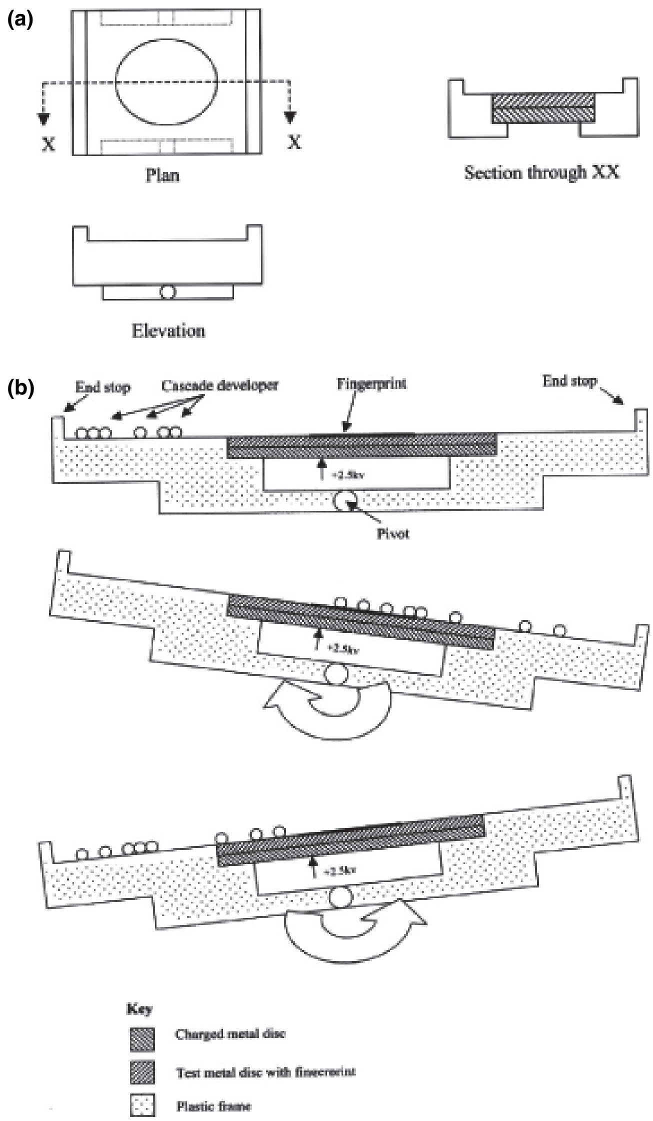

FIG. 20—*Diagrammatic representation of the apparatus used to apply Cascade Developer to the charged metal. (a) shows the design of the apparatus while (b) shows a representation of the tilting movement to enable the Developer to roll back and forth across the metal disk containing the fingerprint.*

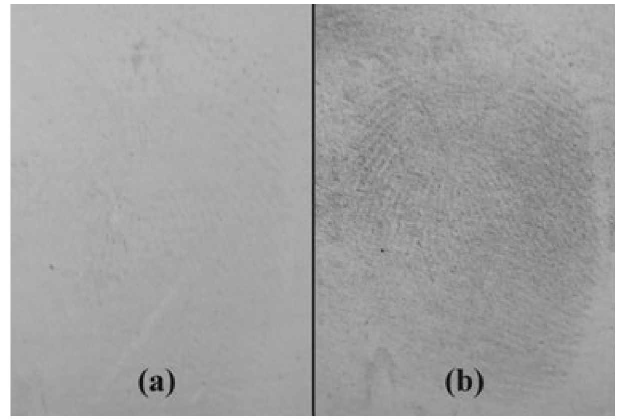

FIG. 21—*Ridge detail development for a fingerprint deposited on brass, 5 days after deposition. (a) shows the degree of redox corrosion visible after washing in water, acetone, and then water, while (b) shows the same fingerprint after subsequent electrostatic enhancement.*

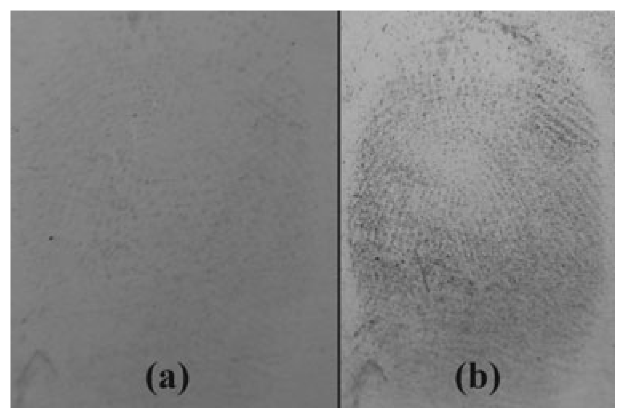

FIG. 22—*Ridge detail development for a fingerprint deposited on brass, 5 days after deposition. (a) shows the degree of redox corrosion visible after washing in water, acetone, and then water, followed by warm water containing a few drops of commercial detergent while (b) shows the same fingerprint after subsequent electrostatic enhancement.*

Fig. 21*a* showing a fingerprint after washing while Fig. 21*b* shows the same fingerprint enhanced using the electrostatic technique. The negative results obtained with the small particle reagent are not surprising as this technique relies on an adherence of the reagent to the fatty constituents of the fingerprint residue, which would be substantially removed by the washing regime (2,19).

The electrostatic enhancement was found to be extremely reproducible in that if, for example, an excess of black powder had been applied and the mark was over developed, the metal disk could be washed and vigorously rubbed in the usual solution of warm water containing a few drops of commercial detergent and then the technique repeated. Figures 22*a* and 22*b* show the same fingerprint as in Fig. 21 after washing and the reapplication of the electrostatic technique, respectively. It can be seen that the quality of the fingerprint ridge detail enhancement has not been diminished significantly between Figs. 21*b* and 22*b* by the intervening washing. Leaving the fingerprint deposits only 5 days prior to treatment (rather than the 10 days as in the previous section) reduced the degree of visible corrosion on the metal surface enabling a better demonstration of the electrostatic technique. After electrostatic treatment, the black powder was found to be extremely vulnerable to disturbance once the electric charge had been removed. By heating the brass disk (post treatment) to ~150°C the powder was found to bind to the brass disk producing a more durable sample.

Fingerprint deposits similar to the above were also taken on copper, steel, and aluminum disks. Results for copper were similar to those obtained for brass while, not surprisingly, both steel and aluminum failed, in all 40 samples, to give any grade 3 or 4 results. Eight of the 40 steel disks produced a grade 2 after electrostatic enhancement with the remainder mostly grade 0. Aluminum failed to produce any enhancement after electrostatic treatment. As with the brass disks, all disks were left in air for 5 days, subject to the above washing regime and then, after an initial electrostatic enhancement, washed, and vigorously rubbed in warm water containing a few drops of commercial detergent and the electrostatic treatment retried.

The mechanism for this process is thought to be a consequence of the corrosion on the metal surface that leads to both impurities and lattice imperfections, which will have the effect of locally increasing the resistivity of the metal at the site of the corrosion (30). If a potential is applied to the metal disk then, under electrostatic conditions, the charge will move entirely to the outer surface with the electric field inside the metal being zero. Areas of corrosion with increased resistivity will behave more like a dielectric and the charge density in these areas (σ') will be less than the charge density at other parts of the surface (σ). Using Gauss' Theorem (31), both the electric field and potential at a given point above the disk will be less above a corroded area. Consider Fig. 23, which represents a section through a metal disk under electrostatic equilibrium. α Represents a Gaussian surface drawn partly through the surface of the metal that has a surface area in the plane parallel to the exterior surface of the metal of A. This Gaussian surface contains a charge

$$q = \sigma \cdot A \tag{5}$$

and from Gauss' law

$$q = \varepsilon_0 \oint \underline{E} \cdot \mathrm{d}\underline{A} \tag{6}$$

where ϵ_0 = permitivity of free space and, at all points on the Gaussian surface, E and dA have the same direction.

Assuming that E has the same magnitude at all points on the Gaussian surface then

$$q = \varepsilon_0 E \oint \mathrm{d}A = \varepsilon_0 E \cdot A \quad \text{therefore } E = q/\varepsilon_0 A \tag{7}$$

By the same derivation, if the Gaussian surface α' (drawn through a corroded area) has the same surface area A then

$$q' = \varepsilon_0 E' \oint \mathrm{d}A = \varepsilon_0 E' A \quad \text{therefore } E' = q'/\varepsilon_0 A \tag{8}$$

As $q' < q$ then it follows that $E' < E$. Further, as the potential difference (Δv) between two points separated by a distance d is given by

$$\Delta v = \int_0^{\mathrm{d}} \underline{E} \cdot \mathrm{d}\underline{s} \tag{9}$$

then the potential at a given point above Gaussian surface α' will be less than the potential above α.

It might be thought that this process would be the same as that used to explain the electrostatic detection of perturbations in paper. However, previous research has proposed a different mechanism for this (32).

Finally, in this section, we return to the enhancement of fingerprints deposited on cartridge cases prior to discharge. The 9 mm pistol cartridge shown in Fig. 13 had already been washed in the usual solution of warm water containing a few drops of commercial detergent and so the electrostatic enhancement technique was applied to it with no further washing. Figure 24 shows the resulting

FIG. 24—*Ridge detail development for fingerprint deposited on brass 9 mm pistol cartridge shown in Fig. 13 after electrostatic enhancement.*

improvement in definition of the fingerprint ridge detail compared with simply heating the cartridge case (Fig. 13).

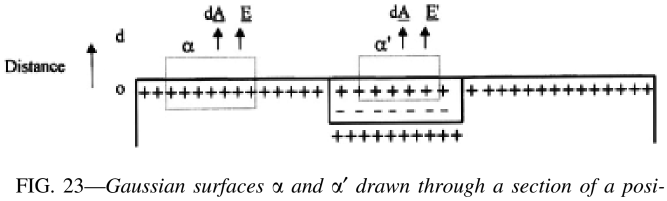

FIG. 23—*Gaussian surfaces* α *and* α' *drawn through a section of a positively charged metal disk.*

Conclusions

We have demonstrated that it is possible for the inorganic salt content of fingerprint residue to produce a sufficiently corrosive redox reaction on metals such as copper, brass, and steel for the ridge detail present in the residue to be visualized. This reaction is greatly enhanced by the application of heat to the metal of the order of several hundred degrees. Such heating has been shown to enable fingerprint visualization after the metal has been in a fire as might be experienced at an arson crime scene and also after surface contamination by, for example, spray painting. The application of this heating technique to enhance fingerprints deposited on brass cartridge cases prior to discharge has shown similar results.

Further experiments have shown that the degree of corrosive redox reaction is very dependent, at room temperature, on humidity. In air at room temperature sufficient reaction can occur for ridge detail in the fingerprint residue to be visualized with no additional treatment.

Although other recently reported techniques have produced similar results in terms of ridge visualization, this technique is attractive for police scientific laboratories as ease of use and durability of the enhanced ridge detail after vigorous cleaning are obvious attractions, as is the ability to speculatively search an object for fingerprints.

This research has highlighted variation in the amount of salt secreted by different individuals, which is an important consideration for workers developing techniques where success relies on the salt content of the fingerprint residue. Clearly, more work would be required to better understand the factors that influence the amount of salt secreted by individuals and its variation over time.

Electrostatic charging of metal has been shown to enable the preferential adherence of a conducting powder to the corroded areas of the metal surface coincident with fingerprint ridges from the original deposition. This technique has been applied to the practical, and important, problem of fingerprint enhancement on spent brass cartridge cases with a degree of success.

Further work is currently being undertaken to better understand the processes involved in the electrostatic enhancement technique on a wider range of metals and also how its use might be extended and improved for day-to-day use in police scientific laboratories.

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