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TECHNICAL NOTE

CRIMINALISTICS

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Nanoscale Analysis of the Interaction Between Cyanoacrylate and Vacuum Metal Deposition in the Development of Latent Fingermarks on Low-Density Polyethylene*

ABSTRACT: Vacuum metal deposition (VMD) has been previously demonstrated as an effective development technique for latent fingermarks and in some cases has been shown to enhance prints developed with cyanoacrylate (CA) (superglue) fuming. This work utilizes scanning electron microscopy (SEM) to investigate the interactions of the two development techniques when applied to latent fingermarks on low-density polyethylene. CA is shown to act principally on the eccrine deposits around sweat pores, where polymerization results in long polymer fibrils a few 100 nm in width. Subsequent VMD processing results in additional areas of development, for example, between pores. However, the primary mode of deposition of zinc is by interaction with the polymerized CA, the fibrils of which become decorated with zinc nanoparticles. Areas with limited CA deposition and no significant polymerization are also enhanced with the VMD process, resulting in increased print development.

KEYWORDS: forensic science, latent fingermark, cyanoacrylate fuming, vacuum metal deposition, nanoparticle, microscopy, superglue, friction ridge impression, fingerprints

Vacuum metal deposition (VMD) is an established technique for fingermark development. Conventionally, a thin, discontinuous layer of gold is deposited, and nanoclusters of gold subsequently act as nucleation sites for zinc deposition (1,2). This has shown to be a particularly effective technique for development of latent prints on various papers (2–5) and polymers (1,2,5–9). Research has shown that VMD may be the optimal technique for some surfaces, including papers exposed to moisture (3), plastics submerged in water or exposed to body fluids (5), and semiporous polymer banknotes, such as those first introduced in Australia in 1988 (6). Studies have shown that VMD is particularly useful in the development of older prints on nonporous surfaces, showing effectiveness on latent prints over 24 months old in laboratory trials (10) casework prints approximately 6 years old, subsequently leading to an identification (5) and enabling development of prints described as at least 16 years old (5).

It has been shown that the effectiveness of VMD and other development techniques is strongly influenced by the type of polymer substrate (1,8,11). Research studies and casework have highlighted a number of problems with VMD, some of which are substrate dependent. These include reverse development (1,10), excess gold deposition that inhibits zinc nucleation and hence latent print development (8) and empty prints, where the VMD processing deposits zinc around the latent print on the general background, but no metal is deposited on or between the fingermark ridges (7,10).

A number of groups have proposed improvements to the VMD process to enable increased development efficacy, including additional treatment with increased gold deposition (8) and a single-metal silver deposition process, after or as an alternative to the existing gold–zinc deposition (12). Other works have shown that cyanoacrylate (CA) fuming can act as an effective pretreatment for VMD development (5–7,10,13); VMD following CA fuming can lead to improved ridge detail, making identification possible (7,10,13) or alternatively can lead to the development of additional marks (5). Previous works (11,14,15) have demonstrated the importance of nanoscale analysis of both developed fingermarks and surfaces to improve the understanding of development technique processes and interactions. Electron microscopy techniques have been previously used to study the variation between commercial development agents for prints on adhesives (14), polymer surfaces developed with powder suspension (11), and for elucidating interaction of multiple techniques for development of bloodied prints (15). This work utilizes scanning electron microscopy (SEM) to examine the interaction between the CA and VMD processes, to better understand the mechanisms of development enhancement.

Experimental

Latent fingermarks on low-density polyethylene (LDPE) substrates were collected at the Home Office Scientific Development Branch (HOSDB) from seven donors. Depletion series of 10 natural prints were collected from each donor. Utilizing a similar process to an earlier study (11), no grooming procedure for loading with sebaceous or eccrine material was applied, although donors were

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asked not to have washed their hands for at least 30 min before donation. Variability was minimized by lightly rubbing fingertips together prior to deposition.

Once donated, the fingermarks were aged for 24 h. The first mark in each depletion series was removed and stored as a control. CA (superglue) fuming was then carried out (MVC 5000 fuming cabinet with "Cyanobloom" glue; Foster and Freeman Ltd., Evesham, U.K.) at room temperature and 80% relative humidity. Again, example fingermarks were removed and retained as controls. The remaining marks were dyed with basic yellow (BY40) *c.* 1 h after the cabinet fuming cycle had been completed. Once more example marks were removed for comparison. Finally, VMD processing with gold–zinc method (VMD900 metallizer; West Technology Systems Ltd., Yate, U.K.) was carried out 3 days after superglue treatment on the remaining marks. A 3- to 4-mm-length on 0.25-mm-diameter gold wire was completely evaporated; subsequently, zinc evaporation was carried out until marks were visualized and judged to be at greatest contrast with the background. More details on all these procedures are provided elsewhere (16).

Sections were taken from representative samples and mounted on aluminum stubs, utilizing carbon-loaded adhesive and conductive silver paint. To enable accurate comparison, this study shows images from a single donor: one sample with CA fuming, a second with CA followed by BY40 dye, and a third sample with CA fuming, dye, and VMD in sequence. Mounted samples were examined within a Supra 35VP scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany), with secondary electron and backscattered electron analysis. Study of electrically insulating samples by this method usually requires additional coating to ensure conductivity, and a thin layer of carbon, gold, or platinum is often applied. In this instance, however, as we aim to study the interaction of vacuum-deposited metal with the treated fingermark, it was essential to allow examination of samples without any additional metal coating. This is achieved through utilizing variable pressure (VP) mode, here with nitrogen at pressures of 15–60 Pa and accelerating voltages of 5–20 kV. Although not always allowing highest-quality images, this technique allows the study of nonconducting samples. Elemental evaluation was conducted by utilizing backscatter electron images and with an INCA energy dispersive X-ray analysis system (EDX; Oxford Instruments plc, Abingdon, U.K.) operating with this microscope.

Results and Discussion

Figure 1 shows SEM images of the latent fingermark on LDPE developed with CA fuming only. The low magnification images, Fig. 1*a*,*b*, show the macrofeatures of the developed fingermark and indicate that the formation of polycyanoacrylate appears to be primarily associated with eccrine secretion from sweat pores. Figure 1*c* shows a section of one such pore at a higher magnification, showing the boundary of developed and undeveloped areas and microstructure of polycyanoacrylate, with characteristic fibrils from the development of the fingermark. Figure 1*d* shows the polycyanoacrylate at higher magnification. However, here the polycyanoacrylate fibrils are strongly affected by the electron beam, causing the distortion that has been previously observed when studying structured polymer samples without application of a conducting layer (14).

Scanning electron microscopic images of the latent fingermark sample developed with CA followed by BY40 dye are shown in Fig. 2. The macrofeatures of the developed fingermark, shown in Fig. 2*a*, show strong similarity to the sample without the dye process (Fig. 1*a*), and no additional areas of development are visible. Higher-magnification images, Fig. 2*b*,*c*, show no additional development mechanisms, and characteristic CA fibrils retain the structure seen in the CA development. The highest magnification (Fig. 2*d*) clearly shows the fibril structure in this area, without the beam-induced distortion previously (Fig. 1*d*). These images are consistent with the dyeing process that is used to increase contrast and visualization rather than to extend the developed area (2,17).

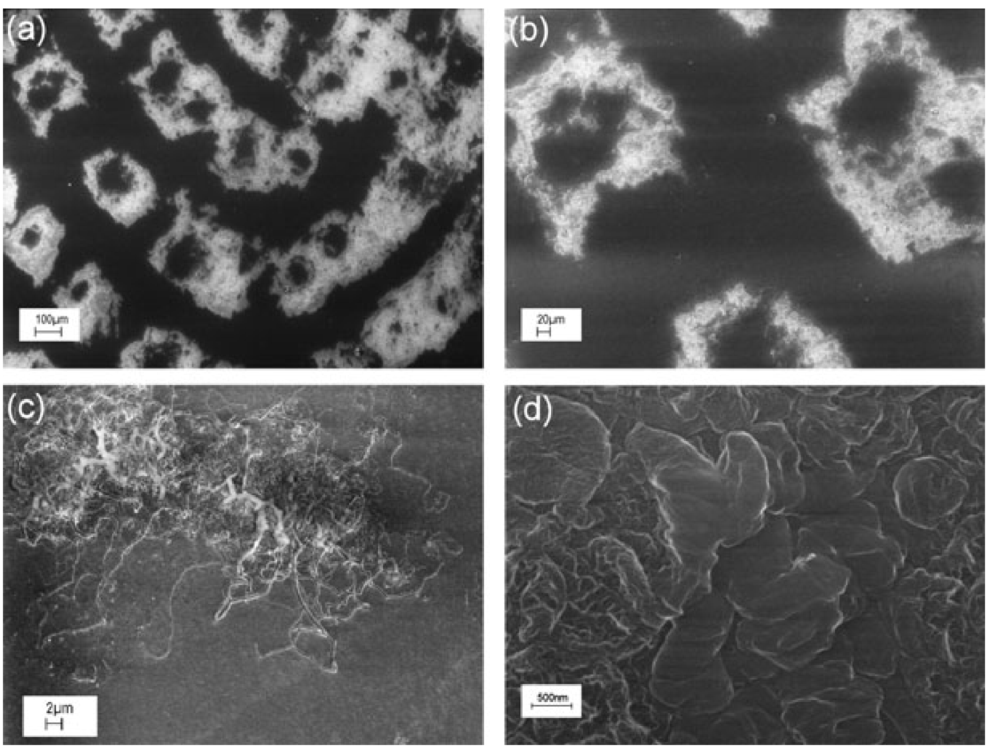

FIG. 1—*Scanning electron microscopic images of fingermark developed with cyanoacrylate fuming.*

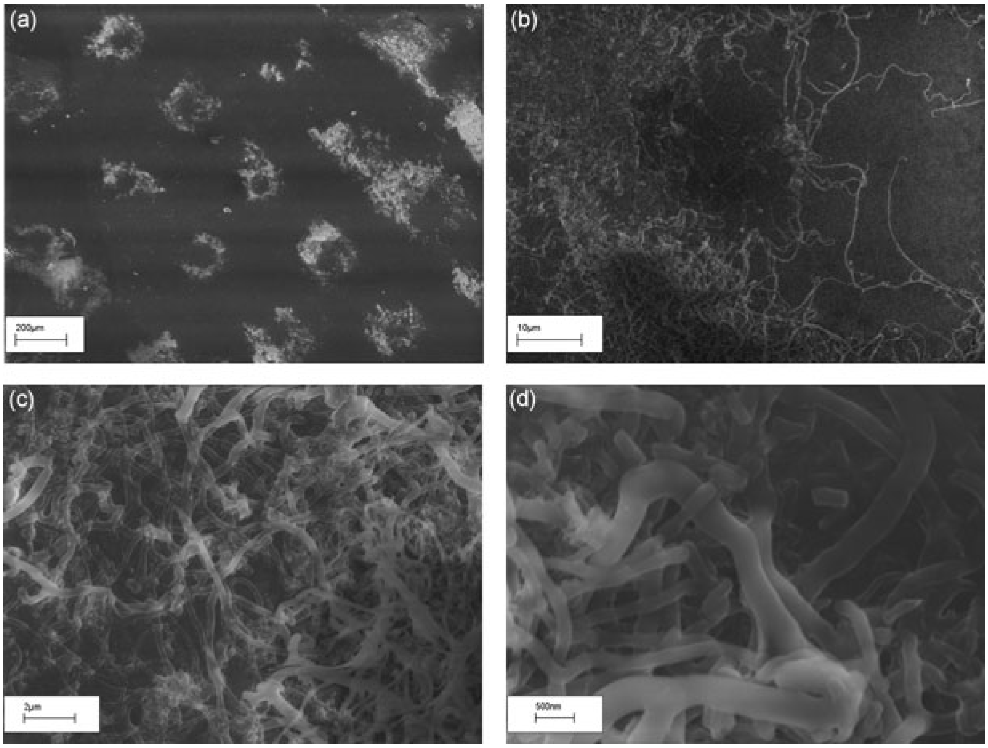

FIG. 2—*Scanning electron microscopic images of fingermark developed with cyanoacrylate fuming followed by BY40.*

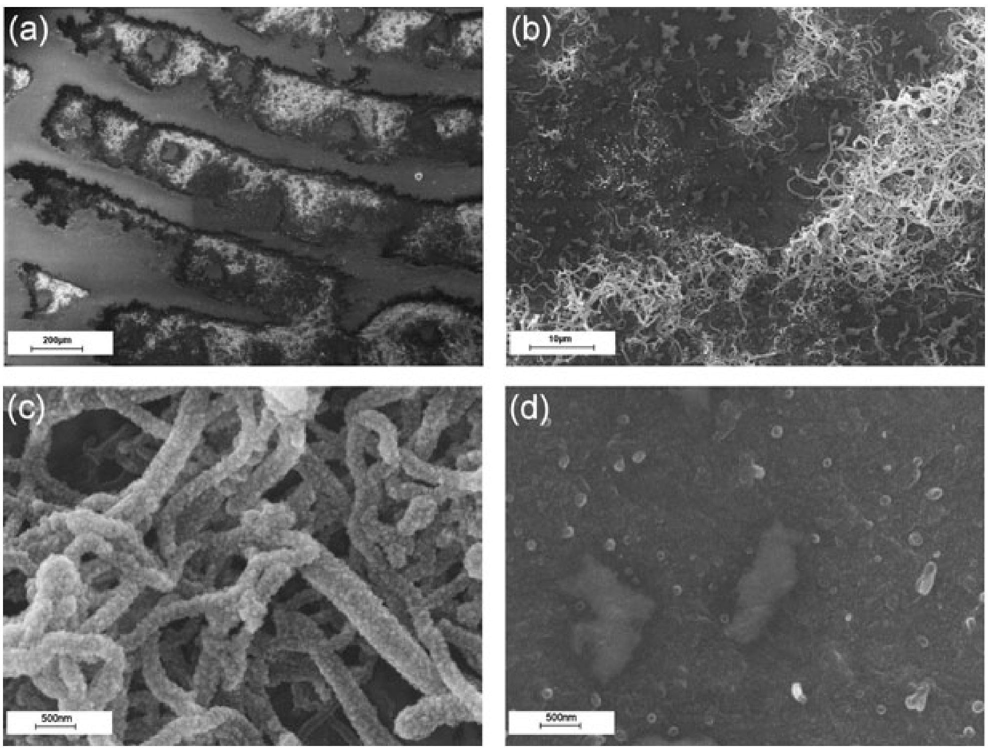

FIG. 3—*Scanning electron microscopic images of fingermark developed with vacuum metal deposition following cyanoacrylate fuming and BY40.*

Figure 3 shows SEM images of the latent print on LDPE developed with a sequence of techniques: a CA fuming process and BY40 dye, followed by VMD of gold and zinc. Figure 3*a* is an SEM image at low magnification, showing the macrostructure of the developed fingermark; by comparison with development shown in Figs 1*a,b* and 2*a* additional developed areas away from the CA deposition are readily identifiable. Figure 3*b* shows the characteristic polycyanoacrylate fibrils from the CA process, partially covering the developed fingermark ridge.

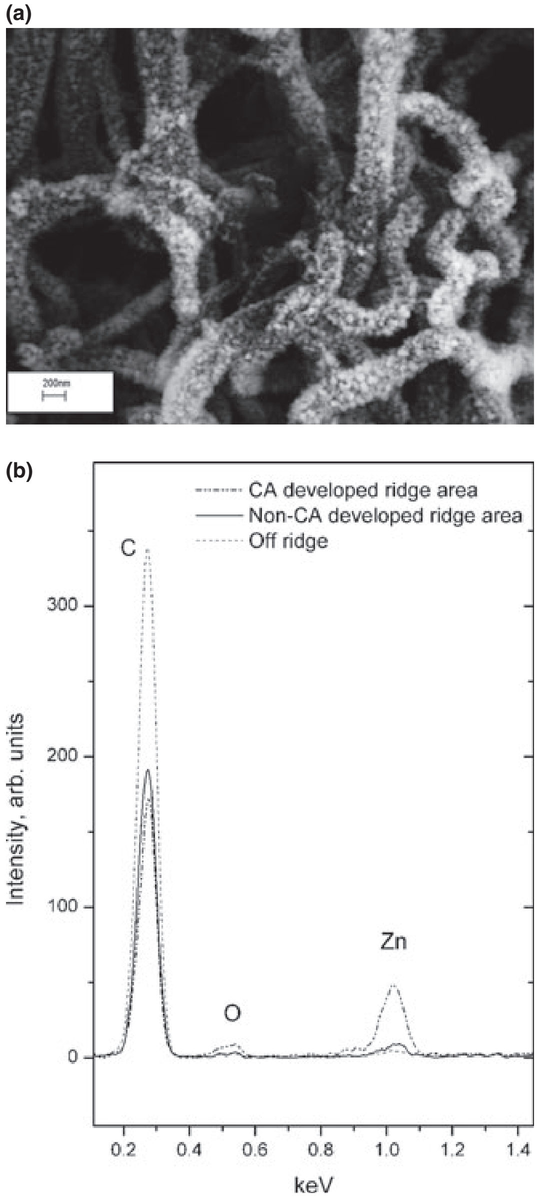

FIG. 4—*Compositional analysis of fingermark developed with cyanoacrylate (CA) and vacuum metal deposition. (a) Backscatter electron image of CA fibrils with zinc nanoparticle decoration and (b) energy-dispersive X-ray analysis of an area off fingermark ridge and areas of ridge with CA polymerization and without extensive polymerization.*

Figure 3*c* shows an area with significant development from superglue fuming, showing polycyanoacrylate fibrils, which after the VMD process are now coated with a particulate decoration. At the same magnification, Fig. 3*d* shows an area of developed fingermark ridge with no significant superglue deposit. Here, a nodular structure related to the initial stages of CA polymerization is apparent.

An SEM backscatter electron image of the sample developed with CA and VMD process is shown in Fig. 4*a*. This elemental contrast technique shows atomic number distinction between CA fibrils and the decorating particulates observed in Fig. 3*c*. Small-area elemental analysis by EDX was conducted over areas of the developed print, and representative spectra are shown in Fig. 4*b*. High levels of zinc are associated with the areas of CA polymerization, consistent with the zinc particulate decoration of the CA fibrils observed in Figs. 3*c* and 4*a*. There are also lower levels of zinc content in areas of the fingermark ridge, which are developed with the VMD process but which do not contain significant areas of CA polymerization. Figure 4*b* also shows that there is no detectable zinc content in the areas of fingermark between ridges. These analyses indicate zinc nanoparticle decoration of polycyanoacrylate fibrils, as well as zinc deposition associated with areas of fingermark ridges away from effective CA development. This process may relate to the improved definition of the print seen in other works (2,5,11) through zinc deposition on the nodular structure formed by superficial CA treatment, without extended polymerization. This appears to aid VMD but does not assist with contrast development with the CA process and would not interact with dyeing agents in the same manner as the polymer chains. However, detection enhancement with this process may be affected by development reversal through the VMD method, which can relate to substrate surface, process parameters, and age or condition of the fingermark (1,7,8,10).

Conclusions

Latent fingermarks on LDPE were developed by CA fuming and by a sequence of CA fuming followed by VMD of gold and zinc. The developed prints were studied by variable pressure scanning electron microscopy. Initial examination shows that CA fuming produces polymerized CA mainly focused around pores in the latent fingermark. The application of gold and zinc through a VMD technique to a sample previously treated with CA causes the development of additional areas not coated with polycyanoacrylate, which relates to the improved definition of the print seen in other works (2,5,11). However, the primary interaction of the zinc deposition appears to be with the polycyanoacrylate, decorating the polymer chains with nanoscale particulates. The other areas of the fingermark ridges that are also developed contain zinc at lower levels. It is possible that the nodularization of areas without extensive CA polymer chains, related to initial polymerization without extended polymer growth, may enhance metal deposition and therefore promote visualization following the VMD process.

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