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Micronised Egyptian blue pigment: A novel near-infrared luminescent fingerprint dusting powder

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In this paper we demonstrate that micronised Egyptian blue pigment can be used as a safe and simple material to visualise latent fingerprints on non-porous surfaces as near-infrared luminescent impressions. This allows the detection of latent fingerprints on highly patterned and reflective surfaces that have proven challenging with existing techniques.

1. Introduction

The detection of latent fingerprints is extremely useful in forensic investigations to establish evidence of contact between the criminal, the victim, and/or the crime scene [1–3]. To that end, a wide range of chemical and physical methods have been developed to aid in their detection and recovery, the choice of which is dependent on the nature of the surface involved [1,2]. The most common approach to detecting latent fingerprints on non-porous items has been the use of dusting powders, which work through physical adhesion to the latent fingerprint deposit [1–5]. It has been estimated that in the United Kingdom, approximately 50% of the 60,000 fingerprint identifications per annum arise from powdered fingerprints [1]. Historically, a wide range of materials have been utilised as fingerprint powders; including carbon black, iron oxide-based magnetic powder and titanium dioxide; in attempts to achieve improved visualisation across a wide variety of surfaces and conditions [1–5]. In recent times, this has included attempts to use natural products such as turmeric as safe and inexpensive powders [6]. Several commercially available powders exhibit luminescence in the visible region of the electromagnetic spectrum, which to some extent can negate the interferences exhibited by highly patterned or coloured surfaces [1,2,4]. However, there remain many fluorescent, highly patterned and/or reflective surfaces that continue to prove troublesome [7–9].

An alternative approach is to use dusting powders that exhibit near-infrared (NIR) luminescence [10–12]. As very few substrates luminesce in the NIR region of the spectrum, such powders can highlight ridge detail while avoiding interference caused by inherent background luminescence [9–13]. To date there are limited examples of such powders in the open literature. Chadwick and co-workers reported an NIR luminescent fingerprint powder based on adsorption of an organic dye (STaR 11®) on finely powdered aluminium oxide, mixed with commercial magnetic fingerprint dusting powder. However, the developed impressions were still affected by underlying patterns on the surface, and the luminescence intensity of the developed fingerprints was observed to decrease over time. In addition, the powder itself had a limited shelf life [10]. More recently, King et al. have demonstrated that a biorganic powder based upon an algae, *spirulina platensis*, can be used to develop fingerprints with imaging in the NIR region [11].

Egyptian blue (also known as cuprorivaite) is the earliest known synthetic pigment; first prepared in ancient Egypt around 3600 BCE and used extensively until the 4th century CE [14–18]. Qualitative studies by Sir Humphrey Davy and others revealed that the pigment was likely to be copper-based, and contained large

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proportions of silica and calcium oxide [16,18–20]. Subsequent evidence from X-ray diffraction (XRD) established its primary composition to be calcium copper silicate ($CaCuSi_4O_{10}$) [21,22]. Researchers have demonstrated that Egyptian blue exhibits strong photoluminescence in the NIR region when excited at around 630 nm, with a quantum yield of 10.5% at the maximum emission of 910 nm [23–26]. Egyptian blue is also very stable, with painted artefacts dating several thousand years old still showing strong NIR luminescence [18,26]. The high stability to light, oxygen, pH and temperature of Egyptian blue, as well as its long luminescence lifetime, have been noted in a recent application to the development of novel optical sensors [27]. These characteristics led us to investigate Egyptian blue as a NIR luminescent latent fingerprint dusting powder for highly patterned surfaces.

2. Materials and methods

2.1. Materials

A single source of Egyptian blue pigment (Rublev Colours, CA) was used for this research. The following commercially available fingerprint dusting powders were used: Velvet Black, titanium dioxide, Blitz Red® fingerprint powder (Criminal Research Products, LLC), and bichromatic powder donated by the Western Australia Police Fingerprint Bureau. The following substrates were used during the course of the study; white glazed porcelain bathroom tiles, aluminium soft drink cans and various glass surfaces.

2.2. Collection of fingerprint specimens

Latent fingerprints were collected from male and female donors (aged between 19 and 25 years) on a variety of substrates. Two varieties of fingerprints were deposited; charged and uncharged. Charging is achieved by rubbing the tips of the fingers across the nose and forehead to transfer sebaceous lipids to the contact ridges of the fingers before touching the substrate [28,29]. Uncharged fingerprints were obtained by simply touching the substrate.

2.3. Micronising process

A McCrone micronising mill was used to micronise the Egyptian blue. This uses 48 corundum (crystalline alumina) cylindrical grinding pellets held in a plastic screw-topped jar. A slurry was made of the pigment (around 1 g) in ethanol (5 mL). This slurry was then added to the screw-topped jar containing corundum pellets. The jar was loaded horizontally into the mill and clamped into place, before micronising for the desired time period. Once micronising was completed, the jar was removed from the mill and its contents poured into an evaporating basin over low heat to evaporate off the solvent.

An estimate of the average particle size of the powders produced was obtained using optical microscopy. Particles in the recorded images were measured against the scale bar (included by the camera in each image) and recorded. If the particle measured was not approximately spherical, the average of the height and width of that particle was used. The average of all of the particles contained in the images was then calculated.

2.4. Application of fingerprint dusting powders and micronised Egyptian blue

Fingerprint powders and micronised Egyptian blue were applied using fingerprint brushes donated by the Western Australia Police Forensic Division. The two types of brushes used were based on natural fibre (camel hair) and synthetic fibre (fibreglass).

2.5. Luminescence spectroscopy

Uncorrected steady state emission and excitation spectra were recorded on an Edinburgh FLSP980-S2S2-stm spectrometer equipped with a 450 W xenon arc lamp and a Hamamatsu R5509-42 photomultiplier. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by a calibration curve supplied with the instrument.

2.6. X-ray diffraction measurements

XRD was performed using a Bruker D8 X-ray diffractometer using a position sensitive detector (PSD). The range examined was 7.5°–90° with an interval of 0.0015° every 0.7 s.

2.7. Photography

A modified Canon 40D camera was mounted on a benchtop macro stand in a darkened room. Modification was made by removal of the internal infrared blocking filter that reduces the natural sensitivity of CCD and CMOS sensors to infrared radiation. The camera was then connected to a live feed television screen. This aided both focusing and reviewing of the images captured. The camera was fitted with a Canon EFS 18–55 mm lens and a lens-mounted RM90 filter, which transmits radiation from approximately 900 nm. The lens-mounted filter was removed for photographs in the visible region.

Developed fingerprints on various substrates were illuminated either with a white LED square array (Camera Electronics, North Perth) or a forensic light source (Rofin Polilight PL500, white light setting). The light source was kept at a 45° incident angle to the substrate and a distance of 22 cm.

3. Results and discussion

Initial experiments were carried out with a commercial sample of Egyptian blue pigment, which was used without further treatment. Excitation and emission spectra of the pigment were obtained, which aligned well with literature values for both the excitation and emission characteristics of Egyptian blue [23,24]. (Fig. 1).

The blue colour of the material and its luminescent nature strongly suggested that this was indeed cuprorivaite, but chemical analysis by XRD was carried out to confirm that the commercial

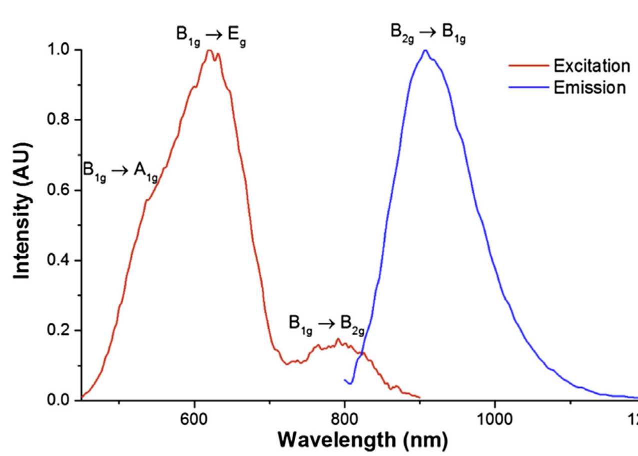

Fig. 1. Excitation and emission spectra of commercial sample of Egyptian blue with associated electronic transitions.

pigment was indeed Egyptian blue (see electronic supplementary information Fig. S1).

Charged fingerprints from one donor were collected on glass petri dishes. A small amount of Egyptian blue pigment was deposited on the fingerprints, and the excess brushed away. While the pigment was highly luminescent when illuminated with a broad-band white LED light and viewed through a Hoya RM90 filter, the particles were too large to adhere sufficiently to the fingerprints, which were subsequently revealed as featureless smudges.

The supplied pigment had a particle size of approximately 50 μm, while the commercially available fingerprint powder (Velvet Black) used as a reference comparison had an average particle size of around 2 μm (Fig. 2). Attempts to manually grind the Egyptian blue using a mortar and pestle were unsuccessful in reducing particle size. However, it was found that a micronising mill, normally utilised in the preparation of samples for XRD analysis, was effective in producing appropriately sized particles (Fig. 2).

The micronised Egyptian blue was applied to both charged and uncharged latent fingerprints on glass and porcelain tile surfaces using a camel hair brush. It was found that the Egyptian blue could consistently develop the latent fingerprints, revealing good ridge detail in the NIR region (Fig. 3).

Egyptian blue samples were micronised for different time periods (1, 5, 15, 30, 60 and 120 min) and compared in terms of size and for their ability to successful develop latent fingermarks (Figs. 4 and 5).

NIR photographs of the developed fingerprint series showed that all of the samples of micronised Egyptian Blue adhered to the fingerprints and showed good levels of ridge detail (Fig. 4). The best results were obtained from samples micronised for 15 and 30 min, with the luminescence intensity then reducing.

The longer the time period that the sample spent in the microniser, the lighter its' colour (Fig. 6). This change in the tone of the colour in relation to particle size for Egyptian blue has been observed previously and has been attributed to its dichroic properties [30]. An additional explanation may be the introduction of corundum as a contaminant into the sample. The constant agitation of the corundum grinding pellets against themselves and the sample gradually wears off a fine layer of corundum. This finely powdered light pink solid is then incorporated into the sample and

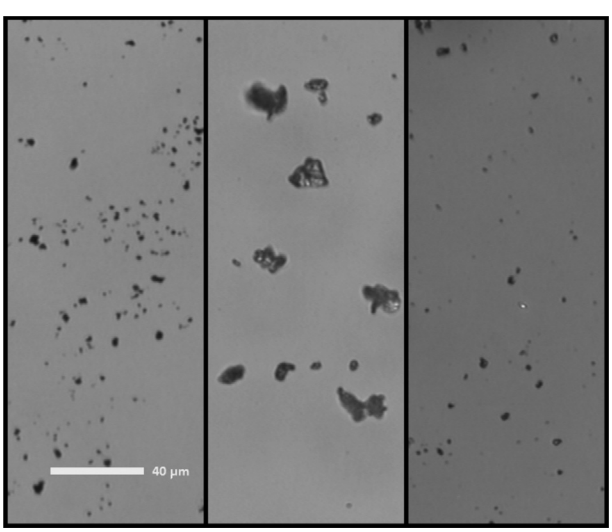

Fig. 2. A comparison image of (from left to right) Velvet Black, Egyptian blue unmicronised, and Egyptian blue micronised for 30 min.

Fig. 3. Latent fingerprints on a glass surface dusted with micronised Egyptian blue. Illumination by a white LED array and recorded with a Canon 40D modified for use in the NIR region, fitted with a Canon EFS18-55 lens with a Hoya RM90 visible light-blocking filter, 2 s exposure time, f 3.5 aperture.

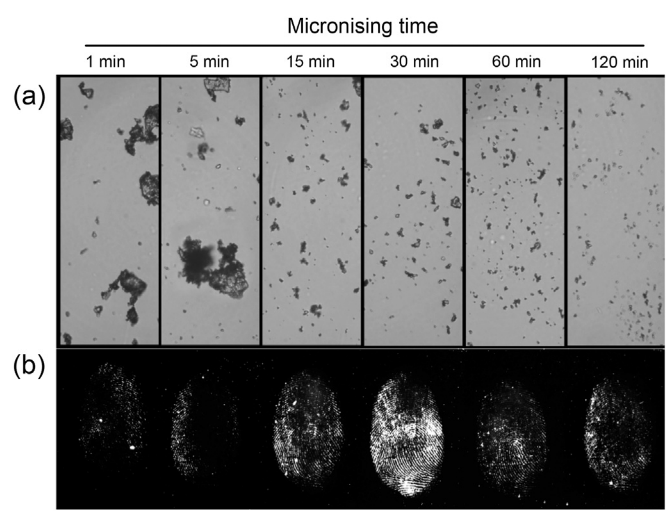

Fig. 4. (a) Photomicrographs of samples of the commercial Egyptian Blue pigment following micronising for differing periods of time; (b) Latent fingerprints dusted with the corresponding micronised samples. Illumination by a white LED array and recorded with a Canon 40D modified for use in the NIR region, fitted with a Canon EFS18-55 lens with a Hoya RM90 visible light-blocking filter.

dilutes the observed colour of the final sample of micronised pigment. This may also partially explain the decrease in luminescence in developed fingerprints dusted with Egyptian blue micronised for longer than 30 min.

A result of the reduction in colour intensity of the micronised pigment is that Egyptian blue developed fingerprints are very faint under normal lighting. The issue of low visibility under normal lighting conditions is also a feature of the algae based powder

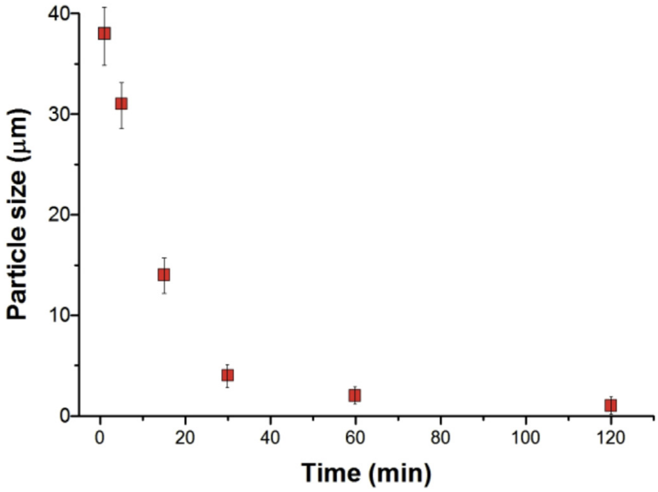

Fig. 5. Relationship between particle size and time spent in the microniser. Error bars indicate the range of particles found in each sample.

reported by King and co workers [11,31]. It should be noted that due to the photographic conditions required to capture the photoluminescence of Egyptian blue (i.e. removal of external light sources), its use would be limited to the forensic laboratory rather than field examination. The poor contrast of Egyptian blue therefore would not be a disadvantage in operational situations.

A variety of brush types, including those with fibreglass filaments and those with bristles of animal hair or feathers, are used for applying fingerprint powder to suspected latent fingerprints [1,32]. In order to carry out a preliminary assessment of the effect of brush type, latent fingerprints on white porcelain tiles were dusted with the micronised pigment using two different brushes; natural fibre (camel hair) and synthetic fibre (fibreglass). Fingerprints could be successfully developed with both types of brushes, however the camel hair brush gave the best results and was used for subsequent experiments. A more extensive evaluation using a wider variety of commercially available brushes is required to best establish the most appropriate brush(es) for this powder.

To examine the performance of the powder for developing impressions on more challenging surfaces, a series of charged fingerprints were deposited on aluminium soft drink cans. These are known to be difficult substrates for dusting powders as they have highly patterned and reflective surfaces, which can reduce contrast between the developed fingerprint and background [10]. The individual latent impressions were split such that one half could be dusted with Egyptian blue, and the other half with a range of commercial powders for direct comparison. Egyptian blue performed better than all of the commercial powders in these tests, allowing visualisation of the fingerprint without any conflicting background pattern and showing excellent levels of ridge detail (Fig. 7). In order to obtain a measure of any potential interdonor

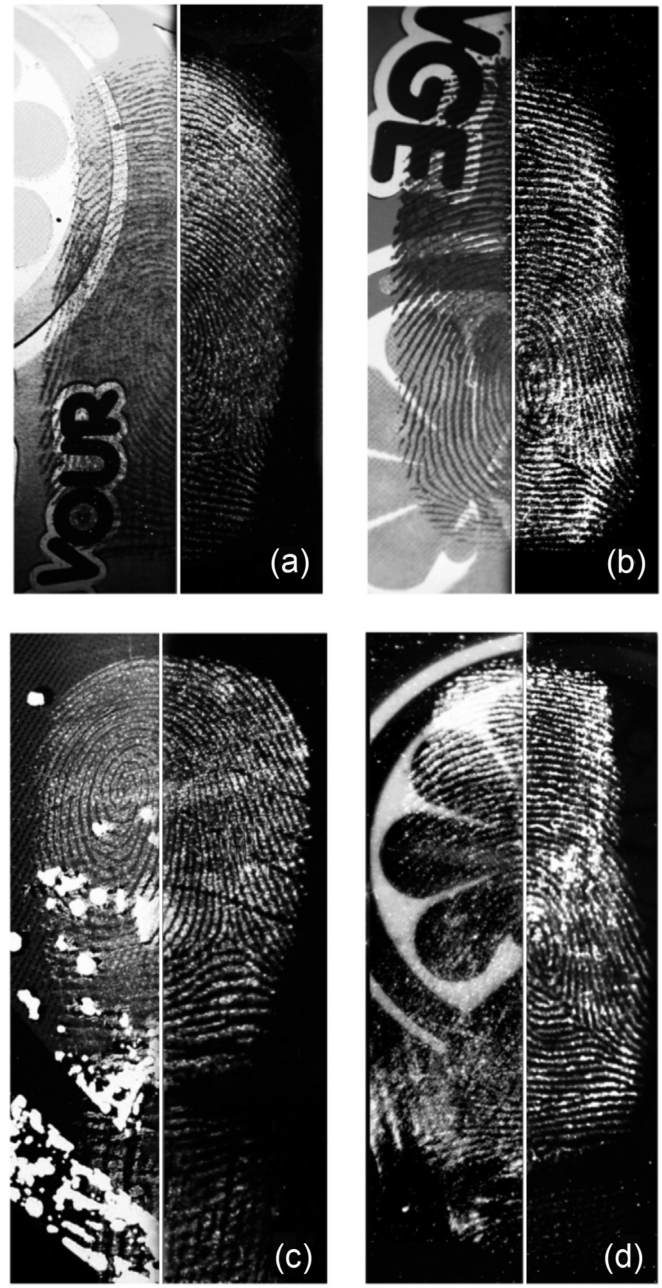

Fig. 7. A comparison between commercially available fingerprint dusting powders (left sides) and Egyptian blue (right sides) on soft drink (Fanta®) can substrates. a) Bichromatic, b) Velvet Black, c) Titanium dioxide, d) BlitzRed®. Illumination by a white LED square array and recorded with a Canon 40D modified for use in the near infrared spectrum, fitted with a Canon EFS18-55 lens with a Hoya RM90 visible light-blocking filter. Filter removed for photography of non-NIR luminescent powders.

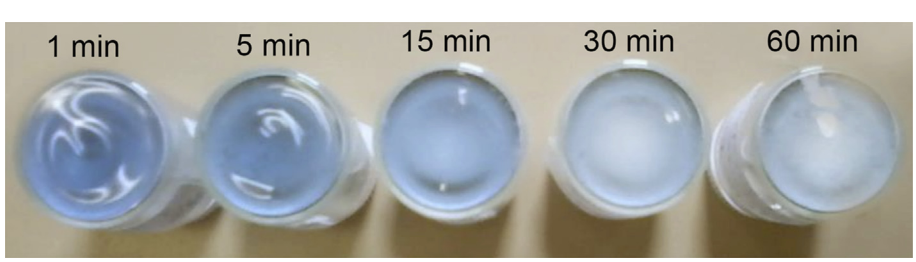

Fig. 6. Lightening of colour resulting from increased time spent micronising. From left to right: samples micronised for 1, 5, 15, 30 and 60 min.

Fig. 8. Fingerprints on white porcelain tile developed with micronised Egyptian blue ~29 months after deposition. Illumination by a Polilight PL500 (white light mode) and recorded with a Canon 40D modified for use in the near infrared spectrum, fitted with a Canon EFS18-55 lens with a Hoya RM90 visible light-blocking filter.

variation [29], uncharged fingerprints from six additional donors were obtained on the same substrates. Fingerprints from all donors exhibited good ridge detail when treated with Egyptian blue.

One potential advantage of Egyptian blue is it well known stability in terms of its photoluminescence [26,27]. Developed fingerprints on a white porcelain tile were left on a window ledge in full ambient light for a period of over 2 years. When viewed in the NIR region they still showed a high level of luminescence (Fig. 8), thus demonstrating the stability of the pigment.

4. Conclusions

This paper demonstrates a proof of concept for Egyptian blue as a NIR luminescent dusting powder for the development of latent fingerprints on non-porous surfaces. Aside from the initial particle size reduction, no treatment or special storage conditions are required for its use as a latent fingerprint powder. In this work we used an inexpensive white light source to demonstrate the simplicity of the approach, improved performance is possible through the use of a dedicated forensic light source, due to increased intensity and ability to control excitation wavelengths. We also used a readily available camera with a simple modification, however specialized forensic imaging systems, as utilised by King et al., [11] would also be highly suitable. Through its long use as an artist's pigment it is known to be non-hazardous and stable, retaining its luminescence characteristics for millennia. This study is preliminary in nature and further systematic studies are required using a wider range of substrates and donors to establish the operational usefulness of this powder, following the guidelines recommended by the International Fingerprint Research Group [28,29]. In addition, the potential to modify the powder to improve its visibility while retaining its luminescent characteristics, as well as its possible use in a slurry as a wet powder technique [1,4], are currently under investigation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.05.008.

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