Title Page (with authors and addresses)

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Dynamics and Mechanism of the Physical Developer Process for Visualization of Latent Fingerprints on Paper

Jodie L. Coulston[a#], Vaughn Sears[b], Stephen Bleay[c] and A. Robert Hillman[a]*

[a] School of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, UK

[b] Home Office Science, Centre for Applied Science and Technology, Woodcock Hill, Sandridge, St Albans, Herts, AL4 9HQ, UK

[c] Division of Human Sciences, School of Applied Science, London South Bank University, London SE1 0AA, UK

Now at: School of Criminology and Criminal Justice, University of Portsmouth, Portsmouth, Hampshire, PO1 2HY, UK

* Corresponding author (email: arh7@le.ac.uk)

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Graphical Abstract (for review)

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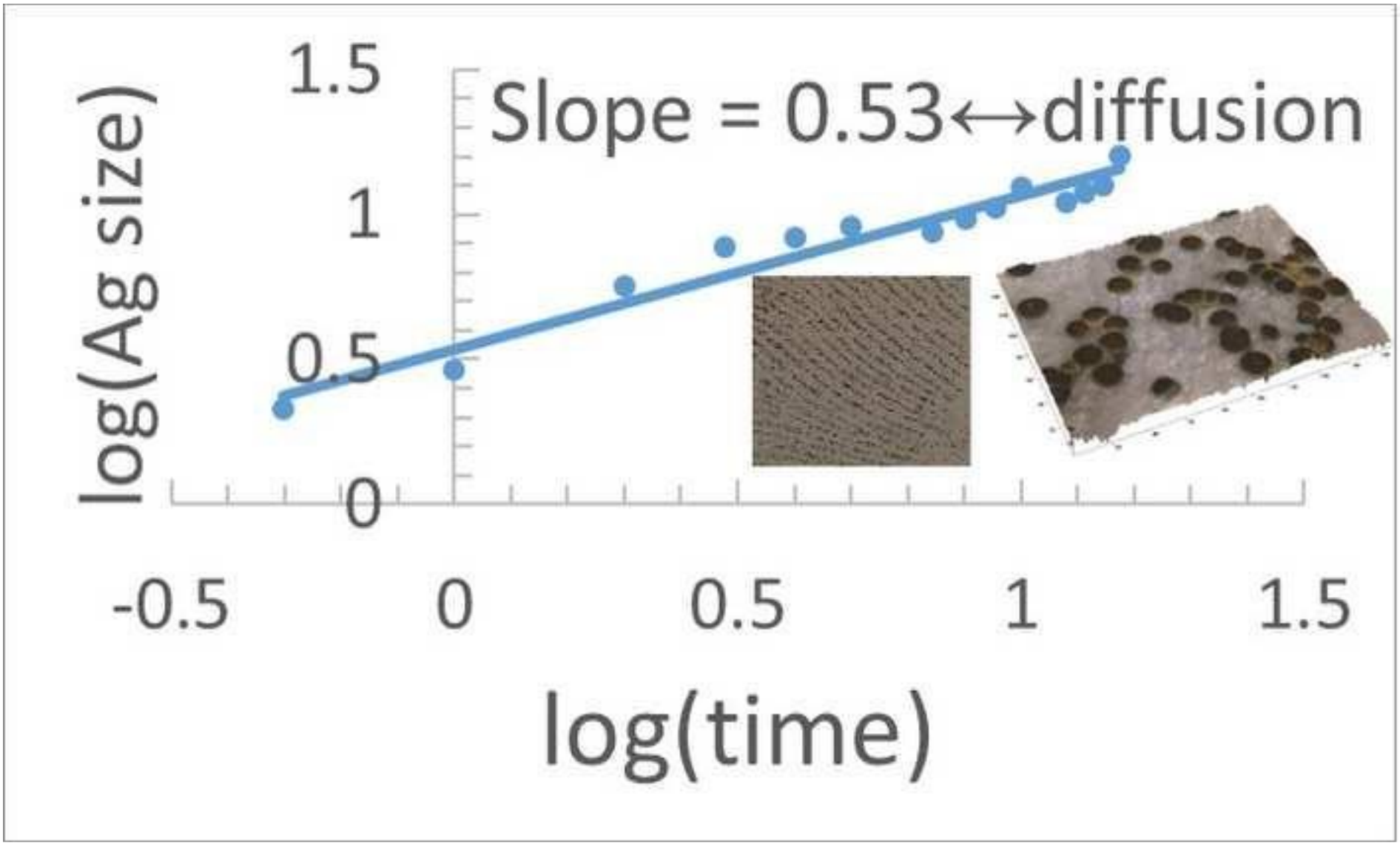
Slope = 0.53↔diffusion
log(Ag size)
1.5
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Dynamics and Mechanism of the Physical Developer Process for Visualization of Latent Fingerprints on Paper

Highlights

- Latent marks on diverse paper types respond mechanistically similarly to the PD reagent
- Silver particles in PD working solution have a size distribution peaked at 880 nm
- Silver particles are deposited instantaneously, then grow under diffusional control
- There is no evidence for iron components of the PD redox system in surface deposits

Dynamics and Mechanism of the Physical Developer Process for Visualization of Latent Fingermarks on Paper

Abstract

We present a detailed mechanistic study of the PD process, focused on the nucleation and growth dynamics of silver particles on fingermarks deposited on a paper surface, from macroscopic (whole fingermark) and microscopic (particle level) perspectives. Conceptually, we separate the outcomes into aspects that *precede* exposure of the exhibit (relating to the reagent formulation), that relate to the development of the fingermark *during* immersion in the PD formulation, and that characterise the fully developed mark *subsequent* to immersion. Initially, dynamic light scattering shows the silver particles in solution to be relatively monodisperse, with a peak particle size of 880 nm. In the second instance, the issue is whether the particles grow to final size in solution then deposit on the surface *or* deposit as relatively small particles then grow on the surface. To the naked eye, silver deposition is evident after 2 minutes; corresponding optical profilometry images show evidence of surface-bound particles (mean diameter 2.13 µm) after 30 s. Across the development time (15 minutes) the particle population density (2.36 (±0.52) x 10^5 cm^{-2}), is independent of time. During this time, the mean particle diameter increases with the square root of development time to 16.09 µm. The dynamics suggest essentially instantaneous (shorter than observation time) nucleation and diffusionally controlled growth. Surface analysis (EDS) shows the expected high (low) levels of silver on ridge detail (in furrows) but no evidence of iron (from the redox component of the formulation) entrapment at any point on the surface.

Keywords: forensic science; latent fingermark; physical developer; nucleation and growth; silver

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1. **Introduction**

Physical developer (PD) is acknowledged as an effective technique for the development of latent fingermarks on porous surfaces, predominantly paper, and finds wide application in the examination of currency, documents and correspondence evidence. While widely used by practitioners, particularly for porous surfaces that have been wetted, there has been surprisingly little research into the underlying fundamentals of the PD process. Here we address this through a detailed microscopic exploration of the nucleation and growth dynamics of silver particles on the surface, manifested macroscopically as the temporal development of the latent fingermark. For immediate purposes, this provides insight into aspects of optimisation of the current formulation [1]. Looking forward, it provides investigational strategies and benchmarks for next generation PD formulations.

Two factors motivate the present study. Firstly, although PD is an effective technique, the operational success rate of reproducible high quality developed marks is low; this may be attributed to a combination of the practical demands of the process and limited understanding of the mechanism, thereby limiting optimal implementation. Second, a reagent formulation change has been enforced as a result of one of the surfactants, Synperonic N, being environmentally outlawed [2]. Identification of a suitable replacement reagent requires that the role of the surfactant be identified and, more widely, the fundamentals of the process be understood, facilitating optimisation of (any variant of) the PD process. In pursuit of this, the present study will reveal the silver particulate size in solution, particle population (as a function of time) on the surface, the dynamics of silver growth on the surface, and compositional analysis of the developed marks.

The PD process was first implemented for the fabrication of printed circuit boards in the electronics industry. In this context, Jonker *et al* introduced the cationic surfactant n-dodecylamine acetate (nDDAA) in order to stabilise the working solution, and the non-ionic surfactant Lissapol N (now named Synperonic N) to aid solubilisation of the cationic surfactant [3]. (NB: since the liquid phase contains colloidal particulates, it is strictly a *dispersion* rather than a *solution*. Throughout, we recognise this factual distinction but, given the common usage of the latter term by practitioners in this context, we will use the terms interchangeably.) Morris extended the use of PD for latent fingermark development under contract to the Police Scientific Development Branch (PSDB, more recently known as the Centre for Applied Science and Technology, CAST) for the Atomic Weapons Research Establishment (AWRE) utilising Jonker's formulation [4]. This led to a comprehensive review for latent fingermark development techniques, including PD [5]. The non-ionic surfactant, Synperonic N, has been used for over 30 years but its manufacture has recently been banned in Europe and the USA, due to its environmental degradation to an endocrine disruptor. This motivates research for alternatives: for example, a Tween 20 formulation is currently being used outside Europe, although this surfactant is still undergoing evaluation as a replacement for Synperonic N [6-9], having recently been deemed unsuitable for use in the UK [10].

A fine balance of components governs the chemistry of the recommended working solution [4, 11-13] which has been modified [14, 15] and compared to other PD formulations [6], to promote the application of PD for fingermark development [5, 16, 17]. The redox chemistry of the PD solution has been extensively studied [13, 14, 18-20]. It is established that ferrous ions (Fe^{2+}) reduce silver ions (Ag^{+}) to elemental silver (Ag^{0}). Silver atoms – clearly highly unstable in solution - aggregate to particulates whose size is in the colloidal domain, although we note that the focus of attention to date in this respect has been for particle size on the *surface*. Since colloidal particles are thermodynamically unstable with respect to bulk material, kinetic stability must be established. This is believed to occur via the silver particles being surrounded by the cationic surfactant molecules [11, 13]. These amendments to the simple redox components significantly increase the shelf life of the working solution, possibly in part due to the presence of adventitious contaminants. The guideline for correctly stored solution in the Fingermark Visualization Manual is 5 days [1]; we work within this guideline.

As with any colloidal dispersion, the particulates seek nucleation sites on which to deposit and grow. This highlights the conflicting demands of PD users: a reagent system with a long shelf life (dispersion stability) that rapidly deposits silver (a manifestation of *in*stability). Overall, the surfactant plays the crucial role of placing the system at the edge of (in)stability; both the absolute and relative concentrations of the components (here Synperonic N and n-DDAA) influence the outcome. Under conditions in which the silver dispersion is unstable, its deposition must be spatially selective, i.e. only on fingermark residue, so practical constraints in the use of PD solutions include meticulous reagent preparation and clean/scratch-free glassware. Without this attention to detail, control over silver deposition (solely on fingermark residue) is relinquished.

In the light of the above operational challenges, alternative methods and reagents have been studied. These include Oil Red O and Nile Red, both of which are lipid stains chosen to target water-insoluble components of the fingermark, as this is what PD is believed to target. Comparison studies concluded that neither of these techniques outperformed PD and in some cases they were only more efficient for purposely loaded marks [8, 21-23]. An important discriminator between PD and these purely lipidtargeting reagents is that the effectiveness of Oil Red O and Nile Red is negligible after 4 weeks, whereas PD still works for marks aged for up to 90 years [24]. Clearly, they do not target the same species. Since PD is highly effective for fingermarks which have been exposed to water, it is widely theorised that it targets water-insoluble material. However, following later studies [25, 26] which suggested that PD benefits from the presence of both the water-insoluble *and* water-soluble components of the fingermark to develop the highest quality fingermark, we have recently observed [27] that eccrine components entrapped by (or emulsified with) sebaceous components can significantly enhance PD development efficacy. The mechanism by which silver deposits onto the fingermark residue is still unknown.

The aims of this paper focus on the underlying chemistry of the PD process. After an initial qualitative survey encompassing different secretion types on different paper substrates, we elect to explore the

development of natural marks on standard copy paper as the most representative practical scenario. The first specific objective is silver particulate *size in the solution* (strictly, dispersion), prior to exposure to the exhibit. The second is determination of the surface *population* of silver particulates as a function of exposure time of the exhibit to the formulation. The third is rate of increase with time of particle *size on the surface*. The fourth objective, complementing the physical character of the preceding objectives, is surface chemical composition, i.e. determination of which formulation components – together with silver - are ultimately transferred to the surface. These objectives are pursued at the *microscopic* level. In a strategic advance on previous works, we correlate these *microscopic* outcomes with simultaneous *macroscopic* observations of fingermark development and their relationship with operational procedures.

2. Materials and Methods

2.1 Chemicals

Maleic acid (Analytical grade), iron (III) nitrate nonahydrate (Analytical grade), ammonium iron (II) sulfate hexahydrate (Analytical grade), citric acid (anhydrous) (Analytical grade) and silver nitrate (ACS reagent, >98%) were used as supplied (by Sigma Aldrich). The detergent solution was formulated from n-dodecylamine acetate (DDAA, used as supplied by ICN) and Synperonic N (used as supplied by BDH). The Synperonic-N was stored under refrigeration to prevent degradation.

2.2 Fingermark deposition and substrates

A single donor was used for all samples. We acknowledge the widely appreciated variability of fingermark residue composition and mass with donor identity. This can lead to significant variations in developed mark quality, which can complicate evaluation of reagent performance. However, this is not a factor in the present study, which is focused on mechanistic issues, not performance. Use of a single donor has the advantage, in the present context, of ensuring continuity of similar fingermark residue for all samples. The donor was asked to deposit natural fingermarks by washing their hands in warm, soapy water at least 30 minutes prior to deposition [28]. Fingermarks deposited and aged for 1 day under ambient conditions are referred to as “dry” samples. Fingermarks deposited and left under ambient conditions for 1 hour, then immersed in water for 1 day to simulate wetted conditions, are referred to as “wetted” samples.

White copy paper (80 gsm; Inacopia) was used as the primary substrate. The preliminary survey (see Figure 2, below) also included vellum laid paper (100 gsm; Amazon), archival (acid-free) paper (100 gsm; Amazon) and Basildon Bond writing paper (90 gsm; Ryman).

2.3 Physical developer procedure

In overview, the maleic acid pre-wash and PD working solutions were prepared in accordance with the method outlined in the Home Office Fingermark Visualisation Manual [1]. Given the sensitivity of the method to conditions, we set out the procedure explicitly. The maleic acid solution was produced by dissolving 12.5 g maleic acid in 500 mL deionised water (Elga) until fully dissolved. In accord with the

recommended protocol, each sample was immersed in the maleic acid solution for at least 10 minutes or until bubble evolution had ceased, whichever was the longer [1].

The physical developer solution is formed from three solutions. The first is the redox solution made up according to the following steps: (i) to 900 mL deionised water (Elga), add 30 g of iron (III) nitrate nonahydrate and stir until fully dissolved; (ii) add 80 g of ammonium iron (II) sulphate and stir until fully dissolved; (iii) add 20 g of anhydrous citric acid and stir until fully dissolved.

The detergent solution used was supplied by CAST and was made up by adding 2.8 g n-dodecylamine acetate (DDAA) and 2.8 g of Synperonic-N to 1 L of deionised water; the mixture was stirred until the solutes were fully dissolved. The silver nitrate solution was prepared by added 10 g silver nitrate to 50 mL deionised water, with stirring until fully dissolved. The final PD working solution was prepared by slowly adding 40 mL of the detergent solution to the redox solution and stirring for at least 10 minutes. 50 mL of silver nitrate solution was then added slowly and stirred for a further 10 minutes.

Each sample was immersed in the working solution for times up to 15 minutes (see figure legends), washed in deionised water three times to remove any excess solution, then air dried for imaging.

2.4 Instrumentation

Images of developed marks were taken using an HD Inspex camera with integrated focus and lighting controls to adjust the brightness and DCS-5 imaging system (Foster and Freeman) with the Polytec ring light and gooseneck light sources. The images were converted to black and white to assist with contrast. A Zeta 20 Optical Profiler with 0.5 x Coupler was used to obtain the microscopic images, using 5x magnification for visualization of the fingermark ridges. Particle diameters were measured under 50x magnification using the built-in Zeta software. A Philips XL30 environmental scanning electron microscope coupled with Oxford Inca energy dispersive X-Ray analysis (EDS) was used for surface imaging and compositional analysis. Dynamic light scattering was performed using a Malvern Zetasizer Nano S dynamic light scattering system (courtesy of STFC ISIS Facility, Didcot, UK). A 1 day old working solution of PD was pipetted into a disposable cuvette; three replicate measurements were taken to acquire an average reading. Data analysis was performed using the built-in Malvern software.

3. Results and discussion

The complete set of combinations of parameters (fingermark composition, paper type and possible immersion in water) generates an impractically large matrix of experiments. We therefore present a preliminary survey of the similarities and variations associated with the different secretion types (fingermark composition) and paper types (in section 3.1), before restricting our attention to so-called natural marks (i.e. those for which no attempt was made to restrict the mark to purely eccrine or sebaceous secretion) on standard copy paper (in sections 3.2-3.5). The approach permits detailed exploration of the most probable exhibit type, combined with a reasonable notion of how straightforwardly the outcomes might be extended to less common circumstances.

Consistent with the prominence of temporal factors in the objectives (see above), we present the data in a format that represents the life-cycle of a developed latent fingermark. Conceptually, one may think of stages before, during and after exposure of the exhibit to the PD reagent. First, we consider the nature of the solution (strictly, dispersion) prior to contact with the exhibit (section 3.2). Second, we follow the development of the mark during immersion of the exhibit in the PD formulation (section 3.3). Third, we undertake analysis of the surface of the developed mark in morphological (section 3.4) and compositional (section 3.5) terms.

3.1 Overview of PD interaction with different fingermarks and paper substrates

In this section we consider the effectiveness of PD to develop fingermarks of various origins on different types of paper, subject to "dry" and "wetted" conditions (see above). Split prints [28] provide a reliable means of comparison of different sample histories. The purpose of these observations is to provide context for the more detailed focus of this study.

Figure 1 shows PD development of eccrine, sebaceous and natural marks subject to "dry" and "wetted" exposure (compared by split print methodology). *Eccrine* marks show no development, irrespective of ageing environment. This is not unexpected given that PD involves exposure to an aqueous medium so water soluble components would be expected to be washed from the surface. While there are some Ag particulates on the surface, they do not represent fingermark development; rather this is low level (*cf.* other images in **Figure 1**) background development. *Sebaceous* marks show similar levels of development by PD, irrespective of prior exposure to dry or wet conditions; in practice, use of the PD formulation levels the situation to the "wetted" scenario. Silver deposition is evident and reveals a clear ridge pattern. *Natural* marks (see above) exposed to dry and wet environments are developed, although they appear more 'dotted' compared to sebaceous marks.

Wetted natural marks are enhanced to essentially the same quality as dry marks. We have conducted spot tests involving PD treatment of single component and binary mixtures of compounds known to be present in fingermark residue. Our qualitative observations indicate that the presence of mixed deposits containing components of *both* eccrine and sebaceous secretions – essentially, a simplistic "natural mark" – promotes visualisation of the latent fingermark. Collectively, these split print and spot test observations support the theory that, from a chemical perspective, PD targets – and requires the presence of - water insoluble residue components, as concluded in other studies [25, 26].

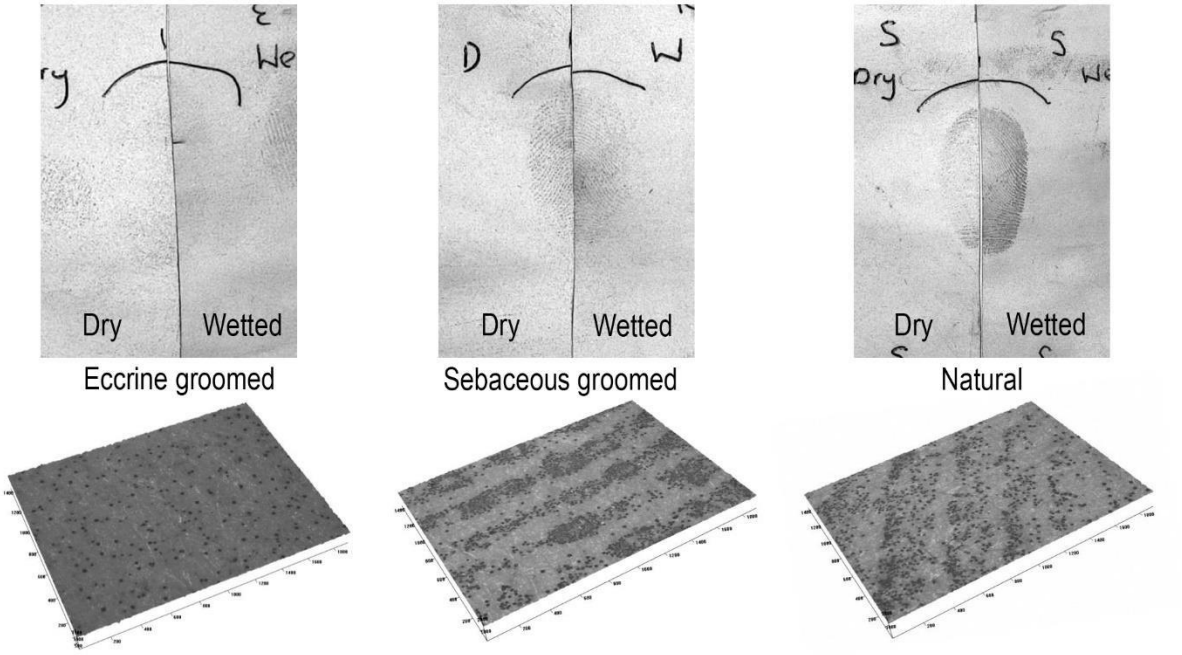


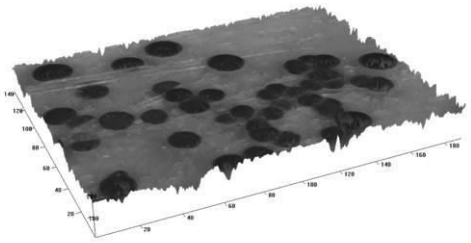
Figure 1. Dry *vs* wetted split prints (left to right: eccrine, sebaceous and natural) with corresponding microscopy images (see section 2.4) for the "dry" samples; microscopy images for wetted marks were indistinguishable from those for the paired dry marks. Prints were deposited onto white copy paper and aged for 1 day under ambient conditions ("dry" marks) and for 1 day immersed in water ("wetted" marks) (see section 2.2). Tick marks on microscopy images every 200 µm in (x,y)-directions.

Figure 2 shows PD development of natural marks deposited on a range of paper types, then subject to "dry" and "wetted" environments prior to development. Whole mark images are complemented by microscopy images that show the size, density and disposition of Ag particulates on the surface.

At a macroscopic (whole mark) level, fingermark development quality and development times are relatively similar across all paper types tested; variations between paper types do not exceed those for replicate samples. Microscopic images were acquired using the Zeta software of the optical profiler as outlined in section 2.4. Image areas evaluated contained 20-100 silver particles (according to sample) and revealed narrowly dispersed (see section 3.2, re. polydispersity index) silver deposits for individual samples. The primary qualitative empirical observation is that smaller Ag particles are seen when the fingermark ridges have developed better and silver has deposited across all areas of the fingermark, whereas larger particles are observed when only partial areas of the fingermark have developed. In each individual case, the particles were uniform in size. For white copy paper, the particle size ranges were 13-20 □m (dry) and 12-20 □m (wetted); for vellum 6-10 □m (dry) and 6.5-8.5 □m (wetted); for acid free paper 18-25 □m (dry) and 13-26 □m (wetted); and for writing paper 13-18 □m (dry) and 12-16 □m (wetted). With the arguable exception of vellum, the type of paper does not appear to affect the mechanism of silver deposition; across all paper types studied, the particle diameter ranges from 6-20 □m.

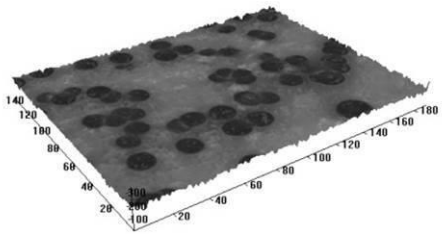
a (i) – dry

a (ii) – dry



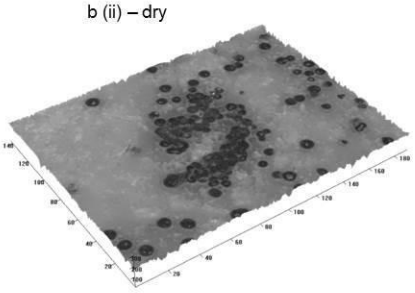
a (iii) – wetted

a (iv) – wetted



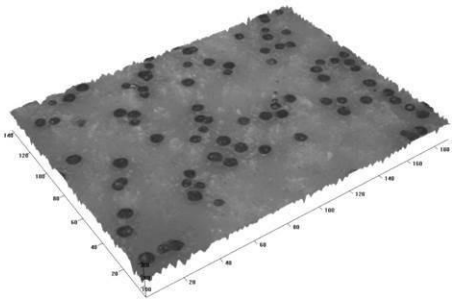
b (i) – dry

b (ii) – dry



b (iii) – wetted

b (iv) – wetted



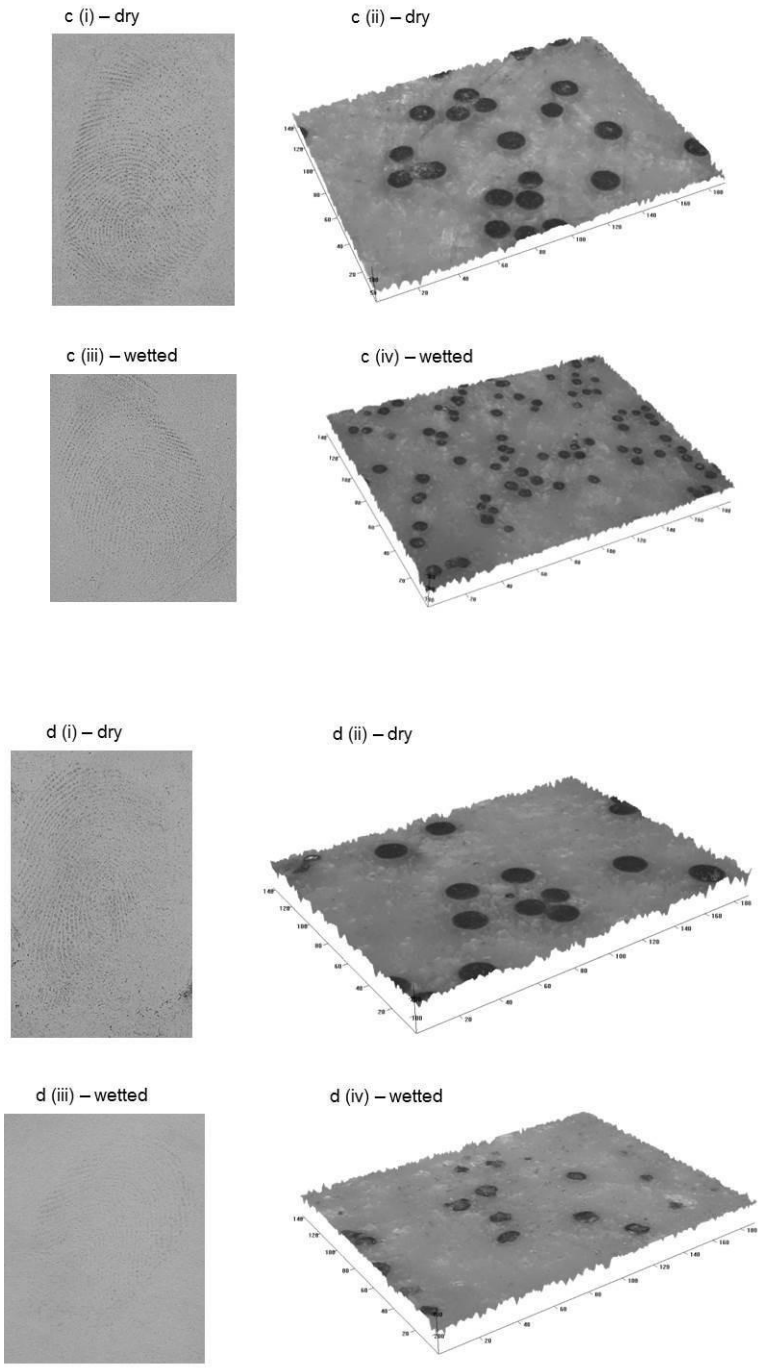


Figure 2. PD development of 1 day old latent fingermarks. Paper type: a: white copy paper; b: vellum laid paper; c: archival paper; d: writing paper (see main text for sources). Ageing conditions: images (i) and (ii) "dry"; images (iii) and (iv) "wetted". Images (i) and (iii) capture whole mark, and images (ii) and (iv) are the corresponding 3D microscopy images (tick marks every 20 µm in (x,y)-directions).

3.2 Silver particle dispersion in PD formulation

Although microscopy (SEM) has been used to observe the silver particles on developed samples [1, 13] subsequent to removal from the PD reagent, the size of the silver particles in the PD formulation has not been previously reported. The issue here is whether the particles grow to final size in solution then

deposit on the surface *or* deposit as relatively small particles then grow on the surface. Resolution of this point requires particle size determination in the liquid *and* on the surface.

Figure 3 shows the particle size distribution in the reagent solution, as determined using dynamic light scattering. The average diameter of the silver particle size distribution is ca. 880 nm, which is attributed to the largest peak by intensity as the silver particles are thought to be the largest component of the working solution. While the particles are not monodisperse, the distribution of sizes is relatively narrow (supported by a polydispersity index of 0.28) and essentially all the metal is present in the colloidal size range; the latter emphasises the importance of the surfactant(s) in maintaining reagent stability. Interestingly, this is broadly the same size regime as the particles in a surfactantstabilised iron oxide powder suspension used for latent fingermark visualisation [29]. Looking ahead to exposure of the exhibit to the reagent, the question then is the evolution (or otherwise) of silver particles as they transfer from solution to the surface.

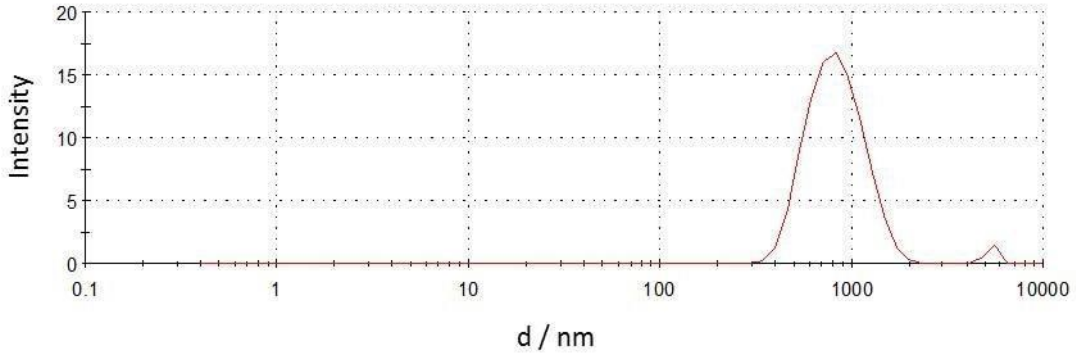


Figure 3. Silver particle size distribution in PD working solution (as detailed in section 2.3). Data determined using dynamic light scattering. Data represent particle diameter.

3.3 Dynamics of surface deposition and growth of silver particles

Previous studies by Cantu [13] reported silver particles on developed marks to have diameters on the order of 5 □m. To presage the data of the next section, we find silver particles a factor of 2-4 larger than this at the end of the development period. The qualitative deduction is that the particles deposit as (relatively) small entities and grow – potentially by an order of magnitude – on the surface. The issues we explore in this section are the time course of this process and the ways in which this is manifested – colloquially, "seen" – on macroscopic and microscopic observational scales.

The typical development time for the PD formulation used is ca. 15 minutes [1]. In order to study the dynamics of silver deposition and growth, *nominally* identical fingermarks (see section 2.2) were aged for 1 day under ambient conditions then developed for different intervals of time in the range 30 s to 15 minutes (see above for procedural details). A different finger was used to deposit a mark for each development time to allow for subsequent microscopic analysis and avoid destruction of the substrate after repeated immersions during the PD process. The exhibits were then imaged at low and high spatial resolution, respectively, by photography (such that the whole mark was captured) and by

microscopy on a scale commensurate with a typical ridge width (such that individual particulates were resolved).

Figure 4 shows a collection of different developed marks as a function of development time using the formulation described in section 2. To the naked eye, silver deposition is evident after 2 minutes, suggesting that silver deposition from solution onto the surface is relatively rapid. Thus, the surfactants are optimally formulated to maintain reagent stability in the absence of suitable nucleation sites but are unable to maintain stability when such sites – in the form of fingermark residue – are provided. The visible background staining observed could be attributed to sample processing or incomplete washing of the PD solution. Corresponding optical profilometry images on selected areas of the same samples are shown in **Figure 5**. After 30 s there is some evidence of particles on the surface; note that particles of the size indicated in **Figure 3** should be visible (even if not accurately measurable) at the resolution of these images. After 1 minute, there is a low but clearly visible population of small silver particles on the surface. From 2 minutes onwards, there is an increasingly visible population of growing silver particles. The authors note that to the eye, the size of the silver particles at 10 minutes look larger than the particles observed at 11-14 minutes in **Figure 5.** This is due to having to use a separate sample for each development time to avoid destruction of the paper substrate as discussed above.

The next step is characterization of the size(s) and population of the particles as a function of time. A plot of mean particulate size as a function of development time is shown in **Figure 6**, for the experiments of **Figures 4** and **5** and replicates. Though not readily visible to the naked eye, silver deposition after only 30 seconds resulted in a mean particle diameter of 2.13 µm; this is effectively double the particle size in solution, emphasising the high selectivity of the PD process in targeting the fingermark residue. After 2 minutes the average particle diameter was 5.69 µm, ca. 5x larger than the silver particle size in solution. Thereafter, progressive growth resulted in a particle diameter of 16.09 µm at the end of the recommended [1] 15 minute development time. The slight anomalies present at 6 and 10 minutes in Figure 6 are due to the methodological practicalities discussed above, however the general trend of progressive growth is still evident.

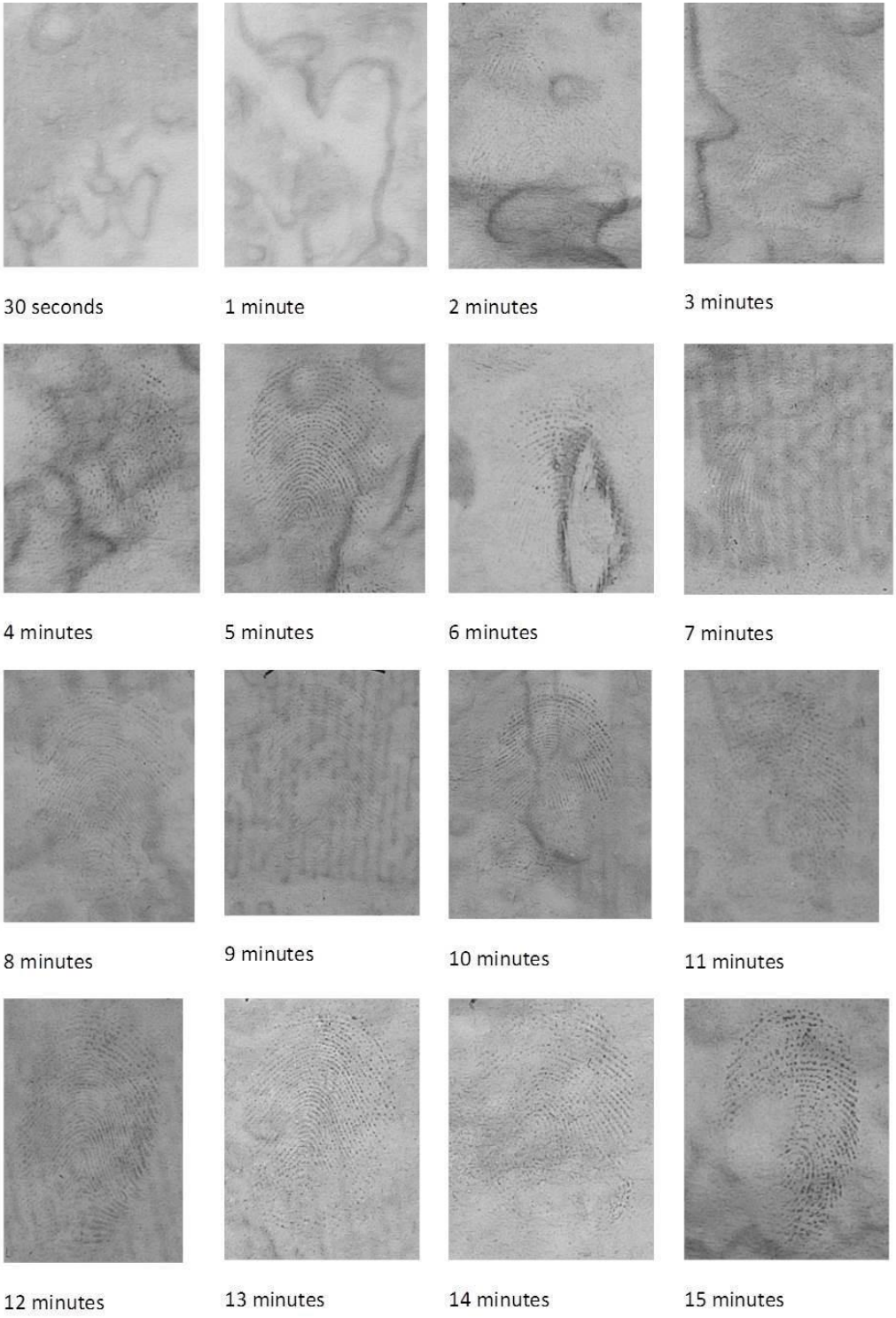


Figure 4. Whole mark photographs of representative natural fingermark development using PD (see section 2 for details) at a range of development times (as indicated). Subsequent to deposition on plain copy paper, the marks were left under ambient conditions for 24 hours before development.

Figure 5. Corresponding microscopic images of selected regions (on residue representing ridge detail) of the marks shown in **Figure 4**. Images acquired using 3DM instrument (see section 2.4) at 50x magnification; scale markers ("tick marks") on x- and y- axes of images at 20 □m intervals.

The conclusion from these data sets is that silver deposition on the surface (residue) occurs almost instantaneously and silver growth then occurs on surface-immobilised particles. We have no evidence for silver particle growth in solution, followed by deposition of "fully developed" (no longer growing) particles on the surface. This is consistent with the inherent low stability of the colloidal working solution, and its reputation for requiring clean (nucleation site-free) glassware and reagents.

Subsequent to silver nucleation on the surface, an interesting question is whether particle growth is dictated by kinetic or diffusional factors. Typically, diffusional phenomena are characterised by a dependence on the square root of time. **Figure 7** shows the data of **Figure 6** plotted in double logarithmic form; in this format, the slope is the power law. The value observed (0.53) is a strong indicator of diffusional control, i.e. "square root" relationship. In these experiments the solution was quiescent; superficially, this is inconsistent with the common practice of rocking the development bath to prevent localised depletion of reagent. However, the diffusion length associated with species in aqueous media after ca. 100 s is on the order of 100 □m, which is similar to the natural convective length; this adventitious "stirring" imposes a practical upper limit on the diffusion layer thickness and ensures that local depletion does not become problematical.

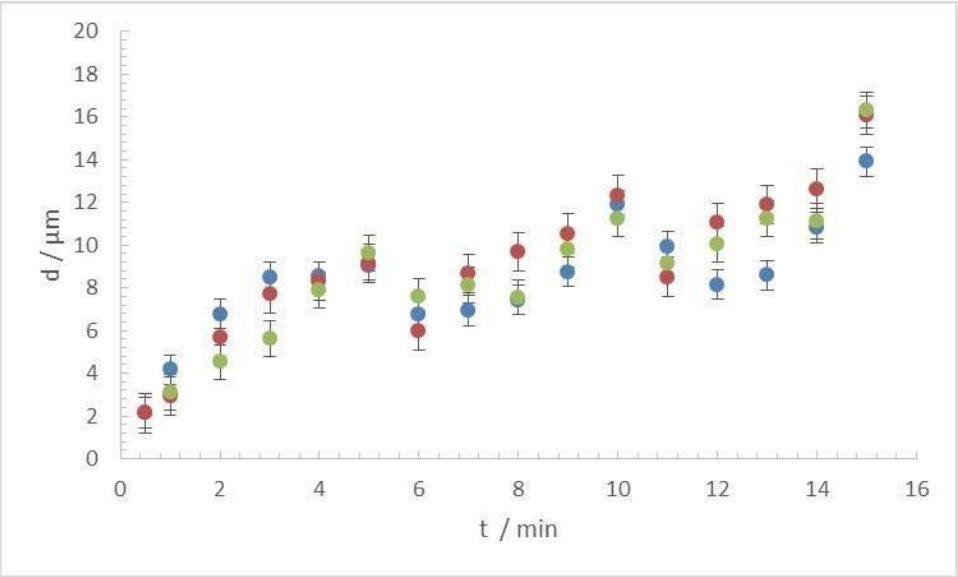


Figure 6. Plot of silver particle diameter as a function of development time. Data from images of **Figure 5** and replicates (indicated by different coloured symbols), presented as average values (symbols) and standard deviations (error bars) for detected particles in each sample.

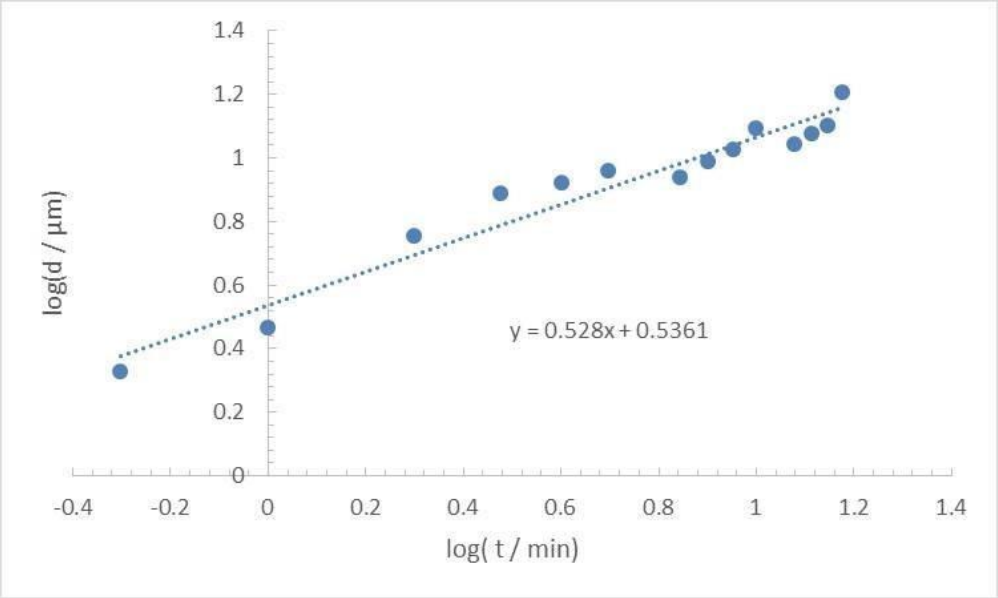


Figure 7. Variation of silver particle diameter with time, plotted in double logarithmic format. Data from **Figure 6.**

Exploration of particle deposition and growth is extended by the data of **Figure 8**, showing the particle population within each image of **Figure 5** as a function of time. To convert the data from a sample to a materials basis, i.e. particle density per unit area, the raw particle counts in **Figure 5** were divided by the sample area. Interpretation of the data requires account being taken of two factors. First, although every effort was taken to maintain equivalence of the deposited marks – most notably use of a single donor following the same protocol – each data point does represent a different mark. Second, at short times, the particles are small and not readily seen; population counts are less reliable at early times. With these caveats, the deduction from **Figure 8** is that the particle density is independent of time, i.e.

nucleation on the surface is “instantaneous” (shorter than the observation time) and subsequent observations relate solely to their growth. The mean particle density is 2.36 (±0.52) x 10^5 cm^{-2}.

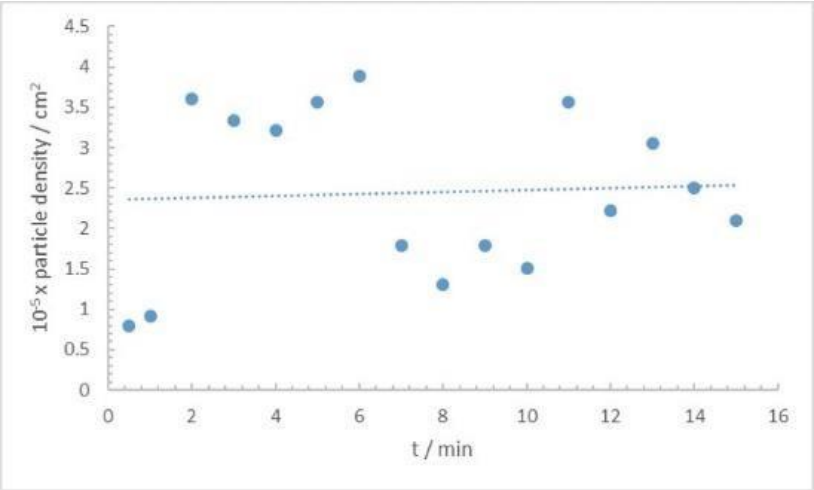


Figure 8. Plot of silver particle population as a function of development time. Data from images of **Figure 5**.

As indicated above, the move to quantitative data treatment requires an appreciation of reproducibility of mark deposition. Due to repeated immersions and practicality issues, simultaneous deposition from different fingers was used for different development time samples. This raises the issues of pressure of fingermark deposition and amount of residue on each finger. To eliminate these issues, the growth study was repeated with extension of the established split print strategy to a 4component split, in which the quadrants were exposed to PD development for different times, namely 1, 4, 8 and 15 minutes (to reflect different regimes within the overall development process as depicted in **Figure 4**).

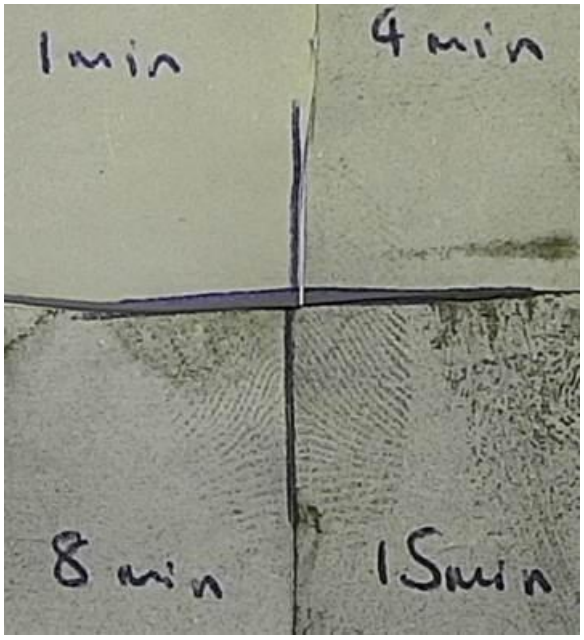


Figure 9. Quadrant-divided whole mark photographs of natural fingermark development using PD (see section 2.3 for details) at four development times (as indicated). Subsequent to deposition on plain copy paper, the mark was left under ambient conditions for 24 hours before development.

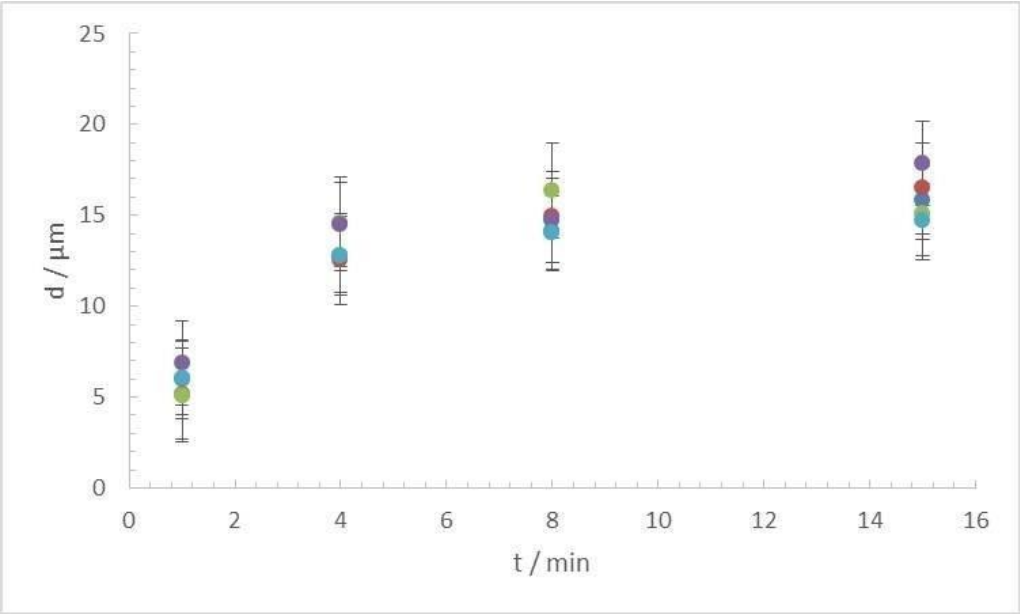


Figure 10. Plot of silver particle diameter as a function of development time for quadrant split prints. Data from images of **Figure 9** and a further four replicates (five samples in total, indicated by different coloured symbols), presented as average values (symbols) and standard deviations (error bars) for detected particles in each sample.

Figure 9 shows a representative outcome of this approach. Progressive development of the fingermark is entirely consistent with the images of **Figure 4**. Microscopic observation of five replicate image sets (analogous to those of **Figure 5**) yielded the data of **Figure 10**. The growth of silver and progressive quality of a *single* fingermark development is very obvious in this study, with the ridge detail improving in contrast and clarity from 1 to 15 minutes. **Figure 10** underpins the earlier conclusion that the greatest changes occur between 1 and 4 minutes, with progressive growth thereafter.

3.4 Surface morphology post-development

The dynamic studies of the previous section revealed the silver particles deposit very rapidly after immersion, then grow on the surface to a size of 15-20 µm, compared to 880 nm in solution. In the previous section, the emphasis was on temporal variations at a given observational length scale (see **Figure 4** and **Figure 5**). In this section, we focus on a single development time – corresponding to full development – and explore observational length scale as a variable.

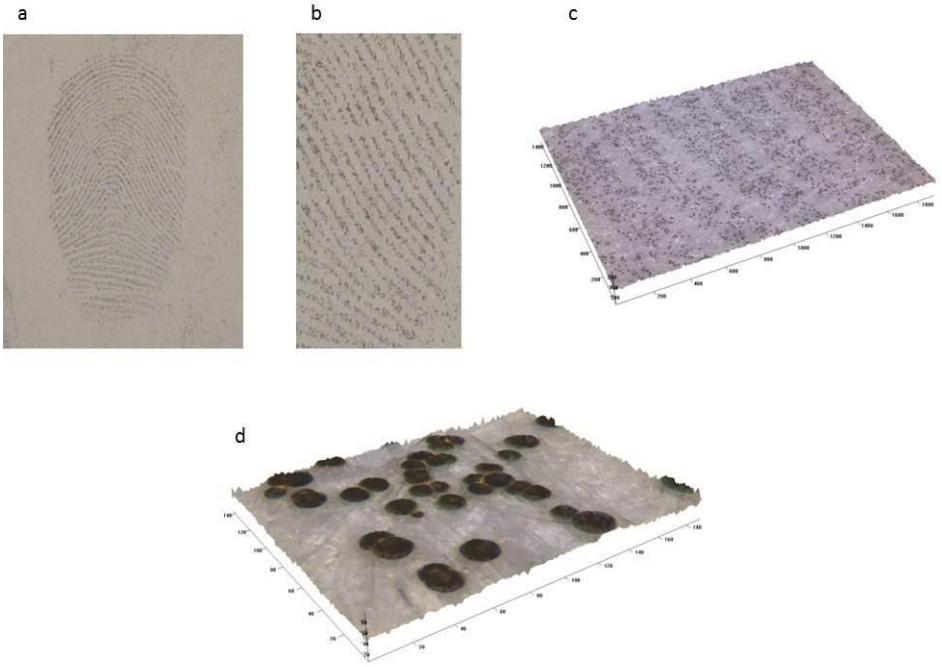


Figure 11. (a) Whole mark photograph of a fully developed (15 minutes) natural mark. Fingermark deposition, ageing and development conditions as in **Figure 4**. (c, d) Corresponding microscopic images of selected region (on residue representing ridge detail) of the marks shown in (b). Images acquired using 3DM instrument (see section 2.4); scale markers ("tick marks") on x- and y- axes of images at 200 □m intervals (c) and 20 □m (d)

Figure 11 shows a series of images at progressively greater magnification, from macroscopic to microscopic. To the naked eye, marks developed with PD appear as solid grey lines against the white paper background. Magnifying these images further starts to reveal the 'dotted' nature of the developed marks. Rather than a series of continuous ridges, individual silver particles are seen as a series of dots along the ridges. Linking these observations back to the time sequences of **Figure 4** and **Figure 5**, it is interesting to correlate the perception of development when viewing the mark on different length scales. When viewed as a whole mark, development is not obvious until 4 minutes. However, looking at the magnified images (compare those at 2 – 4 minutes in **Figure 5**), one would anticipate being able to see useful development from as early as 2 minutes. While we do not explore this question further here, we speculate that this is an interesting manifestation of visual perception.

3.*5 Surface compositional analysis*

Scanning electron microscopy (SEM) has been used previously to observe surface particulates, but with the presumptions that (i) the particles are silver and (ii) no other component(s) of the formulation are present, i.e. compositional analysis of the developed marks has not been reported. While it might be presumed "obvious" (albeit unproven) that the particles are at least predominantly silver, the primary point of ambiguity is whether iron species are entrapped. **Figure 12** shows a representatative SEM image of a small section of a developed fingermark. X-ray analysis (EDS) was conducted on an

area presumed to be silver and an area away from this (annotated spectrum 1 and spectrum 2, respectively). Panels b and c in **Figure 12** show the EDS results. As expected, the (notional) silver particle is predominantly silver and the area away from the silver particle comprises carbon and oxygen. The interesting additional points are the presence of chlorine and the absence of iron. Since the PD formulation does not contain chloride, this is presumed to arise from the fingermark residue. The absence of iron indicates that the iron species are restricted to the Fe^{2+}/Fe^{3+} redox partners involved in the reduction of silver in solution; these are not entrapped by the deposition process.

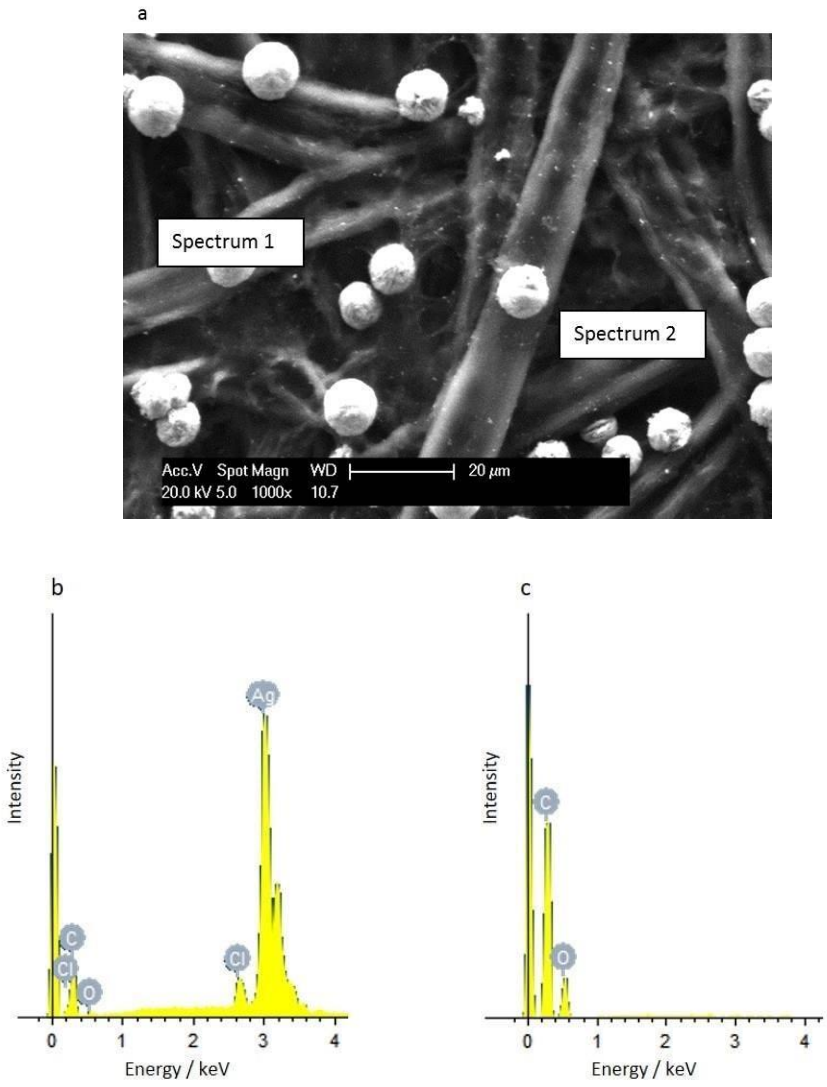


Figure 12. (a) SEM image of a fully developed fingermark, focused on a section of ridge detail; (b) EDS spectrum of a notionally silver particle (annotated "spectrum 1" in panel a); (c) EDS spectrum of a notionally silver-free region (annotated "spectrum 2" in panel a). No peaks observed beyond 4 keV. Local surface analysis (weight %): (b) Ag: 52, C: 35, O: 12, Cl: 1 (c) C: 58, O: 42.

4. Conclusions

The first qualitative conclusion is that *both* eccrine and sebaceous components are associated with optimal PD performance; the complete picture is more complicated, but requires component-

bycomponent spot test analyses that are outside the scope of the present study. Second, within the restricted range explored, variations in paper type have effects on outcome that are within the variations observed between *nominally* identical samples. In particular, irrespective of performance, we find no evidence for changes in PD mechanism. Third, whatever the outcome for a particular set of circumstances (see below), exposure to water does not influence the silver deposition at a microscopic level; use of the so-called split print protocol avoids the ambiguities associated with nominal replicates. In more detail, water exposure has minimal effect for a given mark type (eccrine, sebaceous or natural), but has dramatically different effects for different mark types. Specifically, water exposure removes the water-soluble components that dominate eccrine deposits but not the relatively insoluble components that dominate sebaceous deposits and that are prevalent in natural marks.

The first specific objective of the study was silver particulate *size in solution* (strictly, dispersion), prior to exposure to the exhibit. In the presence of the Synperonic N/DDAA surfactant combination, silver particles whose size lies within the colloidal domain are stabilised. The peak of this size distribution is 880 nm. Upon contact of the paper exhibit with the silver dispersion, silver particulates deposit rapidly (on a timescale of seconds or faster).

A combination of macroscopic (whole mark) and microscopic (micrometre scale) observations has advanced understanding of the PD process. Microscopy observations showed the silver particles to lie within the range 6-20 □m. Within any given sample (paper type, residue type, environment) the silver particles are uniform in size, typical of instantaneous nucleation. In cases when the ridges were better developed (as evaluated macroscopically) and the entire mark was enhanced, the silver particles were at the smaller end of this range. In cases where there was only partial development, larger silver particles were observed. Conceptually, one may separate the outcomes into aspects that *precede* exposure of the exhibit (relating to the reagent formulation), that relate to the development of the fingermark *during* immersion in the reagent formulation, and that characterise the fully developed mark *subsequent* to immersion in the reagent.

Subsequent objectives related to the surface population of silver particles and the dynamics of their growth. We find that deposition and growth are temporally distinct. Silver deposition on the surface (fingermark residue) occurs almost instantaneously and silver growth then occurs on these surfaceimmobilised particles. We find no evidence for silver particle growth in solution followed by deposition of fully developed particles on the surface. Across the recommended development time (15 minutes), we find the mean silver particle density is 2.36 (±0.52) x 10^5 cm^{-2}, independent of time. The particles are approximately monodisperse and their size increases with the square root of development time, suggestive of diffusionally controlled growth, to a diameter of ca. 16 □m (ca. 20 times initial diameter, i.e. 8000 times initial volume) at the end of the recommended 15 minute development time. Interestingly, clear visualisation of silver particulates (with the benefit of

microscopy) is seen at an earlier stage of development than macroscopic ("by eye") visualisation of the whole mark.

Complementary chemical analysis (using EDS) shows the silver particles to be associated with some chlorine, which we attribute to chloride from the fingermark residue. Interestingly, there is no evidence for occlusion of iron species from the redox component of the PD reagent system.

We identify four areas for future study that build on, and that will benefit from, the present study. First, we recognise interesting further exploration of the relationship between visual perceptions of PD developed fingermarks viewed at macroscopic and microscopic scales. Second, we are pursuing neutron reflectivity studies of surfactant adsorption on silver at the molecular level. Third, we are engaged in the further characterisation of PD formulations in which the environmentally outlawed Synperonic N is replaced with alternative surfactants [10]. Finally, we wish to explore the effect – if any – of donor characteristics on the surface-bound particle populations and sizes. These will be described in subsequent publications.

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Authors' contributions

ARH conceptualised and designed the experiments, jointly wrote the manuscript, and acted as corresponding author. JLC undertook the experimental work and associated data analysis, and jointly wrote the manuscript. VS provided guidance for the execution of the experimental work, and reviewed and critiqued the manuscript. SB reviewed and critiqued the manuscript.