

# Polymerisation of $S_2N_2$ to $(SN)_x$ as a tool for the rapid imaging of fingerprints removed from metal surfaces

Stephen M. Bleay,<sup>a</sup> Paul F. Kelly\*<sup>b</sup> and Roberto S. P. King<sup>b</sup>

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

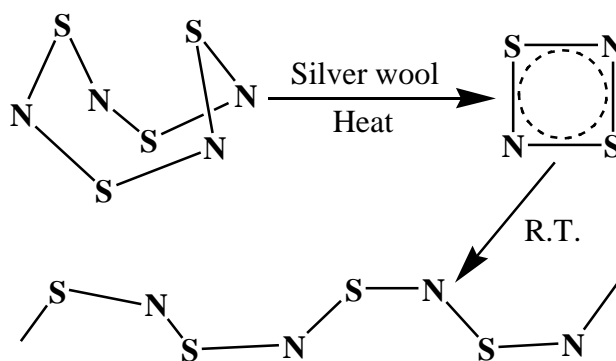
**Polymerisation of  $S_2N_2$  to  $(SN)_x$  on metallic surfaces is induced by interaction with the minute corrosion signatures of removed (by washing) fingerprints; as vapour-phase  $S_2N_2$  is employed, it follows that the process has the potential to rapidly screen large/convoluted metal pieces, such as explosive device fragments whose prints were wiped by the detonation.**

The imaging of latent fingerprints continues to be an immensely important weapon in the forensic arsenal<sup>1,2</sup> and, despite the maturity of the discipline, work on extending capabilities continues. Recent years have witnessed a number of innovative applications of instrumental and synthetic techniques (e.g. the use of mass spectrometry)<sup>3-6</sup> driven, in part at least, by the need to develop methods of obtaining prints in operationally challenging scenarios.<sup>7</sup> One very significant - and timely - example comes in the form of situations where prints have been removed, either deliberately through the washing of items, or through the effects of percussion/explosion (e.g. in the case of gun cartridges or explosive device fragments). Here we show that an image of a print may be rapidly retrieved from metallic surfaces even after it has been physically removed by washing, thanks to the interaction of disulfur dinitride with the print's corrosion signature.

In the case of fingerprints deposited on metallic surfaces, the notion that ionic salts (such as NaCl) present within eccrine secretions of the palmar ridge skin readily undergo redox type interactions with the metal surfaces to which they are in contact,<sup>8,9</sup> has allowed changes in the potential difference of the metal substrate to be exploited. Pioneering work by Bond<sup>10</sup> and Williams<sup>11</sup> has revealed that instrumental techniques such as Atomic Force Microscopy and Scanning Kelvin Probe can image the minuscule surface corrosion effect generated by prints which have been laid down on metallic surfaces, even after the prints themselves have been removed through various rigorous cleaning regimes. These results highlight the immense potential of such minor corrosive action on forensically pertinent substrates; however, the imaging techniques themselves suffer realistic limitations, such as the length of time required to process a macroscopic area, cost and problems analysing irregular surface forms.

Such limitations could be circumvented by a rapid

chemical imaging technique. Despite the frequent use of various chemical treatment methods for fingerprint detection on both porous and non-porous materials, the procedure of choice is predominantly determined by sample surface composition and likely environmental stressors experienced (wetting, heat, friction, *etc.*). Chemical treatment methods typically rely on the reaction of one (or more) fingerprint constituents with the working chemical, in a manner that produces a visible print. Physical removal of the fingerprint deposit itself therefore renders many, if not all, conventional techniques inadequate.



Scheme 1. Structure of the sulfur nitrides employed.

In earlier work we showed that polymerisation of disulfur dinitride ( $S_2N_2$ ) (Scheme 1) on latent fingermarks resulted in the prints being visualized in dark blue  $(SN)_x$ .<sup>12</sup> Although the mechanism of this effect is as yet uncertain, it clearly involves interaction of the nitride with one, or more, of the myriad components within fingerprints. This constituted an intriguing new twist to the capabilities of the polymer, a material whose conductivity properties incited tremendous interest in the late 1970s. The metallic character exhibited by  $(SN)_x$  stimulated much fundamental research, and potential applications for the material were eventually highlighted through patents involving its use in both solid-state devices and electrode assemblies.<sup>13</sup> Ultimately, however, significant practical applications have, hitherto, remained elusive; the previous findings reported within our group<sup>12</sup> alongside the work herein, do perhaps signify the first fundamental mainstream application of this fascinating material.

During the course of these forensically pertinent studies, it became evident that the polymerisation process ( $S_2N_2$  vapour to solid  $(SN)_x$ ) also appeared to target localised physical imperfections on the substrate surface (note the scratches due to the washing process which are picked out in Figure 1c).

<sup>a</sup> Home Office Scientific Development Branch, Sandridge, St. Albans, Hertfordshire, AL4 9HQ.

<sup>b</sup> Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU. Tel: +44 (0)1509 222578; E-mail: P.F.Kelly@lboro.ac.uk

This superficial 'damage' was routinely enhanced by (SN)<sub>x</sub> on materials pre-disposed to topographical alterations: paper and metals, for example. Accordingly, and in light of topical forensic concerns, the study of S<sub>2</sub>N<sub>2</sub> interaction with cleaned fingerprints on metal surfaces, became paramount.

In contrast to standard chemical fingerprint detection techniques, the key feature of the results presented here is that even when the print is no longer *chemically* present, interaction with S<sub>2</sub>N<sub>2</sub> persists *via* the print's corrosive modification of the surface; crucially, this occurs even when the print has had a relatively short time to manifest the corrosion. Figure 1 shows this effect in practice<sup>‡</sup> on brass plates. In the case of Figure 1a, a print was laid down on the brass and left for 30 seconds before being washed off. Successful removal of the print is confirmed by the fact that no evidence of the latter is seen upon exposure to S<sub>2</sub>N<sub>2</sub>. To generate Figure 1b, the print was left on the brass for 30 minutes, before being removed in the same way. Now exposure clearly (to the naked eye) results in an image of the print in question, picked out by the polymer. Crucially, similar results can be obtained from other metal surfaces, including stainless steel and copper. In the former case, the print shown in Figure 2 was obtained after just a two hour pre-wash contact time, and indeed usable prints have been retrieved from shorter contact times than this (down to 30 minutes in tests undertaken thus far). While the anti-corrosion properties of the grade of steel involved would appear to preclude this, the key to the effect appears to be the interaction of the print with the oxide layer present on steel. It is well known that inorganic salts can attack this tenuous layer, and it seems that in this case the washing of the print, and then exposure to the S<sub>2</sub>N<sub>2</sub>, results in preferential polymer growth on the revealed oxide-free surface. This is confirmed by the fact that if prints are laid on the steel, washed off and then the whole surface treated with NaCl solution, subsequent exposure to S<sub>2</sub>N<sub>2</sub> does not result in print visualization. The implication of this is that complete wiping of the oxide surface has removed the pitting effect of the print's corrosion.

#### Fig.1 Here

Figure 1. Brass plates upon which a fingerprint was deposited for (a) 30s, (b) 30 mins, (c) 3 hours and (d) 24 hours before washing and exposure to S<sub>2</sub>N<sub>2</sub>; image (e) shows the print from (b) viewed under polarised light.

Importantly, though, if prints are washed from the steel surface and the sample allowed to sit in air long enough for oxide re-growth prior to exposure, then prints are still obtained. This implies that some aspect of the re-formed oxide surface which grows back on the position of the fingerprint ridges is still sufficiently different to the rest of the surface to allow the polymer to preferentially deposit upon it. Thus even steel surfaces which have had long exposure to air subsequent to print removal should be amenable to this technique. In terms of the image shown in Figure 2, as the detail (*via* microscope) shows, not only are fingerprint pores visible within the ridge impressions, but one can also observe extremely fine scratches that have been picked out by the polymer. We presume these represent either initial surface

features of the steel as obtained, or they show the effects of the buffing process during washing of the plate. Either way, the results highlight the ability of the polymer to respond to exceptionally small surface changes, often in exquisite detail.

As Figure 1 confirms, the quality of images increases (up to a point) with longer deposition time. However, even the image from the 30 minute contact print seen here (Figure 1b) shows complete development over the entire area of contact, with many features of interest to identification experts visible. In the case of brass, contrast between the developed fingerprint ridges and the metal substrate can be further enhanced by viewing under polarized lighting conditions (Figure 1e), and by application of digital image processing (NB all images herein are taken directly from the output of the imaging system in question, with no further processing beyond cropping). The right hand image in Figure 2 does, however, help illustrate just how much microscopic detail is present in raw images. It is worth adding that while specialist apparatus was used to obtain the images in Figure 1, perfectly usable images may be obtained by simple photography or the use of a desktop scanner (as in Figure 2), highlighting the visual quality of the imaged prints.

#### Fig.2 Here

Figure 2. Left - stainless steel plate upon which a print was deposited for 2 hours before washing and exposure to S<sub>2</sub>N<sub>2</sub>; Right - ridge detail photographed microscopically (75X).

Upon exposure to S<sub>2</sub>N<sub>2</sub>, visualization of removed prints starts quickly, and confirmation of the presence of a print can usually be obtained within ten minutes (with full development taking in the order of one hour). In addition, the development agent is in the gas phase, thus opening up the possibility of exposing large, contorted surface areas, e.g. from bomb fragments. Both aspects of this technique provide significant advantages over the instrumental methods and indicate that rapid screening of structurally complex metallic remains (e.g. explosive devices, improvised or otherwise) should prove feasible. While, ironically, the starting material for the whole process, S<sub>4</sub>N<sub>4</sub>, does have friction sensitivity, the reality is that the whole process can be safely contained within the kind of apparatus described previously. Accordingly, this has very real potential as a viable forensic technique; in addition the novel application of the well established polymerization process does serve to illustrate the fact that challenges are still in place and await addressing by the novel utilization of well known materials.

## Notes and references

<sup>‡</sup> **Important safety note: Both S<sub>4</sub>N<sub>4</sub> and S<sub>2</sub>N<sub>2</sub> are friction sensitive explosives. Work in this area by any researchers not already experienced in handling these materials should only be undertaken after careful reading of the safety notes available in the [Electronic Supplementary Information](#).**

Prior to fingerprint deposition, the donor washed their hands 20 minutes before print placement. No excess secretions were loaded onto the fingers either through deliberate grooming of sebaceous content or the wearing of gloves. Latent fingerprint deposits were laid onto metal plates for the

required duration (as per the figure captions) and then removed by washing under running water with soap and gloved rubbing, followed by rinsing in acetone with gloved rubbing and finally vigorous buffing of the dry plate with paper towel. Exposure to  $S_2N_2$  was achieved using the vacuum apparatus described previously,<sup>12,14</sup> with the nitride being freshly prepared from  $S_4N_4$  for each experimental run.

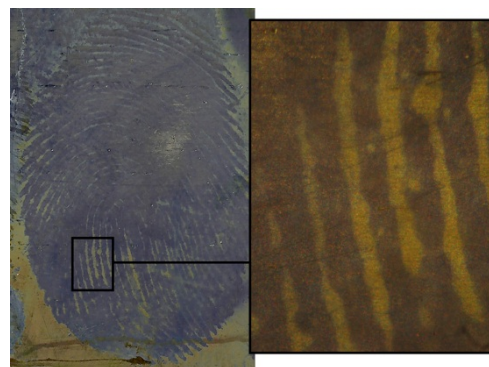
Typically, metal plates of dimensions 2x3 cm were utilised for single prints, or 2x6 cm for pairs of prints. In the case of the two samples used in Figs. 1 and 2, the brass was 0.3 mm thickness CZ108 alloy and the stainless steel 0.5 mm thickness 316 grade. After exposure, brass samples were imaged without any further treatment; steel samples were gently rinsed in  $CH_2Cl_2$  to remove residual  $S_4N_4$  which can sometimes deposit on the steel's oxide layer. The images in Fig. 1 were taken using a Foster and Freeman VSC6000 digital imaging system and captured using incident visible light illumination. The main image in Fig. 2 was obtained using an HP Deskjet F2480 printer/scanner in a high contrast setting, while the inset picture was taken via a Samsung Digimax V800 camera connected to a Leica Zoom 2000 microscope, with a combined magnification of x75.

1. H. C. Lee and R. E. Gaensslen, *Advances in fingerprint technology*, CRC Press, Boca Raton, Florida, ed. 2, 2001.
2. C. Champod, C. Lennard, P. Margot and M. Stoilovic, *Fingerprints and Other Ridge Skin Impressions*, CRC Press, Boca Raton, Florida, 2004.
3. D. R. Iffa, N. E. Manicke, A. L. Dill and R. G. Cooks, *Science*, 2008, **321**, 805.
4. M. I. Szykowska, K. Czerski, J. Rogowski, T. Paryjczak and A. Parczewski, *Forensic Sci. Int.*, 2009, **184**, e24-e26.
5. M. I. Szykowska, K. Czerski, J. Rogowski, T. Paryjczak and A. Parczewski, *Surf. Interface Anal.*, 2010, **42**, 393-397.
6. S. J. Hinder and J. F. Watts, *Surf. Interface Anal.*, 2010, **42**, 826-829.
7. J. W. Bond and C. Heidel, *J. Forensic Sci.*, 2009, **54**, 892-894.
8. J. W. Bond, *J. Forensic Sci.*, 2008, **53**, 1344-1352.
9. J. W. Bond, *J. Phys. D: Appl. Phys.*, 2008, **41**, 1-10.
10. A. J. Goddard, R. Hillman and J. W. Bond, *J. Forensic Sci.*, 2009, **55**, 58-65.
11. G. Williams and H. N. McMurray, *Forensic Sci. Int.*, 2007, **167**, 102-109.
12. P. F. Kelly, R. S. P. King and R. J. Mortimer, *Chem. Commun.*, 2008, 6111-6113.
13. see references noted within: A. J. Banister and I. B. Gorrell, *Adv. Mater.*, 1999, **10**, 1415-1429.
14. R. S. P. King, P. F. Kelly, S. E. Dann and R. J. Mortimer, *Chem. Commun.*, 2007, 4812-4814.

Fig.1:



Fig.2:



---

5

10

15