

PAPER**CRIMINALISTICS**

Ann L. Beresford,¹ M.Chem.; Rachel M. Brown,¹ M.Chem.; A. Robert Hillman,¹ D.Phil.; and John W. Bond,^{2,3} D.Phil.

Comparative Study of Electrochromic Enhancement of Latent Fingerprints with Existing Development Techniques*

ABSTRACT: To address the challenge of capturing latent fingerprint evidence from metal surfaces, a new method of latent fingerprint enhancement based on electrochromic polymer films has recently been developed. Here, we present a study comparing the development and visualization of nonvisible fingerprints on stainless steel substrates using this electrochromic enhancement approach with three classical methods (dusting, wet powder, and cyanoacrylate fuming). Two variants of the electrochromic enhancement method were utilized with polyaniline and poly(3,4-ethylenedioxythiophene) as the electrochromic materials. Fingerprint samples were taken from different donors (varying in age and gender) and were exposed to different environments for systematically varied periods of time (up to 28 days). The environments represent plausible evidential scenarios: left under ambient conditions, washed with aqueous soap solution, washed with acetone, submerged in water, and maintained at elevated temperature. The electrochromic enhancement procedure frequently outperformed the traditional methods, particularly for samples exposed to more challenging histories.

KEYWORDS: forensic science, latent fingerprint, electrochromic, electroactive polymer, thin film, polyaniline, poly(3,4-ethylenedioxythiophene)

When fingerprints are deposited on metal surfaces, the most widely used visualization techniques are dusting, cyanoacrylate fuming (“superglue”), and the use of wet powder. In all these cases, the applied reagent interacts with the fingerprint deposit to make the ridge detail visible. Subsequent application of dyes and/or illumination with light of various wavelengths is sometimes used in conjunction with these development techniques to ensure optimal enhancement (1). We begin by briefly summarizing the features of these methods and the new electrochromic enhancement procedures with which they are compared.

The most common procedure for the development of latent prints is powder dusting. This method relies upon physical adherence of the powder to the sticky sebaceous components of the fingerprint residue (2). Selection of the color of the powder used to achieve maximum contrast is based on the color of the surface. Application of the powder with a brush to dust over the substrate can have destructive effects on ridge detail but has the practical advantage of giving instant development.

Small particle reagent—sometimes referred to as wet powder—works in much the same way as dusting. This technique has been

shown to work well on wet nonporous surfaces, although the scope of color variation for the adhering particles is limited for achieving good visual contrast on metal surfaces (3,4).

“Superglue” treatment involves the reaction of cyanoacrylate with the fingerprint deposit, leading to polymerization of the monomer along the ridges of the print (5,6). Use of chemical dyes often accompanies superglue fuming; this requires an additional step to develop the items, which then have to be photographed under illumination with light of an appropriate wavelength. Although widely used, the efficacy of this technique is limited to fingerprints that either have been wetted or have been aged.

In overview, despite efforts to improve the development of fingerprints from particular types of evidence, notably aged or previously wetted samples, the success rate of fingerprint recovery is low. This is especially the case for metal substrates (7–9), the surfaces upon which we focus here. In light of increasing gun crime that is associated with terrorism and organized crime, an example that has attracted appreciable interest in recent years is the development of fingerprints from the metal surfaces of gun cartridge cases (10–15). One issue that makes the visualization of fingerprints from cartridge cases more difficult is that of the curved surface.

The electrochemically controlled deposition of the so-called conducting polymers on metal (electrode) surfaces has been a topic of huge interest over the last two decades (16). The resultant polymeric films are electroactive: their electronic conductivity and optical properties may be manipulated by the application of relatively modest voltages. Electropolymerization of pyrrole, aniline, and thiophene (and numerous chemically substituted derivatives) and consequent polymer deposition onto metallic surfaces have been studied extensively (16–23) (see Fig. 1). These three families of polymers comprise monomer chains chemically linked by strong

¹Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, U.K.

²Scientific Support Department, Northamptonshire Police, Wootton Hall, Northampton NN4 0JQ, U.K.

³Forensic Research Centre, University of Leicester, Leicester LE1 7RH, U.K.

*Financial support provided by the Northamptonshire Police, the University of Leicester, and EMDA/ERDF.

Received 25 Aug. 2010; and in revised form 4 Nov. 2010; accepted 14 Nov. 2010.

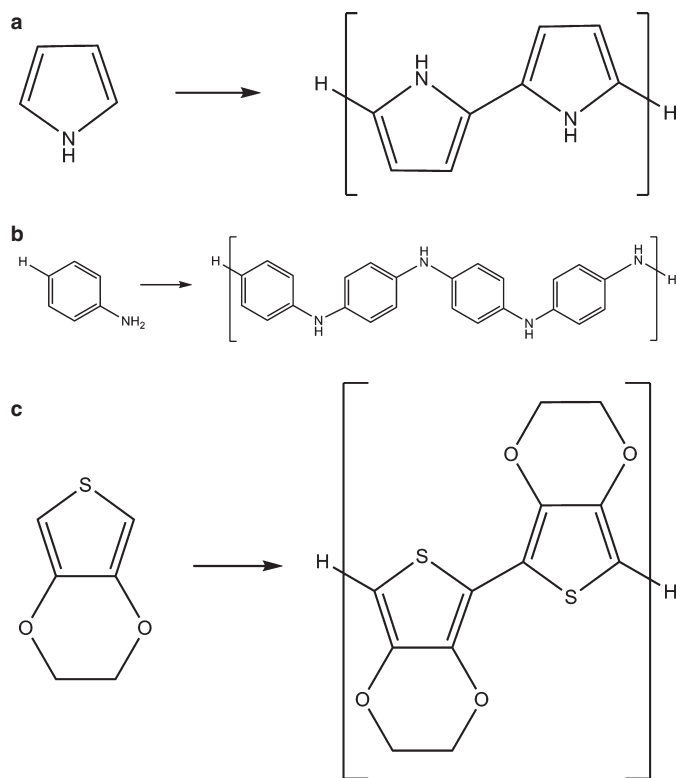


FIG. 1—Pyrrole, aniline, and 3,4-ethylenedioxythiophene monomers and their respective polymers [polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene)].

covalent bonds, making them suitable materials for composite, coating, and adhesive applications owing to their resistance to heat-softening and solvent attack (24). We studied films of polyaniline (PAni) and a derivative of the polythiophene family, poly(3,4-ethylenedioxythiophene) (PEDOT), generated by anodic electropolymerization of aniline, and 3,4-ethylenedioxythiophene (EDOT), respectively.

During PAni formation, electro-oxidation of aniline results in a condensation process involving loss of two hydrogen atoms from each monomer and *para*-coupling (24). PAni has an electronic structure that permits subsequent interconversion among three redox states with distinct electrical and chemical behavior (25): leucoemeraldine (yellow/clear), emeraldine (green/blue), and pernigraniline (blue/violet); only the emeraldine salt is electrically conductive.

Based on the fact that fatty acids present within a fingerprint deposit cause it to act as an insulating layer on the substrate, selective electropolymerization of pyrrole on the exposed (bare) metal substrate between ridge deposits has been used to visualize fingerprints (12). We have recently used this approach with aniline and EDOT to generate PAni (26) and PEDOT (R. M. Brown, personal communication) films that allow visualization of the fingerprint deposit. The strategy is based on the fact that the fingerprint deposit locally masks regions of the metal surface inhibiting polymerization. Thus, spatially selective deposition of the polymer takes place on nonmasked sections of the metal substrate, between the fingerprint ridges. This results in a *negative* image of the print. The process is complementary to existing techniques (such as those with which we make a comparison in this study) in which the reagents interact with the fingerprint itself to generate a *positive* image of the print. The significant extension of our recent work is that, after transfer to a monomer-free solution, potential control of the object (as the working electrode in an electrochemical cell) allows

variation of the well-documented optical properties of the conducting polymer. In the case of PAni, one can access yellow, green, and blue polymer oxidation states. The ability to vary the polymer color allows optimization of visual contrast between the substrate (fingerprint deposit) and the polymer.

While proof of concept of the electrochromic enhancement method has been established for PAni (26) and PEDOT (R. M. Brown, personal communication) with freshly deposited (practically somewhat ideal) fingerprints, the technical performance of this approach under more practical conditions was unknown. Exploration of this was the general objective of this study. Specific objectives related to the relative efficacy of the electrochromic enhancement method and more traditional methods for visualizing fingerprint deposits subject to a range of histories (environments and time scales) that are more representative of plausible scenarios that may arise in a criminal investigation. In particular, we assessed the abilities of three existing techniques (dusting, wet powder, and superglue fuming) and two variants of the electrochromic enhancement method (using PAni and PEDOT) to recover fingerprints. The surfaces from which the fingerprints were to be recovered were subject to five environments: ambient, extended immersion in water, washing with acetone, extended heating, and washing with aqueous soap solution. In each case, the fingerprints were taken from donors of varying age and gender and were left for varying time periods. Overall, the study encompassed 600 samples. From a practical perspective, the objectives were to determine the most appropriate development methods for samples for which the age or environment—or both—were unknown.

Materials and Methods

Substrates and Fingerprint Deposition

Stainless steel plates (25 mm × 25 mm) were polished for 5 min with a proprietary metal polish (Brasso, Reckitt Benckiser plc, Slough, UK), washed with soapy water, and rinsed with acetone. Fingerprint deposits were collected from five individuals, three men and two women, varying in age from 21 to 42 years. Although not quantified, these represented a range of deposit composition and amount, that is, quality. Prior to fingerprint deposition, donors washed their hands with soap and dried them with paper towel. They rubbed their fingertips over their forehead and nose and then rubbed their hands together to ensure a deposition of a rich and even sebaceous fingerprint. Donors deposited their prints by contact with the stainless steel surface for 1–2 sec with minimal pressure. The prints were left overnight under ambient conditions before being subjected to their respective environments. In the case of the 1-day-old prints, pretreatment commenced *c.* 4 h after deposition.

Environments

The five environments to which fingerprints were exposed prior to enhancement are described in Table 1.

Enhancement Techniques

Dusting—Samples developed by dusting with standard black powder (WA Products, Burnham on Crouch, Essex, UK) were gently dusted back and forth with a mop head squirrel brush.

Wet Powder—A mixture of iron oxide and detergent (Kodak Professional Photo-Flo 200 [Kodak Eastman Company, Rochester, NY] and distilled water) was made to a consistency viscous enough

TABLE 1—Descriptions of the five environments to which fingerprints were exposed.

Environment	Sample Conditions Prior to Enhancement
Ambient	In open box at room temperature/pressure
High temperature	Placed on metal tray stored in oven at 150°C
Water	Kept submerged under water at ambient temperature
Soap wash	Rubbed in warm (40°C) soapy water for 30 sec; rinsed in soap-free water; left to dry naturally; stored under ambient conditions
Acetone wash	Agitated in acetone for 30 sec; rinsed in water; left to dry naturally; stored under ambient conditions

to coat a surface but sufficiently optically transmitting that one could see the underlying surface through the resultant film. Wet-powdered samples were developed by painting on the mixture in perpendicular directions to ensure that particles attached to the deposited fingerprint ridges. Samples were then rinsed under slow-running water to remove excess wet powder mixture and placed in a drying cabinet (60°C) for 1 h.

Superglue—The superglue fuming cabinet (MVC 5000; Foster and Freeman, Evesham, U.K.) was prepared by the addition of distilled water and sufficient cyanoacrylate to cover the incorporated hot plate. Samples were placed in the cabinet set to auto glue. After *c.* 8 min, 78.9% of humidity was reached; this was followed by 15 min of fuming at 119.4°C. The samples were then removed from the cabinet, dipped in a solution of Basic Yellow 40 dye (2 g/L in aqueous 60% ethanol), and then rinsed under slow-running water. Samples were left in a drying cabinet (60°C) for 1 h.

PAni Deposition—PAni films were deposited potentiostatically ($E = 900$ mV vs. Ag/AgCl/saturated KCl) from a solution containing 0.1 M aniline in aqueous 1 M H₂SO₄ solution. A one-compartment three-electrode cell of standard configuration (27,28) was used with the sample as the working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The electrode configuration was such that the fingerprinted sample (working electrode) could be visually monitored. When a suitable film was deposited, the working electrode (sample) was disconnected (with the film in the oxidized state), removed from the cell, rinsed with deionized water, and left to dry naturally. This *ex situ* observation potentially underplayed the strength of the electrochromic method for PAni (26) in that fine control of optical contrast was sacrificed, but was adopted as a most critical appraisal of the new technology.

PEDOT Deposition—PEDOT was deposited and the films handled under similar conditions to PAni deposition. The deposition potential was 900 mV. The deposition solution contained 0.01 M EDOT/0.01 M sodium dodecylsulfonate (SDS) in aqueous 0.1 M H₂SO₄. The role of the SDS surfactant was to solubilize the EDOT monomer in the aqueous medium; this obviated the need for organic solvents. As for PAni, this *ex situ* observation potentially underplayed the strength of the electrochromic method for PEDOT (R. M. Brown, personal communication).

Photography

Samples were photographed immediately prior to and following enhancement. In the cases of samples kept in an oven or under water (see Table 1), they were removed from these environments and left to reach ambient conditions (cool/dry, respectively)

naturally in air before being photographed. Samples washed with either aqueous soap solution or acetone were left under ambient conditions for the entirety of their aging time. Samples developed by dusting, wet powder, or electrochromic enhancement (PAni or PEDOT) were photographed using a Canon PowerShot A480 digital camera (Canon UK Ltd, Bedfordshire, UK). Images of samples developed by superglue fuming were captured with DCS-3 Image-ProPlus 5.0.1.11 image software (Foster and Freeman, Evesham, UK) acquired by a Fuji FinePix S2 Pro digital camera (Fujifilm UK Ltd, Bedfordshire, UK) with a 55-mm Nikkor micro lens (Nikon UK Ltd, Surrey, UK) and visualized through a 476-nm filter by a 4 × 4 crime-lite LED ($\lambda = 430\text{--}470$ nm).

Grading

The quality of fingerprint ridge detail prior to and following development was assessed using a 5-point scale (0 = lowest to 4 = highest) developed by Bandey (29). Simplistically, grade 0 represents no discernible ridge detail and grade 4 represents a fully developed print with complete ridge detail. As a guide to practical relevance, samples graded 0–2 would not be expected to be of evidential value and samples graded 3–4 would be expected to show sufficient detail for unequivocal identification of an individual. All fingerprints were independently graded by two individuals.

Results and Discussion

Overview

The fundamental electrochemical aspects of the PAni (26) and PEDOT (R. M. Brown, personal communication) electrochromic enhancement processes have been discussed elsewhere. Here, we focus on practical aspects of the efficacy of the methodology in a range of situations. To give an impression of the origins of the data, it is useful to view representative examples. Typical outcomes are shown in Fig. 2 for two nominally identical fingerprints (i.e., taken from the same donor), one of which was immersed in water for 7 days and then electrochromically enhanced using PAni and the other was heated for 28 days and then electrochromically enhanced with PEDOT. The deliberate use of reagents (polymers) for which a range of colors is accessible means that viewing a black-and-white image necessarily discards a significant amount of information; accessing this will be an avenue of future enquiry. Nonetheless, it is clear that the enhancement process has, from the starting point of a grade 0 print (zero detail visible; image not shown), revealed significant secondary-level detail.

The task was to make comparisons among fingerprints from five donors, subjected to five environments (see Table 1) that represent plausible evidential scenarios, left for different periods of time (different print ages), and subjected to no enhancement or one of five enhancement protocols. For each of these 600 samples, a grade (according to the scale proposed by Bandey [29]) was assigned prior to and following enhancement. We note that all of the nonenhanced prints were grade 0 (the overwhelming majority) or grade 1.

We assessed the effectiveness of the enhancement protocols by addressing three questions: (i) Does the “enhancement” protocol actually result in a higher grade print? (ii) Does the enhancement protocol result in a useable print (grade 3 or 4 on the Bandey scale)? (iii) For given combinations of circumstances (specified age and/or environment, averaged across the five donors), which enhancement protocol results in the largest number of useable (grade 3 or 4) prints? For convenience, in the presentation of graphical and tabular data, we

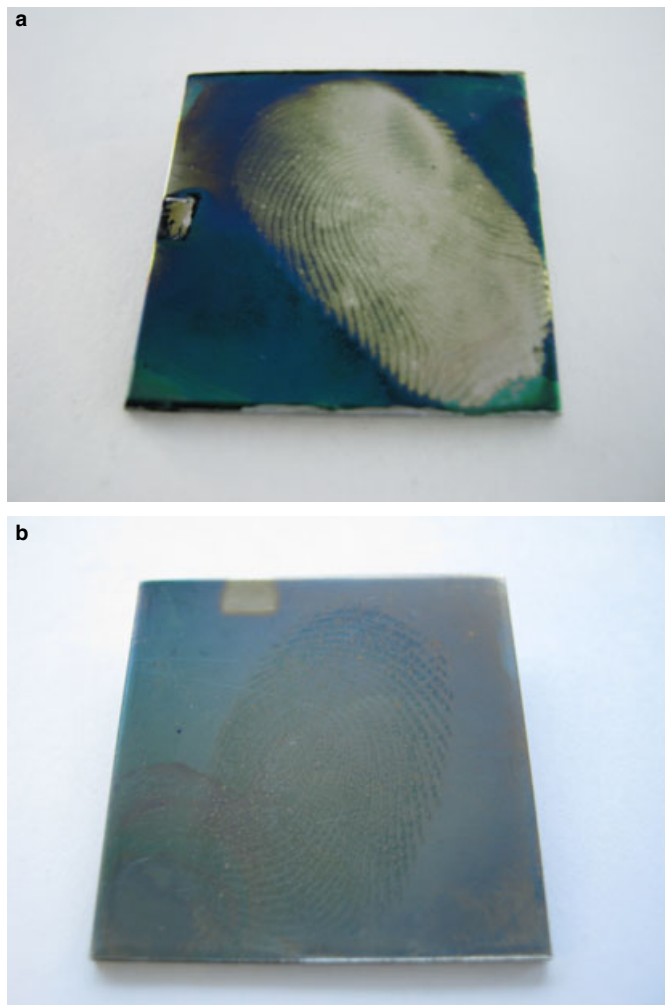


FIG. 2—Panel a: Polyaniline-enhanced fingerprint on stainless steel, following immersion for 7 days in water. Panel b: poly(3,4-ethylenedioxythiophene)-enhanced fingerprint on stainless steel, following heating for 28 days. Both fingerprints were from the same donor.

will refer to outcomes of these questions in terms of the *fraction improved*, the *fraction useable*, and the *optimum enhancement protocol*, respectively. Thus, in terms of the first question, no negative responses are possible. Similarly, in terms of the second question, a useable print is only achievable with enhancement.

Performance of Individual Treatment Protocols

In this section, we consider the fraction (expressed as a percentage) of samples for which the fingerprint was enhanced to any extent (represented by *fraction improved*) and to a useable level (represented by *fraction useable*) by each technique. In the latter instance, “useable” is characterized by a grade of 3 or 4 according to the Bandey scale (29). The results are shown in Figs 3–7. Each individual figure relates to one exposure environment; within this, we explore the effects of varying age of the fingerprint (moving forward in the diagram) and the enhancement method. In each figure, panel *a* relates to the *fraction improved*, and panel *b* to the *fraction useable*.

Inspection of panels *a* in Figs 3–7 shows that, with the exception of soap-washed samples, most techniques offered some element of enhancement; this is hardly surprising, but does not reveal whether the enhancement was at a worthwhile level.

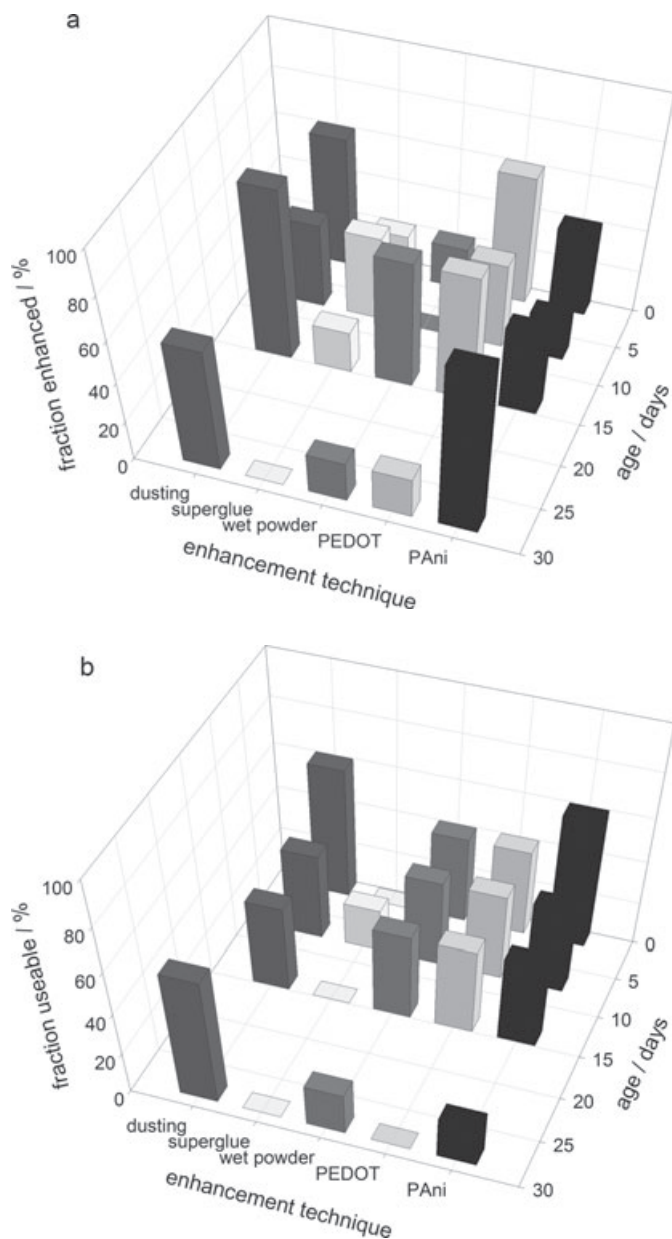


FIG. 3—Three-dimensional bar charts showing the percentage improvements achieved by each of the development techniques for samples subject to storage under ambient conditions. Each column represents the combined outcome from the five donors; the figure captures data from 100 prints. Panel a: percentage of prints enhanced by the designated protocol; panel b: percentage of prints enhanced to a useable level (grade 3 or 4) by the designated protocol.

Interestingly, cyanoacrylate fuming appeared to be the least effective treatment. Simplistically, with obvious variations that are explored below, the most effective procedures were either simple dusting or one of the electrochromic polymer treatments we wished to assess.

The more searching question was what level of enhancement was achieved; for this, we turn to panels *b* in Figs 3–7. For ambient conditions (Fig. 3), the variations in performance of the enhancement methods were generally not large, for a given age of print. The two exceptions to this were the low enhancement levels from cyanoacrylate fuming (at all print ages) and the better recovery rate for the oldest prints (28 days) using simple dusting. Overall, with these two exceptions, this relatively unchallenging scenario was tolerant to the choice of enhancement procedure.

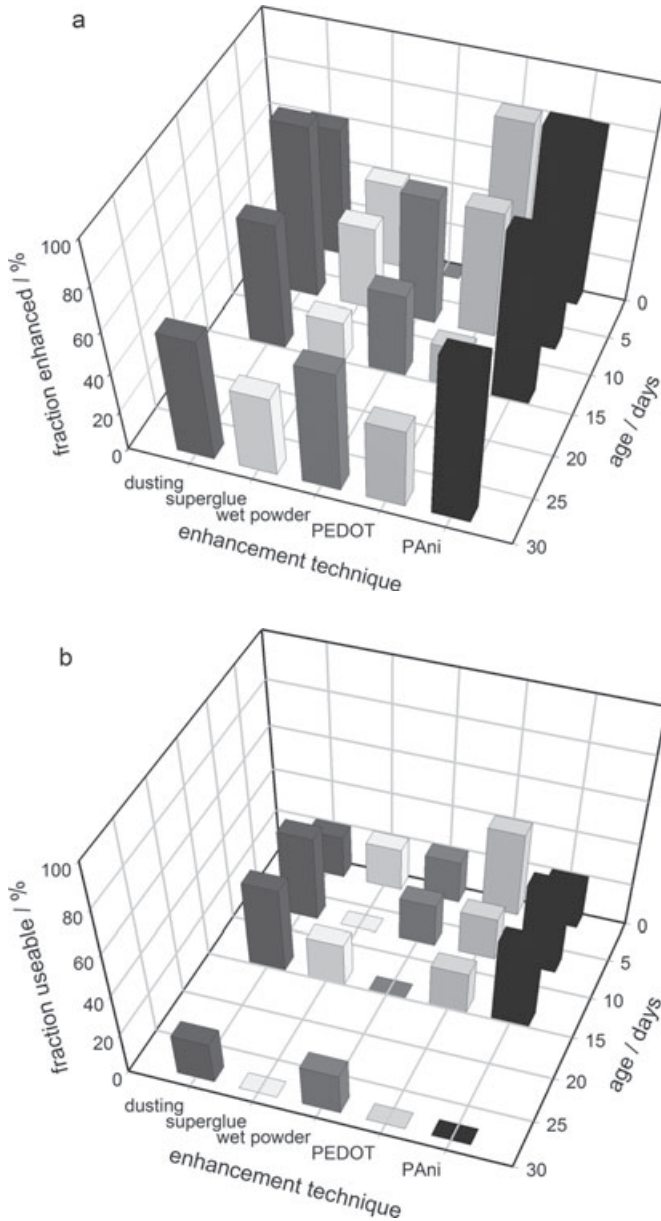


FIG. 4—Three-dimensional bar charts showing the percentage improvements achieved by each of the development techniques for samples subject to continuous immersion in water. Each column represents the combined outcome from the five donors; the figure captures data from 100 prints. Panel a: percentage of prints enhanced by the designated protocol; panel b: percentage of prints enhanced to a useable level (grade 3 or 4) by the designated protocol.

At the other extreme, this more discriminating survey showed that samples subject to heat treatment (Fig. 6) or washed with aqueous soap solution (Fig. 7) were associated with very low recovery levels. PEDOT deposition offered the best prospect of recovery in the former instance and was the only enhancement procedure that appeared to offer any prospect of success in the latter instance.

Between these extremes were the cases of an acetone wash and continuous immersion in water (Fig. 4). In the acetone wash case (Fig. 5), dusting was the most effective treatment. Success levels for this treatment were generally very poor for older samples. The reason for this marked decrease in recovery rate with age was not clear, because acetone wash was early in the storage period; nevertheless, the outcome was clear. Continuous immersion in water

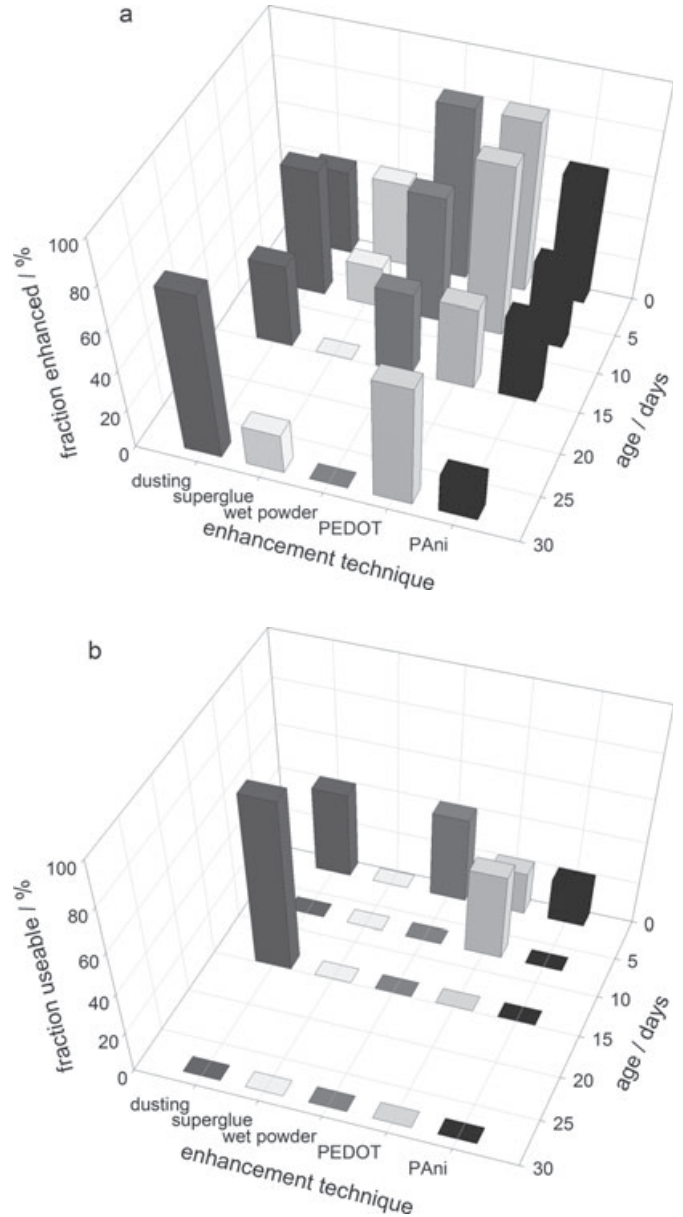


FIG. 5—Three-dimensional bar charts showing the percentage improvements achieved by each of the development techniques for samples subject to an acetone wash. Each column represents the combined outcome from the five donors; the figure captures data from 100 prints. Panel a: percentage of prints enhanced by the designated protocol; panel b: percentage of prints enhanced to a useable level (grade 3 or 4) by the designated protocol.

provided more complex outcomes. The effectiveness of wet powder was not high, but it seemed relatively insensitive to the duration of immersion. One might postulate that anything removed by water was lost quickly and would in any case be removed by the wet powder treatment; thus, the time response was flat. The electrochromic polymer treatments and dusting show modest performance over the first 14 days, with only dry powder dusting (and possibly wet powder) effective after 28 days.

An interesting general observation was that recovery rates, for a given sample history/environment and enhancement technique, were relatively insensitive to fingerprint age for the first 14 days, but drop sharply at 28 days. The practical significance of this for scheduling the processing of evidence is obvious.

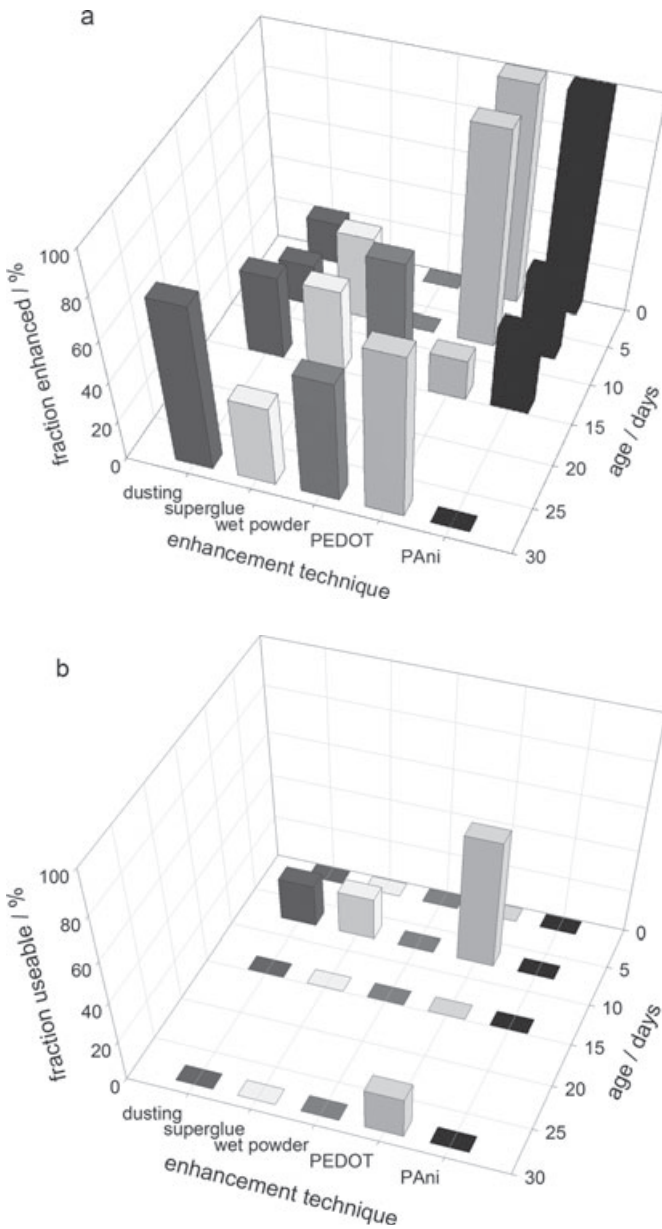


FIG. 6—Three-dimensional bar charts showing the percentage improvements achieved by each of the development techniques for samples subject to continuous heat treatment. Each column represents the combined outcome from the five donors; the figure captures data from 100 prints. Panel a: percentage of prints enhanced by the designated protocol; panel b: percentage of prints enhanced to a useable level (grade 3 or 4) by the designated protocol.

Selection of Optimum Enhancement for Samples of Incompletely Known History

In this section, we focus on the interpretation of the data for improvement in fingerprints to useable levels (panels *b* of Figs 3–7) and integrate the data in two different directions. First, we consider the situation that a print was of known age but had been subjected to uncertain conditions. This corresponded to summation of the corresponding columns for each technique in Figs 3*b*–7*b*; the outcomes are shown in Fig. 8, where panels *a*–*d* correspond to fingerprints sampled after 1, 7, 14, and 28 days. In the data sets shown, summing the results across donors and environments means that each column represents a sample of 25 prints. Thus, anomalous behavior of a single print (i.e., “bit error” associated with an outlier

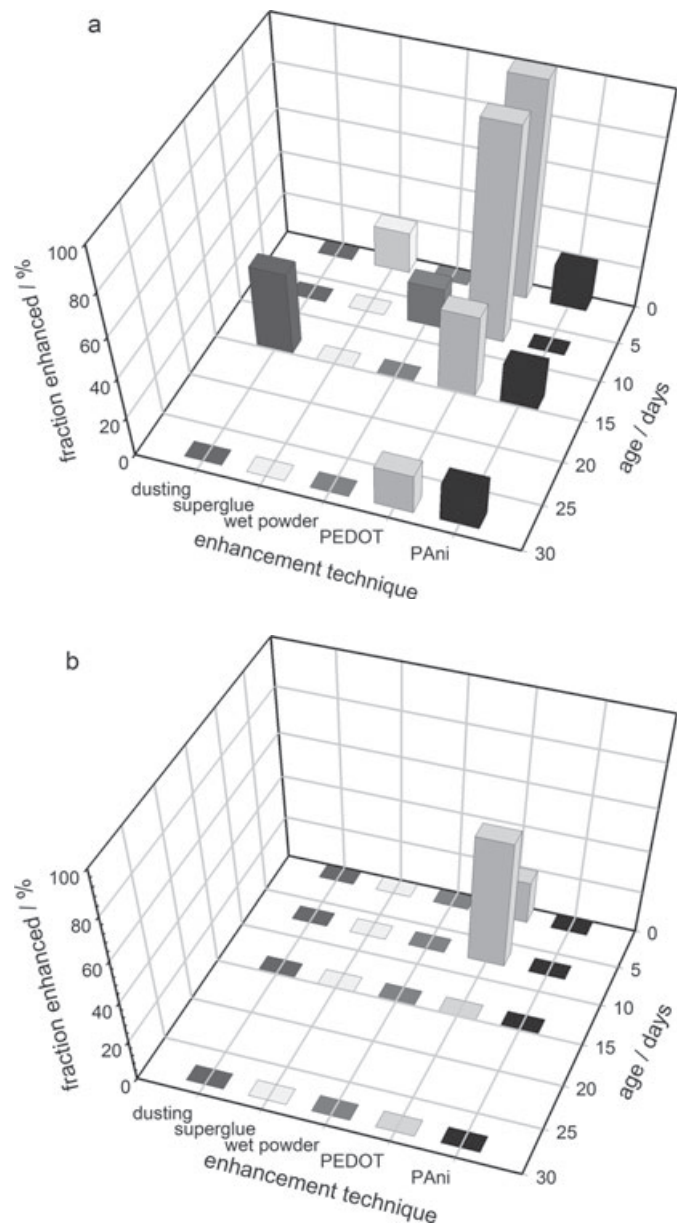


FIG. 7—Three-dimensional bar charts showing the percentage improvements achieved by each of the development techniques for samples subject to washing with aqueous soap solution. Each column represents the combined outcome from the five donors; the figure captures data from 100 prints. Panel a: percentage of prints enhanced by the designated protocol; panel b: percentage of prints enhanced to a useable level (grade 3 or 4) by the designated protocol.

in terms of underlying print quality, enhancement protocol, or assessment) is 4%. In practical terms, this scenario is realistic in that (on the basis of other evidence) one may frequently know when a crime was committed but have little or no knowledge of the history of the object in question.

Inspection of the data in Fig. 8 reveals four interesting features. First, superglue treatment was not effective on these samples subject to these environments. This is not an indictment of this approach, which is extremely successful on a range of nonconducting substrates (e.g., plastics), for which the electrochromic film technology cannot be used. Nonetheless, in view of this outcome, we do not include data obtained using this method in the subsequent discussion. Second, for relatively fresh (1-day-old) prints, there was no significant difference in the effectiveness of the

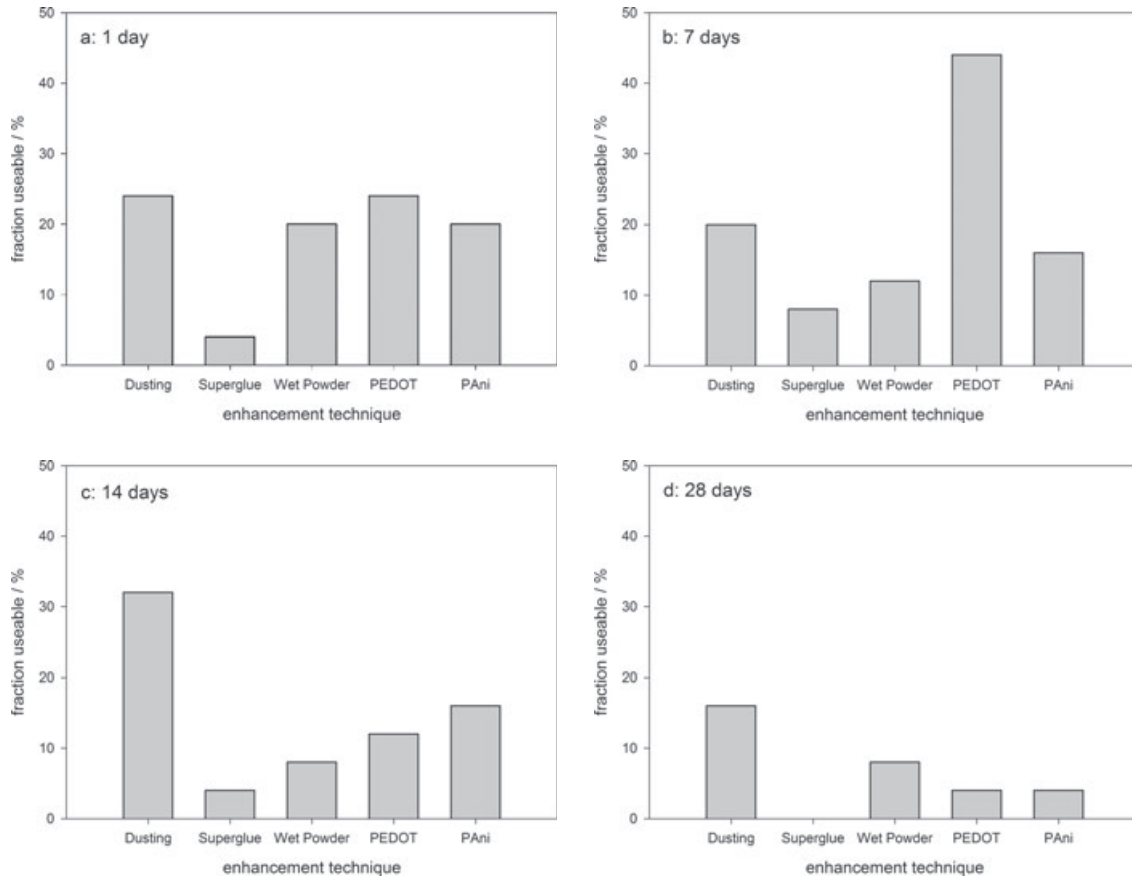


FIG. 8—Enhancement to useable levels of prints of “unknown” environmental exposure (obtained by summing results for the five environments listed in Table 1). Panels a–d, respectively, represent results for prints aged for 1, 7, 14, and 28 days prior to enhancement.

remaining four treatments. While this point was made earlier, the improved statistics offered by this larger sample made the result very clear. Third, for 7-day-old prints, the PEDOT variant of the electrochromic film treatment was unequivocally the best method. Interestingly, this method gave a better outcome for 7-day-old prints than 1-day-old prints. We speculate that this may be associated with some form of compaction of the fingerprint deposit during aging, which made the masking action of the deposit more effective. Third, for 14-day-old prints, dusting was the most effective treatment. Fourth, for 28-day-old prints, dusting was again the most effective treatment, but now even this optimum recovery level was low.

We now consider the complementary situation of fingerprints of known environment, but unknown age. This corresponds to summation of the columns within the individual panels of Figs 3b–7b. We make five observations on the outcomes, shown in Fig. 9. First, cyanoacrylate fuming was the least effective for three cases and not effective in the other two. Second, for the relatively unchallenging situation of prints on substrates kept under ambient conditions, there was relatively little variation among the effectiveness of the remaining four treatments: dusting provided 50% recovery, and PANi electrochromic treatment provided 40% recovery. Third, for samples kept in water, dusting and PANi electrochromic treatments were the most effective methods, with recovery rates of 30% and 24%, respectively. Fourth, for acetone-washed samples, only dusting provided significant enhancement. We deduced that acetone was effective at removing the insulating nonpolar organic components upon which the masking effect underlying the electrochromic film deposition approach relied. Finally, we note that the rather

more challenging environments of extended heat treatment and soap washing prevented significant recovery by all but the PEDOT electrochromic film technique.

Finally, we consider integration of data both within the age rows in Figs 3b–7b and, for each treatment, between the panels in these figures. This corresponds to prints of unknown age and environment. In these aggregated data sets (see Fig. 10), the outcome for each enhancement method was assessed over 100 prints (exposed to five environments, of four ages and originating from five donors), so one may be more confident about the observed variations in performance.

The overall outcome was that the two variants of the electrochromic enhancement technique were of comparable general performance to dusting and outperformed superglue and wet powder for the types of sample studied. Of the two electrochromic films, PEDOT slightly outperformed all other methods and PANi was slightly less effective than dusting. In the absence of “history” information for an object, the statistically best option would be to use PEDOT. However, as the individual data sets for different film histories (see Figs 3–7) show, some knowledge about an object’s age or the environment to which it has been subjected may modify this conclusion. An alternative way of representing this latter issue is summarized in Table 2, which shows the enhancement technique that gave the highest number of improved samples (to a useable grade) for each environment and print age at enhancement. There are a few situations where no samples were improved to a useable extent. In these cases, the technique that gave the best improvement was used; these cases are indicated by italic text. For samples washed with acetone and aged

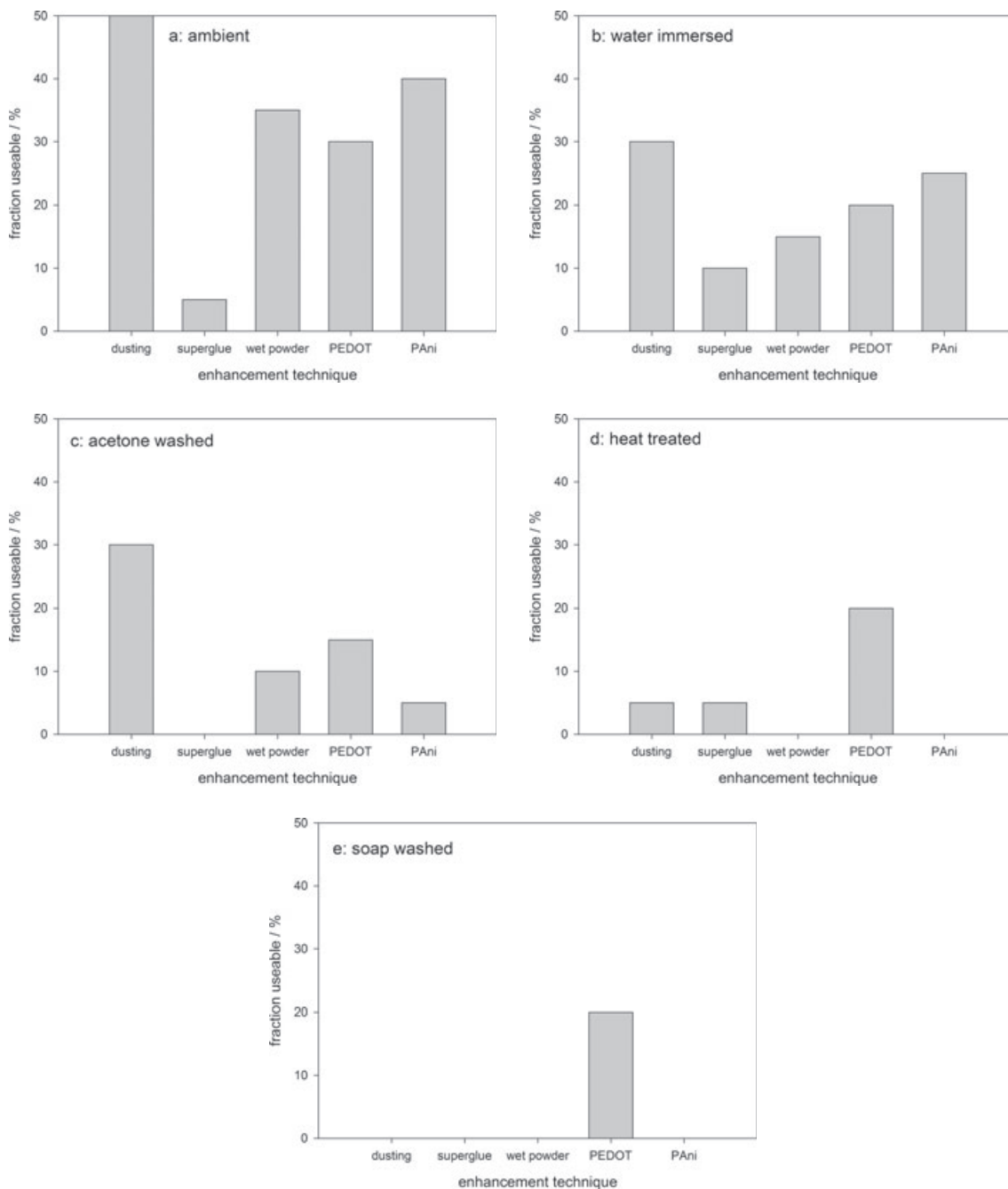


FIG. 9—Enhancement to useable levels of prints of “unknown” age (obtained by summing results for the four sampling times of 1, 7, 14, and 28 days). Panels a–e, respectively, represent results for prints subject to storage under ambient conditions, immersion in water, acetone rinse, heat treatment, and soap wash (see Table 1).

for 28 days, there was no distinction between the two techniques, dusting and PEDOT.

Focusing on the electrochromic enhancement method, we make three pertinent observations. The performance of the electrochromic polymers was better in more scenarios than the other three techniques combined. PEDOT was very effective at enhancing soap-washed samples and those kept at elevated temperature. Despite not producing the highest amount of useable prints, PANi was the most effective at improving water-treated samples of varying ages; further refinement of the technique (e.g., making full use of *in situ* potential control) may be valuable here.

We end with some caveats. Despite efforts to produce prints of consistent quality and composition for a given donor, variations are unavoidable even between fingers on the same hand or from the same finger. The survey of 600 prints was designed to allow exploration of key variables. However, for any given combination of circumstances (donor, print age, environment, and enhancement method), this does not allow for replicates. Additionally, we have not considered all widely used enhancement methods: a useful future activity will be comparison of electrochromic polymer enhancement with methods based on gun blue and related materials (30,31) and on the deposition of metals such as palladium (10,11).

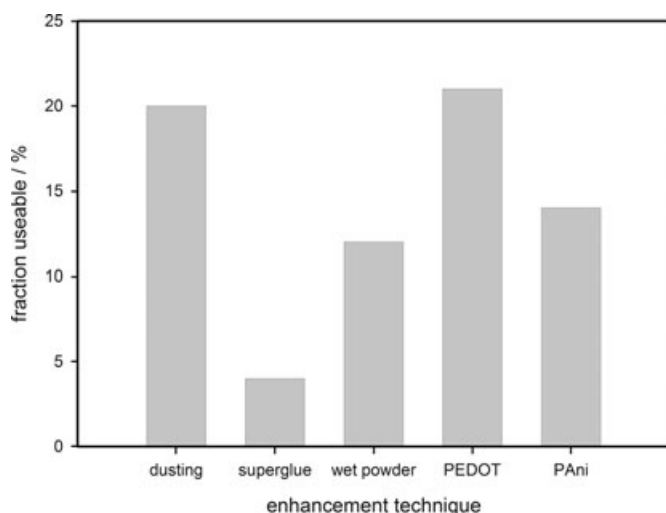


FIG. 10—Enhancement to useable levels of prints of “unknown” age (obtained by summing results for the four sampling times of 1, 7, 14, and 28 days) and “unknown” environmental exposure (obtained by summing results for the five environments listed in Table 1).

TABLE 2—Enhancement technique giving the highest frequency of improvement (increase in fingerprint grade, according to the Bandey scale) for fingerprints of each age and environment studied.

Print Age	Ambient	High Temperature	Water	Acetone Wash	Soap Wash
1 day	PEDOT	PAni	PEDOT	Wet powder	PEDOT
7 days	Dusting	PEDOT	PAni	PEDOT	PEDOT
14 days	PEDOT	PEDOT	Dusting	Dusting	PEDOT
28 days	Dusting	PEDOT	Wet powder	Dusting/PEDOT	PEDOT

PAni, polyaniline; PEDOT, poly(3,4-ethylenedioxythiophene).

Nonetheless, the survey has shown the value of the new electrochromic enhancement approach, identified the scenarios where it is most likely to be effective, and highlighted those areas where a larger survey (with many replicates) might sensibly be focused.

Conclusion

A survey has been carried out on the effectiveness of a new electrochromic method for the enhancement of latent fingerprints on metal substrates. Fingerprints were deposited on stainless steel substrates, exposed to a range of environments representative of plausible crime scene situations and left for varying periods prior to enhancement. Two variants of the electrochromic enhancement methodology, involving PAni and PEDOT films, were compared with three traditional methods, dusting with dry powder, wet powder, and cyanoacrylate fuming (“superglue”). The outcomes were assessed using the 5-point scale devised by Bandey, taking the view that prints of grade 0–2 are not useable and prints of grade 3 or 4 are useable.

Cyanoacrylate fuming was generally the least effective method. This methodology, which is widely used to good effect on insulating materials (plastics), is complementary to the electrochromic methodology, which requires a conducting substrate. In broad terms, the best method for any selected example of the scenarios explored was either dusting or electrochromic enhancement; wet powder offered some enhancement but to a lesser extent.

Performance of the different techniques was assessed from the fine detail of fully known sample history through partially known history

to totally unknown history. For the relatively unchallenging case of samples stored under ambient conditions, with the exception of superglue treatment, there was little difference in the performance of the different techniques for a given age of print. As the prints aged, the recovery rate declined, particularly in the step from 14 to 28 days. Samples washed with acetone prior to storage were best treated by dusting. The poorer performance of the new electrochromic technique here was attributed to dissolution by acetone and surface removal of the nonpolar organic components that form the insulating “mask,” upon which the technique relies. Continuous and prolonged immersion in water generated a complex pattern of enhancement performance. Wet powder did not perform particularly well, but its performance did not decline greatly with immersion time. Dusting and electrochromic enhancement methods worked relatively well for samples up to age 14 days, but recovery rates declined sharply thereafter. For the most challenging environments of extended heat treatment and washing with soap solution, only the electrochromic enhancement procedure (with PEDOT as reagent) was effective.

Aggregation of the data by summation over all print ages (retaining environments separate), or over all environments (retaining print ages separate), or over both print ages and environments was considered. This allowed the assessment of optimum approaches for evidence of unknown age, environmental exposure, or both. Overall, in the absence of any sample history information, electrochromic enhancement by PEDOT provided the best chance of recovering a useable print; dusting and PAni electrochromic enhancement, in that order, were the next best methods. As one acquires more information on sample history, particularly environmental exposure, discrimination between dusting and electrochromic enhancement as the method of choice becomes possible.

We concluded that electrochromic fingerprint enhancement will be competitive with presently used methods across a broad range of scenarios and may be preminent in particular scenarios. There are two respects not explored in the simplistic assessment used here in which the electrochromic film methodology may further excel. The first is diversification to polymer films of different colors; a number of suitable materials are available. Second, the traditional approach involves the use of monochrome black-and-white images but, by definition, electrochromic materials allow the manipulation of optical properties (color) by application of an external stimulus (voltage). Acceptance of this concept, for example using spectral imaging, would yield the benefits of an additional dimension of information.

Acknowledgments

We thank Mark Rowe at Northamptonshire Police for helpful comments and the anonymous donors for their time and patience.

References

- Bowman V, editor. Manual of fingerprint development techniques, 2nd rev. edn. Sandridge, UK: Police Scientific Development Branch, Home Office, 2004.
- Sodhi GS, Kaur J. Powder method for detecting latent fingerprints: a review. *Forensic Sci Int* 2001;120:172–6.
- Haque F, Westland AD, Milligan J, Kerr FM. A small particle (iron oxide) suspension for detection of latent fingerprints on smooth surfaces. *Forensic Sci Int* 1989;41:73–82.
- Polimeni G, Foti BF, Saravo L, De Fulvio G. A novel approach to identify the presence of fingerprints on wet surfaces. *Forensic Sci Int* 2004; 146:S45–6.
- Czekanski P, Fasola M, Allison J. A mechanistic model for the superglue fuming of latent fingerprints. *J Forensic Sci* 2006;51:1323–8.

6. Wargacki SP, Lewis LA, Dadmun MD. Understanding the chemistry of the development of latent fingerprints by superglue fuming. *J Forensic Sci* 2007;52:1057–62.
7. Wargacki SP, Lewis LA, Dadmun MD. Enhancing the quality of aged latent fingerprints developed by superglue fuming: loss and replenishment of initiator. *J Forensic Sci* 2008;53:1138–44.
8. Cuce P, Polimeni G, Lazzaro AP, De Fulvio G. Small particle reagents technique can help to point out wet latent fingerprints. *Forensic Sci Int* 2004;146:7–8.
9. Zhang M, Girault HH. SECM for imaging and detection of latent fingerprints. *Analyst* 2009;134:25–30.
10. Migron Y, Mandler D. Development of latent fingerprints on unfired cartridges by palladium deposition: a surface study. *J Forensic Sci* 1997;42:986–92.
11. Migron Y, Hocherman G, Springer E, Almog J, Mandler D. Visualization of sebaceous fingerprints on fired cartridge cases: a laboratory study. *J Forensic Sci* 1998;43:543–8.
12. Bersellini C, Garofano L, Giannetto M, Lusardi F, Mori G. Development of latent fingerprints on metallic surfaces using electropolymerization processes. *J Forensic Sci* 2001;46(4):871–7.
13. Bond JW. Visualization of latent fingerprint corrosion of metallic surfaces. *J Forensic Sci* 2008;53:812–22.
14. Williams G, McMurray N. Latent fingermark visualisation using a scanning Kelvin probe. *Forensic Sci Int* 2007;167:102–9.
15. Williams G, McMurray HN, Worsley DA. Latent fingerprint detection using a scanning Kelvin microprobe. *J Forensic Sci* 2001;46:1085–92.
16. Skotheim TA. *Handbook of conducting polymers*. New York, NY: Marcel Dekker Inc., 1986.
17. Rajagopalan R, Iroh JO. Development of polyaniline-polypyrrole composite coatings on steel by aqueous electrochemical process. *Electrochim Acta* 2001;46:2443–55.
18. Hamer WJ, Koene L, De Wit JHW. Formation and electrochemical behaviour of poly(pyrrole) coatings on steel substrates. *Mater Corros* 2004;55:653–8.
19. Hür E, Bereket G, Şahin Y. Corrosion inhibition of stainless steel by polyaniline, poly(2-chloroaniline), and poly(aniline-co-2-chloroaniline) in HCl. *Prog Org Coat* 2006;57:149–58.
20. Fernández I, Trueba M, Núñez CA, Rieumont J. Some features of the overoxidation of polypyrrole synthesized on austenitic stainless steel electrodes in aqueous nitrate solutions. *Surf Coat Technol* 2005;191:134–9.
21. Biallozor S, Kupniewska A. Conducting polymers electrodeposited on active metals. *Synth Met* 2005;155:443–9.
22. Patra S, Munichandraiah N. Supercapacitor studies of electrochemically deposited PEDOT on stainless steel substrate. *J Appl Polym Sci* 2007;106:1160–71.
23. Sakmeche N, Aaron JJ, Aeiayah S, Lacaze PC. Usefulness of aqueous anionic micellar media for electrodeposition of poly-(3,4-ethylenedioxythiophene) films on iron, mild steel and aluminium. *Electrochim Acta* 2000;45:1921–31.
24. Fried JR. *Polymer science and technology*. Upper Saddle River, NJ: Prentice Hall, 1995.
25. Kalaji M, Peter LM. Optical and electrical ac response of polyaniline films. *J Chem Soc Faraday Trans* 1991;87:853–60.
26. Beresford AL, Hillman AR. Electrochromic enhancement of latent fingerprints on stainless steel surfaces. *Anal Chem* 2010;82:483–6.
27. Gileadi E. *Electrode kinetics for chemists, chemical engineers and materials scientists*. New York, NY: VCH, 1993;34–41.
28. Hamann CH, Hamnett A, Vielstich W. *Electrochemistry*. Weinheim, Germany: Wiley-VCH, 1998.
29. Bandey HL. *Fingerprint development and imaging newsletter: the powders process, study 1*. Sandridge, UK: Police Scientific Development Branch, Home Office, 2004; Report No.:54/04.
30. Cantu AA, Leben DA, Ramotowski R, Kopera J, Simms JR. Use of acidified hydrogen peroxide to remove excess gun blue-treated cartridge cases and to develop latent prints on untreated cartridge cases. *J Forensic Sci* 1998;43:294–8.
31. Smith K, Kauffman C. Enhancement of latent prints on metal surfaces. *J Forensic Identif* 2001;51:9–15.

Additional information and reprint requests:

A. Robert Hillman
 Department of Chemistry
 University of Leicester
 University Road
 Leicester LE1 7RH
 U.K.
 E-mail: arh7@le.ac.uk