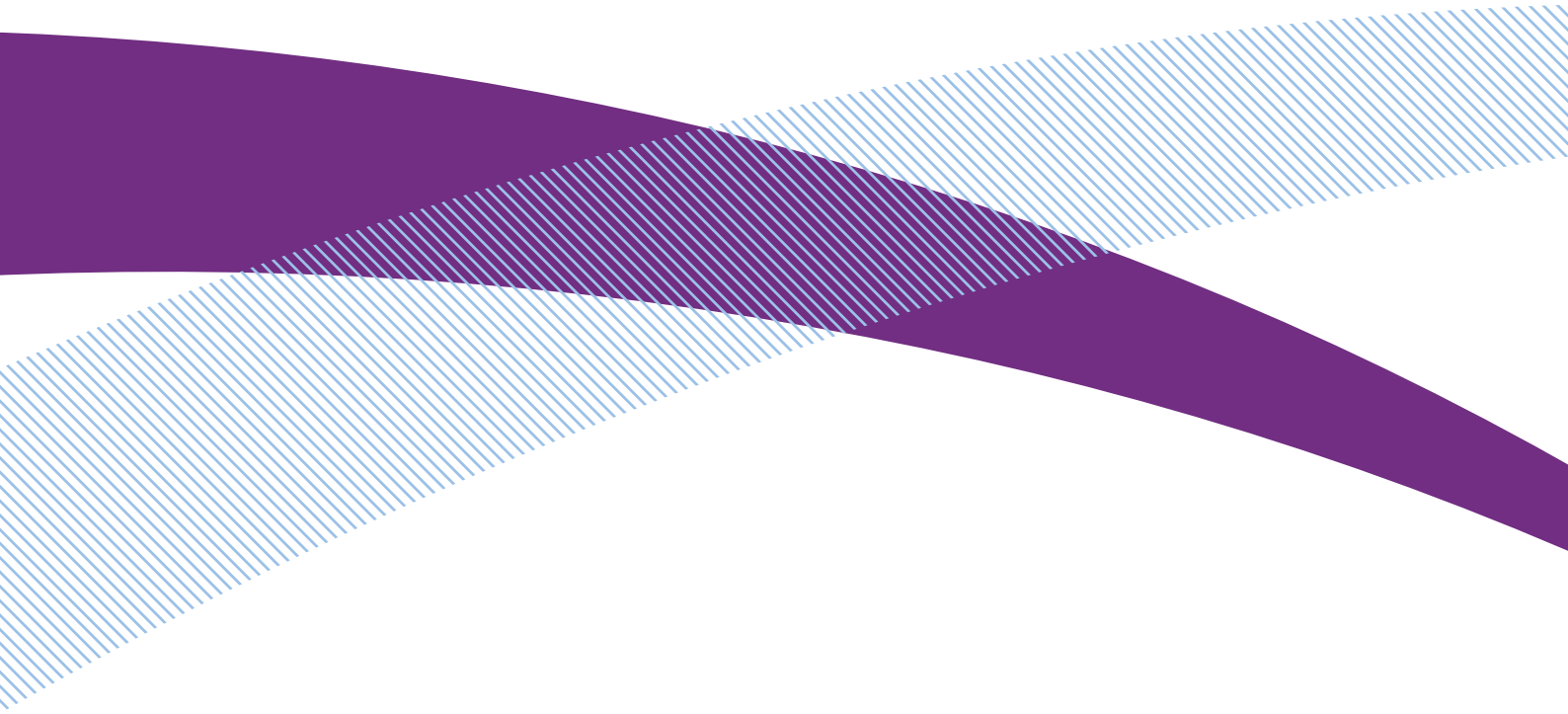
Home Office

Fingerprint Source Book

S M Bleay
V G Sears
H L Bandey
A P Gibson
V J Bowman
R Downham
L Fitzgerald
T Ciuksza
J Ramadani
C Selway

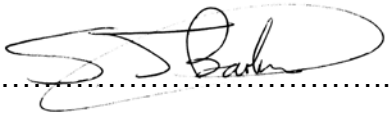


Authorisation

This *Fingerprint Source Book* has been signed off to my satisfaction and is authorised for circulation, as appropriate.

CAST recognises that the information contained within it, while believed to be correct at the time of writing, may be subject to change as more information becomes available. We would welcome feedback from those using the book, which will be subject to regular review to incorporate appropriate changes.

Chief Technical Officer (Home Office CAST) ……Steve Barber……

Signature ……  …….. Date ……12 March 2012……

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Preface

This preface places the publication of this *Fingerprint Source Book* into context, and represents the situation at the time of writing (October 2011).

The *Fingerprint Source Book* was not originally intended as an external publication. It was prepared as an internal reference document, drawing together all of the information held by the Home Office Centre for Applied Science and Technology (CAST) regarding internally managed experimental work on finger mark enhancement techniques. The preparation of the document was carried out in anticipation that supporting evidence would be required for validation of the techniques within the *Manual of Fingerprint Development Techniques*, as part of the ISO 17025 accreditation of the CAST forensic laboratories. The original purpose of the document was to demonstrate to UKAS (the ISO 17025 assessors) and the Forensic Science Regulator that the processes and sequences outlined in the manual had been experimentally tested and that the advice presented in the manual was valid.

As CAST and police force laboratories have progressed with the ISO 17025 accreditation process, the *Fingerprint Source Book* has become regarded as a more widely important document. Because it provides the validation of the techniques contained within the manual, and hence the techniques used by police forces, it has become necessary for the document to be formally issued and controlled. This means that the data contained within it can be directly referred to by individual police forces seeking ISO 17025 accreditation, thus reducing the requirement on police forces to conduct lengthy validation experiments of their own (although local verification experiments will still be required). The Forensic Science Regulator has also requested that the data contained within the *Fingerprint Source Book* is made publicly available for reasons of transparency.

The document is now presented for use as a controlled document. It is not produced as a formal, numbered Home Office document because this is incompatible with the contents. However, the document has been reviewed by the Home Office communications team to ensure that fundamental formatting is acceptable, and a technical review has been carried out covering both internal and external peer reviews of the contents.

A user of the *Fingerprint Source Book* should be aware of the original purpose for which it was prepared. Although it may be a useful source of data for those wishing to conduct research or learn more about various enhancement processes, it is not intended to be a text book. It has been prepared for laboratories that are currently working to the Home Office CAST *Manual of Fingerprint Development Techniques*, therefore the principal formulations described in the source book are those recommended by CAST in the manual. Less attention is given to formulations produced by other organisations, and to processes that are not included in the manual. Significant numbers of the references may refer to reports produced by students working at CAST rather than external journal publications. The user

must therefore be aware that it will not always be possible to obtain copies of every document referred to in the text.

Most sections in the *Fingerprint Source Book* were last extensively reviewed in mid-2010. There have been developments in several areas since then, and CAST has also conducted additional research. It must therefore be recognised that the information contained within this document may not be fully up to date, although a review schedule has been put in place for ongoing maintenance of the document.

Table of contents

Chapter 1: Introduction

The *Fingerprint Source Book* is primarily intended to provide the background and validation for the techniques currently (up to 2011) recommended by the Home Office Scientific Development Branch (HOSDB), now the Centre for Applied Science and Technology (CAST), and to publish, in some cases for the first time, data collected over 35 years of research. It will therefore often present information in an 'CAST-centric' way, emphasising research that was carried out at Sandridge or Horseferry House, possibly sometimes at the expense of research carried out elsewhere. It is not the intention of the authors to ignore the significant contributions made by other research groups and apologies are made in advance if this sometimes appears to be the case. The document is also aimed at providing the UK Forensic Science Regulator and the United Kingdom Accreditation Service (UKAS), which will carry out ISO 17025 accreditation in the UK, with the background evidence behind the advice given in the *Manual of Fingerprint Development Techniques*.

The priorities of CAST in issuing and supporting the *Manual of Fingerprint Development Techniques* and the *Fingerprint Development Handbook* are to provide techniques that are highly effective, safe to use, and can be applied by staff who are not necessarily highly-qualified scientists. When developing formulations the approach is to maintain the effectiveness of the technique while minimising or eliminating any components that have health and safety issues associated with them. In some cases, more effective formulations or processes may be available, but if they are not felt to be safe to use they will not be recommended.

It should be emphasised that all testing and optimisation of processes by CAST has been carried out under UK climatic conditions. It is recognised that in many parts of the world the conditions of temperature and humidity will differ significantly from those in the UK and in some cases this may affect performance. It is likely that optimised formulations in different countries may differ for this very reason.

Throughout the report, references are made to the two main fingerprint research groups in the UK, CAST and the Forensic Science Service (FSS). These organisations have changed names several times in the 35 years covered, and in the text reference is usually made to the name of the group at that time. However, inconsistencies may arise. In summary, previous names for each organisation have been:

CAST

Police Research and Development Branch (PRDB) 1969 -1971
Police Scientific Development Branch (PSDB) 1971 - 1981
Home Office Scientific Research and Development Branch (HO SRDB) 1981 - 1991
Police Scientific Development Branch (PSDB) 1994 -2004
Home Office Scientific Development Branch (HOSDB) 2004 - 2011

FSS

Home Office Central Research Establishment (HO CRE) 1967 – 1988
Home Office Forensic Science Service (FSS), Central Research and Support Establishment (CRSE) 1988 - 1992
Aldermaston Laboratory closed (1992), Metropolitan Police Forensic Support Laboratory (MPFSL) absorbed by the FSS (1996). Fingerprint research subsequently split between FSS Lambeth and FSS Trident House, Birmingham.

Early research also conducted by the Atomic Weapons Research Establishment (AWRE) under contract to CAST.

Chapter 2: Finger mark examination techniques within scope of ISO 17025

2.1 Visual examination

1. History

1.1. Visual examination was the first technique proposed for the detection of fingerprints, with Henry Faulds suggesting the use of finger marks in blood, impressions in clay or marks left on glass for identification of criminals in his letter to the journal *Nature* in 1880. Many of the early landmark cases in fingerprint identification involved marks detected visually [1]; in Argentina in 1892 Vucetich used a mark deposited in blood on a door frame to disprove an account of a murder; in 1897 fingerprints in blood on a book cover were used to identify a murderer in India; and in 1902 impressions of fingerprints in paint were used to identify a burglar in the first trial using fingerprint evidence in the UK.

1.2 Detection of a mark by visual examination did not necessarily mean that it could be easily captured. In many cases the lighting conditions required to detect the mark were difficult to recreate and maintain for photography, but as the use of fingerprint evidence increased a range of techniques were developed or adapted for the photography of both developed and latent marks. Those described for operational use in 1954 [2] included transmitted light, vertical/specular illumination, dark ground illumination, oblique illumination, oblique top illumination and duo filtering.

1.3 Practical examples of the use of backlighting, vertical/specular illumination and oblique illumination were presented in subsequent publications [3,4]. The detection of fingerprints in both grease and dust was demonstrated using the range of lighting techniques above. Olsen [3] also recommended visual examination of metals and firearm articles for latent prints that may not be developed by powdering, with marks occasionally being etched into metal by the fingerprint constituents or ridge impressions left in the oil coatings often found on firearms. Pfister subsequently reported the application of specular lighting techniques using a semi-silvered mirror for the capture of latent fingerprints on glossy surfaces [5].

1.4 Other photographic techniques such the use of polarising filters [6] began to be employed in the imaging of latent fingerprints, improving the contrast between the fingerprint ridges and the background by suppressing the reflections from the background regions. A combination of polarisation and specular reflection techniques has recently been suggested for the detection of latent fingerprints [7]. The use of specialist tilt/shift lenses has also been demonstrated for the capture of marks on mirrors, where the image of the mark may otherwise be obscured by background reflections [8].

1.5 It has also been proposed that marks detected by visual examination need not always be photographed in situ; if it is considered that powdering or chemical development would be of no benefit and photography is difficult, lifting of the mark may be carried out using either transparent lifting tape or gelatine lifters (black, white or transparent) [9]. Lifting of latent marks, either after visual examination or as a speculative technique, should not be carried out as an alternative to treatments such as powdering if the application of a development technique is feasible. The Home Office Centre for Applied Science and Technology (CAST) has recently carried out a comparison of the effectiveness of gel lifting and powdering for development/capture of latent marks [10] and has demonstrated that powdering is the more effective process.

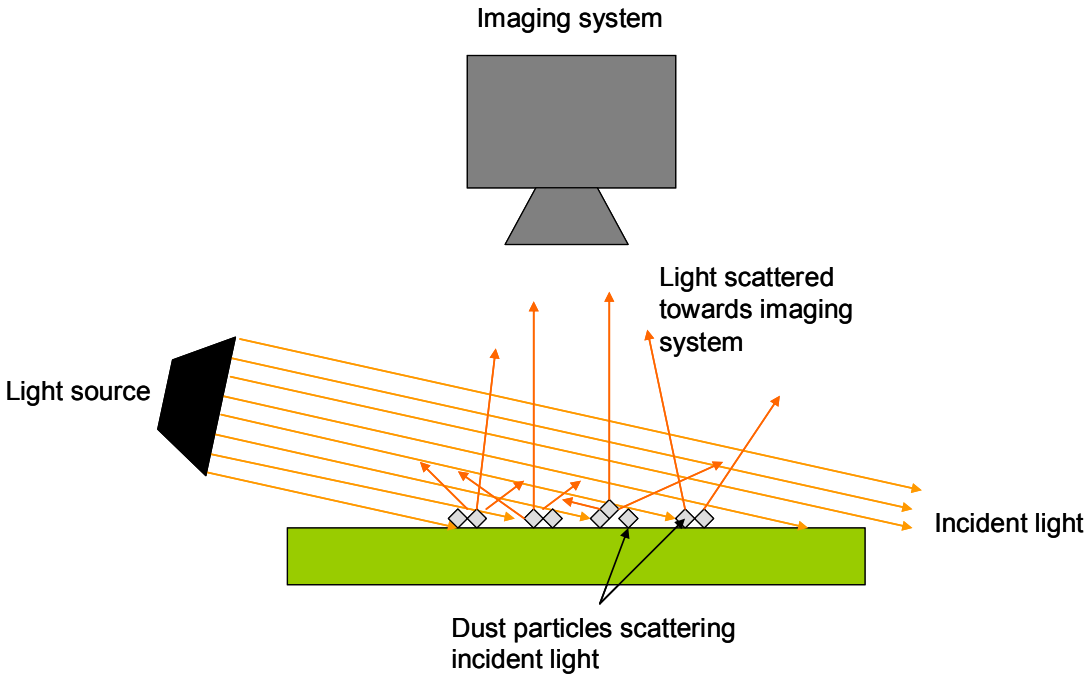
1.6 It has long been recognised that in some circumstances latent fingerprints may be developed by the environment they have been exposed to and fingerprints developed by heat have been found on paper articles at arson scenes [3]. Recent studies by CAST and others have found that there are a wide range of mechanisms by which fingerprints can be developed by the soot and heat at arson scenes [11-14], and visual examination of articles recovered from such scenes is essential.

2. Theory

2.1 The principle of visual examination is to utilise lighting in such a way as to provide as much contrast as possible between fingerprint ridges and the background, if possible suppressing any patterned backgrounds. For the initial detection of marks this is done by trying different lighting angles, but once a mark has been located there are several techniques that can be used to capture it in the optimum way. Some of these are described below, together with the situations that they are most appropriate for.

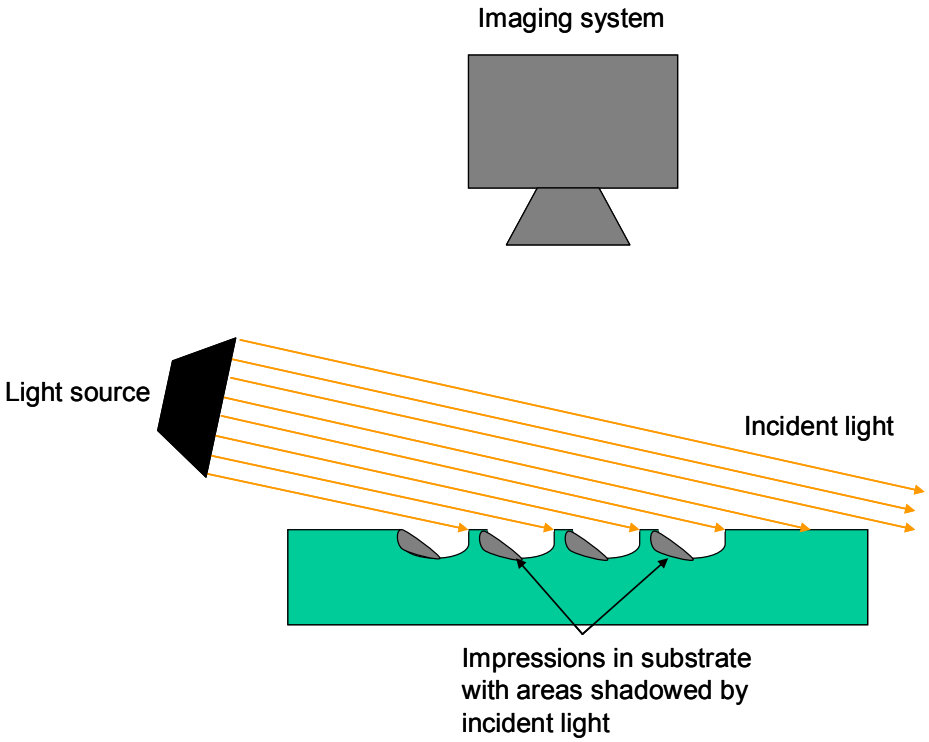
2.2 Oblique illumination

Oblique illumination may be used to capture marks where fingerprints are deposited in dust. The low angle illumination is scattered by particles of dust on the surface being examined, resulting in more light reaching the imaging system from these regions than in areas where no dust is present.



Schematic diagram illustrating the use of oblique lighting to detect marks deposited in dust

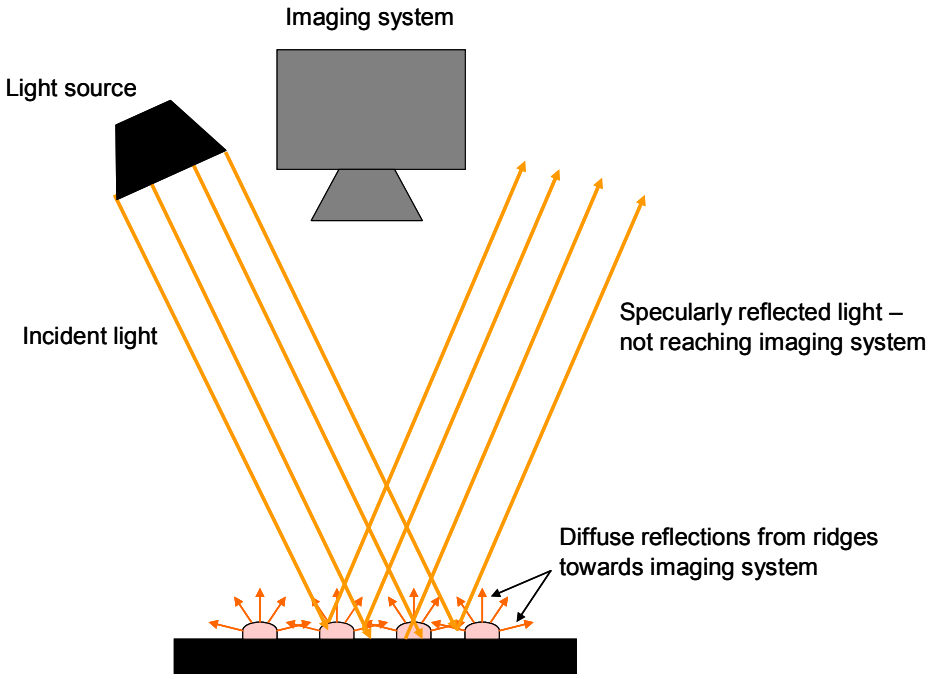
2.3 Oblique illumination can also be used in the capture of fingerprint impressions in wax or putty. In this case the low angle illumination casts shadows in the depressions left by the fingerprint ridges, thus aiding in their visualisation.



Schematic diagram illustrating the use of oblique lighting to detect marks left as impressions in a soft surface

2.4 Specular (oblique top) illumination

Specular illumination can be used for latent marks or marks in contaminant on reflective surfaces. It is essentially the opposite of oblique illumination, with the light source being placed at a high illumination angle in close proximity to the imaging system. Where light falls upon a reflective region of the background, it is specularly reflected at an angle where the reflected light does not reach the imaging system. Where light falls upon fingerprint ridges, it is either scattered or diffusely reflected, resulting in some light being reflected to the imaging system. The ridges will therefore appear lighter than the background in the image.

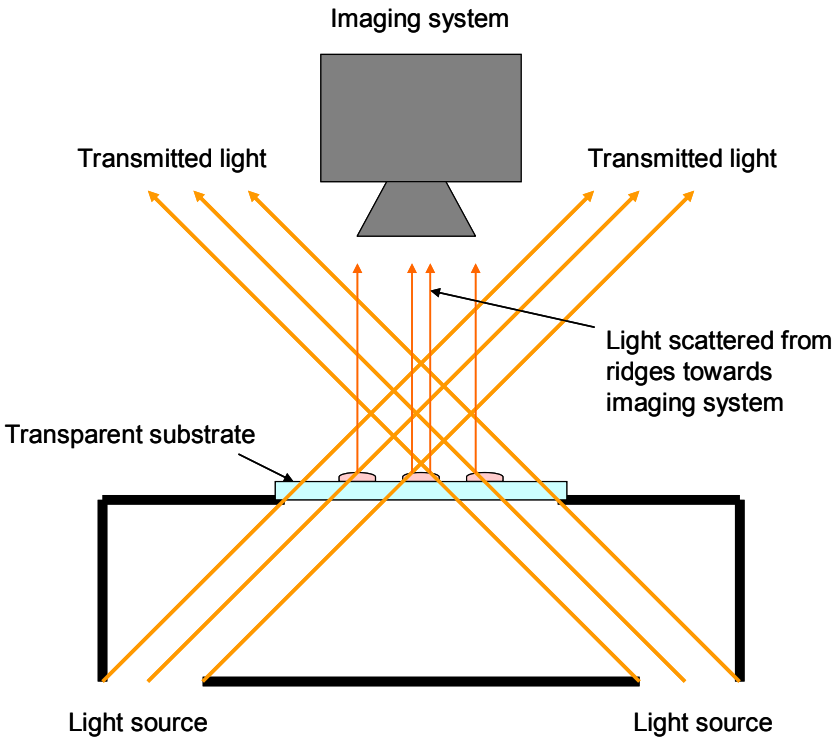


Schematic diagram illustrating the use of specular illumination to detect marks on smooth, reflective surfaces

2.5 This principle is utilised in the BVDA GLScan system, developed for the imaging of trace evidence lifted on black gelatine lifters [15].

2.6 Dark field illumination

Dark field illumination is suited to cases where fingerprints in sweat, oil or grease are present on transparent substrates, such as glass or plastic packaging. The sample is illuminated from underneath at oblique angles. In regions with no fingerprint deposit, light is transmitted and does not reach the imaging system Where there is a fingerprint deposit present the light is scattered, some of it reaching the imaging system. The resultant image shows light fingerprint ridges against a dark background.

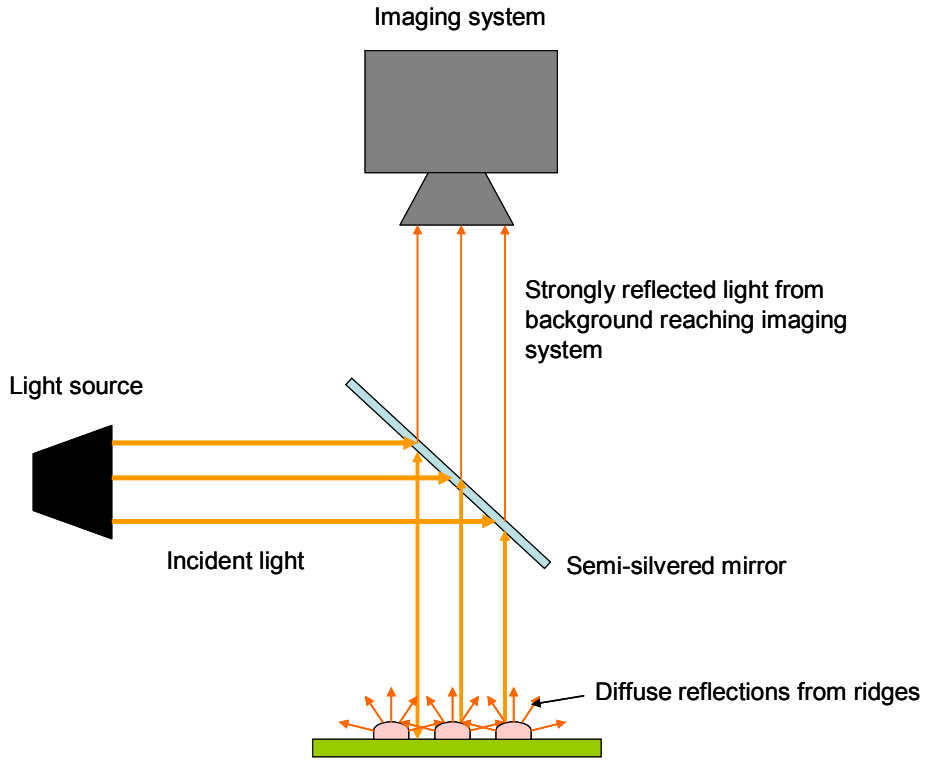


Schematic diagram illustrating the use of dark field illumination to detect marks on transparent substrates

2.7 Co-axial illumination

Co-axial illumination can be used where a latent mark or a mark in contaminant is present on a patterned, reflective background. A semi-silvered mirror at 45º to the axis of the imaging system is used essentially to provide co-axial illumination. The incident light is reflected downwards onto the sample. Where it meets the reflective surface it is strongly reflected and some passes through the semi-silvered mirror to reach the imaging system. Where the light hits ridges, it is scattered or a diffuse reflection occurs. The amount of light reflected back towards the imaging system from these regions is correspondingly less, and the fingerprint will appear as dark ridges against a light background.

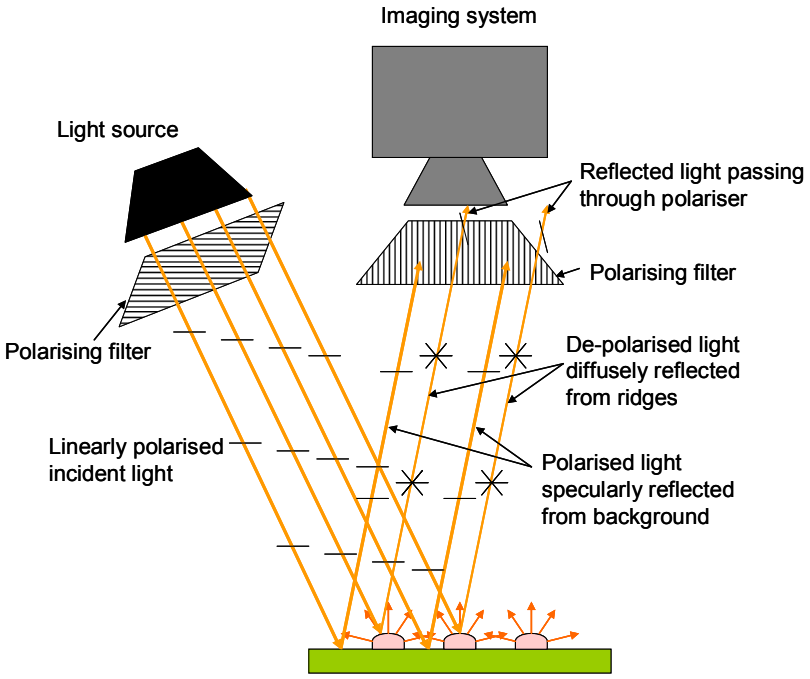
Several commercial systems have been developed incorporating co-axial or epitaxial illumination although these are mostly marketed for machine vision applications and none has been widely adopted for finger mark detection and imaging.



Schematic diagram illustrating the use of co-axial illumination to detect marks on smooth, reflective surfaces

2.8 Polarised light

Polarised light can also be used to detect a latent mark or a mark in contaminant on a reflective background. A linear polarising filter is used in front of the light source to produce linearly polarised light. When this reaches the reflective surface it is reflected and retains its polarisation. Where it hits the finger mark ridges it may be scattered or diffusely reflected, resulting in a depolarised component of light being reflected from the surface. A cross-polarised filter is placed in front of the imaging system, which blocks the specularly reflected light and allows a component of the de-polarised light through, resulting in an image with light ridges against a dark background.



Schematic diagram illustrating use of cross-polarised light to detect marks on reflective backgrounds

3. CAST processes

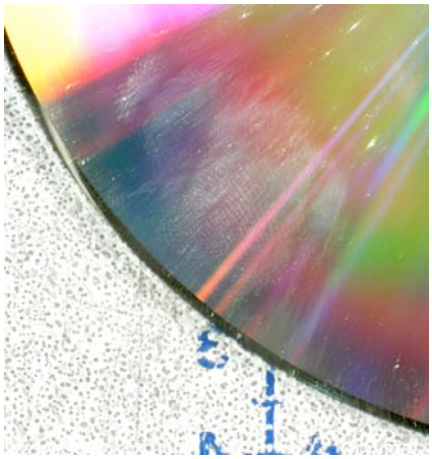
3.1 The CAST *Manual of Fingerprint Development Techniques* [9] identifies five generic types of fingerprint that may be visible.

- Type 1 – where the fingerprint is present in a semi-transparent material, such as sweat, oil or grease.
- Type 2 – where the fingerprint is deposited in a coloured material, such as blood, ink or paint.
- Type 3 – where the fingerprint is in dust.
- Type 4 – where the fingerprint is present as a result of a reaction between a fingerprint and the surface, e.g. fingerprints visible on ferrous, silver and copper articles as a result of surface corrosion or tarnishing.
- Type 5 – where there are fingerprint impressions in wax or putty.

Subsequent to the work carried out on articles recovered from an arson scene [11-14], a further type is proposed.

- Type 6 – where fingerprints have been developed by the effects of an environment the article has been exposed to, e.g. fingerprints developed on paper by the action of heat.

Examples of all these types of mark are illustrated below.

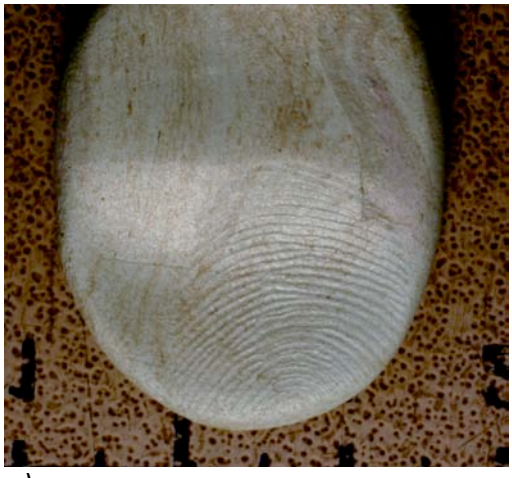


a)

b)

c)

d)



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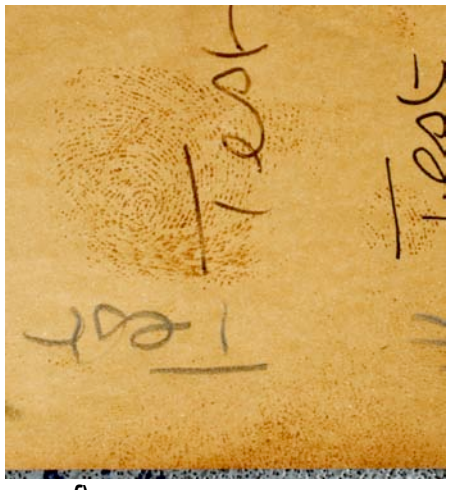


f)

Different types of marks that may be detected by visual examination a) Type 1 mark in grease on CD b) Type 2 mark in soot on mug c) Type 3 mark in dust d) Type 4 mark on metal sheet e) Type 5 mark in plasticine f) Type 6 mark developed by heat on paper.

3.2 The process recommended by CAST for all of these types of marks consists of examination under natural light, turning the article so that illumination falls on it from different angles. This should be followed by an examination using an even, white light source, again altering the angle of illumination from perpendicular to the exhibit to oblique.

3.3 Any fingerprints detected using this examination process should be imaged using the most appropriate technique outlined in the 'Theory' section above.

4. Critical issues

4.1 Visual examination must be performed before commencing any other form of examination or chemical treatment because potentially useful marks may otherwise be missed.

5. Application

5.1 Suitable surfaces: Visual examination is applicable to all types of surface, but will yield most marks on non-porous surfaces.

5.2 Visual examination can be applied to all types of articles, including examination of surfaces at crime scenes. Because it is a non-destructive technique and marks detected in this way may not be subsequently developed by any chemical/physical process, it should be the first stage in any sequential treatment process and any marks found should be imaged before proceeding.

5.3 Because there are a wide range of mechanisms by which latent marks or impressions may occur on articles, a thorough examination using different lighting conditions should be carried out, using both natural light and an even illumination from a white light held at different angles.

6. Alternative formulations and processes

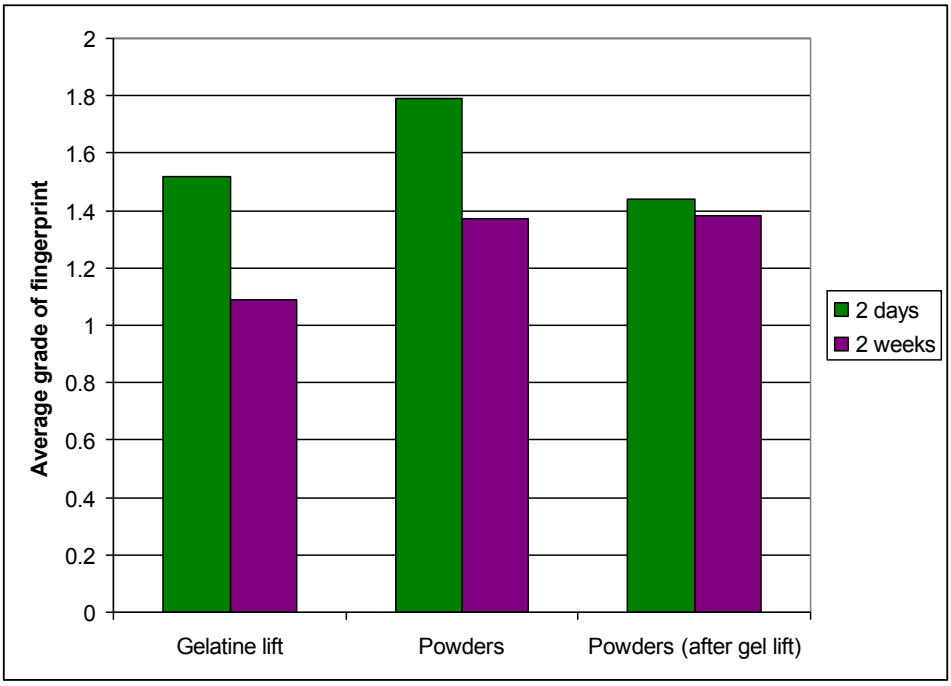
6.1 There are no alternative treatments or processes to those described in this section.

7. Post-treatments

7.1 If the latent mark detected is thought to be eccrine or sebaceous in nature, appropriate chemical/physical development techniques should be selected from the manual [9] taking into account the surface it has been deposited on. Similarly, if the mark is thought to be in blood or another

contaminant that could be developed by techniques in the manual, an appropriate sequential treatment regime should be selected.

7.2 For other types of contaminant/particulate, marks found by visual examination may be lifted using adhesive tape or gelatine lifts. However, this should only be carried out if the type of mark or surface precludes the use of subsequent development techniques, and/or the mark has already been captured, or cannot be captured in situ. The results of a comparative study between gel-lifting of latent marks and powdering are illustrated below, based on 1,260 graded marks.



Relative effectiveness of powders and gelatine lifts for fingerprint recovery from a range of surfaces

7.3 It can be seen that gel-lifting latent prints is less effective than powdering and can be detrimental to subsequent powder application, especially on fresher marks where the deposits are more easily lifted by the gel. On older marks where the deposits are more robust, gel-lifting appears to be less detrimental to subsequent powdering but in general gel-lifting should only be carried out in exceptional circumstances.

7.4 Impressed marks can also be cast and lifted using silicone rubber casting compounds, and the ridges of such casts enhanced by the application of black ink.

7.5 For marks on paper that have been developed by heat, subsequent fluorescence examination using the Quaser 473–548 excitation band and 549 viewing/camera filters may reveal additional detail [12-14].

8. Validation and operational experience

8.1 Because visual examination is a non-destructive process and should be used as the first stage in any sequential treatment regime, few documented operational trials have been carried out. There are many reported examples of where visual examination has revealed fingerprints at crime scenes and on articles in laboratories, and it is not considered necessary to extensively validate what should be an intuitive process.

8.2 Recently, studies have been carried out by Hampshire Constabulary and the Metropolitan Police [16], using a wide range of light sources to examine exhibits prior to chemical treatments. Both of these studies incorporated white light sources and visual examination. Results indicate that visual examination will detect marks that are not found by any other light source or developed by subsequent chemical treatment. In the Hampshire study 11% of marks were only detected by a combination of visual and fluorescence examination, and of this visual examination using white light was the sole means of detection for 3% of marks.

8.3 A summary of the results obtained from the study on operational work at Hampshire Constabulary is given in the tables below.

Surface type	Articles	White light	Quaser 2500	Laser (532nm)	Laser (577nm)	Chemical treatment
Porous	169	3	10	42	15	240
Non-porous	192	43	36	34	54	277
All	361	46	46	76	69	517

Summary of the performance of different light sources on porous and non-porous surfaces.

8.4 The types of article that marks were detected on using visual examination included cowlings and knife blades for non-porous items, and marks in dirt on paper for porous items. The results indicate that, as expected, subsequent chemical treatment develops appreciably more marks. However, it is also of interest to consider the number of unique fingerprints attributable to each process. In this analysis, the following information is obtained.

Light source	Total fingerprints	Not developed chemically	Unique fingerprints to process
White light	46	18	18
Quaser 2500	46	27	8
Laser (532nm)	76	46	36
Laser (577nm)	69	39	24

Detailed analysis of fingerprints detected by different light sources.

8.5 As stated above, it is evident that although visual examination detects comparatively few fingerprints (<10% of all marks detected), 40% of the marks that are detected by visual examination are unique to that process and it is therefore an essential element in a sequential treatment regime.

8.6 The Metropolitan Police study indicated that use of light sources accounted for ~8% of all marks detected on over 1,000 exhibits, although this included white light, long-wave ultraviolet and laser examination. On some non-porous surfaces (e.g. vehicle bodywork), the number of unique marks found by visual examination with a white light source was much higher than the average value above and reinforces the recommendation that visual examination should ideally be carried out before commencing any chemical treatment sequence.

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2.2 Fluorescence examination

1. History

1.1 The use of fluorescence examination for the enhancement of developed fingerprints was being considered as early as the 1930s, with materials such as anthracene and zinc sulphide being proposed for use as fingerprint development powders. Both of these powders fluoresced when illuminated with ultraviolet (UV) radiation and could be used to enhance the contrast of the mark against the background. In the case of zinc sulphide, the longer term phosphorescence of the material could also be utilised by imaging the mark once the light source had been removed. In 1954, Cherrill [1] described the use of barrier filters in combination with fluorescent powders to reduce reflected light from the background.

1.2 Most early investigators used UV radiation to produce fluorescence in fingerprints. In 1970 Ohki [2] carried out an investigation into the constituents of fingerprints and found several components that had inherent fluorescence when illuminated with UV radiation. Developments in chemical reagents for fingerprint development in the mid-1970s identified several systems that produced reaction products with fluorescence in the visible region when illuminated in the UV, including fluorescamine and o-phthaladehyde. However, these reagents did not provide any advantages in performance over ninhydrin and were not widely adopted.

1.3 The most significant development in fingerprint detection by fluorescence examination was the observation by Dalrymple *et al.* [3] that latent, untreated fingerprints could be detected on a range of substrates using a 1.5W argon ion laser line at 514.5nm with an appropriate barrier filter. Duff and Menzel were working in the Xerox Mississauga research laboratory and were also involved in using dye lasers in the same laboratory. It is now thought that the high success rates initially observed in these studies may have been attributable to some latent fingerprints being contaminated with laser dyes. Fluorescence was also observed by the same authors using a filtered xenon arc lamp, but this light source was of lower power (filtered output measured at 0.5W) and the fluorescence was correspondingly weaker. The authors recognised the future potential of fluorescent stains and powders, and attempted to enhance marks by powdering with the fluorescent Coumarin 6. Initially this did not reveal any ridge detail, but subsequent spraying with methanol and laser examination showed some powder preferentially adhering to the ridges. Thornton [4] was more successful, dissolving Coumarin 6 in ethanol, mixing with a black powder and then evaporating the ethanol to produce a fluorescent tagged dusting powder.

1.4 This prompted further studies into development techniques compatible with laser examination and Menzel and Duff investigated a range of fluorescent powders and chemical reagents [5] and the use of

phosphorescent powders in combination with a light chopper to reduce the interfering effect of background fluorescence [6]. This 'time resolved imaging' approach was later explored using a range of substances with long fluorescence decay times.

1.5 Laser examination was also becoming used on operational work and in 1979 Dalrymple [7] was able to record casework successes where laser examination had revealed marks by fluorescence that were not subsequently developed by chemical treatment. Dalrymple also identified the potential of fluorescing the background to enhance the contrast with a non-fluorescent fingerprint.

1.6 The published papers attracted worldwide interest in the technique and in 1979 a Police Scientific Development Branch (PSDB) delegation visited Duff and Menzel at the Xerox laboratories and the FBI [8] to assess the technique on a range of test substrates and to discuss its operational applications. Fluorescent marks were detected on low density polyethylene and matt aluminium, and some fainter marks seen on paper and adhesive tape. Overall the process performed poorly in comparison with traditional methods on 19 surfaces and 300 fingerprints. The PSDB group concluded that the coherent output of the laser was not essential to promote fluorescence, just the output power and wavelength specificity, and this initiated the programme of work into filtered light sources that ultimately led to the production of the Quaser 30 in the early 1980s, followed in turn by the Quaser 80, 100, 40 and finally the Quaser 2000.

a) b)

Different generations of Quaser, a) Quaser 80 and b) Quaser 2000.

1.7 PSDB demonstrated a prototype lamp system to Professor Warrener from Australia and John Watkin from Canada in 1980/81. These other groups also recognised the potential and the significantly lower cost of filtered light sources and research programmes to develop these systems were initiated in both Canada [9] and Australia [10,11]. Comparisons carried out between a filtered light source and a laser [11]

indicated little difference in performance between the systems available at that time.

1.8 The PSDB research programme investigated the constituents of fingerprints, in particular those fluorescing under UV and green light [12,13]. Several constituents that fluoresced under laser illumination were detected although it was not possible to conclusively identify all of them. PSDB (by now part of the Home Office Scientific Research and Development Branch) also began a comprehensive programme to assess the optimum excitation and viewing filter combinations for the Quaser filtered light sources, and to devise health and safety guidelines for use with all types of light sources that could be used for fluorescence examination. This included work in close consultation with leading ophthalmologists to ensure that the safety guidance given was directly relevant to the light sources used and to the end application. The culmination of this work was *Fingerprint Detection by Fluorescence Examination – A Guide to Operational Implementation* [14].

1.9 Another advance in fluorescence examination was made by Herod and Menzel [15] during studies into techniques for enhancing fingerprints developed using ninhydrin. It was already known that complexes formed between some metal ions and ninhydrin could result in colour changes to the mark, but not that some of these products were fluorescent. Herod and Menzel found that spraying the ninhydrin marks with zinc chloride resulted in a colour change in the fingerprint from purple to orange, and the formation of a fluorescent reaction product excited by the 488nm line of the argon laser. Subsequent studies showed that zinc toning used after ninhydrin detected significant numbers of additional marks and this became an important sequential processing technique until somewhat superseded by the development of reagents such as 1,8-diazafluoren-9-one (DFO) and 1,2 indandione, which yielded inherently fluorescent reaction products.

1.10 Other refinements considered to the fluorescence examination process were the use of a scanning laser spot to build up a fluorescence intensity map of a surface by Herod and Menzel [16] and the use of narrow bandpass filters in combination with a long-pass barrier filter to improve the contrast between the fluorescing mark and the background by Dalrymple [17].

1.11 Other types of laser were also considered for fluorescence examination and reviews of the options available were made by Menzel [18,19]. By the early 1980s copper vapour and neodymium:yttrium aluminium garnet (Nd:YAG) lasers had become available and although the copper vapour laser had similar attributes to the argon laser, the Nd:YAG laser was more portable (albeit with much lower output power at that time) and could be taken to crime scenes.

1.12 Research was also conducted into the use of time-resolved fluorescence imaging, combined with the assessment of reagents with longer

fluorescence decay time compatible with this technology. Europium compounds [20] and other lanthanides [21] were proposed by Menzel for this purpose, the potential advantage of the technique being that background fluorescence can be separated from the fluorescence of the fingerprint by the difference in decay time.

1.13 Since the early 1980s, advances in fingerprint development techniques have meant that fluorescence examination has become an integral process in sequential treatment regimes, being used to detect latent fingerprints and to enhance developed fingerprints. Fluorescent dyes have been developed for use with superglue, DFO is available as a technique for developing fluorescent marks on porous surfaces, acid yellow 7 can be used as a fluorescent blood dye on dark surfaces and marks developed using basic violet 3 may also be enhanced by fluorescence. All of these processes are described in greater detail in Chapters 3.1, 3.2 and 3.3, respectively.

1.14 Most recently, the advances made in light emitting diode (LED) technology have resulted in hand-held torches with equivalent output power to some filtered arc lamp systems. However, the output spectra of LEDs are typically broader than filtered systems and usually require additional filtering to avoid reflected light from the light source passing through the viewing filter. Further increases in LED power are anticipated and such systems are already becoming useful tools in fluorescence examination.

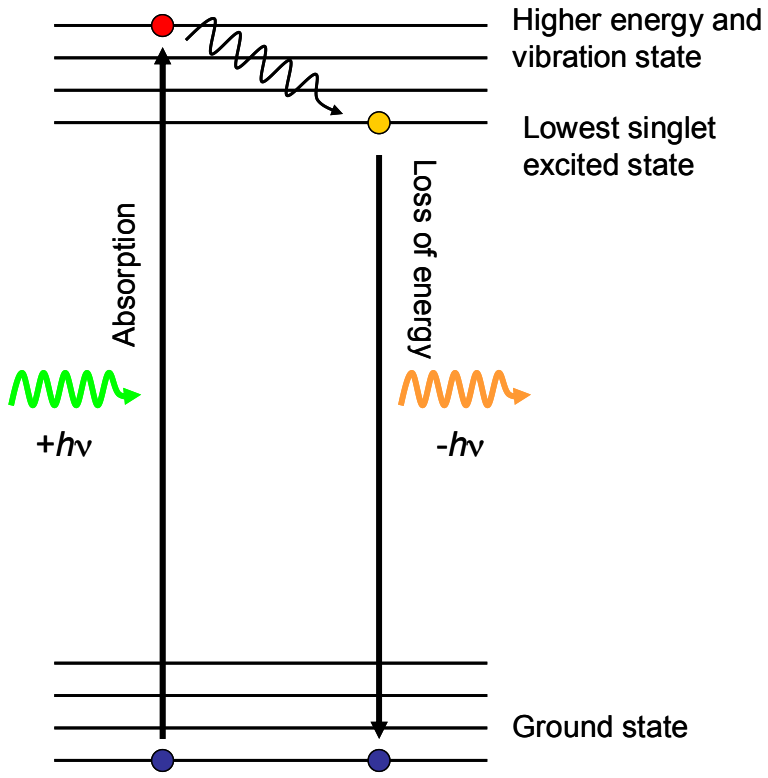
1.15 Lasers have also become more lightweight and portable, and scene portable, suitcase-sized Nd:YAG (and semiconductor diode) green lasers with output powers up to 8W are now available. Semiconductor lasers with outputs of 2W in the blue and 5W in the yellow regions of the spectrum have also been developed; both of these have been demonstrated to detect marks (and other types of forensic evidence) not found by the green laser. The use of as many different light sources as possible is therefore recommended to maximise evidence recovery.

2. Theory

2.1 Fluorescence is one of a number of processes that are broadly described by the term ‘luminescence’, which means that a substance emits light in response to an external stimulus. Other examples include chemiluminescence, where light is emitted as a result of a chemical reaction (as in the blood detection technique luminol) and triboluminescence, where light is emitted as a result of a material being rubbed, broken or abraded.

2.2 In fluorescent chemicals, light of a specific colour is absorbed and some of this absorbed energy is subsequently emitted as light of a different colour and longer wavelength. This can occur because the molecule has potential electronic energy excited states with levels compatible with the

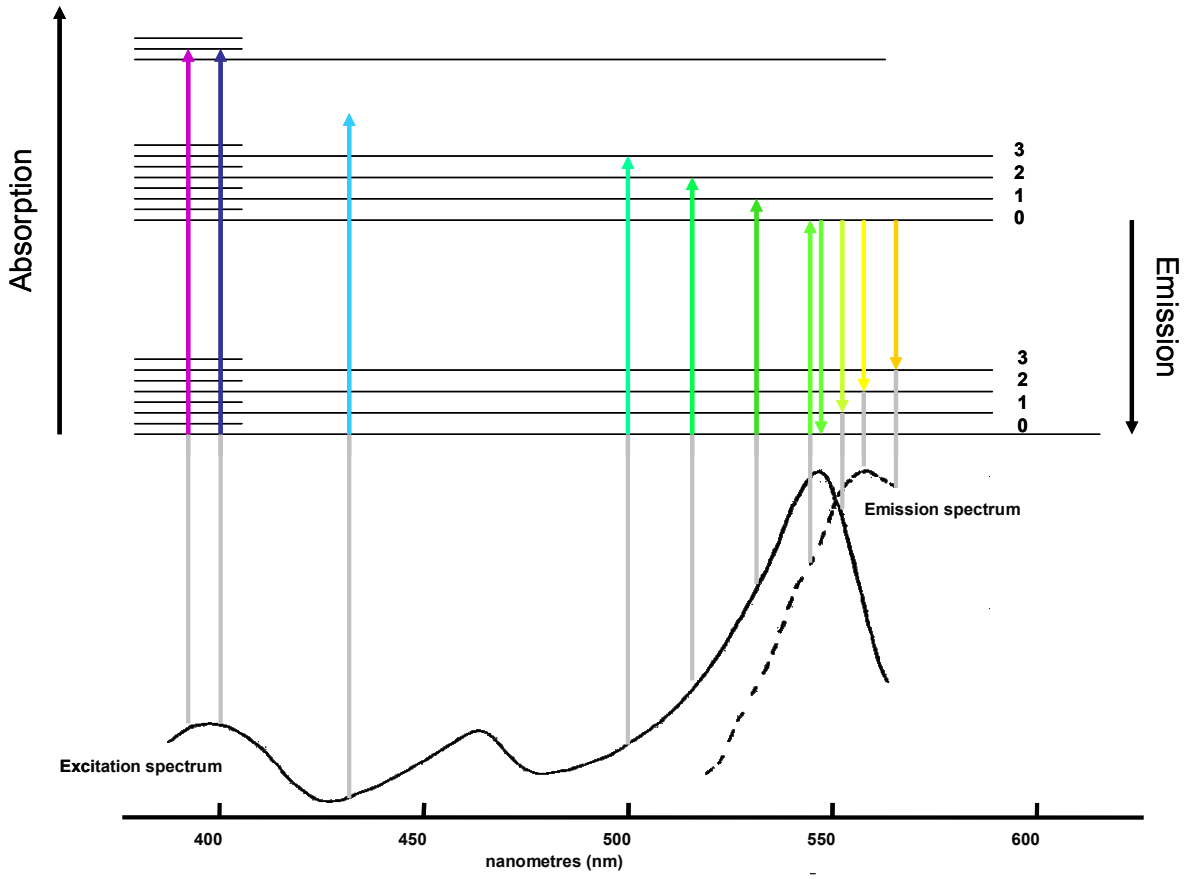
absorption and emission of visible light. The mechanism of fluorescence is shown schematically below.



Schematic diagram showing the mechanism by which fluorescence occurs.

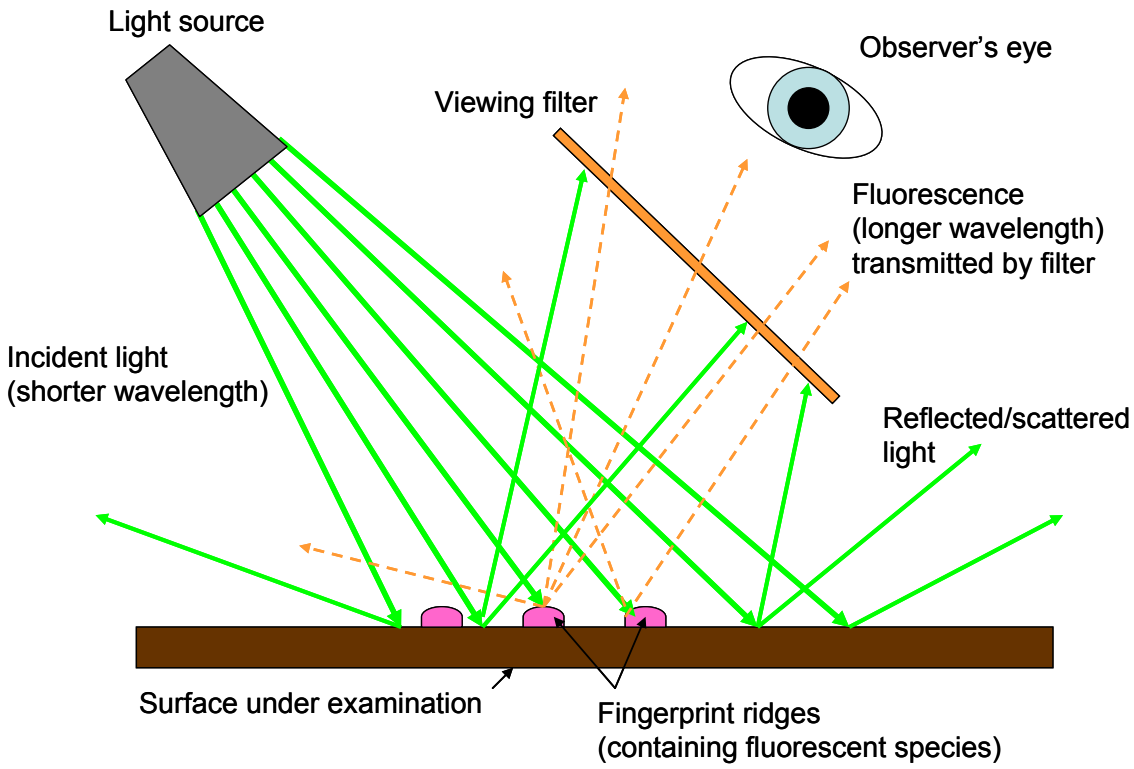
2.3 When a fluorescent molecule is excited with light of an appropriate wavelength, the electrons absorb energy from the light and are promoted from the ground state to a higher energy electronic state. Radiationless energy loss transitions resulting the vibrational energy level of the excited electron dropping. The electron then drops to a lower electronic level with the emission of a photon of a lower energy and lower wavelength than the original absorbed photon. If the transition between excitation and emission takes place in less than 10-8 seconds it is generally regarded as fluorescence. There are other 'delayed fluorescence' and phosphorescence mechanisms that can occur in ome molecules.

2.4 There are in practice several excited states to which electrons can be promoted and several ground states to which they can return, so that absorption and emission actually occur over ranges of the electromagnetic spectrum. A schematic illustration of a representative emission and absorption spectrum and the corresponding excited states is shown below.



Representation of excitation/emission spectra of a chemical with corresponding transitions between excited and ground states.

2.5 Typically, light in the UV, blue, green or yellow parts of the spectrum is used to excite fluorescence, which may result in the emission of light in the yellow, orange, red or infra-red (IR) regions. Most of the illuminating light is not absorbed but scattered or reflected from the surface being examined. Filters that transmit the fluorescence but not the illuminating light are therefore placed in front of the eye and/or image capture device to enable the fluorescence to be seen and recorded. This is shown schematically below.



Schematic diagram illustrating the viewing of fluorescence from fingerprint ridges containing a fluorescent species

2.6 In optimising fluorescence examination it is essential to ensure that the illuminating wavelengths of light correspond closely to the excitation of the fluorescent species present (if known), and that the viewing filter used blocks all illuminating wavelengths and transmits the maximum emission peak of the fluorescent species.

2.7 It is this philosophy that has been used to determine the excitation wavelengths and corresponding viewing filters recommended in the 'CAST processes' section below.

3. CAST processes

3.1 Comprehensive descriptions of the processes used for fluorescence examination are given in the HOSDB publication *Fingerprint Detection by Fluorescence Examination – A Guide to Operational Implementation* [14]. A shorter summary is given here. This section does not cover the use of UV radiation for the detection of fingerprints, which is dealt with in greater detail in Chapter 4.1, Ultraviolet imaging.

3.2 In common with visual examination, there are many ways in which fluorescence examination can used to detect fingerprints. There are two principal forms of examination, subdivided into eight types, which are described below.

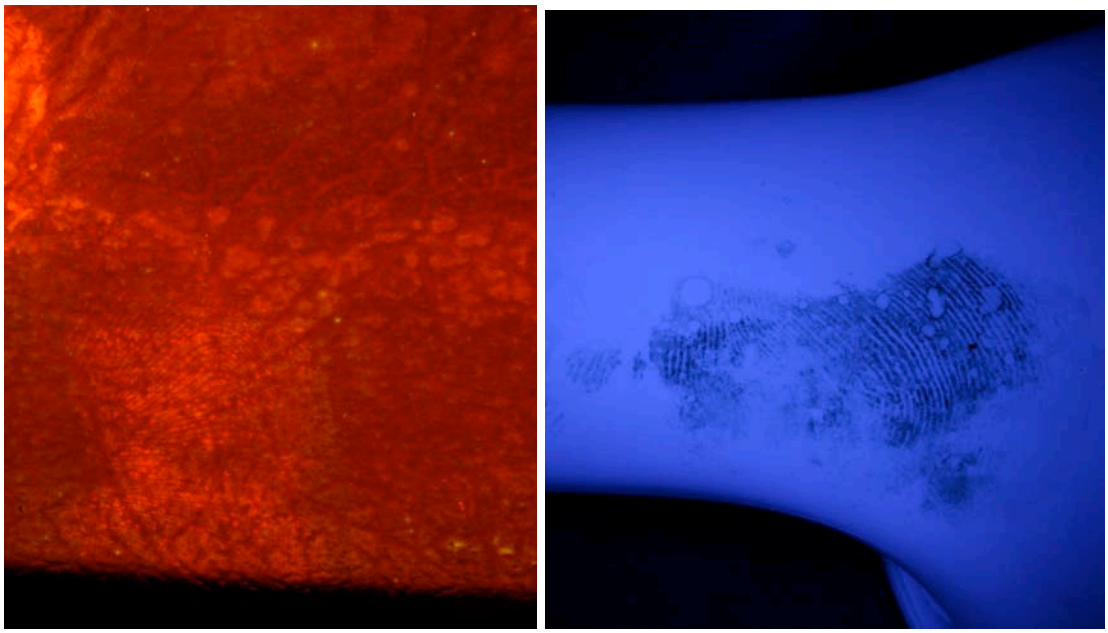
3.3 Initial examination of untreated fingerprints

3.3.1 Fluorescence examination is an essentially non-destructive process and may be used as the initial stage in a sequential processing regime. There are three types of fingerprints which may be revealed during initial examination.

Type 1 – Fingerprints may be detected due to the inherent fluorescence of constituents that may be present in sweat.

Type 2 – Contaminants present in the fingerprint, such as ink, drugs or grease, may exhibit enhanced fluorescence over those consisting of sweat alone.

Type 3 – Some surfaces, such as paper or cardboard, may exhibit background fluorescence, which can improve the contrast of fingerprints contaminated with substances such as blood or dirt that absorb light and appear dark against the light fluorescing background.



a) b)

Marks detected during initial examination a) Type 1 or 2 mark detected by inherent fluorescence of fingerprint and b) mark in blood revealed against fluorescent background.

3.4 Enhancement of developed fingerprints

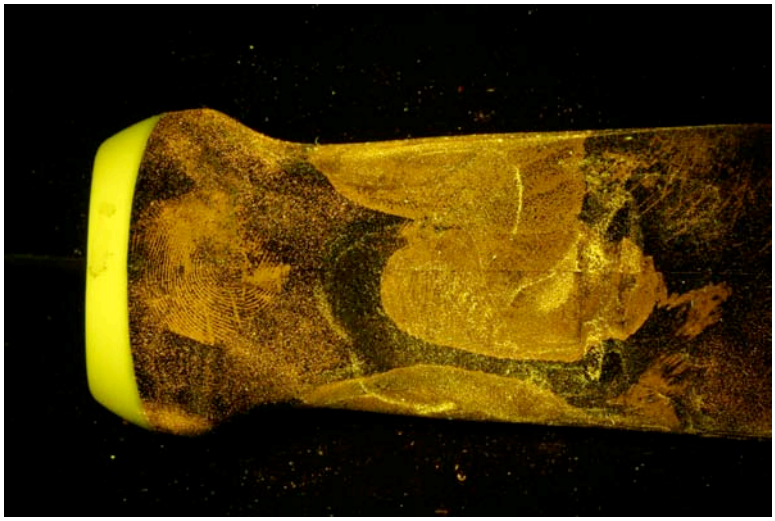
3.4.1 Fluorescence examination may also be used as a method of improving the contrast of fingerprints developed with other processes. There are four principal types of fingerprint to which fluorescence examination can be applied.

Type 4 – The treated fingerprint may itself fluoresce because the chemical used to stain it is fluorescent, examples being basic violet 3 and acid yellow 7. In this way, fingerprints that are faint or invisible under normal light may be revealed by fluorescence. However, heavy blood deposits or heavily stained fingerprints may quench fluorescence.

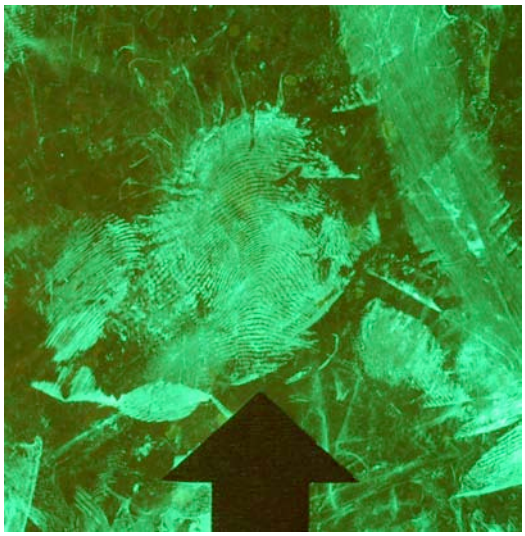
Type 5 – The background surface may fluoresce and the fingerprint may absorb or scatter the incident light and appear black. Examples of this may be seen for ninhydrin and physical developer.

Type 6 – The treated fingerprint may be treated with a secondary reagent or stain prior to fluorescence examination. This converts it from a non-fluorescent to a fluorescent mark, thus improving the detail that can be imaged. Examples of this include the zinc salt toning of ninhydrin marks and the staining of superglue marks with fluorescent dyes.

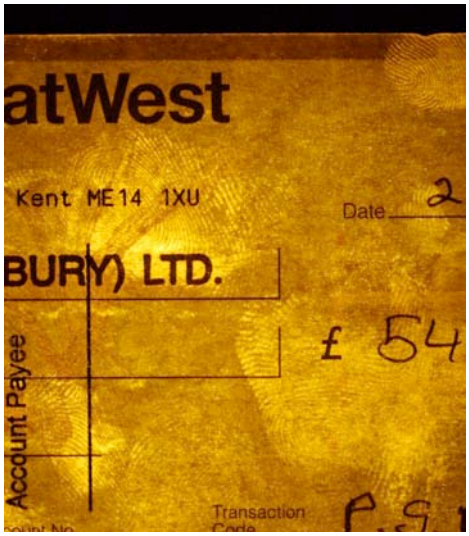
Type 7 – The reagent used may react directly with fingerprint constituents to form a fluorescent product, e.g. DFO and 1,2 indandione. Fluorescent fingerprint powders also fall into this category.



a)



b)

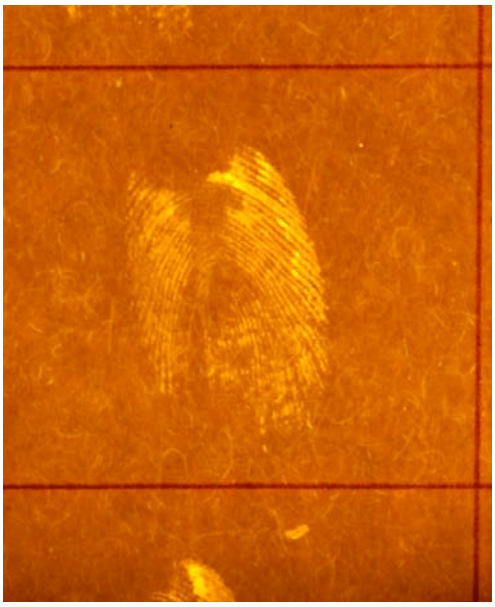


c)

Fingerprints enhanced using fluorescence examination a) Type 4 mark, mark in blood enhanced using acid yellow 7 b) Type 6 mark, superglue stained with basic yellow 40 and c) Type 7 mark, fingerprints developed using 1,8-diazafluoren-9-one.

3.4.2 More recently, work on the recovery of fingerprints from arson scenes has revealed a further category of mark that can be revealed or enhanced by fluorescence examination.

Type 8 – The action of the environment (e.g. heat) on a latent fingerprint may result in the formation of fluorescent products.



Type 8 mark – eccrine mark on paper becoming fluorescent after exposed to 150ºC.

3.4.3 The excitation and viewing conditions recommended for these situations by HOSDB are summarised below.

3.5 Nd:YAG laser (single wavelength)

3.5.1 Initial examination and enhancement of developed fingerprints

Application	**Excitation wavelength (nm)**	**Schott viewing filter**
Examination of all surfaces	532	OG570
DFO	532	OG570
Superglue dyed with basic red 14	532	OG570

Data given are for the Coherent 'Tracer' green laser, and the Laser Innovations 'Revelation' green laser.

3.6 Yellow semiconductor laser (single wavelength)

3.6.1 Initial examination and enhancement of developed fingerprints.

Application	**Excitation wavelength (nm)**	**Schott viewing filter**
Examination of all surfaces	577	RG610
Basic violet 3	577	RG610
DFO (on backgrounds highly fluorescing under green illumination)	577	RG610

Data given are for the Coherent 'Tracer' yellow laser.

3.7 Blue semiconductor laser (single wavelength)

3.7.1 Initial examination and enhancement of developed fingerprints.

Application	**Excitation wavelength (nm)**	**Schott viewing filter**
Examination of all surfaces	460	GG495
Marks contaminated with body fluids	460	GG495
Superglue dyed with basic yellow 40	460	GG495

Data given are for the Coherent 'Tracer' blue laser.

3.8 Argon Ion Laser (multiple, selectable wavelengths)

3.8.1 Initial examination.

Application	**Excitation wavelength (nm)**	**Schott viewing filter**
Examination of all surfaces	514.5	OG550
Surfaces with low background	488.0	OG530

fluorescence		
Fingerprints in dark materials, e.g. blood, where fluorescence of background may improve contrast	488.0	OG530

3.8.2Enhancing developed fingerprints.

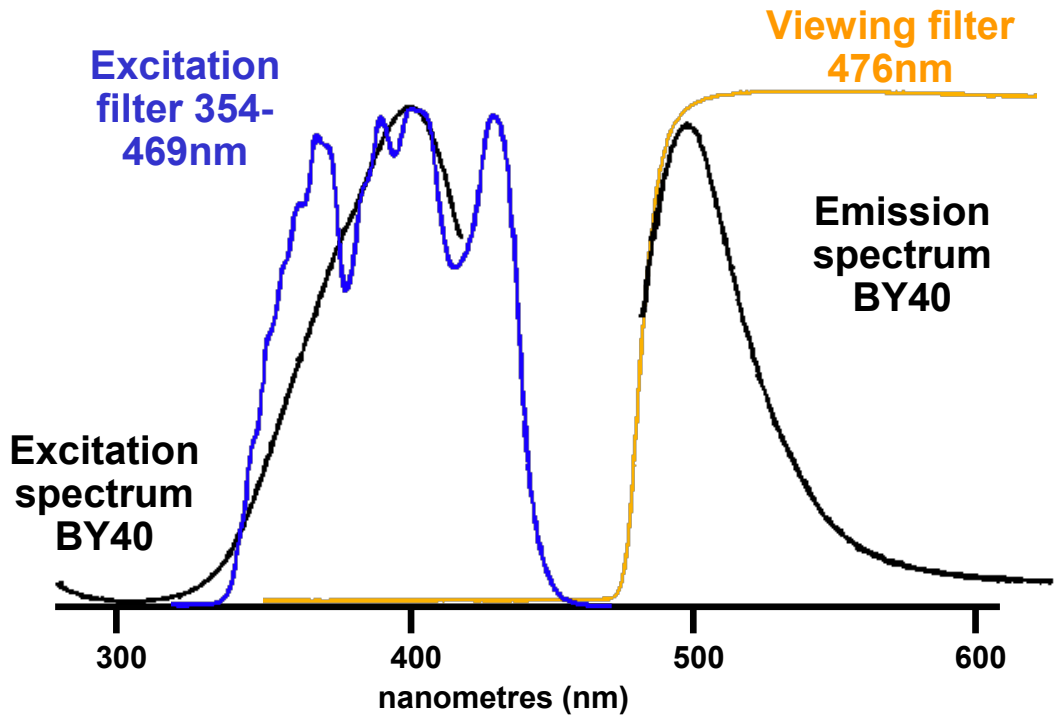
Application	**Excitation wavelength (nm)**	**Schott viewing filter**
Absorbing treatments, e.g. ninhydrin, acid black 1, acid violet 17, Powders (background fluorescence)	457.9 or 476.5 or 488.0	GG495 OG515 OG530
Acid yellow 7	514.5	OG550
DFO	514.5	OG550
Basic violet 3	528.7 or 514.5	RG610 OG550
Ninhydrin toned with zinc salts	488.0	OG530
Superglue dyed with basic yellow 40	457.9 or 476.5 or 488.0	GG495 OG515 OG530
Superglue dyed with basic red 2	514.5	OG550

Where alternative wavelengths are given, users should investigate which is the best combination for their particular laser.

Data obtained from Hardwick *et al.* [14].

3.9 Quaser (multiple, selectable excitation bands)

3.9.1An example of excitation and viewing filter selection for different applications is illustrated below.



Selection of appropriate Quaser filters to fit with excitation/emission of basic yellow 40 dye.

3.9.2Initial examination.

Application	**Excitation filter (nm)**		**Viewing filter (1% transmission point)**	
Examination of all surfaces. Background fluorescence may obscure some fingerprints	Blue	352–509 385–509 354–519 385–519 400–519	Yellow/ Orange Orange	510 or 515 529
Reduces background fluorescence	Blue/ Green	468–526	Orange	529
Reduces background fluorescence further	Green	473–548	Orange	549
Detects some fingerprints on polythene packaging and possibly other surfaces	Green	491–548	Orange	549
Fingerprints in dark materials, e.g. blood, where background fluorescence may improve contrast	Violet/ Blue	350–469 385–469 400–469	Yellow	476
Fingerprints in dark materials, e.g. blood, where background fluorescence may improve contrast. Some fingerprints in oils and greases and some	Ultra-violet	280–413 340–413	Yellow	415

absorbing fingerprints on glossy papers				

Where multiple excitation filters are listed, the set supplied will depend on the Quaser system used.

3.9.3Enhancing developed fingerprints.

Application	**Excitation filter (nm)**		**Viewing filter (1% transmission point)**	
Absorbing treatments, e.g. ninhydrin, acid black 1, acid violet 17, powders (background fluorescence)	Violet/ Blue	350–469 385–469 400–469	Yellow	476
Acid yellow 7	Blue	352–509 385–509 354–519 385–519 400–519	Yellow/ Orange Orange	510 or 515 529
DFO for maximum contrast on most types of paper	Green	473–548	Orange	549
DFO to reduce background fluorescence	Green	491–548	Orange	549
DFO to reduce background fluorescence further	Green/ Yellow	503–591	Red	591
Basic violet 3	Green/ Yellow	503–591	Red	591
Ninhydrin toned with zinc salts	Blue/ Green	468–526	Orange	529
Superglue dyed with basic yellow 40	Violet/ Blue	350–469 385–469 400–469	Yellow	476
Superglue dyed with basic red 14	Green	473–548	Orange	549

Where multiple excitation filters are listed, the set supplied will depend on the Quaser system used.

Data obtained from Hardwick *et al.* [14] and from the CAST *Manual of Fingerprint Development Techniques* [22].

3.10 LED light sources

3.10.1 Data given are for Foster and Freeman ‘Crime-lite 80S’ range, correct as of 28/01/2010

3.10.2 Initial examination.

Application	**Excitation filter (nm)**		**Viewing filter (1% transmission point)**	
Examination of all surfaces.	Blue	430–470	Yellow	476

Background fluorescence may obscure some fingerprints				
Reduces background fluorescence	Blue/ Green	460–510	Orange	529
Reduces background fluorescence further	Green	500–550	Orange	549
Detects some fingerprints on polythene packaging and possibly other surfaces	Green	500–550	Orange	549
Fingerprints in dark materials, e.g. blood, where background fluorescence may improve contrast	Violet/ Blue	395–425 430–470	Yellow	476

3.10.3 Enhancing developed fingerprints.

Application	**LED colour and excitation (nm)**		**Viewing filter (1% transmission point)**	
Absorbing treatments, e.g. ninhydrin, acid black 1, acid violet 17, powders (background fluorescence)	Violet	395–425	Yellow	476
Acid yellow 7	Blue	430–470	Yellow	476
DFO for maximum contrast on most types of paper	Green	500–550	Orange	549
Ninhydrin toned with zinc salts	Blue/ Green	460–510	Orange	529
Superglue dyed with basic yellow 40	Blue	430–470	Yellow	476
Superglue dyed with basic red 14	Green	500–550	Orange	549

4. Critical issues

4.1 There are several issues that need to be considered and addressed when performing fluorescence examination, some concerned with technique effectiveness and other relating to health and safety.

4.2 The light source used must output at a wavelength or spectral bandwidth that overlaps with the absorption bands of the dyes/contaminants in the fingerprint and thus excite the fingerprint into a state where it can fluoresce.

4.3 The light source used must have an effective radiated power that produces a sufficient intensity of fluorescence in the mark for it to be detected and captured.

4.4 The filters used for both viewing and capture of fluorescent marks must be correctly designed and selected so that they block all of the

wavelengths output by the illumination source, and transmit as much of the fluorescence output from the mark as possible.

4.5 The potential background fluorescence of the surface should be considered. It may be necessary to move to other wavelengths or wavebands to reduce the impact of background fluorescence, even though these may not be optimum for exciting the fluorescent constituents in the mark.

4.6 It is essential to carry out a full safety assessment prior to carrying out fluorescence examination to ensure that all operators are wearing appropriate protective eyewear and that unprotected personnel cannot be accidentally exposed to harmful levels of stray light. Safety procedures should be put in place to enforce this.

4.7 The light levels needed to detect weakly fluorescent materials present serious hazards to the eyes and in some cases the skin. It is possible to cause retinal burns in less than the eye blink response time of ¼ second. Some of the light source and filter systems marketed are potentially hazardous and may have inadequate or incorrect safety advice. Those providing safety features to avoid accidental exposure to harmful levels of light are preferable.

4.8 Changes to the wavelength, power, barrier filter or light delivery optical system may dramatically affect the risks to human eyes. The only effective way to carry out a safety assessment of a system is by calculation, and/or by measurement of the radiance levels for visible light systems and irradiance for UV or IR systems.

5. Application

5.1 Suitable surfaces: Fluorescence examination can be used for detection of latent fingerprints on all types of untreated surface, but success rates are higher on non-porous articles. Fluorescence examination is also useful on all types of surface after chemical treatment provided that an appropriate fluorescent chemical has been used to develop the fingerprint, or the surface has appreciable background fluorescence while the chemically treated print absorbs.

5.2 Fluorescence examination has two principal applications in fingerprint detection, firstly in the detection of latent fingerprints prior to commencing a sequence of chemical treatments and secondly in the enhancement of marks that have either been treated to produce fluorescent products or are absorbing on a fluorescent background.

5.3 In the first role, fluorescence can be an invaluable tool because it may detect marks that contain small quantities of fluorescent contaminants. Because fingerprint development processes primarily target natural

secretions, many of these marks will never be found during subsequent chemical treatment.

5.4 Fluorescence examination may also detect marks present in contaminants, such as blood. Many surfaces fluoresce when excited by high-intensity light in the UV and violet regions of the spectrum. This is coincidently where the haem group in blood is most absorbent, with a peak around 421nm (known as the Soret Band) [23] and why blood-contaminated fingerprints will appear dark against a light background. Fluorescence examination may be used before any other fingerprint enhancement techniques as it is non-destructive, and if long-wave UV or violet light (350–450nm) is used then DNA typing is also unaffected.

5.5 In the enhancement of chemically treated fluorescent marks, fluorescence examination is used to reveal marks that may not be visible to the eye and to enhance the contrast between ridges and background. More powerful light sources (of the correct excitation wavelength) will cause even very weakly developed marks to fluoresce sufficiently for imaging.

5.6 Marks in blood may also be detected by fluorescence, even though the original chemical treatment is not intended to produce fluorescence. If haem-specific enhancement processes are used, the use of a strong organic acid in conjunction with hydrogen peroxide breaks up the haem group so that it is no longer as effective at absorbing light. When subsequently excited by green (500–550nm) light it will fluoresce orange. This effect has also been noted as blood ages.

5.7 Wherever possible, fluorescence examination should be carried out in a darkened room free of highly fluorescent articles and surfaces, and users should allow themselves to become dark adapted before commencing examination. All safety precautions appropriate to the light source being used should be taken [14] to ensure the safety of both the operator and others in the vicinity. The light source should be passed slowly over the article to be examined, taking care to minimise exposure time on articles that may be damaged by the heat associated with some high-power light sources. Handling of the article during examination should be minimised to avoid damage to any marks present on the surface. Any marks detected should be photographed using an imaging system fitted with an appropriate barrier filter.

5.8 Fluorescence examination can be carried out both in a laboratory and at a crime scene, provided that appropriate health and safety precautions are taken. For optimum results, it is essential that the operator takes time to become fully dark adapted before commencing examination.

Examination of a crime scene using a portable laser.

6. Alternative formulations and processes

6.1 There are many suppliers of light sources, covering the range of lasers, filtered arc lamps and LEDs, but regardless of which is selected the essential examination process is the same. The light source should be selected to provide maximum illumination in the excitation region of the fluorescent chemical (if known), and the viewing filter selected to block the illumination wavelengths and transmit the excitation wavelengths of the chemical. Provided that this approach is adopted, many different combinations of fluorescent dye, illumination light source and viewing filters can be successfully employed in fluorescence examination.

7. Post-treatments

7.1 There are no post-treatments used in fluorescence examination.

8. Validation and operational experience

8.1 Because fluorescence examination is essentially a non-destructive examination technique and is recommended for use as the second stage in a sequential treatment (after visual examination), its operational implementation for this purpose should not require extensive validation.

8.2 Laboratory trials

8.2.1 Few laboratory trials have been conducted using deliberately deposited fingerprints. This is because it is known that the proportion of marks that will be detected in this way is low, but this is accepted for operational use

because fluorescence examination is non-destructive and will find marks in contaminants not developed by chemical reagents.

8.2.2 A limited study has been carried out by CAST to compare the effectiveness of fluorescence examination with other non-destructive examination techniques, including short-wave UV imaging on porous surfaces. These results are reported in Chapter 4.1, Ultraviolet imaging, and illustrate that both green and yellow lasers will detect marks not found by any other light source, although they are not particularly effective on most porous surfaces.

8.3 Pseudo-operational trials and operational experience

8.3.1 Data are available that demonstrate the benefit of fluorescence examination in sequential treatments. As early as 1979, the FBI reported that from 1,500 articles examined using an argon ion laser, 76 fingerprints were found that were not subsequently developed by any other process [8].

8.3.2 Creer reported early results from the use of an argon ion laser at the Serious Crime Unit of the Metropolitan Police in 1983 [24], stating that from 396 exhibits examined, 121 identifiable fingerprints had been found. Many of these exhibits had been considered unsuitable for other treatments due to surface scratches or patterned backgrounds, which would make conventional photography difficult. Creer also noted that in some cases on plastic bags, the laser detected marks that were totally different to those subsequently developed by vacuum metal deposition. The broader forensic applications of the laser were also presented.

8.3.3 More recently CAST has purchased a 5W, 532nm green laser and have loaned it to police forces for trials on operational work. The laser has been compared with the Quaser 100 operating in the green excitation band for both initial fluorescence examination and for examination of marks developed using DFO [25]. The results of this trial, conducted on articles from over 70 cases, are summarised below.

Application	**Total number of marks found**	
	Quaser 100	**Nd:YAG laser**
Initial examination	10	52
DFO enhancement	70	77

Summary of results obtained using a laser compared with a Quaser 100.

8.3.4 It can be seen that the higher power and higher wavelength specificity of the laser compared with the Quaser 100 provide benefits in the number of marks detected using fluorescence examination. Similar successes have been reported from the use of the laser at crime scenes.

8.3.5 On a limited number of operational cases processed by CAST [26], similar observations to those of Creer [24] were made in that marks were

detected on plastic bags using fluorescence examination that differed totally from those developed by subsequent vacuum metal deposition. One set were identified to a householder, the other to a suspect. This type of result demonstrates that fluorescence examination is a complementary tool to chemical treatments, and fully justifies its position within a sequential treatment process.

8.3.6 As prototypes of lasers operating at different wavelengths became available, CAST carried out a small-scale pseudo-operational trial examining items recovered from waste bins and in and around the laboratory. These items were examined using four different light sources and the number of fingerprints recorded. The results of this study are recorded below.

	Blue laser (460nm)	**Green laser (532nm)**	**Yellow laser (577nm)**	**Quaser 101 (503–587nm)**
Items	56	56	56	56
Total fingerprints	2	15	20	16
Common fingerprints	1	13	12	16
Missed fingerprints	0	0	4	0
Unique fingerprints	1	3	8	0

Summary of results obtained from different light sources in a laboratory trial.

8.3.7 These results suggested that the green and yellow lasers were effective in detecting fingerprints, with the yellow laser finding more fingerprints, and more unique fingerprints overall. Even though the blue laser found very few fingerprints, it was still capable of finding marks not detected by other light sources.

8.3.8 More recently, studies have been carried out by Hampshire Constabulary and the Metropolitan Police [27], using a wide range of light sources to examine exhibits prior to chemical treatments. Both of these studies incorporated fluorescence examination at different wavelengths using a range of light sources. Results confirmed that fluorescence examination will detect marks that are not developed by subsequent chemical treatment. In the Hampshire study, reported in Chapter 2.1 Visual examination, fluorescence examination was the sole means of detection for ~8% of marks recovered from 361 exhibits over a period of 6 months. In contrast to the earlier CAST study, the green laser was found to be most effective in detecting marks on operational exhibits, although both green and yellow lasers found marks not detected by other techniques.

8.3.9 CAST also included fluorescence examination as the initial stage in a pseudo-operational trial to establish the optimum processing sequence

for plastic bags. In this study, 100 plastic bags of varying types (e.g. supermarket bags, black bin bags, clear magazine wrappings) were divided into quarters and each quarter was assessed using a different fluorescence examination regime followed by a different chemical treatment sequence. The total number of fingerprints and the number of fingerprints unique to each process were recorded. The fluorescence examination regimes used were: exclusively laser examination, using green, yellow (and blue when available) lasers; exclusively Quaser examination, using each waveband of a Quaser 101; solely LED examination, using a green Crime-lite 80S; and finally a full examination using all of the light sources available. The results of this exercise are summarised below.

Light source(s)	Total fingerprints found with light source	Total developed chemically	Unique fingerprints to light source
Laser sequence (460, 532, 577nm)	46	379	24
Quaser 101	34	335	10
Green Crime-lite	19	392	5
Full (Quaser, Crime-lite, lasers)	65	380	21

Summary of results obtained using fluorescence examination during a pseudo-operational trial on 100 plastic bags.

8.3.10 It can be seen that on plastic bags, fluorescence examination sequences utilising lasers typically recover ~10–15% of the marks found overall, with up to 50% of the marks found by fluorescence examination not being subsequently developed by any other process. The lower power Quaser and Crime-lite sources are less effective, but still find several unique marks.

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Chapter 3: Finger mark development techniques within scope of ISO 17025

3.1 Acid dyes (acid black 1, acid violet 17, acid yellow 7)

1. History

1.1 Fingerprints may deposited in a number of contaminants at crime scenes, and of all these blood is the most commonly observed This is possibly because, when present even in small quantities, it is easily seen as it strongly absorbs light throughout the visible spectrum. However, when present in minute amounts, or on dark, patterned or multicoloured confusing backgrounds, the blood may require enhancement to make it more useful for evidential purposes. Additionally, proof that a stain is actually blood rather than an innocuous substance may be important in assessing guilt or innocence, and may even be a matter of life or death in some cases.

1.2 The history of proving the presence of blood evidence in forensic investigation dates back over 150 years using chemical means, and further still when microscopical methods are considered. Anton van Leeuwenhoek was said to be the first person to describe and illustrate blood cells in the latter part of the 17th century, although this is disputed.

1.3 The earliest tests for blood were of two types, both relying on the presence of the haem group present in the red blood cells. The early tests included those that reacted with haem to produce crystals and those that relied on its catalytic nature. More recently (1999) a third test relying on antibodies has been introduced.

1.4 The crystal or confirmatory tests were formulated by Teichmann in 1853 [1], producing crystals of haematin, and by Takayama in 1912 [2], producing crystals of haemochromogen. However, these tests require that the blood be scraped from the surface, and therefore they can only be used where blood is easily observed, and cannot be used speculatively. Having to scrape blood also gives no regard to the forms of physical evidence that may be present, such as fingerprints, footwear impressions or splash patterns.

1.5 Catalytic or presumptive tests that attempted to keep much of the physical evidence intact were produced by Van Deen in 1862 based on guaiacum [3], Schönbein in 1863 using hydrogen peroxide [4] and by Adler and Adler in 1904 using benzidine [5]. They also pioneered the use of leuco-malachite green in 1904 [5]; their method being later modified by Medinger in 1933 [6] to make it more sensitive.

1.6 In 1901 Kastle and Shedd [7] developed another catalytic test using phenolphthalein, which Meyer in 1903 [8] modified to detect blood. Further investigation by Kastle and Amos in 1906 [9] proved the phenolphthalein to be reacting with haemoglobin present in blood. This test is known as the Kastle-Meyer Test.

1.7 Other presumptive tests for blood were developed for forensic use by Ruttan and Hardisty in 1912 using o-tolidine [10]; by Specht in 1937 using luminol (3-amino-phthalhydrazide); [11] and by Gershenfeld in 1939 using o-toluidine [12].

1.8 In 1911 Abderhalden and Schmidt [13] reported the development of fingerprints on the bottle label of triketohydrindene hydrate (ninhydrin). This discovery was not exploited for the detection of fingerprints or blood until 1954 when Oden [14] produced his ninhydrin formulation based on acetone. The use of this method for the enhancement of fingerprints in blood revolutionised thinking in this area of forensic investigation. The emphasis was shifted away from presumptive tests for haem, which generally require expert opinion to interpret the test results correctly, to easier to use reagents, which produce intensely coloured products with other components of blood, usually protein or its breakdown products.

1.9 Use of the protein dye amido black (acid black 1) quickly became popular with forensic investigators. Its use by the Metropolitan Police Laboratory, in a solvent base of methanol and acetic acid, was discussed at a forensic science symposium in 1961 by Godsell [15]. This formulation, with a change away from the fixing of the mark by the use of heat to immersion in methanol in 1981 [16], along with a water-based formulation of the same dye [17] continued to be recommended for the enhancement of fingerprints in blood by the UK Home Office until 2004 [18] when a new formulation by Sears and Prizeman [19] was adopted.

1.10 Many other protein stains for the enhancement of both fingerprints and footwear impressions in blood have also been proposed; coomassie blue (acid blue 83) and Crowle's double stain (acid blue 83 and acid red 71) by Norkus and Noppinger in1986 [20], fuchsin acid (acid violet 19, Hungarian Red), patent blue V (acid blue 1) and tartrazine (acid yellow 23) by Barnett *et al.* in 1988 [21], benzoxanthene yellow and acid violet 17 by Sears *et al.* in 2001 [22] and acid yellow 7 by Sears *et al.* in 2005 [23].

1.11 Although the use of protein dyes became most popular for enhancing fingerprints in blood, research on presumptive enhancement methods continued and in 1976 Garner *et al.* [24] proposed the use of tetramethyl-benzidene (TMB) as a safer and more effective technique than benzidine. Suggestions for other presumptive tests continued; tetraamino-biphenyl (TAB, also known as diaminobenzidine, DAB) in 1989 by Hussain and Pounds [25], fluorescein in 1995 by Cheeseman and DiMeo [26] and leucocrystal violet (LCV) in 1996 by Bodziak [27].

1.12 In addition there have been many modifications made to ninhydrin formulations to increase its effectiveness and safety by Crown in 1969 [28] and Morris and Goode in 1974 [29]. Further changes were forced on the fingerprint community because of The Montreal Protocol on Substances That Deplete the Ozone Layer in 1987 and new formulations were proposed by Watling and Smith in 1993 [30] and Hewlett *et al*. in 1997 [31]. The use of transition metal toners to change the colour or make the reaction product between amines and ninhydrin fluoresce have also been proposed by Morris in 1978 [32], Everse and Menzel 1986 [33] and Stoilovic *et al.* in 1986 [34].

1.13 It was also suggested that the use of one of several ninhydrin analogues would improve sensitivity and many have been proposed; benzo[f]ninhydrin in 1982 by Almog *et al.* [35], 5-methoxyninhydrin by Almog and Hirshfield in 1988 [36], 1,8-diazafluoren-9-one (DFO) in 1990 by Grigg *et al.* [37] and 1,2 indandione by Ramotowski *et al.* in 1997 [38]. All of these techniques, although primarily

intended to target with amino acids in latent fingerprints on porous surfaces, will react strongly with the proteins present in blood to coloured and/or fluorescent products.

1.14 More recently in 1999 Hochmeister *et al.* [39] validated a one-step immunochromatographic test for using anti-human Hb antibodies to prove the presence of human blood. However, this method requires the removal of blood from the surface so it cannot be used to enhance the physical evidence in situ, although if this test could be carried out after the application of the more sensitive protein dyes this would then cover all issues. In 2008 Johnston *et al.* [40] compared several of these tests with luminol and concluded the latter was more sensitive.

1.15 It was observed from the earliest times that blood strongly absorbed light and a number of researchers in the mid- to late-19th century tried to use this as a way to identify that a stain was blood. Among them were Hoppe in 1862 [41], who investigated the spectral properties of the colouring matter in blood; Stokes in 1864 [42], who was able to recognise the difference between haemoglobin and oxy-haemoglobin; and Soret in 1883 [43], who characterised the absorption bands of haemoglobin in the violet and ultraviolet (UV) regions of the spectrum. In 1865 Sorby [44] studied the spectra of various haemoglobin derivatives and proposed these as a means of identification for blood stains.

1.16 In the late 1970s and early 1980s it was observed by those developing high-intensity light sources that one of their most useful properties was that shorter wavelengths of light in the UV and violet make surfaces fluoresce strongly and this can give extra detail if a fingerprint is in a strongly light-absorbing material [45]. This is an especially valuable method for the enhancement of fingerprints in blood as the haem group absorbs light throughout much of the visible part of the spectrum [46,47].

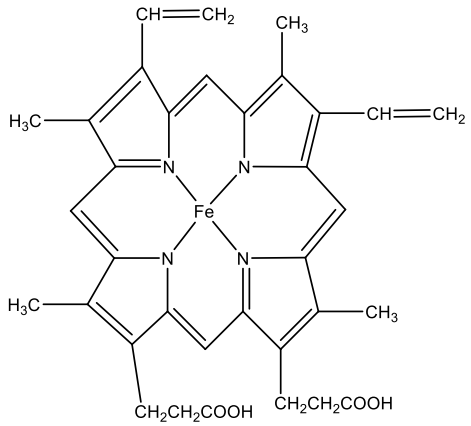
1.17 All these developments meant that by the late 1990s there were so many reagents and formulations existing for the enhancement of blood-contaminated fingerprints and footwear impressions with little or no comparative data that they were causing immense confusion among practitioners. Also the emergence of DNA analysis heaped even more uncertainty over which techniques could or should be used for the enhancement of blood. Vital evidence was likely to be lost by the wrong choices. Therefore the UK Home Office set out to clarify the situation and began a programme of work to review and compare the most commonly used of these techniques [19, 22, 23]. Resulting from this colossal task there were a number of key findings that were incorporated in a comprehensive update to *The Manual of Fingerprint Development Techniques* in 2004 [18], which included the current formulations for acid black 1, acid yellow 7 and acid violet 17.

2. Theory

2.1 Blood consists of red cells (erythrocytes), white cells (leukocytes) and platelets (thrombocytes) in a proteinaceous fluid called plasma, which makes up roughly 55% of the whole blood volume. The red cells principally contain the haemoglobin protein, but also have specific surface proteins (agglutinogens)

that determine blood group. The white cells, which form part of the immune system, have a nucleus that contains DNA.

2.2 Haemoglobin makes up roughly 95% of red cells' protein content and is made of four protein sub-units each containing a haem group. The haem group is made of a flat porphyrin ring and a conjugated ferrous ion.



Chemical structure of haem.

2.3 As mentioned above, chemical blood enhancement methods fall broadly into two types; those that react with the haem grouping and those that interact with proteins or their breakdown products. The last type are not at all specific for blood; however, because of the high proportion of protein and its products present in blood, and the fact that they do not rely on the effectiveness of cell lysation (as do the haem-specific type) the techniques that interact with proteinous material are the most sensitive available to the forensic investigator [23].

2.4 Many researchers measure the sensitivity of their techniques by diluting blood with water [23,26,48,49,50]. This method favours techniques that utilise the haem as all the red cells would be lysed because of osmotic pressure during dilution, something that will not happen when these techniques are used operationally. Dilution with a buffer at the same osmotic pressure as blood serum would give a clearer indication of ultimate technique sensitivity.

2.5 There is also one other major advantage of the protein staining techniques, in that they generally incorporate a stage that either denatures or fixes proteins to the surface; as most proteins, including haemoglobin, are water soluble, the blood-contaminated fingerprint is not then diffused during treatment.

2.6 There are two types of techniques that can be used to target proteins in blood; those that react with amines (e.g. ninhydrin), and those that stain proteinous material (e.g. acid dyes). It is this class of protein dyes that constitute the processes recommended by the Centre for Applied Science and Technology (CAST), i.e. acid black 1, acid violet 17 and acid yellow 7.

2.7 As stated above, the protein dyes used by HOSDB for the enhancement of fingerprints in blood are a group known as acid dyes. They are often characterised by the presence of one or more sulphonate ($-SO_3$) groups, usually the sodium (Na^+) salt. These groups function in two ways; firstly to provide solubility in water or alcohol, the favoured major solvents from which to apply these dyes, and secondly by virtue of their negative charge (anionic). If acidic conditions are used (acetic acid being the favoured option), the blood protein molecules acquire a positive charge (cationic) and this attracts the acid dye anions. Hydrogen bonding and other physical forces such as Van der Waals bonds may also play a part in the affinity of acid dyes to protein molecules [51].

2.8 Protein stains are applied via a three-stage process.

- Firstly the marks are fixed using a solution of 5-sulphosalicylic acid in water; this precipitates the basic proteins and thus prevents diffusion of the marks and any associated loss of detail. This fixing stage gives the protein dyes another advantage over the presumptive tests for fingerprint development because as well as being more sensitive, it is often found that the fingerprint ridges are more sharply defined and the detail is clearer.

- The marks are then treated with an acidic protein stain that dyes the precipitated basic proteins in the manner described above to give a coloured product.

- A washing stage is required post-staining. On non-porous surfaces this just removes excess dye, however on porous surfaces this also acts as a de-stainer, removing dye that has been absorbed by the background surface. The wash solution has to be carefully constructed so that it dissolves the dye, does not either diffuse or wash away the dyed fingerprint and retains the intensity of colour of the dye in the fingerprint. For this reason the same solvent mix as that used for the dyeing process, or some small variation of it, is generally most effective in this application [11].

2.9 Fluorescence examination can also assist in the subsequent visualisation of marks developed using the acid dyes. The use of acid black 1 or acid violet 17 can further intensify the contrast between the fingerprint and the background by increasing the light absorption properties of the blood, and this may aid visualisation of developed marks during fluorescence examination.

2.10 Acid yellow 7 stains blood with a fluorescent species that can be excited by blue (420–485nm) light. The resultant fluorescence from the stained mark can be less pronounced on heavy deposits of blood as the haem group retains its ability to absorb both the excitation light and that emitted as fluorescence.

2.11 It has also been observed that acid violet 17 has weak fluorescence in the deep red and near infra-red (IR) regions of the spectrum when excited with green/yellow and yellow wavelengths, and this fluorescence could also be utilised to view developed marks.

3. CAST processes

3.1 CAST recommends the use of a number of fingerprint development and blood enhancement processes for use on fingerprints in blood, the ultimate process selection being dependent on the characteristics of the surface the blood is present on [18]. Three acid dyes (acid black 1 [naphthlene black, naphthol blue black, CI 20470], acid violet 17 [Coomassie brilliant violet R150, CI 42650] and acid yellow 7 [brilliant sulphoflavine, CI 56205]) are recommended only for use on blood. DFO and ninhydrin will also develop marks in blood, but are also the most sensitive techniques for the development of latent fingerprints on porous surfaces [19,22,23].

3.2 A holistic approach has been adopted for the acid dyes: the formulations for fixing, staining and de-staining have been very carefully constructed so that the blood is fixed effectively, then it is kept from diffusing during the staining and de-staining stages, and finally the strong coloration from the dye is retained during de-staining [19].

3.3 The most effective formulation for the three recommended acid dyes is as follows [23]:

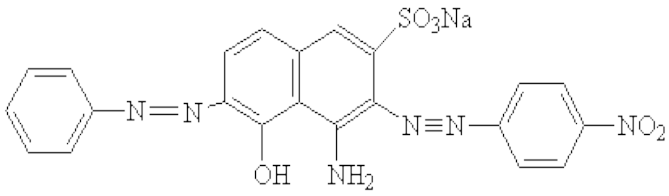
fixing solution – 23g 5-sulphosalicylic acid dihydrate dissolved in 1 litre water;

staining solution – 1g acid dye (acid black 1, acid violet 17 or acid yellow 7) dissolved in 700mL distilled water, 250mL ethanol and 50mL acetic acid;

washing solution – 700mL water, 250 mL ethanol and 50 mL acetic acid.

3.4 If acid dye formulations are applied directly to fingerprints in blood without a fixing stage, the blood will dissolve and the ridges will either diffuse or be completely washed away. A number of different fixing agents have been investigated, but the most effective are 5-sulphosalicylic acid and methanol. Which fixing agent is used will depend upon the major solvent used in the dyeing process; in the current (post-2004) formulations where water is the main solvent, a solution of 5-sulphosalicylic acid is most effective. However, in the previously recommended formulations where the main dyeing solvent was methanol, methanol was found to be the best fixing agent [19]. These fixing agents act in different ways; 5-sulphosalicylic acid precipitates basic proteins and methanol dehydrates the blood. All-in-one formulations that stain and fix are generally not stable for more than a day or two and are not as effective as a two-stage process, both in fixing and dyeing.

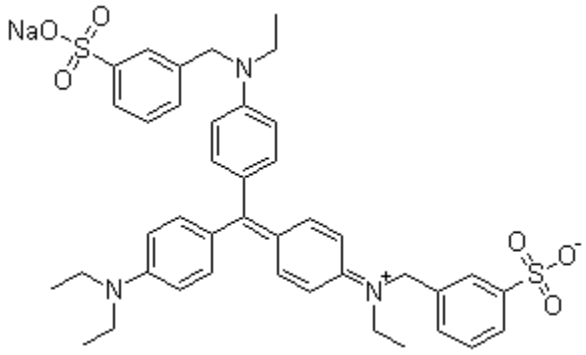
3.5 Acid black 1 (also commonly known as amido black) is a protein stain that dyes the proteins present in blood to give a blue/black colour. It can be absorbed by some porous surfaces so an area away from the mark to be enhanced needs to be tested first to ensure that there is no background staining.



Structure of acid black 1.

Fingerprints in blood on paper enhanced using acid black 1.

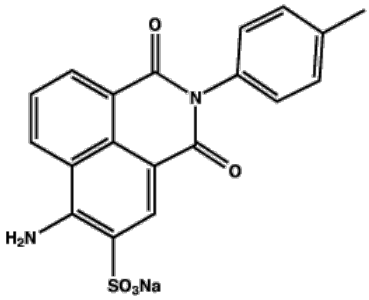
3.6 Acid violet 17 is a protein dye that stains the proteins present in blood to give a bright violet product. It can also be absorbed by some porous surfaces, therefore an area of the substrate away from the target enhancement area should be tested to assess background staining.



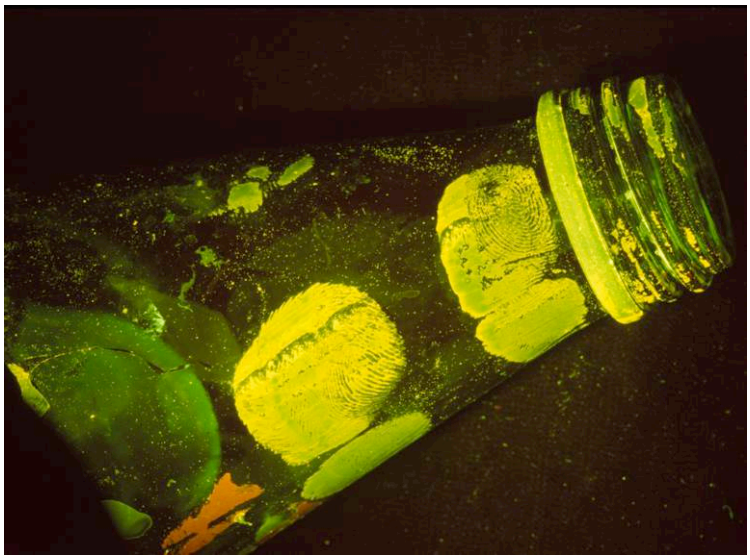
Structure of acid violet 17.

Fingerprints in blood on a wooden handle enhanced using acid violet 17.

3.7 Acid yellow 7 stains the proteins present in blood to give a pale yellow product that fluoresces bright yellow when viewed under blue/green 385–509nm illumination. The haem group acts as an energy sink that improves the enhancement of lighter marks. Acid yellow 7 is recommended in the *Manual of Fingerprint Development Techniques* [18] for use on dark non-porous surfaces only because it can not easily be removed from the background of porous surfaces.



Structure of acid yellow 7.



Fingerprints in blood on a dark glass bottle enhanced using acid yellow 7.

3.8 It was found that concentrations of these dyes of less than 0.1w/v resulted in less effective staining [19] and therefore the dye concentration used in the

formulation above is selected to minimise dye content yet retain staining effectiveness.

3.9 The presence of a short chain alcohol in the dyeing solution helps to prevent the blood from diffusing during the dyeing stage [19]. Ethanol is preferred as this offers lower toxicity and flammability than methanol. The use of water as the major solvent gives the solution a flash point of around 30°C enabling this formulation, containing water, ethanol and acetic acid, to be used at scenes of crime with a few simple precautions [18].

4. Critical issues

4.1 The entire scope of blood evidence (blood pattern analysis, footwear enhancement, DNA recovery) should be taken into account before deciding on a treatment for fingerprint evidence alone. In some cases the correct sequence of application will be essential in order to maximise evidential opportunities and the use of protein stains may affect other forms of evidence.

4.2 The protein stains should not be used as the sole means of determining whether a mark is in blood, because they give positive reactions with a number of other protein-containing substances (e.g. egg white). Other presumptive tests should be used to confirm the presence of blood (preferably using an area that does not contain ridge detail) before proceeding to enhancement with protein stains.

4.3 The fixing stage is essential for the process to be effective. If a fixative is not used, the blood marks will diffuse as the dye solution is applied to them, possibly destroying the ridge detail.

4.4 The current (post-2004) solutions are flammable, with a flash point of 30°C. The solutions should not be used in situations where the flash point is likely to be exceeded or where sources of ignition are present.

5. Application

5.1 Suitable surfaces: The three protein dyes recommended are suitable for use on all non-porous surfaces where blood contamination is suspected to be present. Acid black 1 and acid violet 17 are also suitable for use on porous surfaces contaminated with blood, whereas acid yellow 7 is not recommended for porous surfaces because it is more difficult to wash the dye out of the background, making fingerprints more difficult to see.

5.2 Currently (2011) it is considered that combinations of fluorescence examination, two amino acid reagents and three acid dyes are the most effective means of enhancing fingerprints in blood [23]. The most appropriate and effective techniques to use, either individually or in a sequence, depend on the porosity of the surface to be treated. This applies to both latent fingerprint development and enhancement of blood-contaminated fingerprints.

5.3 Fluorescence examination of the surface should always be carried out before any other technique to see if any marks are revealed as dark absorbing ridges against a fluorescing background. High-intensity light sources with outputs between 350–450nm are most effective.

5.4 When the blood-contaminated or latent fingerprints are on porous surfaces the most effective sequence of techniques is DFO, ninhydrin, either acid black 1 or acid violet 17, after carrying out a spot test to see which is most suitable, and then finally physical developer [23].

5.5 When the blood-contaminated or latent fingerprints are on non-porous surfaces the most effective sequence of techniques is vacuum metal deposition (VMD), powders, acid yellow 7, acid violet 17 then finally either powder suspensions or solvent black 3 (Sudan Black). Superglue may be used instead of VMD or powders but this will inhibit the dyeing process for blood by sealing the surface and preventing the dye reaching the blood [23].

5.6 The three recommended acid dyes, acid black 1, acid violet 17 and acid yellow 7, should all be applied to blood that has been fixed for at least five minutes with a solution of 5-sulphosalicylic acid. Dyeing of fixed blood is most effective if immersed in the dyeing solution for at least three minutes for acid black 1 and acid violet 17 whereas acid yellow 7 requires at least 5 minutes. Areas heavily contaminated with blood need longer dyeing times. If it is not possible to immerse the bloodied fingerprints then the dyeing solution should be applied above the area of interest and allowed to flow down over it, keeping the area damp for the specified time. A well may be constructed around the area of interest on horizontal surfaces, which may be flooded and drained as appropriate, or tissues soaked in dye may be applied to the surface [52]. Ethanol-containing staining or de-staining solutions should never be sprayed because this lowers the flash point by at least 100°C making it impossible to work without creating a flammable atmosphere.

5.7 Areas of interest will then need to be washed or de-stained to remove excess dye. The most effective solution for doing this is the same solvent composition as the dye solution, washing as required to remove dye or de-stain the background.

5.8 High-intensity light sources capable of delivering output wavelengths between 420–485nm must be used to excite fluorescence from blood dyed with acid yellow 7. The fluorescence emitted is between 480–550nm. The use of shorter wavelengths between 350–450nm to excite background fluorescence after acid black 1 or acid violet 17 treatment may be beneficial.

5.9 Work carried out by CAST has demonstrated that positive DNA identification may be made after fluorescence examination and any single chemical treatment provided simple guidelines are followed. If more than one fingerprint development technique is used in sequence then the chances of successfully carrying out DNA identification are much reduced [18].

6. Alternative formulations and processes

6.1 There are a great number of blood reagents, only some of which have been mentioned above, and there can be many different formulations of each of those reagents to consider. Some of these will be described in more detail in Chapter 5.1. The water-based formulation of the acid dyes are probably the most practical alternative formulations because they can be used at all times, although methanol-based solutions might prove beneficial under some specialised circumstances.

	Water-based method	**Methanol-based method**
Fixing solution	20g 5-Sulphosalicylic acid 1,000mL Distilled water	Methanol (99%+)
Staining solution	2g Acid dye 20g Citric acid or 5% v/v acetic acid 1,000mL Distilled water	2g Acid dye 900mL Methanol 100mL Acetic acid
De-staining solution 1	Distilled water (5% v/v acetic acid helps to retain coloration)	900mL Methanol 100mL Acetic acid
De-staining solution 2	Distilled water (5% v/v acetic acid helps to retain coloration)	950mL Distilled water 50mL Acetic acid

Methanol-based and water-based acid dye and de-staining formulations.

6.2 Originally these formulations were developed for use with acid black 1, but both can be used equally well with acid violet 17 and acid yellow 7.

6.3 Advantages of methanol-based and water-based acid dye formulations

6.3.1 The water-based formula does not use flammable or toxic solvents and can therefore be used safely regardless of the temperature at the scene of a crime. It can also be used in a laboratory if extraction is not available. It is an easy process to use and cheap to carry out.

6.3.2 The methanol-based formula is very effective, cheap and an easy method to use for enhancing fingerprints in blood. It gives good ridge definition, little background staining and produces dark blue-black fingerprints.

6.4 Disadvantages of methanol-based and water-based acid dye formulations

6.4.1 The water-based formula does not always produce optimum results as it may give diffuse fingerprint ridges and weaker coloration with less contrast, especially on porous surfaces. More coloration may be retained by the inclusion of 5% v/v acetic acid in the de-staining solutions. Also on porous surfaces, the contrast between the fingerprint and the background can sometimes be poorer than that achieved when using the methanol-based formulation because of relatively high background staining and the lower colour intensity of the developed ridges.

6.4.2 The methanol-based solutions are toxic by ingestion and skin absorption. Methanol is also a highly flammable solvent. Although this formulation can be used safely in a laboratory, its use at scenes of crime is not recommended due to potential ignition or the possibility of absorption of methanol through the skin. Leaching of blood from heavy deposits also occurs with this formulation unless long fixing times (> 10 minutes) are used. The methanol-based formulation may also soften or destroy some surfaces including paints, varnishes and some plastics, damaging or obliterating ridge detail.

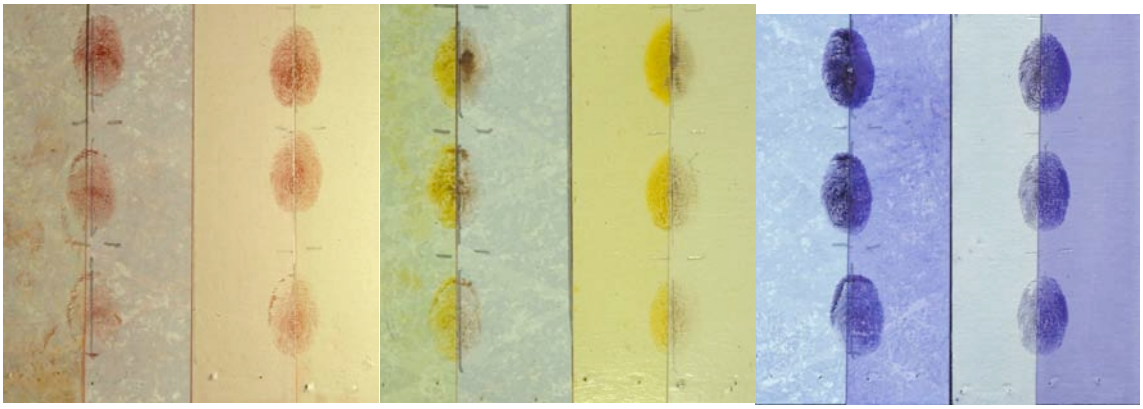
6.5 Rejected dyes and techniques

6.5.1 The CAST blood enhancement project investigated many dyes and reactive techniques that proved less effective, and considered many others that were not ultimately studied because of health and safety concerns. The dyes and techniques that were investigated in practical experiments are listed below in categories.

6.5.2 Protein dyes [22] : Acid blue 74 (indigo carmine), acid blue 83 (Coomassie brilliant blue R250), acid blue 90 (Coomassie brilliant blue G250), acid blue 92 (Coomassie blue R), acid blue 147 (xylene cyanol FF), cid red 1 (amido naphthol red G), acid red 71 (Crocein scarlet 7B), acid red 87 (eosin y), acid red 88 (roccellin), acid red 112 (Ponceau S), acid violet 19 (fuchsin acid, Hungarian Red), acid yellow 23 (tartrazine), benzoxanthene yellow (Hœchst 2495), brilliant sulphaflavine, Crowles double-stain *(acid blue 83 and acid red 71)*, direct yellow 12 (chrysophenine), MBD (7-[p-methoxybenylamino] -4-nitro-2,1,3-benzoxadiazole).

6.5.3 Haem-specific reactive techniques [23]: Azino-di-benzthiazoline sulphonic acid (ABTS); diaminobenzidine (DAB) or tetraamino-biphenyl (TAB); guaiacol; leucocrystal violet (LCV); leucomalachite green (LMG); luminol; organic acid (formic or acetic) and hydrogen peroxide (hæmatoporphyrin); fluorescein.

6.5.4 Amine and protein reactive techniques [23]: ATTO-TAG™ CBQCA; ATTO-TAG™ FQ; fluorescamine; Lucifer Yellow vinyl sulphone (VS) ; SYPRO® Ruby Protein Blot Stain.

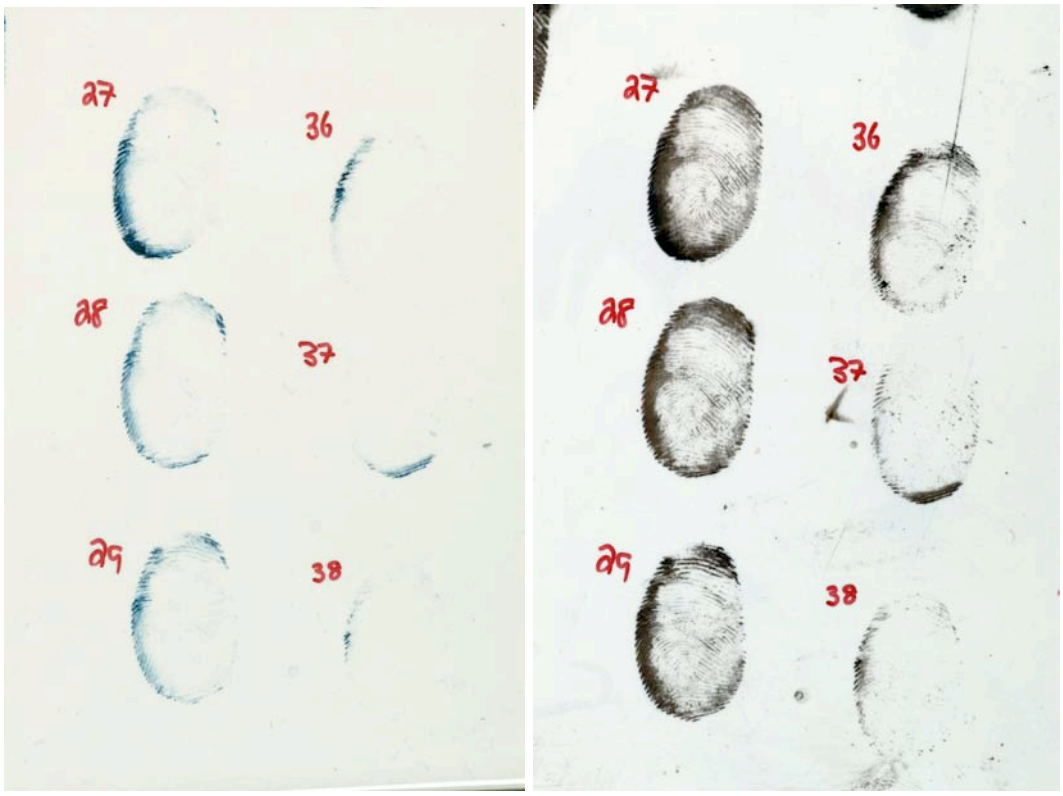


Examples of split depletion experiments carried out on wallpaper and painted wall surfaces using a range of alternative protein stains.

7. Post-treatments

7.1 Fluorescence examination is the most notable post-treatment process and this has been discussed fully above in sections 2.9 and 2.10.

7.2 However, it appears from more recent studies on footwear marks that powder suspensions may have an affinity for blood and can be used as an enhancement technique after the protein dyes [52]. It should be noted that the current (post-2009) application methods will cause potentially disastrous over-development on heavy blood deposits, but on faint fingerprints on non-porous surfaces there may be significant enhancement. Powder suspensions are not specific for blood and cannot be used to determine that any additional ridge detail is in blood.



Finger marks in blood in a depletion series on a ceramic tile showing deposited marks numbers 27,28,29,36,37,38,39, a) enhanced using acid black 1 and b) subsequently treated using iron oxide-based powder suspension.

8. Validation and operational experience

8.1 The validation of blood dyes is carried out both in terms of the number of graded marks, and also in terms of sensitivity to diluted blood. The first test will give an indication of how far down a depletion series the blood reagent will work (i.e. how many multiple contacts from a single finger contaminated with blood at normal concentration can be detected) and the second will indicate how sensitive the technique is to dilute traces of blood (as may be experienced where efforts have been made to clean a crime scene). Because blood is being targeted as a contaminant, the results obtained for fingerprints will be applicable to development of other types of blood evidence, such as footwear marks (and vice versa). There will be some exceptions to this, e.g. luminol is recommended as a footwear development process for carpets, a surface for which there is no recommended fingerprint development process, but would not be recommended as a primary technique for development of fingerprints because the requirement for spray application without fixing may diffuse fingerprint ridges and destroy evidence.

8.2 Laboratory trials

8.2.1 During the late 1990s and early 2000s, HOSDB conducted a series of experiments to optimise the Acid Black 1 formulation and to identify alternative blood enhancement agents with potentially improved performance [19,22,23]. Experiments to assess the effectiveness of protein dyes were carried out by

using series of 6 split depleted blood-contaminated fingerprints on 9 or 15 surface types, depending on whether or not the technique was appropriate for both porous and non-porous surfaces. However, it became obvious that this experiment was not sufficient to resolve the differences in sensitivity of some fluorescent dyes on non-porous surfaces, so the number of depletions was increased to 18.

8.2.2 Additionally, in the literature it is common to compare the sensitivity of blood enhancement techniques by diluting blood with distilled water. Accordingly it was decided to assess techniques in this manner so a series of 12 dilutions from 1/100 to 1/100,000 were used along with a distilled water control. These tests were carried out on photocopy paper and glass using 5μL of solution for each spot.

8.2.3 Of the 17 protein stains investigated, 2 absorbing (acid violet 17 and acid violet 19) and 2 fluorescent (brilliant sulphaflavine and benzoxanthene yellow) dyes were identified for further study. Ultimately the original fluorescent dyes became unavailable and Acid Yellow 7 (brilliant sulphoflavine) was identified as a suitable substitute. Further comparisons showed that acid violet 19 was less effective than both acid black 1 and acid violet 17. The lighter coloration of marks stained with Acid Violet 19 produced ridge detail with less contrast with the background than the other two dyes.

8.2.4 On porous surfaces acid violet 17 proved to be more effective than both the water- and methanol-based formulations of acid black 1, and was very similar in performance to the newly developed water/ethanol/acetic acid (WEAA) formulation of acid black 1.

8.2.5 Experiments on a further 24 porous surfaces failed to show conclusively whether one of these dyes was more effective than the other. However, there were some surfaces where one dye performed better than the other. It proved impossible to define before treatment whether the acid violet 17 or the acid black 1 would give greatest contrast.

8.2.6 Some of the results of comparing and grading fingerprints developed using acid black 1, acid violet 17 and acid yellow 7 across eight different non-porous surfaces are shown below.

Grade	24 Hours after deposition		2 Weeks after deposition	
	Acid black 1	Acid violet 17	Acid black 1	Acid violet 17
0	0	0	0	0
1	0	0	0	0
2	42	46	46	49
3	35	26	31	20
4	167	160	166	174

Grade	24 Hours after deposition		2 Weeks after deposition	
	Acid black 1	Acid yellow 7	Acid black 1	Acid yellow 7
0	0	0	0	0
1	0	0	0	0
2	50	46	51	70
3	39	40	33	38
4	185	188	191	167

Examples of comparative grading exercises carried out between acid black 1, acid violet 17 and acid yellow 7 on non-porous surfaces including glass, ceramic tile, polymers and metals

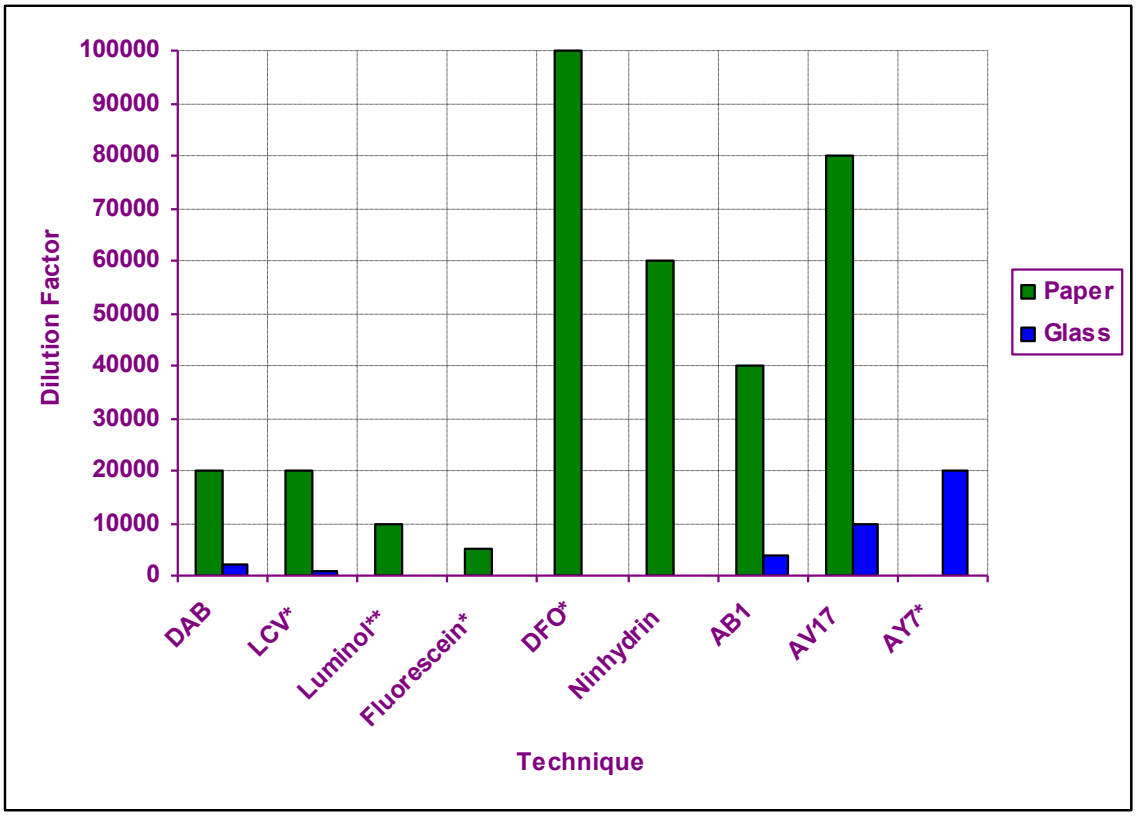
8.2.7 It can be seen that the performance of each of the recommended acid dyes is closely equivalent and the three dyes can be used interchangeably according to which dye will give the best contrast on the particular surface.

8.2.8 The comparative performance of the recommended protein dyes with other types of blood enhancement techniques and with alternative formulations of the same dyes on split depleted fingerprints are shown in the table below.

Technique	Type (H = haem, A = amine, P = protein)	Subjective performance assessment ***** = excellent, * = poor		
		Porous	Semi-porous	Non-porous
DAB	H	**	**	*
LCV	H	**	**	-
Acid Violet 19 + organic acid/peroxide	H	**	**	*
Fluorescein	A	*	*	-
DFO	A	*****	**	-
Ninhydrin	A	****	**	-
SYPRO ruby protein blot stain	A	***	**	**
Acid Black 1 (methanol)	P	***	***	****
Acid Black 1 (water)	P	***	***	**
Acid Black 1 (water/ethanol/acetic acid)	P	****	***	***
Acid Violet 17 (water/ethanol/acetic acid)	P	****	***	***
Acid Yellow 7 (water/ethanol/acetic acid)	P	-	-	*****

Summary table showing subjective overview of the comparative effectiveness of several regularly used blood enhancement agents.

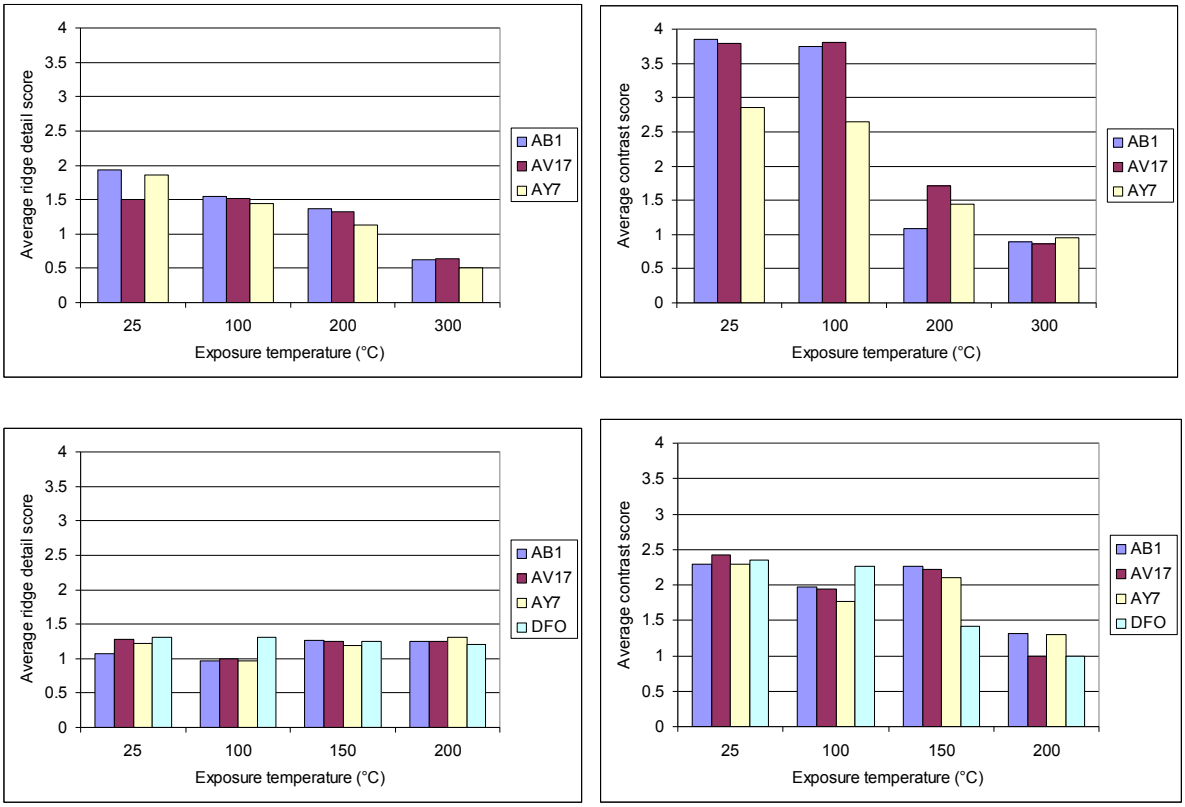
8.2.9 The graph below illustrates the sensitivity of each dye at developing the diluted blood spots on photocopy paper and glass. The sensitivity achieved with diluted blood is not always consistent with the results of experiments with depleted fingerprints, so it is believed that comparative dye performance cannot be measured using dilution series alone. The results below do not take into account the contrast between the stained spots and the background. If spots could be seen then they were counted, even if the contrast between them and the background was very poor.



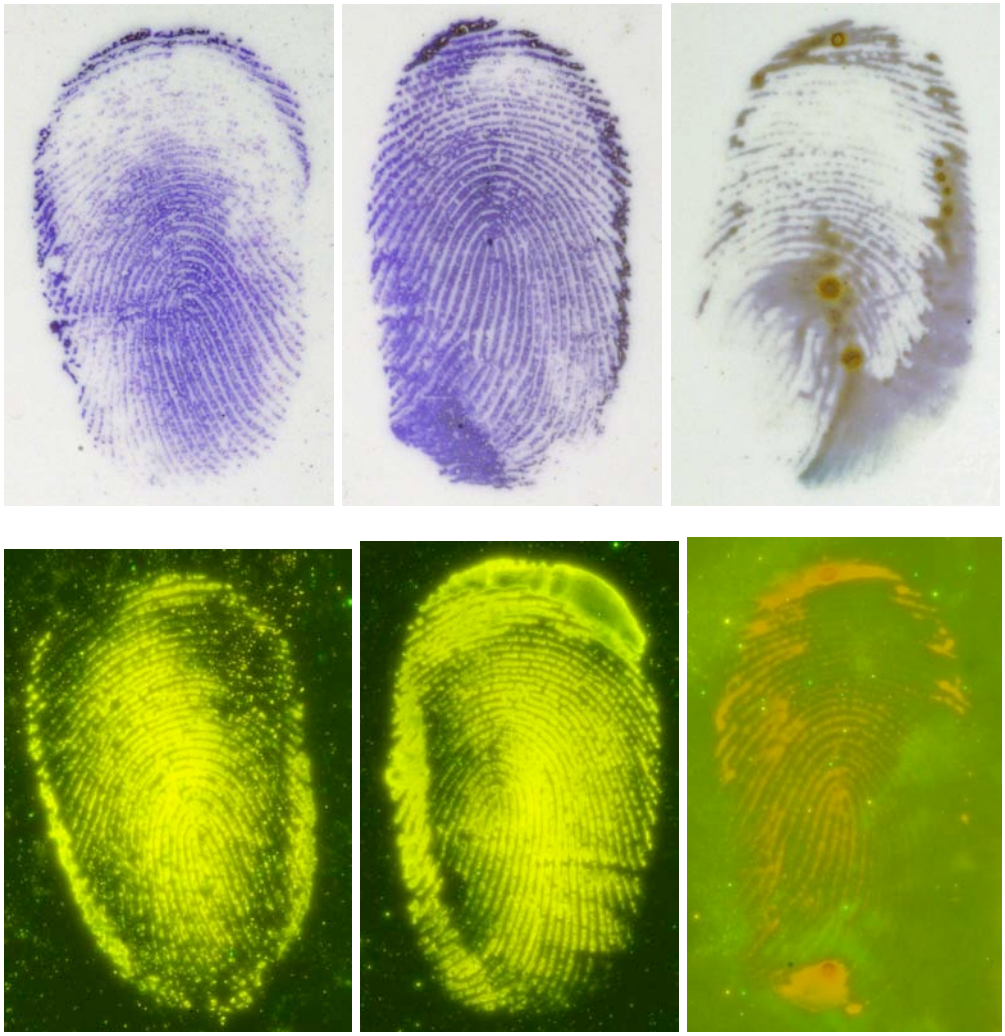
Graph to show the relative performance of various blood enhancement agents in the spot dilution sensitivity test. = visualised by fluorescence, ** = visualised by chemiluminescence.*

8.2.10 It should be noted that the graph above shows the sensitivity of luminol to be relatively poor. This may be because the viewing conditions used were not optimised. Subsequent research to investigate enhancement of footwear marks in blood has shown that dark adaption and optimised viewing conditions are essential and that the sensitivity of luminol may be far greater than is represented here.

8.2.11 Other laboratory trials that have been carried out using the acid dyes include an assessment of the technique's effectiveness on marks in blood that had been exposed to elevated temperatures [53]. In these studies marks were deposited on a range of surfaces and exposed to temperatures in the range 100–300°C for periods between one and eight hours. Marks were graded in terms of both quality and contrast, because it was observed that the contrast of the developed mark decreased as exposure time and temperature decreased.



Recorded results of fingerprint quality and contrast for marks enhanced using blood dyes on a ceramic tile (top row) and white card (bottom row), after exposure to different temperatures.



a) *b)* *c)*

Series of images for acid violet 17 (top row) and acid yellow 7 (bottom row) showing how quality of developed mark and contrast degrade with increased exposure temperature and exposure time, a) control, b) 8 hours at 100°C and c) 8 hours at 200°C

8.2.12 The results of this study demonstrated that the acid dyes were capable of developing marks exposed to 200°C for eight hours, albeit with reduced effectiveness. Once again, there was little significant difference between the performance of the three recommended dyes. A further important observation from the study was that the haem specific reagent leucocrystal violet had stopped enhancing marks after exposure to temperatures of 150°C, further supporting the recommendation of the acid dyes for operational use in scenarios such as arson scenes.

8.3 Pseudo-operational trials and operational experience

8.3.1 Pseudo-operational trials have not been conducted on the acid dye formulations because this is not practical with articles contaminated with blood. Because the contaminant is known, unlike 'real' fingerprints that are variable in composition, the performance in operational use will be the same as that in laboratory tests. Since the introduction of the new formulation of acid black 1 and the new dyes acid violet 17 and acid yellow 7 in 2005, feedback from operational work has been favourable. Feedback has been especially good for acid yellow 7, which has resulted in, for the first time, the capability of enhancing blood-contaminated fingerprints on dark non-fluorescing surfaces. The new dye has been successfully used to develop marks on exhibits including a black Maglite torch and a dark wood banister, surfaces for which no previous treatment would have been effective. The dyes have also been used for the successful enhancement of footwear marks on large areas of non-porous flooring.

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3.2 Basic violet 3 (Gentian Violet)

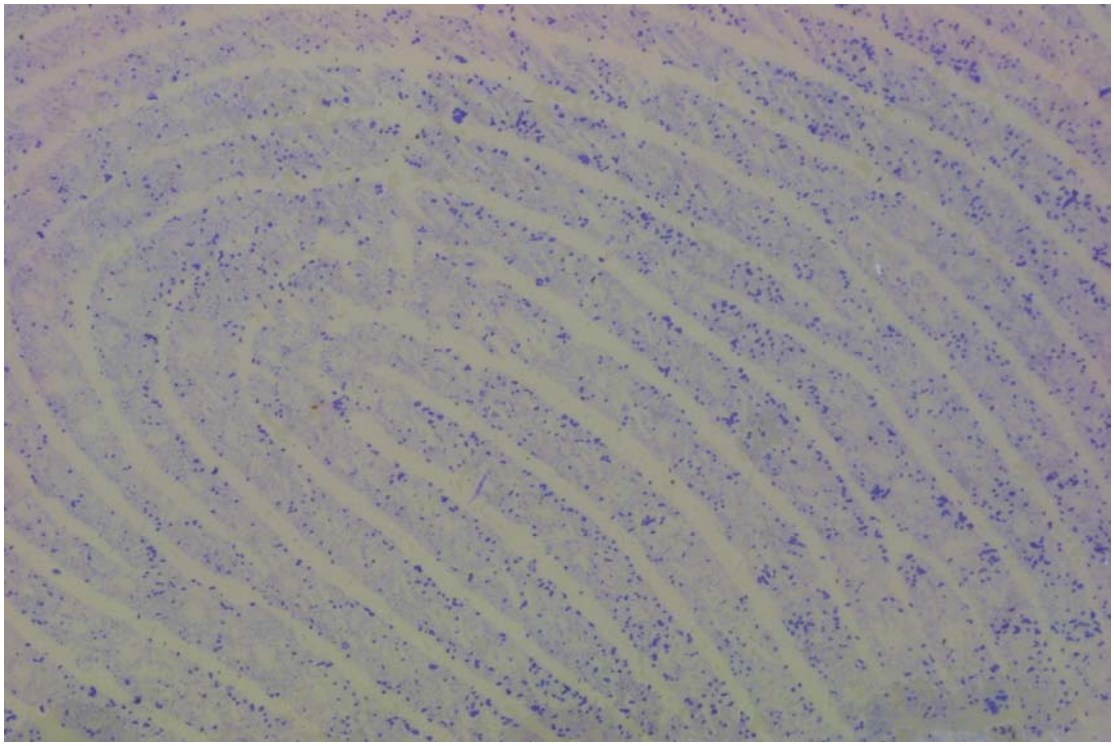
1. History

1.1 The history of basic violet 3 begins with the discovery of the first synthetic dye, 'Mauve', by W. H. Perkin in 1856. In the following years a series of aniline dyes were synthesised for the dyeing of textiles, including methyl violet (basic violet 1) by Lauth in 1861 [1]. A range of closely related compounds were subsequently synthesised including basic violet 3 (also known by several alternative names including gentian violet and crystal violet).

1.2 The applications of these dyes were not confined to the textile industry and microbiologists began to explore the potential of synthetic dyes for the staining of biological sections. The German biologist Paul Ehrlich used aniline water and gentian violet to stain bacteria cells, the gentian violet targeting the lipids in the cell walls to give a purple stain. In 1884 the Danish physician Hans Christian Joachim Gram further developed this staining process for selectively staining bacteria and providing information about the structure of the cell walls. The test is still known as Gram staining to this date. Basic violet 3 has since been used for a variety of medical applications, including treatments for ringworm and scabies, where the ability of the dye to inhibit bacterial action is beneficial.

1.3 Aniline dyes (of which basic violet 3 is one) have been proposed as fingerprint reagents since the early part of the 20th century. In 1917 Bock [2] patented a process for recording latent fingerprints by brushing the fingerprint with a powder of aniline dye and then fixing the mark by heating. In 1920 Mitchell was reporting the use of aniline dyestuffs in powder form as a means of detecting fingerprints [3], with the observation that basic dyestuffs were preferable.

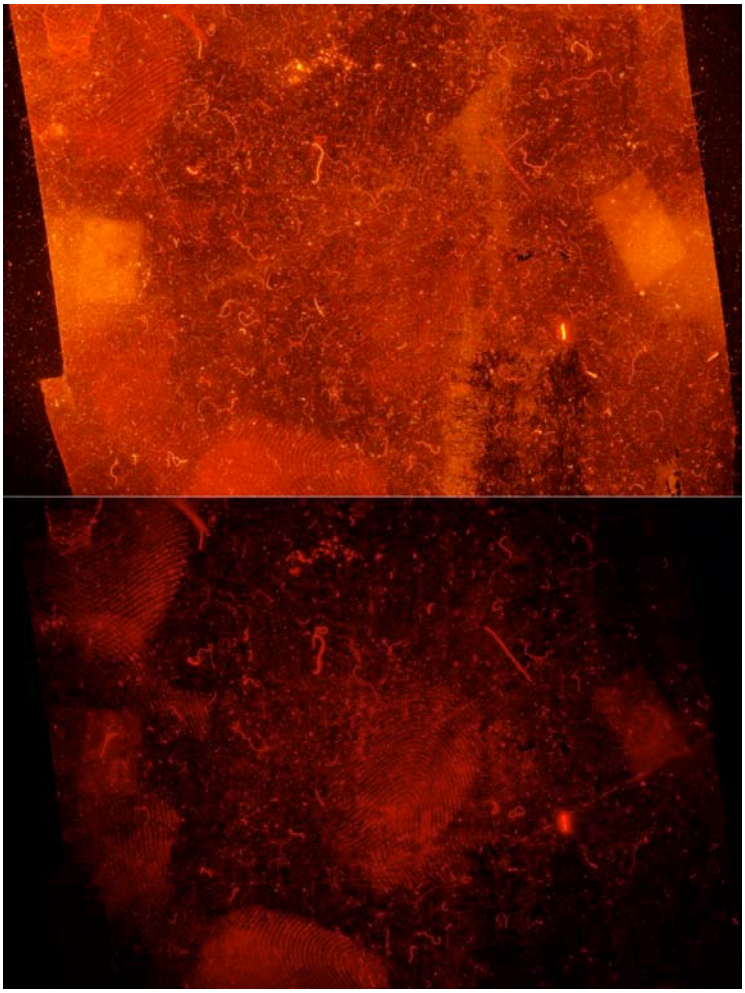
1.4 As research work into the constituents of fingerprints progressed in the 1960s, reagents were proposed that targeted particular components of fingerprint residues. Basic violet 3 was proposed as a technique for the selective staining of epithelial cells and fatty components of fingerprint residues. Epithelial cells are most likely to be present on the adhesive side of tapes, where a layer of dead cells may be pulled off the fingerprint ridges when the tape is touched. The use of basic violet 3 in this application was reported by the Italian Police in the late 1960s and it their recommended phenolic formulation was adopted by PSDB and some forces in the UK during the late 1970s [4,5].



Photograph of adhesive side of tape sample treated with basic violet 3, showing violet staining of lipids in ridges and of epithelial cells in particular.

1.5 Basic violet 3 continued to be used worldwide for development of latent fingerprints on adhesive surfaces [6] but although good results were obtained for a wide range of tapes the detection of marks on black tapes remained problematic, the only technique available for visualisation being photography under oblique lighting. This was overcome by the development of the transfer process by the Police Scientific Development Branch (PSDB) [7,8] and others [9]. This process involved the sandwiching of the tape between sheets of photographic paper, resulting in the transfer of the purple stain from the developed fingerprint to the surface of the white paper.

1.6 It has been found that marks developed using basic violet 3 on adhesive tapes are also fluorescent, and can be visualised using green/yellow light to excite the fluorescence and a deep red viewing filter [10]. It was found that the fluorescence had a peak at 720nm in the deep red region of the spectrum and extended to a small degree into the near infra-red region [11]. More recently, yellow (577nm) lasers have become commercially available and studies have shown that this gives excellent results when used to image fluorescent marks developed using basic violet 3 [12].

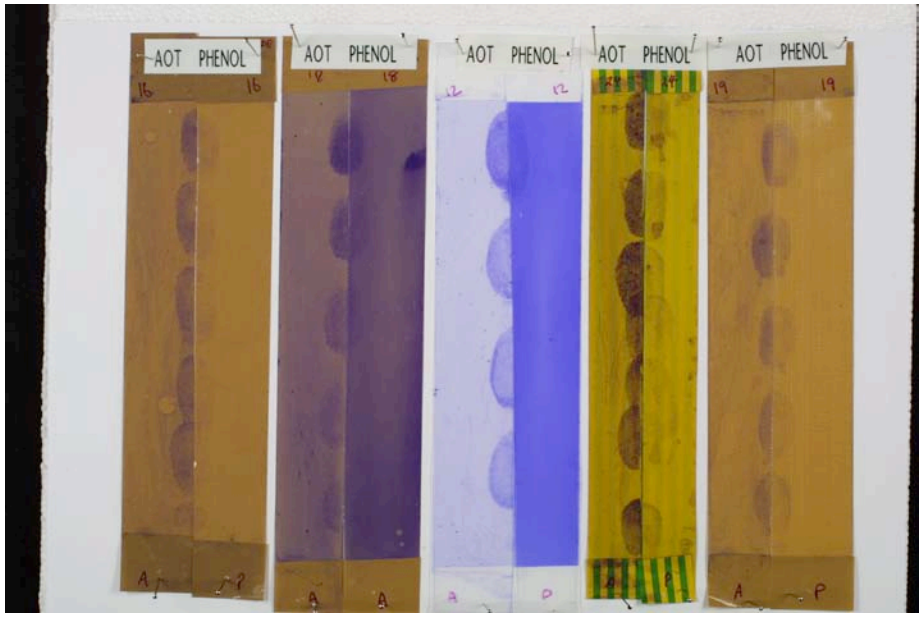


Photograph of basic violet 3 fluorescence in fingerprints developed on adhesive tape, imaged using a 5W 532nm green laser (top) and a 5W 577nm yellow laser (bottom)

1.7 Basic violet 3 can also be used for detection of fingerprints on a wide range of non-porous surfaces and can be especially useful where contamination may be present on the surface.

1.8 The work carried out by CAST on basic violet 3 includes the development of the transfer process for black tapes in the late 1970s. More recently, concerns about the toxicity of phenol have prompted in-depth studies into the development of an effective phenol-free formulation for basic violet 3 [13] and a comparative study between basic violet 3 and a possible alternative dye, basic violet 2 [14]. These studies have culminated in the recent issue of a revised formulation of basic violet 3 based on Aerosol OT™ (AOT), also known by its chemical name of dioctyl-sulfosuccinate, sodium salt [15], which in laboratory trials has consistently out-performed the phenol formulation in terms of number, quality and contrast of marks developed, and has exhibited a reduced amount of background staining. However, recent reclassification of chemicals has resulted in basic violet 3 itself being classed as a suspect

carcinogen and both phenol and AOT-based formulations must be used under controlled conditions.

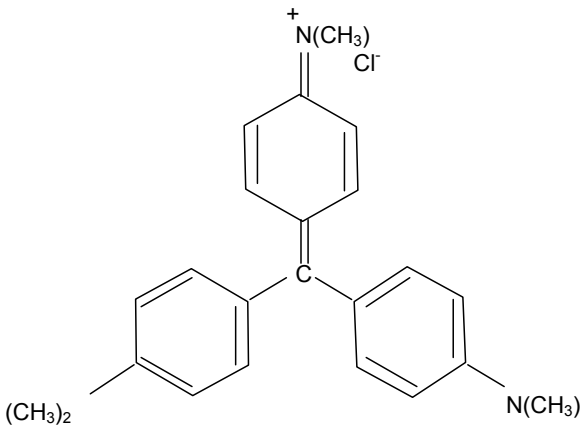


Photograph of different adhesive tapes, showing difference in fingerprint development between phenol and Aerosol OT-based basic violet 3 formulations.

2. Theory

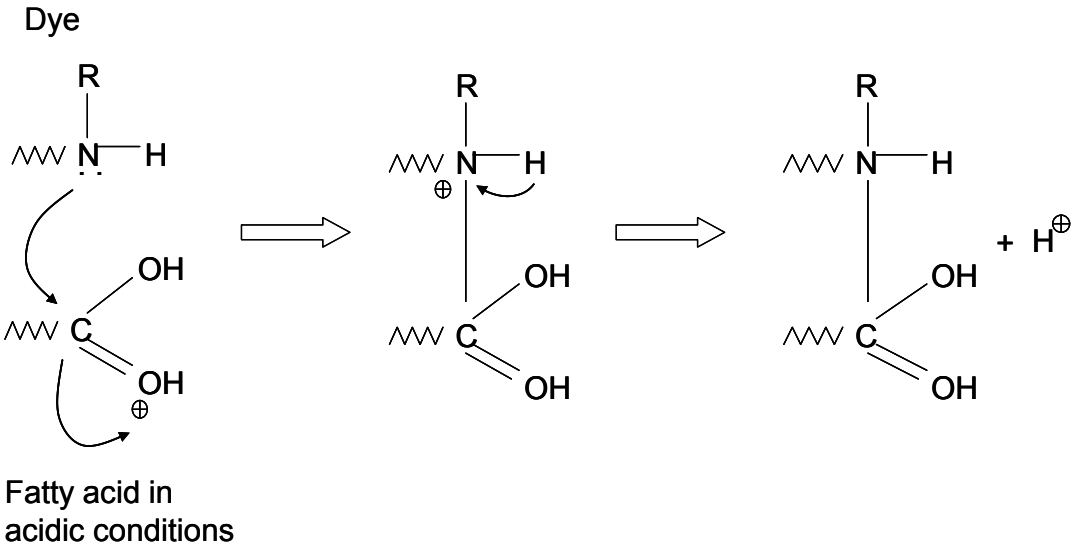
2.1 The exact mechanism by which basic violet 3 selectively dyes fingerprint deposits is not known, nor has it been determined which individual fingerprint constituents are targeted by the dye. However, there are two mechanisms that have been proposed for the interaction of the basic violet 3 dye molecule with the lipids in the fingerprint.

2.2 The basic violet 3 molecule is shown below:



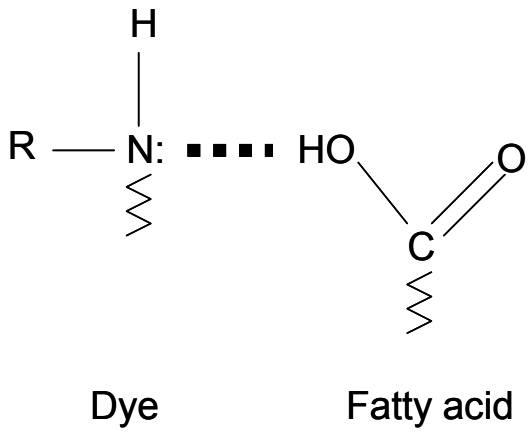
The basic violet 3 molecule.

2.3 Gurr [16] proposes that the basic groups such as amines (NH_2, or in this case NH-R) of neutral dyes such as basic violet 3 could form a chemical union with the acidic group of the lipids being stained. It is thought that the staining action occurs via a reaction between the amine group of the dye and the acidic group of a lipid component (such as a fatty acid). The possible reaction is shown below.



Possible reaction mechanism for staining action of basic violet 3.

2.4 Another proposal is that the dye could link to fatty acids by the formation of a hydrogen bond between the nitrogen in basic violet 3 and the hydroxyl group in the fatty acids, as shown below.

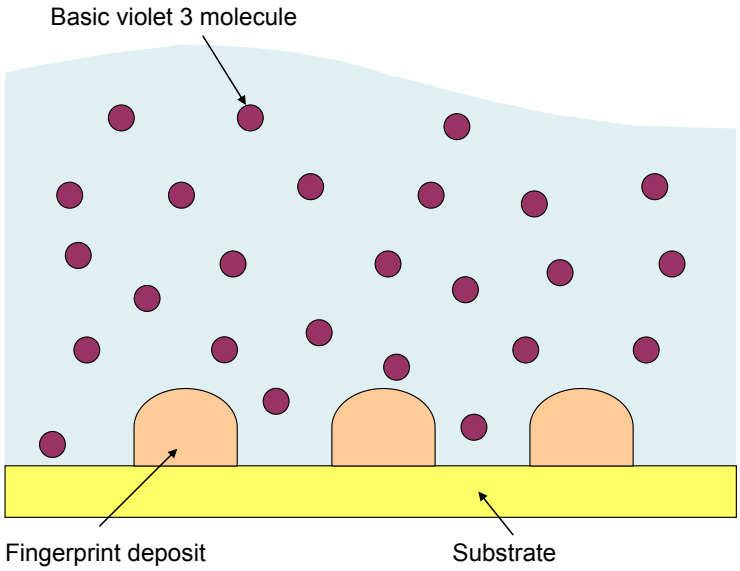


Alternative reaction mechanism for staining action of basic violet 3.

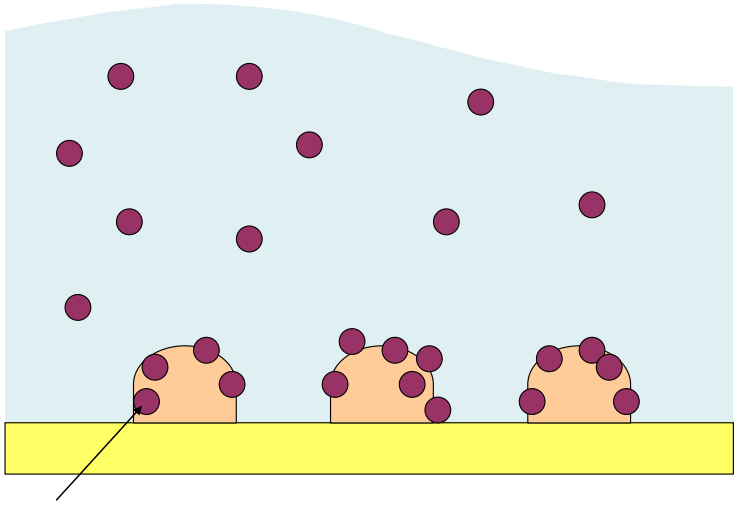
2.5 Both the mechanisms are applicable to the phenolic water solution used in the basic violet 3 formulation currently (as at 2011) recommended in the *Manual of Fingerprint Development Techniques* [17].

2.6 It is also known that the basic violet 3 molecule is fluorescent, but when basic violet 3 is used as a development reagent on non-porous surfaces fluorescence is not observed in most cases. However, on adhesive tapes fluorescence is observed, and weak marks that are not visible under conventional lighting may be revealed by these means. The fluorescence observed on adhesive surfaces is attributed to the fact that for fluorescence to occur the structure of the compound must be rigid [18]. It is thought that the adhesive promotes fluorescence by binding with the dye molecule and making it more rigid. This theory has been investigated by spraying non-fluorescent marks developed using basic violet 3 with spray adhesive. In these studies a significant increase in fluorescence was observed [13]. It is thought that additional marks are revealed by fluorescence examination because the more strongly developed, visible marks 'self quench', i.e. the dye absorbs the fluorescence from the fingerprint, whereas for the weakly coloured marks that are not visible by eye the fluorescence is not re-absorbed and the marks are detected.

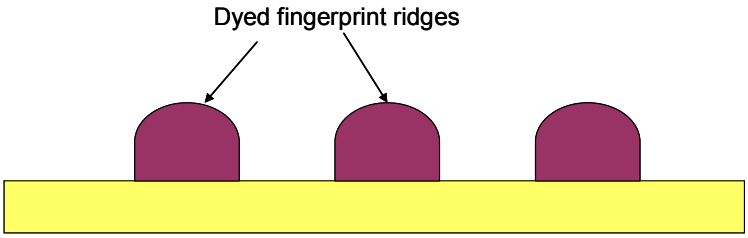
2.7 The fingerprint development process using basic violet 3 is shown schematically in the series of figures below.



a)



b) Basic violet 3 molecules reacting with or bonding to lipids in deposit



c)

Schematic illustration of the basic violet 3 development process a) basic violet 3 molecules in solution b) basic violet 3 molecules preferentially binding to skin cells and lipids in fingerprint ridges and c) dried mark leaving dyed fingerprint ridges.

3. CAST processes

3.1 There are two formulations recommended for use by CAST, one based on phenol and the other based on AOT.

3.2 The phenol formulation is produced by first mixing a stock solution comprising 5g basic violet 3 and 10g of phenol dissolved into 50mL of 96% ethanol.

3.3 A working solution is produced by measuring 1mL of stock solution and progressively adding distilled water until the gold film formed on the surface of the solution disappears.

3.4 The role of basic violet 3 in the formulation is to selectively stain the fingerprint deposits. The quantity used is sufficient to produce a supersaturated solution of basic violet 3, thus promoting the transfer of the dye into the lipids in the fingerprint.

3.5 The role of phenol in the formulation is not fully understood. The presence of phenol has been found to promote the staining ability of basic violet 3 and appears to make it more specific to fingerprint constituents. Several theories have been proposed [13], including:

- the pH change due to the addition of the mildly acidic phenol aids staining;
- phenol aids the wetting of the lipids;
- phenol increases the solubility of the dye, forming a supersaturated solution;
- phenol replaces the dye anion forming a phenolate, which acts as a dye carrier and aids penetration of the fats;
- phenol disaggregates dye molecules, increasing their diffusion rates.

3.6 Experiments have been carried out to investigate some of these theories and while these did not provide conclusive evidence it is thought more

likely that phenol acts by affecting the solution properties, either making it supersaturated or by changing its surface tension and increasing staining.

3.7 The ethanol component of the formulation provides a common solvent for both phenol and basic violet 3.

3.8 The AOT formulation of basic violet 3 is produced by first producing a stock solution by dissolving 5g of basic violet 3 in 50mL of absolute ethanol. A separate 1% w/v AOT solution is then produced by dissolving AOT in distilled water, stirring for at least 12 hours to allow the AOT to dissolve. The working solution is produced by placing 1mL of concentrated stock solution into a clean, dry beaker, then adding 25mL of AOT solution.

3.9 Similarly to phenol, the role of AOT in the formulation is not fully understood. AOT is an unusual detergent, being preferentially soluble in non-polar solvents and forming reverse micelles. One theory is that basic violet 3 molecules could become contained within the reverse micelles, which are in turn preferentially soluble in the fingerprint lipids compared with the polar water/ethanol solution [13].

4. Critical issues

4.1 Basic violet 3 is classified as being carcinogenic and phenol (a major constituent in one of the formulations) is mutagenic. Although the solution can be used safely in a laboratory environment if the procedures outlined in the *Manual of Fingerprint Development Techniques* [17] are followed, it should not be used in the uncontrolled environment of a crime scene.

4.2 If a gold film forms on the surface of the basic violet 3 working solution it should be discarded because this may give a high background staining on the surface being treated.

4.3 In general strongly stained fingerprints either do not fluoresce or fluoresce weakly, this is believed to be due to quenching effects. Fluorescence is therefore most valuable for detection of weakly stained fingerprints. However, this means that on dark tapes strongly dyed fingerprints may be missed unless a transfer technique is used.

5. Application

5.1 Suitable surfaces: Basic violet 3 is suitable for use on the adhesive side of adhesive tapes and on surfaces contaminated with fats. It is also suitable for use on all non-porous surfaces as the final process in a sequential treatment. Its use should be restricted to small articles because of issues with carcinogenicity of the solution.

5.2 The principal application for basic violet 3 is in the development of fingerprints on the adhesive side of adhesive tapes, where it can be used as a single treatment or in sequence to develop additional marks after powder suspensions or superglue [19].

5.3 The AOT-based basic violet 3 formulation can be used on tapes of any colour and also on tapes with both acrylic and rubber-based adhesive. However, if used as a single treatment, laboratory trials indicate that it is less effective than powder suspensions and superglue and it is more appropriate for use as part of a sequential processing regime.

5.4 Basic violet 3 is also recommended as a treatment for contaminated surfaces, where its specificity as a lipid dye may be capable of selectively dyeing the fingerprint ridges without background staining of the contaminant. This is only recommended for small articles because of the toxicity issues associated with the phenol-based formulation. Solvent black 3 can be considered as an alternative treatment for contaminated surfaces and although laboratory trials indicate that solvent black 3 may be more effective than basic violet 3 on latent prints, the most effective treatment on contaminated surfaces has not been conclusively identified.

5.5 Basic violet 3, used in the form of the Forensic Science Service (FSS) crystal violet formulation, see below, has also been proposed as a treatment for soot-covered articles retrieved from arson scenes, where the phenol in the formulation was believed to assist in lifting surface soot and developing the fingerprint. More recent experiments indicate that other chemical treatments and soot removal techniques may be more effective in this application [20].

5.6 Most recently, studies on plastic packaging materials show that basic violet 3 will develop additional marks if used as the final stage in a sequential treatment regime, and it is now recommended for these purposes on plastic packaging and non-porous surfaces.

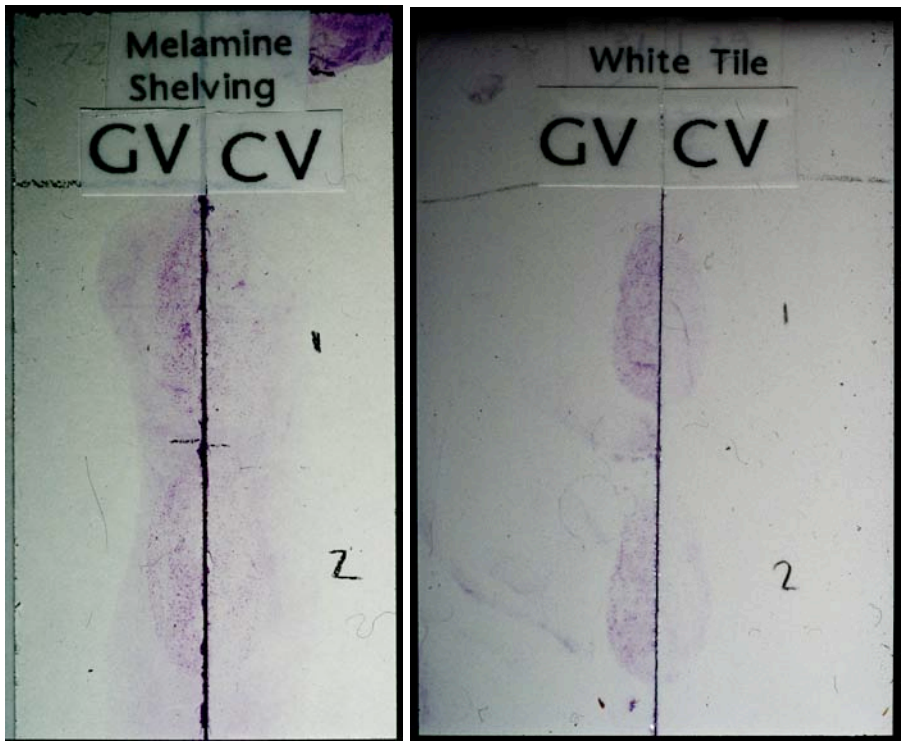
6. Alternative formulations and processes

6.1 An alternative composition based on basic violet 3 is used in the UK by the FSS [21]. This formulation (known as the FSS crystal violet formulation) consists of the following:

- 50g of basic violet 3 dissolved into 2.5 litres of ethanol (min. 95% assay) to form a stock solution;
- 200ml of stock solution added to 4.8 litres of water to form a working solution.

6.2 This formulation was tested against the phenolic formulation in the *Manual of Fingerprint Development Techniques* [17] on a range of substrates, including clear, black and white polythene sheet, laminate,

ceramic tiles, melamine and white hardboard using split depletion series. In this comparison [22] it was found that the formulation in the manual produced stronger staining and more ridge detail than the FSS crystal violet formulation.



Images showing relative effectiveness of Home Office Centre for Applied Science and Technology basic violet 3 formulation (GV) and Forensic Science Service crystal violet formulation (CV) on non-porous surfaces.

6.3 CAST has also conducted an extensive evaluation of alternatives to phenol in the formulation, including disinfectants and antibacterial agents, substances with similar chemical structures, properties or functional groups, detergents and surfactants, and substances used as phenol replacements in other formulations [13]. These are summarised in the table below.

Disinfectants / antibacterials	**Similar structure, properties, functional groups**	**Detergents / surfactants**	**Other phenol replacements**
Hexachlorophene	Cyclohexanol	Aerosol OT (AOT)	Ammonium hydroxide
Benzalkonium Chloride	Phenylalanine	Aerosol 22	Sodium chloride
Cetrimide	Aspargine	1-pentane sulfonic acid	Ammonium oxalate
Chlorhexidine	Arginine	1-hexane sulfonic acid	Pyridoxamine.2HCl

Chlorhexidine diacetate monohydrate	L-Ascorbic acid	1-heptane sulfonic acid	Pyridoxine.HCl
Chlorhexidine digluconate	Salicylic acid	1-octane sulfonic acid	Pyridoxal.HCl
2,4,6-Trichlorophenol	Sulfosalicylic acid	1-decane sulfonic acid	
	Oxalic acid	Cholic acid	
		Deoxycholic acid	
		Aurocholic acid	
		Dehydrocholic acid	
		Alginic acid	
		Caprylic acid	
		N-Lauryl Sarcosine	
		LOC High Suds	
		Arylan PWS	

Alternatives to phenol investigated for basic violet 3 formulations.

6.4 Of these, only AOT gave performance equivalent to or better than the phenol-based formulation and hence was the only compound considered in further, more focused studies. These subsequent studies [14,23] confirmed the observation that the AOT formulation consistently out-performed the phenol formulation in laboratory trials and this formulation was ultimately recommended for operational use on adhesive tapes after a brief operational trial.

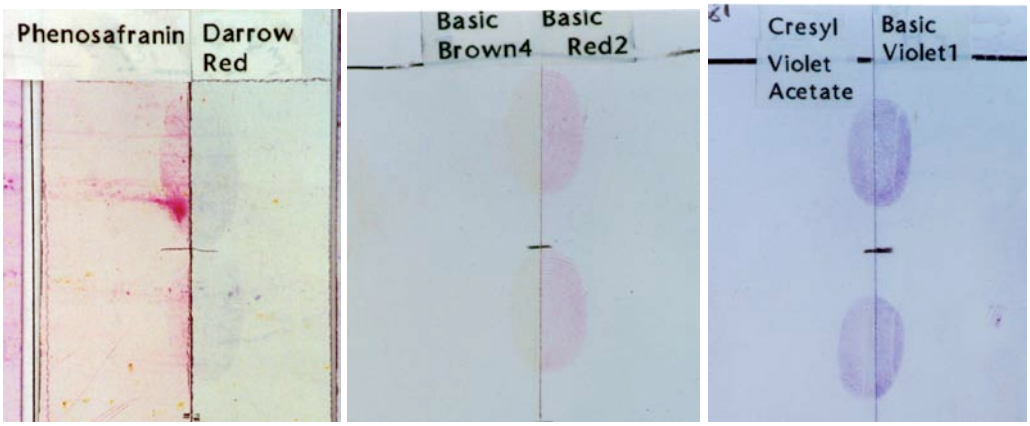
6.5 CAST has also assessed a wide range of alternative lipid dyes, some water soluble, some ethanol soluble and some soluble in both solvents. In addition, some other dyes containing NH_2 groups were also evaluated because this characteristic appeared to be important in the staining of fingerprints. The full list of dyes evaluated is given in the table below.

Common name	**Colour Index name**	**Colour Index number**
2,7-Dichlorofluorescein	–	–
Basic fuschin	Basic red 9	42500
Bismark brown R	Basic brown 4	21010
Cresyl violet acetate	–	–
Darrow red	–	–
Indophenol blue	–	49700
Lucifer yellow CH	–	–
Methyl violet	Basic violet 1	42535
Methylene blue	Basic blue 9	52015
Neutral red	Basic red 5	50040
New fuschin	Basic violet 2	42520
Nigrosin	Solvent black 5	50415
Nile blue Chloride	Basic blue 12	51180

Nile red	–	–
Oil blue N	Solvent blue 14	61555
Oil red O	Solvent red 27	26125
Phenosafranine	–	50200
Primulin	Direct yellow 59	49000
Pyronine B	–	45010
Rose engal	Acid red 94	45440
Safranine O	Basic red 2	50240
Sudan green 4B	Solvent green 3	61565
Sudan III	Solvent red 23	26100
Sudan orange G	Solvent orange 1	11920
Solvent violet R	Disperse violet 1/solvent violet 11	61100
Thiazol yellow G	Direct yellow 9	19540
Thionin	–	52000
–	Acid black 48	65005

Dyes investigated as possible alternatives to Basic Violet 3.

6.6 Of this selection of dyes, basic red 5, direct yellow 59, phenosafranine, basic red 2, cresyl violet acetate, basic violet 2 and basic violet 1 were considered worthy of further investigation. Optimised formulations based on basic violet 2 were ultimately developed, but in comparative trials with an experimental formulation of basic violet 3, the basic violet 2 formulation was found to be less effective [14].



Examples of some of the split depletion experiments conducted using alternative lipid dyes.

7. Post-treatments

7.1 The principal post-treatment used for fingerprints treated with basic violet 3 is the transfer process [7], used for fingerprints on the adhesive side of dark tapes where the violet colour of the dye cannot be seen. In this process the tape is placed in contact with the glossy surface of photographic paper and pressed. Dye is transferred to the surface of the

white paper and the violet dye can be easily visualised. Another advantage of this process is that the fluorescence of the marks is generally increased because the concentration of the dye transferred is less than that present in the original developed fingerprint, reducing the self-quenching effect of the dye.

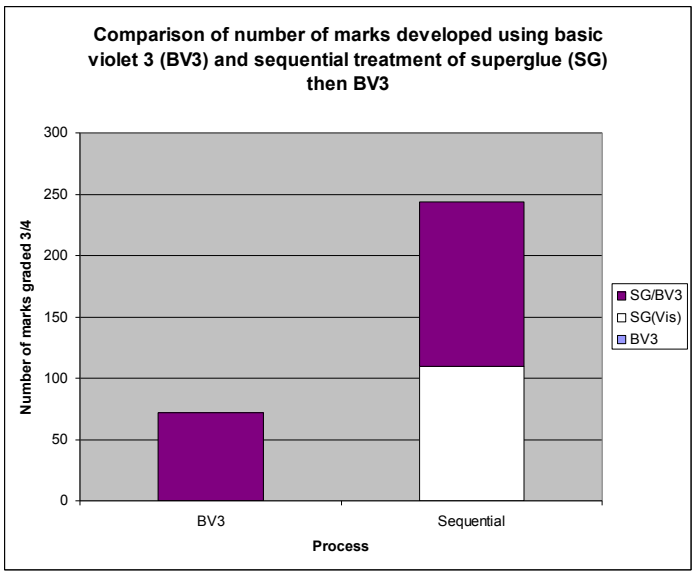
8. Validation and operational experience

8.1 Laboratory trials

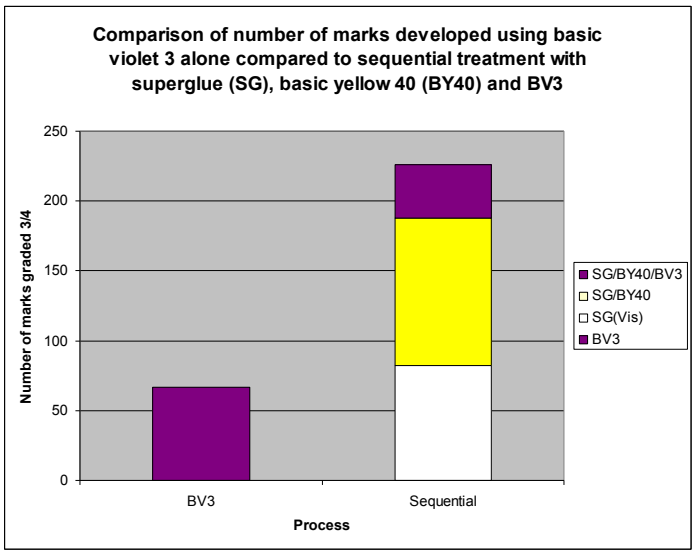
8.1.1 Extensive laboratory trials have indicated the following.

- Basic violet 3 alone is not the most effective treatment for any type of adhesive tape.
- Basic violet 3 can be effectively used as a final sequential treatment for adhesive tapes after either superglue or powder suspensions.
- The AOT-based basic violet 3 formulation appears to develop better quality fingerprints with better contrast, causes less background staining and has fewer health and safety issues associated with it than the phenol-based formulation.
- Basic violet 3 can also be used on contaminated, non-porous surfaces but it has not been conclusively shown whether basic violet 3 or solvent black 3 (or indeed iodine or powder suspensions) are the optimum treatment in these circumstances. Basic violet 3, solvent black 3 and iodine all stain fats, whereas powder suspensions will not stain fats but will develop latent fingerprints laid on contaminated surfaces.

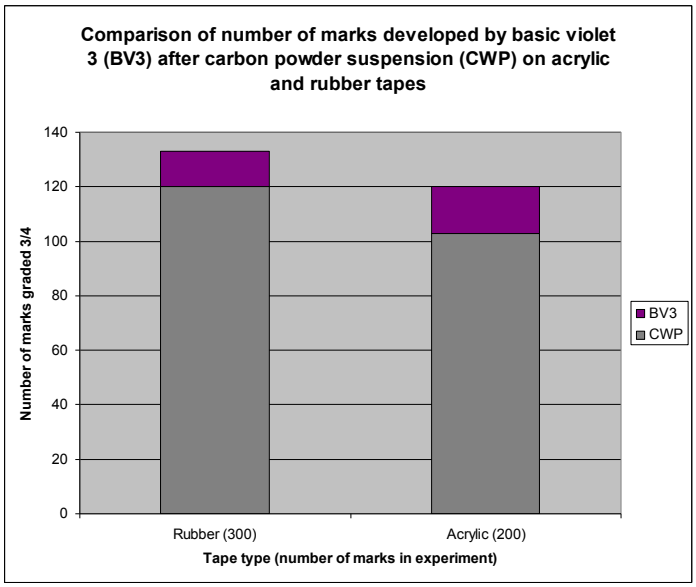
8.1.2 The experiments conducted to support the statements above are summarised below. During studies on optimum treatments for adhesive tapes, basic violet 3 was compared with superglue as a single treatment, and as a secondary treatment after superglue. It was also investigated as a secondary treatment after carbon-based powder suspensions. In total, over 1,000 marks were graded during this study. The results are shown graphically below.


Comparison of number of marks developed using basic violet 3 (BV3) and sequential treatment of superglue (SG) then BV3
Number of marks graded 3/4
300
250
200
150
100
50
0
BV3
Sequential
Process
SG/BV3
SG(Vis)
BV3

a)


Comparison of number of marks developed using basic violet 3 alone compared to sequential treatment with superglue (SG), basic yellow 40 (BY40) and BV3
Number of marks graded 3/4
250
200
150
100
50
0
BV3
Sequential
Process
SG/BY40/BV3
SG/BY40
SG(Vis)
BV3

b)

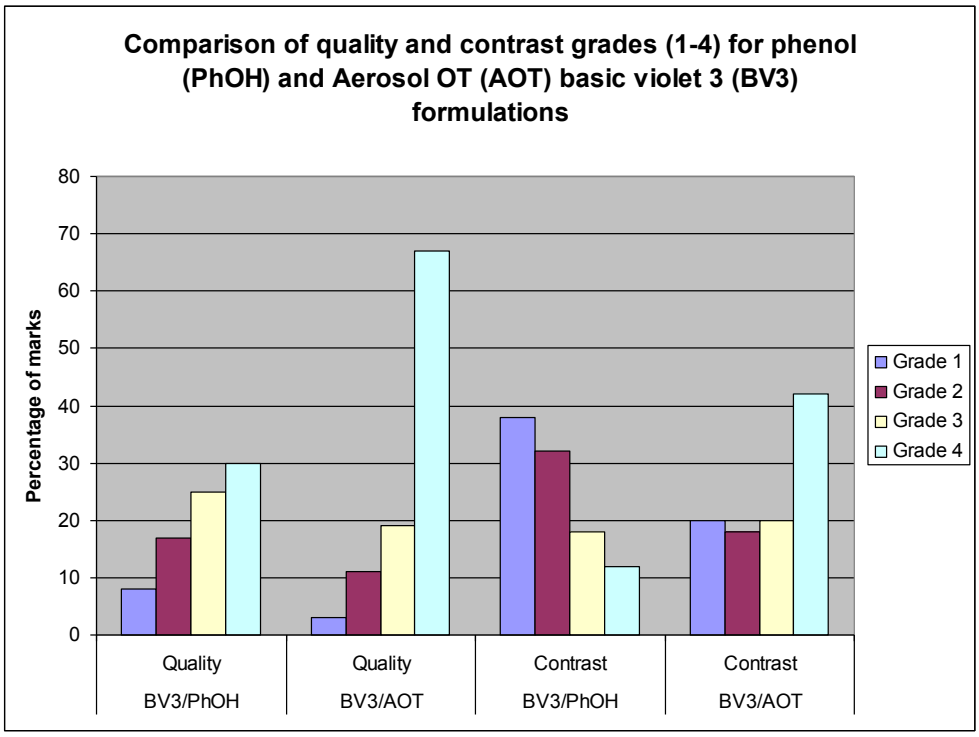

Comparison of number of marks developed by basic violet 3 (BV3) after carbon powder suspension (CWP) on acrylic and rubber tapes
Number of marks graded 3/4
140
120
100
80
60
40
20
0
Rubber (300)
Acrylic (200)
Tape type (number of marks in experiment)
BV3
CWP

c)

Graphs showing additional marks developed using basic violet 3 (BV3) in sequence on adhesive tapes a) comparison of BV3 alone with superglue (SG) followed by BV3 b) comparison of BV3 alone with superglue followed by basic yellow 40 (BY40), followed by BV3 and c) BV3 after carbon powder suspension (CWP) on both acrylic and rubber-based adhesives.

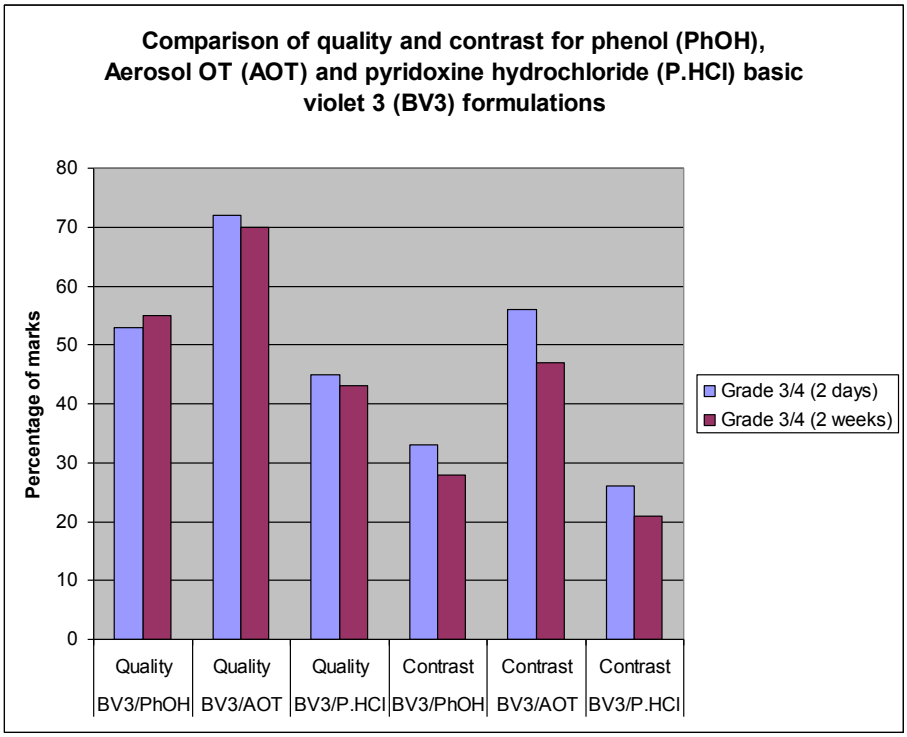
8.1.3 It can be seen that basic violet 3 is not as effective as superglue, but does develop additional marks after both superglue and powder suspensions on adhesive tapes.

8.1.4 Research into phenol replacements evaluated a range of surfactants, of which AOT gave performance equivalent to, or better than, the phenol-based formulation and hence was the only compound considered in further, more focused studies on adhesive tapes.

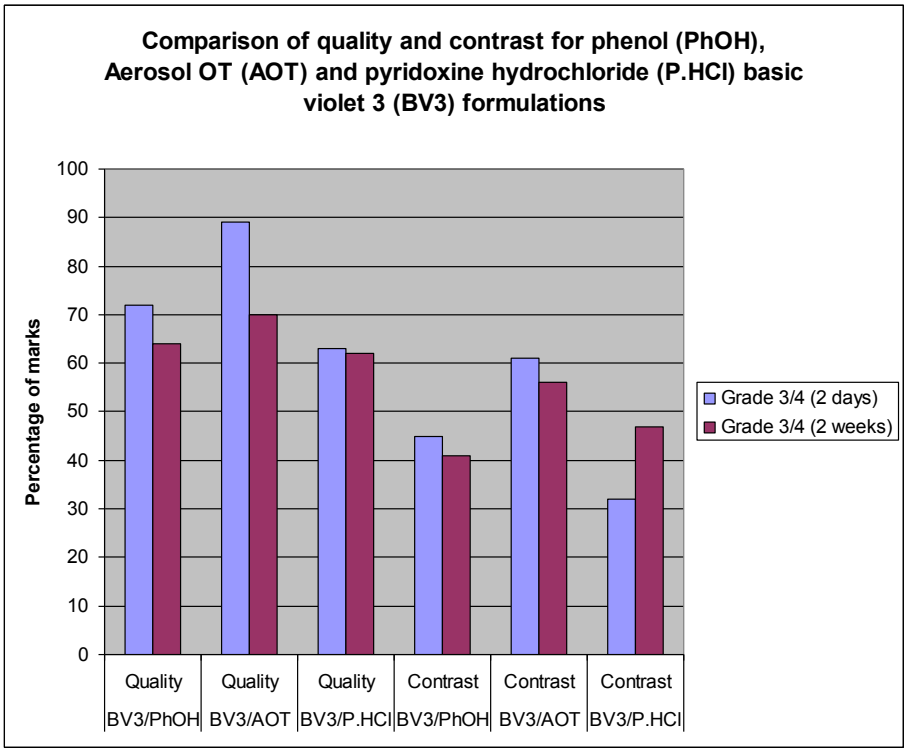


Graph comparing effectiveness of phenol (PhOH) and Aerosol OT (AOT)-based basic violet 3 (BV3) formulations, results based on grading of 1,920 half prints.

8.1.5 These subsequent studies [14,23] incorporated further phenol alternatives and confirmed the observation that the AOT formulation consistently out-performed the phenol and pyridoxine hydrochloride formulations in laboratory trials and this formulation was ultimately recommended for operational use on adhesive tapes after a brief operational trial.

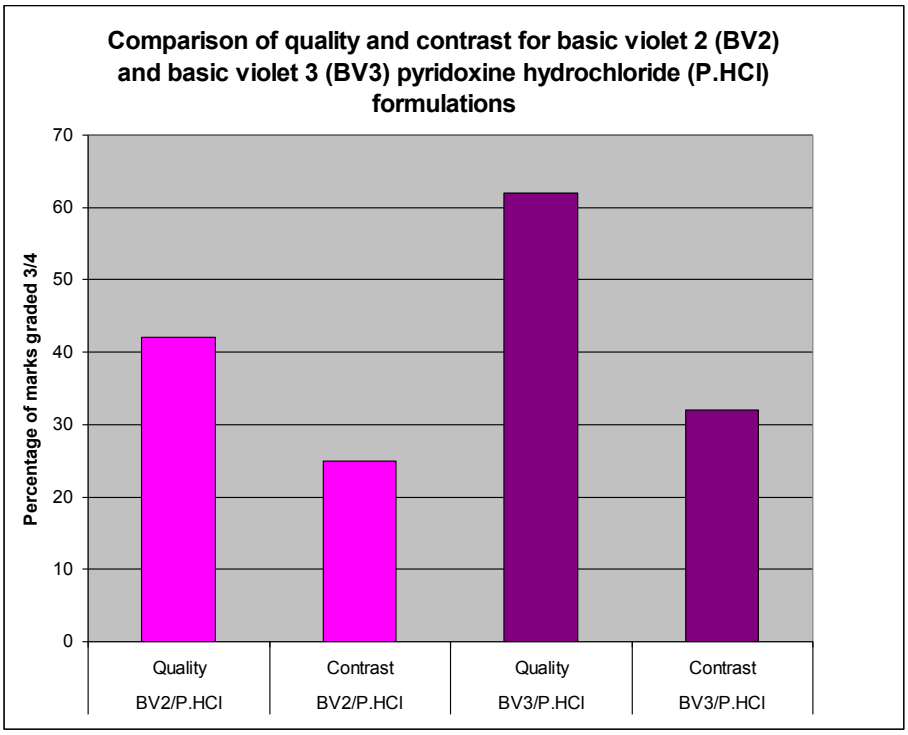


Three-way comparison of phenol, Aerosol OT and pyridoxine hydrochloride basic violet 3 formulations on tapes peeled off plastic bags, based on 4,494 half prints.



Three-way comparison of phenol, AOT and pyridoxine hydrochloride basic violet 3 formulations on tapes removed from plastic bags using freezer spray, based on 1,798 half prints

8.1.6 Of all of the alternative lipid dyes evaluated, the most promising was basic violet 2. Comparative studies were conducted between basic violet 2 and basic violet 3, the results indicating that basic violet 2 was inferior in performance based on the colour of marks developed and hence no further research was carried out on this dye.

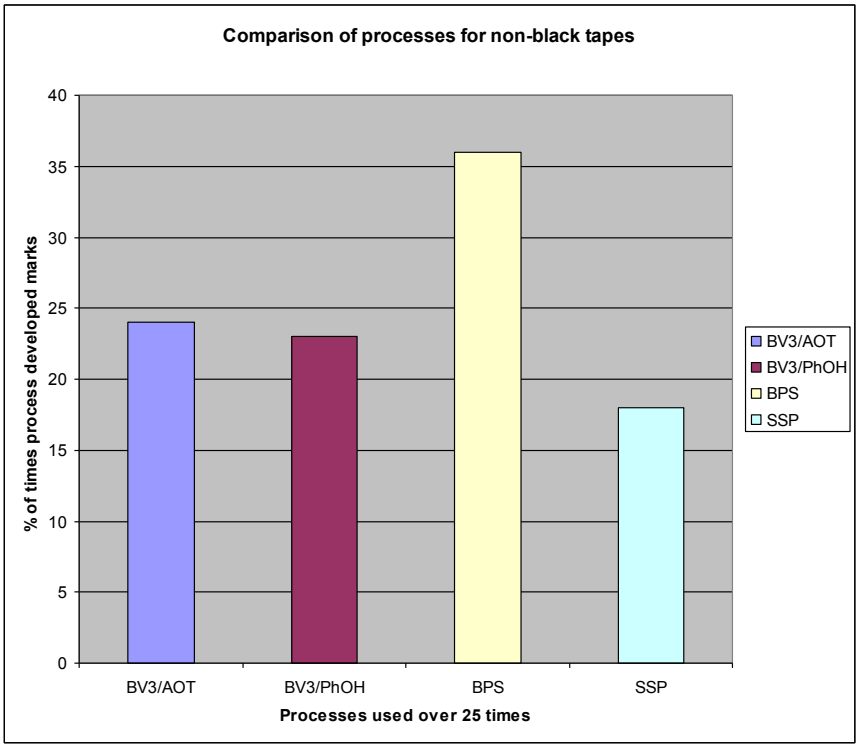


Comparison of pyridoxine hydrochloride-based basic violet 2 and basic violet 3 formulations (pyridoxine hydrochloride-based basic violet 3 subsequently found to be less effective than phenol and AOT-based basic violet 3). Results obtained from grading 300 half fingerprints.

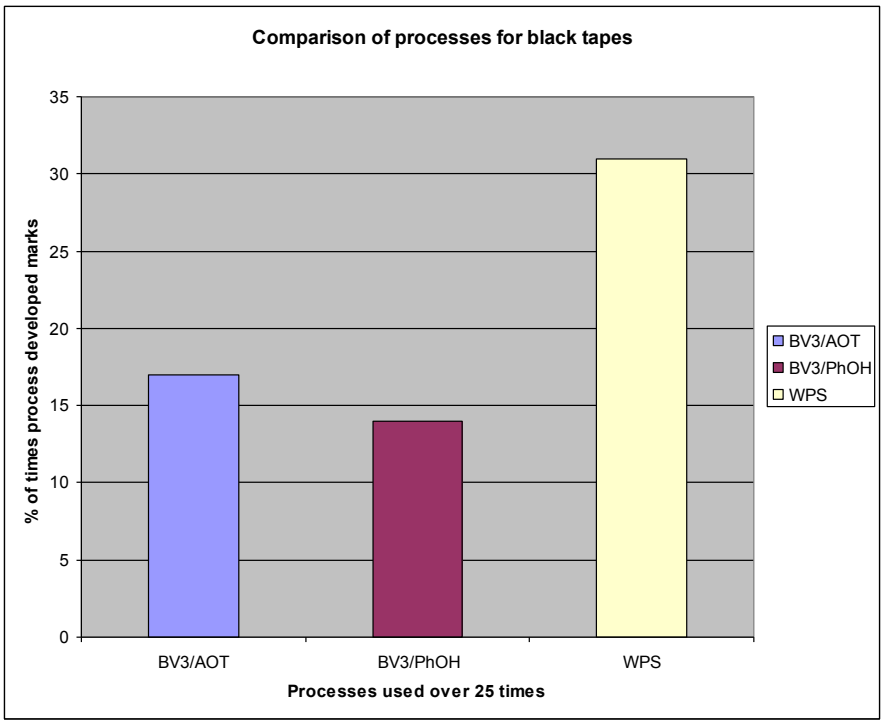
8.1.7 Comparative studies were also carried out between basic violet 3 and solvent black 3 on a range of non-porous surfaces. These are reported in Chapter 3.9 and show that there is no clear difference between the two processes in this application.

8.2 Pseudo-operational trials and operational experience

8.2.1 An operational trial was conducted, comparing the effectiveness of both phenol- and AOT-based basic violet 3 formulations with CAST-formulated powder suspensions and a commercial powder suspension. Results were obtained on both black tapes (where a white powder suspension was used) and light tapes (where black powder suspensions were used). These were conducted with police forces traditionally receiving large numbers of tape exhibits over a period of 18 months. However, tapes are not common exhibits and it took a considerable time to generate sufficient data for a reasonable comparison to be made.



a)



b)

Results of operational trial on adhesive tapes, comparing Aerosol OT and phenol-based basic violet 3 formulations with a) Home Office Centre for Applied Science and Technology black powder suspension and Sticky-Side Powder on non-black tapes and b) Home Office Centre for Applied Science and Technology white powder suspension on black tapes.

8.2.2 The trial effectively confirmed the results of the laboratory trials in that the AOT-based formulation was more effective than the phenol-based formulation on adhesive tapes and that powder suspensions were more effective than basic violet 3 as a single treatment. As a consequence, formulations for AOT-basic violet 3 and black and white powder suspensions were issued by HOSDB in 2006 [15].

8.2.3 A pseudo-operational trial was recently conducted on plastic wrapping materials, which incorporated basic violet 3 as the final process in a sequential treatment scheme. The results of this trial are more fully reported in Chapter 3.7 Powder suspensions, and demonstrate that basic violet 3 develops up to 10% additional marks in both visual and fluorescence modes after sequences involving other treatments. As a consequence, basic violet 3 has been incorporated as the final stage in the processing treatments for non-porous surfaces and plastic packaging materials.

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3.3 1,8-Diazafluoren-9-one (DFO)

1. History

1.1 1,8-Diazafluoren-9-one (DFO) was first synthesised by Druey and Schmidt in the CIBA laboratories in Switzerland in 1950 [1]. The potential of the chemical for the labelling of amino acids and detection of fingerprints was not recognised until the late 1980s, when the Central Research Establishment (CRE) of the then Home Office Forensic Science Service (FSS) placed a contract with Queens University, Belfast to investigate ninhydrin analogues. During the course of this research DFO was identified as a highly promising alternative to ninhydrin, producing marks of a reddish colour when viewed under normal light. The most significant feature of the product formed by the reaction between the DFO reagent and fingerprint residues was that it was inherently fluorescent and eliminated the need for toning with metal salts, the process used to make ninhydrin marks fluorescent.

1.2 Before open publication of information on the effectiveness of DFO, quantities were sent to selected fingerprint research laboratories worldwide for evaluation. Operational trials were also conducted at two UK police forces, Surrey [2] and the Metropolitan Police [3]. A comparative assessment of DFO with ninhydrin and 5-methoxyninhydrin was carried out in both Israel [4] and New Zealand [5]. The Israeli study looked at results obtained on a series of paper samples and banknotes and found DFO to out-perform both forms of ninhydrin. The New Zealand researchers investigated sequential treatment and found that DFO could be used before ninhydrin, and did not affect the subsequent use of physical developer. However, ninhydrin used after DFO was far less effective and did not produce any additional marks. The fluorescence of DFO was also superior to that of both ninhydrin forms after toning with zinc chloride. Another observation made by the New Zealand group was that DFO also enhanced blood, and could be used in sequential treatments before amido black (acid black 1).

1.3 With all researchers reporting significant improvements in the number of marks developed using DFO over the numbers found with ninhydrin, the first information on the new reagent was published in open literature in 1990 [6,7,8]. The initial formulation issued was based on the chlorofluorocarbon (CFC) 1,1,2-trifluorotrichloroethane (CFC113) solvent, with small quantities of methanol and acetic acid, and required the exhibits to be dipped twice in the solution, allowing them to dry each time before finally heating in a dry oven at 100ºC for 10 minutes to develop the marks. Excitation and emission spectra for DFO were also presented, with the UK laboratories initially using an argon ion laser to promote fluorescence. However, it was also found that a high intensity light source (i.e. the high intensity filtered light sources then becoming available) could also be used to produce fluorescence [9,10].

1.4 Fundamental research into DFO continued, with studies carried out into the reaction products formed between DFO and amino acids [11]. Assessments of the relative sensitivity of DFO and different ninhydrin analogues were also carried out [12], looking at their relative detection limits for serine. This study indicated that DFO was similarly sensitive to ninhydrin in colorimetric mode and as sensitive as 5-methoxyninhydrin toned with zinc chloride (the best of the ninhydrin analogues) in fluorescence mode.

1.5 The issue of the first DFO formulation and the subsequent commercial availability of the reagent prompted further investigations worldwide, with assessments being carried out of alternative solvents to CFC113 including petroleum ether [13] and a petroleum ether/xylene mixture [14]. Sequential treatments were also reassessed, with Masters *et al.* [14] studying a range of different paper types and finding that the DFO-ninhydrin sequence was far superior to ninhydrin-DFO. Corson [13] also investigated sequential treatment and indicated that occasionally DFO could develop additional marks after ninhydrin, but did not state which sequence was best. Masters *et al.*[14] also studied a range of different light sources and filter combinations for excitation and viewing of the fluorescent fingerprints. A red camera/viewing filter was recommended to reduce the background fluorescence that was sometimes observed on coloured papers and from some writing inks.

1.6 The Home Office Scientific Research and Development Branch (HO SRDB) studies into DFO also began in 1990, initially looking at the components of the formulation and the dipping and heating stages. In a split depletion comparison carried out over seven different paper types using five donors, it was found that there was no benefit in dipping the article twice. The purpose of double-dipping was stated to be to increase the uptake of DFO by the fingerprint, but the HO SRDB study showed no difference in either the visible appearance or the intensity of fluorescence between single-dipped and double-dipped articles. Single-dipped articles, in particular cheques, showed less evidence of background staining and therefore single dipping was recommended. Heating experiments were also conducted, monitoring the change in fluorescence with increasing exposure time in an oven using a luminance meter. At 100ºC, optimum fluorescence was reached after 20–30 minutes, whereas at 50ºC development took several hours [15]. Temperatures in excess of 100ºC were not considered because of potential charring to the paper, although development rates were increased; Australian researchers suggested that development occurred in approximately 20-30 seconds at 160˚C [16]. A dry oven was found to be more effective than a heat gun in delivering the optimum heating conditions. It was considered important that the oven used in processing had a laminar air flow across each shelf as opposed to being a convection oven, because paper articles were loaded on cardboard in the same way as used for the processing of ninhydrin treated articles. Further studies also investigated alternative solvent systems and reductions in the amount of DFO in the formulation. It was found that the quantity of DFO could be reduced from

0.5g to 0.25g without any detriment to the intensity of fluorescence produced. This also overcame issues with instability of the working solution, where DFO precipitated rapidly, sometimes before processing had commenced. Operational trials were conducted between the original and revised formulation and processing conditions, with the revised formulation giving marginally better performance. A summary of these studies was published in 1993 [15].

1.7 Other extensive studies of DFO, its reactions and optimum viewing conditions were conducted by Cantu *et al.* [17] and Stoilovic [16]. Cantu *et al.* compared the effectiveness of DFO with a range of ninhydrin analogues on the amino acid glycine and concluded that DFO was the only compound acting as a fluorescer without secondary treatment, with the intensity of fluorescence exceeding that of any of the zinc or cadmium complexes formed with ninhydrin. Cantu *et al.* also demonstrated that the presence of acetic acid in the formulation was essential for fluorescence to occur. Formic acid will also produce a good reaction, but when used in combination with methanol the two constituents react rapidly to produce the unwanted methyl formate. Stoilovic also investigated changes to the formulation, adding chloroform and reducing the methanol and acetic acid components in order to reduce inks running when treating documents. He also conducted a sensitivity study and concluded that DFO was equivalent in sensitivity to ninhydrin toned with zinc chloride. Samples were treated by heating with an ironing press at 160ºC, which was thought to give superior results to oven heating (although the oven used in this case was a convection, rather than a laminar flow oven). The optimum excitation and viewing conditions were also investigated using a filtered high intensity light source (Polilight).

1.8 The introduction of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987 and the subsequent prohibition on the use of ozone-depleting solvents, including CFC113, meant that from the mid-1990s efforts were directed towards an ‘ozone-friendly’ DFO formulation. In 1995 Lennard [18] proposed petroleum ether, which was in wide scale use in the US as a solvent for ninhydrin, as a replacement for CFC113, but it was also desirable to identify a solvent replacement without the associated issues of high flammability. During the period 1994–1997, PSDB evaluated a range of candidate replacement solvents including hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs). Of these HFC4310 and 1-methoxynonafluorobutane (HFE7100) [19] both showed promise, but required other additives to produce the same level of reaction as CFC113. HFE7100 had also been supplied to French researchers for evaluation, and they too developed a DFO formulation based on this solvent [20]. HOSDB carried out an operational trial of the most promising new DFO formulations, comparing them with the existing CFC113 formulation and an optimised 1,2 indandione formulation based on HFE7100. In this trial, conducted on 650 articles in an operational police laboratory, the HFE7100-based DFO formulation gave the best

results [21] and was therefore recommended for operational use in the UK. A fuller description of the alternative formulations investigated by PSDB was later published by the researchers [22].

1.9 Further fundamental research was carried out on the DFO system. Wilkinson studied the reaction mechanism between DFO and amino acids [23] and the synthesis of DFO analogues [24]. Conn *et al.* [25] investigated whether metal salt treatment of DFO would give any further benefits in fluorescence but concluded that, in contrast to ninhydrin, there was little effect on the fluorescent product.

1.10 The impact of DFO on other types of forensic evidence was also studied. The emergence of DNA and its importance as an identification tool prompted studies into the effect of DFO treatment of blood on the subsequent recovery of DNA profiles [26]. The authors concluded that DFO had no detrimental effect on DNA. PSDB and the FSS also showed that DFO treatment had little impact on the recovery of DNA from latent fingerprint residues [27]. Strzelczyk [28] considered the effects of DFO treatment on subsequent document examination, comparing the PSDB HFE7100 formulation with the CFC113 formulation. The HFE7100 formulation was found to be less detrimental to handwriting evidence.

1.11 A survey of fingerprint development processes for porous surfaces conducted in 2004 [29] showed that DFO had become the second most widely used reagent for this surface worldwide, with 86% of those responding to the survey saying that they used it in their laboratory.

1.12 More recently, the development of formulations of 1,2 indandione incorporating zinc salts have resulted in claims that 1,2 indandione-zinc is actually more effective than DFO. As a consequence several groups of researchers have carried out further comparative work [30-32]. To date the results of these have given conflicting results with most favouring 1,2 indandione-zinc but some favouring DFO. It is clear that further research is required to establish whether DFO should remain the primary chemical treatment in sequential processing regimes for porous surfaces. This further work should take into consideration the overall effectiveness of sequential treatment routines, as well as the effectiveness of individual techniques.

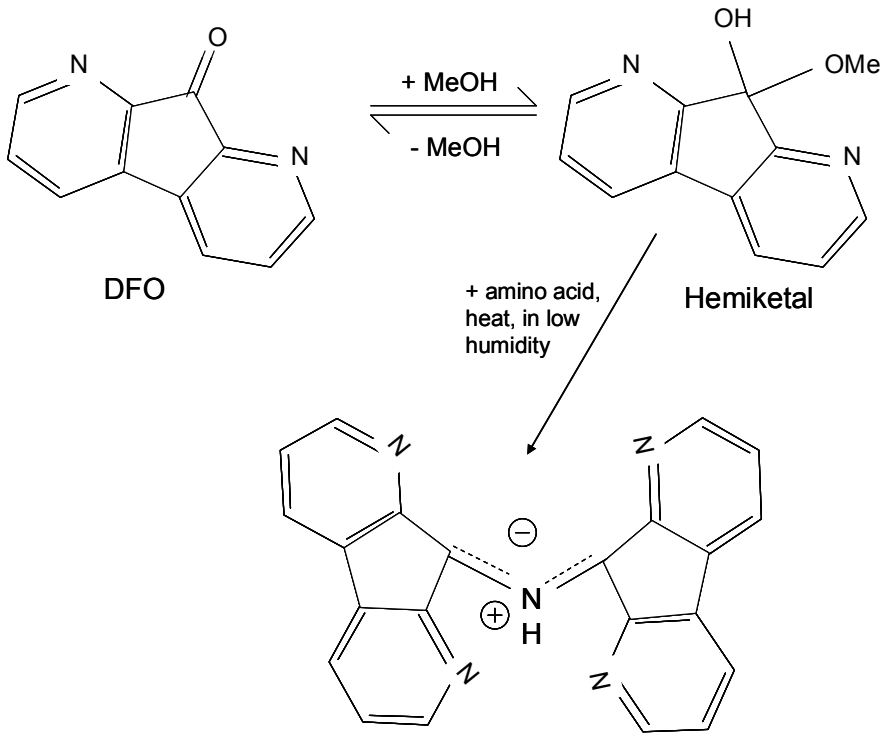
2. Theory

2.1 The reaction mechanism for DFO has been studied by both Grigg *et al.* [11] and Wilkinson [23, 24]. Grigg *et al.* isolated the red reaction product between DFO and various α-amino acids and found it to be closely related to the protonated Ruhemann's purple structure developed with ninhydrin.

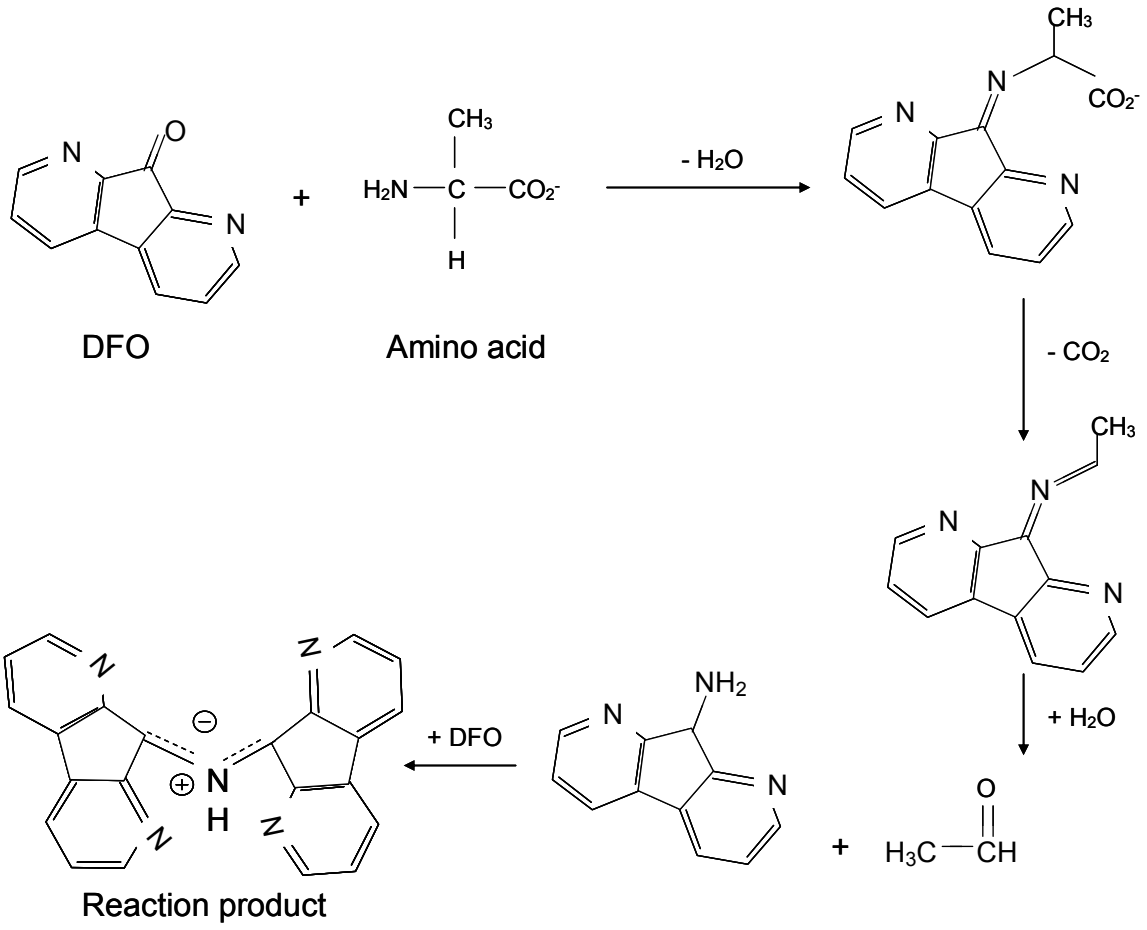
a) b)

Reaction products formed between 1,8-diazafluoren-9-one (DFO) and 0.1M solutions of amino acids and other fingerprint constituents a) visible and b) fluorescence.

2.2 The analytical studies carried out by Wilkinson used a range of techniques including nuclear magnetic resonance spectroscopy (NMR) and gas chromatography – mass spectrometry (GC-MS) to isolate and identify reaction products. A reaction mechanism was proposed, which is illustrated below.



Proposed mechanism for formation of hemiketal.



Proposed reaction path of 1,8-diazafluoren-9-one (DFO) with amino acids [24]

2.3 Wilkinson [24] proposed that the DFO reaction follows a very similar path to that of ninhydrin with amino acids. DFO reacts with the methanol in the solvent mixture to form a hemiketal, which has a higher reactivity with amino acids than the DFO molecule. The nitrogen atom of the amino acid is able to attack the hemiketal at the electron deficient carbon in the polarised carbonyl, with the loss of water. This forms an aromatic imine, which retains the alkyl fragment of the amino acid and undergoes decarboxylation to form a further intermediate product. Hydrolysis then occurs at the nitrogen-carbon double bond, which forms an aromatic amine and acetaldehyde. The aromatic amine finally reacts with another DFO molecule to form the red, fluorescent reaction product identified in this and previous studies [11, 24]. X-ray crystallography carried out on the reaction product between DFO and L-alanine [23] indicated that the structure of the reaction product consisted of two DFO molecules linked by a bridging nitrogen atom, and was therefore in close agreement with Grigg *et al.*'s original predictions [11]. In the crystalline product analysed, molecules of the reaction product were shown to be linked by hydrogen-bonded bridges with water molecules.

2.4 The reaction between DFO and amino acids is not thought to proceed to completion, which accounts for the observation that ninhydrin will develop additional marks when used after DFO. Alternatively (or additionally), there may not be sufficient DFO to completely react in a 2:1 ratio with all amino acids present.

3. CAST processes

3.1 The process currently (as of 2011) recommended by CAST is to add 30mL of methanol and 20mL of acetic acid to 0.25g of DFO, stirring to produce a yellow solution. To this is then added 275mL of HFE71DE followed by 725mL of HFE7100, stirring together to produce a working solution.

3.2 Working solution is poured into a shallow tray, and articles to be treated drawn slowly through the solution with forceps, then removed and allowed to dry on a sheet of tissue. Alternatively, DFO solution may be applied with a soft brush.

3.3 Once dry, articles are heated in a non-humidified oven at 100ºC for 20 minutes, followed by examination in white light (where developed marks may be detected due to their pale pink colour) and subsequent fluorescence examination.

3.4 The role of DFO in the formulation is to react with amino acids present in fingerprint residues to give a fluorescent reaction product. The CAST formulation makes the assertion that the primary purpose of DFO is to produce a fluorescent product, and therefore the presence of any coloured reaction product is of secondary importance. The formulation

uses 0.25g of DFO per litre, found to give the maximum intensity of fluorescence. Any increase in DFO content will make the coloured product more intense (although still far less visible than the purple of ninhydrin) but does not enhance fluorescence. Quantities of > 0.2g DFO are essential for the reaction to occur, and quantities of > 0.75g cannot be dissolved.

3.5 Methanol is an essential component of the DFO formulation, its presence allowing DFO to form hemiketals, which in turn have greater reactivity with amino acids. Longer chain alcohols are not as effective, using ethanol, propan-1-ol or propan-2-ol reduces the yield and fluorescence of developed fingerprints and *t*-butanol inhibits the reaction completely. Studies have shown that 30% of DFO reacts with methanol, whereas only 10% reacts with ethanol. The formulation uses the minimum amount of methanol possible due to its toxic nature.

3.6 Acetic acid is added to acidify the solution. If acidification is not carried out, virtually no fingerprints are developed. Propanoic acid can be used in place of acetic acid but has no benefit, whereas formic acid rapidly esterifies with the methanol component of the formulation, producing water as an unwanted by-product. The presence of water causes phase separation of the solution, reducing the amount of DFO in the non-polar phase available for fingerprint development, although a small amount of water is essential for the reaction to take place. Dried solutions are brown in colour and do not produce fluorescent marks if used to treat fingerprints.

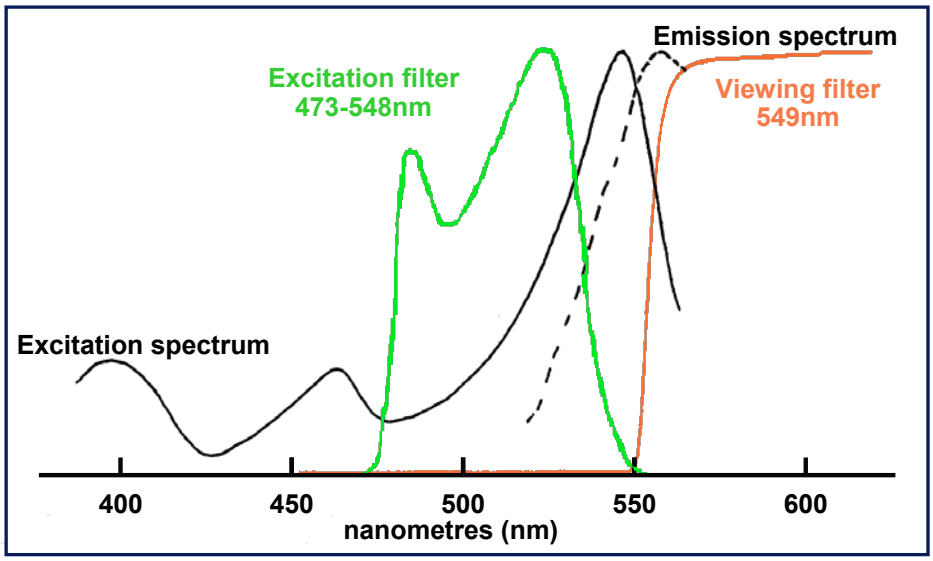
3.7 HFE7100 is used as the principal carrier solvent for DFO. However, during reformulation work it was found that it could not be used as a straight replacement for CFC113 because CFC113 appeared to catalyse the reaction between DFO and amino acids in some way, whereas HFE7100 did not. If HFE7100 was used on its own, the developed fingerprints appeared noticeably less fluorescent and fewer in number. The addition of *trans*-1,2-dichloroethylene as a co-solvent (i.e. in the HFE71DE component of the formulation) is essential for the development of greater quantities of brighter fluorescent fingerprints.

3.8 CAST recommends only a single dip in the DFO working solution. Early studies indicated that double dipping had no benefit in terms of number or intensity of marks developed, and may lead to increased background staining.

3.9 The heating temperature of 100ºC is selected to give a combination of a reasonably short development time combined with a low risk of damage to exhibits, such as paper charring and melting of plastic windows in envelopes. It is also compatible with the upper temperature limit of the ninhydrin oven, enabling a single piece of equipment to be used for both processes. Early studies using a luminance meter showed that optimum fluorescence was obtained after 20 minutes for a significant majority of

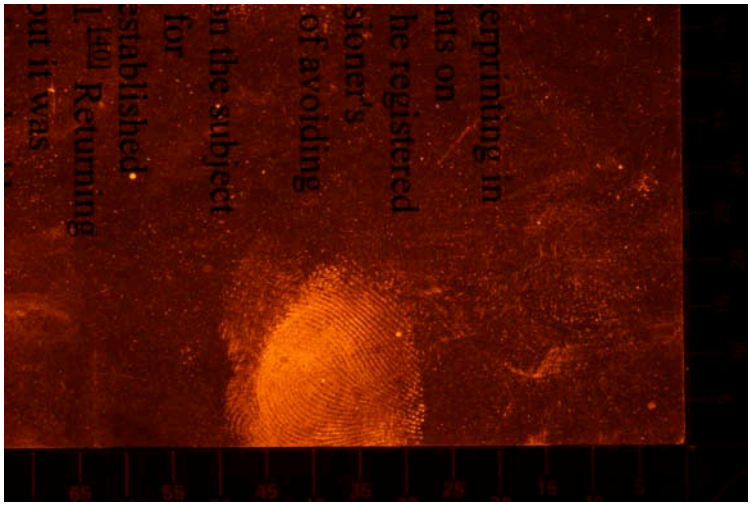
exhibits and this was therefore recommended in place of the original 10-minute period.

3.10 CAST recommends the viewing of marks developed using DFO using excitation in the green region of the spectrum (the 473–548 excitation band of the Quaser series of light sources) and viewing fluorescence through an orange, Schott glass OG570 (549nm long-pass) filter. This gives the optimum match with the excitation and emission spectra for DFO, with the illumination waveband overlapping the DFO excitation and the viewing filter transmitting close to the optimum emission wavelength.



Emission and excitation for 1,8-diazafluoren-9-one, overlaid with the Quaser excitation waveband used and the corresponding transmission of the viewing/camera filters recommended.

3.11 In some circumstances, such as coloured papers, background fluorescence from the paper or ink may make the developed marks more difficult to visualise and in these situations the narrower green excitation waveband of the Quaser (491–548) should be used instead, in combination with a 593 (Schott RG610) filter to cut background fluorescence. More recently, green neodymium:yttrium aluminium garnet (Nd:YAG) lasers with output at 532nm have become more widely available. This output is further towards the optimum excitation wavelengths for DFO, and being single wavelength will cause far less background fluorescence. Therefore, 532nm lasers in combination with 549 (Schott OG570) long-pass filters are recommended for optimum viewing of fluorescent marks developed using DFO.



Fingerprints developed using 1,8-diazafluoren-9-one, illuminated with green (532nm) light and viewed using a 549 long-pass (Schott glass OG570) filter.

3.12 The broad excitation and emission spectra of DFO means that for surfaces where background fluorescence is appreciable when illuminated with light in the green region of the spectrum, better results may be obtained using yellow illumination sources (such as the new 577nm laser) in conjunction with 593 long-pass filters. DFO will still fluoresce under these conditions whereas the background fluorescence may be considerably reduced. This is particularly relevant for many types of brown and coloured paper.

4. Critical issues

4.1 The presence of methanol and *trans*-1,2-dichloroethylene in the formulation is essential for the optimum operational effectiveness. Formulations that substitute or omit these constituents will develop less highly fluorescent marks and fewer marks overall.

4.2 Heating of DFO-treated exhibits should be carried out in a dry oven with even heating via laminar airflow across each shelf; high levels of humidity equivalent to those used for ninhydrin are not beneficial for the reaction.

4.3 Appropriate excitation wavelengths and viewing filters must be selected when visualising developed marks. These are detailed in paragraphs 3.10–3.12 above. Light sources with higher output powers (e.g. lasers) will detect more marks.

4.4 If any separation of the working solution into oily droplets is observed, the solution should be discarded and not used for processing.

5. Application

5.1 Suitable surfaces: DFO is suitable for use on all porous surfaces, including paper, cardboard, raw wood and matt painted walls.

5.2 The principal application of DFO is in the development of fingerprints on porous items, in particular paper. It has been found to be the single most effective treatment for this surface and can be used as the first process in a sequential processing routine consisting of DFO – ninhydrin – physical developer. The use of DFO does not destroy marks that could have been developed by ninhydrin or physical developer and both processes can reveal further marks that have not been developed by DFO.

5.3 DFO is not as widely used as ninhydrin because it requires access to a forensic light source and appropriate viewing filters to see many of the marks developed. Consequently, ninhydrin is the method of choice for many laboratories processing volume crime exhibits because the marks are visible under normal lighting conditions and can be easily captured. However, ninhydrin is a less effective process (DFO typically develops 1.6 times more marks) and potential marks will be missed if it is used as a sole treatment.

5.4 DFO is also an effective blood dye, reacting strongly with the protein constituents in the blood to produce highly fluorescent marks. Heavy deposits of blood will reabsorb the fluorescence making this process less effective in these areas. It can therefore be used to enhance marks in blood on porous surfaces, but is not specific to the 'haem' component of blood and cannot be used to determine whether a mark is blood or not. The application of DFO has been shown not to affect subsequent recovery of DNA from marks deposited in blood [26].

5.5 DFO is applied in the laboratory by solution dipping, passing the exhibit through a shallow tray containing the DFO working solution, allowing it to dry then heating it in an oven at 100ºC for 20 minutes. Neither the exhibit nor the oven are humidified in any way. For larger items, such as boxes, DFO can be applied as a solution using a soft brush, again allowing the exhibit to dry before placing it in an oven.

5.6 DFO cannot be effectively used at scenes of crime. Although the solution can be applied using a brush, the conditions of temperature required to develop fingerprints in a reasonable time are not compatible with working at scenes. It is possible to apply heat locally using equipment such as a heat gun, but this is less effective than oven treatment and will still require long periods of heat application to develop marks, depending on the particular system used. Some heat guns are capable of heating to several hundred degrees centigrade and must therefore be used with caution.

6. Alternative formulations and processes

6.1 Since 1990 and the introduction of DFO, several different formulations have been investigated. Many of these were prompted by the search for alternative solvents after the banning of CFCs. A summary of some significant alternative formulations proposed is given below.

6.2 Bratton and Juhala [33] proposed a variation of the DFO formulation and process called 'DFO-Dry', which involved impregnating sheets of filter paper with a solution of DFO, allowing them to dry, then sandwiching paper exhibits between the impregnated sheets and applying heat from a steam iron filled with 5% acetic acid solution. Samples were then placed in a dry press at 110ºC for 10 minutes to complete development. The formulation used to impregnate the filter papers sheets was:

200mL methanol, 200mL ethyl acetate, 40mL acetic acid, 1g DFO.

6.3 Marks developed in this way were equal in intensity to those developed using a solution dipping process using the same formulation diluted with petroleum ether. The principal advantages of the dry process were that there was no ink run, no background staining and no background fluorescence.

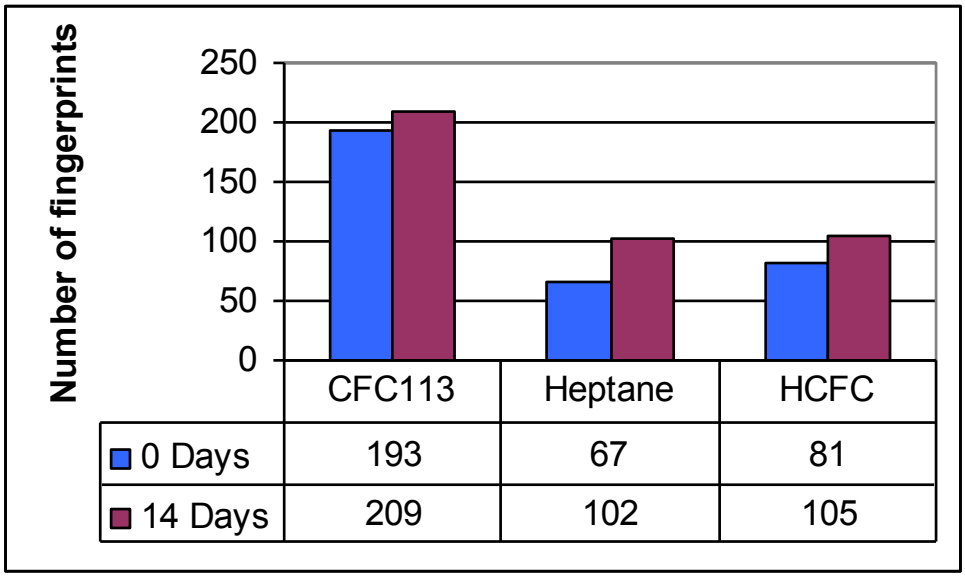
6.4 Petroleum ether was also proposed as a replacement solvent for CFC113 [14,18] but CAST would not recommend the use of this, or any other, highly flammable solvent in a laboratory because of the fire and explosion risks. It was found during testing by CAST that the formulation proposed by Masters *et al.*[14], containing propan-2-ol, xylene and acetone in addition to petroleum ether, developed brightly fluorescent fingerprints but caused significant damage to writing inks and was unstable when stored.

6.5 CAST carried out extensive studies into the identification of replacement solvents for CFC113, using a range of different solvent types including hydrocarbons, HCFCs and HFCs [22]. During these studies, initial evaluations were carried out using split depletions. Any formulations showing promise were taken forward to more detailed trials involving the treatment of a batch of 75 fraudulently passed cheques, using each formulation and counting all developed fingerprints with more than eight minutiae visible.

6.6 The best performing hydrocarbon and HCFC formulations are given below, together with their performance relative to the CFC113 formulation of batches of 75 cheques.

	CFC113	**Hydrocarbon**	**HCFC**
DFO	0.25g	0.25g	0.25g
Methanol	30mL		25mL
Acetic acid	20mL	20mL	20mL
Ethanol		100mL	

Ethyl acetate		50mL	
Methyl acetate			5mL
Heptane		850mL	
CFC113	1 litre		
HCFC141b			1 litre



Formulations based on hydrocarbons (heptane) and hydrochlorofluorocarbons (HCFCs) and their performance relative to the 1,1,2-trifluorotrichloroethane (CFC113) formulation.

6.7 Despite promising results from laboratory split depletion tests, neither of these formulations performed well when compared with the CFC113 formulation in a realistic trial.

6.8 Another non-CFC formulation evaluated was provided by the Bundeskriminalamt (BKA), Weisbaden, Germany, and consisted of:

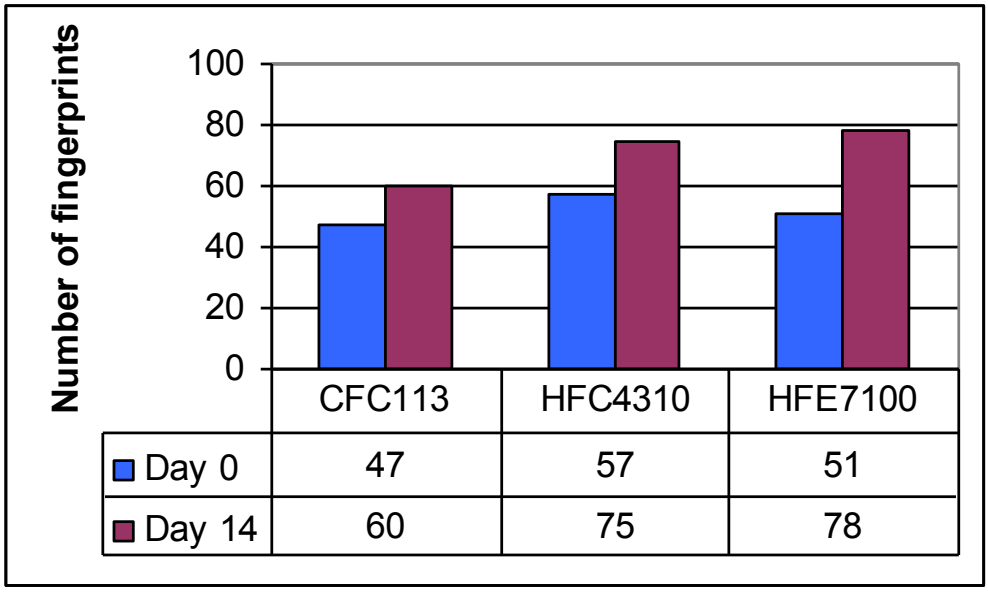
0.5g DFO, 40mL methanol, 20mL acetic acid, 1 litre *t*-butyl methyl ether.

6.9 This gave more fluorescent prints than the heptane formulation, but caused significant ink running. The solvent posed an explosion risk, and did not perform as well as the CFC formulation in comparative trials on batches of cheques.

6.10 The final class of solvents evaluated were HFCs, the most suitable of those evaluated being HFE7100 and HFC4310mee. The formulations were trialled against CFC113 and the results are shown below.

	CFC113	**HFC4310mee**	**HFE7100**
DFO	0.25g	0.25g	0.25g
Methanol	30mL	30mL	30mL
Acetic acid	20mL	20mL	20mL

trans–1,2 dichloro-ethylene		100mL	150mL
HFC4310mee		1 litre	
HFE7100			850mL
CFC113	1 litre		



Formulations based on hydrofluorocarbons and hydrofluoroethers and their performance relative to the CFC113 formulation.

6.11 Both formulations appeared to give superior performance to the CFC113 system and were taken to a full operational trial alongside it [21]. From this trial, the HFE7100-based formulation (with minor modifications) was ultimately recommended for operational use and is described in more detail in the CAST processes section above.

6.12 There are several DFO formulations in operational use worldwide. A survey of these has recently been conducted by Wallace-Kunkel *et al.* [29], the most commonly used being summarised in the table below.

% usage	DFO (g)	Methanol (mL)	Ethyl acetate (mL)	Acetic acid (mL)	Dichloromethane (mL)	Petroleum ether (mL)	HFE7100 (mL)	HFE71DE (mL)
18	0.25	40		20			940	
14	0.5	40		20			940	
11	0.5	100	100	20		780		
7*	0.25	30		20			725	275
4	0.2	50		20	50	880		

* currently (2011) recommended HOSDB formulation.

Compositions representative of 1,8-diazafluoren-9-one formulations used worldwide.

6.13 The two most commonly used formulations use HFE7100, but do not incorporate *trans*–1,2 dichloroethylene. CAST has found that

formulations without this component are less effective and would therefore recommend its inclusion.

6.14 Formulations based on petroleum ether are not recommended by CAST because of the fire and explosion hazards associated with the solvent, and CAST would seek to minimise use of dichloromethane where possible due to health and safety concerns.

6.15 A modified formulation has been proposed by CAST for the treatment of thermal receipts [27]. When thermal receipts are treated with DFO they blacken due to reaction between acetic acid and the thermal ink layer, blackening also occurring due to the heat ion the oven used to develop marks. To counteract this, CAST carried out trials and devised a formulation with the amount of methanol increased to 60mL. This dissolves away the thermal ink layer and significantly reduces subsequent blackening. The thermal paper is retained in the dip bath until all black deposit is removed from the surface of the paper, then placed into the oven. In practice, this did reduce the problems associated with blackening of thermal receipts but as ink compositions changed it did not prove possible to remove easily all of the ink layer in this way. Pre-dipping the receipt in ethanol until all text disappears and then allowing it to dry prior to dipping in a solution of the standard formulation has proved more effective [34].

7. Post-treatments

7.1 There are no post-treatments used with DFO other than the examination of the developed mark using fluorescence, which is described above. Toning using metal salts is ineffective and does not increase the fluorescence of the mark.

8. Validation and operational experience

8.1 Laboratory trials

8.1.1 Although laboratory trials were conducted during the initial development of DFO formulations in the early 1990s, most of these results no longer survive. It has been found from experience that planted prints rarely give operationally representative results in such trials, typically performing worse than seen on casework. This is possibly because perpetrators of crimes may be under increased stress and sweat more, giving more eccrine prints than seen in the laboratory. As a consequence, development of revised formulations at HOSDB is usually carried out using small-scale comparative tests until best performing formulations are identified, after which testing proceeds to pseudo-operational trials using realistic items such as bundles of cheques.

8.1.2 One exception to this is the recent comparison between DFO and 1,2 indandione/zinc, carried out using split depletions on a range of different substrate types. This study showed closely equivalent performance between DFO and the 1,2 indandione/zinc formulation studied, and is more fully reported in Chapter 5.7, 1,2 Indandione.

8.2 Pseudo-operational trials and operational experience

8.2.1 Several pseudo-operational trials were conducted on alternative DFO formulations during research into a replacement solvent for CFC113. The results of these have been summarised in the section on 'Alternative formulations' above. The outcome of these studies was that the formulation based on HFE7100 solvent was selected for comparative trials with the CFC113-based DFO formulation.

8.2.2 There have also been several pseudo-operational and operational trials conducted to establish the relative effectiveness of the DFO and ninhydrin techniques and also to establish the best sequence of treatment. Before publication of the initial reports on DFO, operational trials were conducted at Surrey Police and the Metropolitan Police Serious Crimes Unit.

8.2.3 The trial at Surrey [2] involved treatment of the exhibits using DFO followed by laser examination, then ninhydrin treatment. An assessment was made of the number and quality of the marks developed using each process. The results of this trial were:

DFO > Ninhydrin 139 articles (69.8%);
Ninhydrin > DFO 13 articles (6.5%);
DFO = Ninhydrin 47 articles (23.6%).

8.2.4 The Metropolitan Police trial [3] involved a direct comparison of the effectiveness of DFO and ninhydrin when used as a single process on casework, and also looked at the impact of zinc chloride treatment on marks developed using ninhydrin. The results are summarised below:

DFO – 510 prints from 168 articles;
Ninhydrin – 1,135 prints from 1,356 articles;
Ninhydrin + zinc chloride – 1,249 prints from 1,356 articles.

8.2.5 Both these trials indicated significant benefits in the use of DFO, with more marks being developed than found using ninhydrin. DFO was found superior to ninhydrin even after zinc chloride toning had been used to make marks fluorescent.

8.2.6 HO SRDB also conducted pseudo-operational trials in 1990 [35], looking at the numbers of marks developed on batches of brown and white envelopes using DFO, ninhydrin and the DFO-ninhydrin sequence. Articles were examined visually and then using fluorescence examination

to enhance the DFO marks. The results of this exercise are tabulated below.

Visible examination				
	Ninhydrin		**DFO**	
	Brown	White	Brown	White
Articles	93	93	93	93
Fingerprints	18	24	6	16
Articles with fingerprints	11	14	6	11
% Articles with fingerprints	12	15	6	12

Fluorescence				
	Ninhydrin		**DFO**	
	Brown	White	Brown	White
Articles	93	93	93	93
Fingerprints	19	24	60	91
Articles with fingerprints	12	14	33	50
% Articles with fingerprints	13	15	35	54

Ninhydrin after DFO				
	New fingerprints		**Overall**	
	Brown	White	Brown	White
Articles	93	93	93	93
Fingerprints	9	10	15	26
Articles with fingerprints	7	8	12	16
% Articles with fingerprints	8	9	13	17

Results obtained from pseudo-operational trial on batches of envelopes.

8.2.7 Hardwick *et al.* [15] also carried out trials at PSDB in the early 1990s, comparing the original formulation issued by Pounds *et. al*. [7] with revisions to the process suggested by PSDB, including reductions in the amount of DFO, single dipping and increasing the heat treatment time to 20 minutes. The study looked at 200 cheques, 100 from each of two banks, divided into two sets with 50 cheques from each bank. In this trial, both formulations developed just over 200 prints with >8 points ridge detail and so the reduction in DFO (and therefore in the cost of the formulation) was not felt to be detrimental to performance and was

recommended operationally. Subsequent treatment of these exhibits with ninhydrin developed an additional 10% of marks.

8.2.8 A direct comparison of the effectiveness of ninhydrin and the revised DFO formulation was also carried out. This study looked at 300 cheques, 100 from each of three banks, divided into batches containing 50 cheques from each bank. In this study DFO gave 60% more fingerprints than ninhydrin, in accordance with all previous studies.

8.2.9 All the studies above utilised DFO and ninhydrin formulations based on CFC113. As this solvent was being withdrawn from operational use, operational trials were conducted to compare the effectiveness of the replacement solvent formulations with CFC113, also to compare the effectiveness of DFO with 1,2 indandione, a new reagent being proposed as an alternative one-step fluorescent treatment for porous surfaces (see Chapter 5.7, 1,2 Indandione for further details).

8.2.10 Merrick *et al.* [21] carried out an operational trial at West Midlands Police in conjunction with PSDB. This was carried out over 7 weeks, examining over 650 articles at an average of 2.26 articles per case and counting fingerprints containing >8 points. The trial compared the CFC113 DFO formulation, the DFO formulations based on HFC4310mee and HFE7100 described in the section above, and a 1,2 indandione formulation based on HFE7100. The results are summarised in the tables below.

Formulation		**Week**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
DFO (CFC)	Prints	86	91	109	132	156	201	214
	Cases	67						
DFO (HFC)	Prints	46	59	76	99	104	158	171
	Cases	66						
DFO (HFE)	Prints	93	97	130	144	174	213	218
	Cases	70						
IND (HFE)	Prints	70	89	92	105	116	149	164
	Cases	68						

Cumulative number of identifiable fingerprints developed with 1,8-diazafluoren-9-one and 1,2 indandione formulations, and total number of cases processed.

Formulation	**Week**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
DFO (CFC)	69.6	61.3	61.5	59.2	57.9	61.5	59.7
DFO (HFC)	56.0	60.6	61.0	58.8	55.2	59.1	59.7
DFO (HFE)	78.3	71.0	69.2	65.3	63.2	66.2	62.5
IND (HFE)	52.4	51.6	46.5	49.0	49.1	55.4	54.2

Cumulative proportion of cases producing identifiable fingerprints.

8.2.11 The results showed that the HFE7100-based formulation gave equivalent, if not better, performance to the CFC113 formulation and this was therefore recommended for operational use by PSDB.

8.2.12 A similar trial was carried out by the Royal Canadian Mounted Police (RCMP) [36], assessing the HOSDB DFO formulation based on HFE7100, an alternative DFO formulation based on HFE7100 but without *trans*-1,2-dichloroethylene, and a 1,2 indandione formulation based on HFE7100.

8.2.13 Preliminary trials were conducted on 80 cheques, which indicated that the HOSDB formulation gave the best results. The study then proceeded to an operational field trial, the interim results of which are summarised below:

DFO (alternative HFE7100 formulation): 303 exhibits, 66 identifiable marks;
DFO (HOSDB HFE7100 formulation): 440 exhibits, 126 identifiable marks;
1,2 indandione (HFE7100-based):165 exhibits, 7 identifiable marks.

8.2.14 The PSDB DFO formulation was therefore adopted by RCMP for operational work.

8.2.15 More recently there have been several papers reporting reformulations of 1,2 indandione to incorporate zinc salts as an integral constituent of the dip solution rather than as a post-treatment. Research has been conducted to compare the effectiveness of these revised formulations with DFO [30-32]. To some extent the results of these have been conflicting, with some researchers [30, 32] finding 1,2 indandione performing better, and others [31] finding DFO to give marginally better performance. Further refinements have since been made to the 1,2 indandione-zinc formulations and indications are that this reagent may now give improved performance over DFO under UK conditions. However, further validation work will be required to demonstrate this, and the overall impact of replacing DFO with 1,2 indandione on the total number of marks recovered during sequential processing will need to be assessed.

8.2.16 Another recent pseudo-operational trial that has been conducted by HOSDB has been the comparison of DFO, ninhydrin and 4-dimethylaminocinnamaldehyde (DMAC) for the development of marks on thermal receipts [37]. In this study DFO was found to significantly outperform the other two processes, yielding almost twice the number of marks. This study is more fully reported in Chapter 5.2, 4-Dimethylaminocinnamaldehyde (DMAC).

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3.4 Ninhydrin

1. History

1.1 Ninhydrin was first synthesised by Ruhemann in 1910, and soon after this the development of a purple (‘dark blue’) reaction product was observed between the new compound and amino acids and proteins [1]. This reaction was further investigated by Adberhalden and Schmidt [2]; they tested a large number of compounds, both singly and in combination, in terms of the reaction products formed with ninhydrin. The purple reaction product was observed to form with proteins and polypeptides. Adberhalden and Schmidt also investigated the reactions with amino acids and different types of body fluid, noting that purple reaction products could be formed with sweat [3], and this could contaminate analyses unless it was ensured that reaction vessels, stirrers, etc. were clean.

1.2 The sensitivity of ninhydrin for proteins and amino acids resulted in its use for detection of amino acids by chromatography techniques and for quantitative measurements of amino acid contents. The first published suggestion that ninhydrin could be used for fingerprint detection was made by Oden and von Hofsten in 1954 [4] based on observations of fingerprints accidentally developed on paper items. They proposed a solution of ninhydrin dissolved in acetone and tested it on fingerprints deposited on a range of different types of paper. Oden later patented a refined formulation [5] that also included acetic acid and this soon became adopted worldwide as an alternative to the iodine and silver nitrate techniques then in use for detection of fingerprints on paper.

1.3 In 1969 Crown [6] proposed an alternative ninhydrin formulation based on petroleum ether solvent in place of acetone, with minor additions of methanol. Diethyl ether was also investigated as a solvent, but this was regarded as too volatile for spraying on documents because of the flammable atmospheres created. The reason for using these non-polar solvents was to minimise ink run on the documents being treated with ninhydrin, thus preserving evidence for subsequent document examination. Crown observed that the reaction could be accelerated by heating, but did not recommend temperatures in excess of 100ºC because this caused unwanted background reactions that could obscure prints. Crown also reported improved results when placing bowls of water in treatment ovens to produce more humid atmospheres.

1.4 Lesk [7] reported the use of both acetone and petroleum ether-based formulations in combination, with petroleum ether being used in most cases to minimise ink running. However, it was also observed that occasionally additional marks could be developed by retreatment of the article in the acetone-based formulation.

1.5 In the early 1970s the Police Scientific Development Branch (PSDB) contracted researchers at the Atomic Weapons Research Establishment

(AWRE) at Aldermaston to investigate improvements to chemical reagents then in use for fingerprint development. Ninhydrin was investigated as part of this contract. An initial observation was that the formulation developed by Crown [6] could be improved in sensitivity by the addition of acetic acid. In 1971/2 a police officer from the Kent constabulary contacted PSDB and asked whether one of the chlorofluorocarbon (CFC) solvents such as 1,1,2-trifluorotrichloroethane (CFC113) could be used as a safe solvent for ninhydrin. His idea was passed on to the AWRE team and as a result the so-called non-flammable, or new formulation, ninhydrin (NFN) was developed by Morris and Goode [8]. This solvent had the additional benefits that it minimised ink running when used to treat documents [8].

1.6 At about the same time Linde [9] observed that processing exhibits treated with ninhydrin in a high humidity oven at 60ºC gave superior results to dry treatment at 100ºC. At first this was not universally accepted. In comparisons of oven processing and treatment with a steam iron, Morris and Gray [10] noted that oven treatment was superior and specifically stated that the steam setting of the iron should not be used during processing. Despite this advice, and although not approved of by PSDB, a number of police forces, in particular Avon and Somerset, regularly used steam irons to speed up the ninhydrin reaction. The recommended procedure at the time was to put treated articles in a brown envelope and wait for three weeks, and the use of a steam iron gave results in a significantly shorter time. Jones and Pounds [11] reinforced the earlier work of Linde, presenting the beneficial effects of steaming exhibits for 10–15 seconds prior to heating in an oven at 80ºC for 3 minutes. Subsequent work by PSDB confirmed the importance of humidity for the optimum development of marks and found the optimum to be around 65% relative humidity [12]. PSDB worked with Gallenkamp around 1980/81 to modify one of their production humidity cabinets to provide rapid humidification for the ninhydrin process. Subsequently these were installed in all UK police forces.

1.7 Ways of adapting the ninhydrin reaction product began to be considered. The contrast between the developed mark and the background could be improved by using coloured filters, and green filters to enhance the purple mark were in common use by police photographers in the 1970s. Contrast between the fingerprint and the background could be improved by other means, and Morris found that post-treatment of the purple reaction product with different metal salts resulted in the formation of complexes with different colours, including blue, red, pink and orange [13]. The best results were obtained with the salts of zinc, cadmium and lead.

1.8 It was also found that marks developed using ninhydrin could be enhanced by illuminating the exhibit using light of a wavelength where the Ruhemann's purple product absorbed and the background fluoresced [14]. This was followed by the discovery that some of the coloured reaction products produced by treating purple ninhydrin marks

using metal salts were fluorescent [15] and could be revealed using an argon ion laser [15] or an appropriately filtered xenon arc lamp [16]. It was also shown that the intensity of this fluorescence could be increased by cooling the exhibit to low temperatures using liquid nitrogen [16]. Subsequent researchers also investigated a wider range of metal compounds for complexation [17, 18] and concluded that zinc and cadmium gave products with the optimum fluorescence. It was also suggested that moisture and elevated temperature during processing were necessary to achieve the optimum fluorescence from the reaction products [19,20]. Rare earth elements were also proposed for metal complexation with ninhydrin, the long fluorescence decay time for toning elements such as Europium offering potential for use with techniques such as time-resolved imaging to reduce background fluorescence [21].

1.9 Researchers also began to synthesise analogues of ninhydrin, either to change the colour of the principal reaction product with amino acids, e.g. benzo(f)ninhydrin [11,22], or to give reaction products that gave greater fluorescence intensity when treated with metal salts, e.g. 5-methoxyninhydrin. Some of these analogues are covered in greater detail in Chapter 5.8, Ninhydrin analogues, but at the present time (2011) none have displaced ninhydrin in regular operational use.

1.10 The principal driver for further changes to the ninhydrin formulation arose as a consequence of the Montreal Protocols in 1987 banning the use of ozone depleting solvents, including CFCs. Researchers worldwide began investigating alternatives to the non-flammable ninhydrin formulation. In 1992 Jungbluth [23] proposed the use of a mixture of hydrochlorofluorocarbon (HCFC) and hydrochlorocarbon (HCC) solvents as a substitute to CFC113 in both ninhydrin and 1,8-diazafluoren-9-one (DFO) formulations. Lennard and Mazella [24] proposed reverting to a formulation based on petroleum ether with additions of methanol, acetic acid and ethyl acetate and reported that it gave superior performance to the CFC113 formulation. Watling and Smith [25] suggested using heptane as the primary solvent. However, both formulations presented the issue of solvent flammability and ideally a non-flammable formulation with equivalent (or better) performance to the CFC113-based system was required.

1.11 PSDB alerted the UK police forces to the potential issues that would be caused by phasing out CFCs, and began a comprehensive programme to identify replacement solvent systems. PSDB also investigated a range of alternative, solvent-less carrier systems including supercritical carbon dioxide (CO_2) [26]. The extensive CFC solvent replacement programme was conducted over 3 years and evaluated approximately 300 formulations to an initial stage, with several formulations taken through substantial operational trials. This programme considered the previously published formulations based on heptane and HCFC solvents, refining these formulations and comparing them with CFC113 [27]. A heptane-based formulation giving good results for fingerprint development was produced but was not considered safe to use because of the flammable

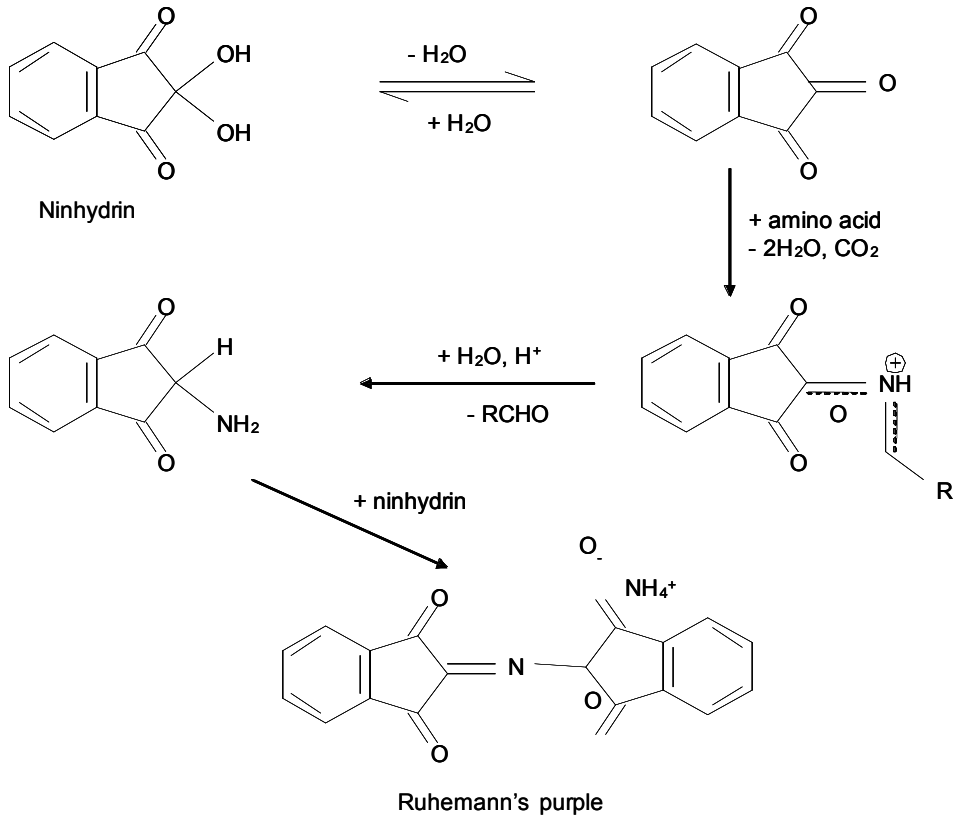
atmospheres generated around articles that were apparently dry, and the large quantities of solvent that would need to be evaporated from ninhydrin-treated articles. Adoption of the heptane-based formulation would have required specially adapted cabinets and laboratories for safe working, and this was considered impractical. HCFC-based formulations caused excessive ink running and were not considered further.

1.12 The next classes of solvents investigated were hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) and it was found that excellent results could be obtained from formulations based on two solvents, 2,3-dihydrodecafluoropentane (HFC4310mee) and 1-methoxynonafluorobutane (HFE7100) [28]. These out-performed the CFC113-based formulation in laboratory trials and therefore the evaluation proceeded to a full operational trial of all three formulations [29]. The results of this two-month study indicated that the HFE7100-based formulation gave the best results overall and this was recommended for operational use in the UK. Petruncio [30] independently reported results of a comparative study between HFC4310mee-, HFE7100- and petroleum ether-based formulations and found the HFC- and HFE-based systems gave better results in terms of the number of marks developed and reductions in ink run damage caused to treated documents.

1.13 As a consequence of this development work, the HFE7100-based formulation is currently (2011) the only one recommended for operational use by CAST, although work to investigate possible alternative solvents is ongoing.

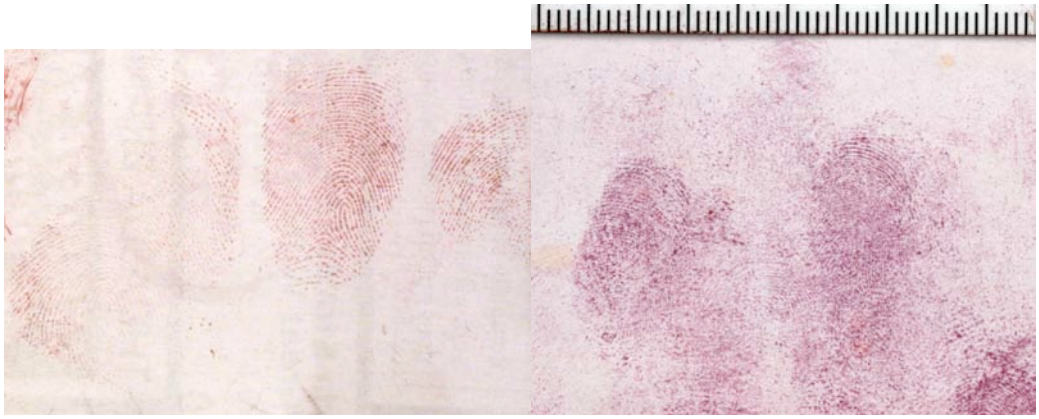
2. Theory

2.1 Many comprehensive studies of the reaction mechanisms, colour formation and kinetics of reaction have been carried out and published for the formation of Ruhemann's purple by reactions of ninhydrin with amino acids. These include the studies by McCaldin in 1960 [31]; Friedman and Sigel in 1966; Friedman and Williams (1974 [32,33]; Yuferov in 1971; [34] and most recently by Joullie *et al*.in 1991 [35]. Some of these papers propose detailed reaction mechanisms for ninhydrin with individual amino acids under different conditions, and seek to identify all intermediate forms that arise during the reaction. The reaction mechanism outlined below is typical of the generally accepted reaction pathway between ninhydrin and amino acids. For amino acids it is the amine group that ninhydrin is reacting with to form Ruhemann's purple, whereas the anomalous reactions that occur with other compounds do not proceed all the way to the formation of the purple product.

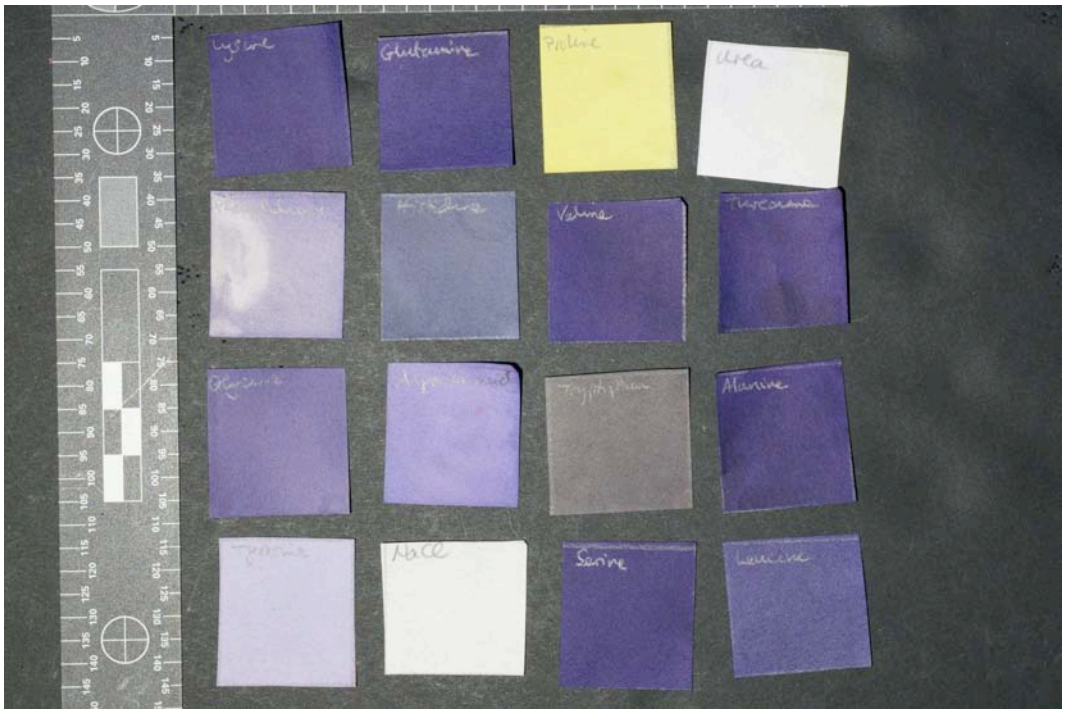


Generally accepted reaction pathway between ninhydrin and amino acids to form Ruhemann's purple.

2.2 The reaction products formed between ninhydrin and different amino acids are not all purple and the colour of the developed fingerprint can vary from nearly red to deep violet, depending on the composition of the fingerprint. Some examples are shown below. Another contributing factor to this difference in colour may be that the reaction above may not have proceeded to completion. There is a coloured intermediate (an imine or an aldimine) in the full ninhydrin reaction scheme that is also coloured, and the reaction may stop at this point if the acidity (pH) is not high enough. A pH of less than five is required for the reaction to proceed past the intermediate product, although if the pH is less than two the reaction proceeds to formation of the colourless hydrindantin product instead of to Ruhemann's purple. The colour of the intermediate imine compound is dependent on the R groups attached to the active species.

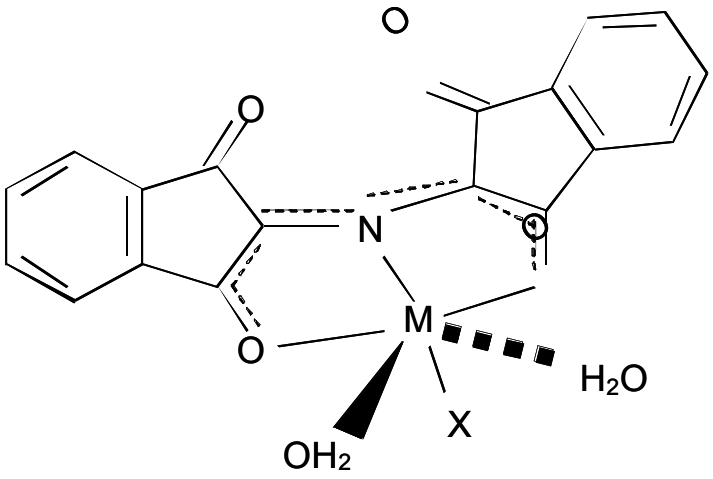


Fingerprints of differing colours developed by treatment using ninhydrin.



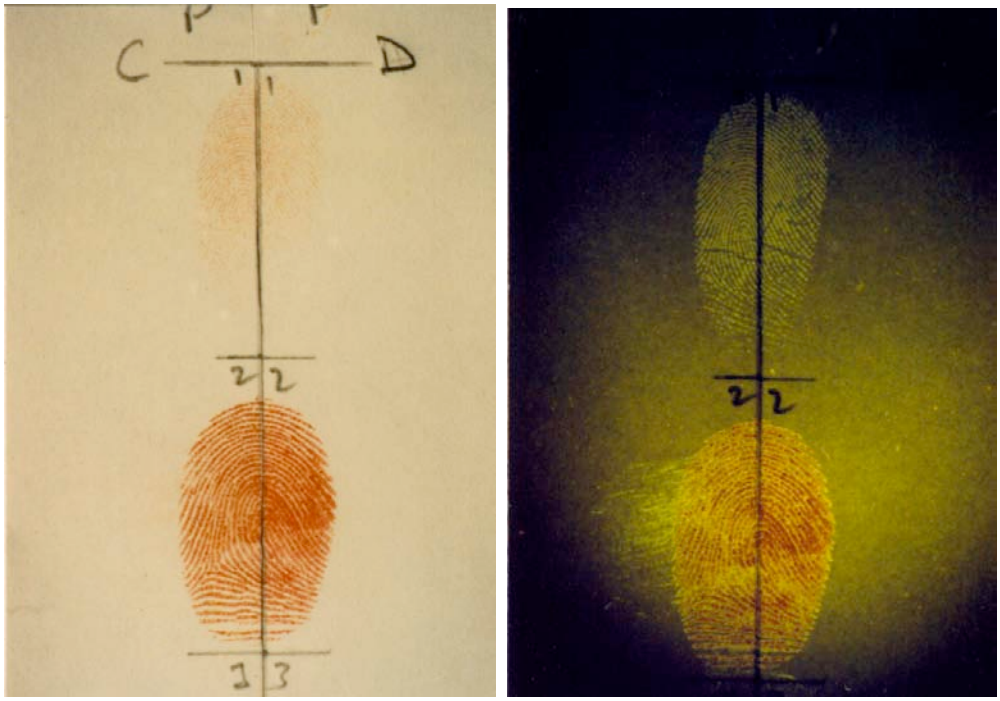
Reaction products formed between ninhydrin and 0.1M solutions of amino acids and other fingerprint constituents.

2.3 Studies have also shown that the subsequent complexation reaction with metal salts gives a complex of the generic structure below.



Complex formed between metal salt and Ruhemann's purple, in some cases giving rise to colour changes and fluorescence.

2.4 In the case of zinc and cadmium, the complexes formed are fluorescent in nature. The pictures below illustrate the visible appearance of marks treated with zinc chloride toning solution and the same marks when viewed using fluorescence examination. Studies by Australian researchers [20] identified two different coloured zinc/Ruhemann's purple complexes, one appearing orange and the other magenta/pink. The magenta/pink complex was found to be more fluorescent than the orange one, the differences being attributed to the amount of water bound into the complex. The importance of water in the formation of the more fluorescent complex makes humidification an important stage in the toning process.



a) b)

Ninhydrin marks toned with zinc chloride solution a) viewed under room lighting and b) viewed using fluorescence examination.

2.5 It should also be noted that ninhydrin does not only react with amino acids. A wide range of coloured reaction products can also be obtained from different amine-containing substances. Dent [36] carried out an extensive study in 1947 of 60 different compounds that reacted with ninhydrin, recording both colour of the reaction product and their natural occurrence. Although these substances react with ninhydrin the reactions cannot proceed to the Ruhemann's purple product because they do not have the structure to react beyond the coloured intermediate compounds. Cashman *et al.* [37] and Dutt and Poh [38] also report the use of ninhydrin for the detection of phenethylamines and other basic drugs, and some of these substances or their metabolites may occur in fingerprint residues. As a consequence, the reaction mechanism given above may not be the only one operating and ninhydrin may detect additional fingerprints that do not contain amino acids.

3. CAST processes

3.1 The process currently (2011) recommended by HOSDB involves the initial preparation of a concentrated solution, followed by the preparation of a working solution when required. This is because the working solution only has a limited stability in air before precipitation occurs.

3.2 The concentrated solution is produced by weighing 25g of ninhydrin and stirring 225mL of absolute ethanol into it to form a slurry. To this should

be added 10mL of ethyl acetate and 25mL of acetic acid to form a clear yellow concentrated solution, which should be stored in a cupboard.

3.3 To produce the working solution, 52mL of concentrated solution should be measured out and 1 litre of HFE7100 added to it. This solution is then poured into a shallow tray and exhibits either pulled through it with forceps or immersed for a maximum of five seconds. Treated articles are then allowed to dry on a sheet of cardboard before being placed into a humidity-controlled oven at 80ºC and 65% relative humidity for a time that will depend on the particular conditions during loading of the oven, but that will typically be between five and seven minutes. Developed fingerprints can be photographed immediately but further marks will continue for up to 2 weeks (although additional marks have still been observed to develop after 13 weeks in some cases) during which exhibits should ideally be kept in the dark. The time marks take to develop is dependent on the surface and may be related to the pH because more acidic papers, such as cheques, generally develop more marks.

3.4 The role of the constituents in the CAST formulation can be identified as follows.

3.5 Ninhydrin is the principal active component and reveals fingerprints by means of the (primarily) purple product formed in its reactions with amino acids and proteins. It has limited solubility in the main carrier solvent and is present in as high a concentration as possible without making the working solution rapidly unstable.

3.6 Ethanol is required to ensure solubility of ninhydrin in the carrier solvent.

3.7 Ethyl acetate is added as a co-solvent to inhibit the esterification reaction by shifting its equilibrium towards formation of ethanol and acetic acid, thus preventing water droplet production during processing, which may diffuse fingerprint ridges.

3.8 Acetic acid and water are required to catalyse the reaction of ninhydrin with amino acids, the water being supplied in a controlled manner in the humidity oven. The acetic acid content is kept as low as possible to minimise any ink diffusion on documents being treated, but there is also a balance to be achieved in having sufficient acid present to ensure the reaction proceeds to the formation of Ruhemann's purple. This is of particular relevance for alkaline paper types, such as magazine pages, which have high filler contents and may remove the hydrogen ions provided by the acetic acid [27].

3.9 HFE7100 is the main carrier solvent for ninhydrin and meets the criteria of being non-toxic, non-flammable and causing minimal damage to documentary evidence. It is, however, expensive and the use of specially designed shallow dipping trays is recommended to minimise the volumes of solution required.

3.10 Heating accelerates the reaction and the development of fingerprints, but temperatures in excess of 100ºC may cause unwanted background reactions and possibly damage to the paper.

3.11 PSDB carried out studies into the effect of humidity on processing in the late 1980s/early 1990s [12] which indicated that settings producing 65% relative humidity in the treatment areas of the oven gave the best results. These results are summarised in section 8 below.

3.12 If toning is to be carried out after development of marks, CAST recommends the use of a zinc chloride-based toning solution, produced by mixing 50mL of ethanol, 10mL of propan-2-ol, 10mL of acetic acid and then stirring in 6g of zinc chloride. To this is added 200mL of HFE7100 (used as a direct replacement for the CFC113 in the original formulation), stirring to produce a clear solution. This solution is then sprayed lightly over the marks and they are retreated in the humidity oven at 80ºC and 65% relative humidity.

Zinc chloride solution being applied to an exhibit.

3.13 PSDB also carried out studies into the effectiveness of zinc toning [39] and confirmed the observation that humidity was required to accelerate the complexation reaction with the metal salt [20]. The approximate times for the formation of the orange complex are given below.

Relative humidity	42	47	56	57	60	78	83
Development time	> 1 hr	> 1 hr	< 5 mins	< 5 mins	< 5 mins	< 1 min	< 1 min

Approximate development times for different treatment temperatures.

3.14 Zinc chloride is preferred over cadmium salts for producing fluorescent marks because of the toxicity issues associated with the use of cadmium.

4. Critical issues

4.1 In common with many of the chemical development processes there are several important issues to consider when using ninhydrin.

4.2 The reaction will proceed under conditions of room temperature and humidity, but will be considerably accelerated and enhanced by the use of elevated temperature (80°C) and humidity (65%). Treatment at temperatures over 100°C may cause excessive background development. Design of the humidity oven is critical. Since the exposure time required is relatively brief, about 3 minutes, it is essential that the humidification system provides a substantial quantity of water vapour immediately after the door is closed otherwise the true exposure time will be unknown. Many humidity cabinet designs are constructed for long term environmental testing and do not have this required rapid umidity and temperature recovery time.

4.3 Marks developed using ninhydrin may begin to fade and should be imaged as soon as possible after development. Conversely, marks may continue to develop on items treated using ninhydrin for several days afterwards, and items should be re-examined after two weeks.

4.4 Cloudy solutions or solutions that have separated into oily droplets should not be used to treat articles and must be discarded.

4.5 Ninhydrin cannot be used to treat articles known to have been wetted because the amino acids targeted by the reagent will have been washed away.

5. Application

5.1 Suitable surfaces: Ninhydrin is suitable for use on all porous surfaces including paper, cardboard, raw wood and matt painted walls.

5.2 Ninhydrin is the most widely used process around the world for the development of fingerprints on porous surfaces. This is not because it is the most effective process – DFO and 1,2 indandione will develop higher numbers of marks overall [40,41], but the reason ninhydrin is so widely used is because it develops visible marks that can be quickly and easily captured using a range of equipment (e.g. cameras, scanners, photocopiers). It is thus well suited to applications in volume crime, where it is necessary to process large numbers of exhibits rapidly and it is considered that DFO treatment and subsequent fluorescence

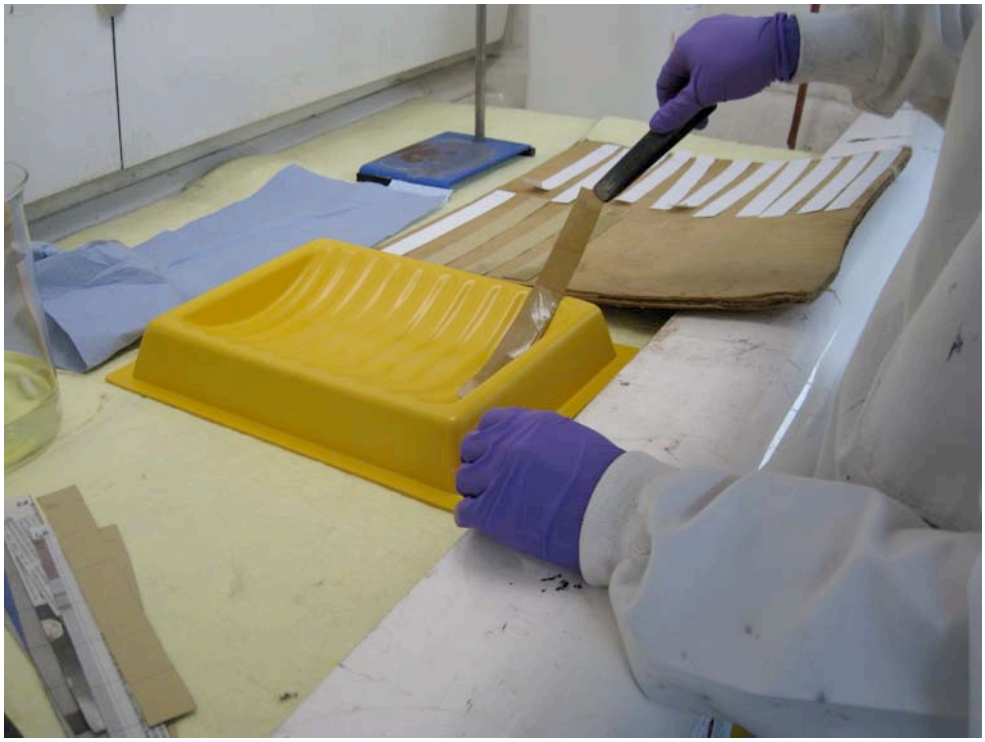
examination is too time-consuming. However, caution should be exercised if ninhydrin is to be used in this way because a) it is less effective than other processes and b) marks continue to develop up to two weeks after treatment. Potentially identifiable marks will missed for these reasons if ninhydrin is used as the sole process.

5.3 Ninhydrin is best suited to be used as part of a sequential processing regime for porous exhibits. Although it is not as effective as DFO, it will regularly develop additional marks if used sequentially after it because the DFO reaction with amino acids does not proceed to completion and some residue will be left to react with ninhydrin. In addition, ninhydrin may react with some non-amino acid compounds that may be present in fingerprints, which are not targeted by DFO. Use of ninhydrin does not preclude subsequent treatment of the exhibit with physical developer.

5.4 Ninhydrin will also react with proteins and can be used for the enhancement of marks in blood on porous surfaces. It will not be possible to determine whether a mark is actually in blood by this method alone, but ninhydrin can be used as a sensitive enhancement reagent if blood is known to be present. The application of ninhydrin for the enhancement of marks in blood has not been found to be detrimental to the subsequent recovery of DNA [42, 43].

5.5 If ninhydrin has been applied, it is not possible to go back and retreat an exhibit using DFO so if a mark has been developed on a surface where it may subsequently benefit by converting the mark to a fluorescent product the zinc toning process can be applied. Examples where this may be relevant are banknotes treated by ninhydrin, where parts of the developed mark are obscured by patterned backgrounds. However, previous work by CAST [39] indicates that zinc toning is only truly effective on predominantly white backgrounds that do not fluoresce. Cooling the marks to liquid nitrogen temperatures was sometimes also required to optimise the fluorescence viewed.

5.6 Ninhydrin is a versatile process and can be applied both in a laboratory and at scenes of crime. In a laboratory thin paper exhibits can be drawn through a shallow tray and allowed to dry before processing in a humidity-controlled oven. A recommended specification for a humidity oven suitable for developing marks on articles treated with ninhydrin is given in the *Manual of Fingerprint Development Techniques* [44].



Use of a shallow dipping tray for treatment of paper items with ninhydrin.

5.7 Small paper items should be placed into the oven and treated on sheets of cardboard. This minimises the time taken to load the oven and also avoids direct contact with any condensation that may have formed on the shelves. Treatment time for exhibits will vary according to the time taken for the oven to recover the temperature and humidity levels once the door is opened to insert exhibits and then closed. This can be recorded for a particular oven, and the treatment time used will be the recovery time plus two minutes. This typically results in a treatment time of between four and seven minutes. It is recommended that the oven parameters are regularly checked to ensure that the temperature and humidity values are being displayed accurately, and that the wick in the oven is checked before each run to ensure that it is moist.

5.8 For larger articles that can be fitted into the humidity oven but cannot be drawn through the dip bath, the ninhydrin solution can be applied with a soft brush and the exhibit allowed to dry before treating it in the oven. If articles are particularly dense (e.g. cardboard, wood or plasterboard), they should be heated before being placed in the humidity oven to ensure that the entire exhibit reaches the required reaction temperature and to prevent a thin layer of condensation forming on the surface. The formation of such a layer may have the detrimental effect of diffusing the amino acids in the latent fingerprints. A pre-heating stage in a dry oven at 80°C for 1 hour is recommended.

5.9 Ninhydrin solution can be used at scenes, again using a soft brush to apply it to the surface being treated. The marks produced in this way may require time (up to two weeks) to develop. Development rate can be

increased by raising the temperature in the room and increasing humidity if possible. Ninhydrin should never be spray applied at scenes; spray application is less effective and the solvent, although not toxic or flammable, may rapidly displace oxygen if used in this way.

5.10 Ninhydrin solution will keep for 12 months if stored at room temperature, although any solution appearing cloudy should be discarded. Precipitation of ninhydrin from the working solution will occur with time after exposure to air. This is attributed to the fact that as the HFE7100 evaporates it lowers the temperature of the solution to a point where ninhydrin precipitates. As a consequence, the solution should only be poured out immediately before treating the articles. The ninhydrin working solution should be discarded after use.

5.11 Articles to be treated with ninhydrin should not be stored in high humidity environments (e.g. in non-porous bags with other damp articles) as this will cause diffusion of amino acids. After treatment articles should be kept in the dark because developed marks may fade on exposure to light. For this reason developed marks should be photographed as soon as possible after treatment, but because additional marks may continue to develop the article should be re-examined after ten days.

6. Alternative formulations and processes

6.1 Formulations for standard papers

6.1.1 Many other ninhydrin formulations have been proposed since its first reported use for fingerprint development in 1954. The formulation first used by Oden and von Hofsten [4] in1954 consisted of a 0.4% solution of ninhydrin in acetone. Oden (1957) patented a revised formulation consisting of 0.2% ninhydrin and 4% acetic acid in acetone or diethyl ether. These formulations would not be recommended by CAST because of the ink running that would potentially be caused by the solvents, combined with their high flammability.

6.1.2 The formulation proposed by Crown in 1969 [6] consisted of 7.5g ninhydrin in 40mL methanol, then the addition of 960mL of petroleum ether. The main purpose of this formulation was to reduce the damage caused to documents by the acetone solvent. The formulation satisfied these criteria, but again is based on a highly flammable solvent and would not be recommended by CAST. The absence of acidity in the formulation would also reduce effectiveness.

6.1.3 The non-flammable ninhydrin (NFN) formulation developed by AWRE under contract to CAST in the early 1970s consisted of 25g ninhydrin, 50mL acetic acid, and 100mLethanol mixed to form a stock solution. Subsequently, 30mL of stock solution was added to 1 litre of CFC113 to give a working solution. This equates to 5g ninhydrin, 10mL acetic acid, 20mL ethanol, and 1 litre CFC113 in the working solution. This was the

formulation published in the first edition of the *Manual of Fingerprint Development Techniques* [45] and continued to be recommended until 2002, when it was replaced by the HFE7100 formulation. It would not now be used because the use of CFC113 is banned under the Montreal Protocol.

6.1.4 Studies by PSDB indicated that supercritical CO_2 could be used as a solvent for ninhydrin [26], with the advantage that the solvent caused minimal damage to the document being treated. However, specially built reactors were required to produce the supercritical CO_2 and it was considered unlikely that these would produce sufficient material for the processing of large numbers of exhibits.

6.1.5 Another formulation that is in operational use is the formulation based on petroleum ether solvent proposed by Lennard and Mazella [24]. This is formulated by dissolving 4g of ninhydrin in 20mL methanol, adding 10mL of acetic acid and 70mL of ethyl acetate, then adding 900mL of petroleum ether. CAST would not recommend this formulation because of the flammability of the solvent, but other researchers have indicated that similar ninhydrin formulations based on petroleum ether also give inferior results in terms of fingerprints developed and the effect on the documents being treated.

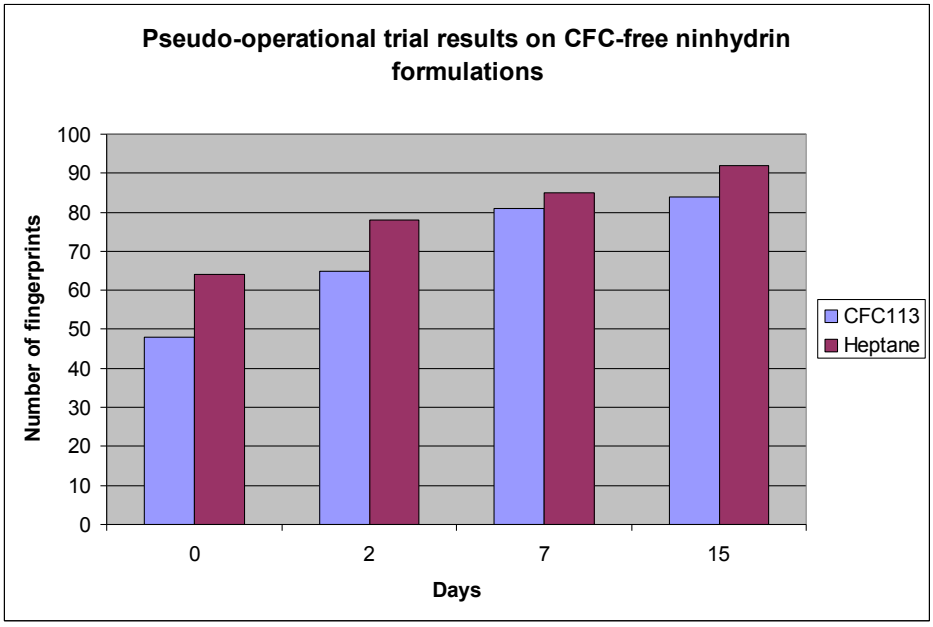
6.1.6 In the comparative study carried out by Petruncio [30], a ninhydrin formulation consisting of 5g ninhydrin, 20mL methanol, 10mL acetic acid and 1 litre petroleum ether was trialled against the PSDB formulations based on HFE7100 and HFC4310mee. The study compared ink run and contrast and clarity of latent prints, and produced the results below.

	HFE7100 better	**Equal**	**Pet. ether better**
Latent print quality	47.8%	45.6%	6.7%
Ink run	33.3%	66.7%	0%

	HFC4310 better	**Equal**	**Pet. ether better**
Latent print quality	48.9%	45.6%	5.6%
Ink run	41.7%	58.3%	0%

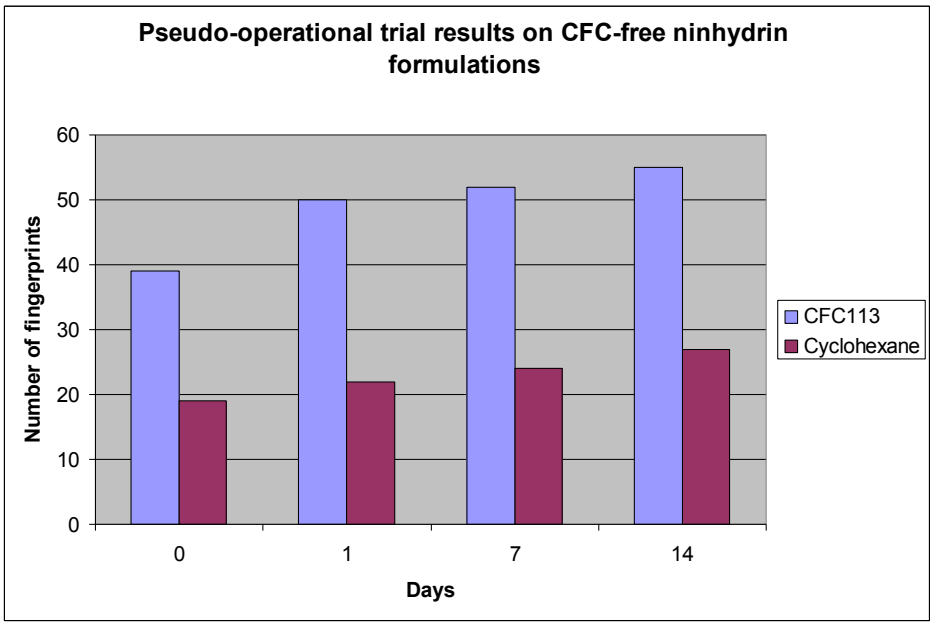
Comparison of the effectiveness of HFE, HFC and petroleum ether-based ninhydrin formulations.

6.1.7 Other comparative trials conducted by PSDB in the search for a CFC113 replacement used the heptane-based formulation proposed by Watling [25] as a starting point for an optimised heptane system [27]. This comprised 5g ninhydrin, 75mL ethanol, 25mL ethyl acetate, 3mL acetic acid and 1 litre heptane, and performed well against the CFC113 formulation. However, at the time it was not recommended by PSDB because of its high flammability.



Comparative test results on batches of 75 cheques for different ninhydrin formulations.

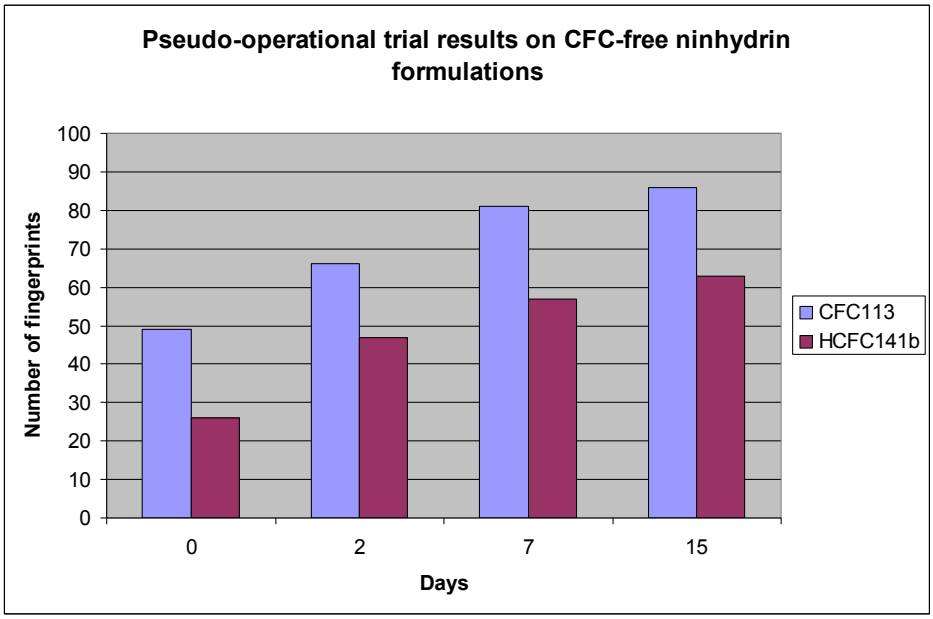
6.1.8A cyclohexane-based solution was also developed, containing 5g ninhydrin, 20mL ethanol, 10mL propan-2-ol, 10mL acetic acid and 1 litre cyclohexane. In trials, this was significantly worse than the CFC113 formulation and was not recommended.



Comparative test results on batches of 75 cheques for different ninhydrin formulations.

6.1.9The final class of solvents assessed in the initial phase of solvent replacement studies were the HCFCs [27] and the following formulation was identified for trial: 5g ninhydrin, 15mL ethanol, 5mL ethyl acetate,

10mL acetic acid, 1 litre of HCFC141b. In comparative trials this did not perform as well as the CFC113 system, caused more ink running and there were concerns at the time that HCFCs would also ultimately be banned. As a result, the formulation was not pursued further.



Comparative test results on batches of 75 cheques for different ninhydrin formulations.

6.1.10 Although effective, the cost of the HFE7100 solvent makes the volume use of ninhydrin expensive and if cheaper, similarly effective, alternatives were to be identified this would assist police forces in cost savings. CAST has recently been assisting in research conducted by police laboratory staff to evaluate novel, cheaper solvent systems and further work is anticipated. The system showing most promise to date is Asahiklin AE-3000, produced by the Asahi Glass Company in Japan [46]. This was originally projected to be priced around 30% less than HFE7100, but more recent estimates by the supplier indicate that there will be little, if any, cost savings.

6.2 Formulations for thermal papers

6.2.1 A modified formulation has been proposed by CAST for the treatment of thermal receipts [47]. When thermal receipts are treated with ninhydrin they blacken due to reaction between acetic acid and the thermal ink layer. Blackening also occurs due to the heat applied to the exhibit in the oven used to develop marks. To counteract this, CAST carried out trials and devised a formulation with an additional 45mL of ethanol added per litre. This dissolves away the thermal ink layer and significantly reduces subsequent blackening. The thermal paper is retained in the dip bath until all the black deposit is removed from the surface of the paper, then placed into the oven. In practice, this did reduce the problems associated with blackening of thermal receipts but as ink compositions changed it

did not prove possible to remove all of the ink layer easily in this way. Pre-dipping the receipt in ethanol until all the text is removed and then allowing it to dry prior to dipping in a solution of the standard formulation has proved more effective [48].

6.2.2 Two other ninhydrin formulations have been proposed for the development of fingerprints on thermal papers. In the 'Nin-Dry' process proposed by McMahon [49], 30–50g of ninhydrin is dissolved in 1.5 litres of acetone and this solution is used to impregnate sheets of paper by soaking the paper and then letting it dry in a vented fume cupboard. The document to be treated is placed between two impregnated sheets of paper in a sealed plastic bag and left for three to seven days. If faster development is required, the sandwich of document and impregnated paper sheets can be covered in a moist towel and an iron used to apply gentle heat and humidity.

6.2.3 The final process is the commercially available 'ThermaNin' product marketed by BVDA, which consists of a hemiketal of ninhydrin with the water molecule exchanged for an alcohol. On contact with the water present in paper (or in the atmosphere) ThermaNin converts to ninhydrin The combination of alcohol and the ninhydrin then becomes available for reaction with the fingerprint residues. The working solution suggested by BVDA consists of 4–5g ThermaNin, 5mL propan-2-ol, 15mL ethyl acetate and 980mL of HFE7100 (petroleum ether or heptane may be used as alternatives). Fingerprints are developed by dipping the exhibit in the solution and leaving the exhibit overnight at elevated humidity (~80% relative humidity), at room temperature in the dark. Thermal papers treated in this way retain all printed text while developing the characteristic purple fingerprints. CAST has initiated a comparative trial between ThermaNin and other techniques capable of developing fingerprints and leaving printed text intact [50]. The results of this exercise are summarised in Chapter 5.2, 4-Dimethylaminocinnamaldehyde (DMAC), but ThermaNin performed well, giving results closely equivalent to physical developer. No direct comparison has been conducted between ThermaNin and the standard ninhydrin formulation.

7. Post-treatments

7.1 Post-treatments for ninhydrin can be divided into two main categories: optical techniques that increase the contrast between the ninhydrin mark; and the background and chemical treatments that change the colour and/or fluorescence properties of the mark.

7.2 Marks developed using ninhydrin are non-fluorescent over broad regions of the visible spectrum, and this can be used to make the marks appear dark against a light background where appropriate light sources are used to produce background fluorescence [14].

7.3 The spectral reflectance curve of ninhydrin exhibits two minima in the region of 410nm and 535nm, which may be utilised to enhance the contrast of the mark. By either illuminating the marks with monochromatic light of these wavelengths [51] or using narrow bandpass filters passing these wavelengths in front of the imaging system significantly enhanced the contrast of the ridges that can be obtained. A green (~535 nm) bandpass camera filter is most commonly used for the capture of marks developed using ninhydrin. Alternatively, modern digital imaging systems and processing tools allow digital filtering of the red, blue and green channels to achieve a similar end product.

7.4 The use of metal salt spray treatments to form metal complexes with Ruhemann's purple has been described in sections 2.3, 2.4, 3.12 and 3.13. Originally this was investigated as a means of producing a colour change in the mark although in most cases the colour change was only slight, typically from purple to red, orange or pink, and insufficient to significantly enhance the mark. However, the observation that some of these complexes are also fluorescent has proved more useful as a post-treatment, with the complexes produced using zinc and cadmium giving the most intense fluorescence. For safe, practical purposes, zinc toning is the only chemical post-treatment for ninhydrin recommended by CAST. Cooling of the exhibit enhances the intensity of fluorescence produced and ideally zinc toning should be combined with fluorescence examination with the exhibit cooled to liquid nitrogen temperatures. Fluorescence examination should be carried out using the 468–526 excitation band of a Quaser and a 529nm cut-on long-pass viewing filter.

8. Validation and operational experience

8.1 Laboratory trials

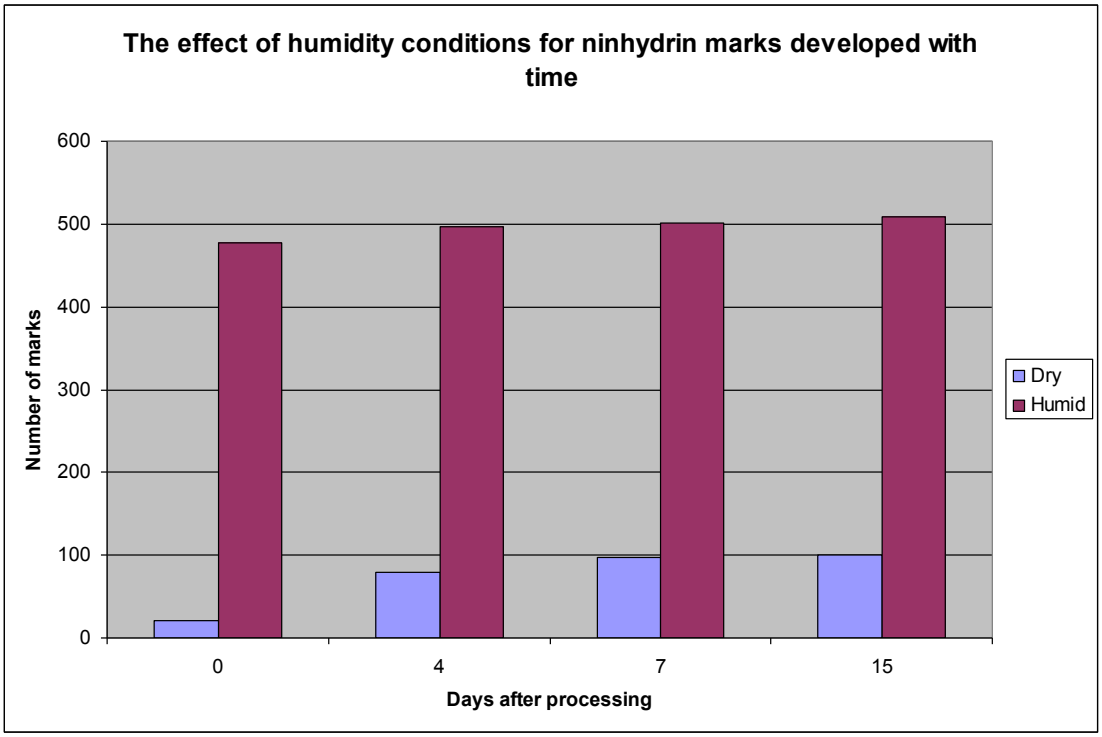
8.1.1 Although laboratory trials were conducted during the initial development of ninhydrin formulations in the mid-1970s, these results are no longer available. It has been found from experience that planted prints rarely give operationally representative results in such trials, typically performing worse than seen on casework [52]. This is possibly because perpetrators of crimes may be under increased stress and sweat more, giving more eccrine prints than seen in the laboratory. As a consequence, development of revised formulations at CAST is usually carried out using small-scale comparative tests until best performing formulations are identified, after which testing proceeds to pseudo-operational trials using realistic items such as bundles of cheques, as can be seen in many of the results reported in this section.

8.1.2 A recent exception to this is precursor work carried out to evaluate possible alternative solvents to HFE7100, which carried out tests on split depletion series deposited on a range of different paper substrates [53]. The two solvents investigated in this study were Asahiklin AE-3000 (1,1,2,2-tetrafluoroethyl-2[2,2-trifluoroethyl ether]) and Lenium (75%

1,1,1,3,3-Pentafluorobutane + 25% 1,1,1,2,2,3,4,5,5,5-Decafluoropentane). The results showed no significant difference between the performance of the three solvents when used for fingerprint development, although the Lenium solvent did cause more ink running on treated documents. Lenium ultimately became unavailable and subsequent pseudo-operational trials focused on the AE-3000 solvent [46].

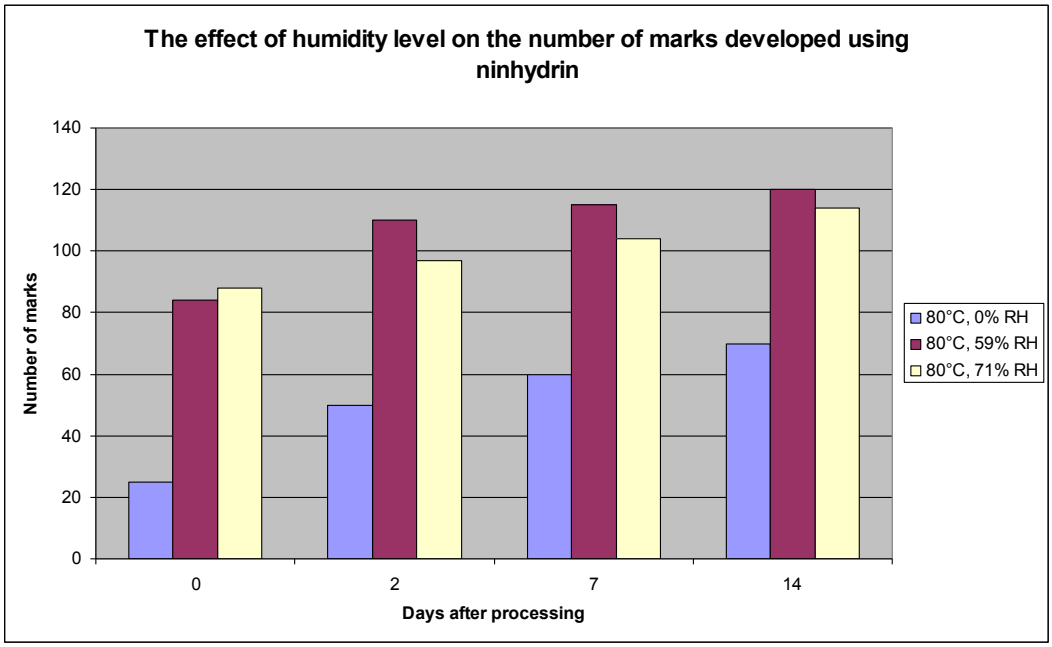
8.2 Pseudo-operational trials and operational experience

8.2.1 An important element in optimising the ninhydrin process was to establish the role of humidity in fingerprint development. Work to investigate this was conducted by HO SRDB, later PSDB in the late-1980s/early-1990s [12]. Initial trials carried out by counting fingerprints developed on 250 cheques representing 77 separate cases clearly demonstrated that humid processing conditions produced up to 5 times more marks, and that these marks developed more quickly.



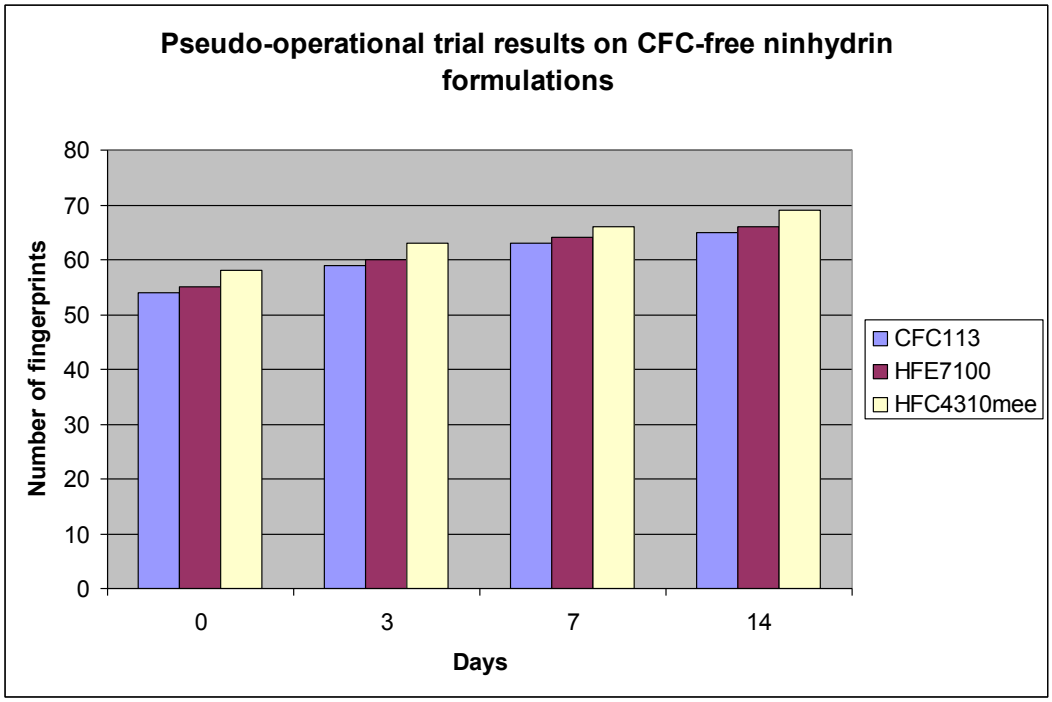
Results of trials carried out on cheques to establish the effect of humidifying exhibits treated with ninhydrin during processing.

8.2.2 Later trials in 1992 refined the humidity conditions required and tests on batches of 100 cheques, 25 from each of 4 banks, indicated that an oven humidity setting of 59% relative humidity gave the best results. This setting actually equates to a higher humidity (65%) in the region where the exhibits are treated, but means that the oven should be set to 59% relative humidity to achieve optimum development, which avoids issues associated with 'overshoot' in the humidification system. This is described in the *Manual of Fingerprint Development Techniques* [44].



Results of trial to refine the optimum humidity level required for development of marks using ninhydrin

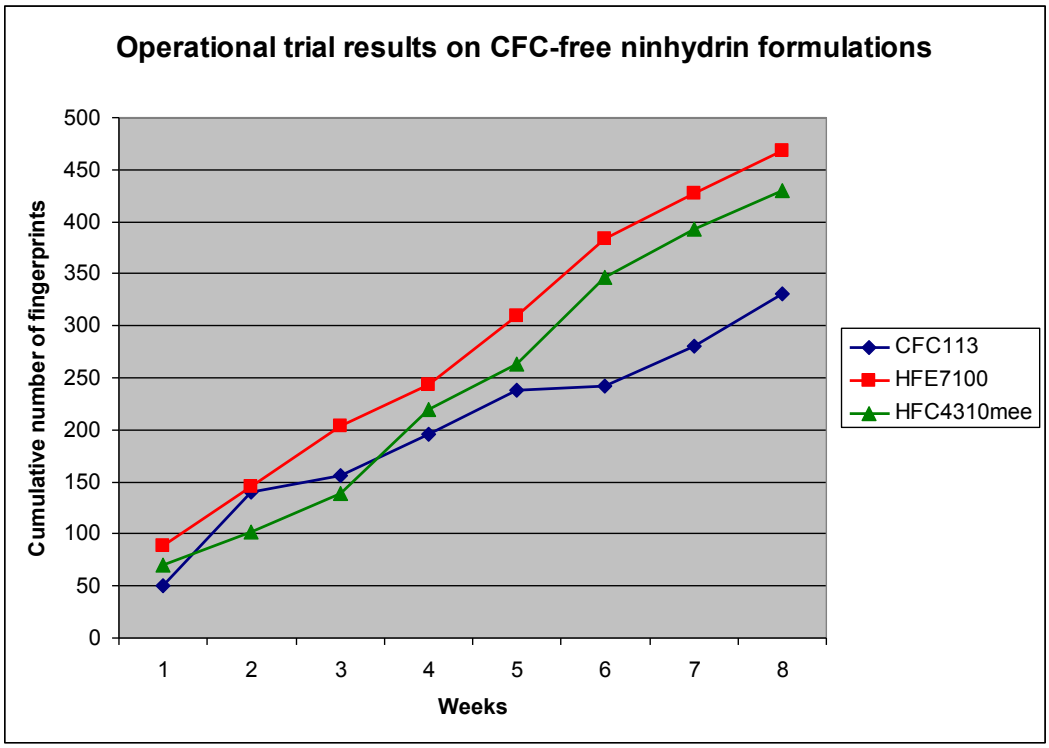
8.2.3 The HFE7100-based formulation now recommended in the CAST *Manual of Fingerprint Development Techniques* [44] has been trialled under UK conditions and found to be superior in performance to the CFC113-based formulation previously used. As part of the programme to find a suitable CFC-free ninhydrin formulation, Hewlett and Sears first tested a number of CFC-free formulations against the CFC113 formulation then in use. Some of these early studies are reported under section 6 'Alternative formulations and processes' above. A pseudo-operational trial, counting numbers of fingerprints with >8 minutiae developed using each technique on batches of 75 fraudulently passed cheques, gave the following result for the most promising HFC and HFE compounds.



Pseudo-operational trial results obtained on batches of fraudulently passed cheques.

8.2.4 These results indicated that both formulations had the potential to give equivalent, if not better, performance compared with the CFC113 formulation and fingerprints were developed over a similar timescale. As a consequence, both formulations were carried forward to a full operational trial carried out over a period of eight weeks at Essex Police. Articles suitable for ninhydrin treatment were separated into three batches, one treated with the CFC113 formulation, one based on HFE7100 solvent and the other based on HFC4310mee solvent. The number of fingerprints with > 8 minutiae was recorded, with exhibits being examined for fingerprints after 2 days and again after 2 weeks. Over the 8 weeks, 110 cases were treated by each process with an equivalent number of articles treated by each process overall. The results are tabulated and displayed graphically below.

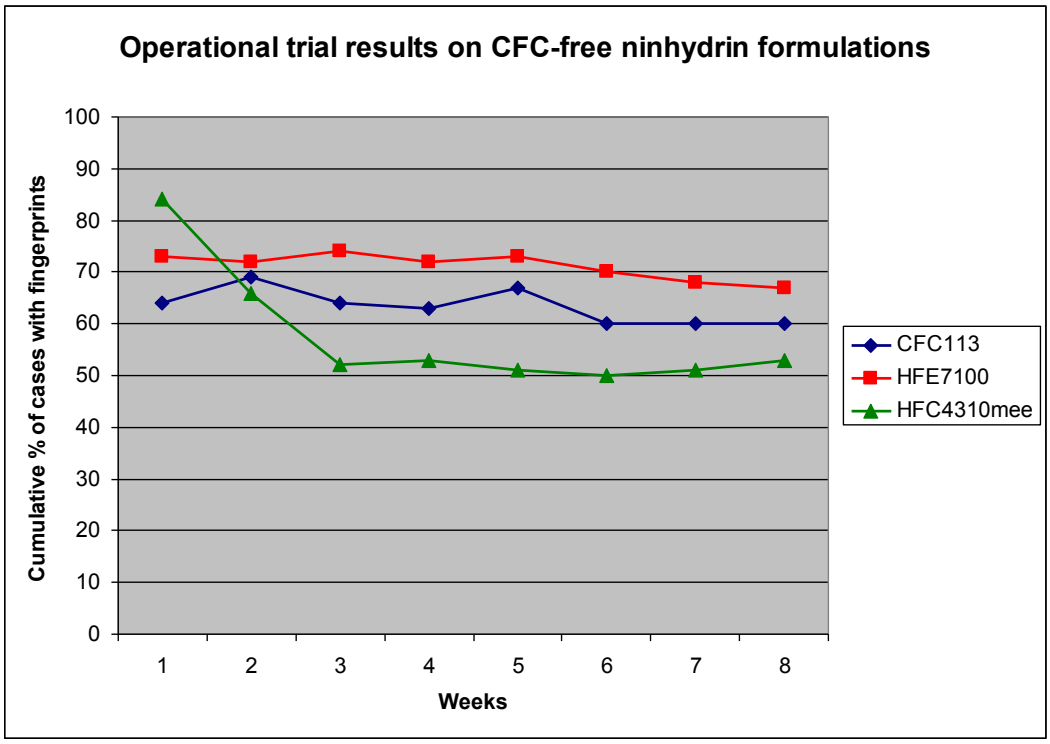
Week	**Cumulative figures**					
	CFC113		**HFE7100**		**HFC4310mee**	
	Cases	F'prints	Cases	F'prints	Cases	F'prints
1	14	50	15	89	12	70
2	29	140	32	146	29	102
3	39	156	42	204	42	139
4	54	196	54	243	55	220
5	69	238	66	309	68	263
6	80	242	83	384	79	347
7	102	280	102	427	102	393
8	110	331	110	468	110	430



Number of fingerprints developed in operational trial on chlorofluorocarbon-free ninhydrin formulations.

8.2.5 Although this analysis shows HFE7100 and HFC4310mee to perform better than CFC113 it was considered that these results may be misleading because single cases could yield disproportionate numbers of fingerprints; one-sixth of all fingerprints developed using HFC4310mee coming from a single case. It is statistically good practice to remove 'outliers' (i.e. the largest and smallest figures) from such analyses for the reason given above. The data were therefore also analysed in terms of the proportion of cases where fingerprints were developed, and these results are given below.

Week	**Cumulative figures**					
	CFC113		**HFE7100**		**HFC4310mee**	
	Cases	% with f'prints	Cases	% with f'prints	Cases	% with f'prints
1	14	64	15	73	12	84
2	29	69	32	72	29	66
3	39	64	42	74	42	52
4	54	63	54	72	55	53
5	69	67	66	73	68	51
6	80	60	83	70	79	50
7	102	60	102	68	102	51
8	110	60	110	67	110	53



Proportion of cases yielding fingerprints in operational trial on chlorofluorocarbon-free ninhydrin formulations.

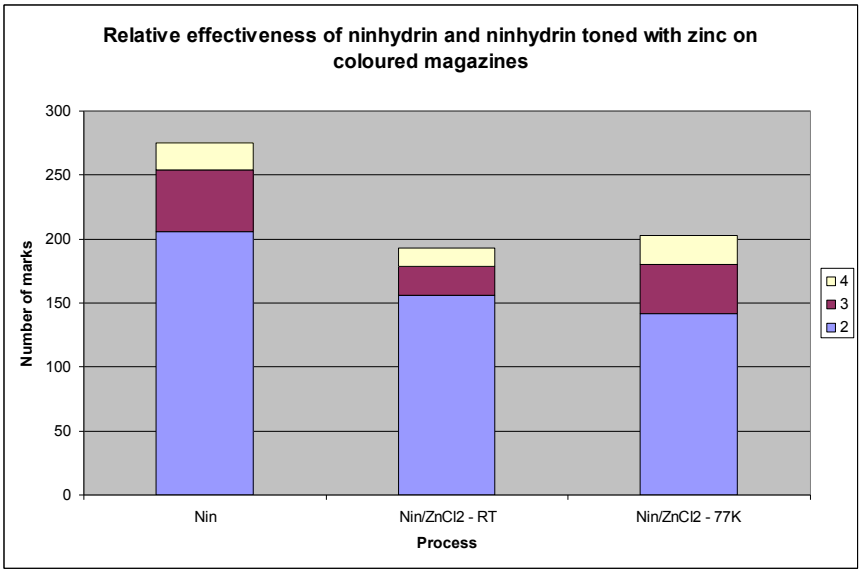
8.2.6 Under this analysis it appeared that the HFE7100-based formulation was the most effective, having the dual advantage of being non-ozone depleting and more effective than CFC113-based ninhydrin on operational work. This formulation was therefore recommended for operational use. It was also observed that the HFC-based formulation became less effective as the solution used became older, indicating that there may have been additional interaction between the HFC4310mee solvent and other constituents. The reasons for this were not explored further.

8.2.7 This study only refers to the use of ninhydrin as a single treatment, where in practice it may be used in sequence after DFO. Studies reported in Chapter 3.3 1,8-Diazafluoren-9-one (DFO) demonstrate that as a single process ninhydrin is less effective than DFO, but if used sequentially after DFO, ninhydrin will develop additional marks.

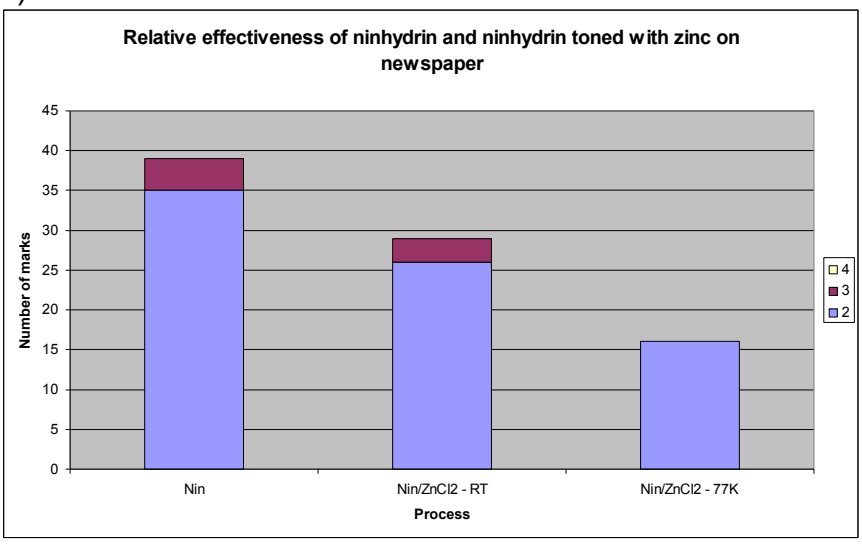
8.2.8 Results reported in Chapter 3.5 Physical developer also indicate that the application of ninhydrin is not detrimental to subsequent physical developer treatment and that physical developer can develop additional marks after ninhydrin. The recommended sequence of DFO-ninhydrin-physical developer for porous exhibits continues to be used successfully in the UK.

8.2.9 The effectiveness of zinc toning was also investigated in a pseudo-operational trial in the late-1980s, looking at marks deposited on cheques, coloured magazines and newspaper. The results of this trial

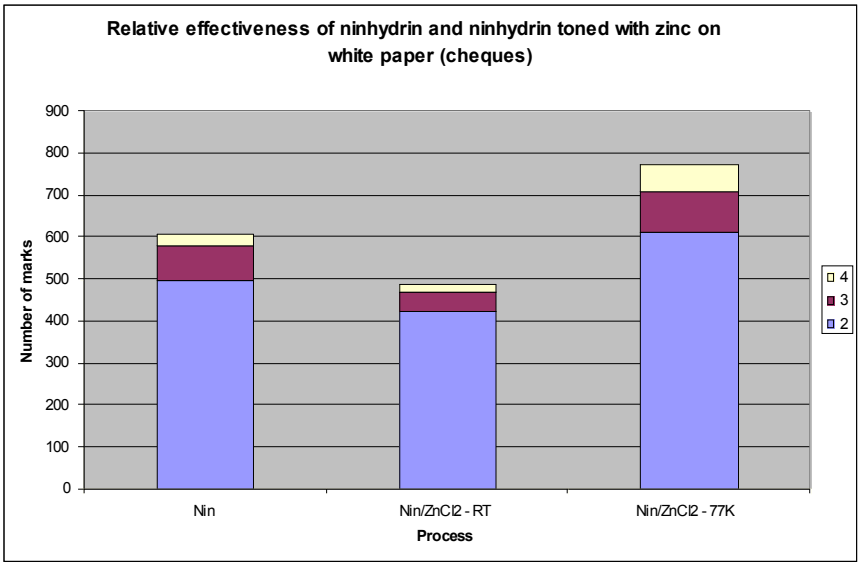
indicated that results were poor on newspaper and obscured by background fluorescence on coloured magazines, but on cheques (based on white, non-fluorescing paper) zinc toning and fluorescence examination increased the number of marks recovered if the paper was chilled to liquid nitrogen temperature.



a)



b)



c)

Psuedo-operational trial results (marks graded 2, 3 and 4) on naturally handled items treated with ninhydrin and subsequently toned with zinc.

8.2.10 The most recent assessment of ninhydrin has been a pseudo-operational trial to compare the effectiveness of the HFE7100-based formulation with a revised formulation based on the alternative solvent AE-3000 [46, 53]. This trial utilised items representative of casework, including envelopes, receipts from retail shops, newspapers and letters. The items were divided into 8 experimental batches of 50 exhibits and 4 control batches of 10 exhibits, the types of exhibits being evenly distributed among the groups. These exhibits were then processed using the standard ninhydrin conditions, comparing the effectiveness of the two formulations and gathering additional information about long-term stability. The results were analysed in several different ways: using the basic CAST grading scheme; using a grading scheme taking into account additional factors, such as ridge continuity and background development developed at Staffordshire University; and also by running the developed marks on an Automated Fingerprint Identification System (AFIS) system. The results were analysed statistically using several different models, and all results indicated that there was no statistical difference between the effectiveness of the HFE7100 and AE-3000-based formulations.

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3.5 Physical developer

1. History

1.1 Physical developer solutions had been in use for many years in the photographic industry for the development of film. These worked with exposure to light causing silver bromide or silver iodide crystals in the film to reduce to specks of silver, these specks becoming sites for the subsequent deposition of silver from solution. In 1969, Jonker *et al.* at the Philips Research Laboratory in Eindhoven published a series of papers on physical developers when investigating methods for making printed circuit boards. These began with a review of classic physical developer solutions [1] but most importantly also included the description of a stabilised physical developer formulation [2,3] with the addition of surfactants and ferrous ions to suppress spontaneous deposition of silver from solution.

1.2 In common with many processes, the potential for fingerprint development was recognised when fingerprints were accidentally developed during the processing of photographic plates. Work to evaluate the technique as a fingerprint development process began at the Atomic Weapons Research Establishment (AWRE) Aldermaston in the early 1970s [4,5], with Morris and Goode recognising that although the process could develop marks on both non-porous and porous surfaces, it was most effective on porous items. The process was assessed against ninhydrin and osmium tetroxide on paper, both in the dry condition and after wetting. It was found that although the performance was not as good as ninhydrin or osmium tetroxide on dry paper, physical developer was the only process to develop marks on wetted paper and it was concluded that further trials should be conducted by the Police Scientific Development Branch (PSDB).

1.3 These studies included background research on the electrochemical characteristics of the formulation, together with investigations of alternative metals to silver [6]. This work primarily focused on taking the existing formulation towards operational use. Laboratory trials were conducted across a range of different paper types, both fully wetted and exposed to high humidity environments [7]. Rigorous testing, leaving paper samples in cages in the Thames, indicated that fingerprint ridge detail was still detected on paper samples which were close to physival disintegration.

1.4 The use of a radioactive toner based on ^{35}S for the revelation of developed marks on patterned backgrounds was also proposed, using autoradiography of the radioactive toned item to separate the mark from the background. The recommendation of the original study was to proceed to a one-year operational trial for both the basic process and the toning technique This commenced at Sussex Police and the Metropolitan Police in 1976, with HOSDB staff processing the exhibits in police laboratories [8]. The operational trial confirmed the laboratory

observations; additional marks were developed using physical developer after ninhydrin treatment, marks were developed on items known to have been wetted, and the radioactive toning process was successfully used to reveal marks on patterned backgrounds. The trial was continued without HOSDB involvement, using trained police staff to process exhibits [9] and it was shown that similar results could be achieved. However, during the early stages of this phase of the work it was observed that the physical developer solutions were unstable, resulting in rapid 'fogging' of the entire exhibit. Work was carried out by PSDB to establish the reason for this [10] which concluded that the principal cause was excessive exposure of the solution to light. With elimination of this factor, results improved significantly. It was also discovered that water quality was crucial for the production of stable solutions, so there was a move to use only distilled, not deionised water. After further testing, PSDB progressed with the operational implementation of the process across the UK at the beginning of the 1980s [11].

1.5 Although the technique had been introduced into operational use, the fingerprint constituents responsible for influencing development were still not firmly established. Early work by Morris [5] had suggested that cholesterol esters, hydrocarbons or triglycerides may trigger deposition but in later tests by Gray [12] using a range of model compounds it was not possible to identify clearly which were actively promoting deposition and it may be that combinations of substances are responsible rather than any constituent in isolation.

1.6 A problem sometimes observed during operational use of physical developer was that background interference could occur. In some cases this was seen as light greying, which did not affect visualisation of the developed mark, but in other cases dark grey/black patching occurred, which could obscure marks. Investigations at PSDB established that this was caused by the calcium carbonate filler present in many papers, which made them alkaline in nature. This caused silver hydroxide to be formed, which was subsequently converted to the brown/black compound silver oxide (Ag_2O). The proposed solution was to neutralise the paper before the application of physical developer and a range of acids were tested in this role, with maleic acid ultimately being selected by PSDB (dilute nitric acid being recommended as an alternative by the Home Office (HO) Forensic Science Service (FSS) laboratory at Aldermaston). Another refinement to the formulation made by PSDB (now renamed HO SRDB) in the mid-1980s was the reduction in the concentration of surfactants used, made possible by the availability of higher purity surfactant grades.

1.7 The technique began to be used worldwide, with published papers promoting the benefits of the technique and giving case studies where success had been obtained on wetted items [13, 14] and on items over 30 years old [14]. The importance of using an acid pre-wash to neutralise alkali fillers in most commercial papers was emphasised [15]. As discussed above, without this pre-wash a reaction occurred that caused

the paper to darken, obscuring developed marks and inhibiting more widespread use of the technique. A range of commercially produced, pre-mixed physical developers were evaluated by the same researcher [16], none of which supplied, or commented on, the need for a pre-wash. All were capable of giving reasonable performance if a pre-wash was used, but the researcher expressed concern that the lack of this advice may cast doubt on the effectiveness of the process. Few commercially produced packs explicitly state the constituents used, and CAST encourages UK police forces to make their own solutions for operational work to optimise performance.

1.8 The basic formulation recommended for operational use by CAST is little modified from that originally described by Jonker *et al.* in 1969 and has continued in use to the present day. Research into alternative formulations has been predominantly carried out in the USA, with the objectives of reducing cost, simplifying the process, reducing the time taken to process exhibits and to improve visualisation of the developed marks. Saunders experimented with a range of different physical developer solutions at different dilutions [17], starting to process exhibits with dilute solutions and if development did not occur silver nitrate was progressively added until success was obtained.

1.9 Other adaptations investigated included:

- copper-based physical developers [18]
- toning of marks to make them fluorescent [18]
- bleaching of marks to make them more visible on darker backgrounds [19].

1.10 A revised formulation was published by the US Secret Service in 2003, incorporating malic (as opposed to maleic) acid in the solution and reductions in the amount of silver, surfactants, ferrous salt and citric acid [20, 21]. Split comparisons with the established process suggested that the revised formulation gave equivalent, if not better, development. A comprehensive review of the physical developer process and alternative formulations investigated has been produced by Cantu [22].

1.11 More recently, acid-free formulations have been suggested for the development of marks on porous and non-porous surfaces [23] but other researchers have not been able to recreate these results. There has also been concern about the continued availability of Synperonic N, one of the surfactants used in the formulation, and work has been carried out both in the USA and by HOSDB in the UK [24] to assess possible alternatives. None of those investigated has yet proved to be as effective as Synperonic N.

1.12 Physical developer remains an important reagent for fingerprint development on porous surfaces. It appears to target different fingerprint constituents to the amino acid reagents 1,8-diazafluoren-9-one (DFO) and ninhydrin, and will regularly develop additional marks if used sequentially after them. It has also been shown to develop marks on

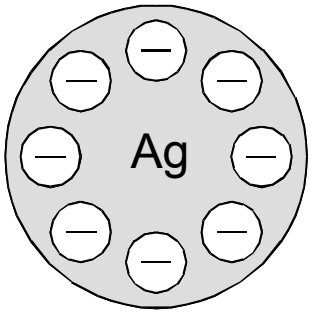
exhibits exposed to some of the harshest environments, including long periods of water immersion, charring [25], gamma ray irradiation [26] and on paper nearly 60 years old [27].

1.13 More recently there have been published papers demonstrating that Oil Red O can also develop fingerprints on wetted surfaces and in some situations may be more effective than physical developer. This debate is more fully addressed in Chapter 5.12 Oil Red O, but the CAST position is that physical developer remains more effective under typical operational conditions and should continue to be the technique of choice for use on wetted paper. Many of the studies on Oil Red O have used freshly deposited, 'groomed' marks and this is not representative of marks encountered operationally.

1.14 A number of workers overseas have indicated that they have problems implementing the physical developer process, in particular the development of high backgrounds. A team from PSDB carried out trials during a visit to Israel in the late 1990s and concluded that local differences in paper manufacture, possibly including the nature of the inorganic fillers used, can affect the levels of background development. Similar problems have been reported in China and in Taiwan. Some of these issues may arise from water quality but others may result from differences in paper manufacture.

2. Theory

2.1 In conventional physical developer solutions, spontaneous, homogeneous nucleation of silver nuclei occurs by reduction of silver ions. These nuclei carry a negative charge, and grow by progressive silver deposition from solution, the negative charge being maintained throughout their growth.



Negatively charged silver nuclei.

2.2 In stabilised physical developer solutions, several other chemicals are added to suppress the reduction of silver ions to elemental silver unless a suitable initiation site is present. In the case of the physical developer

solution used for fingerprint development, the initiation sites are the fingerprint ridges (although as mentioned above it is not fully clear which constituents actually initiate deposition).

2.3 The physical developer solution contains both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, setting up a ferrous/ferric couple reaction that acts as a reducing agent for the silver ions. The reversible reaction below is set up:

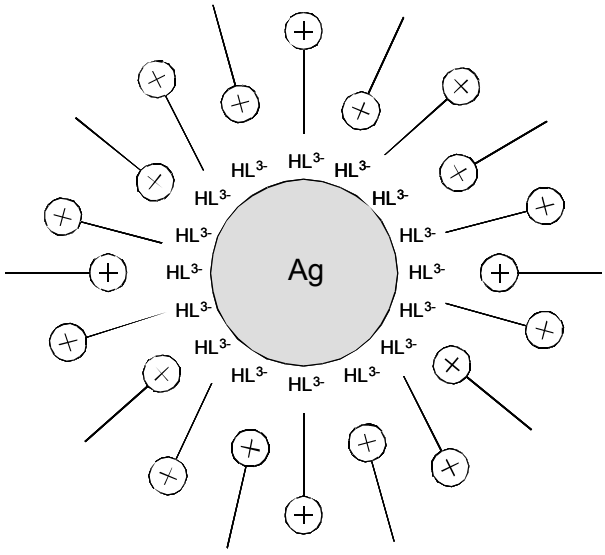
$$Ag^{+} + Fe^{2+} \leftrightarrow Ag + Fe^{3+}$$

2.4 Addition of citric acid reduces the ferric ion concentration by the formation of ferric citrate, which releases three protons and essentially drives the overall reaction in the direction of suppressing elemental silver deposition.

$$Ag^{+} + Fe^{2+} + H_3Cit \leftrightarrow Ag + FeCit + 3H^{+}$$

2.5 By adjusting the relative concentrations of each component, the reduction reaction can be balanced so that it only occurs on fingerprint ridges (or other sites where initiators are present) rather than in solution. However, once a silver nucleus has formed, it acts as a site for further silver deposition and this will result in depletion of silver ions from the solution unless the initiation capability of the nucleus is suppressed.

2.6 Surfactants are added to the formulation in order to inhibit the growth of the colloidal silver particles. As stated above, the silver nuclei formed in solution are negatively charged, attributed to the adsorption of the negatively charged citrate anions on the surface. A cationic surfactant is therefore added to suppress particle growth, with the molecules of the surfactant arranging around the silver particle in a staggered fashion to form a micelle.

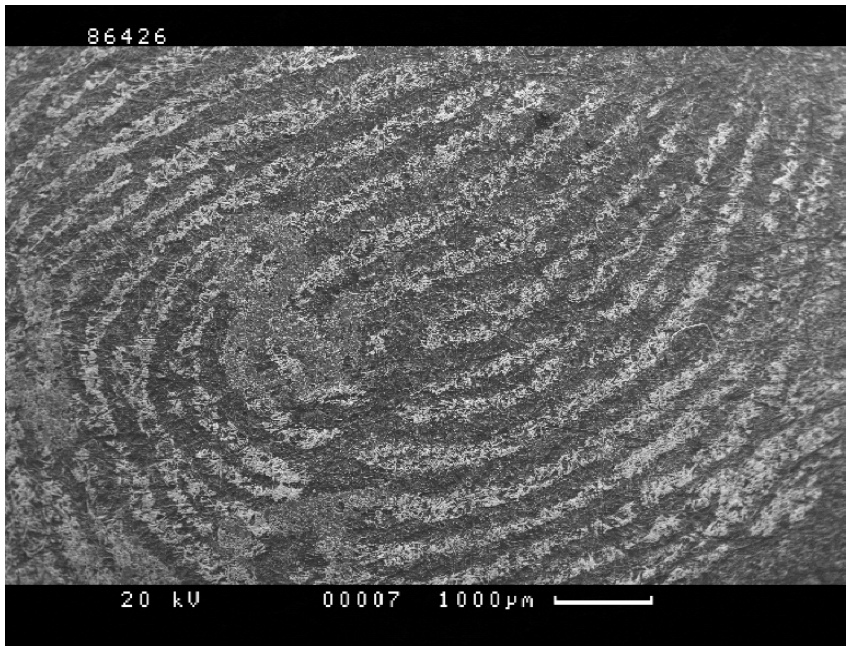


Micelle formed around silver particle by cationic surfactant molecules interacting with citrate anions (HL^{3-}).

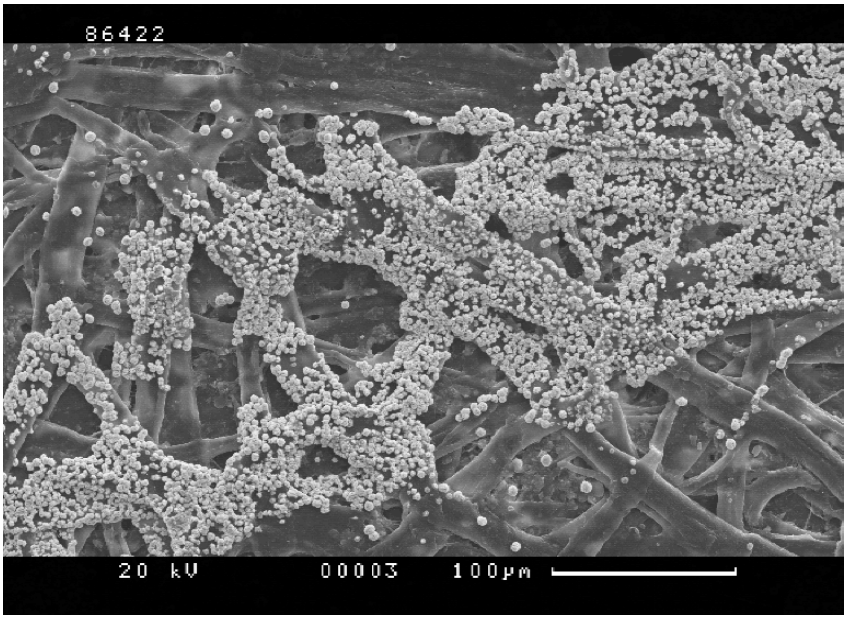
2.7 A further non-ionic surfactant is added to prevent the cationic surfactant being precipitated out of solution.

2.8 Despite several studies failing to identify conclusively individual fingerprint constituents responsible for triggering nucleation, it is thought that the essential element in the selective deposition of silver on fingerprint ridges is that the fingerprint residue becomes positively charged when exposed to the acidic (pH < 3) conditions of the physical developer solution. This may be due to protonation of the amine groups of proteins held within the emulsion of the fingerprint deposit, or by olefins in the residue acquiring a positive charge. A brief study by Wright [24] showed that physical developer gave weak positive development with an amino acid mixture, a strong development with a lipid mixture and the strongest reaction with a mixture of lipids and amino acids. The mixed chemical environment within the fingerprint residue may create a better environment for protonation and subsequent deposition to occur.

2.9 As described above, any silver nuclei formed in the solution will be negatively charged. It is likely to be enveloped by the cationic surfactant molecules, but close to the fingerprint ridges there is competition from the positively charged components of the residue. In this environment the micelle may be destabilised and the silver nucleus deposited on the ridge, where it becomes neutralised. Once a metallic silver particle has formed it can grow autocatalytically, resulting in a series of silver particles 10–40μm in diameter deposited along the length of the fingerprint ridge.



a)



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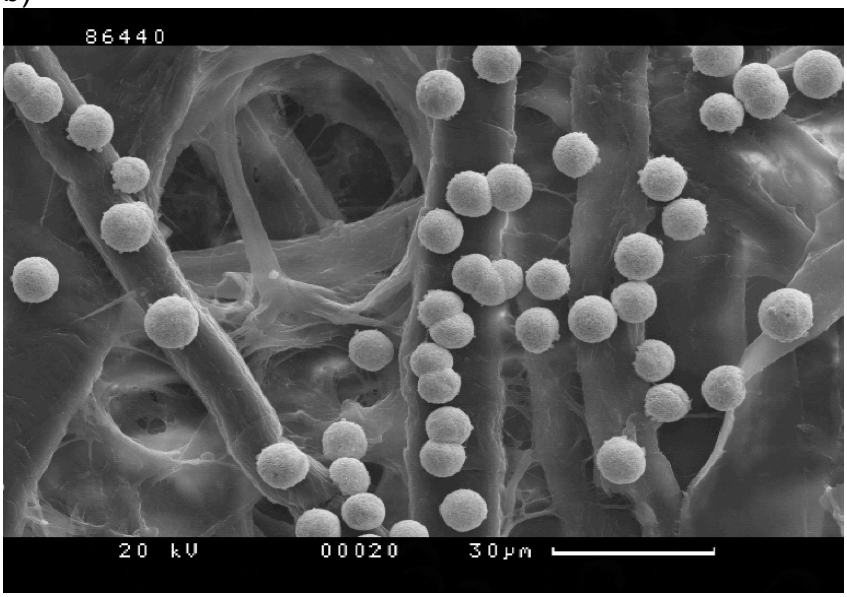


c)

Scanning electron micrographs of a fingerprint treated with physical developer a) low magnification, showing fingerprint structure b) medium magnification showing fingerprint ridge and c) high magnification showing individual particles.

3. CAST processes

3.1 The process recommended by CAST consists of three stages. In the first stage, the exhibit is exposed to an acid pre-wash to ensure that the substrate is neutralised and that darkening of the background will not occur. In the second stage the exhibit is placed in the physical developer working solution and agitated until it is considered that optimum development has occurred. In the final stage, the exhibit is taken through a series of water wash baths, removing all traces of the physical

developer solution and stopping the reaction. It is recommended that the glassware used for all these treatment baths is kept scrupulously clean to prevent silver depositing on residual impurities such as dust particles.

3.2 The acid solution used for the pre-wash is a 2.5% w/v solution of maleic acid, prepared by dissolving 25g of maleic acid in 1 litre of de-ionised water. The role of the maleic acid is to neutralise the calcium carbonate filler found in many papers. Maleic acid reacts with calcium carbonate to form calcium maleate, releasing bubbles of carbon dioxide. The reaction is considered to be complete when bubbles are no longer seen forming on the surface of the paper.

3.3 The physical developer working solution is produced by adding a pre-mixed stock detergent solution and a pre-mixed silver nitrate solution to a further solution containing the ferrous and ferric ions and citric acid.

3.4 The stock detergent solution is produced by adding 2.8g of n-dodecylamine acetate to 1 litre of distilled water then stirring. Once it has dissolved, 2.8g of Synperonic N is added and stirred for 24 hours, with the container being covered in clingfilm to prevent ingress of foreign particles. The role of n-dodecylamine acetate is to act as the cationic surfactant, forming micelles around any silver nuclei forming in the physical developer working solution. Synperonic N is the non-ionic surfactant, primarily added to prevent precipitation of the cationic surfactant from solution although it is thought that it may have other functions in the development reactions. It is known that without the non-ionic surfactant being present, physical developer solutions do not work. It is essential that the resultant working solution is clear at this stage for optimum performance, cloudy solutions giving poor results. Cloudy solutions may arise if the temperature in the laboratory is too low (<20°C) or from contamination in one of the components; both causes should be investigated if this issue begins to arise.

3.5 Silver nitrate solution is produced by dissolving 10g of silver nitrate in 50mL of distilled water, then storing it in a dark cupboard until required. Silver nitrate is the source of the silver ions (Ag^{+}) in the redox reaction leading to silver deposition.

3.6 To prepare the working solution, 900mL of distilled water is measured out and then, in order, the following chemicals are stirred into solution: 30g iron (III) nitrate, 80g ammonium iron (II) sulphate, 20g citric acid. To this are then added 40mL of the stock detergent solution and all of the silver nitrate solution. The iron (III) nitrate is the source of the ferric (Fe^{3+}) ions for the redox reaction, and ammonium iron (II) sulphate provides the ferrous (Fe^{2+}) ions. Citric acid acts as a buffer for the reaction, reducing pH to below three and suppressing formation of elemental silver.

3.7 The concentrations of each component have been selected such that the redox reaction is balanced in favour of silver deposition on initiation sites among the fingerprint residue, and not in solution.

3.8 It is possible to reduce the time taken for the washing stage of physical developer by introducing a fixing bath after treatment with physical developer [28]. A commercial photographic fixing agent can be used for this purpose, following the manufacturer's instructions. This has the advantage of reducing the overall treatment time but means that it will not be possible to retreat the exhibit with physical developer if faint marks are present that could have benefited from a longer development time.

4. Critical issues

4.1 There are several critical issues relating to the successful implementation of the physical developer process.

4.2 An acid pre-wash is essential for paper items so that the alkali fillers present in most papers are neutralised. If this stage is omitted heavy background development may occur, which obscures marks.

4.3 The glassware used to carry out the process must be kept scrupulously clean because scratches and impurities may act as preferential nucleation sites and cause silver to precipitate out of the solution.

4.4 Distilled, rather than deionised, water should be used to make the solutions because this has been shown to improve performance.

4.5 The presence of a non-ionic surfactant in the formulation is essential for development to occur. The process is critically dependant on the surfactants used and their purity. The early work conducted at AWRE used a stock of dodecylamine acetate which was subsequently found to be of low purity but produced excellent results. A subsequent purchase of dodecylamine acetate, believed to be of higher purity, produced acceptable results but the concentration recommended in the formulation was revised downwards from 4g to 2.8g per litre for this batch. There are still some questions over the performance of current sources of dodecylamine acetate and no definitive comparisons have been reported.

4.6 The process should be carried out at temperatures above 20°C to avoid the formation of cloudy solutions, which are less effective in developing marks.

5. Application

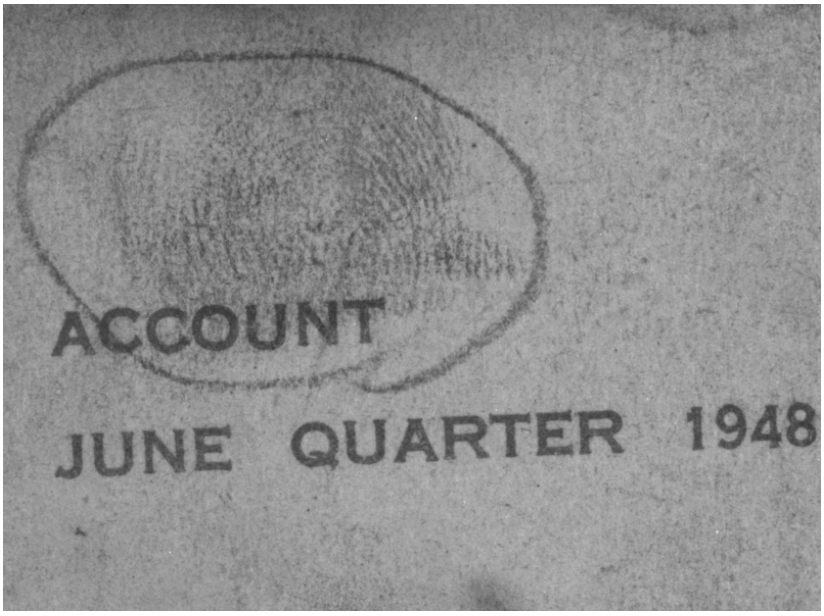
5.1 Suitable surfaces: physical developer is suitable for use on all porous surfaces, including paper, cardboard and raw wood.

5.2 The principal application of physical developer is the final stage in any sequential treatment process for porous items. It has been repeatedly demonstrated that physical developer targets different components within fingerprint deposits than DFO and ninhydrin, and will frequently develop additional marks if used sequentially after them. It should not be used before DFO and ninhydrin in a sequence because on its own it is less effective than either reagent and the aqueous solutions used will dissolve the amino acids targeted by these processes.

5.3 Physical developer is also the reagent of choice when it is known a porous item has been wetted. Because it targets insoluble components of the fingerprint residue (or soluble components retained within an emulsion of insoluble components) it is capable of developing fingerprints after long periods of immersion in water. Operationally, fingerprints have been developed on exhibits immersed for over three months [13].

5.4 Physical developer has also been shown to develop marks on exhibits exposed to temperatures in excess of 200ºC [25], providing evidence that the components targeted by the process are resilient to adverse conditions. Supporting this are other results obtained during treatment of articles known to be nearly 60 years old [27], where physical developer produced several identifiable marks. It is therefore a process that can be applied when it is known that an exhibit has been exposed to extreme conditions.

a)



b)

Photographs of marks developed on articles exposed to extreme conditions using physical developer a) marks on charred paper and b) mark on a bill nearly 60 years old.

5.5 In a laboratory, physical developer is applied to articles by processing them through a series of shallow dishes. The paper article is first placed into a dish containing the acid pre-wash, agitating the dish gently until bubbles are no longer formed on the surface. It is then transferred to a dish containing the physical developer working solution, which is rocked gently until optimum development of the marks has been observed. This typically takes 10–15 minutes, but may take longer. Finally, the paper is removed to a series of water wash baths before being allowed to dry in air on an absorbent surface. Once the article is dry and developed marks have been examined, a decision can be made about whether a retreatment with physical developer is required or a post-treatment should be used to improve contrast. It is important to control the temperature during processing, with temperatures below 17ºC inhibiting successful development by destabilising the developer solution [24].

5.6 Physical developer is not a technique suited to application at scenes of crime, although there are occasions where improvisations are known to have been made, such as half-fish tanks pressed against walls and successively filled with each treatment solution in turn.

6. Alternative formulations and processes

6.1 Alternatives have been considered to all elements of the physical developer formulation.

6.2 Several different acids were considered for the pre-wash before maleic acid was selected. More recently nitric acid and malic acid have been

studied as possible alternatives, but none of them have given noticeably better performance over maleic acid.

6.3 With regard to the metal component of the formulation, early studies by Fuller and Thomas [6] indicated that solutions based on palladium, rhodium and gold were investigated and although these deposited metal on the surface as expected they did not appear to develop fingerprints. Ramatowski and Cantu [18] reported research into a copper-based physical developer using copper sulphate in place of silver nitrate. Although development was obtained via this route, it has not proved as sensitive as the silver-based system and is not recommended as a replacement for it.

6.4 As part of a drive to reduce the cost of the large quantities of physical developer used by the US Secret Service, revisions to the CAST formula were investigated. These resulted in a revised formulation incorporating malic acid [20,21], with reductions in the concentrations of ammonium iron (II) sulphate, citric acid, both surfactants and silver nitrate. The proposed formulation (based on 1 litre of water for each stage) is given below:

malic acid 13g;

iron (III) nitrate 30g;
ammonium iron (II) sulphate 70g;
citric acid 15g;
n-dodecylamine acetate 0.056g;
Synperonic N 0.056mL;
silver nitrate 8g.

6.5 The results presented suggested that the above formulation was as effective as the CAST formulation, if not more so. However, no comprehensive trial has yet been reported that compares the two formulations either in laboratory tests or on operationally representative exhibits, so it is not yet possible to state whether a revision to current (2011) UK practice is required. An adaptation of this formulation using Tween 20 in place of Synperonic N was developed by the US Secret Service, as a precaution against the possibility of Synperonic N becoming unavailable. This formulation was tested against the CAST formulation in trials of Synperonic N-free systems, and although it gave better results on one-day-old prints it was poorer on prints that were two weeks old. Further details of this trial are given below.

6.6 Another revised formulation omitting the maleic acid pre-wash was issued by Yapping and Yue [23], but attempts by other researchers to reproduce this formulation and the results claimed for it were unsuccessful and at present it is discounted.

6.7 Concerns have been expressed about the environmental issues associated with compounds closely related to Synperonic N. These are

becoming banned because they closely mimic oestrogen in structure and as these compounds enter the environment they may lead to reduced sperm count and increases in testicular cancer. Recent research in both the USA and the UK has therefore investigated alternative surfactants to Synperonic N. In the UK study [24], the following alternative compounds were considered.

Surfactant	General description
Tween 20	Polyoxyethylene sorbitan (fatty acid ester)
Tween 80	Polyoxyethylene sorbitan (fatty acid ester)
Synperonic 91/5	Fatty alcohol ethoxylate
Synperonic 91/6	Fatty alcohol ethoxylate
Synperonic 13/6.5	Fatty alcohol ethoxylate
Synperonic 13/8	Fatty alcohol ethoxylate
Caflon-N	Fatty alcohol ethoxylate

Surfactants used in the comparative study.

6.8 The solutions containing the different surfactants were compared with the Synperonic N-based solution and applied to split depletions of several thousands of marks deposited on a range of paper types. The results showed that none of the proposed replacements for Synperonic N gave equivalent performance, the nearest being the formulation based on Tween 20 recommended by the US Secret Service from their own internal research. The long-term availability of Synperonic N remains a concern and therefore it is likely that this study will have to be revisited at some point in the future. One observation that has been made subsequently by the US Secret Service is that the Tween 20 formulation benefits from being used after ageing for several days, and that the solution used in the HOSDB comparative studies may have been 'too fresh'. This is another factor that requires further investigation.

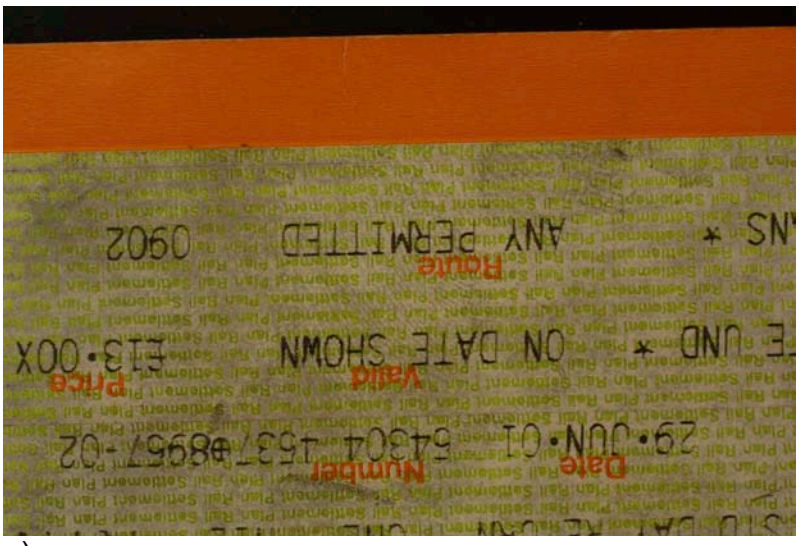
7. Post-treatments

7.1 A range of post-treatments have been proposed for enhancing marks. One of the earliest treatments proposed [6], and still outlined in the CAST *Manual of Fingerprint Development Techniques* [29] is the treatment of developed marks with a radioactive toner, then using autoradiography to capture the marks. The principal application of this technique was to reveal developed marks that would otherwise be obscured by highly coloured or patterned backgrounds. In the radioactive toning process, the exhibit is treated with radioactive sodium sulphide. This converts the silver particles to silver sulphide, resulting in the radioactive sulphur being bound into the fingerprint ridges. The treated exhibit is then sandwiched between sheets of film for several days, during which radiation emitted from the sulphur causes the film to darken in regions where it is present. On development the film will show all the

regions of the film that have become radioactive. The fingerprints will only be more useful if the underlying background, ink or contamination, has not taken up the radioactive sulphur. The technique has not been used for many years and will be removed from future editions of the manual.

7.2 Bleaching has also been proposed as a technique for both revealing fingerprints on dark papers or as an initial step in the coloured toning of developed marks [19,22, 30]. Several techniques have been proposed for treating developed marks, the most widely used formulation operating by the conversion of silver to silver iodide by first converting it to Ag_2O then converting Ag_2O to the silver halide. To carry out the process, a stock solution of 20g potassium iodide in 100mL of distilled water is prepared and one part of this solution added to 19 parts of the standard physical developer working solution. The article to be treated is then immersed in the solution until the paper background becomes blue-black (this is thought to be due to the starch in the paper reacting with iodine) and good ridge detail is observed. This may take between 15 minutes and 2 hours. On dark paper or against dark backgrounds, the bleaching process alone can reveal marks. For faint, developed marks on pale backgrounds a weaker concentration of potassium iodide can be used to treat the mark without darkening the background.

7.3 Alternatively, developed marks can be treated with standard photographic colour toning solutions, e.g. Fotospeed Blue Toner (BT20), using the manufacturer's instructions to change the colour of the mark and enhance its contrast [31]. Any silver deposited on the background will also be toned in this way.



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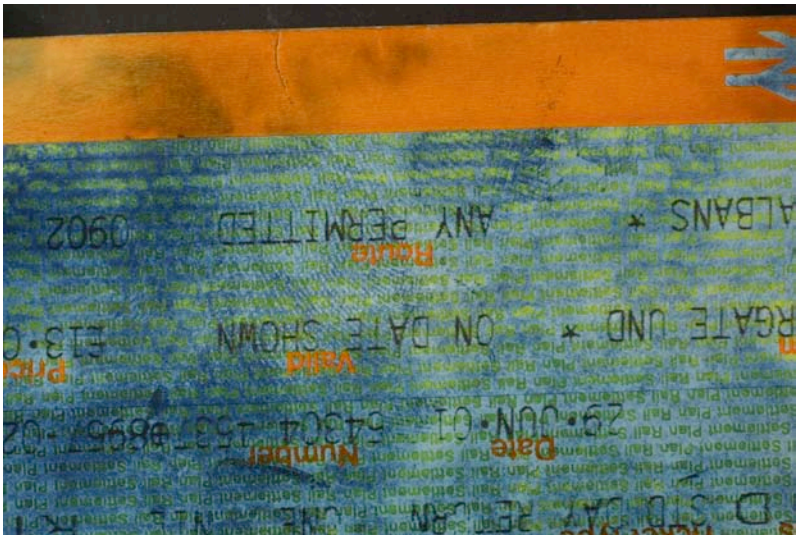

b)

Marks on a rail ticket obtained by using physical developer a) as developed and b) after bleaching and treatment with blue photographic toner.

7.4 A final post-treatment that can be applied to articles treated using physical developer is infra-red (IR) imaging, described in detail in Chapter 4.2 Infrared imaging. The principle used is that the marks produced using physical developer remain visible in the near IR and many printing inks use organic pigments that are IR transparent. If a camera sensitive in the near IR is used in combination with an appropriate light source and a long-pass filter blocking the visible region of the spectrum, it may be possible to suppress the background pattern and reveal the features of the mark.

8. Validation and operational experience

8.1 There have been a limited number of extensive trials carried out on physical developer, primarily because of its position within sequential processing regimes. Physical developer is only going to be used as the first process on items that are known to have been wetted, where until recently it was the only process that could be considered for this role. It is accepted that physical developer is less effective than DFO and ninhydrin, but because it develops additional marks when used after them rather than being considered in place of them, large-scale validation has been considered unnecessary.

8.2 Laboratory trials

8.2.1 The first reported comparative studies of the effectiveness of physical developer were carried out at AWRE Aldermaston in 1975, where it was compared with the non-flammable ninhydrin formulation being developed by the same research group, and to osmium tetroxide [5].

8.2.2 In this study, single fingerprints from two separate fingers from the same donor were used and these were aged for different periods of time. One set of exhibits was then wetted, and the paper processed using the three processes being compared. A basic, non-numeric grading system was used where:

none = no trace of fingerprint;
very poor = traces of fingerprint only;
poor = just sufficient for general classification;
good = sufficient detail for identification;
very good = easily identifiable;
excellent = all ridge detail developed.

The results are summarised below.

Age of mark	Number of prints	Dry			Wet		
		Ninhydrin	OsO_4	PD	Ninhydrin	OsO_4	PD
1 day	1	Excellent	Excellent	V. good	None	None	V. good
	2	Excellent	Excellent	V. good	None	None	V. good
5 months	1	Good	Good	Good	None	None	V. poor
	2	Fair	Good	Poor	None	None	Poor
6 months	1	V. good	V. good	Good	None	None	Poor
	2	V. good	V. good	Good	None	None	Good
7 months	1	V. good	V. good	Good	None	None	Poor
	2	V. good	V. good	Good	None	None	Poor
8 months	1	Good	V. good	Good	None	None	Good
	2	Good	V. good	Good	None	None	Excellent
10 months	1	Good	Good	Good	None	None	Poor
	2	Good	Good	Good	None	None	None

Results of early comparative trials on both dry and wetted paper articles.

8.2.3 It was evident that physical developer was not as effective as ninhydrin or osmium tetroxide for marks on dry surfaces, but was the only process to develop marks on paper soaked for 24 hours.

8.2.4 Continuation of this work was carried out at HOSDB in 1975 and 1976 and focused on evaluating the effectiveness of physical developer against ninhydrin on paper kept in conditions where the surface became wet [7]. Two trials were conducted, both using split palm prints where one-half were kept indoors under dry conditions and the remainder were exposed to the wet environment.

8.2.5 The first trial exposed palm prints on paper kept exposed to the atmosphere in an outside test rig at PSDB Sandridge over the period November 1975 to January 1976. The grading system below was used.

1 = no reaction;
2 = reaction, no useful ridge structure;

3 = useful, poor contrast;
4 = useful, good contrast;
5 = useful, very good contrast;
6 = excellent.

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	2+	2	3	4	5	4	3+	3
2	5	3+	5	4	4	4	3	4
4	4	5	3	3+	5	4	5	5
9	-	-	3	4	-	-	5+	4+

Ninhydrin comparison

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	3+	1	3+	1	4	1	4	1

Results of early trials on paper items exposed to outside environments.

8.2.6A follow-on test was carried out holding samples in a water immersion rig in the River Thames. This gave the following results.

Day	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	1	3	3	2	3	4	2	3
2	3	2	3+	4	3	4	3	1
3	4	3	1	1	3	4	5	1
4	3	1	5	3	5	1	5	3

Ninhydrin comparison

Week	£5 Banknote		Kraft paper		Glazed paper		Bond paper	
	Control	Test	Control	Test	Control	Test	Control	Test
1	3+	1	3+	1	3+	1	3+	1

Results of early trials on paper items immersed in the River Thames.

8.2.7It was evident that for wetted surfaces ninhydrin gave no reaction, and that physical developer should be the development technique of choice.

8.2.8The most recent laboratory trials conducted by HOSDB focused on comparisons of the existing physical developer formulation with those based on the alternative surfactants identified in the 'alternative formulations and processes' section above. The solutions containing the different surfactants were applied to split depletions of several thousands of marks, deposited on a range of paper types consisting of:

- brown envelope;
- white envelope;
- parchment paper;

- magazine;
- newspaper;
- printer paper;
- green card;
- silk finish paper;
- wove paper.

8.2.9 The number of marks scoring three and four (equating to clearly identifiable marks) were recorded for each process on test strips aged for one day and two weeks. The differential between the number of marks graded three and four between the two techniques is recorded below, with negative scores indicating that the surfactant performed worse than Synperonic N.

	One-day differential	**Two-week differential**	**Average differential**
Tween 20 (US Secret Service formulation)	11	-15	-2
Synperonic 91/6	-3	-7	-5
Tween 80	-6	-6	-6
Caflon-N	-7	-9	-8
Synperonic 91/5	-5	-18	-11.5
Synperonic 13/6.5	-22	-18	-20
Tween 20	-33	-40	-36.5

Performance of different surfactants in physical developer solution relative to Synperonic N.

8.2.10 The results show that none of the proposed replacements for Synperonic N gave equivalent performance, the nearest being the formulation based on Tween 20 recommended by the US Secret Service from their own internal research. Production of Synperonic N is being discontinued so it is necessary to implement a revision to the surfactant used, and it is likely to be detrimental to the performance of physical developer for fingerprint development unless a more suitable replacement is identified.

8.3 Pseudo-operational trials and operational experience

8.3.1 The results of the operational trials conducted in 1977 prior to implementation of physical developer throughout the UK [9] are summarised below.

	Number of marks			%		
	New Scotland Yard	Sussex (1–29)	Sussex (30–90)	New Scotland Yard	Sussex (1–29)	Sussex (30–90)
Neither process +ve	11	0	6	28.9	0	10
Ninhydrin +ve PD -ve	6	13	8	15.8	46.4	13.3
Ninhydrin -ve PD +ve	11	0	8	28.9	0	13.3
Both processes +ve	10	15	38	26.4	53.6	63.4
Total cases	38	30	60	-	-	-
Total articles	433	69	234	-	-	-

Operational casework results obtained by applying physical developer after ninhydrin on a range of porous articles.

8.3.2 There were differences between the results obtained at different sites and between different phases of the work at the same site, but in general it was observed that physical developer consistently developed additional marks when used after ninhydrin. In the first phase of the work at Sussex the physical developer solution was degraded by exposure to light and results were poor, in the work at New Scotland Yard exhibits were selected because they were less likely to give positive results using ninhydrin, hence the results obtained in the second phase of the work at Sussex (where all exhibits passing through the laboratory were processed) were probably most representative. In the course of the trial the value of the technique in developing marks on wetted items was confirmed, as was the usefulness of the radioactive toning post-treatment for revealing marks on patterned backgrounds. The subsequent operational recommendations that physical developer should be used sequentially after ninhydrin and as a treatment for wetted paper items were supported by the results above.

8.3.3 This recommendation is still supported by operational results where physical developer continues to develop additional marks as the final stage of sequential treatments and as the sole treatment for wetted items. In some cases the items treated have been over 25 years old and have been immersed in water.

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3.6 Powders

1. History

1.1 The use of powders is one of the oldest reported techniques for development of latent fingerprints. Faulds, in his publication 'Dactyloscopy, or the study of fingerprints' of 1912 [1], refers to the experiments conducted by Forgeot in the late 19th century as the first studies into the powdering technique, and also comments on subsequent experiments of his own [2]. By 1912 Faulds [1] was able to describe formulations and application techniques for both black and white powders, and by 1920 many more types of powders had been reported for development of fingerprints, including mercury-chalk (hydrargyrum–cum–creta), graphite, lamp black, ferric oxide, magnesium carbonate, aniline dye stuffs, lycopodium powder-Sudan Red mixture, red lead oxide, lead carbonate, lead iodide and lead acetate [3]. By the end of the decade a further selection of fingerprint development powders had been reported, including the first references to the use of aluminium powder. The purpose of many of these materials was to provide investigators with a range of different coloured powders that could be used to both develop a crime scene mark and provide contrast with coloured backgrounds. Some of these early powders persisted in use for many years. Mercury-chalk was still in use in the UK in the 1970s, and carbon black-based powders remain in use worldwide to the current day (2011).

1.2 Another technique for providing contrast between the developed mark and the substrate and considered relatively early in the history of fingerprint development was fluorescence. Zinc sulphide and anthracene were proposed as fluorescent dusting powders in the 1930s [4], with the developed marks being illuminated with long-wave ultraviolet (UV) radiation to promote phosphorescence and luminescence respectively. Variants of these powders were still being recommended for development of latent fingerprints on multi-coloured surfaces in 1954 [5].

1.3 The range of powders that have been formulated and marketed for fingerprint development in the intervening years far exceeds the number of chemical development techniques, and more enter the market every year. Some examples of powder 'recipes' that have been used by police forces in the past [6,7] but that are now predominantly obsolete, are given in the table below.

Colour of powder	Constituents	Wt% of constituent
Black	Lamp black Graphite Gum acacia	70 20 10
	Black magnetic ferric oxide Rosin Lamp black	50 25 25

White	Titanium dioxide Kaolin French chalk	67 16.5 16.5
	Titanium dioxide Basic lead carbonate Gum arabic	33.3 33.3 33.3
Grey	Mercury Chalk Aluminium powder	25 50 25
	Basic lead carbonate Gum arabic Aluminium powder Lamp black	87.5 12.5 trace trace to give colour
Red/orange	Red lead oxide Rosin	33 67
	Lycopodium Sudan Red III	90 10
Fluorescent	Anthracene White tempera	50 50

Published formulations for various types of early fingerprint powders.

1.4 These early powder formulations do not appear to have been devised by any standardised testing system, nor were any recorded comparative trials carried out to establish which formulations were most effective. Their use was often according to the personal preferences of the person treating the marks at the crime scene rather than any scientific assessment of which powder was most appropriate for a particular type of surface. As a consequence, no single type of powder predominated and many local variations in practice arose worldwide.

1.5 Some of the constituents used in early fingerprint powder formulations were toxic or carcinogenic and their prolonged use could cause health problems. The best documented of these problems is the occurrence of mercury poisoning among officers in UK police forces [8,9], initially reported in the late 1940s and caused by the use of mercury-chalk powder. Although most of these powder formulations have since been withdrawn, it is still recommended that users consult material safety data sheets before employing any new type of powder.

1.6 Many powders used for fingerprint development in the first half of the 20th century were also granular in nature, typically applied with animal hair brushes. Photography of the marks developed by powdering was almost exclusively carried out in situ. Developments in the 1960s meant that alternative types of powders began to become more widely used. The first of these developments was the ‘Magna brush’ in the early 1960s [10], consisting of a retractable bar magnet within a non-magnetic cover material. When dipped into a pot of magnetic powder, a brush-like head of powder became attracted to the magnet, which could then be drawn across the surface like a hairbrush. A range of magnetic powders

were soon developed for use with this brush. The second development was the increasing recognition that aluminium flake powder, already in operational use in the 1950s, had a combination of properties that made it ideally suited for use with lifting media, thus overcoming the need for photography in situ and enabling the separation of the developed mark from backgrounds that may have made photography difficult.

1.7 PSDB has carried out several unpublished surveys of the types of powders in use in police forces around the UK, showing the progressive change in the types of powders used. The use of aluminium flake powder and subsequent lifting of the mark was adopted by the Metropolitan Police around 1971 after observing the practice in the USA. The principal objective of this change in practice was to avoid the transport of exhibits for photography; although it was argued that results were as good as or better than previous procedures. It was widely adopted around the UK over the next 5–10 years, although two forces were still almost exclusively using white and black powders into the late 1980s.

1.8 Since then, aluminium flake and magnetic powders have been increasingly used in place of granular powders and the types of powder currently (2011) in widespread use can be grouped into four main classes, namely:

- metal flake powder (e.g. aluminium and bronze);
- granular powder (black and white);
- magnetic powders;
- fluorescent powders.

1.9 The categories above represent a general classification, the actual number of powder formulations that are available on the world market can be numbered in the hundreds and some formulations actually fall into more than one category. Each of these different powder types have particular types of surface to which they are most suited – there is no one powder that will consistently develop marks of optimal quality on all surfaces. However, despite this recognised performance variation there is very little reported evidence of large-scale comparative studies to demonstrate the relative effectiveness of powders other than the experiments carried out by the Home Office Scientific Development Branch (HOSDB) [11,12,13]. These comparisons were limited to a small number of powders identified as being representative of the general categories by a survey of police force scene of crime units and by preliminary evaluations. By tracing the commercial powders back to source it was established that many differently labelled products were in effect the same powder, and some other less-used powders performed poorly in early trials and were therefore eliminated from subsequent studies. This enabled the large-scale trials to focus on powders that were effective, and/or widely used. A methodology is presented [11] that allows researchers to carry out similar comparative assessments for any new powder system.

1.10 Powdered marks probably account for the largest number of fingerprint identifications worldwide, in the UK alone approximately 50% of the 60,000 fingerprint identifications per annum arise from marks developed using this process. It is therefore evident that even the small proportional improvements that can be achieved by the selection of the optimum powder and brush combination for a particular surface have the potential to provide significant operational benefits, and further study of this area may be required.

2. Theory

2.1 The development of fingermarks by powdering occurs by preferential adhesion of powder particles to the ridges, with the background material having less affinity for the particles. This means that powders should not be used where surfaces are sticky or heavily contaminated because the particles will not be able to discriminate between the constituents in the fingerprint residues and the contaminant, and will adhere across the entire surface.

2.2 The factors that are thought to play a role in promoting powder particles to adhere to fingerprint ridges are:

- particle shape;
- surface chemistry of the powder particle;
- electrostatic charge on the particle;
- adhesion to grease or liquid;
- low(er) adhesion to the substrate.

The overall adhesive effect of a particle to a fingerprint ridge is likely to be a combination of all these factors and therefore no one dominant mechanism can easily be identified.

2.3 In terms of particle shape, it has been suggested that flake powders are more sensitive than granular powders because their shape gives them a higher surface area and hence better contact with the fingerprint deposits.

2.4 With regard to surface chemistry, it is known that the adhesion of a powder particle to a solid surface in air or a gaseous medium is partly due to molecular forces [14]. It is therefore anticipated that changing the molecules on the surface of the powder particle will have an effect on the interaction between that particle and the medium it adheres to. It has been demonstrated that surface coatings do play a role in the effectiveness of metallic flake powders for fingerprint development. Experiments conducted by James *et al.* [15,16] demonstrated that flake powders without stearic acid coatings were poor for fingerprint development, irrespective of flake diameter. Further investigation of stearic acid coating thickness showed that optimum results were obtained for a coating thickness of 70nm.

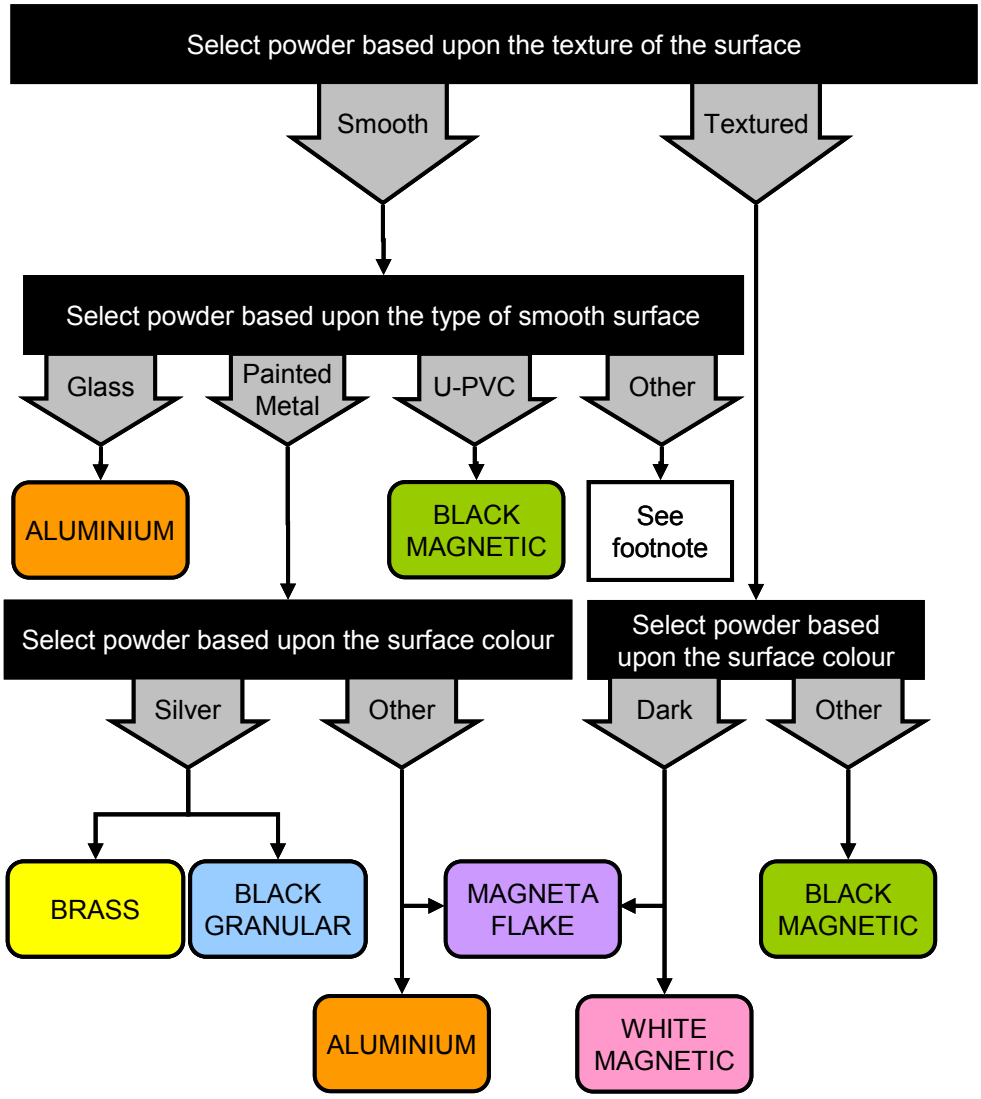
2.5 Electrostatic charge can potentially make large contributions to adhesion. It has been stated [14] that if particles are highly charged, the value of the attractive Coulomb forces exceeds that of other contributions to adhesion. Researchers have investigated various ways of utilising this effect for enhancing fingerprint development using powders, but it is not the major mechanism used in any of the types of powder widely used at crime scenes.

2.6 The presence of liquid or grease in a fingerprint deposit will promote adhesion of the particle to it for two principal reasons. The first is that the liquid is able to wet the surfaces, thus giving a greater contact area for the powder particles. The second is the capillary force of the liquid caused by surface tension. In atmospheres of relative humidity in excess of 70% the increase observed in the adhesion of microscopic particles is due to capillary forces. It has been suggested that in dry climates or for fingerprints that have dried out, ‘huffing’ (blowing warm, humid air or breath over the mark) or rehumidification prior to powdering may improve the quality of the developed print [17].

2.7 Once the initial layer of powder particles have adhered to the fingerprint ridge, the process of auto-adhesion (the interaction between individual powder particles) becomes important. In the case of aluminium powders it is suggested that repeated passes of the brush are used to ‘build up’ the mark, indicating that strong auto-adhesive bonds do exist between aluminium powder particles. For powdering with magnetic flake powders, a single sweep of the applicator is suggested, with further passes thought to ‘fill in’ or reduce the quality of the fingerprint. This indicates that auto-adhesive forces between magnetic flake particles are weak, and there is a possibility that the magnetised particles may repel each other.

3. CAST processes

3.1 CAST recommendations suggest the use of several different generic types of powder, the advice regarding selection being dependent on the type of surface being treated. The current (2011) recommendations are as follows [18]:



Home Office Centre for Applied Science and Technology flowchart for the selection of powders.

3.2 Aluminium flake powder is the most effective powder on glass, but shows similar performance to several alternative powders on other smooth, non-porous surfaces. For these surfaces aluminium may still be the powder of choice as it is easy to apply and develops good contrast marks on most smooth surfaces. The most effective brush for use with aluminium powder is the glass fibre, Zephyr-style. Although monitored trials established that exposure to aluminium dust in normal usage is an order of magnitude lower than allowable exposure limits, dust masks should be used with this powder when used in confined environments.

3.3 Brass (copper/zinc alloys commonly referred to as ‘bronze’ or ‘gold’ due to their colour) flake powders perform similarly to aluminium flake powder, but should only be used on smooth, silver coloured surfaces where aluminium would give low contrast. An appropriate dust mask must be worn when using this type of powder because the exposure

limits for this type of powder are lower than those for aluminium flake and can be exceeded during normal use.

3.4 Black granular powder may be used on some smooth surfaces only and can be considered as an alternative to brass flake powder on silver coloured surfaces. Dust masks should be worn when using this powder.

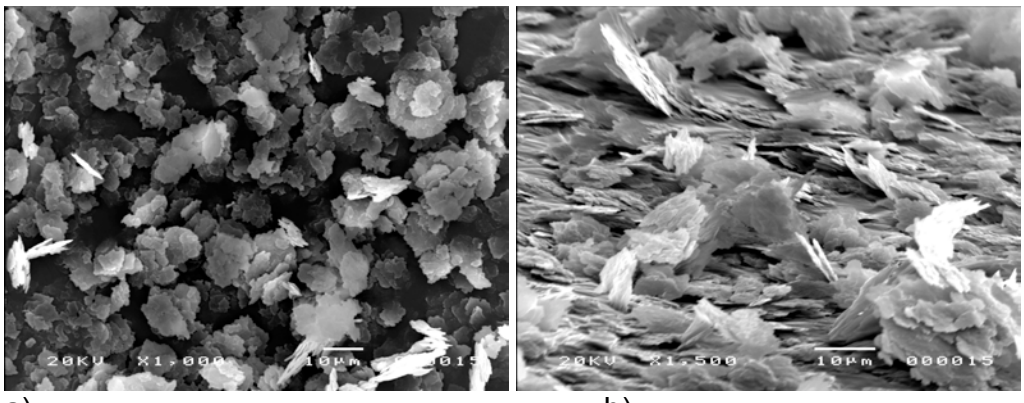
3.5 Black magnetic powder is the most effective powder on textured surfaces and unplasticised poly vinylchloride (uPVC). Similar results were obtained with 'jet black' magnetic powder, but others (grey, silver, etc.) were found to be considerably less sensitive. White magnetic powder, although less sensitive, may be used on dark, textured surfaces when contrast is an issue.

3.6 Magneta Flake powder is slightly less sensitive than black magnetic powder on textured surfaces, but may offer an alternative on dark textured surfaces. It may also be used on most smooth surfaces although application can be difficult and inconsistent.

3.7 Further information on each type of powder is given below.

3.8 Aluminium powder

The aluminium powder that was widely used throughout the UK was either 'Aluminium Super 8000' or 'Offset 901', both supplied by Wolstenholme International Ltd. Wolstenholme has recently been taken over and a closely equivalent powder is now supplied by the new parent company (Eckart Effect Pigments). Small-scale tests and microscopy indicate no significant differences in morphology or performance. They are metal flake powders, with smooth surfaces and jagged edges. The diameter of the particles falls within the range 1–12μm and the thickness is ~0.5μm. The flakes are coated with stearic acid during the milling process to prevent clumping.



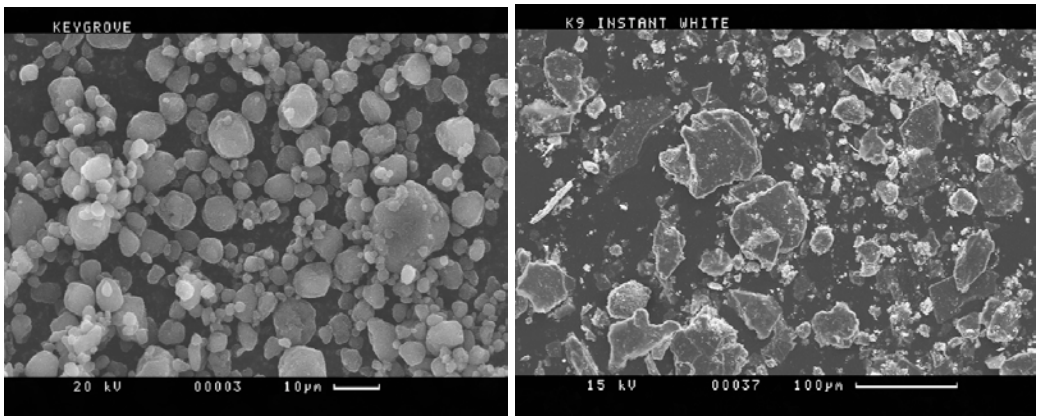
a) b)

Scanning electron micrographs of Wolstenholme Super 8000 aluminium powder showing a) flakes viewed from above and b) flakes viewed from the side.

3.9 Granular powders

Most black granular powders are carbon-based. The main carbon supplier in the UK is Cabot Ltd, which supplies most forensic providers with the Elftex 415 grade of carbon powder. This is an amorphous, elemental carbon with a particle size in the range 5–10μm and a textured, irregular (but smooth) shape.

3.10 White powders may contain more than one particle type. The example shown below consists of large flakes of magnesium silicate (20–100mm in size) with small granules of titanium dioxide (mostly <1μm). The small granules coat the surface of the flakes, suggesting that the flakes act as the carrier for the titanium dioxide granules.



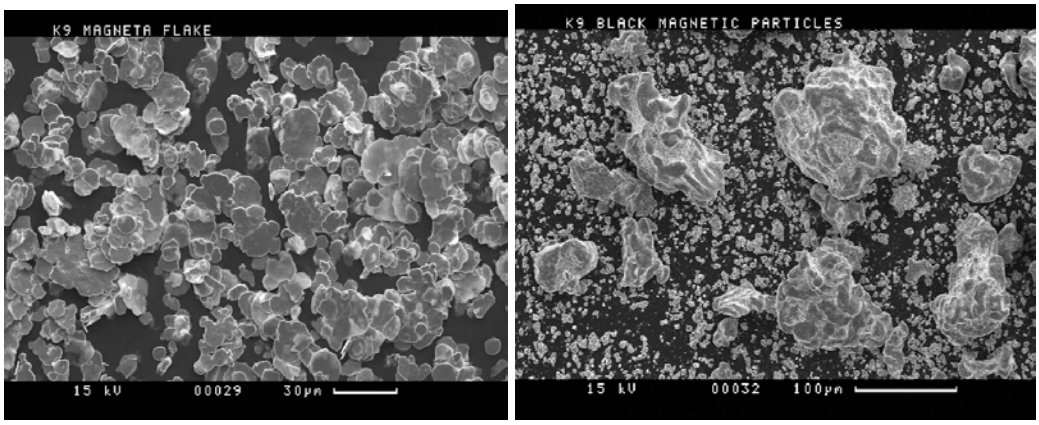
a) b)

Scanning electron micrographs of typical a) black and b) white granular powder.

3.11 Magnetic powder

There are two distinct types of magnetic powder used in the UK, Magneta Flake and black magnetic powder (traditionally called Magna powder). Magneta Flake was developed as part of a joint project between the Home Office and the University of Swansea in the early 1990s [15,16] and is now manufactured and distributed by CSI Equipment Ltd. It is produced by milling spherical carbonyl iron with 3–5% stearic acid in an appropriate solvent to produce a smooth edged flake with particle sizes in the range 10–60μm. Other types of magnetic flake powder are now available from other suppliers.

3.12 Black magnetic powder has a substantially different microstructure, consisting of large magnetic carrier particles of elemental iron (20 – 200μm) and smaller non-magnetic particles of iron oxide (Fe_3O_4) with a particle size in the range 3–12μm. The larger particles act as a carrier medium for the smaller particles, which adhere to the fingerprint ridges and develop the mark.



a) b)

Scanning electron micrographs of magnetic powders a) Magneta Flake and b) black magnetic powder

4. Critical issues

4.1 There are several critical issues to consider before powdering a surface. Before any powder is applied, a search should be made using a white light source to establish whether any visible marks are present. These should be captured before proceeding because not all marks found in this way will subsequently develop using powders.

4.2 An assessment should be made of the surface itself. If the surface is heavily contaminated, highly textured and/or porous, powdering may not be the best technique to use and alternative processes should be considered.

4.3 The type of powder used should be selected according to the nature of the surface, choosing both a powder type known to work well on that surface and a powder colour that gives a good contrast with the background.

4.4 The means of application should be compatible with the powder selected. Aluminium powders are best applied using a glass fibre Zephyr brush, magnetic powders using a magnetic applicator, and granular powders using a soft mop style of brush.

4.5 The decision on whether to lift the mark or to image in situ must be made according to the type of powder used. Aluminium (and brass) flake powders are well suited to lifting, magnetic and granular powders may be better imaged in situ first. However, regardless of the powder used there is always the possibility of damage during lifting and photography of the mark in situ should always be considered as a first option.

4.6 The sequential use of powders should be considered. It is possible that marks will not be developed by one type of powder, but may be subsequently enhanced by use of a different type.

5. Application

5.1 Suitable surfaces: Powders can be used on all non-porous types of surface including glass, plastics, metals, painted and varnished wood and ceramic, although they may not be the most effective process for that surface. In general, as the surface becomes rougher and more porous, the less effective powdering is likely to be.

5.2 The principal application of powders is the development of fingerprints on smooth non-porous surfaces at crime scenes, although recent research has shown them to be a valuable method for finding marks on textured or semi-porous surfaces such as wallpaper. The brush application method allows large areas such as windows, doors and door frames to be speculatively treated without recourse to more messy or time-consuming chemical treatments. The speed and effectiveness of the technique makes powders well-suited to volume crime applications. The fact that other treatments (such as blood dyes, powder suspensions and superglue) can be used sequentially after it also makes it an important first treatment at serious crime scenes.

5.3 In the laboratory, powders can be used on non-porous exhibits where it is suspected there may be a mixture of latent prints and marks in blood. This is because they can develop both types of mark and have no detrimental impact on subsequent treatment with blood dyes (unlike the alternative treatment option, superglue).

5.4 Powders should not be used if it is suspected that a surface is contaminated with any sticky residues (e.g. foodstuffs, oils) because powder will adhere to the entire surface and marks will not be resolved.

5.5 The means by which the powder is applied to the surface can also affect the quality of the mark. It has been recognised [19] that marks may be damaged by poor powdering practice and/or the use of the wrong type of brush. Similarly, brush application may often develop surface texture instead of the mark, and selection of an appropriate applicator may in some cases be more important than selection of the correct powder. HOSDB carried out extensive studies [11,20] to determine the optimum brush for use with aluminium powder and concluded that glass fibre, Zephyr-style brushes gave the optimum combination of ridge detail developed, contrast of the developed mark and minimal brush damage. This is because the glass fibre brush retained the powder well and released it gradually, which is most compatible with the gradual build up of the marks produced with this type of powder. In contrast, squirrel hair, mop style brushes give significantly worse performance in all three respects for aluminium powder, but are the most widely used brush for use with granular powders.

5.6 Magnetic powders (both black magnetic and Magneta Flake) are applied using magnetic wand applicators, where a small magnet in the tip of the wand picks up a 'brush' of powder when dipped into the powder container. This powder 'brush' is then applied to the surface, thus avoiding any direct contact between the applicator and the surface. Although such powders are relatively easy to apply to horizontal surfaces, application to vertical surfaces is less straightforward and powder may drop off. Ease of application to a particular surface should be taken into consideration when selecting the powder to use.

6. Alternative formulations and processes

6.1 There are many different types of powder being sold for fingerprint development applications and it is not possible to evaluate every product on the market. As a consequence, the advice given in the powder selection flow chart above refers to generic powder types only and not to a specific manufacturer's products. It is known that several nominally similar products are now available on the market (e.g. 'Magneta Flake' and 'Mag100') and not all of these have been tested by CAST.

6.2 It is possible that some products may give better performance than those covered in the existing CAST guidance. If the use of a product not currently (as of 2011) within the generic powder types outlined above is proposed, it should be extensively evaluated against the existing powder types in laboratory trials on representative surfaces before being used operationally. The guidance given by CAST originates from tests utilising thousands of developed marks, and any trials recommending changes to that guidance should incorporate an equivalent number.

6.3 PSDB funded work in the mid- to late-1970s to develop an electrostatic powder process for developing fingerprints at scenes of crime [21-25]. The perceived advantages of the technique were that it could develop fingerprints without making any contact with the latent mark, and that the developed mark could be enhanced by removing excess powder without damaging the mark. The concept proposed by Roy 22] was the use of a positively charged high voltage electrode introduced above a quantity of powder within an insulating container to attract a powder coating onto the electrode. Holding the electrode over a surface bearing a fingerprint resulted in the formation of a powder cloud, with charged powder particles moving between powder and surface and some being retained on the fingerprint ridges. Several different powders were studied, the most appropriate for this purpose being found to be the semiconductor calcium tungstate ($CaWO_4$). Work was also carried out to develop a practical apparatus for powder delivery [21] and to explore mechanisms of deposition and cheaper alternative powders to calcium tungstate [23-25]. Ultimately the system did not enter widespread operational use, possibly because of limited benefits over conventional powdering, coupled with the added complexity of the application device compared with brushes.

7. Post-treatments

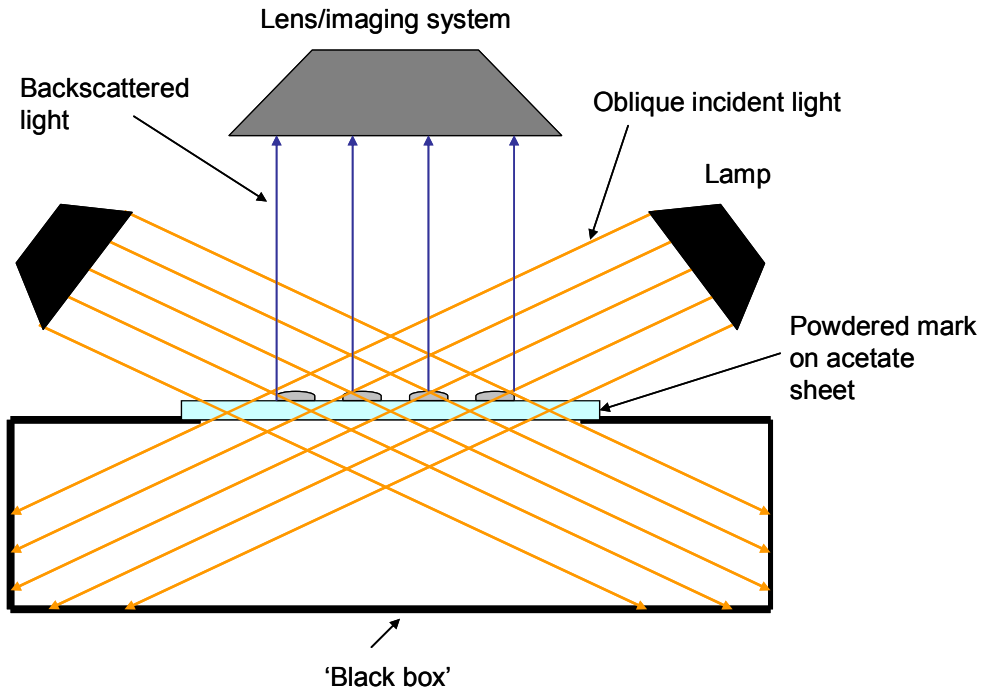
7.1 The main post-treatment for powdered marks is that of lifting. Advantages of this process include the fact that it enables a large number of marks developed using powder to be rapidly collected from a scene, it removes the powdered mark from the background environment it has been developed on and thus makes imaging of the marks in isolation easier, and it removes many issues associated with the level of skill of the crime scene photographer in capturing a good quality image.

7.2 To counter this, some disadvantages are that lifting may remove contextual information about the environment the mark was found in, and the quality of the lifted mark is potentially degraded from the mark developed in situ because some powder remains on the surface while the remainder adheres to the lifting medium. Lifting is most compatible with flake powders, it is less appropriate for granular and magnetic powders and may cause greater degradation to the quality of the lifted mark for these powder types. If it has been decided that the developed mark is to be lifted there are several types of material that can be used as lifting media, including:

- adhesive tapes and sheets;
- gelatine lifts;
- casting compounds.

7.3 In common with powders and brushes, selection of the optimum lifting medium for a particular type of mark may improve the quantity and quality of the marks recovered. However, there are few extensive published studies in this area.

7.4 The lifting process is principally used for aluminium powdered marks, but may be used for marks developed using other types of powder. For marks developed using aluminium flake, clear adhesive tapes are most commonly used as the lifting medium. The lifted mark is stuck to a clear acetate sheet, which is then retained as the exhibit. The contrast between the reflective aluminium powder and the transparent tape and acetate can be utilised to capture images of the lifted mark. Techniques used include contact printing using equipment such as the Camtac (although the advent of digital imaging is leading to this method becoming obsolete), scanning using a glossy black backing sheet, or using a ‘black box’ to enhance the contrast.



'Black box' imaging arrangement used to enhance contrast of aluminium lifts.

7.5 The type of lifting tape used does have an effect on the quality of the mark, and some studies have been carried out to assess this [26]. However, in practice there are few, if any, adhesive tapes produced solely for forensic use and it is difficult to ensure that any particular tape type will perform consistently from roll to roll. For this reason, CAST does not recommend any specific brand of lifting tape. Small-scale tests by CAST indicate that black gelatine lifts may actually be better than adhesive tape in lifting aluminium powdered marks, but this type of lift is more expensive, and more difficult to store and transport than tape lifts and is not routinely used.

7.6 Other recent developments associated with the lifting process include the introduction of wireless transmission of the fingerprint image from the crime scene to the fingerprint bureau. One approach [27] uses a flatbed scanner with a gloss black backing paper to scan the aluminium lift and image compression software to reduce the file size to a level that can transmitted over a mobile phone network in around 30 seconds.

8. Validation and operational experience

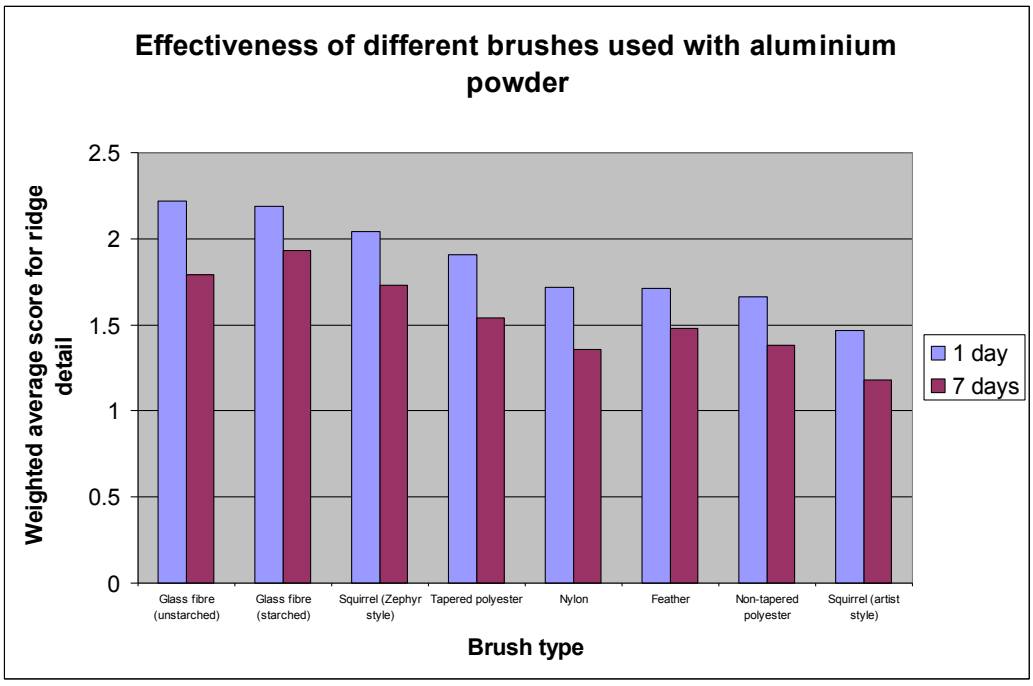
8.1 Powdering is a very important process for fingerprint identification, with approximately 50% of fingerprint identifications (in excess of 30,000 per annum) being obtained from marks developed using this technique. As a consequence, any improvement in the effectiveness of powdering or

guidance associated with its application has the potential to provide a significant number of additional identifications.

8.2 Laboratory trials

8.2.1 CAST has conducted extensive laboratory trials on both powders and the brushes used to apply them. Each study has involved the development and assessment of approximately 10,000 fingerprints.

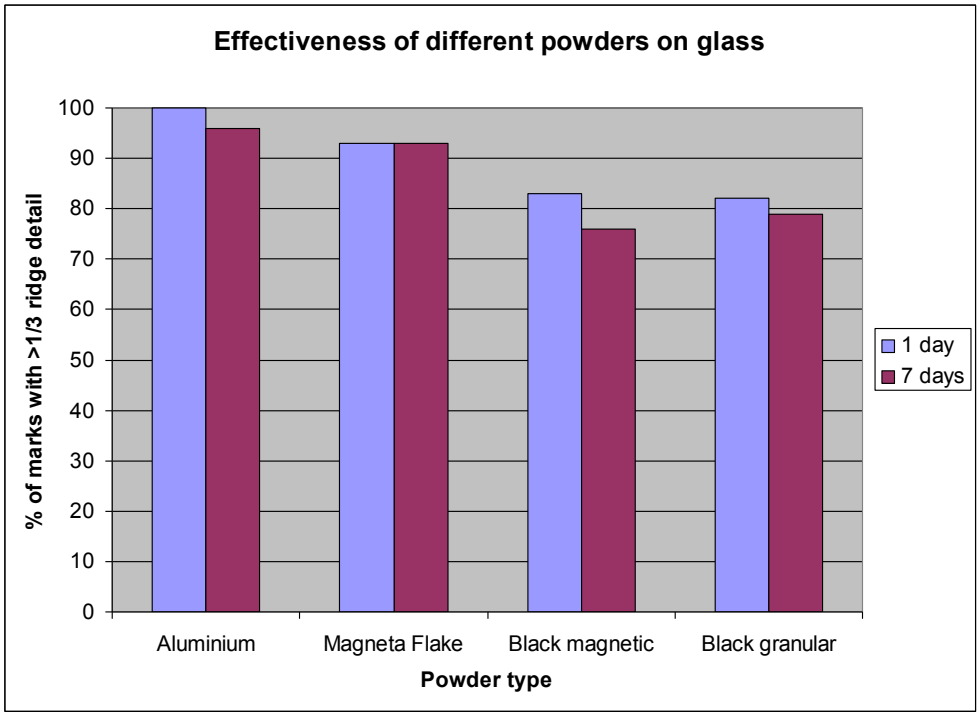
8.2.2 Surveys carried out on powdering practice in the UK confirmed that by far the most widely used powder was aluminium, although many different brushes were being used for its application, including glass and polyester Zephyr, feather, and squirrel hair. The initial study [11,20] looked at the most effective brush type for the application of aluminium powder. Trials were carried out on four surfaces identified by a survey of scene of crime officers (SOCOs) as those most representative of those found at crime scenes, namely glass, uPVC, painted wood and painted metal. In all 12,640 marks were powdered and graded in terms of ridge detail developed, contrast and brush damage. The conclusion of this work was that glass fibre, Zephyr-style brushes gave the best results for this type of powder.



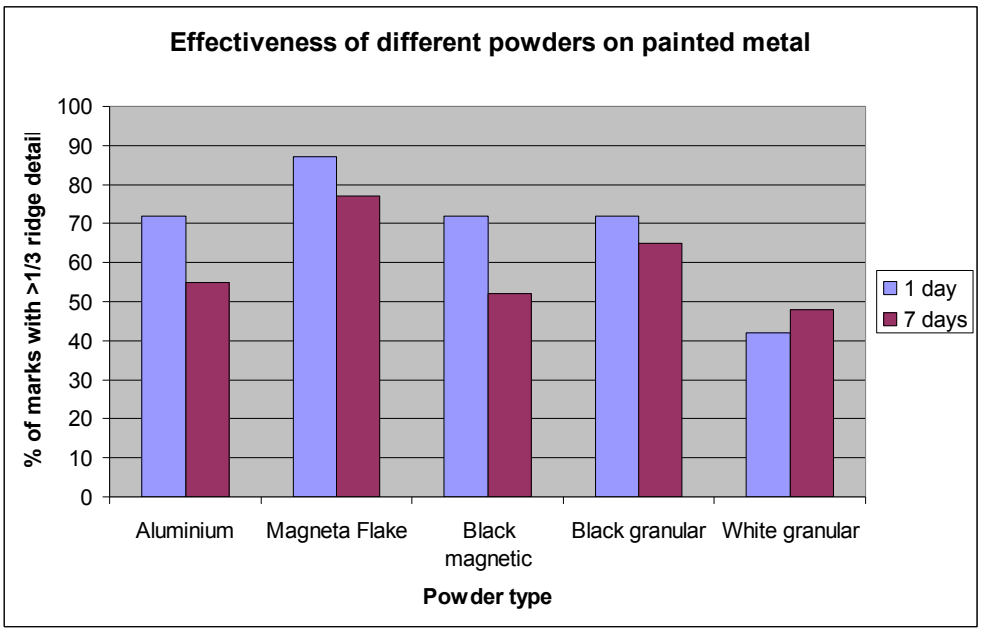
Summary of results obtained comparing the effectiveness of different types of brush used with aluminium powder.

8.2.3 It was recognised that although aluminium is routinely applied to all the surfaces used in the trial summarised above, it may not actually be the best powder to use in all cases. The next stage of the work [12] therefore compared the effectiveness of aluminium against other types of regularly used powder on a series on smooth, non-porous surfaces (glass, painted metal, ceramic and gloss painted wood). Approximately 1,500 marks

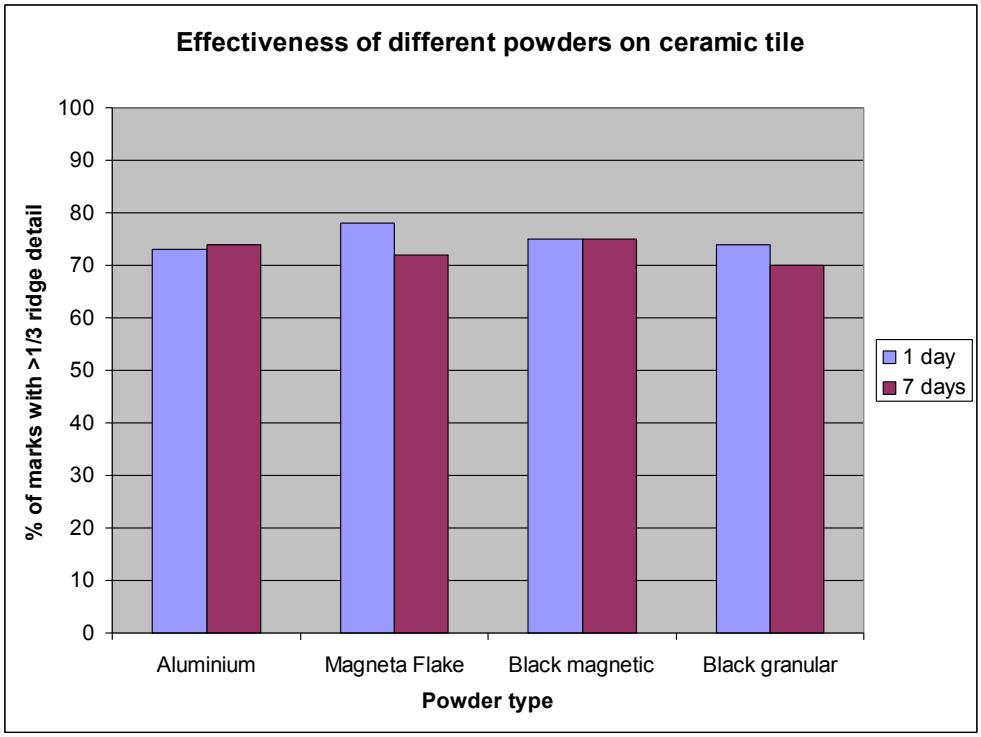
were developed on glass and approximately 2,500 on the other three surfaces. The results are shown below.



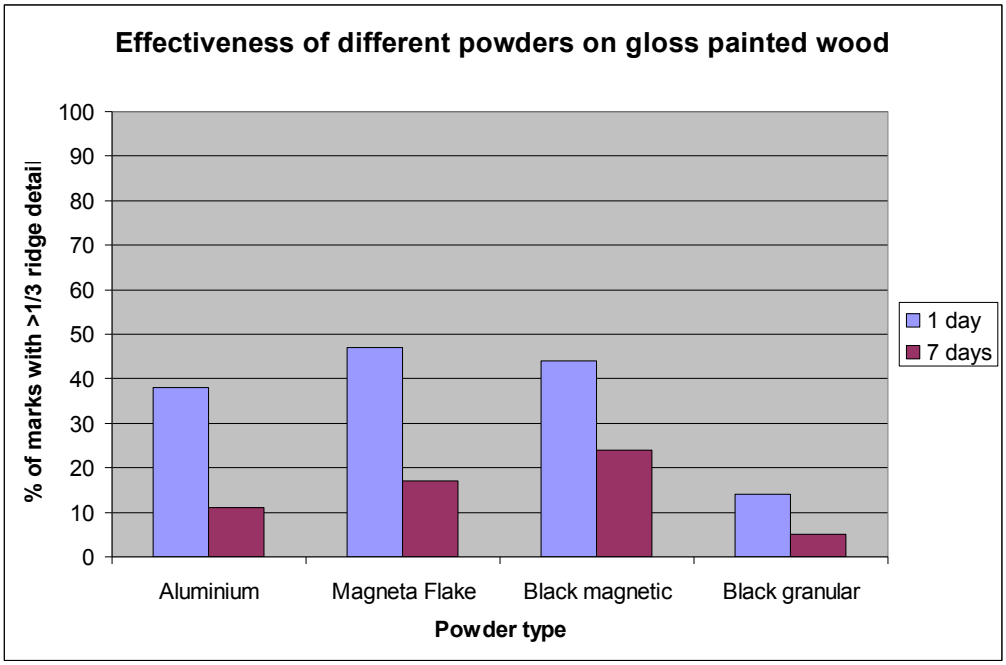
Comparison of different powder types on glass surfaces.



Comparison of different powder types on painted metal surfaces.



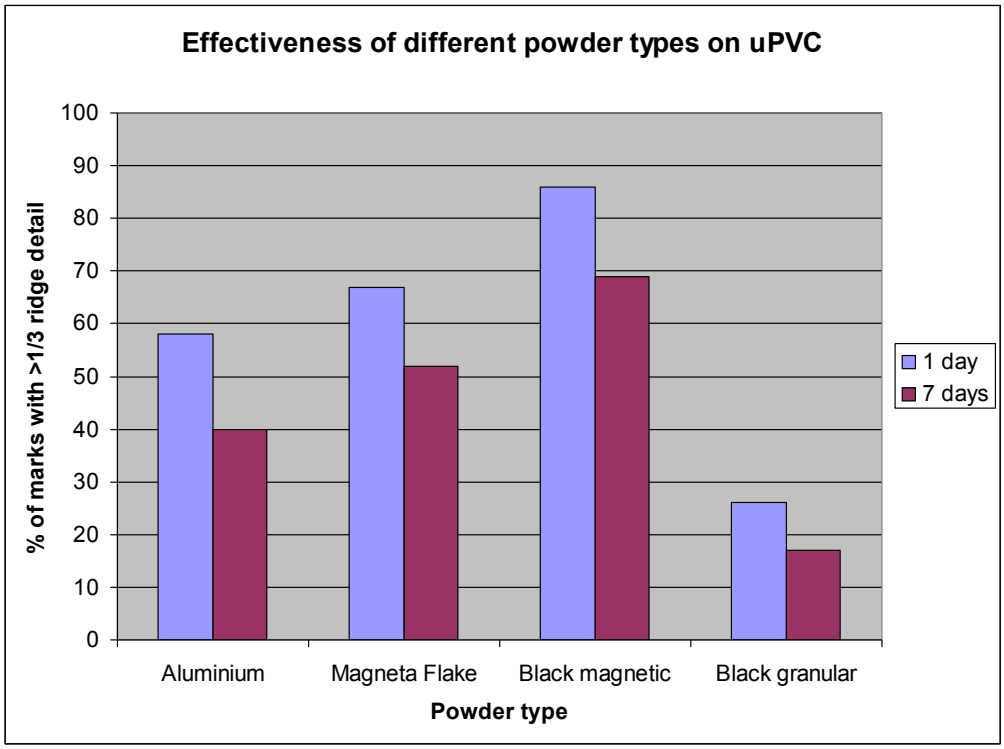
Comparison of different powder types on ceramic tiles.



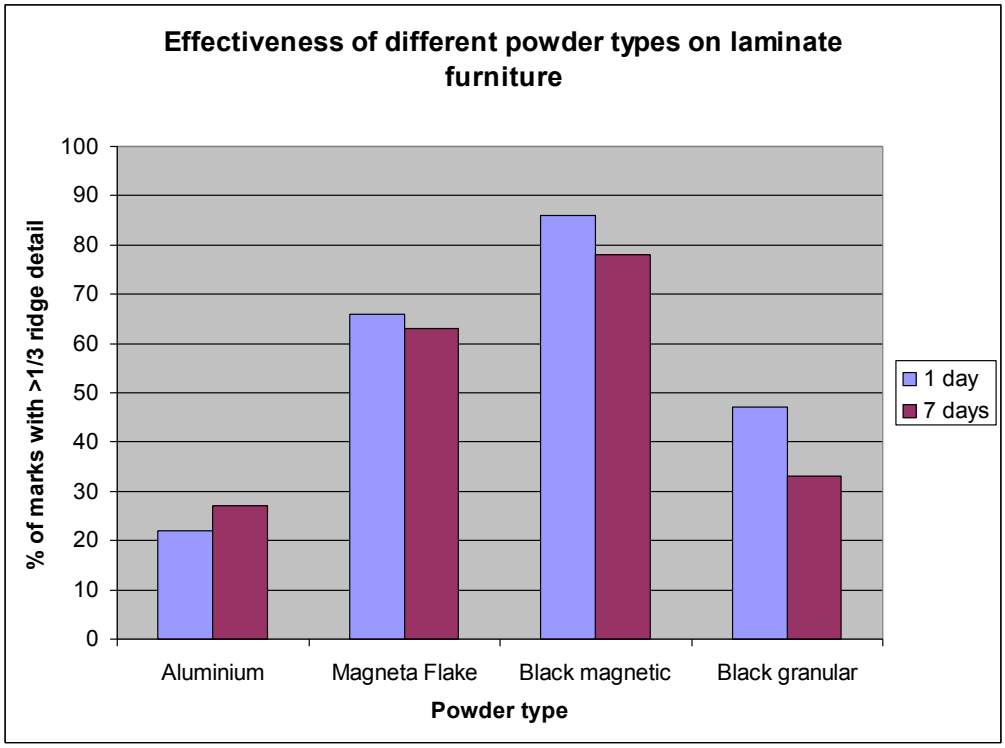
Comparison of different powder types on gloss painted wood.

8.2.4 The results indicate that although aluminium powder is the best performing powder on glass, on other smooth surfaces magnetic powders may actually give slightly better performance. As the roughness of the surface increases the effectiveness of aluminium drops off and both types of magnetic powder are more effective. In order to investigate this further, the next trial compared a range of powders on surfaces with

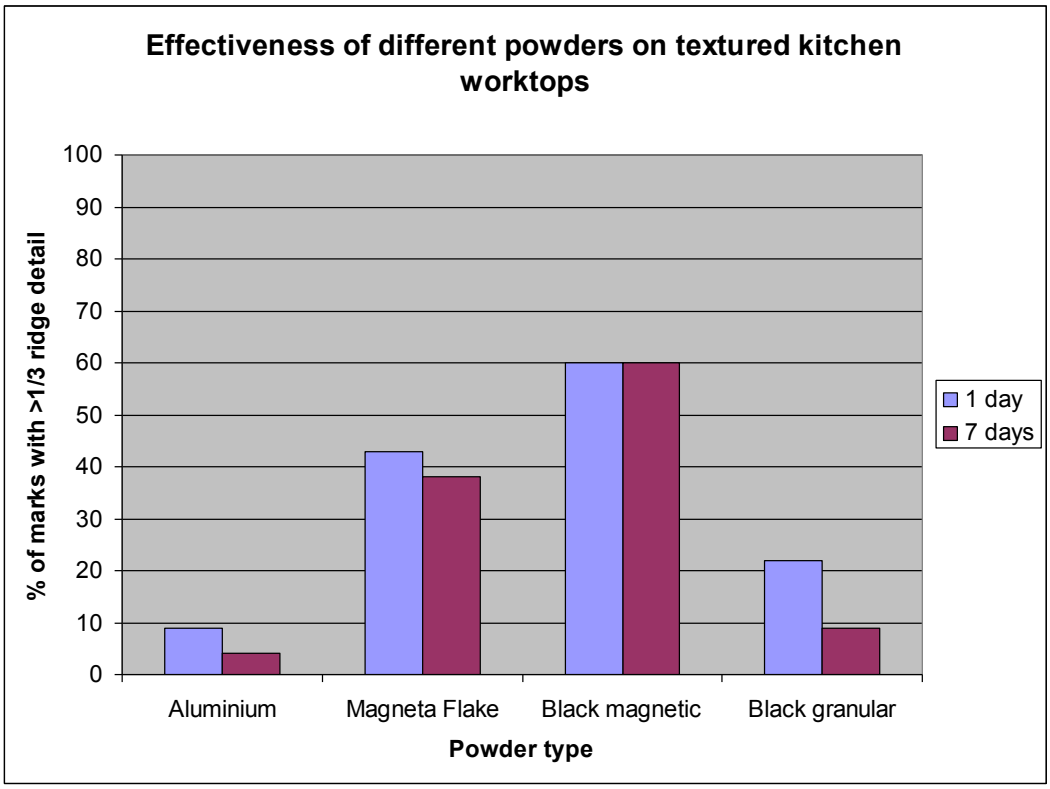
different levels of surface texture including uPVC, laminate furniture, kitchen worktops and wood furniture [13,28]. The graphs below show the results of this study, which developed and graded 9,560 marks.



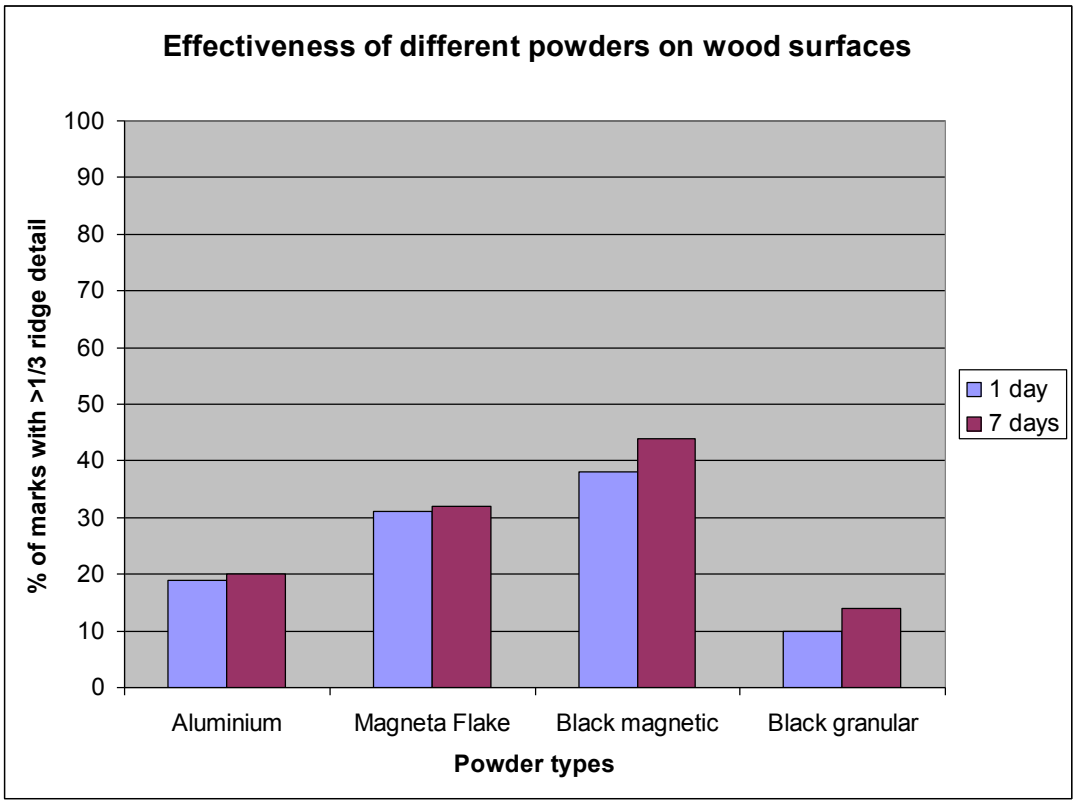
Comparison of different powder types on uPVC.



Comparison of different powder types on laminate furniture.



Comparison of different powder types on textured kitchen worktop material.



Comparison of different powder types on wood furniture.

8.2.5 When considering the results obtained from all surfaces examined, it is evident that as the surface becomes more textured, the effectiveness of both aluminium flake and black granular powder decreases significantly. The effectiveness of both types of magnetic powder also decreases as surface texture increases, but the degradation in performance is not as great and these powders are recommended for use on this type of surface.

8.3 Operational experience

8.3.1 Since the issue of the *Fingerprint Powders Guidelines* [18] in 2007, CAST has supplemented this with several training sessions targeting SOCOs at individual police forces. In some cases there have been reported rises in the use of black magnetic powder at the expense of aluminium flake and an increase in marks developed, but at present (up to 2011) it is difficult to assess whether both trends will be sustained in the long term.

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3.7 Powder suspensions

1. History

1.1 During the development of the small particle reagent in the late 1970s, many other particulates were investigated as constituents in the formulation, including amorphous carbon and graphite and the oxides of the magnetic elements cobalt and iron [1]. All of these gave good results, but none were as consistent as molybdenum disulphide and therefore were not pursued as systems for operational use.

1.2 In a significant development that appears to have been overlooked at the time, Haque and co-workers developed an alternative 'small particle suspension' based on iron oxide (Fe_3O_4) in 1989, and stated that this gave better results than the molybdenum disulphide-based small particle reagent in terms of sensitivity and contrast [2]. The new formulation was also noted to work on wetted surfaces, and to enhance further marks previously developed by powdering. This formulation does not appear to have entered widespread use for non-porous surfaces and was not developed further.

1.3 In the mid-1990s similar formulations were developed by researchers at the National Identification Centre, Tokyo Metropolitan Police, who were investigating simple methods for developing fingerprints deposited on the adhesive side of tapes [3]. This was noted by an American police officer on secondment in Japan and after experimentation with black powder suspensions he contacted the Lightning Powder Company, which developed the 'Sticky-Side Powder' product now sold commercially, consisting of a pre-mixed powder that was blended with Kodak Photoflo surfactant and distilled water. The resulting suspension was painted on to the adhesive side of tapes, then washed off using running water to reveal developed marks.

1.4 The new Sticky-Side Powder system was compared with techniques in general use for adhesive tapes in 1996, primarily basic violet 3 [4]. The powder suspension formulation was found to perform better than basic violet 3, in particular on marks known to be eccrine in nature. Several researchers began to investigate alternative powder suspension formulations, looking at the combination of commercial powders with surfactant/water mixtures. Bratton and Gregus [5,6] looked at Lightning Black Powder with Liquinox surfactant and reported it to give better results than Sticky-Side Powder, noting that the revised formulation reduced the occurrence of background staining that sometimes obscured marks with Sticky-Side Powder. Kimble [7] studied a wider range of powders, including grey and coloured systems, with Photoflo surfactant and water in different ratios. It was concluded that other powders could be used and a formulation incorporating a grey powder was proposed for black adhesive tapes. Other workers also investigated formulations for black adhesive tapes, Parisi [8] testing 'Pink Wop' fluorescent powder and a white fingerprint powder with Liquinox and Photoflo, and Martin [9]

looking at an ash grey powder with Photoflo. White powder in Liquinox and ash grey powder in Photoflo both gave suspensions that developed good quality fingerprints. Further testing of these revised powder suspension formulations against basic violet 3 continued to indicate that powder suspensions were the more effective single process for these surfaces [10].

1.5 The Police Scientific Development Branch (PSDB) began experimenting with powder suspensions for development of fingerprints on adhesive tapes in the late 1990s [11]. An initial assessment was carried out on the original Sticky-Side Powder formulation, characterising the base powder by electron microscopy and looking at optimised formulations. It was found that the base powder consisted of fine (~1μm) particles of iron oxide interspersed with larger (10–20μm diameter) flakes of aluminium. A range of other powder suspension formulations were investigated, with two ultimately being recommended for further research. A black powder suspension based on precipitated, magnetic iron oxide was proposed, together with a white powder suspension based on titanium dioxide powder. Both formulations utilised Photoflo as the surfactant. These formulations were trialled against Sticky-Side Powder, where the black formulation was shown to give superior results.

1.6 The black iron oxide-based formulation was then compared in effectiveness with two other treatments for the adhesive side of tapes, basic violet 3 and superglue followed by dyeing with basic yellow 40 [12]. In these trials powder suspension gave closely equivalent results to superglue, with the contrast of developed marks being slightly better. Basic Violet 3 was found less effective than either powder suspension or superglue, in accordance with previous observations.

1.7 Other researchers also concluded that titanium dioxide was the optimum particulate for white powder suspension formulations. Wade [13] used a commercially available white small particle reagent formulation based on titanium dioxide as a starting point, and demonstrated that improved performance was obtained by concentrating the solution and adding Photoflo. Alternative formulations based on different grades of titanium dioxide were investigated and it was observed that better results were obtained using the rutile, rather than anatase, form of titanium dioxide. Williams and Elliot [14] also looked at modifying white small particle reagent with Photoflo and studied different application methods including spraying, immersion, dipping, painting and pouring. It was concluded that the best development could be obtained by immersion and this method also reduced the risk of over-development but was also the most time-consuming.

1.8 Until the mid-2000s, development of fingerprints on adhesive surfaces was the sole application considered for powder suspensions. In 2004, Auld [15] carried out an investigation into the effectiveness of various fingerprint development techniques for detecting marks on motor vehicles, including vehicles that had been wetted. He compared

powdering, superglue, small particle reagent and Sticky-Side Powder, and found that Sticky-Side Powder was the most effective treatment for several scenarios, in particular where cars had been wetted at some stage prior to fingerprint development.

1.9 Around the same time, Strathclyde Police had begun to investigate the use of black and white powder suspensions for the treatment of articles recovered from arson scenes, the treatment both removing soot deposits and developing marks [16].

1.10 These observations resulted in further experimentation on non-porous surfaces, both by police forces on operational casework and by HOSDB in laboratory trials [17]. The HOSDB studies sought to establish the relative effectiveness of the black powder suspension technique on a range of different surfaces and the position of powder suspensions in sequential processing. It was soon apparent that superglue and powder suspensions are mutually exclusive processes and if one is applied the other cannot be used afterwards. An equivalent study was subsequently carried out for white powder suspensions on dark, non-porous surfaces, which came to similar conclusions, although white powder suspension was found to be less effective than black powder suspension overall [18]. Operationally, police forces applied powder suspensions either at crime scenes after powdering, or in the laboratory as a replacement for superglue on articles likely to have been wetted or contaminated (cowlings, number plates, drugs packaging). In both cases additional marks were found or recovery rates increased.

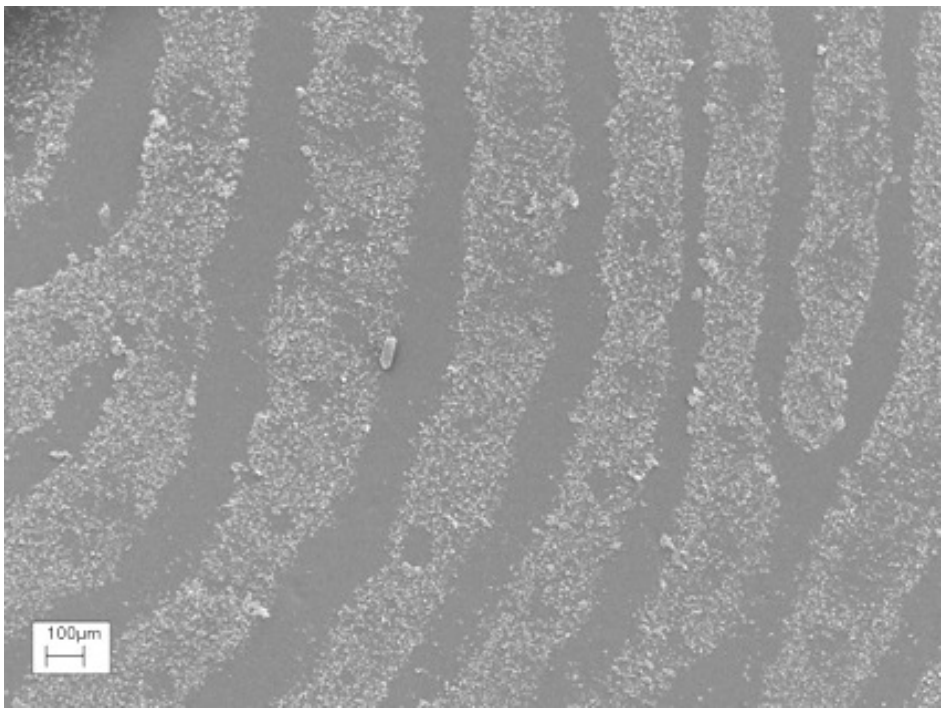
1.11 HOSDB also continued the assessment of powder suspensions for use on adhesive tapes, comparing the formulations developed in earlier work [11] with a range of commercially available powder suspensions. For the white powder suspension [19] it was found that the original HOSDB formulation gave marginally better results and this was used in a subsequent operational trial. For black powder suspensions it was discovered that commercial formulations based on carbon out-performed the HOSDB iron oxide-based formulation and work therefore focused on developing a non-proprietary carbon-based formulation [20]. It was not possible to identify a formulation giving equivalent or improved performance over the commercial systems and therefore commercial, carbon-based systems were included in operational trials. The results from these trials showed that carbon-based, black powder suspensions are the most effective process for the adhesive side of light coloured tapes, whereas for dark tapes superglue/basic yellow 40 is more effective, and white powder suspensions are only recommended for this application if it is known that the article has been wetted.

1.12 Subsequent work both at HOSDB and in operational police laboratories has continued to explore the range of surfaces for which powder suspensions can be used. Recent research has shown that they can be applied to plastic bags [21], semi-porous surfaces [22] and are one of the most effective processes for surfaces contaminated with drugs [23]. It is

anticipated that current (2011) advice regarding the treatment of such surfaces will be updated in due course.

2. Theory

2.1 The exact mechanism for development of marks using powder suspensions is unknown, and studies by CAST to establish which factors are most important are continuing. However, it is thought that the development process is very similar to that for small particle reagent, where the micelles are formed around the particles by the surfactant. Some component or property of the latent fingerprint destabilises these micelles, causing the particulates to deposit preferentially on the fingerprint ridges.



Scanning electron micrograph of fingerprint developed using black powder suspensions on clear adhesive tape, showing particles deposited on fingerprint ridges but not on background.

2.2 Powder suspension formulations contain far higher concentrations of powder than small particle reagent and this may account for some differences in behaviour noted between the two processes.

3. CAST processes

3.1 Powder suspensions have recently (December 2009) been incorporated into the CAST *Manual of Fingerprint Development Techniques* [24] in Charts 1, 2, 5 and 7, and it is likely that they will be incorporated into other charts as research progresses.

3.2 There are three slightly different powder suspensions recommended for operational use, these being outlined below.

3.3 Black powder suspension for use on the adhesive side of adhesive tapes (carbon-based): Commercially available, pre-mixed carbon-based powder suspensions, either Kjell Carlsson Wet Powder (Black) or Armor Forensics/Forensics Source WetWop™ (Black).

3.4 Black powder suspension for use on light, non-porous surfaces (iron oxide-based): Weigh 20g precipitated magnetic iron oxide (Fe_3O_4/Fe_2O_3) into a glass beaker, add 20mL of a pre-mixed 1:1 solution of Kodak Photoflo 200 and distilled water and stir with a brush to form a paste [25].

3.5 White powder suspension for use on dark, non-porous surfaces and wetted dark adhesive tapes (titanium dioxide-based): Commercially available, pre-mixed titanium dioxide-based powder suspensions, either Kjell Carlsson Wet Powder (White) or Armor Forensics WetWop™ (White).

3.6 The ratio of powder to surfactant/distilled water mixture recommended in the CAST formulations for application to adhesive tapes have been determined by laboratory tests [11]. If there is excess surfactant/water present, a thinner suspension is produced, which does develop marks although these are significantly fainter than those obtained with optimum formulations. If there is insufficient surfactant/water present, the suspensions do not flow and clumps of powder may be left behind on the tape.

3.7 For use on non-porous surfaces, it has been observed that the powder suspension can be diluted from the thicker paste applied to adhesive tapes and can still give effective results.

3.8 The role of the detergent in the formulation is to form micelles around the fine particulates and stabilise the suspension against indiscriminate precipitation over the entire surface. The CAST formulations utilise Photoflo, but the commercial formulations may contain other surfactant systems.

4. Critical issues

4.1 Performance of powder suspensions is often critically controlled by the particle size and the shape of the materials concerned which can vary widely with methods of preparation. Use of other generic sources of what is nominally the same chemical may result in very different results and batch testing is recommended.

5. Application

5.1 Suitable surfaces: The full range of application areas for powder suspensions are still being explored, but it is likely that they will be recommended for use in the following circumstances.

- On the adhesive side of light coloured, polymer backed adhesive tapes.
- On non-porous surfaces where it is thought that the surface has been wetted or exposed to high humidity environments.
- On non-porous surfaces where powder or particulate contamination (e.g. soot or drugs residues) is present on the surface.
- On non-porous surfaces where there is a surface layer of oily contamination present.
- On some 'semi-porous' surfaces.
- In a sequential treatment process after powders at a scene of crime and in laboratories.
- As a final treatment after blood dyes on non-porous surfaces.

5.2 Powder suspensions are applied to the surface of interest using a soft brush, ensuring that the brush is well loaded with the suspension mixture to avoid damage that could be caused to the fingerprint by a dry brush and to avoid 'streakiness' in background development. The suspension should be stirred to achieve a paint-like consistency and painted onto the surface, left in situ for 10–15 seconds and then washed off using running water (either from a tap, hose or wash bottle). The temperature of the wash water has not been found to be important.

5.3 Prints can become over-developed if the suspension is left on the surface too long because the suspension starts to dry and fills in ridges. Powder suspensions can also be reapplied, if necessary. There is also evidence to suggest that the different types of powder suspension can be applied in sequence and still develop additional marks.

5.4 The process is suited to application both in a laboratory and at scenes of crime, none of the constituents posing a significant health and safety issue. However, the process is messy to apply and the implications for cleaning of the scene should be considered before application.

6. Alternative formulations and processes

6.1 The initial formulation proposed for powder suspensions [2] was iron oxide mixed with Brij 35 and choline chloride surfactant, diluted with distilled water. This does not appear to have been widely adopted and has not been evaluated by CAST, although the current (2011) formulations are actually similar in nature.

6.2 The first formulation proposed for adhesive tapes was Sticky-Side Powder, consisting of Sticky-Side Powder (a mixture of iron oxide particles and aluminium flakes) mixed with a 1:1 blend of Photoflo and water, added until a thin paint consistency was achieved. Soon after this an alternative formulation was proposed that used 20g of Lightning Black Powder as the particulate, mixed with 20g Liquinox surfactant and 40mL of distilled water.

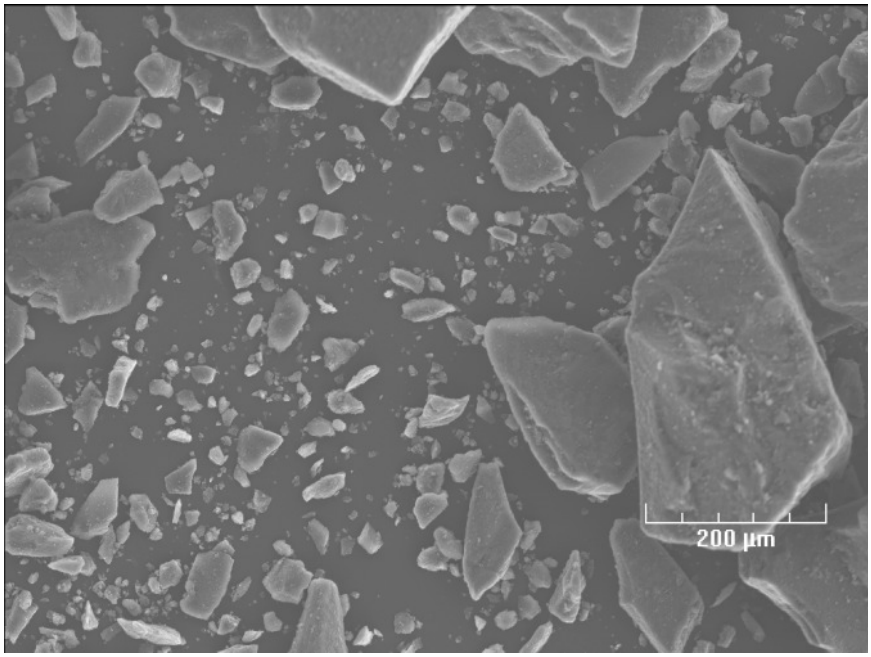
6.3 PSDB evaluated both of these formulations in comparative trials with many different types of particulate fillers in powder suspensions. In the initial investigation of an optimum formulation for the treatment of adhesive tapes [11], the range of powders below were tested in combination with Photoflo surfactant as candidate black powder suspensions.

Powder sample	Specific gravity	Particle size	Manufacturer/ supplier
Fe_3O_4	5.18	> 10μm	BDH Chemicals
Fe_3O_4	5.18	> 5μm	Sigma – Aldrich
Fe_3O_4 – magnetic/ precipitated	5.18	> 1μm	Fisher Chemicals Ltd
Fe_2O_3 – red, precipitated	5.24	> 5μm	BDH Chemicals
Fe powder	-	9 – 110μm	–
Lightning Black Powder	~1.8	> 1 μm (aggregates up to 40μm)	Lightning Powder Company
Lightning Magnetic Black Powder	-	Range from 1–30μm	Lightning Powder Company
Cobalt (II, III) oxide	6.11	> 1μm	Sigma – Aldrich
K9 – Black Fingerprint Powder	1.7–1.9	> 1μm (aggregates up to 150μm)	K9 Scene of Crime Ltd
K9 – Black Magnetic Powder	~1.8	> 1μm (aggregates up to 150μm)	K9 Scene of Crime Ltd
K9 – Jet Black Magnetic Powder	~5.18	> 1μm (aggregates up to 150μm)	K9 Scene of Crime Ltd
K9 – Magneta Flake	7.8	–	K9 Scene of Crime Ltd
K9 – Gold Powder	8.5	–	K9 Scene of Crime Ltd
K9 – Grey Magnetic Powder	~2.7	–	K9 Scene of Crime Ltd
Dactyl Black Fingerprint Powder	~2	> 1–24μm	Speciform
Copper (II) oxide	6.315	–	Sigma – Aldrich
Activated Charcoal	~2	–	BDH Chemicals
Graphite Powder	~2.09–2.23	–	Sigma – Aldrich
Graphite Powder (synthetic)	~2.09–2.23	–	Sigma – Aldrich
Molybdenum disulphide	4.80	–	-
Manganese disulphide	–	–	Sigma – Aldrich
Vanadium (III) oxide	4.87	–	Sigma – Aldrich

Particulates investigated by the Police Scientific Development Branch as the basis for black powder suspensions for adhesive tapes.

6.4 Of these, the precipitated magnetic Fe_3O_4 powder proved most effective (out-performing both formulations originally proposed for adhesive tapes in the literature) and was therefore used in the CAST formulation initially proposed for adhesive tapes. This formulation was subsequently found to give excellent results on non-porous surfaces.

6.5 Commercial, pre-mixed black powder suspensions have recently (post 2004) become available, including Wet Powder – Black (Kjell Carlsson) and WetWop™ – Black (Armor Forensics). An initial assessment of these formulations indicated that they were probably based on a powdered graphitic material.



Scanning electron micrograph of particulates from commercial carbon-based powder suspension.

6.6 It was established by comparative trials that carbon-based black powder suspensions were superior to iron oxide-based formulations on all types of adhesive tapes, and therefore a more in-depth assessment was carried out on carbon particulates. This focused on graphitic powders although several other forms of carbon were also investigated [20], as outlined in the table below.

Powder	Particle size	Manufacturer/supplier
Coke FC800	0.8mm	TIMREX
Graphite T800	0.71mm	TIMREX
Graphite	150μm	Fisher Chemicals Ltd
Activated charcoal	50–150μm	Sigma – Aldrich
Swedish black powder	95μm	BVDA
Natural graphite	75μm	GTC
Synthetic graphite	53μm	GTC
Graphite powder	50μm	VWR
Activated charcoal	40μm	Sigma – Aldrich
KS44	44μm	TIMREX
HSAG 300 AE-109	32μm	Timcal
Graphite	20μm	Sigma – Aldrich
Micronised graphite	10μm	GTC
Graphite KS6	7μm	TIMREX
Dispersion LB1300	7μm	TIMREX
Activated carbon	0.8μm	Sigma – Aldrich
Monarch 280 carbon black	0.41μm	Cabot Carbon
Carbon nanopowder	0.3μm	–
Vulcan VXC 72R	0.3μm	Cabot Carbon
Mogul L	0.24μm	Cabot Carbon

Carbon powders evaluated as constituents for non-proprietary carbon powder suspension formulation.

6.7 Several surfactants were also evaluated in this study, including:

- Photoflo;
- Aerosol OT;
- Liquinox.

6.8 For white powder suspensions, white powders with relatively high density and a spherical shape were researched [11]. Of these, initial trials indicated that zirconium oxide and titanium dioxide gave the best results, with titanium dioxide giving marks of higher contrast. Further studies therefore focused on optimising the titanium dioxide formulation.

6.9 A range of commercial white powder suspensions have also become available, including Wet Powder – White (Kjell Carlsson), WetWop™ – White (Armor Forensics/Forensics Source) and Adhesive Side Powder – Light (Sirchie). These have all been evaluated against the original CAST formulation on adhesive tapes [19] and found to give closely equivalent performance. A comparative trial on non-porous surfaces [18] found that for the limited range of surfaces evaluated there was little significant difference between any of the commercial formulations and the CAST

adhesive tapes formulation, and the white powder suspensions can be used interchangeably.

6.10 Various nanopowders were also been evaluated by HOSDB in 2007 (including aluminium, magnesium, titanium, tin, yttrium, iron, zirconium, copper, neodymium, tungsten, lanthanum, terbium, ytterbium, and bismuth oxides, carbon, and silicon carbide) [20]. Many of these failed to develop fingerprints when used in suspensions, but of those that did the best were found to be iron oxide, titanium dioxide and carbon (the same constituents as used in existing formulations), but none gave better results than the formulations outlined in the CAST processes section above.

7. Post-treatments

7.1 Marks developed using powder suspensions can be lifted once dry in the same way as marks developed using small particle reagent, using either adhesive tape or gelatine lifts.

8. Validation and operational experience

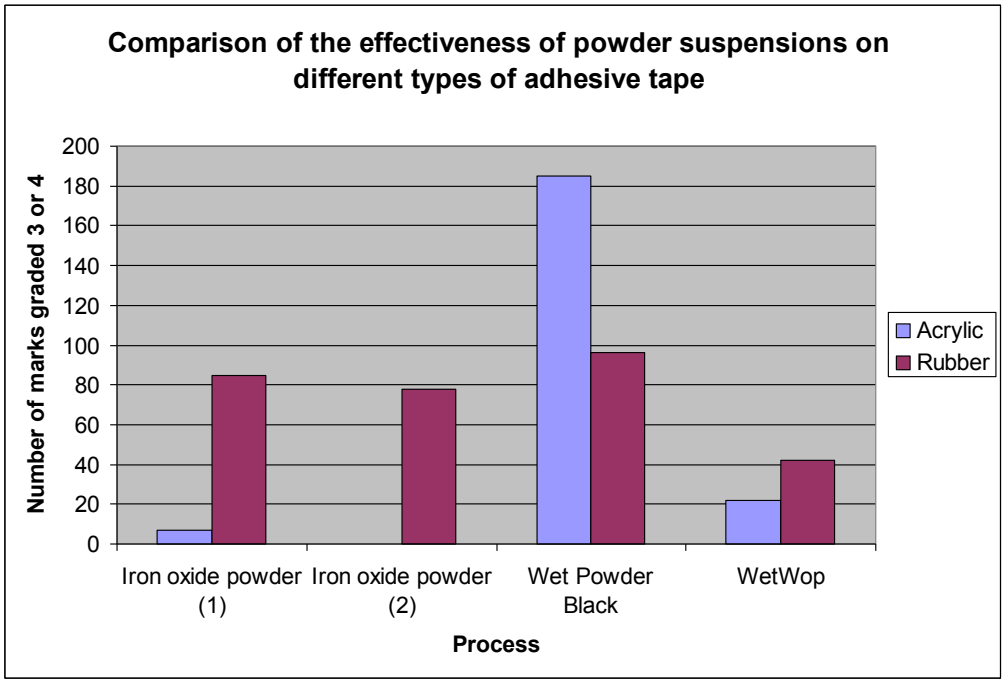
8.1 The operational experience of powder suspensions must take into account two primary applications – their use on adhesive tapes and their use on non-porous surfaces. There is a greater background knowledge regarding the effectiveness of powder suspensions on adhesive tapes, although the application of powder suspensions to other non-porous surfaces is becoming more widespread.

8.2 Laboratory trials

8.2.1 Initial laboratory comparisons on adhesive tapes were carried out at PSDB in 2000 between basic violet 3, iron oxide-based black powder suspension and superglue, with over 1,600 prints being evaluated for each process [12]. In these trials superglue and iron oxide-based black powder suspension gave the best results and were very similar in performance, but powder suspension marks had better contrast. An equivalent trial was carried out using titanium oxide-based white powder suspension, superglue and basic violet 3 (imaged via fluorescence and via the transfer technique). The results were closely equivalent to those observed for light tapes, with white powder suspension and superglue being closely equivalent in performance and both better than basic violet 3. The powder suspension again showed better contrast for developed marks.

8.2.2 During these trials it was observed that some tapes exhibited extensive background staining when treated with iron oxide-based powder suspensions whereas others did not. It was established by infrared (IR) spectroscopy that tapes using rubber-based adhesives did not

background stain while those with acrylic-based adhesives did. This resulted in the initial recommendation that a spot test be carried out to see whether background staining occurred prior to selecting a treatment [25]. However, it was subsequently noted that there were differences between powder suspensions, not all staining the background of acrylic tapes. It was established that the suspensions that did not stain the background contained carbon instead of iron oxide particulate, and a comparison of the relative effective of iron oxide- and carbon-based black powder suspension (WetWop™, Wet Powder Black) was carried out on both rubber and acrylic adhesive tapes. This trial looked at 300 half prints over a range of acrylic tapes and 480 half prints over a range of rubber tapes.



Results of comparative trials using different black powder suspensions on adhesive tapes.

8.2.3 These trials demonstrated that Wet Powder – Black gave the best overall performance, with both carbon powder formulations working on acrylic and rubber-based adhesives. Background staining of acrylic-based adhesive tapes by iron oxide powder suspension formulation was again observed.

a)

b)

Development of marks on adhesive tapes, a) acrylic-based adhesive tape showing background staining by iron oxide-based powder suspension applied to left half, no background staining from carbon-based powder suspension applied to right half b) rubber-based adhesive tape showing no background staining from iron oxide-based powder suspension applied to left half or carbon-based powder suspension applied to right half

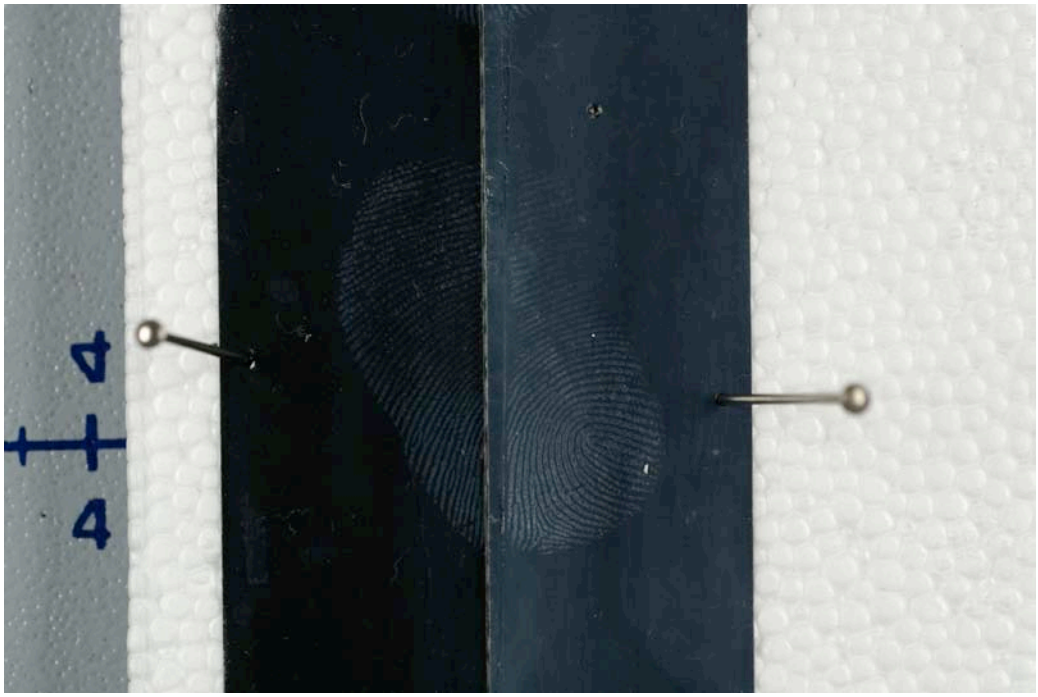
8.2.4 A similar comparison has been conducted for white powder suspensions on tapes. An initial investigation [19] compared the HOSDB formulation against the following commercially available products:

- Wet Powder – White (Kjell Carlsson);
- WetWop™ – White (Armor Forensics);
- Adhesive Side Powder – Light (Sirchie).

8.2.5 The results of these studies are summarised in the table below, but in general all formulations gave similar results, with the HOSDB formulation marginally better. Some differences were observed between the level of background staining, but in general all marks were clearly visible against the background. Approximately 14,400 marks were examined in this study.

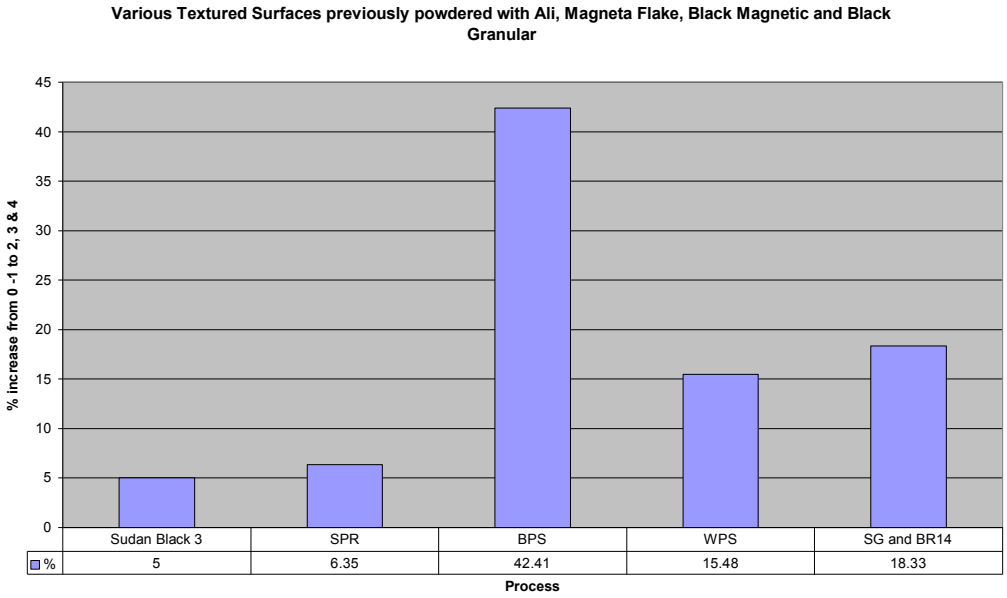
Mark grade	Sirchie	Wet Powder	WetWop	Stan Chem (HOSDB)
0	2.30%	1.63%	0.95%	1.51%
1	7.86%	6.83%	5.99%	4.09%
2	10.52%	13.63%	13.29%	11.88%
3	17.34%	21.79%	22.22%	20.79%
4	61.98%	56.13%	57.54%	61.73%
3s and 4s	**79.33%**	**77.92%**	**79.76%**	**82.53%**

Results of laboratory comparative trials for different white powder suspensions.



Comparison of fingerprint and background development using a) Home Office Scientific Development Branch formulation (left) and Sirchie Adhesive Side Powder (right) on black tapes.

8.2.6 Work on non-porous surfaces commenced with an initial assessment of the number of additional marks developed (or enhanced) by subsequent chemical processing after powdering. Several different processes were studied, including solvent black 3, small particle reagent, superglue and basic red 14 dye, and both white and black powder suspension (formulations, as published by HOSDB)[25]. The results of this exercise are illustrated below and clearly demonstrated that there were potential advantages in applying powder suspensions after powdering.



Results obtained by applying a secondary fingerprint development process (SPR = small particle reagent, BPS = black powder suspension, WPS = white powder suspension, SG and BR14 = superglue dyed with basic red 14) in sequence after powdering.

8.2.7 This prompted a further, in-depth study of the application of powder suspensions and alternative processes, both singly and in sequence [17]. It was soon established that carbon-based black powder suspensions were comparatively ineffective and studies therefore focused on the iron oxide-based black powder suspension formulation instead.

a)

b)

Black powder suspensions applied to a smooth, non-porous surface a) iron oxide-based formulations and b) commercial carbon-based formulation.

8.2.8 The study examined 37,560 marks deposited on 23 different smooth and textured non-porous (and in some cases semi-porous) surfaces representative of those that may be encountered at crime scenes, including ceramic tiles, melamine, painted metal, and uPVC, summarised below together with an outline of the number of marks deposited.

General surface classification	Specific description and designation
Smooth, non-porous	S1 Ceramic tile
	S2a Smooth wood effect laminate
	S2b Shiny, striped laminate
	S2c Beige laminate
	S3a White painted metal
	S3b Red painted metal
	S4 Glass
	S5 Perspex
	S6 Polyethylene
	S7 Polypropylene
Rough, non-porous	R1 Textured ceramic tile
	R2a Cream textured laminate
	R2b Wood effect laminate
	R2c Granite effect laminate
	R2d Grey textured laminate
	R2e Beige textured laminate
	R3 Textured painted metal
	R4 Fake leather texture laminated aluminium
	R5 Varnished wood
Other	O1 uPVC
	O2a Silk emulsion painted plasterboard
	O2b Kitchen/bathroom painted plasterboard
	O3 Textured vinyl wallpapered plasterboard

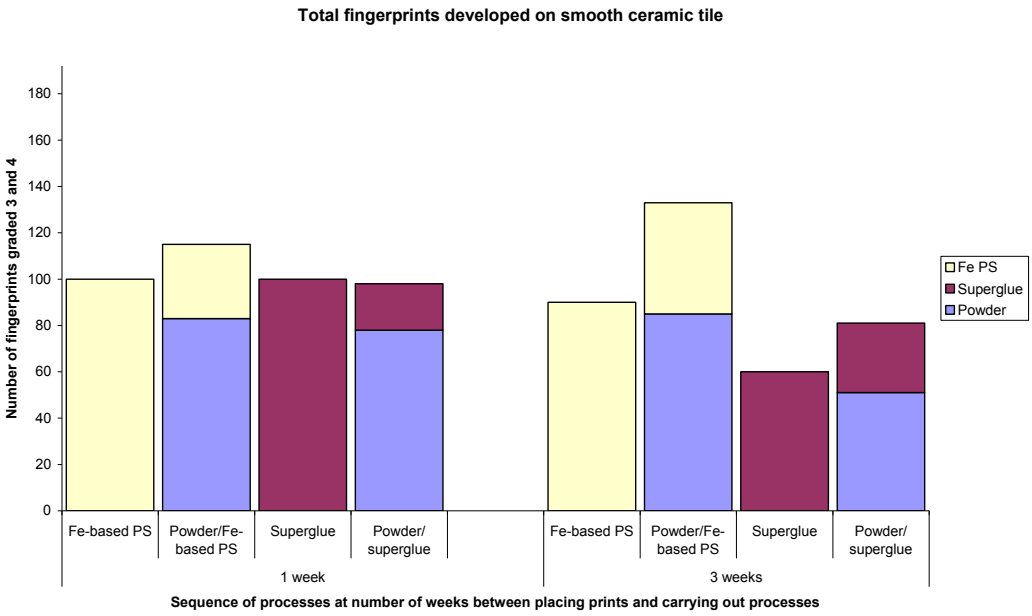
Description of the surfaces used in the comparative study between various sequences of superglue, powders and powder suspensions

Surface	Number of donors	Number in depletion	Number of repeats	Number of panels	Number of ages	Number of fingerprints
S1	40	12	5	50	3	4,800
S2a	35	10	5	50	3	3,500
S2b	14	10	2	20	2	1,400
S2c	7	10	1	8	2	560
S3a	14	10	2	20	2	1,400
S3b	28	10	4	44	3	3,080
S4	14	10	2	16	2	1,120
S5	14	10	2	20	2	1,400
S6	14	10	2	20	2	1,400
S7	14	10	2	20	2	1,400
R1	35	10	5	50	3	3,500
R2a	35	10	5	50	3	3,500
R2b	7	10	1	8	2	560
R2c	7	10	1	8	2	560
R2d	7	10	1	8	2	560
R2e	7	10	1	8	2	560

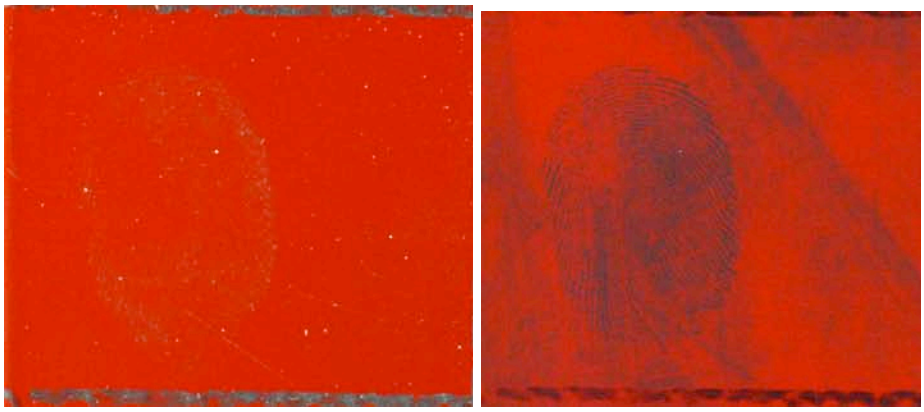
R3	21	10	3	32	3	2,240
R4	14	10	2	20	2	1,400
R5	7	10	1	10	2	700
O1	7	10	1	8	2	560
O2a	7	10	1	12	2	840
O2b	14	10	2	24	3	1,680
O3	7	10	1	12	2	840
					TOTAL	**37,560**

Summary of the experiments carried out in the comparative study and the total number of marks used.

8.2.9 The conclusions were that in many cases the powder-powder suspension sequence was more effective than superglue and dyeing and powder suspensions are clearly a highly effective process. Typical results from some of the surfaces used in the study are illustrated below.

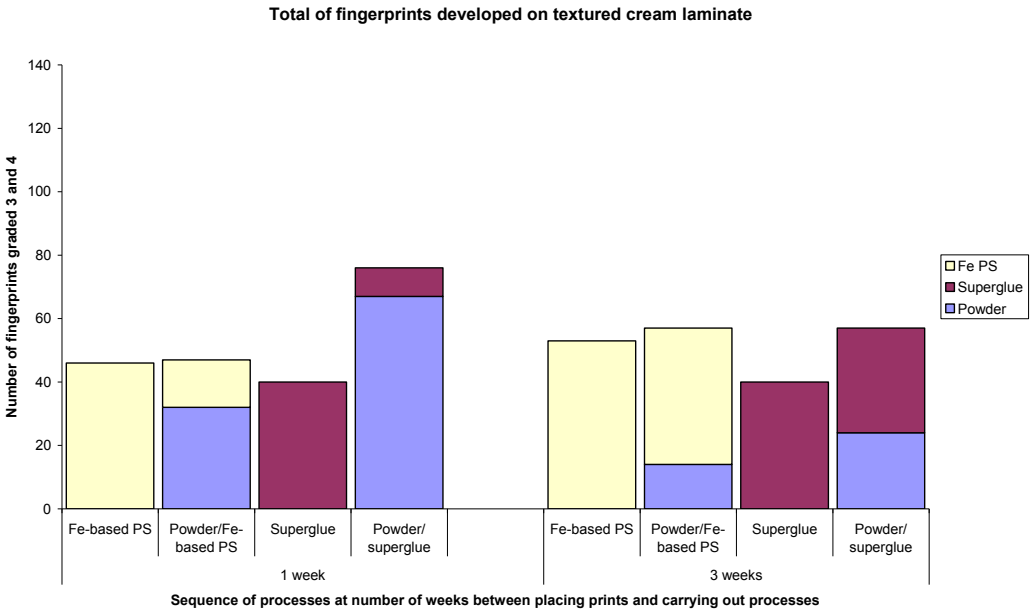


Typical results obtained comparing the effectiveness of powder suspensions, powders and superglue as single treatments and in sequence on a smooth surface.

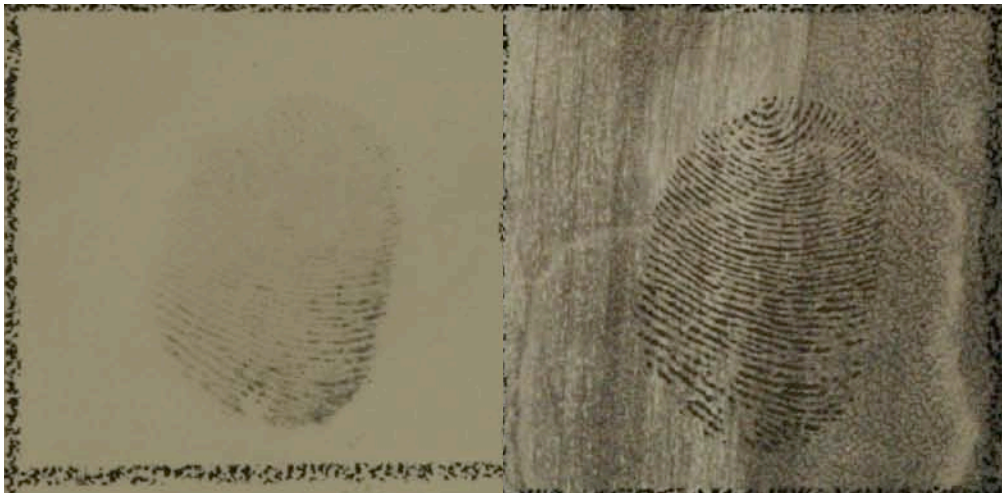


a) b)

Enhancement of a mark on a smooth painted surface a) after application of aluminium powder and b) improvement obtained by subsequent treatment with black powder suspension.



Typical results obtained comparing the effectiveness of powder suspensions, powders and superglue as single treatments and in sequence on a textured surface.



a) b)

Enhancement of a mark on a textured surface a) after application of black magnetic powder and b) improvement obtained by subsequent treatment with black powder suspension.

8.2.10 The overall trends on all surfaces examined are summarised in the table below.

Surface	**Best process/sequence**			
	Fresh marks (1 day)		**Older marks (> 1 week)**	
	Superglue + dye	**Powders + powder suspensions**	**Superglue + dye**	**Powders + powder suspensions**
S1		X		X
S2a		X		X
S2b				X
S2c		X	X	
S3a			X	
S3b		X	X	
S4				X
S5				X
S6			=	=
S7			X	
R1		X		X
R2a	X			X
R2b		X		X
R2c	X		X	
R2d	X			X
R2e		X		X
R3		X	X	
R4				X
R5		X		X
O1		X		X
O2a				
O2b	X		X	

O3		X		X

Best optimum processing process/sequence for different ages of mark across all surfaces studied.

8.2.11 A similar study was conducted with white powder suspensions on dark surfaces to enable firm recommendations to be made [18]. In this study the following surfaces were examined.

General surface classification	**Specific description and designation**
Smooth, non-porous	S1 Grey PVC
	S2 Black polypropylene
	S3 Dark brown wood effect melamine laminate
	S4 Black gloss painted metal
	S5 Dark blue ceramic tile
	S6 Black compressed polystyrene
Rough, non-porous	R1 Mottled grey kitchen worktop melamine
	R2 Black 'fake leather' laminate on aluminium
	R3 Black polythene
	R4 Black matt painted metal
	R5 Black textured compressed polystyrene

Description of the surfaces used in the comparative study between various sequences of superglue, powders and powder suspensions on dark surfaces.

8.2.12 In this study, 21 donors placed depletion series of 10 marks on each of the 11 different surfaces studied. The experiment looked at marks that were 1 week and 3 weeks old, giving a total number of 4,620 graded marks. The purpose of the experiment was to determine the optimum processing sequence, assuming that powders would always be the first process used. White powder suspensions and superglue + basic yellow 40 were compared in terms of their effectiveness as secondary treatments. A summary of the trends observed in the data across all surfaces studied is given below.

Surface	**Best process/sequence**			
	1-week-old marks		**Older marks (> 1 week)**	
	Powders + superglue/dye	**Powders + powder suspensions**	**Powders + superglue/dye**	**Powders + powder suspensions**
S1		X	X	
S2		X		X
S3	X		X	
S4		X		X

S5		X	X	
S6		X		X
R1	X		X	
R2	X		X	
R3	X		X	
R4		X		X
R5		X		X

Best optimum processing process/sequence for different ages of marks across all surfaces studied.

8.2.13 It was observed that the white powder suspensions were less effective than black powder suspensions in developing marks on non-porous surfaces. On smooth, dark surfaces, powders followed by white powder suspensions give closely equivalent performance to powders followed by superglue and both sequences can be recommended with equal weighting. On rougher, dark surfaces the sequence of powders followed by superglue gives better results and would be the sequence of choice, unless it is known that the surface has been wetted.

8.2.14 Comparative work has also been carried out to establish the effectiveness of powder suspensions on wetted non-porous surfaces [26, 27]. The results indicated that on certain wetted surfaces powder suspensions may be more effective than vacuum metal deposition [27]. Slight differences were also observed between the effectiveness of different formulations of powder suspension [26].

8.3 Pseudo-operational trials and operational experience

8.3.1 Initial operational trials have been carried out to compare the effectiveness of basic violet 3 with black powder suspensions on the adhesive side of tapes. The results of these trials are summarised in Chapter 3.2 Basic violet 3, and demonstrate that powder suspensions are the more effective process. However, superglue is also known to be a highly effective treatment for adhesive tapes. A subsequent operational trial commenced comparing iron oxide-based black powder suspensions with the superglue process, looking at marks developed on both adhesive and non-adhesive sides of the tape.

8.3.2 Based on the results obtained using carbon-based black powder suspensions, this operational trial was modified to include a commercial carbon-based formulation in addition to the iron oxide-based formulation. The trial results are recorded below.

Process	Cases	Number of positive results (cases)				% positive
		Non-adhesive	Adhesive	Both	Total	
Superglue/basic yellow 40	59	9	13	1	23	39
Iron oxide powder suspension	45	1	15	1	17	38
Carbon powder suspension	33	1	14	1	16	48

Operational trial results for different processes on light coloured adhesive tapes.

8.3.3 It can be seen that carbon-based black powder suspensions were found to be the most effective process for the adhesive side of tapes, and were therefore recommended for operational use.

8.3.4 The HOSDB white powder formulation was then used in an operational trial, comparing results with those obtained using superglue and dyeing. The trial results are summarised below.

Process	Cases	Number of positive results (cases)				% positive
		Non-adhesive	Adhesive	Both	Total	
Superglue/basic yellow 40	33	1	11	1	13	40
White powder suspension	39	1	11	2	14	36

Operational trial results for different processes on dark coloured adhesive tapes.

8.3.5 Superglue was found to be the more effective process on operational casework and white powder suspensions were not ultimately recommended for use on adhesive tapes, except in circumstances where dark tapes had become wetted.

8.3.6 Most recently, CAST has conducted a repeat of the pseudo-operational trial on plastic bags last conducted in 1986. In this trial, 100 bags and plastic packaging materials from different sources (e.g. supermarket carrier bags, 'bags for life', black bin bags, clear magazine wrappings) were collected from as realistic environments as possible. Each bag was divided into quarters, with each quarter being examined using a different fluorescence examination regime followed by a separate sequence of chemical treatments [21]. The number of marks developed using each

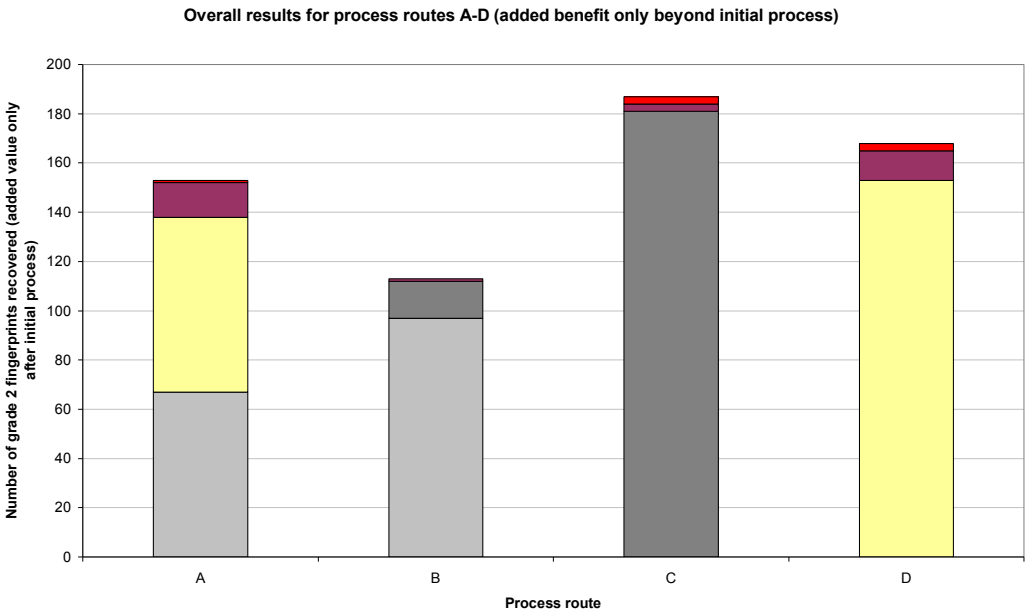
process was recorded. The results from the fluorescence examination stage in the trial have already been included in Chapter 2.2 Fluorescence examination. Iron oxide-based powder suspension was included as a chemical treatment in these trials, both as an initial process and as a secondary treatment subsequent to vacuum metal deposition (VMD).

8.3.7 The results of these trials for the first 50 bags are summarised below:

- Process route A = VMD –superglue – basic violet 3;
- Process route B = VMD –powder suspension – basic violet 3;
- Process route C = powder suspension – basic violet 3;
- Process route D = superglue – basic violet 3.

Process route	1st process	2nd process	Basic violet 3/ visible	Basic violet 3/ 577nm laser
A	67	71	14	1
B	97	15	1	0
C	181		3	3
D	153		12	3

Summary of the marks developed on plastic bags after each stage of sequential processing routes.

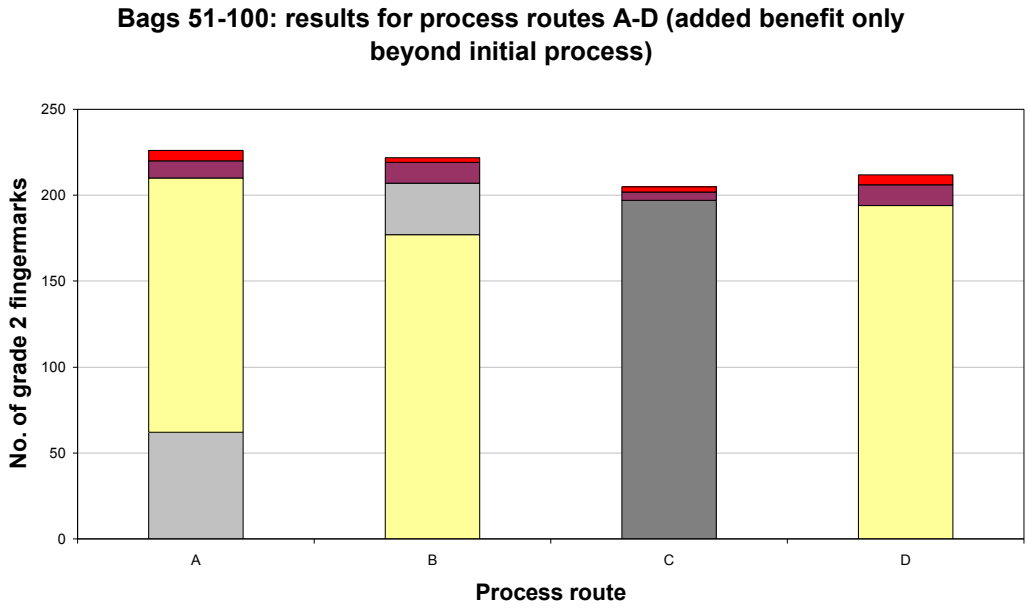


Graphical representation of the data summarised in the table above (light grey = VMD, dark grey = powder suspension, yellow = superglue + basic yellow 40, purple = basic violet 3 (visible), red = basic violet 3 (fluorescence with 577nm laser).

8.3.8 For the second 50 bags, the poorly performing process route B (VMD – powder suspensions – basic violet 3 route) was replaced by superglue – VMD – basic violet 3. The results from these studies are summarised below.

Process route	1st process	2nd process	Basic violet 3/ visible	Basic violet 3/ 577nm laser
A	62	148	10	6
B	177	30	12	3
C	197		5	3
D	194		12	6

Summary of the marks developed on plastic bags after each stage of sequential processing routes.



Graphical representation of the data summarised in the table above (light grey = VMD, dark grey = powder suspension, yellow = superglue + basic yellow 40, purple = basic violet 3 (visible), red = basic violet 3 (fluorescence with 577nm laser).

8.3.9 Powder suspensions performed well in these trials, giving equivalent, if not better, performance than any other single process. However, the superglue/VMD sequence gave the best results and it is this sequence that would be recommended, unless the bag is known to have been wetted. For wetted bags, the powder suspensions process is the main process recommended.

8.3.10 Many police forces have been using both black and white powder suspensions operationally in advance of the update to the *Manual of Fingerprint Development Techniques* [24], both in a laboratory as a replacement for superglue on items that may have been wetted (cowlings, car number plates) or contaminated (drugs wraps), and at

scenes after the application of powders. Results are still being collected but significant increases in the number of marks being developed are reported.

8.3.11 Powder suspensions have also been successfully used to develop marks on items recovered from arson scenes by more than one police force, in accordance with observations during CAST studies [28]. Laboratory tests have indicated that it may also be the best treatment for situations where cars have been sprayed with WD40 to destroy fingerprints [29].

8.3.12 It is clear that powder suspensions are a highly effective process for non-porous surfaces, give superior results to small particle reagent and may supersede superglue in some applications. CAST studies are continuing to establish the optimum position for the techniques within the full range of sequential processing charts.

9. References

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3.8 Small particle reagent

1. History

1.1 Small particle reagent (SPR) was first formulated in the mid-1970s by researchers at the Atomic Weapons Research Establishment (AWRE), Aldermaston, under a Police Scientific Development Branch (PSDB) contract. The objective of the contract was to devise a cheaper alternative to what was then termed surfactant 'stabilised physical developer (SPD)' (now known simply as physical developer) [1,2]. At the time, SPD was being investigated for the development of latent fingerprints on a range of surfaces, including plastics and paper, although it was recognised that the technique worked best on paper samples.

1.2 The SPD system was found to work by the deposition of silver particles, in the presence of a cationic surfactant, onto the surface being treated. Studies into this system showed that finely divided silver particles could also be used to develop latent fingerprints when prepared as a suspension, and that this behaviour was not exhibited when the suspension was dispersed in water alone, prompting studies into fine particle suspensions. This work indicated that the presence of the surfactant was essential if fingerprints were to be developed, and subsequent studies investigated a range of formulations incorporating different powders and surfactants. It was found that formulations containing powders with small particles of about 1μm suspended in a fluid at concentrations of between 1 and 10gl^{-1} were effective [2,3,4,5]. The generic name given to these systems was 'surfactant controlled SPR' and a provisional patent application covering such reagents was filed by Morris and Wells in 1976. A more comprehensive study of powders, surfactants and methods of application then followed [2,5].

1.3 Initial experiments showed that good results could be obtained using dish development with molybdenum disulphide (MoS_2) particulate and this was used as a control against which formulations based on alternative powders could be assessed [2,7]. These experiments identified the best performing powders as cobalt oxide(Co_2O_3), lead oxide (PbO_2), MoS_2, graphite and the pigment Monastral Blue (copper phthalocyanine), although for some of these there was a large batch-to-batch and supplier-to-supplier variation. In this respect MoS_2 was found to be the most consistent in performance across all batches tested. It was also found that all 'ionic' types of surfactant evaluated gave good results, but that poor results were obtained when the surfactant molecule has a 'tail' of fewer than eight carbon atoms (C_8) [2]. On the basis of these studies, a combination of Tergitol 7 and choline chloride was selected as the surfactant solution, although it was subsequently found that the latter constituent was unnecessary and it was omitted from the SPR formulation initially recommended for operational use. Subsequently, Tergitol 7 (3,9 diethyl-6-tridecanol hydrogen sulphate sodium salt) became unavailable because of the harmful impact it could

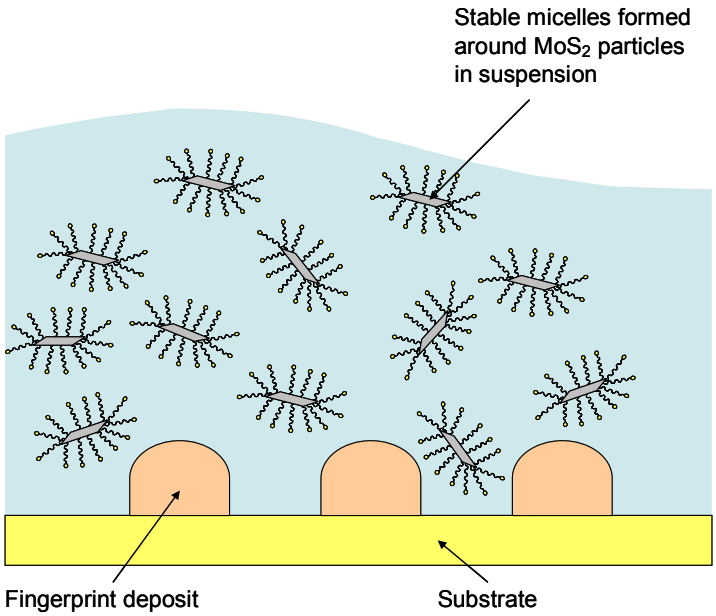
have on the environment, and a revised formulation was developed by the Home Office Scientific Research and Development Branch (HO SRDB) based on Aerosol OT (AOT) surfactant. It is this formulation that is recommended for use in the UK to the present day (2011).

1.4 SPR dish development was trialled operationally against vacuum metal deposition (VMD) for the development of marks on polythene bags [8]. This trial indicated that although SPR was not as effective as VMD for this type of surface, it was far more effective than powdering and the technique was recommended for operational use on non-porous surfaces and wetted items because it was recognised that few police forces had access to VMD.

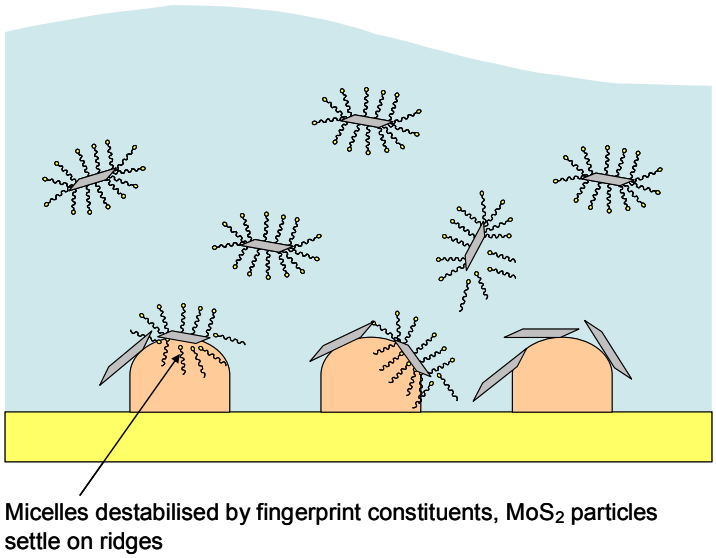
1.5 Work by the Home Office Central Research Establishment (HO CRE) in the early 1980 suggested that spraying of SPR was an effective method for cars which were wet and could not be dried, and for other exterior wetted surfaces such as windows and window frames. SPR was found to be capable of developing marks on surfaces exposed to the outside environment for prolonged periods of time, e.g. window glass. SPR was found to detect marks that had not been developed during aluminium powdering [9], although the presence of excess quantities of aluminium powder on the surface were found to inhibit SPR [10]. Operational trials using SPR alone on wetted surfaces, and surfaces that were still wet, demonstrated that the technique was effective in such circumstances [10] and it was subsequently recommended for operational use. However, it is recognised that spray application of SPR is less effective than dish development, and that use at crime scenes should be restricted to surfaces that cannot be recovered to a laboratory. It remained the principal treatment for fixed outdoor surfaces that are known to have been wetted until the recent development of powder suspensions in 2009.

2. Theory

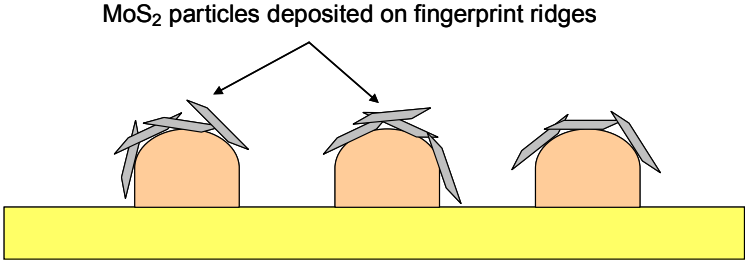
2.1 The mechanism by which SPR is thought to develop fingerprints is shown schematically in the illustrations below.


Stable micelles formed around MoS_2 particles in suspension
Fingerprint deposit
Substrate

a)


Micelles destabilised by fingerprint constituents, MoS_2 particles settle on ridges

b)


MoS_2 particles deposited on fingerprint ridges

c)

Schematic illustration of the small particle reagent process a) stable micelles formed around particles of molybdenum disulphide b) destabilisation of micelles by fingerprint constituents leading to particles settling on ridges and c) dried mark, leaving particles adhering to ridges.

2.2 The fine MoS_2 particles detect high molecular weight constituents and so adhere to the oily and fatty components of latent fingerprints by reaction between the fatty components present and the hydrophobic tails of the surfactant forming micelles around the particles. These tails are linked to a hydrophilic head, which reacts with metal salt to give a black precipitate, hence making the fingerprint visible.

3. CAST processes

3.1 The process recommended by CAST is first to prepare a concentrated solution by mixing 7.5mL of 10% AOT (also known by its chemical name dioctyl sulfosuccinate, sodium salt) solution with 500mL of tap water, then add 50g of MoS_2 powder. It may be difficult practically to prepare a 10% solution of AOT, and therefore the 10% solution should be attempted as the starting point and small quantities of water added until all solids are dissolved. This concentrated solution is then further diluted according to the development process being used. If the dish development SPR process is required, 4.5 litres of water are added to the concentrate and if the SPR is to be used for spray development 3 litres of water should be added.

3.2 The role of the AOT surfactant is to control the deposition of suspended particles onto fingerprint ridges in preference to the background surface. The surfactant will form micelles around the suspended particles and although the nature (anionic, cationic, non-ionic) of the surfactant is not critical there are properties that were found to be favourable in surfactant selection:

- it must be suitably soluble to achieve the optimum working concentration;
- the ‘tail’ of the surfactant should have an open carbon atom chain with no fewer than C_8, with the optimum number of carbon atoms in the chain being between12 and 17.

AOT meets both these criteria.

3.3 The concentration of AOT used is again not critical but must be controlled to be below the critical micelle concentration (CMC), the optimum being between one-third and one times of the CMC. The concentration used in both CAST formulations falls within these limits. If AOT concentration is below this limit, deposition of MoS_2 on the background surface increases and the definition of ridge detail is reduced, while at higher concentrations the clarity of the print diminishes and at best only a very faint outline of the print is observed. At these high

concentrations little general deposition takes place, signifying that micelle formation blocks the process of deposition, perhaps by providing a more attractive species for adsorption on the fingerprint deposit.

3.4 The role of the MoS_2 is to deposit preferentially on the fingerprint ridges and aid the visualisation of the mark. Several different materials can be used in this role, but in general the best results were obtained with materials with a density of ~4 gcm^{-3} and a layer lattice structure, both of which apply to MoS_2. There must be a sufficient quantity of MoS_2 in suspension for the particles to adhere to the fingerprint ridges and give a clear print. However, if the quantity is too great the powder also adheres to the background, giving background staining and smudging the developed ridges. The quantity used in the CAST formulation is sufficient to give good development without background staining.

3.5 Uniform wetting of the powder by the AOT surfactant is difficult to achieve if the powder is directly added to the working concentration solution of surfactant, so the MoS_2 should be added to a concentration greater than the CMC and after dispersion, diluted to the working concentration.

4. Critical issues

4.1 There are no critical issues relating to the application of SPR. The formulation is tolerant of changes in water content and made up solutions will keep indefinitely. In very cold weather additions of ethanol may be required for the spray application method to work effectively.

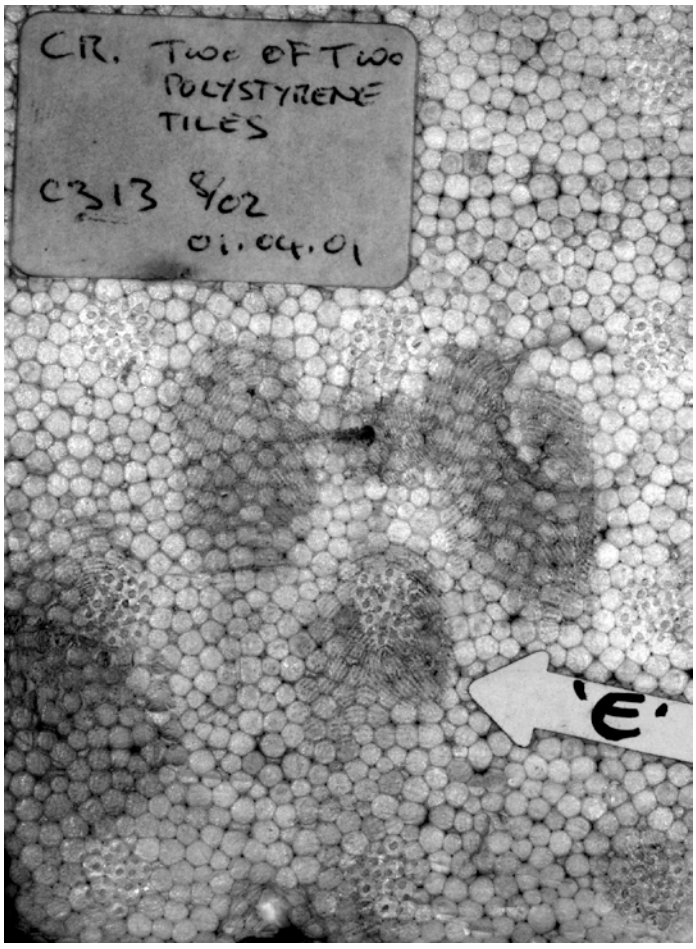
5. Application

5.1 Suitable surfaces: SPR is suitable for use on non-porous surfaces, such as plastic bags, glass bottles, waxed paper and other waxy items, such as candles. It can be used on expanded polystyrene items such as drinking cups. It will still develop marks on surfaces that have been wet, but is not suitable for heavily contaminated surfaces.

5.2 SPR is a process recommended for use on non-porous articles that have been wetted. Because the process targets the insoluble lipid components of fingerprint residues, immersion in water or exposure to rain will in many cases leave sufficient deposits for SPR to continue to develop marks. It is not as sensitive as VMD for this type of exhibit, but for the majority of police forces that do not have VMD equipment, SPR was until 2009 the only option for non-porous articles known to have been wetted. Tests have indicated that SPR may still develop additional marks if used in sequence before powder suspensions on wetted non-porous surfaces.

5.3 The two application techniques recommended for operational use are dish development and spray application. The dish development

technique can be applied to non-porous surfaces, such as plastic bags and packaging materials, waxed and plastic-coated paper, small gloss painted or glass articles and expanded polystyrene articles, such as drinking cups and ceiling tiles. Such items are difficult to treat with superglue, where uptake of the fluorescent dye by the expanded polymer makes any marks developed very difficult to visualise.



Fingerprints developed on expanded polystyrene tile using small particle reagent.

5.4 A tray or tank of sufficient size for the article being processed should be filled with sufficient working solution to enable the article to be submerged 50mm below the surface. The working solution is then stirred to ensure all powder is in suspension before submerging the article with the surface of interest facing upwards. The article is then kept submerged and stationary for 30 seconds while the MoS_2 particles come out of suspension and settle evenly over the object. For small, complex shaped articles the article may be placed in a dish and the working solution poured over it from a beaker. The article is then removed carefully from the dish and the uniform grey deposit carefully washed off by placing the surface of interest face downwards into a second dish of water and agitating it gently. The article should then be dried at room temperature. The dish development technique limits the size of the

article that can be treated in the laboratory, but for use at scenes a formulation for spray application has been developed.

5.5 Spray application may be carried out on all non-porous surfaces, but it is recommended for objects that are outside, awkwardly shaped, large or immovable. Although wet or damp articles can be processed, when treating articles outside, the area being treated needs to be sheltered from direct rainfall.

5.6 For spray application, a simple, commercially available garden spray unit is used. The nozzle of the unit should be set to give a conical, fine spray and the filter unit removed to prevent it clogging. The working solution should be shaken to give an even particulate distribution and the area to be processed should be sprayed liberally, starting at the top edge and working down towards the bottom. As the liquid runs down the surface fingerprints may begin to become visible and spraying should be continued just above the relevant area until there is no more build up of the grey deposit. A second spray unit filled with water is then sprayed above the developed fingerprints before they have dried, allowing the flowing water to carry away excess particles. Prints should not be directly sprayed with water as this may damage them. In cold weather, 200ml of ethanol may be added per 1 litre of suspension to prevent freezing on the surface.

Spray application of small particle reagent to a car.

5.7 The spray formulation is much less effective than the dish formulation and should only be used where dish development is not possible.

5.8 Studies have shown that SPR has potential for developing fingerprints in specialist applications, such as on wetted firearms [11] and on incendiary bottles soaked in accelerant [12].

6. Alternative formulations and processes

6.1 Several other particles have been investigated as the basis of SPR. Some of those investigated in early studies [2] are summarised in the table below.

Material type	**Compound**	**SPR performance**
Metals	Silver powder	Good
	Zinc powder	Fair
	Aluminium powder	Fair
	Aluminium fingerprint powder	Fair
	Lead powder	Poor
	Copper powder	Poor
	Iron powder	Poor
	Manganese powder	Poor
Metal oxides	Iron (Fe_2O_3)	Good
	Cobalt (Co_2O_3)	Excellent
	Chromium (Cr_2O_3)	Good
	Uranium (UO_2)	Good
	Lead (Pb_3O_4)	Poor
	Lead (PbO_2)	Excellent
	Manganese (MnO_2)	Good
	Silver (Ag_2O)	Fair
	Copper (CuO)	Good
Metal sulphides	Zinc (ZnS) Batch 1	Excellent
	Zinc (ZnS) Batch 2	Poor
	Molybdenum (MoS_2) Batch 1	Excellent
	Molybdenum (MoS_2) Batch 2	Good
Other	Tungsten carbide (WC)	Good
	Silicon carbide (SiC)	Good
	Titanium boride (TiB_2)	Poor
	Carbon (amorphous)	Good
	Carbon (graphite)	Excellent
	Monasterol Blue	Good

Summary of compounds investigated as the basis of small particle reagent.

6.2 As described above, MoS_2 was ultimately selected because it gave good performance and was more consistent in performance across different batches and different manufacturers. A further series of powders

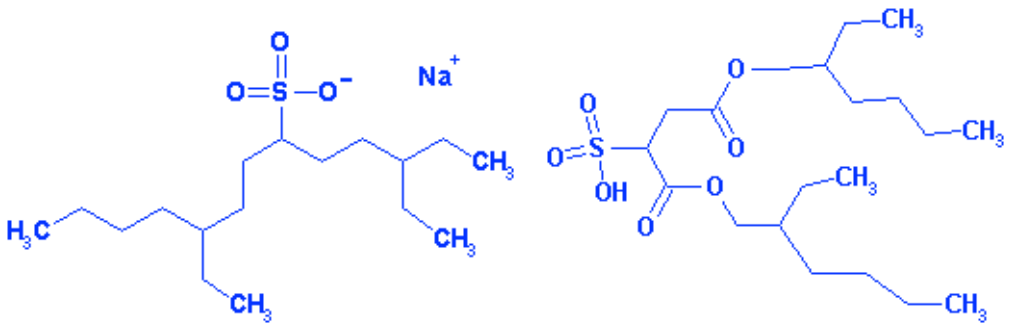
including boron nitride, cadmium sulphide, cadmium selenide, kaolin, molybdenum carbide, silicon nitride and tungsten sulphide were subsequently investigated [13] but none were found to give better performance.

6.3 In addition to the particulate component, a range of different surfactants were investigated [2]. These are also summarised below.

Surfactant			Performance
Name	**Chemical**	**Ionic type**	
Teepol 610	Sodium lauryl sulphate	Anionic	Good
Teepol 514	Sodium lauryl sulphate	Anionic	Good
–	Sodium lauryl sulphate	Anionic	Good
Teepol Green	Sodium lauryl sulphate	Anionic	Good
Tergitol	Heptadecyl sulphate	Anionic	Excellent
Manoxal 1B	Dibutyl sodium sulfosuccinic acid	Anionic	Very poor
Manoxal OT	Diacetyl sodium sulfosuccinic acid	Anionic	Good
Armac 12D	Lauramine acetate	Cationic	Fair
-	Lauramine acetate	Cationic	Fair
Choline citrate	Trimethyl 2 hydroxy ethyl amine citrate	Cationic	Poor
Choline chloride	Trimethyl 2 hydroxy ethyl amine chloride	Cationic	Poor
Hyamine 2389	Methyl, dodecyl benzyl trimethyl amine chloride	Cationic	Good
Hyamine 1622	Di isobutyl phenoxy ethoxy benzyl amine chloride monohydrate	Cationic	Excellent
Brij 35	Phenoxy ethylated lauryl alcohol	Non-ionic	Excellent
Lissapol NDB			Fair
Lissapol D	Sodium acetorley sulphate		Fair
Lissapol LS	Sodium N octyl amino sulphonic acid		Fair
Flow 7X	Unknown		Good
Photoflo	Unknown		Good

Summary of surfactant systems considered for use in small particle reagent.

6.4 A further range of surfactants were subsequently studied [13] including Nonidet P40, Triton GR-5, Triton X405, and the series of Tween surfactants 85, 80, 40, 20. Manoxol OT (another trade name for AOT) gave the best performance and ultimately replaced Tergitol 7 in the operational formulation when the latter surfactant became unavailable.



The structures of Tergitol 7 ($C_{17}H_{35}NaO_3S$) and Aerosol OT ($C_{20}H_{37}NaO_7S$).

6.5 More recently, there has been much interest in the use of powder suspensions for the development of fingerprints on the adhesive side of tapes. These have similarities to some of the formulations evaluated for SPR, albeit with far higher solids content, and are available in black (with carbon or iron oxide particulates) and white (with titanium dioxide particulates) forms. It was found that some of these formulations work very well on non-porous surfaces and recent results indicate that they will supersede SPR in this application on most types of surface. A detailed description of these formulations is given in Chapter 3.7 Powder suspensions.

6.6 SPRs based on other particulates have been reported, including light coloured zinc carbonate [14] and fluorescent particles [15]. Commercial, pre-mixed formulations are also available in various colours. The relative effectiveness of these formulations has not been tested by CAST against the recommended process, and in the case of the commercial pre-mixed products the nature of the filler particles is not known.

7. Post-treatments

7.1 Once entirely dry, marks developed using SPR are essentially the same as a mark developed by a regular powdering technique and can therefore be lifted in the same way by low-tack, clear adhesive tapes [3,11]. On occasions the lifting tape may not adhere to the surface very well, so care must be taken not to let the tape slip when lifting the developed mark. Lifting fingerprint marks is especially useful when dealing with highly patterned and/or coloured surfaces, however damage may be caused to the mark during lifting and the priority should be to photograph the mark in situ first.

8. Validation and operational experience

8.1 Laboratory trials

8.1.1 CAST has carried out few laboratory trials of SPR because the formulation was developed by the Atomic Weapons Research Establishment AWRE and HO CRE, and until recently there has been no other process for treating fixed, outdoor surfaces that have been wetted, to carry out a comparison with. A small-scale study using split depletion series was carried out in 1992 when the surfactant was changed from the discontinued Tergitol 7 to AOT [16]. This test used five different donors, each depositing five prints on three different plastics. These results, and the grading scheme used, are summarised below.

1 = no obvious development
2 = print area visible but poorly defined ridge structure
3 = some clear ridge structure
4 = useful mark

Grade	**John Lewis white plastic bag**		**Sainsbury's white plastic bag**		**Clear plastic**	
	Tergitol 7	AOT	Tergitol 7	AOT	Tergitol 7	AOT
1	4	4	2	9	0	2
2	5	4	7	2	2	7
3	9	12	7	5	8	6
4	7	5	9	9	15	10

Results of comparative studies on plastic bags using different small particle reagent formulations.

8.1.2 It can be seen that the AOT formulation is slightly less effective than the Tergitol 7-based formulation, but a range of equivalent tests carried out using different surfactants showed that AOT was the best performing Tergitol 7 replacement and it was therefore incorporated into the revised formulation for operational use.

8.2 Pseudo-operational trials and operational experience

8.2.1 HO CRE carried out several trials before implementing SPR. In the initial investigation, SPR was compared with powders and VMD on paper, polythene and window glass surfaces [9]. On paper SPR gave reasonable results, but it affected subsequent ninhydrin treatment and therefore could not be used in sequence. On polythene, SPR was shown to be capable of developing marks on polythene that had been exposed to the environment (including rain), but VMD gave better results. This observation was confirmed in a full operational trial [8], the results of which are summarised in Chapter 3.11 Vacuum metal deposition. On window glass SPR gave similar performance to aluminium powder on the inside surface. However, on the outside, which had been exposed to

autumnal weather conditions for two weeks, SPR gave significantly improved performance and could be used in sequence after powders.

8.2.2 An operational trial was then conducted over two winter months using three police forces, spray applying SPR after powdering [10]. These initial trials gave poor results, which were attributed to excessive application of aluminium powder inhibiting SPR, and therefore sequential processing was not recommended at scenes. A second phase of the operational trial was carried out over two months using four police forces, applying SPR to surfaces that had not been previously powdered. During this trial 106 outside surfaces were examined and 55 useful prints recovered from 24 of the surfaces. Of these surfaces, five were examined while still wet (not possible with powders) and seven useful marks were recovered. SPR was therefore recommended for use on wet or damp surfaces and at scenes of crime on articles where powdering is not feasible.

8.2.3 With the development of the superglue process (see Chapter 3.10 Superglue), the effectiveness of SPR was compared with that of superglue and VMD in a pseudo-operational trial on polythene bags. The results are reported in detail in Chapter 3.11 Vacuum metal deposition and indicated that SPR was less effective than superglue and dyeing and VMD on this type of surface, in accordance with earlier studies.

8.2.4 However, until recently (2009) SPR remained the process of choice where non-porous exhibits had been wetted and were either not portable or could not be treated with VMD. In the last two years it has become apparent that powder suspensions give superior performance to SPR on most surfaces studied, and advice is in the process of being updated to reflect this change in recommendations.

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3.9 Solvent black 3 (Sudan Black)

1. History

1.1 Solvent black 3, alternatively known as Sudan Black B, is one of a class of azo dyes. Although some related compounds such as Sudan III (solvent red 23) and Sudan IV (solvent red 24) were available in the late 1800s and early 1900s, solvent black 3 was not introduced until the mid-1930s. Industrially, the dye is used for the coloration of organic solvents, printing inks, lacquers and a range of fats and wax substances [1].

1.2 Soon after its introduction the dye was proposed as a stain for fats and various other microbiological applications and has been successfully utilised in this role to this date (2011). The first published use of solvent black 3 for the development of latent fingerprints was by Mitsui *et al.* in 1980 [2]. They used a solution of solvent black 3 in a mixture of ethylene glycol, ethanol and water to develop prints on water-soaked paper items, the performance of Solvent Black 3 being shown to be superior to ninhydrin on this type of exhibit. This was soon followed by a further study by Stone and Metzger [3], comparing solvent black 3 with black magnetic powder on wetted porous items. In this comparison magnetic powder was found to give the best results.

1.3 In the early 1980s the Home Office Central Research Establishment (HO CRE) conducted an evaluation of over 60 biological dyes for their ability to develop latent fingerprints on both paper and polythene surfaces [4]. These studies also identified solvent black 3 as having particular potential for the development of fingerprints, in this case the best results being obtained on polythene. It was decided to proceed with an operational trial comparing the effectiveness of solvent black 3 with the two existing techniques recommended for polythene at the time, vacuum metal deposition (VMD) and small particle reagent (SPR) [5]. An initial phase of the work suggested that solvent black 3 gave superior results to VMD on polythene bags and the study was extended to a full operational trial. In these more detailed studies both VMD and SPR were found to be more effective than solvent black 3 and the reagent was not considered further for these applications.

1.4 The Police Scientific Development Branch (PSDB) subsequently re-evaluated the reagent and found that it had potential for developing fingerprints in cases where surfaces were contaminated and powdering was not possible. Examples of this type of surface included takeaway food containers or fizzy drinks cans. The process was subsequently included in the CAST *Manual of Fingerprint Development Techniques* [6] and recommended for these applications.

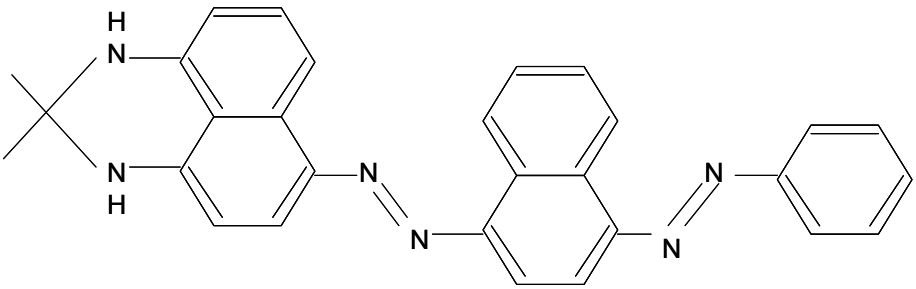
1.5 PSDB carried out a re-evaluation of a range of lipid reagents in 1999–2000 [7] and investigated several other lysochromes including Oil Red O (solvent red 27) and Sudan III (solvent red 23). These studies confirmed solvent black 3 to be the best performing of this type of lipid dye and it

was not considered worthwhile initiating development of formulations based on other dyes. Instead, research was initiated to develop a formulation based on a less flammable solvent than ethanol that gave potential for the reagent to be used at crime scenes. As a consequence of this research 1-methoxy-2-propanol was identified as a suitable solvent and laboratory trials indicated that there was no discernible difference between this and the ethanol-based formulation. This formulation was subsequently published for operational use [8]. The studies did raise the issue of how best to test reagents for contaminated surfaces, because a method for consistently contaminating test surfaces needs to be devised. Several alternative techniques were investigated during the course of the experiments [9] but none of these were regarded as being truly satisfactory.

1.6 In the interim, there has been very little published work on the use of solvent black 3. One recent study assesses the effectiveness of solvent black 3 in both powder and solution form, with the solution treatment found to be more effective. Marks up to 75 days old were successfully detected on porous surfaces using this approach [10]. The authors also recommend the reagent for development of lipstick marks.

2. Theory

2.1 Solvent black 3 is a lysochrome, more commonly known as a fat stain. Most lysochromes are azo dyes, which because of their structure have undergone molecular rearrangement making them incapable of ionising.



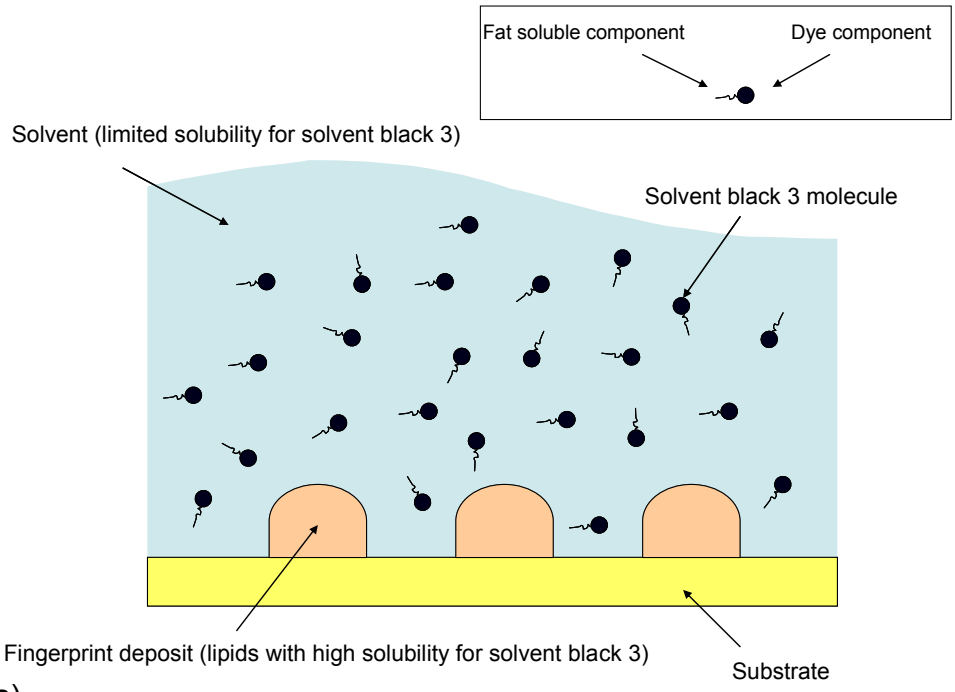
Structure of solvent black 3.

2.2 The basis for these dyes colouring fats is that they dissolve into them. From another perspective, the fat is the solvent for the dye. Lysochromes are mostly insoluble in strongly polar solvents, such as water, and somewhat more so in less polar solvents, such as ethanol. They are quite strongly soluble in non-polar solvents, such as xylene. Triglycerides, being non-polar compounds, dissolve them quite well. Other lipids, having fatty components, may also dissolve them.

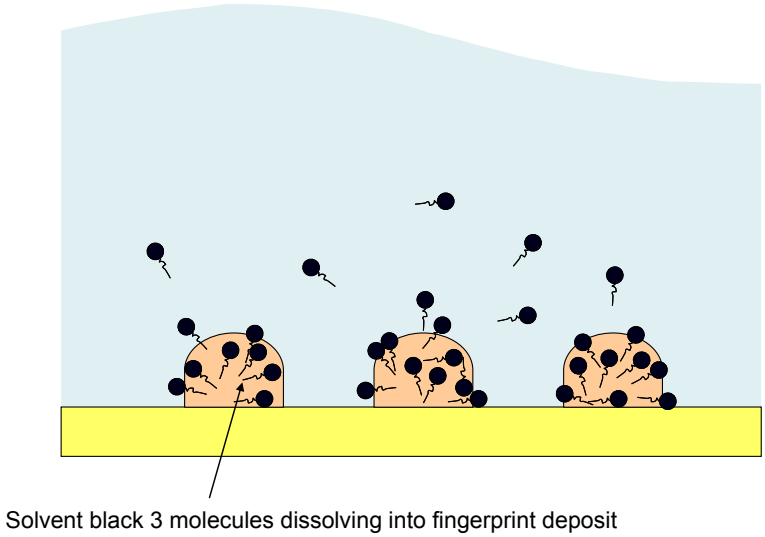
2.3 Lysochromes such as solvent black 3 are applied from solvents in which they are sparingly soluble. As they come into contact with materials in which they are strongly soluble, they transfer to them significantly, often colouring them more strongly than the original solvent. This process is known as preferential solubility.

2.4 Although the primary action of solvent black 3 is to stain lipids by dissolving in them, it can also stain materials ionically. This may result in some background staining.

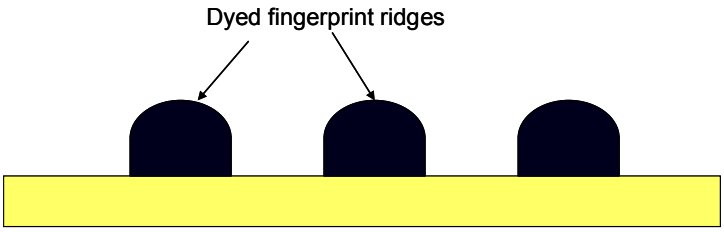
2.5 The dyeing process of solvent black 3 is illustrated schematically below.



a)



b)



c)

Schematic illustration of the solvent black 3 process a) solvent black 3 molecules in solvent with limited solubility b) lipophilic component of solvent black 3 molecule preferentially dissolving into lipids in fingerprint ridges and c) fingerprint after drying, leaving dyed ridges.

3. CAST processes

3.1 The process recommended by CAST does not differ significantly from that originally proposed by the HO CRE. The solution consists of 15g of solvent black 3 dissolved in 1 litre of ethanol, to which is subsequently added 500ml of distilled water.

3.2 The role of solvent black 3 in the formulation is to act as the dye for the fingerprint ridges. The concentration used is such that the limit of solubility in the ethanol/water solvent is almost exceeded, and some precipitation of solvent black 3 is occurring. It was proposed by HO CRE that these precipitating particles may preferentially settle on fingerprint ridges in addition to the dyeing action of solvent black 3 dissolving into the lipids.

3.3 The role of ethanol is to act as the initial solvent for solvent black 3 and it is capable of dissolving the quantity of solvent black 3 outlined above.

3.4 Solvent black 3 is insoluble in water, and the addition of water reduces the solubility of solvent black 3 to the point where precipitation is beginning to occur.

3.5 In the more recently developed, less flammable formulation of solvent black 3, 1-methoxy-2-propanol fulfils the same role as ethanol while having a reduced flammability.

4. Critical issues

4.1 Any metallic films forming on the surface of the working solution should be removed using tissue or blotting paper prior to use. This is because these films will otherwise cause excessive staining of the background and may obscure marks.

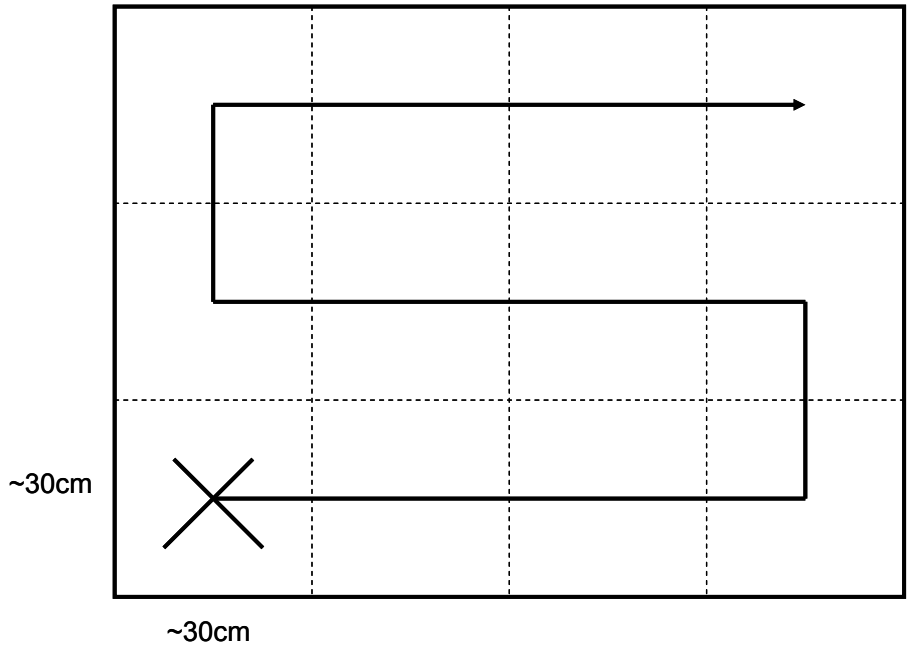
5. Application

5.1 Suitable surfaces: Solvent black 3 is suitable for use on all types of non-porous surface where particular types of contamination are present. The two types of contamination for which solvent black 3 is known to be effective are: fatty deposits (similar in nature to sebaceous fingerprints), and drinks' residues, where chemical discrimination may be of value.

5.2 Solvent black 3 is not recommended as a primary treatment for any particular surface, but appears in several of the processing charts for non-porous surfaces as a treatment for surfaces that have been contaminated. In these situations, the lipid specific nature of solvent black 3 may enable it to selectively stain fingerprint ridges without causing background staining of the contaminant. Basic violet 3 can be considered as an alternative treatment for contaminated surfaces and although laboratory trials indicate that solvent black 3 may be more effective than basic violet 3 on latent prints, the most effective treatment on contaminated surfaces has not been conclusively identified. Examples of the types of exhibit that can be effectively treated with solvent black 3 include fast food containers and drinks cans.

Photograph of beer can treated with solvent black 3, showing developed ridge detail.

5.3 A formulation of solvent black 3 with reduced flammability has recently been developed [11] with the potential for use at scenes. The types of scenes where this formulation could be used include potentially contaminated areas such as kitchens and bathrooms. Guidelines for application are given [7,11], starting application at the bottom of the surface and then working up. This minimises dye running down over unprocessed areas and affecting subsequent development of marks.



a)

b)

Application of solvent black 3 at scenes of crime a) suggested application sequence for vertical surfaces, and b) solvent black 3 being applied to a cupboard.

6. Alternative formulations and processes

6.1 HOSDB carried out an evaluation of a range of alternative solvents with the objective of providing a less flammable solvent black 3 formulation with the potential for use at scenes of crime. These solvents were tested individually, and in some cases diluted with water or heptane. A summary of the systems evaluated is given in the table below.

Solvent	**Formulations examined**	**Flammability**	**Results**
Dichloromethane/ Heptane	Various	Not studied	Only faint staining of prints
Ethyl acetate/ Heptane	Various	Not studied	Only faint staining of prints
Acetone	25, 50, 75, 100%	Similar to ethanol formulation	Similar level of fingerprint development with existing ethanol formulation
Propan-2-ol	25, 50, 75, 100%	Slightly lower than ethanol formulation	Similar level of fingerprint development with existing ethanol formulation
Propylene carbonate	100%	Not studied	Immiscible with water – poor results
Propylene glycol methyl ether acetate (PGMEA)	100%	Not studied	Immiscible with water – poor results
Dipropylene glycol dimethyl ether (DPGDME)	100%	Not studied	Immiscible with water – poor results
2,2-Dimethoxy Propane (2,2-DMP)	100%	Not studied	Immiscible with water – poor results
Propan-1,2,3-triol	Various	Ethanol had to be added to dissolve Solvent black 3, similar	Solvent black 3 not soluble in glycerol or water/glycerol mix
Propan-1,2-diol	25, 50, 75, 100%	Lower than ethanol formulation	Poor performance in staining marks
Propylene glycol methyl ether (PGME)	Various, including 40, 50, 55, 60, 75%	Much lower than ethanol formulation	Equivalent level of fingerprint development to existing ethanol formulation

Dipropylene glycol methyl ether (DPGME)	Various, including 30, 40, 50, 60%	Much lower than ethanol formulation	Equivalent level of fingerprint development to existing ethanol formulation

Solvents investigated as alternatives to ethanol in the solvent black 3 formulation.

6.2 The results indicated that solvent black 3 was soluble in most polar organic solvents and that formulations based on diluted solvents worked better in the development of fingerprints. Water was found to be essential to give good fingerprint development.

6.3 Of the range of solvents investigated, propylene-based glycol ethers were identified as best performing group in terms of reduced formulation flammability and good fingerprint development. Optimised formulations were subsequently developed based on propylene glycol methyl ether (PGME) and dipropylene glycol methyl ether (DPGME). Further detail on both of these solvents is provided below.

6.4 Propylene glycol methyl ether (PGME, 1-methoxypropan-2-ol, dowanol PM)
Molecular formula: $C_4H_{10}O_2$
CAS number: 107-98-2
Boiling point: 118–119°C
Flash point: 33.88°C
Lower Flammability Limit: 1.8%
Upper Flammability Limit: 16.0%
Purity: 99.5+%
Main contaminant: 2-methoxypropan-2-ol

6.5 Dipropylene glycol methyl ether (DPGME, dowanol DPM)
Molecular formula: $C_7H_{16}O_3$
CAS number: 34590-94-8
Boiling point: 90–91°C
Flash point: 74°C
Purity: 97% (mixture of isomers)

6.6 The two best performing systems of those optimised were:

10g solvent black 3, 500mL PGME, 500mL water (50%);
10g solvent black 3, 400mL DPGME, 600mL water (40%).

6.7 The flash points of both PGME and DPGME-based solvent black 3 formulations were also assessed, and found to be:

PGME = 55ºC;
DPGME >87ºC.

6.8 Considering that both these flash points were well in excess of temperatures experienced at scenes and that effectiveness in developing fingerprints was equivalent to the existing ethanol-based formulation, the PGME-based formulation was ultimately recommended for operational use both at scenes and in the laboratory.

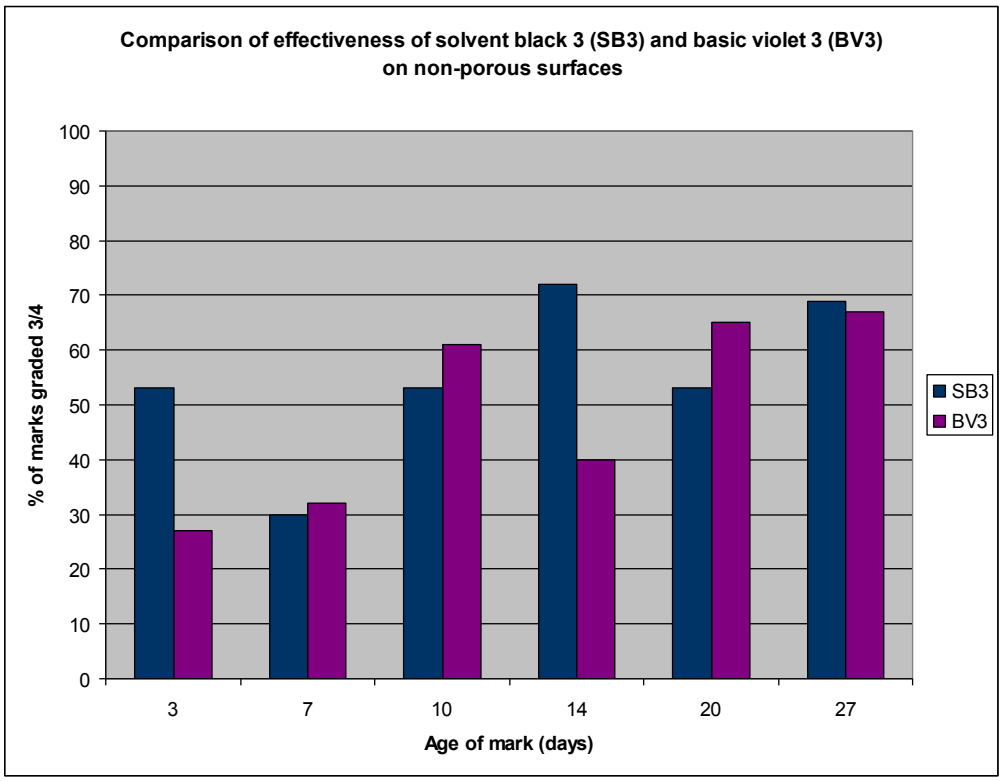
7. Post-treatments

7.1 No post-treatments are used after solvent black 3.

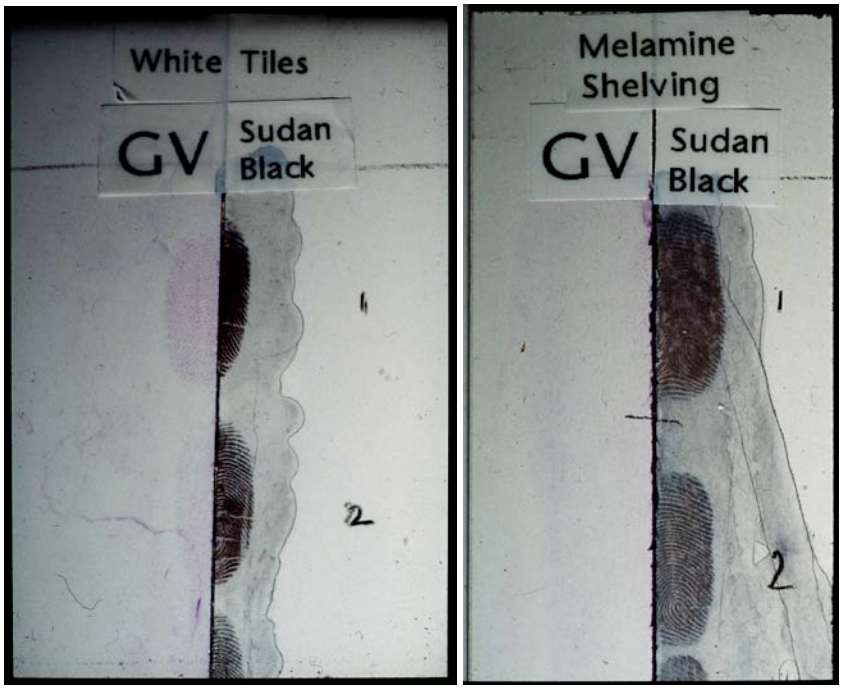
8. Validation and operational experience

8.1 Laboratory trials

8.1.1 The effectiveness of solvent black 3 on non-porous surfaces has more recently been evaluated in a laboratory trial, comparing it with the other reagent recommended for contaminated surfaces, basic violet 3. The results of this trial, carried out on 2,592 half prints, are illustrated below.



a)



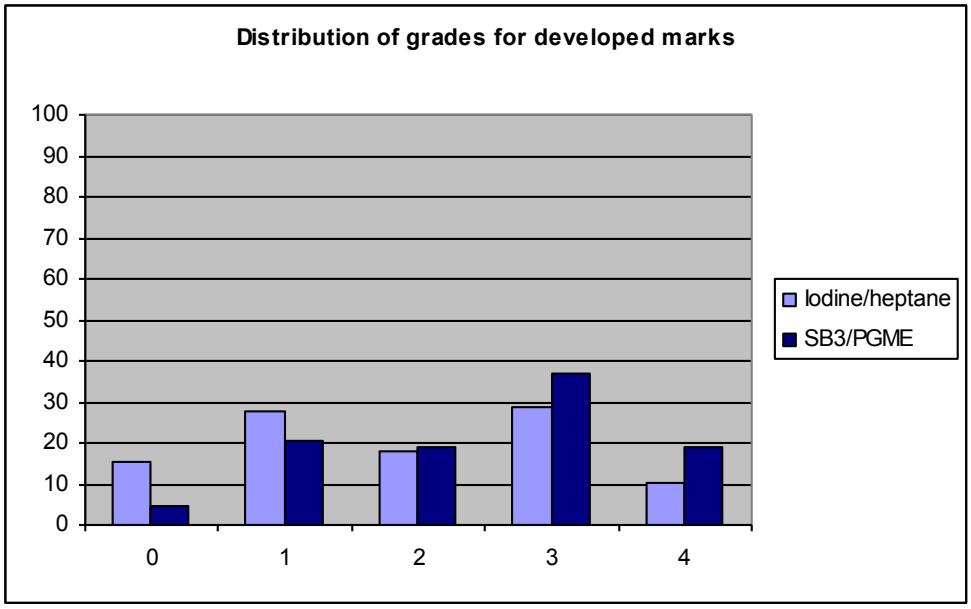
b)

Results from a comparison of the effectiveness of solvent black 3 (Sudan Black) and basic violet 3 (GV) on non-porous surfaces a) results of grading marks of different ages and b) photographs of marks developed on different surfaces.

8.1.2 These results indicate that solvent black 3 may be more effective, but are not conclusive. The trials were conducted on clean non-porous surfaces and are therefore not fully representative of the contaminated surfaces that the techniques are proposed for. However, there are reduced health and safety issues associated with solvent black 3, which may make it preferable to basic violet 3 for operational use on contaminated exhibits.

8.1.3 Comparisons were also carried out between solvent black 3 and a heptane-based iodine solution. This involved grading 2,592 half prints, the results of numbers of mark at each grade being summarised below:

Grade	Technique		
	Iodine/heptane	**SB3 after iodine**	**SB3/PGME**
0	297	63	83
1	361	152	304
2	212	95	245
3	341	326	465
4	85	84	199
Total	**1,296**	**720**	**1,296**

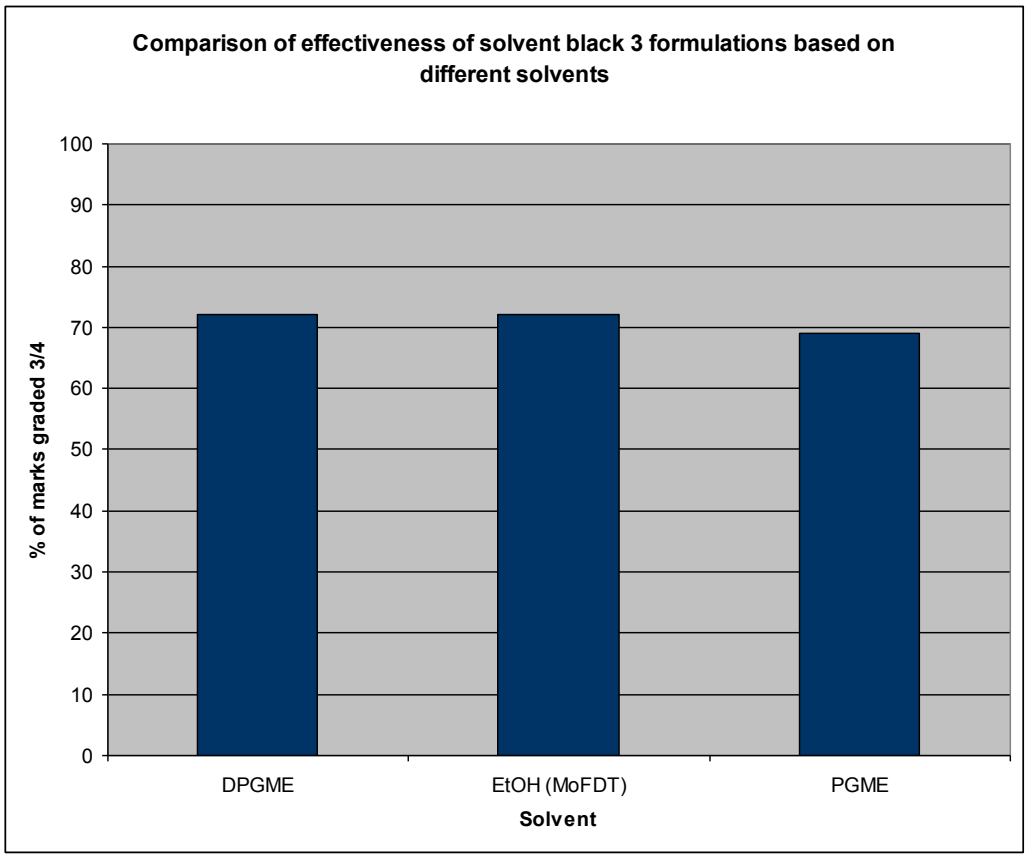


Results of comparative tests between Solvent Black 3 and iodine solution.

8.1.4 In general, the results show that solvent black 3 is a more effective treatment than iodine for latent fingerprints. However, an in-depth analysis of the results across all the surfaces examined (which included various laminates, uPVC, ceramic tile and gloss painted wood) showed that there were certain surfaces (e.g. gloss painted wood) where iodine did out-perform solvent black 3. However, the overall better performance of solvent black 3 combined with the flammability issues of iodine, meant that solvent black 3 continued to be the technique recommended for operational use.

8.1.5 Prior to the publication of the current reduced flammability solvent black 3 formulation in 2005 [8], a three-way trial was carried out comparing PGME- and DPGME-based formulations with the ethanol-based formulation recommended in the *Manual of Fingerprint Development Techniques* [6].

8.1.6 During the course of this three-way trial, 5,040 half prints were graded. The results of this study are illustrated below.



Results of three-way comparison between solvent black 3 formulations based on different solvents

8.1.7 The results demonstrate closely equivalent performance between all three formulations, and it was considered that they could be used interchangeably according to circumstances.

8.1.8 It should be noted that all trials outlined above utilise latent fingerprints. These results are therefore not truly representative of the operational use because solvent black 3 is recommended for use on greasy, contaminated surfaces and fingerprints. However, there are difficulties in producing a model 'contaminant' for such studies in the same way that horse blood is used as a contaminant for studies into blood dyes, and further research is required in this area.

8.2 Pseudo-operational trials and operational experience

8.2.1 Initial operational trials were carried out in 1986 to determine the relative effectiveness of the technique in developing fingerprints on polythene bags. In these trials solvent black 3 was compared with VMD and SPR [5]. The results of this comparison are reproduced below.

	Characteristics				Number of marks	
	>16		8–16*			
	SB3	VMD	SB3	VMD	SB3	VMD
Number of cases	11	18	13	6	24	24
Number of fingerprints	56	81	80	102	–	–

** Number of prints of 8–16 characteristics recorded only when no prints of >16 characteristics were revealed.*

	Characteristics				Number of marks	
	>16		8–16*			
	SB3	SPR	SB3	SPR	SB3	SPR
Number of cases	4	10	5	10	39	28
Number of fingerprints	8	24	21	72	–	–

** Number of prints of 8–16 characteristics recorded only when no prints of >16 characteristics were revealed.*

Results of comparative trials between solvent black 3, small particle reagent and vacuum metal deposition.

8.2.2 These trials indicated that solvent black 3 was not as effective as either VMD or SPR for developing fingerprints on polythene bags and it was not subsequently recommended for this application. However, the potential of the technique to develop marks on greasy, contaminated surfaces was later recognised and the technique was developed for this purpose.

8.2.3 A full operational trial has not been conducted on the use of solvent black 3 on contaminated surfaces, nor has a side-by-side comparison been conducted between ethanol and PGME-based solutions. This is because there are so few cases where the use of solvent black 3 is necessary and to build up statistically meaningful operational data would take several years. Because nature of the contaminant is known, unlike 'real' fingerprints that are variable in composition, the performance in operational use will be the same as that in laboratory tests. In the case of the solvent black 3 formulation, the decision was taken to issue the less flammable formulation because this provided a scene of crime capability where none was previously available. Laboratory results suggest the two formulations are very similar in performance and there is no reason to assume that this would significantly change when applied at a scene.

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3.10 Superglue (cyanoacrylate fuming)

1. History

1.1 Superglue was developed in the 1950s by researchers trying to produce an acrylic polymer for the aircraft industry. It found commercial use as an adhesive system for non-porous surfaces, a main advantage being the very short cure time. Exposure to superglue vapour was reported as a possible method for the development of latent fingerprints in the late 1970s. It was reported apparently independently in Japan, North America [1] and in a private communication with the UK Home Office from Laurie Wood of Northamptonshire Police [2, 3]. Early research in the UK was carried out by the Home Office Central Research Establishment (HO CRE) investigating the relative effectiveness of a range of different commercial superglues [4] and the development of fingerprints on a range of surfaces including polyethylene, PVC and adhesive tape [5]. The use of powdering to enhance developed ridge detail was also investigated [5] and Bristol Black powder found to be most effective for this purpose.

1.2 The first literature publications detailing the use of the process for fingerprint development began to appear in the early 1980s [6]. Initially little was known about the reaction mechanism or the optimum treatment conditions, and fingerprint development was often slow and inconsistent, sometimes taking 24 hours to produce a developed mark. Various police forces around the world used (and some still use) the technique in a relatively uncontrolled way by treating exhibits in containers, such as fish tanks, with various proprietary cyanoacrylate adhesives. Some experimented with heating the glue to speed the process [7, 8]. Others proposed the use of other accelerating agents, including sodium hydroxide [9] and sodium carbonate [10] and comparative trials were reported between these techniques and a commercial system ‘Hard Evidence’, where vapours were released from a cyanoacrylate impregnated gel exposed to the atmosphere[11]. Commercial superglue fuming chambers began to be manufactured, with systems such as the ‘Visuprint’ [12] being available in 1983.

1.3 After finding the technique variable and somewhat unreliable HO CRE handed the work over to the Police Scientific Development Branch (PSDB) in 1982 for further investigation. It was quickly determined that humidity was playing a crucial role in the speed and sensitivity of the reaction [13]. The humidity was optimised primarily for polythene and other plastics, with a relative humidity (RH) level of around 80% being recommended [14]. This is the point at which solid sodium chloride will take up water from the atmosphere. Lower humidity levels resulted in slower and less effective development and higher humidity levels resulted in high background development. These experiments were repeated by HOSDB in 2009, with the results confirming the recommendations of the original study. Several prototype treatment cabinets with controlled humidity were built. A novel electronic humidity

control system was developed by a contractor (Nick Hartley) and by 1986 the commercial 'Sandridge' superglue cabinets were being installed in police forces [15]. This cabinet was designed to carry out development under the optimum conditions of humidity, evaporating ethyl cyanoacrylate at 120°C and venting to the atmosphere.

The prototype 'Sandridge' controlled-humidity superglue cabinet developed by the Police Scientific Development Branch.

1.4 The Sandridge cabinet had a capacity of approximately 0.5 m^2 and controlled the humidity by injection of vapour from an ultrasonic humidifier. The humidity was monitored, during the typical 15–30 minute treatment time, by wet and dry thermocouples linked to an electronic control system. It was manufactured by the Mason Vactron Company in Acton, London and was installed in most police and forensic service provider fingerprint laboratories in the UK and many across Europe, several of these still being in use today. This cabinet produced much more rapid and consistent results than the ad hoc arrangements most had been using and provided police forces with an effective and reliable

process for the development of fingerprints on many non-porous surfaces. In the late 1990s HOSDB was involved in, and funded in collaboration with the USA, the initial development of a larger cabinet with capacity of approximately 2 m^2 [16]. The prototype was purchased by Thames Valley Police and is still in operational use to the present day (up to 2011). The design was substantially modified after the original Mason Vactron Company was purchased by Foster and Freeman and is now marketed as the MVC5000. Cabinets of smaller capacities, the MVC3000 and MVC1000, have subsequently been developed and marketed.

1.5 Superglue development is rarely used in isolation. The white deposit of a superglue-developed fingerprint can be difficult to see and photograph, especially on light coloured surfaces, although ultraviolet (UV) imaging and several of the processes described for visual examination can enhance ridge contrast. Attempts were made to improve contrast by powdering the developed ridges with coloured powders [5], but the best results were obtained by using fluorescent dyes to dye the deposit. The potential of using fluorescent dyes in this way was recognised soon after the first published papers on superglue fuming appeared. Menzel *et al.* [17] suggested the use of Rhodamine 6G (basic red 1), either by evaporation or solution staining, in combination with an argon ion laser light source. The evaporation of Rhodamine was also reported by Vaughn [18]. Stoilovic investigated Coumarin 540 as an alternative solution staining dye [19], for use with the filtered xenon lamp-based forensic light sources then under development in Australia. The high cost and limited availability of lasers and alternative forensic light sources in the early 1980s prompted investigations into dyes excited by long-wave UV [20, 21], for which cheap radiation sources were readily available. As a consequence of these studies, Ardrox was proposed for use [22] as a UV-excited alternative to Rhodamine 6G.

1.6 From the early 1980s through to the current time (2011), Rhodamine 6G has been one of the most widely-used dyes for developed superglue marks. Many formulations used methanol as the solvent. Methanol is extremely hazardous by skin absorption and Rhodamine was a suspect carcinogen. Alternative dye systems to Rhodamine 6G were being investigated by the mid-1980s [23]. In the mid-1980s PSDB set out to find a safer alternative which could be excited in the blue region of the spectrum and that would preferably emit in the green-yellow region. In 1985 the dye basic yellow 40 (BY40) dissolved in ethanol was identified by Sears and this was included in the manual issued in 1986 [14]. BY40 has subsequently proved to be one of the most effective dyes for dyeing marks developed with superglue, combining high fluorescent yield with low toxicity. The absorption of the dye in the violet-blue region of the spectrum and corresponding emission in the green-yellow region are particularly convenient for visualisation of developed marks. The BY40 dye has been shown to enhance the superglue-developed fingerprints to the extent that twice as many identifiable fingerprints are found on some surfaces after dyeing compared with those seen after superglue

treatment alone. The subsequent dye process is therefore an important step in sequential treatment procedures. Attempts have also been made to combine the superglue fuming and subsequent dyeing of the deposit into a single stage by co-volatilising thermal dyes that sublime [24] , and investigations have also been conducted into tagging cyanoacrylates with fluorescent species. However, all these approaches have so far (up to 2011) been unsuccessful in producing as highly fluorescent marks as solution dipping.

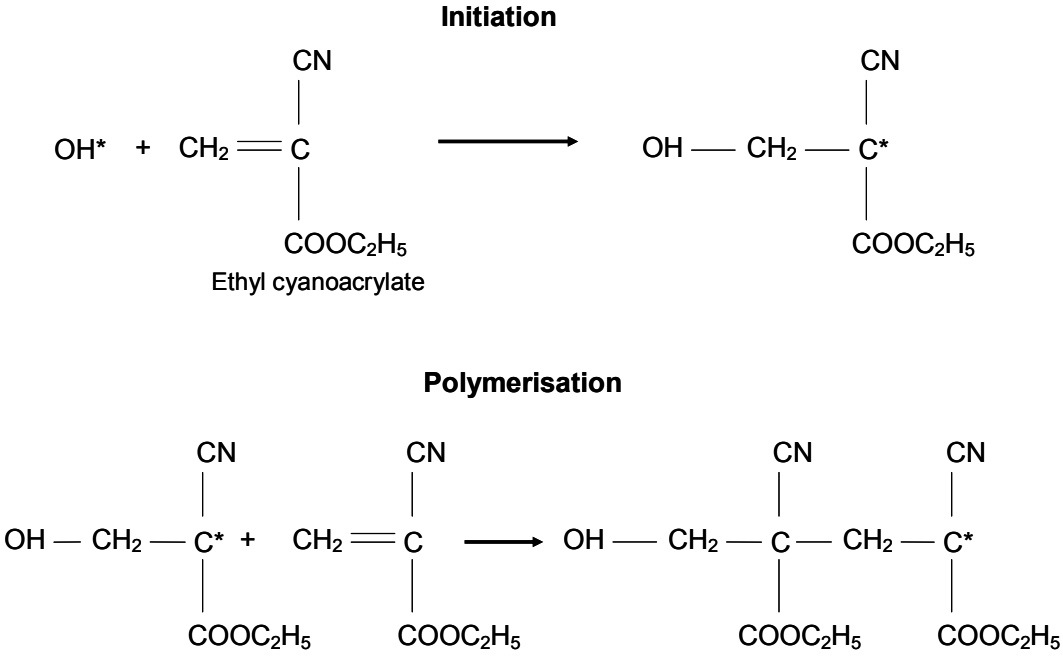
1.7 A less effective water-based version of BY40 was introduced at a later date, this formulation being intended for use on surfaces where ethanol had detrimental effects (such as varnishes and some surfaces printed with inks), or in areas with poor ventilation. HOSDB subsequently reviewed the water-based BY40 formulation and investigated a further range of alternative water-based dyes [25]. The outcome of this study was the issue of a more effective water-based dye formulation incorporating basic red 14 (BR14), published for operational use in 2004. The recent development of portable, high power green lasers offers the possibility of increasing the number of fingerprints detected after staining with BR14 because the output wavelength of the laser (532nm) is well matched to the excitation characteristics of the dye.

1.8 Vacuum superglue fuming has been proposed as an alternative to the atmospheric, high humidity superglue development process and equipment has been developed and manufactured for this purpose [26]. Several comparative studies have been carried out between the vacuum and high humidity techniques [27, 28, 29] which demonstrated that each process has advantages and disadvantages. The high humidity technique develops marks that can be more easily seen without subsequent fluorescent dyeing and absorbs far more dye. It is therefore considered by CAST to be more appropriate to a wider range of exhibits, hence it is the technique recommended for use in the UK. However, studies into the vacuum technique have continued and refinements to the technique and equipment have been proposed [30, 31].

1.9 Superglue fuming, using a range of different systems, has also been used for the development of fingerprints in cars and at scenes for many years [32-35]. None of these systems have been shown to be as effective as treatment in a controlled-humidity cabinet in a laboratory (the effect of humidity and temperature is elaborated in a later sections 2.5 – 2.9, but undoubtedly they have a role in the development of fingerprints on surfaces that cannot be powdered or recovered to a laboratory. PSDB conducted an evaluation of the SuperFume system produced by Foster and Freeman [36], which came to similar conclusions to earlier studies. The SuperFume process has been successfully deployed at scenes such as hydroponics factories growing cannabis within the UK, but the suitability of the surfaces for powdering should also be considered prior to use because in many cases this may give better results.

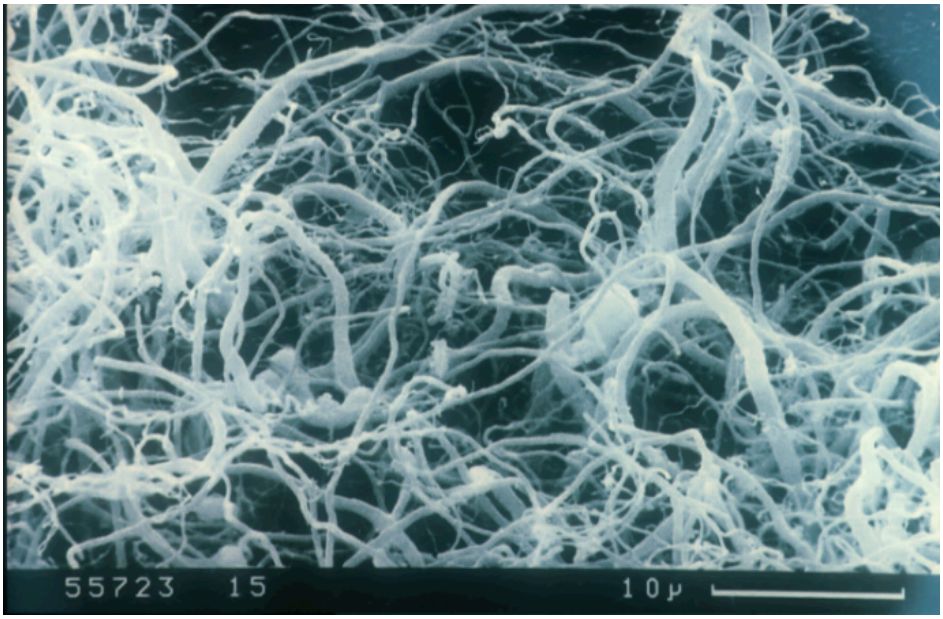
2. Theory

2.1 Marks developed by superglue become visible because white deposits are preferentially formed on fingerprint ridges during treatment. These white deposits are polycyanoacrylate, formed by the polymerisation of the cyanoacrylate monomer. The polymerisation reaction for ethyl cyanoacrylate is shown below; a similar mechanism occurs for methyl cyanoacrylate, which is used as an alternative by some practitioners.



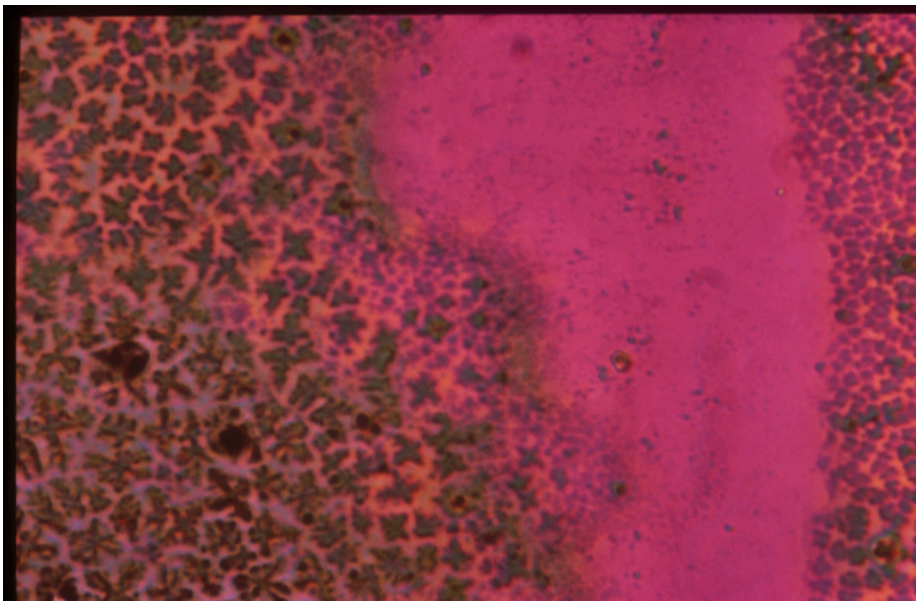
Polymerisation reaction for ethyl cyanoacrylate

2.2 The precise mechanism of the growth of poly-ethyl-cyanoacrylate on fingerprint residue is unclear. Electron microscopy studies by PSDB showed the growth of long fibrous deposits when the humidity was elevated (80% RH), these were not present at lower humidity levels (40% RH). These long fibrous deposits make the developed mark easier to see by eye.



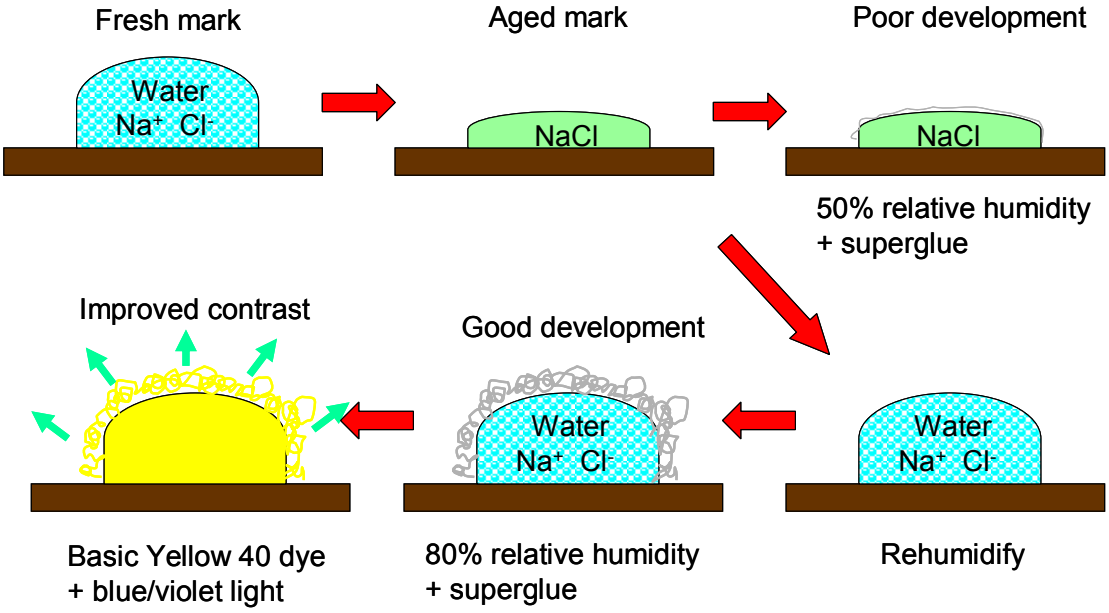
Electron micrograph of the fibrous deposits formed by superglue development at high humidity.

2.3 Cyanoacrylate polymerisation is base-initiated and even weak bases, such as water, will initiate polymer growth. It is believed that elevating the RH to around 80% causes sodium chloride crystals in the latent fingerprint to take up water. A saturated solution of sodium chloride (NaCl) with excess solid in a closed volume will create an RH above the solution of 75% at equilibrium. Therefore, at RH values above this NaCl crystals will absorb water from the environment around it. Similarly, any NaCl crystals in fingerprints will absorb moisture from the environment when the cabinet is set to 80% RH.



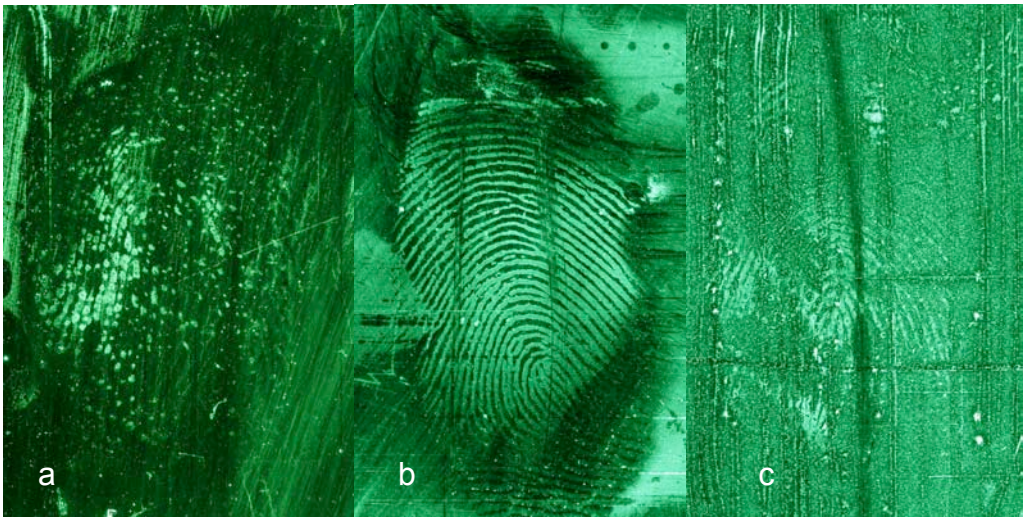
Optical interference micrograph of a dehydrated fingerprint ridge showing the formation of sodium or potassium chloride salt crystals.

2.4 This description explains one possible mechanism for polymer growth. There are undoubtedly other bases within fingerprint residues and some of these may also initiate polymerisation. Most fingerprints, however, have an initially significant water and chloride content, this is therefore likely to be a significant initiation mechanism. It is also suggested that short chains, oligomers, of cyanoacrylate may be formed due to atmospheric humidity, which may take part in further polymerisation on the fingerprint or the substrate. The superglue process is illustrated schematically below.

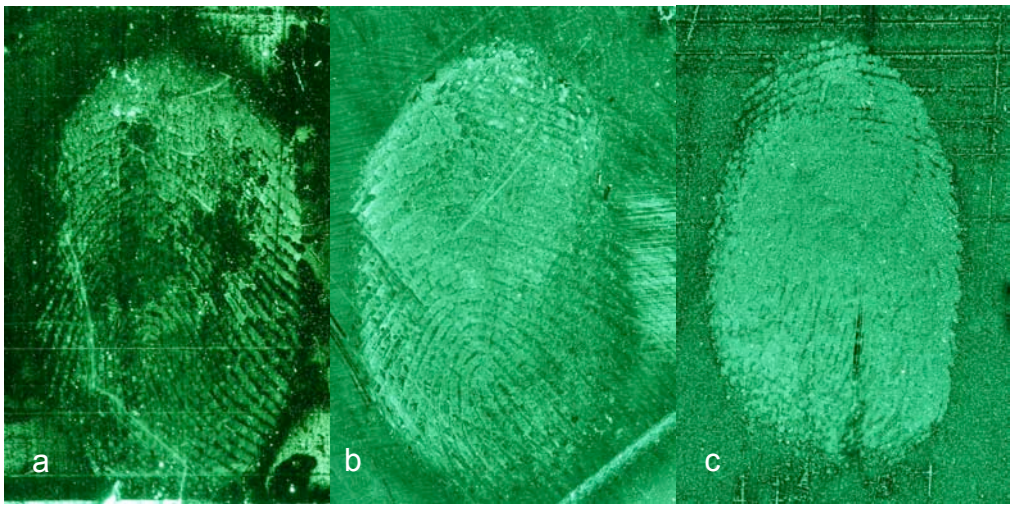


Schematic diagram of the superglue development and dyeing process.

2.5 Humidity levels below 75% RH give underdeveloped marks, humidity levels above 80% RH cause an increased background development and reduced definition of the developed mark. This can be seen in the series of photographs below, obtained for predominantly eccrine and predominantly sebaceous marks [37].

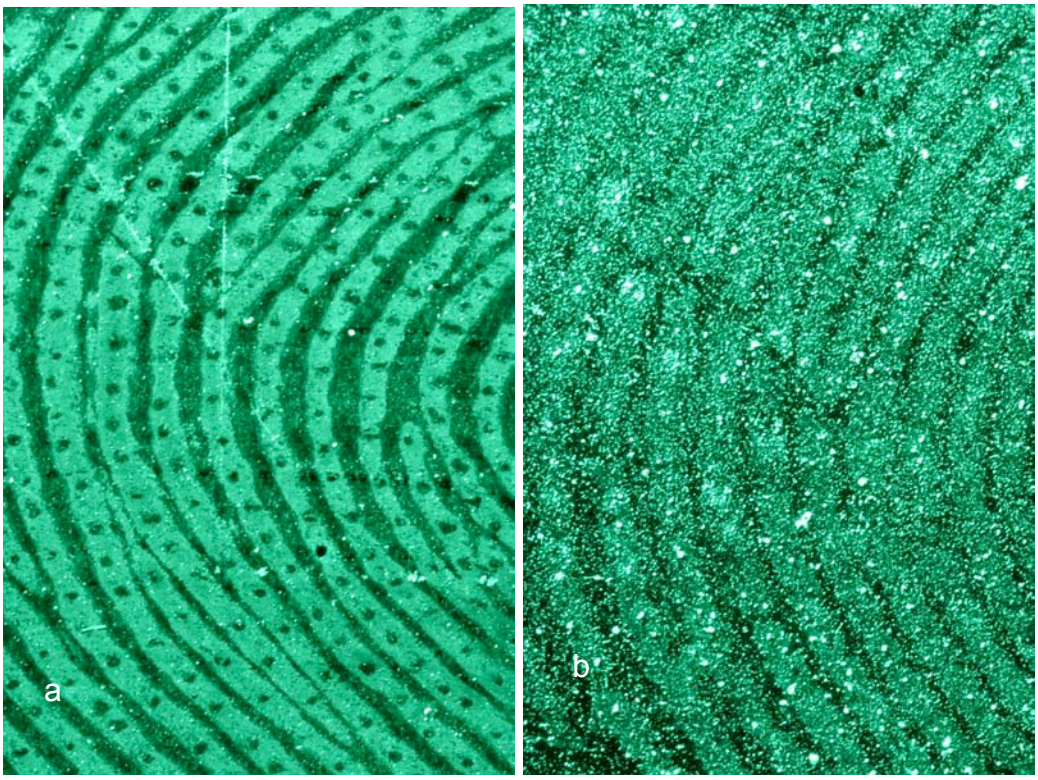


Eccrine fingerprints developed at a) 60% b) 80% c) 100% relative humidity.



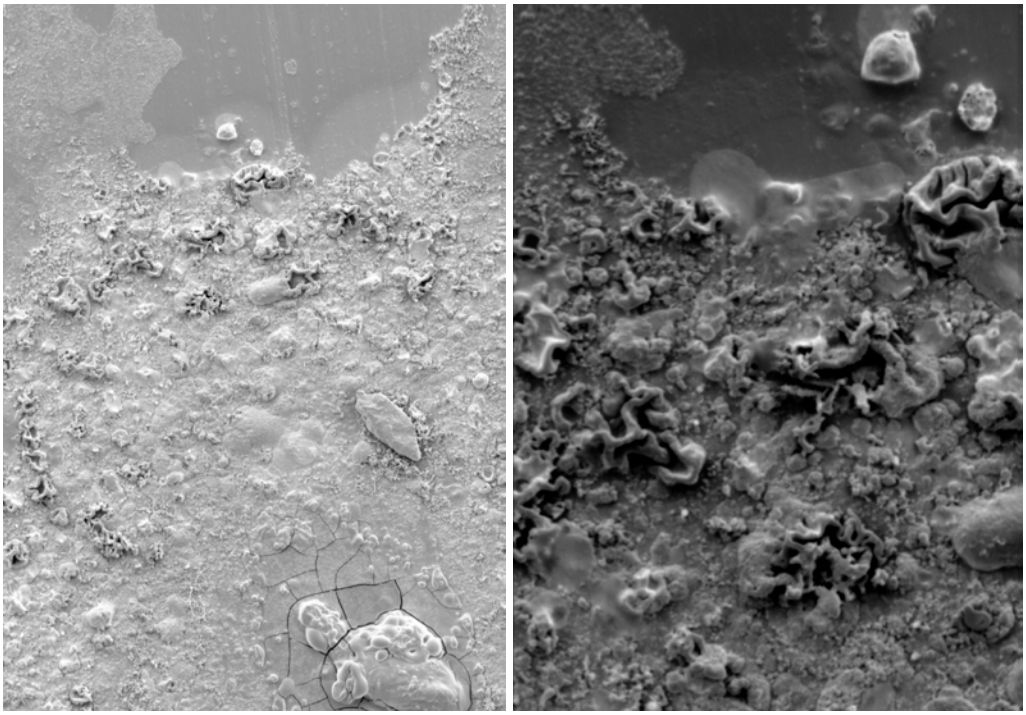
Sebaceous fingerprints developed at a) 60% b) 80% c) 100% relative humidity.

The overdevelopment at higher humidity can be better seen in the higher magnification images below.

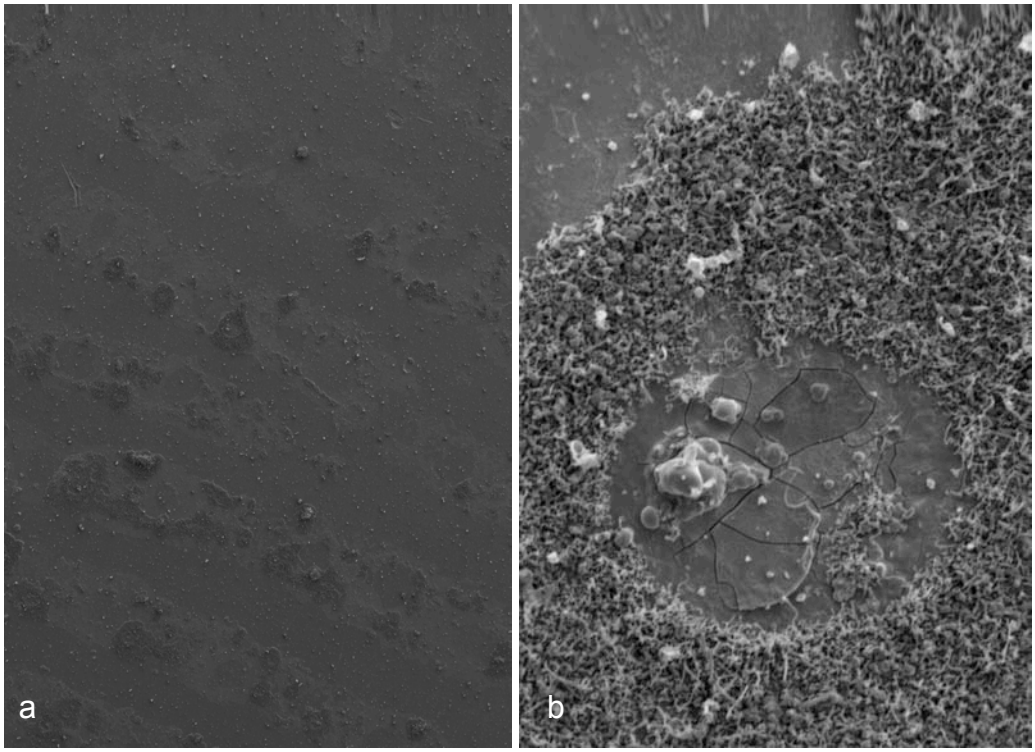


Normal (un-groomed) fingerprints developed at a) 80% and b) 100%.

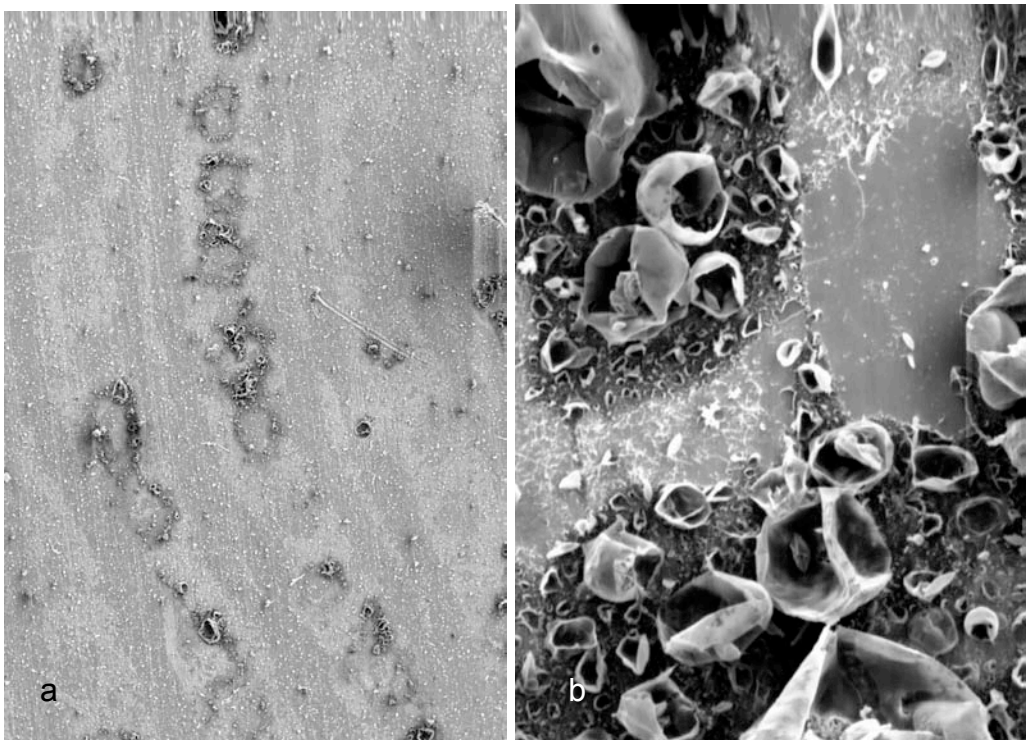
2.6 The different levels of superglue development for fingerprints under different conditions of humidity can be seen to be associated with different microstructures. Scanning electron microscopy has been conducted on samples developed under different humidity conditions [37], some of the results being illustrated below. It should be noted that these microscopy results are from a very limited subset of the donors used in the full study, and further investigation is required to see how consistent such observations are across a range of donors.



Fingerprint ridge developed at 60% relative humidity a) x 580 magnification b) x 1,700 magnification.



Fingerprint developed at 80% relative humidity a) x 50 magnification b) x 1,100 magnification.



Fingerprint developed at 100% relative humidity a) x 50 magnification b) x 1,000 magnification.

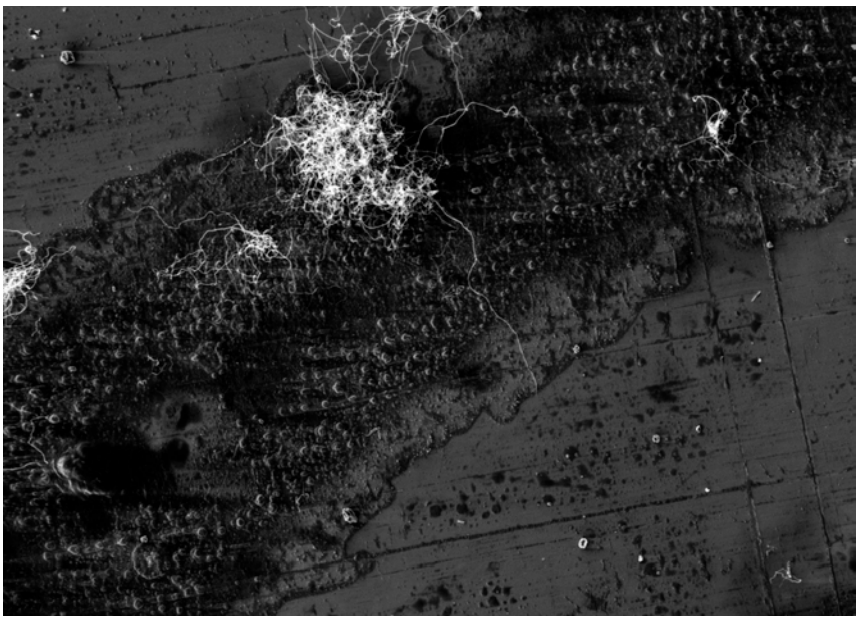
2.7 At 60% RH, the polymer resembled a film that was gathered at some points into a tortellini-like structure. This type of polymer morphology has been observed in fingerprints developed at lower humidity by others [38]. It has been suggested that this polymer film is a result of initiation by a hard anion, leading to rapid initiation and many active centres of polymer growth and hence the polymer grows in many directions, producing a two-dimensional film [39].

2.8 Fingerprints developed at 80% RH had less polymer development between the ridges than those developed at 100%. There was a very high concentration of noodle-type polymer in the ridges, with a particularly high concentration around the pores. This is thought to be because the concentration of eccrine secretion is higher in these areas. It has been suggested that this type of polymer is a result of slower initiation of polymerisation, leading to fewer active centres of polymer growth, and hence growth in a single direction, producing the noodle morphology [39]. It is not clear as to why initiation might be slower at 80% RH than at 60%. If anything, it would make sense for initiation to be faster at 80% because there is a higher concentration of water molecules to initiate polymerisation. It is possible that the presence of the water molecules influences how other constituents of the fingerprint initiate polymerisation.

2.9 Fingerprints developed at 100% RH produced an interesting morphology that seems to be unlike any observed in the literature. The polymer resembles collapsed spheres of varying size and was mostly concentrated around the fingerprint pores. The structure of the

developed marks is predominantly flat in nature for the 60% and 100% RH samples, with some isolated raised features ('tortellini' for 60% RH, and 'collapsed spheres' for 100% RH). The noodle-like structure developed at 80% RH is most effective in retaining the fluorescent dyes used to enhance the marks.

2.10 There has been further investigation into which constituents of fingerprint residues may be responsible for initiation of the polymerisation reaction. Lewis *et al.* [40] found that moisture in the print prior to the fuming process was an important factor in the development of fingerprints. Eccrine marks showed a marked drop-off in quality of developed marks with time, attributed to loss of moisture from the mark. In contrast, sebaceous marks showed less age-dependence. It was thought that sebaceous constituents in the print could retain moisture in the residues, but these constituents were not, in themselves, responsible for initiating the polymerisation reaction. In the recent study conducted by CAST and London South Bank University [37] to investigate the effects of RH on fingerprint development, the microstructure of purely sebaceous marks developed at 80% RH was found to differ considerably from eccrine and 'normal' marks, suggesting a different mode of polymer growth.



Sebaceous fingerprint developed at 80% relative humidity (x 250 magnification).

2.11 In sebaceous marks developed using superglue, there is a large amount of spherical polymer throughout the ridge, as well as clumps of noodle-type polymer, presumably where some eccrine material is present on the ridge. The edge of the ridge shows where the oily material has spread outwards. It has been suggested that the capsule-type polymer morphology is a result of emulsion polymerisation, with fatty acids acting as emulsifiers of aqueous and oily phases [40]. The presence of small clumps of noodle-type polymer would seem to suggest that whatever is

initiating noodle-type growth in eccrine fingerprints is present in unevenly distributed, smaller quantities in sebaceous fingerprints.

2.12 More recent research [41] looked at the role of fingerprint constituents initiating polymerisation and indicated that some of the components of eccrine sweat (lactate and alanine) were both capable of initiating the polymerisation reaction, in both cases initiation occurring via the carboxylate functional group. There was no evidence that the amine functional group in alanine played any role in polymerisation. However, the fingerprint environment is a complex one and it may be that the presence of combinations of constituents is actually more important than individual constituents in the initiation process.

2.13 With regard to the selection of dyes for the enhancement of developed superglue marks, it should be noted that many of the most successful dyes are basic in character. It is believed that basic dyes work better in this application because they form weak Van der Waals bonds with the polycyanoacrylate 'noodles' formed during development, predominantly due to weak binding of the dye cation with the anions associated with cyanide (CN^-) groups in the polymers strands.

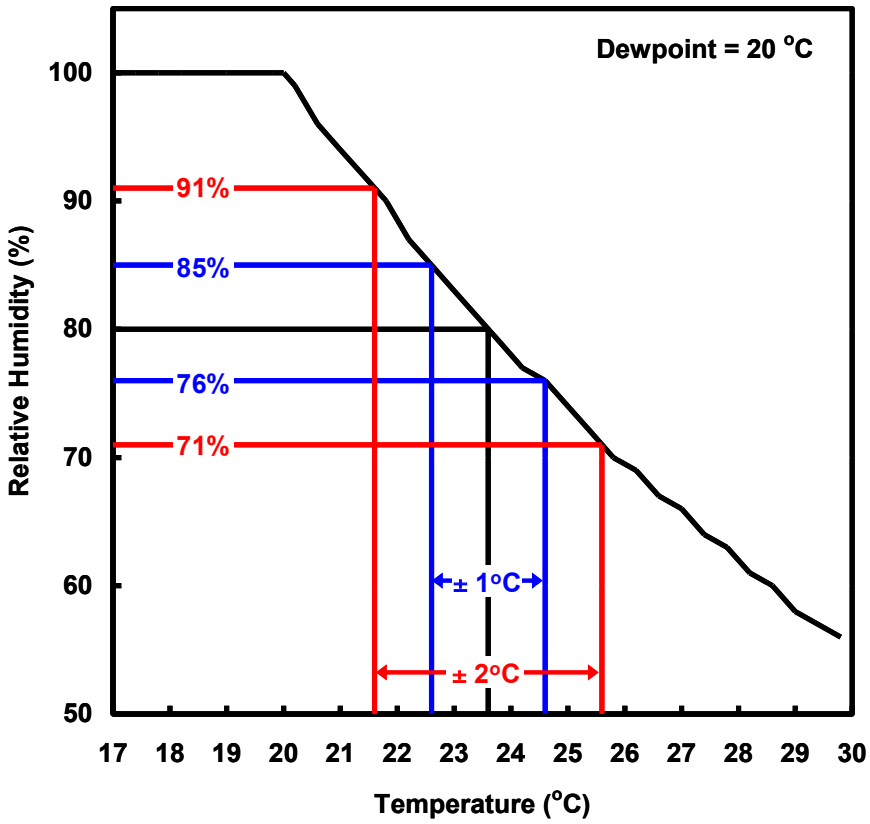
3. CAST processes

3.1 The CAST procedure recommends the use of a controlled-humidity superglue cabinet, four of which are known to comply with the technical specifications devised by CAST. These are the Sandridge cabinet, produced by the original Mason Vactron Company and still in use in some fingerprint laboratories, the MVC5000 and MVC3000 systems produced by Foster and Freeman (the company that purchased Mason Vactron), and the superglue cabinet produced by Labcaire. There are other systems on the market that may meet specifications, but CAST has not carried out an evaluation of them.

3.2 The process involves first raising the humidity in the treatment chamber to 80% RH. This value has been found by empirical testing to give a visible white deposit on the developed fingerprint and minimal background staining for the typical ambient temperature range experienced in the UK.

3.3 Once the humidity in the chamber has reached the required level, superglue is evaporated from an aluminium pot placed on a heater and heated to ~120ºC to speed evaporation. The amount of superglue used varies between different types of chamber depending on capacity, but is selected to give a sufficient concentration of superglue vapour in the atmosphere to allow the polymerisation reaction to proceed to the extent that marks are visible. The quantity actually used should be optimised for a particular cabinet configuration by observing the quantity of residue left in the aluminium pot and adjusting it to ensure very little excess remains at the end of the cycle.

3.4 Obtaining a constant temperature within the closed treatment chamber is essential in order to maintain a constant RH because of the relationship between the two variables in a situation where air currents and fans carry air around a closed system. A theoretical plot derived from a known mass of water contained in the air at 80% RH and 20°C is illustrated below [36].



Relationship between temperature and humidity in a closed system.

3.5 It can be seen that small fluctuations in temperature can have appreciable effects on the local RH, and it is therefore essential to ensure that the temperature profile within the treatment chamber is as even as possible. Within the old 'Sandridge' style cabinet, the heat from the light bulbs used in the chamber was observed to cause fluctuations in temperature (and therefore RH), and a change to 'low energy' bulbs was recommended to overcome this [42].

3.6 The use of low viscosity (unthickened) ethyl cyanoacrylate is thought to give better results than those including thickeners. Methyl cyanoacrylate seems to give similar results to the ethyl system.

3.7 CAST recommends that initial photography of any visible marks be carried out after superglue treatment and prior to proceeding to treatment with a fluorescent dye stain. This is because some marks may be degraded or destroyed by the dye process and to maximise evidence recovery all marks should be recorded before dyeing.

3.8 The primary fluorescent dye recommended by CAST in the 2nd edition of the *Manual of Fingerprint Development techniques* [43] is BY40, dissolved in ethanol. Fingerprints dyed with BY40 are best visualised by illuminating them using the violet/blue (400–469nm) excitation band of a Quaser light source (or equivalent) and viewing the resultant blue/green fluorescence through a Schott glass GG495 filter (which has a 1% 'cut-on' limit at 476nm). BY40 is selected because trials by CAST in the 1980s (for which original data are no longer available) have shown it to be at least as effective in terms of fluorescence intensity as Rhodamine 6G. BY40 is preferred by CAST because it has been demonstrated not to have any of the issues of suspect carcinogenity associated with Rhodamine derivatives. With the recent development of a blue laser operating at 460nm, it may be possible to increase the number of marks detected after dyeing with BY40, although no dedicated study has yet been carried out.

3.9 The dye basic red 2 (Safranine O) was also recommended for use by HOSDB. In comparative studies in the 1980s (for which original data are no longer available) it was found to be slightly less sensitive than BY40 but is excited by the green (473–548) excitation band of the Quaser light source and has an orange fluorescence that is viewed through a Schott glass OG570 ('cut-on' 549nm) filter. This may be a useful alternative dye for situations where the background fluoresces when illuminated by violet/blue light and obscures the developed mark, although BR14 is now preferred for this role.

3.10 The solvent recommended for the dyeing of superglue marks is ethanol. This is selected because it is non-toxic (unlike earlier formulations based on methanol) and has been shown to be effective in delivering the dye into the polymer deposits. However, there are cases where the flammable ethanol-based formulations cannot be used (e.g. in a laboratory that has insufficient extraction, if the dye is being applied at a scene, in cases where ethanol is causing some printed inks to run or there is excessive dye take-up by the substrate) and a water-based BY40 formulation is recommended as an alternative. However, the water-based BY40 formulation is less effective in dyeing the fingerprints and the resultant fluorescence is markedly less intense [25]. More recently CAST has reviewed a number of alternative water-based dyes and have found the most effective of these to be BR14. A formulation for this has been issued [44] for operational use, and further improvements in performance may be possible by using this dye in combination with the green (532nm) laser. There have been some recent issues with availability of the Levercet CC carrier material for the water-based formulation and some work has recently been carried out to identify alternatives [45].

4. Critical issues

4.1 There are a number of critical issues associated with the superglue process as recommended by CAST.

4.2 Superglue development should be carried out in a closed, temperature- and controlled-humidity cabinet at an RH of 80%, because these conditions give the optimum development of marks. There is evidence that some cabinets may overshoot and do not provide close control of humidity. Ideally control limits should be determined and specified. Cabinets should be kept clean and maintained regularly.

4.3 Marks developed using superglue should be imaged wherever possible after superglue development and prior to dyeing. There is no guarantee that marks visible after the development process will still be present after dyeing.

4.4 Superglue should not be used if the surface is suspected of being wetted at any point after fingerprint deposition because the fingerprint constituents that initiate polymerisation will have been dissolved.

4.5 The nature of the surface needs to be taken into consideration prior to dyeing the developed marks. Some surfaces may be damaged by ethanol and require dyeing with a water-based formulation, some surfaces may be strongly background fluorescent under blue/violet light and require a dye excited in a different part of the spectrum, and some surfaces may strongly absorb dye and require the developed marks to be enhanced with another means such as powders.

4.6 Marks may develop on different surfaces at different rates, observation of the development process is recommended and the process should be halted if over-development begins to occur, or extended if it is felt that further development of faint marks is possible.

5. Application

5.1 Suitable surfaces: Superglue is suited for use on all types of non-porous surface, including glass, plastic bottles and plastic packaging, metals, ceramics and both sides of many adhesive tapes. It is superior to powders in developing marks on surfaces that are more textured. Superglue can also be used on some ‘semi-porous’ surfaces, but in such situations the dyeing stage is usually omitted to prevent staining of the background.

5.2 The principal application of superglue is for the development of fingerprints on non-porous surfaces and adhesive tapes (although not on the adhesive side of acrylic adhesive-based tapes). It is an effective process on articles such as plastic bags, drinks cans, bottles, cowlings and vehicle number plates. Superglue generally gives better results than

powdering on textured surfaces, where powders tend to fill in the texture and clog the surface. However, the polymerisation process is thought to be initiated by water-soluble components of the fingerprint and as a consequence the process is not generally suitable for articles that have been wetted because these components are likely to have been washed away [46]. For wetted items the use of an alternative process, such as vacuum metal deposition, small particle reagent or powder suspensions, is recommended instead.

5.3 The technique can be effective on semi-porous items or items with glossy, non-porous coatings on porous backings (e.g. glossy magazines, printed cardboard packaging) but in these situations dyeing the article can lead to severe background staining or uptake in the porous substrate. Marks developed on these surfaces should be imaged under oblique light or UV imaging, or enhanced using a dry process such as powders or vacuum metal deposition.

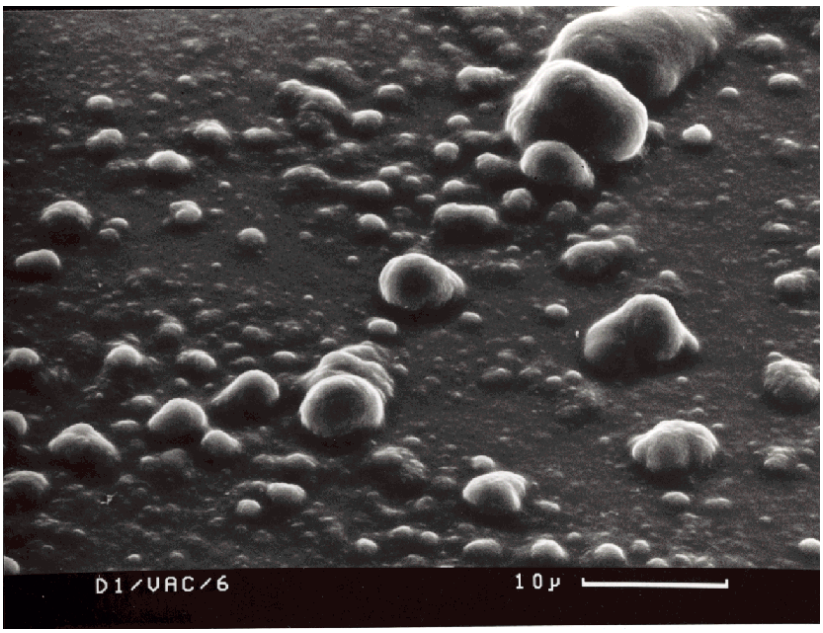
5.4 The use of superglue fuming has been reported for fingerprints deposited on skin, but developed marks are not easy to visualise and require dye staining.

5.5 The method recommended for application of superglue in a laboratory is by the use of controlled-humidity cabinets. The articles to be treated are suspended or placed on shelves within the cabinet, ensuring sufficient space between them for circulation of the vapours and exposure of all surfaces of interest. Ideally, similar items should be treated together in batches. The cabinet is then humidified to the recommended level of 80% RH, and then an appropriate amount of superglue is evaporated from an aluminium foil pot on a heater at approximately 120ºC. The glue cycle can be allowed to run for a set period of time, but it is best practice for the operator to watch development on the samples and halt the cycle if it looks as if overdevelopment of marks is beginning to occur. The cabinet is then placed through a purge cycle to remove fumes of cyanoacrylate vapour before the cabinet is opened and articles are removed. Articles with underdeveloped marks can be replaced into the cabinet and redeveloped. The cabinet allows several items to be treated in a single run unlike some processes, such as vacuum metal deposition, where it may only be possible to treat one item at a time.

5.6 If an article is to be dyed, it is immersed in a tank containing dye solution (either ethanol or water-based), then removed to a second tank containing running water until excess dye has been removed. The dyeing time for the ethanol-based dye is approximately one minute, but longer dyeing times (~ two minutes) may be required when water-based dyes are used. The article is then allowed to dry at room temperature. For larger articles, the fluorescent dye solution may be applied from a wash bottle (but never sprayed), and the dye washed off using a wash bottle, hose, or running tap water.

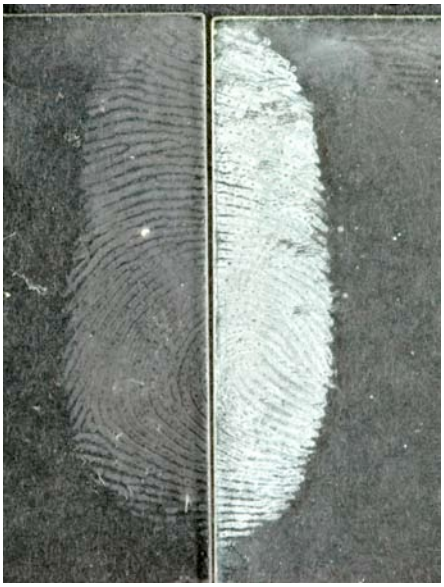
6. Alternative formulations and processes

6.1 The reaction of cyanoacrylates with fingerprints under low humidity and low pressure is also reported in the literature [26-31] and several comparisons have been made to the high humidity technique. In the vacuum superglue technique, the articles to be treated are placed in a chamber with a quantity of superglue, and the chamber is evacuated to a level in the region of 0.3–0.7mbar. When most of the air has been pumped out, the chamber is sealed from the vacuum pump and the superglue continues to vaporise to its room temperature vapour pressure. In general, the 'vacuum superglue' reaction does not give rise to the white fibrous deposit, instead it produces small beads of polymer.



Scanning electron micrograph of superglue deposit formed during vacuum superglue fuming.

6.2 The principal advantage of the technique over the high humidity process is that it is less prone to overdevelopment of marks. However, the developed marks are less easy to see and require dyeing to aid visualisation. Studies by PSDB [28] have indicated that it is more difficult to obtain dye uptake in the bead-like deposits formed by vacuum superglue and consequently it is the high humidity process that CAST has recommended.



a)

b)

Photographs showing differences between vacuum superglue development (left-hand side) and high humidity superglue development (right-hand side) a) showing over-development of high humidity mark and b) showing generally fainter appearance of vacuum developed marks

6.3 Comparative studies carried out by PSDB in the early 1990s [28] involved a pseudo-operational trial, dividing plastic (polyethylene) bags from high street stores into quarters. Two quarters were treated with high humidity superglue and the other two with vacuum superglue. All were then dyed with BY40 and examined using the violet/blue output of a Quaser 100. From this and parallel studies using split depletions deposited on clear polythene substrate, PSDB concluded that vacuum superglue was generally less sensitive or effective in the development of latent fingerprints. However, it should be noted that other researchers reached the opposite conclusion [27, 29] and it is recognised that both techniques have their advantages and disadvantages, vacuum superglue

being preferred where development is not closely observed and the risks of overdevelopment can be mitigated.

6.4 The use of superglue as a fingerprint development technique for use at crime scenes has also been investigated and several systems have been developed for the treatment of car interiors, rooms and localised treatment of small areas [32-35]. It is difficult to control accurately the humidity conditions during treatment at scenes. Consequently, where comparative assessments have been made between portable fuming equipment and treatment in controlled-humidity cabinets, the laboratory results have been superior. In 2002 PSDB assessed the SuperFume system produced by Foster and Freeman, comparing it with both powdering and superglue treatment in the controlled conditions of the MVC5000 cabinet [36]. Over 6,000 marks were deposited across a range of surfaces in a small room. Marks developed at the scene were dyed with water-based BY40, those developed using the MVC5000 were dyed with the ethanol-based formulation.

6.5 It was concluded that although there were a range of surfaces where superglue gave better performance than powders at a scene of crime, if the surface could be recovered to a laboratory and treated under controlled conditions the number and quality of marks developed was increased. The study concluded that scene portable fuming systems such as SuperFume do have an important role to play in treatment of scenes, in particular on textured surfaces that cannot be recovered to a laboratory. However, if articles are portable they should be taken back to a laboratory for treatment unless time and cost considerations indicate in situ treatment is preferable. The use of superglue at a scene will have health and safety implications, both in application and in the subsequent clean up. During application the fumes given off by the superglue must be contained and then safely vented, and after application vapours may still be trapped in porous items such as soft furnishings. The vapours may subsequently be released to the atmosphere, and there is a possibility that superglue deposits on hot surfaces can degrade to form hydrogen cyanide, carbon monoxide and carbon dioxide. It should also be noted that the water-based BY40 dye used in this study has since been superseded by a water-based BR14 formulation and the effectiveness of treatment at scenes should now be improved because the water-based BR14 dye gives more intense fluorescence than water-based BY40, and will be particularly effective if used with the higher power 532nm laser.

6.6 With regard to the dye systems used in combination with superglue, several alternatives to BY40 have been proposed in the literature. A summary of these is given to below, together with some comments about why they are not currently (2011) recommended for regular operational use by CAST.

Dye	Excitation band (nm)/colour	Viewing filter cut-on (nm)/ fluorescence colour	Comments
Rhodamine 6G (Basic red 1)	495–540 (green)	549 (orange)	Unconfirmed health and safety concerns. No better than BY40
Safranine O (Basic red 2)	473–548 (green)	549 (orange)	Recommended in CAST manual 2nd edition, but less sensitive than BY40
Ardrox	365 or 435–480 (UV or blue)	476 (blue/green)	Health and safety issue with prolonged use of UV-A
Basic red 28	470–550 (green)	549 (orange)	Not tested by CAST
Liqui-drox	365 (UV)	415 (blue)	Health and safety issue with prolonged use of UV-A
MBD	415–505 (blue/green)	515 (yellow)	Not tested by CAST
Nile Red	450–560 (green)	549 (orange)	Not tested by CAST as superglue dye
Thenoyl europium chelate (TEC)	365 (UV)	593 (red)	Health and safety issue with prolonged use of UV-A. Tested *vs*. BY40 by CAST, found to be inferior
MRM 10 (Rhodamine 6G, BY40, MBD)	430–530 (blue/green)	549 (529) (yellow/orange)	Not tested by CAST
RAM (Rhodamine 6G, MBD, Ardrox)	415–530 (blue/green)	529 (yellow/orange)	Not tested by CAST
RAY (Rhodamine 6G, BY40, Ardrox)	450–550 (green)	549 (orange)	Not tested by CAST

Some fluorescent dyes reported for use with superglue [19,20,21,23,47,48].

6.7 Not all the above dyes are fully soluble in ethanol, and other combinations of solvents may be recommended.

6.8 In order to minimise background fluorescence and improve contrast between ridges and the background, approaches to maximise the shift between excitation band and emission wavelength have been investigated. Successful approaches have included the use of dye mixtures [47], where energy transfer occurs between the excited states of the combined dyes and emission occurs at the longest wavelength from illumination at the shortest excitation band, and of thenoyl europium chelate, which naturally has a large Stokes shift and emits in the deep red/near infrared after excitation in the long-wave UV [48]. These approaches can be used operationally if it is not possible to distinguish any of the recommended dyes against background fluorescence.

6.9 CAST has researched alternatives to the water-based BY40 formulation, the most promising candidate systems being BR14 and Disperse Yellow 82 [25]. Disperse Yellow 82 proved difficult to dissolve into the water/carrier mix and therefore only the BR14 formulation was taken forward. The resultant formulation proved more intensely fluorescent than the water-based BY40 formulation, but not as intense as BY40 in ethanol. The effectiveness of BR14 in ethanol is closely equivalent to BY40 in ethanol and could be substituted for it, especially if used in combination with the new generation of scene-portable 5W green lasers emitting at 532nm.

a) b)

Comparison of water-based basic red 14 with a) water-based basic yellow 40 (right), showing higher intensity of basic red 14 and b) ethanol-based basic yellow 40 (left), showing higher intensity of basic yellow 40

(this image should be viewed electronically to see the true intensity levels).

6.10 Simultaneous processes for fuming and dyeing in a single step have been investigated [24] and in some cases carry-over of the coloured or fluorescent dye into the developed ridges has been achieved. However, to date (2011) the resultant fluorescence has not been comparable with that obtained in a two-step process and the approach is not recommended. The approaches that have been considered include co-evaporation of a coloured or fluorescent dye with the superglue, and tagging of the monomer molecules with fluorescent species. This has been difficult to achieve because it is hard to get the monomer and dye to evaporate at equivalent rates, and tagging the molecules generally increases molecular weight and increases the temperatures required for evaporation.

7. Post-treatments

7.1 There are several post-treatments that can be applied to marks developed using superglue in order to improve their visualisation. The application of fluorescent (or indeed coloured) dyes has been discussed above; these are most often applied as solutions but sublimation has also been investigated. The intention is to stain selectively the fingerprint ridges to enhance their contrast with the background.

7.2 For marks on surfaces that cannot be solution-dyed, powdering is a possible alternative. Powders may also selectively adhere to developed areas of ridge detail although early trials indicated that not all powders are effective and some trial and error may be required to identify the most appropriate powder to use. Reasonable results have been reported with Bristol Black and black magnetic powder [5], but these are by no means the only powders to use. Powdering may also destroy marks and photography should be carried out before powdering if possible.

7.3 Oblique lighting and UV imaging [49] have also been used to improve the contrast between the ridges and the background. In both cases the scatter of incident light from the rough texture of the developed ridges is used to discriminate the ridges from the smooth background. The advantage of both techniques is that they are non-contact. Further detail on both these techniques is given in Chapter 4.1 Ultraviolet imaging and Chapter 2.1 Visual examination.

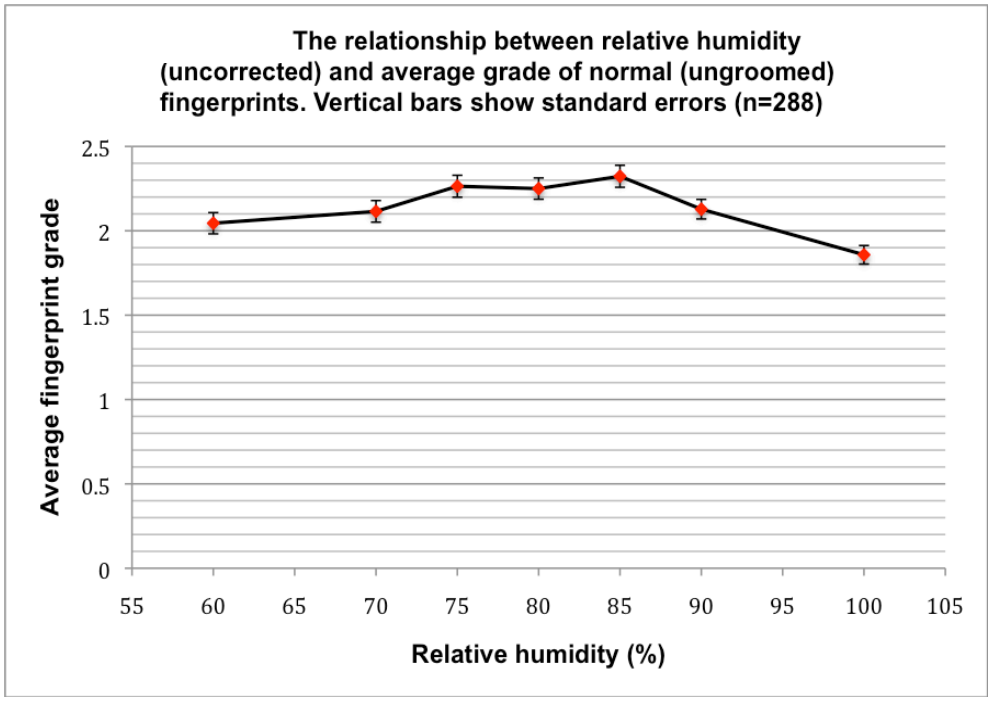
7.4 Another technique that may be used to separate superglue developed marks from patterned backgrounds is lifting using black gelatine lifters. These pick up a loose surface layer of white superglue deposit that can then be easily visualised against the black glossy background of the gel. Where marks have been dyed there is also a limited amount of dye carry-over and the lifted marks can also be viewed by fluorescence.

8. Validation and operational experience

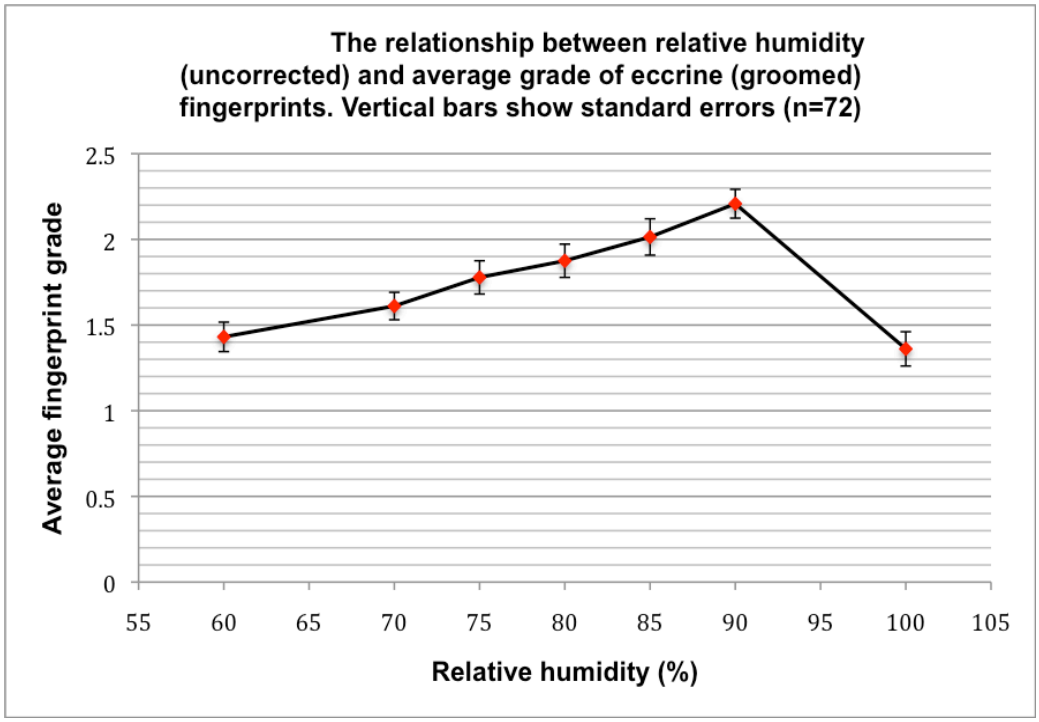
8.1 The effectiveness of superglue has been compared with that of a range of other techniques recommended for use on non-porous surfaces in a series of laboratory and pseudo-operational studies conducted by CAST from the mid-1980s to the present (2011).

8.2 Laboratory trials

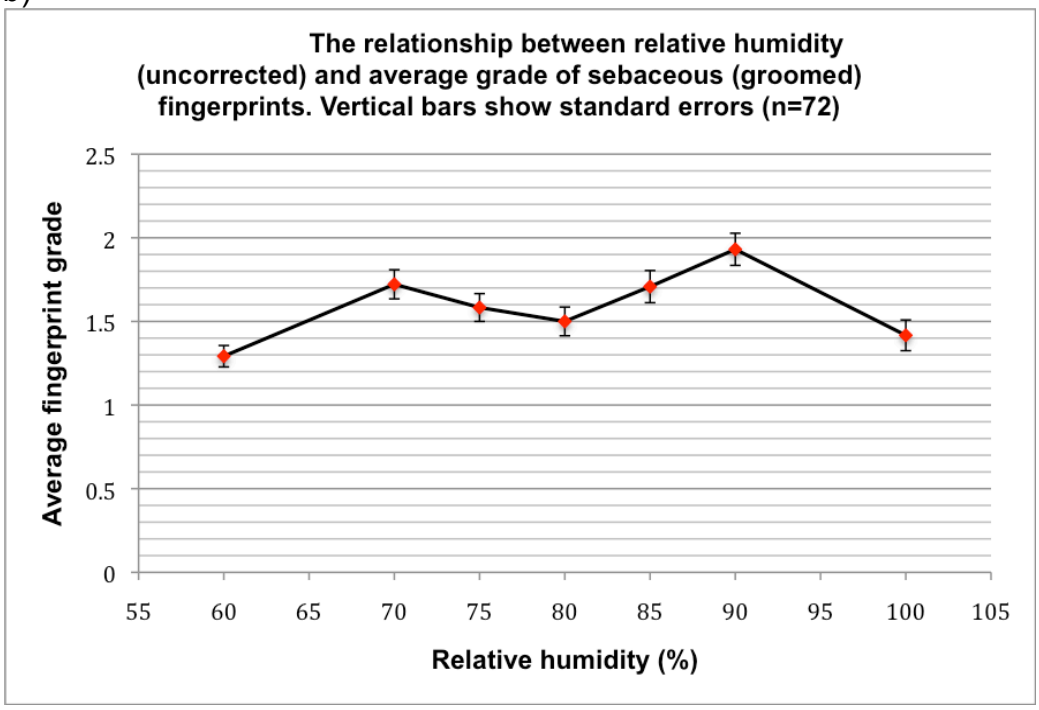
8.2.1 Laboratory trials were first conducted by HOSDB in the mid-1980s to establish the optimum conditions of RH for development of fingerprints. Unfortunately, the results of these trials no longer survive for inspection and the work was repeated in 2009 to re-validate the recommendation for 80% RH during processing [37]. The results of developing and grading 2,016 'normal' marks, 502 'eccrine' marks and 502 'sebaceous' marks are illustrated below.



a)



b)



c)

The effect of relative humidity on the quality of marks developed using superglue a) normal prints b) eccrine prints and c) sebaceous prints

8.2.2 It can be seen that the quality of the marks developed at the extremes of RH investigated, 60% and 100%, were inferior to those developed between 70% and 90% with the optimum actually being between 85% and 90%. The lower value of 80% RH is chosen for operational work because it gives some margin of error during processing and is not too close to 100%.

8.2.3 Laboratory trials have also been carried out to compare the effectiveness of superglue with both powders and powder suspensions on a range of substrates [50,51].

8.2.4 Laboratory trials were carried out in 2003–2004 to establish whether any clear recommendations could be made regarding the use of superglue or powders on non-porous surfaces [50]. A two-way trial was conducted on a range of textured surfaces comparing superglue and subsequent BY40 dyeing, and powdering with black magnetic powder. A subsequent three-way trial was performed on smooth surfaces, comparing aluminium powder, black magnetic powder and superglue, and BY40 dyeing. Both of these studies included marks of ages one day, one week and one month. Almost 10,000 marks were deposited and graded during these trials.

8.2.5 In the trial on textured non-porous surfaces 12 different surfaces were studied, including a range of laminates with different effect facings (e.g. marble, wood, granite), stone floor tiles, uPVC, computer casings and kitchen unit material. The summary of grading over 7,500 marks of all ages on all substrates is recorded in the table below.

Grade of fingerprint[	**Process**	
	Black magnetic powder (%)	**Superglue + BY40 (%)**
0	12.04	16.93
1	29.61	29.19
2	19.09	16.48
3	26.26	21.08
4	13.00	16.32
Total % grade 3 + 4	**39.26**	**37.40**

Results of initial comparative experiments between superglue and powders.

8.2.6 The results obtained by the two techniques are closely equivalent, although when the results were analysed surface by surface, it could be seen that superglue developed more marks of high quality on the rougher surfaces and on older marks. It was therefore concluded that the techniques should be given equal weighting in updates to the sequential processing charts for textured non-porous surfaces in the *Manual of Fingerprint Development Techniques* [43].

8.2.7 In the second trial on smooth surfaces four materials were used, including glass, patterned and white ceramic tiles and smooth plastic-faced chipboard. Over 2,000 marks were graded in this exercise. The results are summarised in the table below.

Grade of fingerprint	Process		
	Aluminium powder (%)	Black magnetic powder (%)	Superglue + BY40 (%)
0	4.6	5.7	9.7
1	20.4	20.3	24.6
2	16.5	17.2	11.9
3	22.4	30.0	25.4
4	36.1	26.8	28.3
Total % grade 3 + 4	**58.5**	**56.8**	**53.8**

Results of further comparative experiments between superglue and powders.

8.2.8 Overall, there was little difference between the three processes, although the observation in previous trials that aluminium powder performed best on smooth surfaces was confirmed. Powdering would marginally be the preferred process on smooth non-porous surfaces, but superglue gave closely equivalent performance.

8.2.9 The comparison with powder suspensions carried out more recently (2007) is more fully reported in Chapter 3.7 Powder suspensions. This was an extensive study looking at over 37,500 marks over 23 different surface types. There were variations in performance across individual surfaces, but general trends could be seen. These indicate that superglue and powder suspensions are closely equivalent in performance when used to develop fingerprints on non-porous surfaces, but the sequence of powders followed by powder suspensions was found to be more effective than superglue and dyeing overall [51].

8.3 Pseudo-operational trials and operational experience

8.3.1 PSDB carried out a pseudo-operational trial on 200 plastic bags in 1986, and demonstrated that superglue combined with dyeing and subsequent fluorescence examination was a highly effective process for this type of surface, although not as effective as vacuum metal deposition. The results of this study are described in greater detail in Chapter 3.11 Vacuum metal deposition. Because not all police forces had vacuum metal deposition equipment, superglue and dyeing was considered an effective alternative.

8.3.2 A comparison between vacuum metal deposition and vacuum superglue was also carried out by Misner [52], who found that vacuum metal deposition developed 180/229 (79%) deposited marks to an identifiable standard compared with 141/229 (62%) marks developed by superglue, a similar margin to that in the PSDB study. Taroni *et al.* [53] conducted a similar study but concluded that superglue and vacuum metal deposition were of a similar sensitivity. However, a further study by Masters and

DeHaan [54] again concluded that vacuum metal deposition was more sensitive than superglue on older marks (> three years) although equivalent on fresher marks (< two months).

8.3.3 PSDB conducted a comparative pseudo-operational trial between high humidity and vacuum superglue in the early 1990s [28], dividing ten plastic (polyethylene) bags obtained from high street stores and donated after use into quarters. Two quarters were treated with high humidity superglue and the other two with vacuum superglue. All were then dyed with BY40 and examined using the violet/blue output of a Quaser 100. The number of fingerprints and scraps of ridge detail developed were recorded, the results being summarised below.

High humidity superglue		**Vacuum superglue**	
Fingerprints	Ridge detail areas	Fingerprints	Ridge detail scraps
32	47	16	29

Results of comparative experiments between vacuum and high humidity superglue techniques.

8.3.4 From this and parallel studies using split depletions deposited on clear polythene substrate, PSDB concluded that vacuum superglue was generally less sensitive or effective in the development of latent fingerprints. PSDB found that there were problems with low dye take-up by marks developed using vacuum superglue, resulting in less developed marks being detected. However, other researchers carrying out similar studies reached the opposite conclusion [27, 29] and it is recognised that both techniques have their advantages and disadvantages. However, high humidity superglue continued to be the primary process recommended for operational use in the UK.

8.3.5 An analysis of the effectiveness of the superglue process on operational work in Essex Police Laboratory was conducted by Taylor [55] over a period of three months in 1995. Results from processing 430 items are summarised below. At the time of the work a 16 point standard was in place for fingerprint identification in the UK, and the marks were assessed by a fingerprint expert in terms of the number of ‘second-level detail’ features present.

Article type	**>16 points**	**8–15 points**	**Items overall**
Adhesive tape	3	6	18
Cash bag	0	4	46
Cowling	3	57	145
Credit cards	0	3	22
Latex gloves	0	0	16
Number[style so far] plates	2	4	42

Screwdrivers	0	0	13
Store cards	0	0	21
Sweet wrappers	0	0	11
Bullets/pellets	0	0	8
Crisp packets	0	1	7
Polythene bags	0	0	7
Miscellaneous	5	31	74

Results of operational work using superglue.

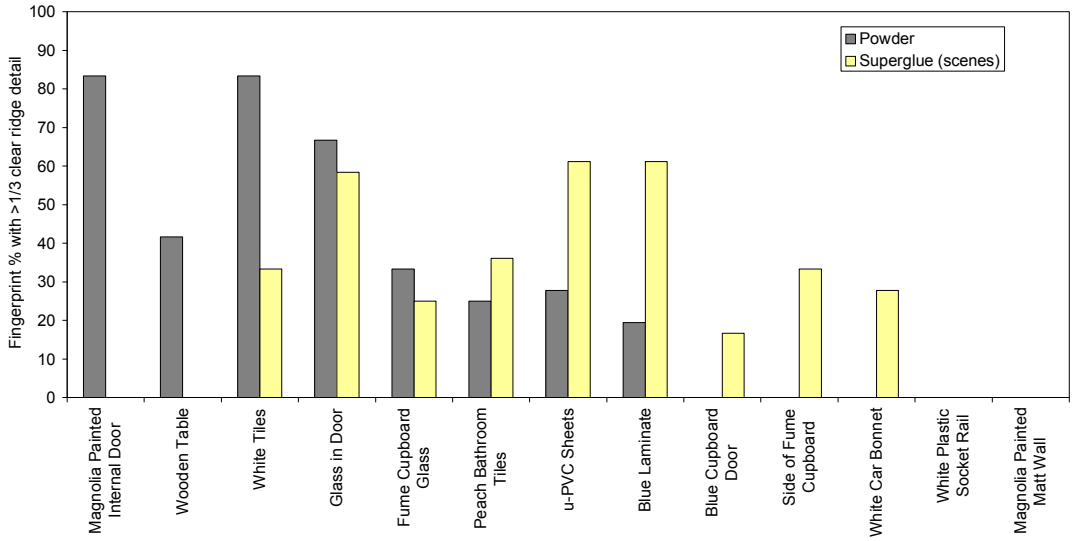
8.3.6 The miscellaneous items where the superglue process had most success included bin liners, a photograph and a telephone. The majority (91%) of items for which marks containing >16 points (the minimum fingerprint quality standard then in place) were recovered were plastics, suggesting that superglue is effective for this type of article. The effect of time before treatment on the number of marks developed was also assessed, as was the effect of any contamination present on the surface on subsequent development. Results indicated that superglue became less effective as the age of the mark increased. Development was still observed on articles contaminated by chemicals, blood or oil, but the presence of drugs residue or powder inhibited development and no marks were found on articles known to have been wetted. At this time, fluorescent dyeing was not being used as a secondary treatment; had this been the case, the number of recorded marks would have increased.

8.3.7 Subsequent operational experience has shown that superglue continues to be highly effective on plastic, non-porous items and the technique is extensively used on plastic bags and cowlings. However, some police forces had found that powders give equally good results on the inside of cowlings and it has recently been observed that powder suspensions may be more effective still. Two police forces recording data and changing from superglue to powder suspensions as a development technique on cowlings have observed increases in the number of marks developed. This is thought to be partly attributed to the fact that such items may be exposed to moist or wet environments, which are less detrimental to the powder suspension process.

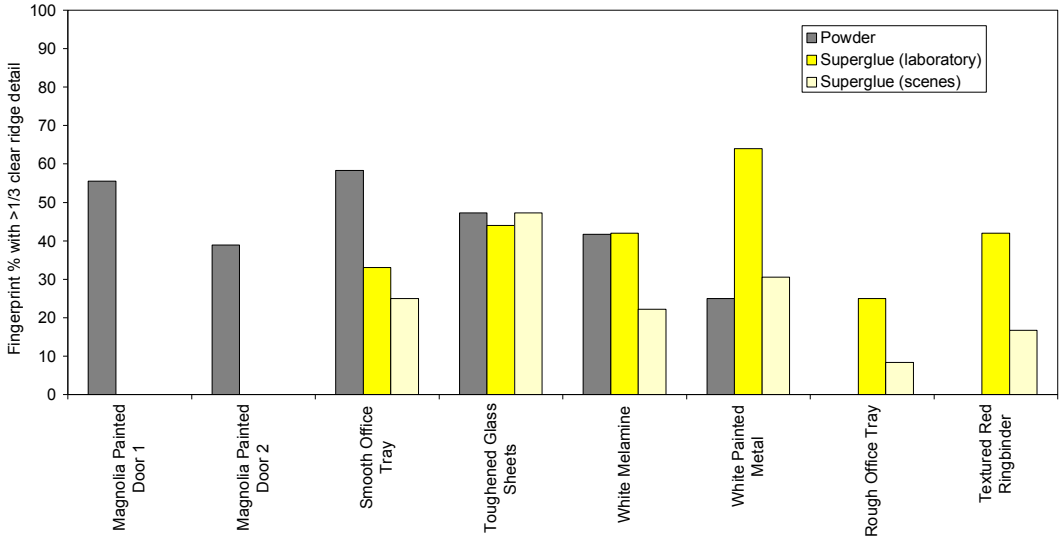
8.3.8 The operational work outlined above also shows that superglue is an effective process for developing fingerprints on adhesive tapes. Recently concluded research by CAST [56,57,58] indicates that superglue is the most effective process for developing fingerprints on the non-adhesive side of tapes, and is closely equivalent in performance to powder suspensions on the adhesive side of tapes with rubber-based adhesives. For treatment of such tapes superglue has the advantage that it develops marks on both sides of the tape simultaneously. However, on tapes with acrylic-based adhesives superglue does not develop marks on the adhesive side and carbon-based powder suspensions should be used instead. An operational trial to compare the effectiveness of superglue and carbon-based powder suspensions was carried out and

indicated that carbon-based powder suspensions were superior in this application, this being reported in Chapter 3.7 Powder suspensions.

8.3.9 Pseudo-operational trials were also conducted to establish the relative effectiveness of superglue carried out at scenes using a SuperFume unit, and those developed under laboratory conditions in an MVC5000 unit [36]. In this study over 6,000 marks were deposited across a range of surfaces in a small room. Marks developed at the scene were dyed with water-based BY40, those developed using the MVC5000 were dyed with the ethanol-based formulation. This was representative of what would be carried out at scenes and in most laboratories. The results of this study are summarised below.



Comparison of the effectiveness of superglue and powders on surfaces treated at a simulated scene [36].



Comparison of the effectiveness of superglue and powders on surfaces treated at a simulated scene, and surfaces treated with superglue in a laboratory [36].

8.3.10 It could be seen that SuperFume gave better results than powdering on several surfaces, although better results still could be obtained where a controlled-humidity superglue cabinet was used. The ultimate choice of technique should take into account effectiveness and time and cost considerations. It should also be taken into account that aluminium powder was used on all surfaces, whereas more recent guidelines may dictate use of an alternative powder. The results obtained from powdering in this trial are therefore less than optimum, and further work may be required to clarify this.

8.3.11 The most recent pseudo-operational trial that has been carried out including superglue has been the reassessment of the optimum processing sequences for plastic bags and packaging material [59]. Once again, the results are more fully reported in Chapter 3.7 Powder suspensions, but indicate that superglue followed by vacuum metal deposition may be the best processing sequence for this type of surface.

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3.11 Vacuum metal deposition

1. History

1.1 Vacuum metal deposition (VMD) is a long-established industrial technique for the application of metal coatings to components such as glass mirrors. In 1964, Professor S. Tolansky, working on the manufacture of interference filters at the Royal Holloway College of the University of London, noted that the deposition of silver in a vacuum system developed accidentally deposited latent fingerprints on glass optical components. An investigation into the process as a fingerprint development technique was proposed to the Home Office by Professor Tolansky. However, this was not pursued at the time by the Home Office because other techniques for fingerprint detection on glass were considered cheaper, easier to use, and sufficiently effective.

1.2 In 1968, it was reported by French workers [1] that VMD from a mixture of zinc, antimony and copper powder was capable of developing latent prints on paper. As a consequence of this paper, interest in the technique was revived in the UK and Tolansky initiated a research programme to investigate the optimum conditions and the potential applications for VMD. One of the early objectives of the research was to establish why the French combination of metals was effective. Closer examination of metal coatings deposited by the French laboratory indicated that the coating was almost entirely zinc, the presence of antimony and copper not being necessary to develop prints [2].

1.3 The research programme initiated by Tolansky [2] investigated the deposition characteristics of a range of metals on paper substrates, identifying single metals and metal combinations giving the optimum print development. Research was also carried out into the ability of the technique to detect latent prints on fabrics. These experiments showed that although some print development was obtained by the use of single metals, in general the best results were obtained by the use of a combination of metals, typically gold or silver followed by cadmium or zinc. The gold/zinc combination is currently (2011) used operationally.

1.4 The potential of VMD to develop fingerprints on fabrics was further explored by the Atomic Weapons Research Establishment (AWRE) under contract to the Home Office [3,4,5]. The work looked at identifying the best metal combinations for developing prints [3], transfer of both latent and developed marks onto photographic paper [3] , and the effect of humidity [3,4]. The researchers considered the effect of different washing and wearing conditions on print survival [4] and expanded the study to look at synthetic fabrics [5]. It was considered that the chances of fingerprints surviving on washed and worn fabrics under ‘field’ conditions was small, but finite.

1.5 In the mid-1970s the increasing of low density polyethylene (LDPE) carrier bags in a variety of crimes, in particular Irish Republican Army

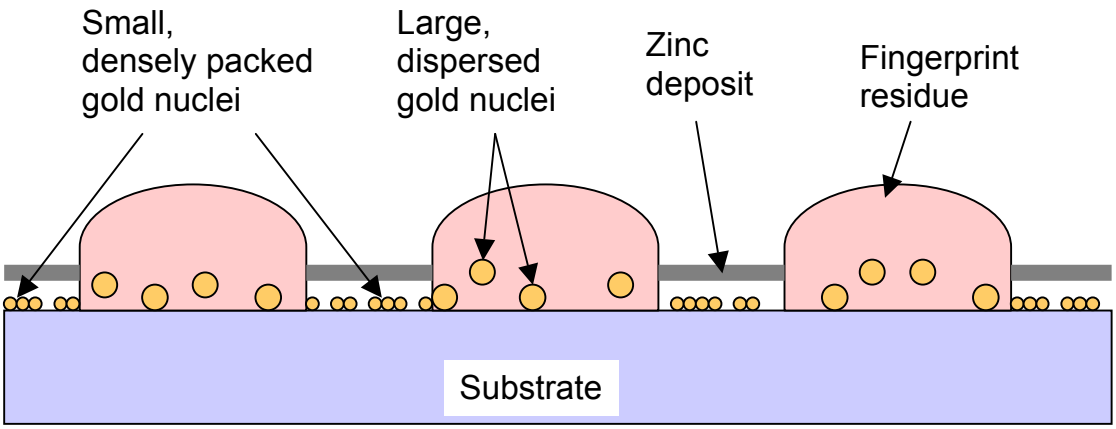
(IRA) improvised explosive devices (IEDs), led the Police Scientific Development Branch (PSDB) to look for better ways of developing fingerprints on polyethylene. A programme of work evaluating the various metal combinations on a variety of plastics and rubbers was set up and considerable success achieved using gold followed by cadmium on polythene and most plastics with the notable exception of plasticized PVC. This and all the early experimental work was carried out on small-scale equipment with 12 inch bell jar coaters. Silver-cadmium combinations gave slightly poorer results than gold-cadmium, with copper-cadmium less good. To make the system more viable for operational casework modification of horizontal 24 inch coaters was investigated and a system purchased by PSDB in 1976. This proved very successful during operational trials with police forces and over the next decade around 20 similar machines were installed [6]. Monitoring of the cadmium levels in the vicinity of the chamber and during cleaning operations in 1977-1978 indicated that figures approaching 10% of the maximum exposure level were being generated and around this time there was also a proposal to reduce the permitted levels for cadmium. Gold followed by zinc deposition was known to give similar results to gold-cadmium although deposition of zinc is slower and more difficult. The decision was made to switch to gold-zinc for all operational police systems as the maximum exposure limits for zinc were many times higher and there was no likelihood of these being exceeded in operational use.

1.6 From the late-1970s until the late-1990s PSDB worked with manufacturers and introduced a number of improvements including larger chambers, liquid nitrogen cold fingers and semi-automated sample loading systems. Over this time most suppliers had moved from manually operated valve systems to automated, or semi-automated, control systems [7]. Several trials were carried out by PSDB between VMD and other techniques for developing fingerprints on polyethylene including small particle reagent, superglue and fluorescence examination [8,9,10] and it was found to out-perform all of these techniques. In particular VMD was shown experimentally and operationally to develop fingerprints that had been exposed to extended water immersion, something that no other technique at the time (late-1970s and early-1980s) could cope with.

2. Theory

2.1 There is general agreement on the theory associated with normal development of prints by the VMD method. The reason that the metal combinations are postulated to work well is due to the condensation characteristics of zinc (and cadmium). These metals will not condense on grease, such as that found in fingerprint residues, even when these substances are only present as a monolayer. However, zinc will deposit on small nuclei of metal, and this is the reason that gold or silver deposition is carried out first. Gold and silver can be deposited over the

entire surface, and begin to form nuclei, the morphology of which depends on the nature of the surface (surface energy, chemical species present) they are being deposited on. The resultant gold coating is very thin (several nanometres only) and discontinuous. However, in the regions coated with the fatty residues of the latent fingerprint, the gold diffuses into fat and hence there are no gold nuclei close to the surface. As a consequence, when zinc is subsequently deposited, it will condense on the regions of gold nuclei (i.e. the background substrate), but not on the regions of the fatty deposit (i.e. the fingerprint ridges). This theory of nucleation was discussed in more detail by Stroud [11,12]. It should, however, be noted that there is no conclusive evidence of nuclei diffusion and it is possible that the effect observed may be solely attributable to zinc growing on regions of different nuclei size at different rates. The normal development process based on nuclei diffusion is depicted in the schematic diagram and photographs below.



Schematic diagram of normal development, showing zinc depositing where gold nuclei are available on the surface.

Photograph of a normally developed mark on a polyethylene bag.

2.2 Tests carried out to determine which components of the latent print were most likely to be responsible for inhibiting metal deposition identified several substances, including stearic acid, palmitic acid, cholesterol oleate, glycerol trioleate and amino acids L-arginine monohydrochloride, L-leucine, and DL-threonine. Most of these substances are non-water soluble or long chain fats or acids with low vapour pressure, which determines their stability and non-migration over the surface during the VMD process. These findings were in accordance with the observation that VMD was capable of developing prints on substrates exposed to wet environments, many of these substances being insoluble in water. In the late 1970s PSDB funded work at Imperial College, London using electron spectroscopy for chemical analysis (ESCA) and ion beam etching in order to establish the depth profile of gold on the surface. This was done to determine whether loss of gold nuclei into the fats of a fingerprint would account for the 'normal' development of light ridges. Experiments to study the diffusion of gold into thin films of stearic acid [13] indicated that 60% of the gold penetrated the stearic acid to a depth greater than the detection depth of the ESCA surface analysis technique, and hence would probably not be sufficiently close to the surface for zinc to nucleate on it. The work was however regarded as inconclusive as although a slight increase in gold was detected during etching down through the

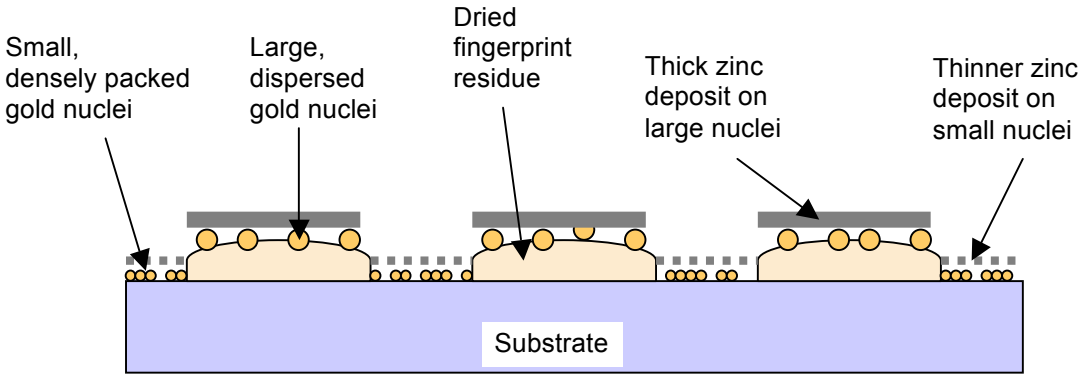
surface layers it was felt that this might have been due to 'knock on' effects of the heavy ion etching.

2.3 Transmission electron microscopy has also been used to confirm that the size and distribution of gold nuclei formed during the deposition process varied greatly according to the substrate and the chemical species present [14]. Transmission electron micrographs of gold films on carbon support grids which had some deposited LDPE crystals showed few large nuclei on the LDPE compared with large numbers of small nuclei on the carbon. This confirmed that a variation in nuclei size could be produced in areas with different binding energies. Rayleigh scattering from the gold films also showed changes in colour indicating variations in nuclei size. It was this difference in nuclei size and distribution, coupled with diffusion of gold into the fatty deposits, that was believed to contribute to the subsequent delineation of the print during VMD.

2.4 In practice, many prints developed using VMD may be 'reverse developed', i.e. zinc preferentially deposits on the fingerprint ridges rather than the background. There are differences in opinion as to why this arises, the main theories being outlined below.

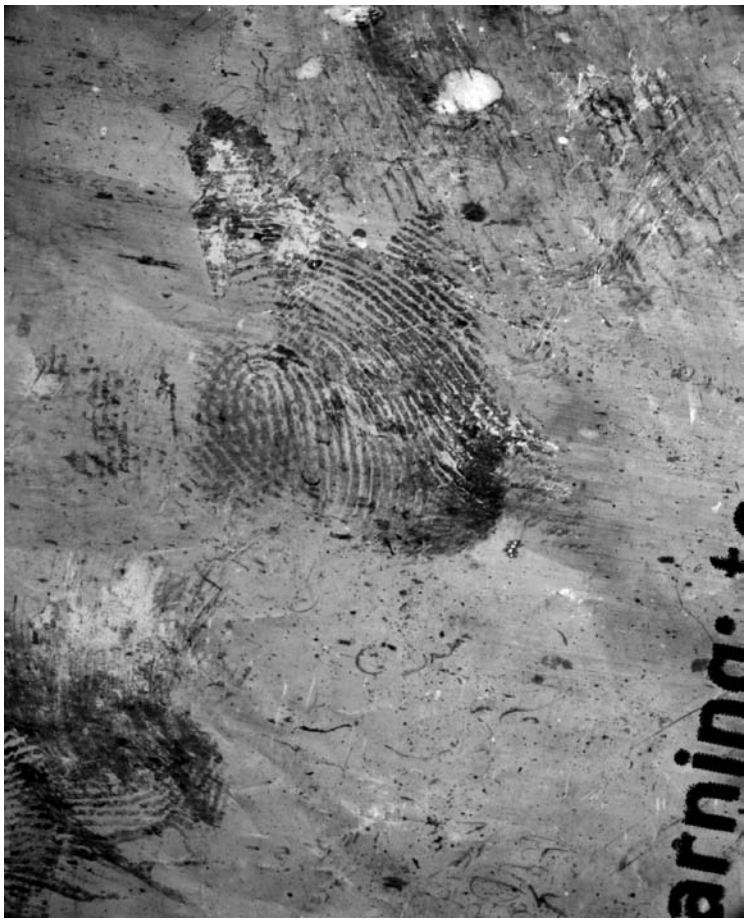
2.5 Kent *et al*. [15] attribute reverse development to absorption of mobile species of the fingerprint residue into the substrate, leaving a solid, primarily inorganic residue that acts as a preferential nucleation site for the zinc. More gold diffuses into the polymer substrate than into the solid residue, hence zinc deposits on the ridges first. Smith, as quoted by Jones *et. al.* [16-18]) proposed that zinc deposits on the ridges because it is able to align crystallographically with some of the crystalline constituents in the deposit (e.g. sodium chloride) and undergo epitaxial growth. Most recently, Jones *et al*. [16-18] have proposed an alternative theory related to the types of gold nuclei formed. The gold nuclei in the ridges form at a different rate to those growing on the substrate and in the furrows, hence a regime exists where the gold film on the background has reached a state where zinc cannot nucleate, but on the ridges the nuclei are a suitable size for zinc to deposit. This theory closely relates the type of print developed to the amount of gold deposited initially.

2.6 Current (2011) CAST thinking is that the reverse development is due to the fingerprint deposits becoming dried out, either by air drying or by the preferential absorption mechanism outlined by Kent, or contaminated, thus inhibiting any diffusion of the gold nuclei into the fingerprint residue. The dried ridge is likely to have a higher surface energy than the background and therefore larger gold nuclei will form in these regions. These larger gold nuclei will sit on the surface of the ridge because their diffusion is inhibited and because the gold nuclei in the region of the ridges are larger, zinc deposition occurs at a faster rate. This is illustrated schematically below.



Schematic diagram of reverse development, showing different rates of zinc deposition according to size of gold nuclei available on the surface.

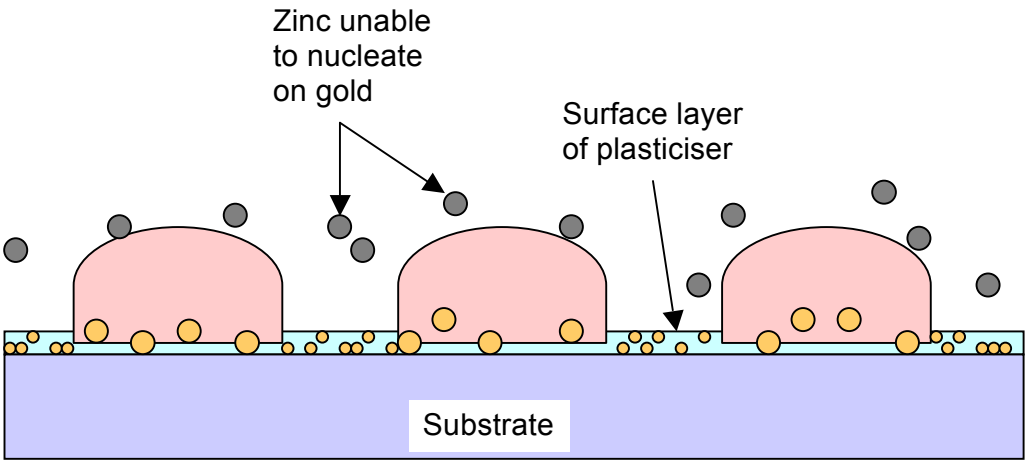
2.7 None of the theories above have been categorically proven, and in some cases reverse and normal development may be observed on the same substrate, although it is stated that this is most common for (if not exclusive to) LDPE substrates. The photograph below shows a 'reverse developed' mark on a polyethylene bag.



Photograph of a reverse developed mark on a polyethylene bag.

2.8 It is recognised that the gold/zinc VMD process does not work well (or at all) on substrates that are heavily plasticised (e.g. clingfilm, plasticised

PVC) or have surface release films or contamination. This is attributed to the fact that gold nuclei diffuse into the surface layer on the substrate as well as the fingerprint deposits, with the result that there are no nuclei on the surface of zinc to deposit on, as is illustrated schematically below.



Schematic diagram of no development, showing zinc unable to find gold nuclei on surface.

3. CAST processes

3.1 The process outlined in the *Manual of Fingerprint Development Techniques* [19] is essentially as follows:

- evaporate ~2mg of gold at a pressure of 3 x 10^{-4} mbar or lower;
- evaporate zinc at a pressure between 3–5 x 10^{-4} mbar until a suitable coating is formed.

3.2 These steps can be repeated until the desired level of coating and fingerprint development has been obtained.

3.3 The reason for choosing these particular materials and conditions can be expanded as follows.

3.4 The role of gold in the VMD process is to act as the 'primer' for subsequent zinc deposition. Gold is not selective in that it will deposit across the entire surface of the exhibit, but the size and dispersion of the gold nuclei formed will be determined by the nature of the surface (chemistry, roughness, etc.). As outlined above, there is usually a sufficient difference between the nuclei formed in the regions of the fingerprint ridges and the background for the print to be delineated during subsequent zinc deposition. Gold is also used as the initial deposition metal because it is inert and does not react with fingerprint residues or atmospheric pollutants. The low deposition pressure is used so that gold can be deposited directly onto the surface without colliding with a significant number of molecules in the chamber, giving an even coating.

3.5 The role of zinc in the process is to delineate the fingerprint, primarily by the difference between the growth rate of zinc on the fingerprint ridges and the growth rate on the background. Zinc is highly effective for this purpose because it easily re-evaporates from the surface unless there is a suitable nucleation site present, thus the gold nuclei formed control the way in which zinc layers subsequently form. The sections above outline the different mechanisms by which differences in zinc growth rate can reveal fingerprints. The evaporation pressure used for zinc is higher than that for gold, and this is to allow the user more control over the zinc deposition process. Allowing more air into the chamber makes the deposition of zinc more uniform across the area of the exhibit. It was thought that the additional air molecules present in the chamber would reduce the kinetic energy of zinc atoms as they reach the surface and could increase development rate, but this has never been proven.

4. Critical issues

4.1 Sealed containers such as aerosol cans, sealed drink cans and bottles, batteries and items with sealed air pockets must not be treated using VMD because the expanding gases may cause the item to explode.

4.2 Articles to be treated by VMD must be dry and free of other residual liquids and solids.

4.3 During the zinc deposition stage of the gold/zinc VMD process it is essential for the operator to observe the development of the marks and to stop the process before any over-development occurs. The filament temperature and deposition time required to coat articles will vary according to the type of material and condition of the surface. For this reason multiple exhibits of different types should not be treated together.

4.4 Multiple deposition runs can be used to build up a coating if the initial run fails to develop any marks.

5. Application

5.1 Suitable surfaces: VMD has traditionally been recommended as the primary process for development of fingerprints on plastic bags and wrappings. Although still effective in this role it is no longer as effective as alternative processes, such as superglue and powder suspensions. The silver VMD process is one of the few techniques suitable for clingfilm. VMD is suitable for use on all types of non-porous surface, and is one of the more effective techniques on ‘semi-porous’ surfaces such as glossy magazines and wrapping paper, and the best process for the non-adhesive side of masking tapes.

5.2 The equipment used for VMD may vary according to manufacturer, but the essential elements of the system are the same. The equipment consists of a vacuum chamber capable of being pumped down to high levels of vacuum (<3 x 10^{-4} mbar), filaments for deposition of gold and zinc, and a viewing window so that the deposition of zinc can be monitored. The chamber may also contain a 'cold finger', chilled to low temperature to aid condensation of contaminants and to reduce pump down times. Articles to be coated are attached to the perimeter of the vacuum chamber, above the coating filaments. A typical system is illustrated below.

Typical vacuum metal deposition equipment.

5.3 The filaments used for deposition of gold and zinc are typically formed from thin sheets of molybdenum. The gold filament usually consists of a shallow dimple in a thin strip of molybdenum. This is because the quantity of gold used is very small (~2–3mg), and it is important that all the gold reaches the substrate. If deeper containers are used, 'shadowing' may occur and not all regions of the article may be coated. Gold deposition takes place when the chamber has reached a pressure of 3 x 10^{-4}mbar or lower, and the current to the filament is increased until the filament reaches a yellow/white heat. Deposition of gold should be complete within ten seconds, but if any residue is observed on the filament as the current is reduced, the temperature should be increased again until all the gold has been evaporated.

5.4 Once gold deposition is completed, the pressure in the chamber is increased to ~5 x 10^{-4}mbar and the current to the zinc deposition filament(s) turned on. The reason for increasing the pressure in the chamber is to increase the uniformity of the coating produced. The zinc deposition filaments are larger and significantly deeper than the gold filament, and the quantity of zinc added is larger, typically 1g per run. The zinc used is in the form of foil, shot or powder. For zinc deposition, the current is increased until the filament glows a cherry red/dull orange colour. Once this occurs, the operator should observe the deposition process through the viewing window, ceasing deposition as soon as marks become visible on the substrate. After zinc deposition, the gold filament should be briefly heated to yellow/white heat to burn off any zinc contamination. The process is described in more detail elsewhere [19].

5.5 There is a great variability in the speed at which different substrates coat, and it may take over ten minutes to obtain a suitable coating on some types of material. In some cases it may be necessary to carry out multiple deposition runs in order to obtain satisfactory results, or to develop all the marks present. The presence of surface contamination, release agents or plasticisers may mean that it is not possible to obtain a zinc coating at all and in these circumstances the deposition of 30mg of silver using the same deposition conditions for gold may yield additional marks.

5.6 The VMD technique initially was adopted as an operational technique for the detection of latent prints on thin polyethylene items such as carrier bags and wrappings, and was shown to be superior to other processes developed subsequent to the initial comparison trials. Although the technique had originally been developed with the intention of being used to detect prints on fabrics, no identifiable prints were successfully obtained in operational trials and VMD is not currently (2011) recommended for operational use on this substrate.

5.7 VMD has now been used operationally for many years, and has been shown to be an effective technique for a wider range of materials than polyethylene. Recent results showing VMD to produce results on a range of substrates include a ticket coated with ferromagnetic ink, and on expanded polystyrene [20]. The use of the technique has also begun to increase in North America, and successful results have obtained from plastic bags, in some cases several years old and exposed to moisture [21].

5.8 The range of exhibits that have been successfully treated using VMD is extensive, and includes:

- plastic bags and packaging;
- glass and plastic bottles;
- firearms;
- glossy card, photographic paper and magazine covers;

- clean leather items (including handbags and shoes);
- adhesive tapes (non-sticky side).

5.9 It is evident that there is much overlap between the types of article that can be treated with VMD and those that are treated using cyanoacrylate fuming. In many cases, the deciding factor as to which technique is to be used is whether the article has been wetted, because VMD remains effective on wetted items whereas cyanoacrylate fuming does not. In practice it is possible to use the two processes in sequence, and more marks may be detected in this way because the two processes work on different fingerprint constituents.

6. Alternative formulations and processes

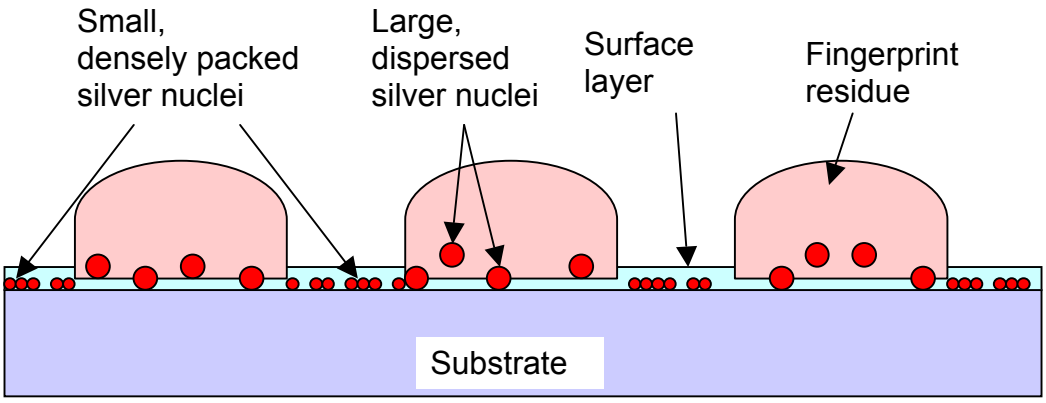
6.1 Several other materials have been investigated in the VMD process, including metal combinations, single metals, and organic materials. A summary of some of these is outlined below.

Metal 1	Metal 2	Comments
Gold	Cadmium	Initially, the gold/cadmium combination was selected as the optimum process, with cadmium giving better results than zinc when used as the second metal. It is also easier to produce coatings using cadmium. However, cadmium is very toxic and its use is no longer recommended on health and safety grounds.
Silver	Zinc	Silver can be used in place of gold as the initial deposition metal and limited evidence suggests that it this would have little effect on the effectiveness of the process. However, silver is more likely to interact with fingerprint constituents or atmospheric contaminants, and for this reason the more inert gold is preferred.
Silver	Cadmium	See comments for silver and cadmium above.
Copper	Zinc	Copper is potentially more reactive than silver or gold, and hence gold is preferred.
Copper	Cadmium	See comments for copper and cadmium above.
Lead	–	Of all the single metals investigated for fingerprint development in early studies (Hambley, 1972)[2], lead gave the best performance. However, lead is very toxic and its use is no longer recommended on health and safety grounds.
Zinc	–	Zinc is capable of developing fingerprints if used as a single metal, but re-evaporates

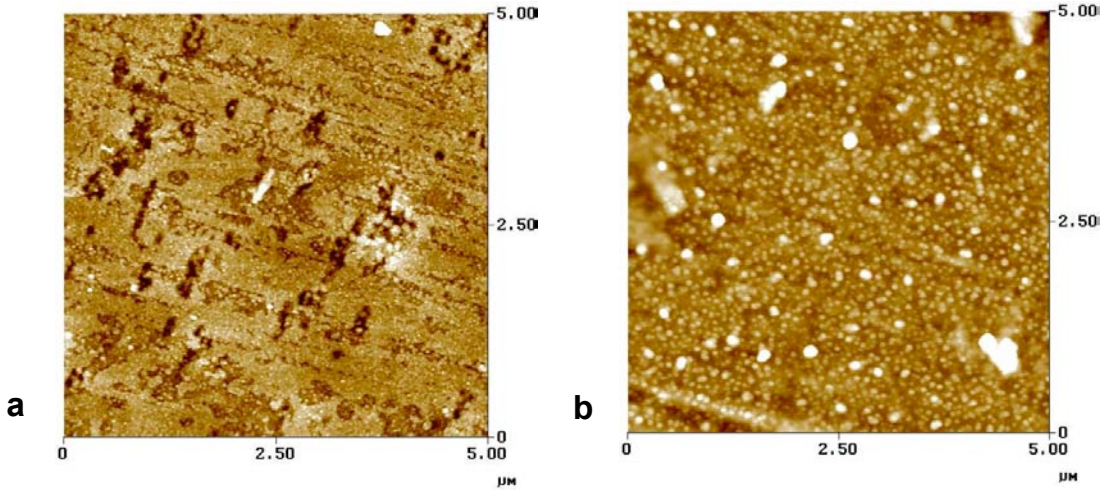
		easily from many surfaces and is best used in combinations.
Gold	–	Gold can be used as a single metal, and gives a blue background coloration with pink ridges. However, it has been found to be less sensitive than silver and copper and the gold/zinc combination when used this way.
Magnesium	–	Gives a silvery background, but less sensitive than most other single metals.
Copper	–	Gives a green/grey background coloration with pale yellow ridges. Effective on PVC-based clingfilm but less effective than silver on all other surfaces studied (Philipson and Bleay, 2007) [22]
Indium	–	Gives a pale brown background coloration with pale yellow ridges. Less effective than silver and marks difficult to see.
Tin	–	Gives a pale brown background coloration with pale yellow ridges. Less effective than silver and marks difficult to see.
Aluminium	–	Gives a silvery coating. Recently proposed as a more effective technique than gold/zinc on black plastic bags (Guraratne *et al.,* 2007)[23]. Ongoing research by CAST suggests no benefit over existing processes.
Silver	–	Identified as an alternative process to gold/zinc for plasticised materials (e.g. clingfilm) and materials with surface layers of contaminant (Philipson and Bleay, 2007)[22], now recommended for operational use by CAST. Can also be used sequentially after gold/zinc to fill in areas where zinc has deposited poorly. Further detail on the silver process is given below.

Summary table of alternative vacuum metal deposition processes.

6.2 The silver VMD technique is thought to work because silver, like gold, deposits uniformly across the surface. The nuclei formed vary in size and distribution between the fingerprint ridges and the background, giving a difference in colour between the two regions. This is shown schematically and as viewed by an atomic force microscope in the figures below.

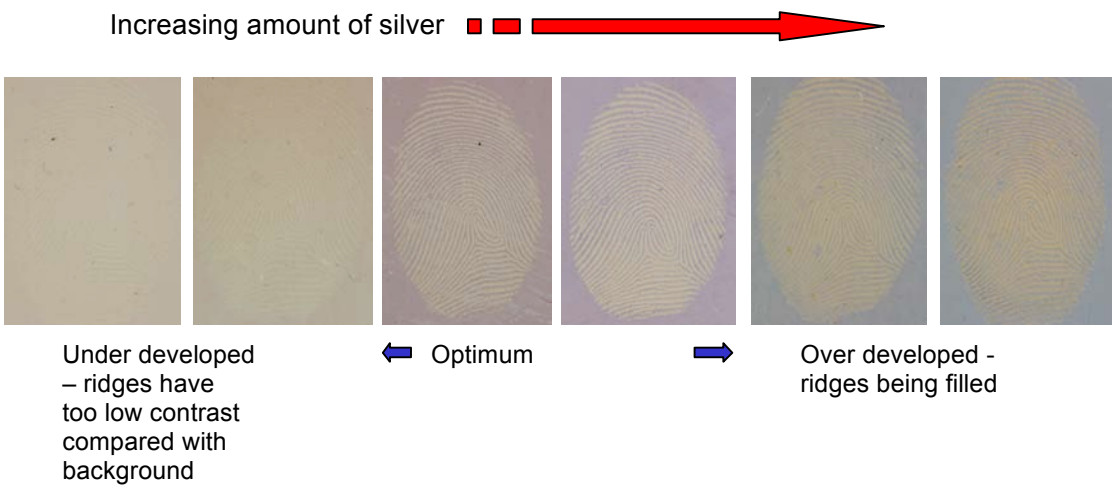


Schematic diagram of silver vacuum metal deposition on a plasticised surface, showing different sizes of silver nuclei in ridges and on surface.



Atomic force microscopy images of polyethylene bag after vacuum metal deposition, showing differences in silver nuclei size and density a) atomic force microscopy image of polyethylene surface, b) atomic force microscopy image of ridge region. Silver nuclei appear as light dots, and are smaller and very tightly packed on the polyethylene surface, and larger and more widely spaced in the fingerprint ridge.

6.3 The silver is deposited using the same conditions as for gold in the gold/zinc combination. The optimum amount of silver to use for most surfaces has been identified as 30mg. If less silver is used, development is too faint – if too much silver is used, ridges start to become filled in and detail can be lost, as seen in the sequence of images below.



Progression of colours developed using increasing amounts of silver in a single metal vacuum metal deposition process on polyethylene.

6.4 It is thought that copper works in a similar way, but the resultant colour of the film formed is different.

6.5 There has been recent interest in the aluminium deposition process [23], but trials at CAST have been unable to replicate the results in the literature. Most marks developed by this process are not easily visible and consequently are difficult to image. Comparisons of carrier bags cut in half and processed using aluminium and gold/zinc indicate that aluminium finds no marks from natural handling, only deliberately placed, 'groomed' marks.

6.6 Fluorescent, organic materials have also been deposited using the VMD process, most notably anthracene. Anthracene is less sensitive than most of the single metals and metal combinations outlined above and there are health and safety concerns regarding its use in this way. More recently, deposition of Rhodamine 6G in combination with an organic precursor has been investigated as a possible alternative to superglue fuming and dyeing [24]. The process was shown to develop fluorescent marks on surfaces, including metal, glass, plastic and thermal paper, but has not yet been developed further.

7. Post-treatments

7.1 A limited amount of research was carried out in the late-1970s on physical developer enhancement of VMD deposits on banknotes and metal images from banknotes transferred onto gelatine emulsions.

8. Validation and operational experience

8.1 The comparative effectiveness of VMD with other fingerprint development processes for the development of fingerprints on plastic (principally polyethylene) bags has been assessed in pseudo-operational and operational trials conducted by HOSDB. The principal results of these trials are reported below.

8.2 Laboratory trials

8.2.1 An initial laboratory trial conducted in 1978 [9] demonstrated that VMD typically developed between 23–27% useful marks on polythene bags compared with 7–10% for aluminium powdering, concluding that VMD was a superior process for this type of exhibit. This trial utilised planted marks deposited on plastic bags, results being obtained from over 1,000 deposited marks. The subsequent successful introduction of the technique into operational use meant that few other laboratory trials were conducted.

8.2.2 Laboratory trials were carried out when research was being conducted into deposition of alternative metals for development of marks on clingfilm [22]. These investigations compared the effectiveness of depositing silver and copper as single metals, on both polyvinylchloride (PVC)- and polyethylene (PE)-based clingfilms. Conventional gold/zinc VMD gave virtually no marks on both these types of clingfilm and was therefore omitted from the trial. Results for one-day-old and one-month-old marks are tabulated below. In the one-day-old experiment, 200 marks were analysed and in the one-month-old experiment, 240 were analysed.

Grade	**Silver**		**Copper**	
	PE	**PVC**	**PE**	**PVC**
3–4	10	20	0	24
2	4	10	0	11
1	36	10	10	10
0	0	10	40	5

One-day-old marks.

Grade	**Silver**		**Copper**	
	PE	**PVC**	**PE**	**PVC**
3–4	14	2	0	37*
2	28	24	3	5
1	1	12	40	0
0	17	22	16	18

* Many marks faint and difficult to image.

One-month-old marks.

Summary of comparative trials carried out on clingfilm using different vacuum metal deposition processes.

8.2.3 The results indicated that copper VMD was ineffective on PE-based clingfilm, but gave better results on PVC-based clingfilm than silver. Copper was only recommended for use if it was certain that the clingfilm found was PVC-based.

8.2.4 Comparative tests were also carried out between gold/zinc and silver VMD on two 'non-standard' clear packaging films, polyester terephthalate (PET) and cellophane, where gold/zinc VMD occasionally had problems with 'empty' prints or rapid fading of developed marks.

Grade	Gold/zinc		Silver	
	PET	Cellophane	PET	Cellophane
3–4	9	28	22	31
2	22	13	18	21
1	29*	19	10	8
0	0	0	0	0

* Many empty prints developed.

One-day-old marks.

Summary of comparative trials carried out on alternative clear packaging materials using different vacuum metal deposition processes.

8.2.5 It was shown that silver VMD offered an improvement over gold/zinc for development of marks on PET, and could also fill in ridge detail in regions where 'empty' prints developed. Although silver VMD performed well on cellophane, the developed marks faded very rapidly and there was no operational benefit in using the technique.

8.2.6 Finally, investigations were carried out into the use of gold and silver in combination, as opposed to silver as a single metal [25]. These showed no benefit in the use of gold-silver as opposed to silver and were not pursued further.

8.3 Pseudo-operational trials and operational experience

8.3.1 With the advent of the small particle reagent (SPR) process in 1979, an operational trial was conducted at Essex Police on plastic bag exhibits submitted to the fingerprint laboratory [26]. Each bag was cut in half, one-half being treated with VMD, the other with SPR. The results are summarised below.

Trial overview	
Number of polythene articles received	204
Number of cases received	57
Total number of fingerprints developed using VMD	117
Total number of fingerprints developed using SPR	61
Number of articles where VMD developed marks	36
Number of articles where SPR developed marks	20

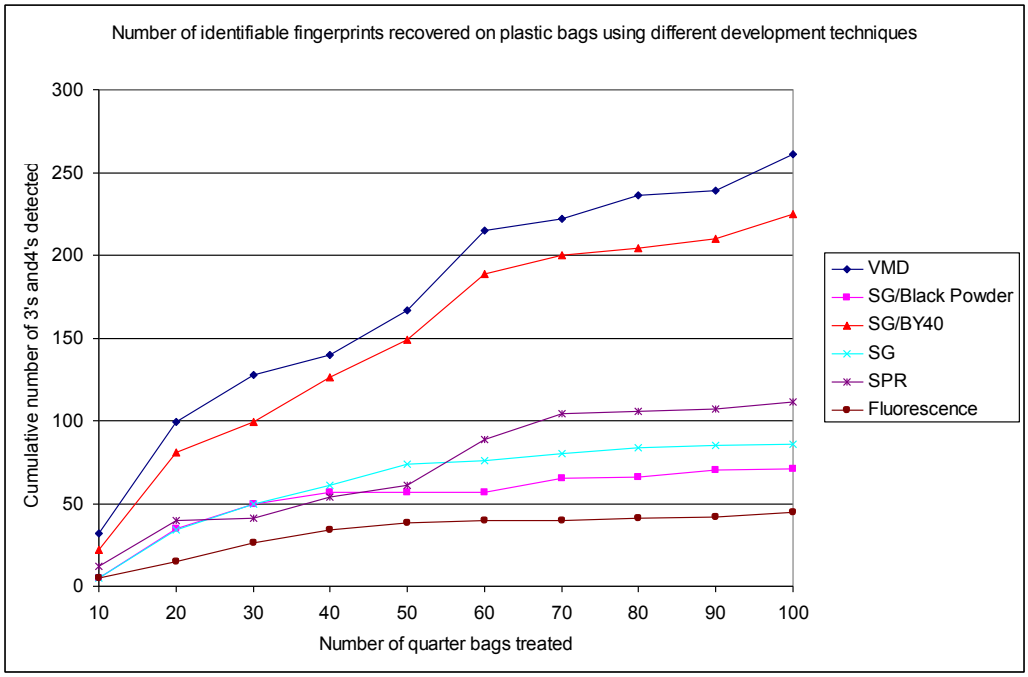
Process effectiveness comparison		
	Number of cases	Percentage from total number of cases
Cases with fingerprints only developed by VMD	13	23
Cases with fingerprints only developed by SPR	3	5
Cases where both VMD and SPR developed fingerprints	13	23
Cases where VMD developed fingerprints	26	46
Cases where SPR developed fingerprints	16	28
Total number of cases where VMD and SPR developed fingerprints	29	51

Early operational trial results comparing small particle reagent and vacuum metal deposition.

8.3.2 It was found that VMD was almost twice as effective as SPR on this type of exhibit. It was also observed that SPR could be used sequentially after VMD, but this was expected to be of only limited benefit.

8.3.3 The subject was revisited when an optimised superglue process became available in the mid-1980s, with a pseudo-operational trial being conducted between VMD, SPR, superglue and superglue followed by dyeing with basic yellow 40 and fluorescence examination. The trial was conducted by HOSDB on a large number of plastic bags using the same methodology as the study above, but not using operational casework.

8.3.4 The VMD process produced the largest number of identifiable fingerprints, producing approximately 12% more fingerprints than a combination of superglue, dyeing and fluorescence, and twice as many fingerprints as fluorescence alone [27]. Results of this exercise are shown below.



Results of pseudo-operational trial carried out on plastic packaging material in 1986.

8.3.5 More recently the composition of plastic bags has changed significantly, typically including more recycled material and observations from police forces using VMD on operational work indicated that the effectiveness had dropped off on this type of exhibit. As a consequence, the pseudo-operational trial above was repeated in 2009, comparing VMD with superglue and powder suspensions in a range of sequential processing scenarios. These studies are more fully reported in Chapter 3.7 Powder suspensions, and confirmed that VMD is no longer the most effective process for plastic bags, but instead should be used after superglue in a sequential processing route.

8.3.6 Operational trials involving silver have been more limited in extent because the process is only recommended as a secondary treatment after gold/zinc VMD. A small-scale study on clear cigarette wrappings (thought to be polypropylene) is summarised below, showing the number of wrappings yielding particular levels of ridge detail.

Result	**Technique**		
	Gold/zinc VMD	**Silver VMD**	**Superglue fuming**
Full print	1 (12.5%)	1 (5.6%)	1(12.5%)
Usable fragment	2(25%)	7(38.9%)	1(12.5%)
Unusable fragment	2(25%)	4(22.2%)	2(25%)
No print	3(37.5%)	6(33.3%)	4(50%)

Results of a short pseudo-operational trial on cigarette wrappers.

8.3.7 Silver VMD gives comparable results to gold/zinc VMD in this study, and better results than superglue. However, due to the limited sample size it is not possible to draw strong conclusions.

8.3.8 The process was trialled by some police forces on operational exhibits, using it after gold/zinc VMD where no development or patchy development was found. In these small-scale trials silver VMD was found to develop additional ridge detail in approximately 10% of cases.

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Chapter 4: Finger mark imaging techniques

4.1 Ultraviolet imaging

1. History

1.1 The existence of ultraviolet (UV) radiation was discovered by Johann Ritter in 1801. He found that emissions beyond the violet region of the electromagnetic spectrum were capable of darkening silver chloride in the same way that visible light at the blue end of the spectrum could. Ritter originally called these rays 'de-oxidising rays' although the term 'chemical rays' was adopted soon after and was in use throughout most of the 1800s. 'Chemical rays' was eventually dropped in favour of the current term 'ultraviolet radiation'.

1.2 By 1931 the forensic applications of UV radiation were already being explored, with UV fluorescence being widely used for document examination and glass identification [1,2]. The results of investigations into the fluorescence of body fluids and drugs under UV illumination were also reported [2].

1.3 In 1970, Ohki carried out an investigation into the potential of UV examination for the detection of latent fingerprints without the need for chemical development [3]. These experiments involved collecting secretions from the human skin by means of gauze wrapped around the hands and feet of several subjects, followed by analysis of these secretions to see if any characteristic UV absorption or fluorescent properties were observed. In these experiments, absorption was observed at 277nm and fluorescence between 300 and 400nm, depending on the solvent used to take the extract. Ohki was able to utilise the UV absorption characteristics of latent fingerprints to capture pictures of untreated latent fingerprints on paper and PVC, those on paper only being visible using a 253nm interference filter but both being visible using a 365nm filter.

1.4 Although the technique was not widely adopted, research continued worldwide to establish the range of surfaces that latent fingerprints could be detected on [4], and to investigate the use of UV image-intensifier viewers for real time observation of latent prints [5,6]. PSDB had demonstrations of some of these early viewing systems. UV-sensitive charge-coupled device (CCD) cameras were also being used for the direct imaging of latent prints by the mid-1990s [7].

1.5 By the 1990s, both long-wave (365nm) and short-wave UV (254nm) imaging techniques were in operational use by the Metropolitan Police [7]. Long-wave UV was found to be useful on glossy magazines, where the fingerprint ridges absorbed and the background fluoresced, and also on stipple surface photographs, where the photographic emulsion absorbed and the fingerprint ridges reflected. Short-wave UV found

application in enhancing marks on patterned backgrounds, where printing absorbed the radiation and the ridges reflected it. Experimental work by the Metropolitan Police group established that the intensity of natural fluorescence in fingerprints was superior in the UV region to that obtained in the visible region [8], with most fluorescence being observed in sebaceous prints. A 266nm neodymium:yttrium aluminium garnet (Nd:YAG) laser was used in these studies, and the level of fluorescence in the fingerprint was observed to decrease with increased exposure time.

1.6 Around the same time, the Rofin company, in conjunction with Israeli researchers, were also developing a short-wave UV-imaging system based on a CCD camera and used this system to image fingerprints in both fluorescence and absorption modes. They also carried out experiments to establish the sensitivity of the system to fluorescence from tyrosine and tryptophan, the amino acids believed to be primarily responsible for the natural UV fluorescence from latent prints [9]. The same group also considered the use of a lower cost imaging system for long-wave UV imaging alone, with the principal applications being the detection of latent fingerprints on smooth surfaces, such as mirrors, and the enhancement of marks developed using superglue without application of fluorescent dyes [10]. The same group also carried out further studies into UV fluorescence [11], showing that for practical casework there were far fewer fluorescent prints present than suggested in the Metropolitan Police study [8], possibly because most prints on paper exhibits are primarily eccrine in character. However, fluorescence was observed in older prints than was suggested in the earlier study. The use of UV imaging for detection of other body fluids was suggested.

1.7 The majority of the imaging systems developed by the Metropolitan Police and the Israel National Police were laboratory-based and not capable of being transported to crime scenes. The US Army Crime Laboratory carried out further experiments with UV image-intensifier systems, which resulted in the commercial production of a scene-portable Reflected Ultraviolet Imaging System (RUVIS) [12]. Several scene-portable RUVIS systems are now available through different manufacturers and reports have been published regarding their practical application to casework [13,14].

1.8 With regard to short-wave UV fluorescence imaging of fingerprints, work has continued in Japan using a tunable laser as the irradiation source and time-resolved imaging to improve fingerprint definition [15]. The equipment used was a laboratory-based imaging system and not suited for use at scenes. The results of the study essentially confirmed the observations of previous researchers regarding optimum excitation wavelengths and the types of fingerprints detected.

1.8 The Home Office Centre for Applied Science and Technology (CAST) has carried out intermittent research into UV imaging. In the mid-1990s a prototype RUVIS system was developed, based on a DEP-Photonis

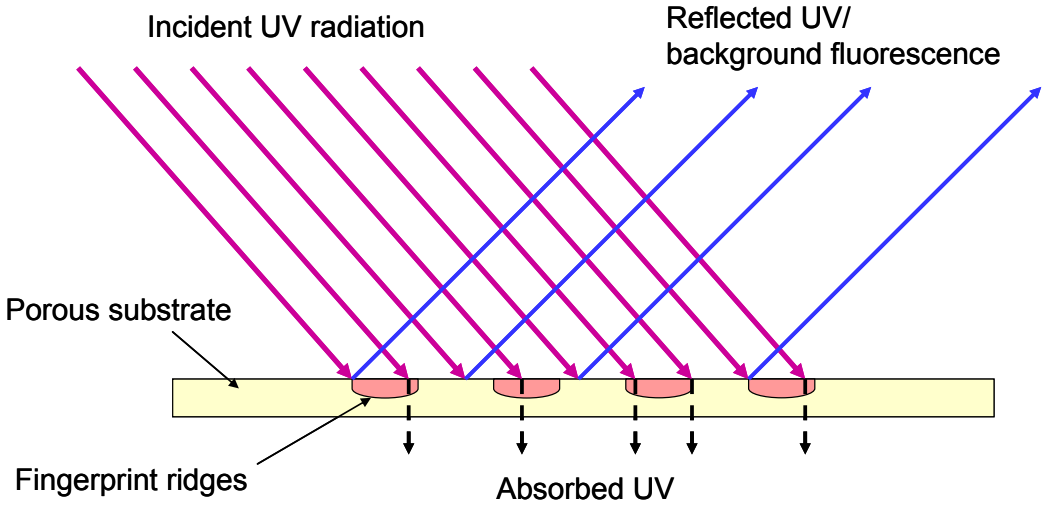
intensifier tube linked to a Nikon 105mm UV lens and a rotatable filter wheel containing a range of different UV filters. This was not pursued any further as a commercial product. A collaborative study was also conducted with the Israeli research group in the late 1990s although this did not result in operational implementation of the process in the UK. Work has also been carried out by CAST to develop safety and best practice guidelines for long-wave UV photography [16], with the focus being on the capture of injury marks and 'smart water' dyed suspects and articles. More recently work has resumed to design and manufacture a laboratory-based UV imaging system based on a UV-sensitive CCD camera (the Alta Apogee U-47 UV) and operated using the software developed for the Integrated Rapid Imaging System (IRIS) digital imaging workstation.

2. Theory

2.1 UV imaging is a broad subject area and there are many processes by which contrast may be obtained between the fingerprint ridges and the background. These include fluorescence, absorption and reflection. Each of these processes is described in greater detail below.

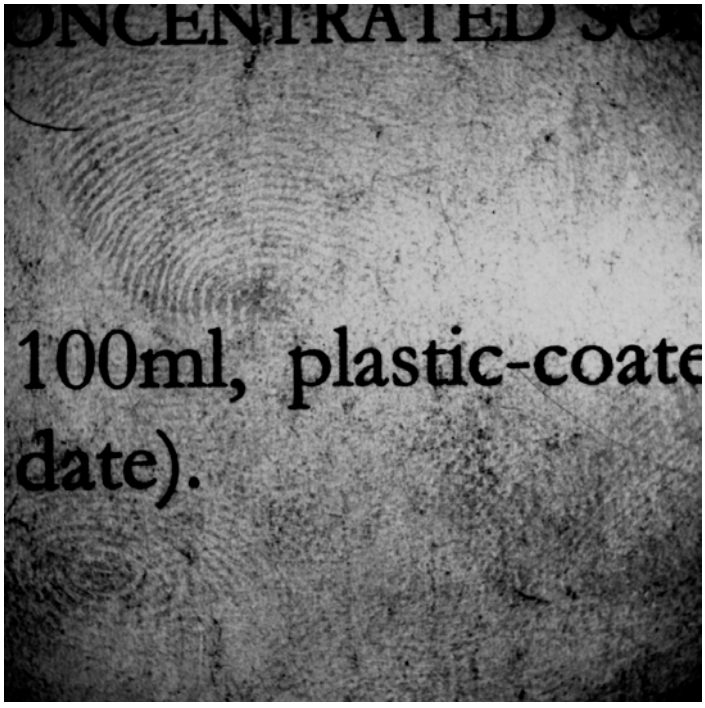
2.2 UV fluorescence. The theory associated with UV fluorescence is identical to that for fluorescence in the visible region of the spectrum. The fingerprint residue is illuminated with short wavelength UV radiation, which promotes electrons within the molecules of certain fingerprint constituents into excited states. These electrons cannot remain in this excited state and drop back to their original electron shell, losing the excess energy by emitting radiation at a longer wavelength (in this case as longer wave UV or into the visible region) than the original excitation. In the case of latent fingerprints, the amino acids tyrosine and tryptophan are believed to contribute most to this fluorescence. UV fluorescence is more applicable to the detection and imaging of latent fingerprints on porous surfaces than to detection of latent fingerprints on non-porous surfaces. However, UV fluorescence is more often used for the enhancement of marks developed using superglue and a range of UV fluorescent dyes are commercially available for this purpose.

2.3 UV absorption. It is known that fingerprint residues absorb strongly at 277nm [3] , primarily due to absorption by fatty acids, and in cases where fingerprints are deposited on surfaces that either fluoresce or reflect UV this phenomenon may be sufficient to provide contrast between fingerprint ridges and the background. This is shown schematically in the figure below.



Schematic diagram showing how ridge contrast of latent marks can be obtained by ultraviolet reflection/absorption.

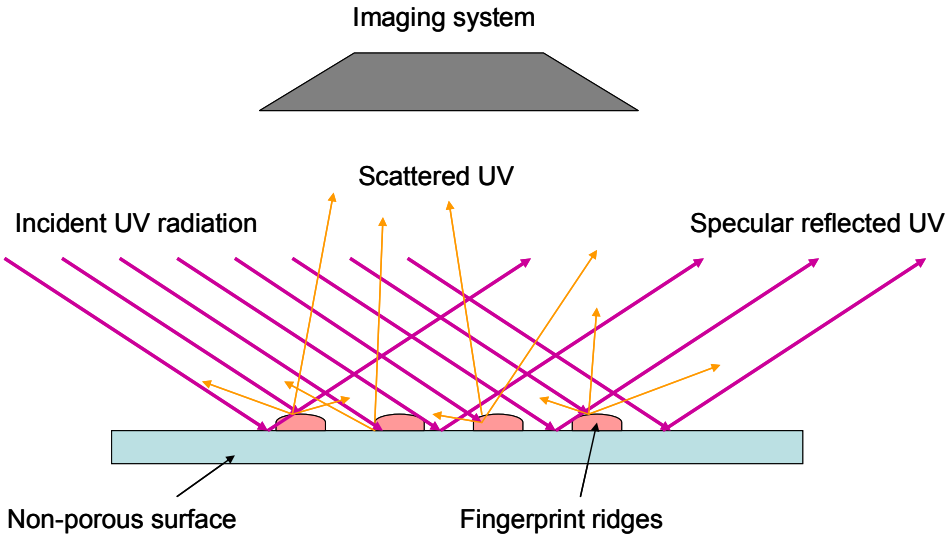
2.4 UV absorption is most applicable to the detection of fingerprints on porous surfaces, in particular on white paper, where optical brighteners fluoresce under UV radiation and provide a stronger contrast with the absorbing fingerprint ridges.



Latent fingerprints detected on glossy paper by reflected short-wave ultraviolet imaging.

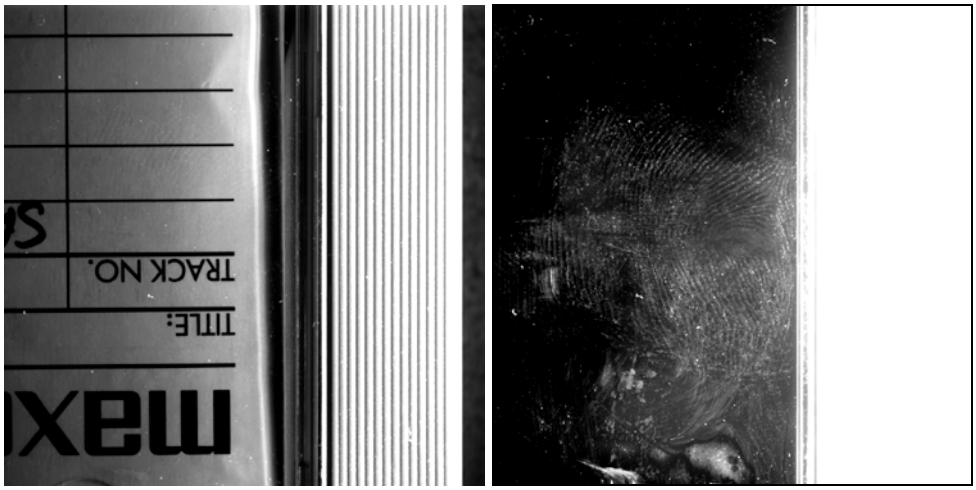
2.5 UV reflection. Reflected UV provides contrast between the fingerprint ridges and the background by means of a greater reflection or scatter from the fingerprint ridges than from the background. This may be due to

the fact the background absorbs UV more strongly than the fingerprint deposits, or by the fingerprint residues being rougher in texture than the background and scattering more UV radiation towards the detection system. This effect is more pronounced in the UV region of the spectrum because the wavelength of the radiation is of a similar scale to the height of the fingerprint ridges, and hence is scattered more strongly than light in the visible region. This is shown schematically below. A short-wave UV band-pass filter may be used in front of the camera to block fluorescence and any reflected visible light emitted by the light source.



Schematic diagram showing how ridge contrast of latent and superglue treated marks can be obtained by ultraviolet reflection/scattering.

2.6 UV reflection is most useful for the detection of latent fingerprints on smooth surfaces, and for the enhancement of marks developed using superglue, where the noodle-like structure of the developed mark scatters strongly.



a) b)

Latent fingerprint on CD case imaged using reflected short-wave ultraviolet a) no filter and b) short-wave ultraviolet band-pass filter.

3. CAST processes

3.1 CAST does not currently (up to 2011) recommend the routine use of short-wave UV imaging for fingerprint imaging because of the health and safety issues associated with short-wave (UV-C) radiation. However, provided that personnel are suitably trained in both UV safety and fluorescence examination, and appropriate precautions are taken in terms of eye and skin protection, there is no reason why UV imaging should not be carried out in a laboratory or at a crime scene.

3.2 Long-wave UV imaging is provided as an option on the IRIS workstation, using either a 365nm fluorescent bulb or the 340–413nm excitation band of the Quaser 2000. IRIS is fitted with a 415nm long-pass (Schott GG435) viewing and camera filter, and will detect fingerprints fluorescing under these illumination conditions. Skin protection (e.g. a pair of latex gloves) is recommended when using the long-wave UV imaging function.

4. Critical issues

4.1 All wavelengths of UV radiation are capable of causing damage to skin and eyes, and personnel using the process should ensure that they are fully trained and aware of the health and safety issues associated with it. Appropriate protective clothing must be worn.

4.2 Exposure to UV radiation (particularly UV-C) will cause progressive damage to DNA and this must be taken into account if it is intended to recover DNA subsequently from the exhibit.

5. Application

5.1 Suitable surfaces: In reflection mode, UV imaging is most appropriate for use on smooth, non-porous surfaces, where the scattering from the ridges is greater than the scattering from the background texture. It is particularly effective on glass where the glass strongly absorbs UV, giving greater contrast between scattering from the ridges and the background. It is also effective on glossy paper surfaces, where fingerprint deposits absorb and the paper surface reflects. In fluorescence mode, UV imaging is capable of detecting fingerprints on all types of surface where UV-fluorescent contaminants are present.

5.2 The main applications of short-wave UV imaging are in the detection and capture of latent fingerprints prior to the application of any chemical treatment. Fingerprints can be detected on both porous and non-porous surfaces by the range of processes outlined above, typically using equipment such as RUVIS for a speculative search of a scene or article and then using specialist equipment to capture marks at the high

resolution required. The advantages of using this technique prior to chemical treatment are that it is non-contact and therefore non-destructive to fingerprints (although if exposure is more than a few minutes it is detrimental to DNA) and that some of the marks revealed will be in the contaminant, and will never be developed by any chemical process. As mentioned above, short-wave UV is destructive to DNA and the process should not be used if DNA recovery is being considered.

5.3 Long-wave UV imaging is more suited to searching for traces of body fluids, but may be capable of revealing marks in this type of contaminant. Latent marks may be revealed by their fluorescence on thermal receipts when illuminated with long-wave UV.

6. Alternative formulations and processes

6.1 There are no alternative processes used for UV imaging in addition to those outlined in the sections above.

7. Post-treatments

7.1 There are no post-treatments used with UV imaging.

8. Validation and operational experience

8.1 CAST has not conducted an extensive study on the effectiveness of UV imaging in operational work. However, the Metropolitan Police has been using UV examination and imaging on operational work for over 20 years. It has been demonstrated that in several cases UV imaging can reveal marks that are not subsequently developed by chemical treatment. It is believed that many of these marks are in contaminants that will not be targeted by chemical or physical development techniques, and hence UV imaging is a valuable tool for operational work. Studies that have been conducted under the control of HOSDB are outlined below.

8.2 Laboratory validation

8.2.1 CAST has conducted limited studies of the relative effectiveness of UV imaging in comparison with other development techniques because the technique is not widely available and is not currently (2011) recommended as a principal treatment. However, a limited investigation has been carried out to compare UV imaging with fluorescence examination on porous surfaces [17]. This study looked at single fingerprints deposited by 36 different donors on 5 different paper types, with the fingerprints aged for 1 day and 1 week. The results are summarised below.

Paper type	Light source	Number of fingerprints detected	Number of identifiable marks	Number of unique marks
Pukka Pad lined paper	Laser (532nm)	3	1	2
	Laser (577nm)	0	0	0
	UV (254nm)	9	3	8
Niceday A4 printer paper	Laser (532nm)	0	0	0
	Laser (577nm)	0	0	0
	UV (254nm)	3	1	3
Hello Silk semi-glossy paper	Laser (532nm)	19	9	1
	Laser (577nm)	14	7	1
	UV (254nm)	28	18	10
Brown envelope	Laser (532nm)	5	2	1
	Laser (577nm)	6	0	2
	UV (254nm)	3	0	0
White envelope	Laser (532nm)	1	0	1
	Laser (577nm)	0	0	0
	UV (254nm)	4	1	4

Results for one-day-old marks using different light sources.

Paper type	Light source	Number of fingerprints detected	Number of identifiable marks	Number of unique marks
Pukka Pad lined paper	Laser (532nm)	4	2	1
	Laser (577nm)	3	0	0
	UV (254nm)	10	3	7
Niceday A4 printer paper	Laser (532nm)	1	0	1
	Laser (577nm)	0	0	0
	UV (254nm)	3	0	3
Hello Silk semi-glossy paper	Laser (532nm)	24	12	1
	Laser (577nm)	18	10	0
	UV (254nm)	29	15	5
Brown envelope	Laser (532nm)	7	0	1
	Laser (577nm)	10	0	4
	UV (254nm)	0	0	0
White envelope	Laser (532nm)	0	0	0
	Laser (577nm)	1	0	0
	UV (254nm)	3	1	2

Results for one-week-old marks using different light sources.

8.2.2 The results demonstrate that short-wave UV imaging is a highly effective process for detection of untreated fingerprints on glossy papers, but less so on rougher paper types. It can also be seen that short-wave UV imaging does detect marks that are not found by fluorescence examination and is a complementary technique for non-contact examination of porous exhibits in cases where chemical treatment is not possible.

8.2.3 A further study looked at the effectiveness of short-wave UV imaging in detection of latent fingerprints on a wider range of surfaces [18]. In this study a depletion series of ten fingerprints were laid by ten different donors, and the marks graded. Marks were examined in a Digital Enclosed Ultraviolet System (DEUS), custom built by the HOSDB workshops. The light sources used were two 8W 254nm mercury vapour lamps, and the imaging system was an Alta Apogee U47-UV camera with a Resolve Optics 60mm forensic lens. For the glass substrate the experiment was repeated three times to give a total of 300 graded marks. The results of this study are summarised below.

Grade	**Substrate (number of marks assessed), percentage at each grade**				
	Glass (300)	Red painted metal (100)	White ceramic tile (100)	Brown parcel tape (100)	Glossy paper (100)
4	56	6	12	0	7
3	20	24	30	13	7
2	9	10	4	14	7
1	13	18	8	22	21
0	2	42	46	51	58

Results of marks found using ultraviolet imaging on a range of substrates.

8.2.4 It can be seen that the proportion of identifiable marks that are detected by the technique ranges from 13– 76% according to the substrate, demonstrating that the process is relatively effective for a non-contact technique.

8.2.5 A study was also conducted on the effect of changing the illumination wavelength. A series of samples were illuminated with long-, mid- and short-wave UV radiation in the DEUS imaging chamber [18]. Two 8W tubes were used for each wavelength, the tubes being incorporated into the same mountings for each wavelength. These results of examining depletion series of 10 marks from 10 different donors (i.e. a total of 100 marks) are summarised below.

Wavelength	**Number of marks detected using optimum filter**	
	Paper	**Glass**
365nm (UV-A)	1	45
302nm (UV-B)	6	83
254nm (UV-C)	10	98

Results of marks found using ultraviolet imaging at different wavelengths.

8.2.6 The results show the increased effectiveness in fingerprint detection as the wavelength of illumination decreases, and demonstrates why UV-C is preferred if fingerprint detection is the priority.

8.3 Pseudo-operational trials and operational experience

8.3.1 CAST has not conducted any pseudo-operational trials using short- or long-wave UV imaging. The Metropolitan Police routinely uses long-wave UV to search crime scenes, and has recently conducted an analysis of the number of unique marks detected by light source examination, including long-wave UV, white light and laser examination [19]. This demonstrated that light source examination accounted for ~8% of unique marks detected, although the proportion of those that were uniquely identified using long-wave UV was not identified.

8.3.2 The Metropolitan Police also uses short-wave UV imaging under controlled conditions in a laboratory, and there are several documented examples of where it has detected marks not subsequently developed by chemical techniques.

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4.2 Infra-red imaging

1. History

1.1 The existence of infra-red (IR) radiation was discovered in 1800 by William Herschel, building on Newton's observation that sunlight could be separated into different colours by refraction through a glass prism. Herschel was investigating the theory that different colours could contain different levels of heat, and confirmed this by placing thermometers in different colour ranges of the spectrum. Herschel observed that the measured temperature increased from the violet to the red end of the spectrum, but made the additional observation that the measured temperature continued to increase beyond the red portion of the spectrum indicating that non-visible radiation was present. This radiation was termed 'calorific rays' by Herschel, with the term 'infra-red' being adopted in the late 19th century.

1.2 The practical applications of IR radiation were limited until the development of the first detector materials towards the end of World War I. Military imaging applications continued to be the main driver for the development of IR detectors and imaging systems for several decades, with the first IR imaging devices developed in the 1940s.

1.3 Forensic applications of IR imaging did not begin to be widely explored until the advent of detectors linked to video displays, allowing live imaging in the IR region of the spectrum. Specialised IR photography could be carried out using conventional cameras with IR sensitive film [1], but this was often speculative, carried out under the assumption that a feature of interest would be present. With live imaging capability, investigators could see whether there were any IR reflection or fluorescence effects occurring and subsequent photography could be targeted appropriately. Some early experiments were carried out in the Metropolitan Police Forensic Science laboratory and elsewhere using first generation military image converter tubes utilising S1 photocathodes and subsequently S20 photocathodes.

1.4 The principal application of IR imaging in forensic science was in document examination and from the 1950s onwards various researchers [2-5] used IR sensitive vidicons to investigate the potential of reflected IR and IR fluorescence for applications such as detection of forgeries, revelation of erased writing and ink comparison. As the cost of image converters and IR detectors reduced, bench-top document examination equipment became available in the late 1970s/early 1980s, enabling routine examination of documents in forensic laboratories. IR imaging systems utilising vidicons based on those developed in the Birmingham Forensic Science laboratory [4] were commercialised by Foster and Freeman and marketed as the Video Spectral Comparator (VSC).

1.5 In addition to document examination, IR photography was also found to be a valuable tool for the imaging of blood spatter patterns on surfaces

appearing dark under visible light [6]. Similarly, IR photography has also been used in the imaging of injuries (such as bruising) on skin [7].

1.6 The potential use of IR imaging for visualisation of fingerprints was being considered in the 1970s. Wilkinson [8] makes an early reference to the use of IR microscopy to enhance a powdered mark (IR opaque) on a dark green bottle (IR translucent) and a US Patent issued around the same time [9] makes specific reference to the IR responsive nature of a fingerprint powder. This does not appear to have resulted in a significant increase in the use of IR imaging for fingerprint applications. However, the Metropolitan Police was using reflected IR for photography of marks revealed using physical developer in the mid-1980s [10]. The same group subsequently reported the use of IR long-pass filters to detect IR fluorescence from latent fingerprints illuminated with an argon ion laser at 514.5nm [11]. In the early 1980s PSDB conducted trials at the laboratories of STC Harlow on the use of a scanning thermal imaging microscope for the detection of finger marks on difficult surfaces such as adhesive tape and some metals, hoping to exploit differences in emissivity. This was not pursued at the time due to the limited resolution of the systems available and low contrast observed.

1.7 Later research using a live capture digital imaging system demonstrated that in addition to IR fluorescence of latent prints, existing fingerprint reagents such as basic violet 3 (Gentian Violet) exhibited some fluorescence in the IR region of the spectrum. This fluorescence could be used to aid visualisation of the developed mark [12].

1.8 Subsequent work by the Home Office Scientific Development Branch (HOSDB) [13] demonstrated that IR reflection was an effective technique in suppressing background patterns when metallic or inorganic development reagents (e.g. vacuum metal deposition, powders, powder suspensions and physical developer) were used, although marks developed using organic reagents such as ninhydrin became transparent and could not be seen in the IR. HOSDB also demonstrated that IR fluorescence can be observed for the protein dyes acid black 1 and acid violet 17 [14]. Although IR fluorescence is observed for the pure acid violet 17 dye, much stronger fluorescence is seen for batches of acid violet 17 mixed with dextrin and this may offer a route for producing IR fluorescent reagents in the future.

1.9 All of the above forensic applications utilise the near IR region of the spectrum where the interactions of the incident radiation with the fingerprint residue and the substrate are very similar to those occurring in the visible region. Further into the IR region the incident radiation can promote molecular vibrations, such as bond stretching and rotation, and characteristic absorption peaks associated with these motions can be used to characterise chemical species present in the fingerprint. This approach was applied in a study to compare fingerprint residues of males, females and children, investigating compositional differences between these groups and between eccrine and sebaceous deposits

[15]. This study used spectromicroscopy and focused on a small portion of an individual ridge. A later study looked at the same technique to detect and identify particles trapped in the fingerprint ridges, such as illicit drugs [16].

1.10 More recently the use of the short- and mid-wave IR regions of the spectrum has been considered for the imaging of fingerprints, using wavelengths where absorption mechanisms characteristic of chemical species in the fingerprint ridges occur. The systems used to image fingerprints in this way are currently (in 2011) highly specialised pieces of equipment more suited to research than operational work, mostly using Fourier Transform IR (FTIR) spectroscopy techniques. A FTIR focal plane array detector has been used to scan a fingerprint on an Australian banknote in a series of lines, stitching these together to form the final image [17]. Other researchers have used FTIR imaging to detect both latent and treated fingerprints on a range of porous and non-porous surfaces [18]. In an alternative approach researchers have used arrays of FTIR sensors in the attenuated total reflection (ATR) mode [19], which significantly reduced the time taken to produce the image, but there is still the potential to increase the size of the array and reduce the imaging time for the whole area of the fingerprint. The limitation of this approach has been that the sample bearing the fingerprint needs to be flat and in intimate contact with the detector. This limits the type of exhibit that can be examined using ATR-FTIR equipment, but to overcome this limitation the lifting of marks and other forensic evidence from exhibits using gel lifters and tape has been investigated [20,21]. This technique offers the potential to bring marks back from a crime scene for subsequent laboratory analysis.

1.11 Other regions of the IR spectrum may also offer potential for fingerprint detection, and one approach that has been proposed is to pass humidified air over latent fingerprints and utilise an IR thermography camera to detect temperature differences between the fingerprint ridges and the substrate [22]. This does not appear to have been progressed further in recent years.

2. Theory

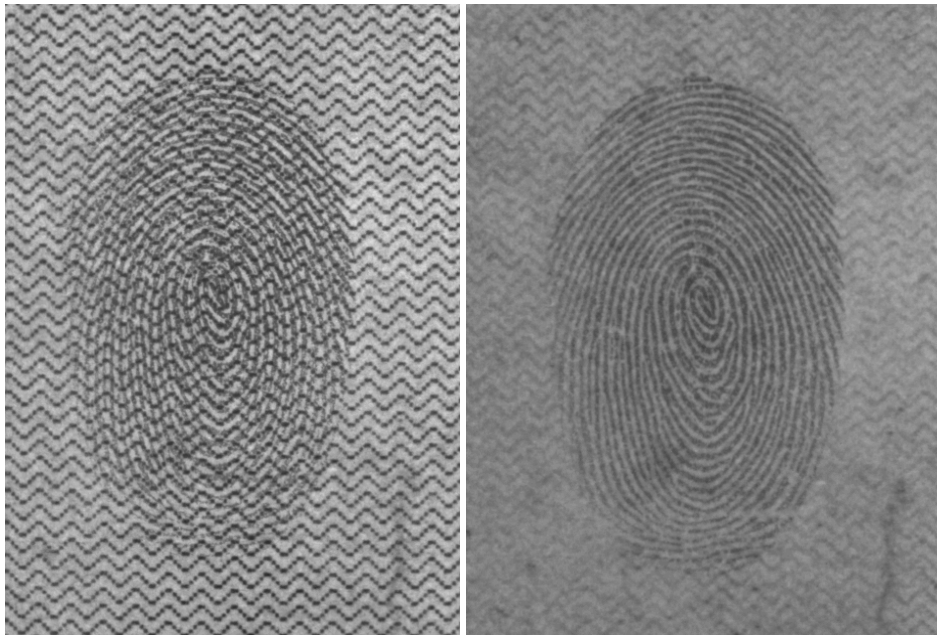
2.1 IR imaging is a broad subject area and there are many processes by which contrast may be obtained between the fingerprint ridges and the background. In the near IR regions these include fluorescence, absorption and reflection. At longer IR wavelengths there are other mechanisms that can be used to distinguish fingerprints, including IR absorption characteristics associated with chemical species present in the fingerprint but not in the substrate, and thermography using differences in emissivity between the fingerprint and the substrate. Each of these processes are described in greater detail below.

2.2 Near IR (700–1,100nm)

2.2.1 In this region of the IR spectrum, the mechanisms used for fingerprint visualisation are essentially the same as those used in the visible and ultraviolet (UV) regions, namely fluorescence and absorption/reflection. The principal difference from imaging in the visible region is that many of the organic pigments used in printing inks are IR transparent, and surfaces that appear highly patterned and/or coloured under 'daylight' conditions in the visible spectrum may appear devoid of printing when viewed in the near IR. This can be a significant advantage when trying to resolve minutiae in fingerprints developed on articles like banknotes.

2.2.2 It has already been established that some fingerprint reagents do have some fluorescence in the IR when illuminated with green/yellow and yellow light, most notably basic violet 3 and acid violet 17 (although much of the emission of basic violet 3 is actually in the red spectral region). However, the use of longer wavelength illumination such as orange, red and IR, and the resultant fluorescence from existing reagents has not yet been extensively explored. The potential to develop IR fluorescent dyes and reagents for fingerprint detection clearly exists and could be exploited in future. Preliminary investigations have indicated that there may be some constituents of latent fingerprints that have fluorescence in the near IR, but optimum illumination conditions have not yet been identified.

2.2.3 For fingerprint imaging using IR reflectivity, a light source emitting in the near IR is required. As stated above, many inks used for printing are IR transparent and highly patterned surfaces may be suppressed. To date, it does not seem that latent fingerprints can be detected in this way. It has not yet been established whether there are any fingerprint constituents that have characteristic absorption mechanisms in this region, but the background fluorescence of most surfaces is low and the contrast between the substrate and ridges is insufficient for fingerprint visualisation. However, it is possible to image some developed fingerprints in IR reflection mode. Many organic reagents and dyes, including ninhydrin, solvent black 3 and superglue, are transparent in this region of the IR spectrum and developed marks are not visible. Those developed using inorganic or metallic processes, including vacuum metal deposition, powders and powder suspensions, either absorb or scatter IR more than the background and developed marks remain visible when imaged in the IR.



a) b)

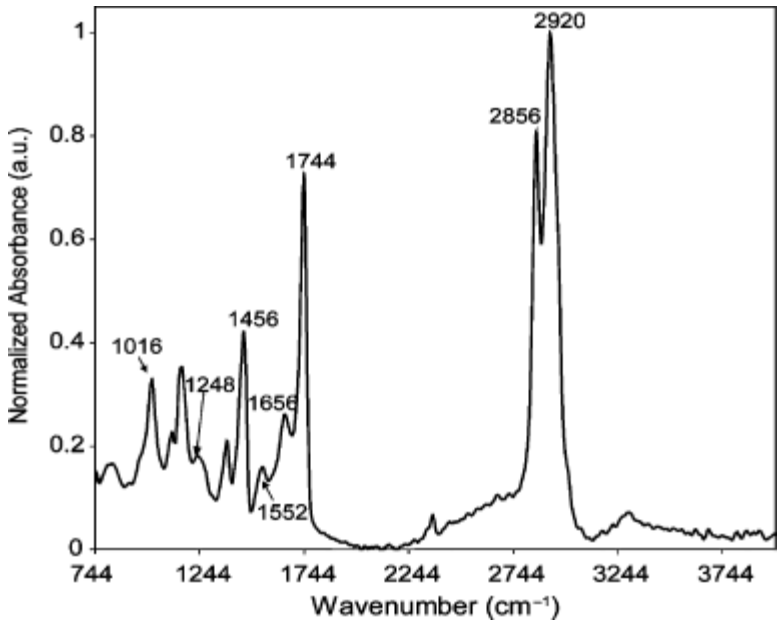
Images of fingerprint developed using physical developer on patterned background a) imaged under tungsten illumination and b) imaged under tungsten illumination using an infra-red long-pass filter (Schott glass RG780).

2.3 Short-wave IR (1,100–1,700nm)

2.3.1 This region of the IR spectrum has not yet been extensively studied for the detection of fingerprints and there is no established process for fingerprint detection. However, there are some known processes, such as water absorption bands at around 1,300nm, that could be exploited in future.

2.4 Medium-wave–long-wave IR (1,700–25,000nm)

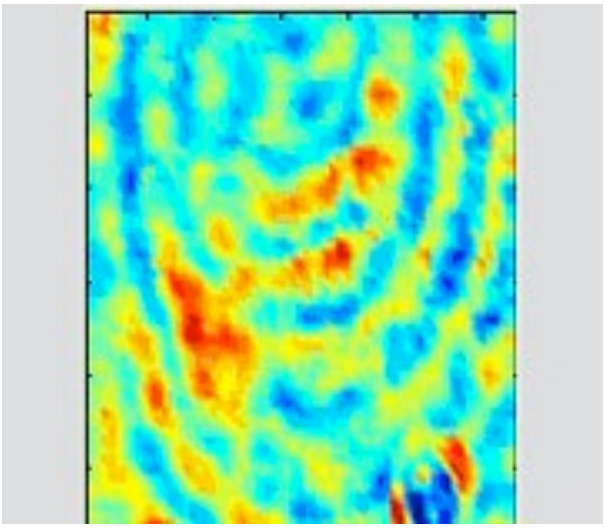
2.4.1 Further into the IR spectrum, many organic compounds have characteristic absorption peaks associated with vibration of organic sidegroups or stretching of chemical bonds. This chemical specificity can be utilised to discriminate different compounds using techniques such as FTIR spectroscopic imaging.



Wavenumber (cm^{-1})	**Assignment**
1,016	Asymmetric O–C–C stretch, ester
1,248	Asymmetric C–C–O stretch, ester (C bonded to the O included in the carbonyl)
1,456	CH_2 scissors
1,552	N–H bend combined with C–N stretch, protein amide II feature
1,656	C=O stretch, protein amide I feature
1,744	C=O stretch, saturated ester
2,856	Methylene C–H stretch
2,920	Methyl C–H stretch

Fourier Transform infra-red spectrum from fingerprint residue and molecular motions associated with peaks [18]

2.4.2 Researchers have begun to investigate the potential of this for fingerprint detection. It is possible to use a peak wavelength characteristic of a particular constituent of the fingerprint residue or fingerprint development reagent (but not present in the substrate) to obtain an image giving enhanced contrast between the fingerprint and the background.



Attenuated total reflection-Fourier Transform infra-red image of a fingerprint, showing distribution of lipid components.

2.4.3 This has been successfully demonstrated for fingerprints developed using cyanoacrylate fuming on the highly patterned background of an Australian banknote. The technique may also be able to detect the presence of other characteristic compounds (e.g. drugs, explosives) in fingerprint residues, giving investigators additional information about the person depositing the fingerprint.

2.4.4 At longer wavelengths, other mechanisms can be utilised to image fingerprints. IR imaging systems in this region can be used in non-destructive evaluation applications, such as thermography. There is the possibility of obtaining a contrast between fingerprint ridges and the substrate by exploiting differences in emissivity or differences in thermal conductivity between the two materials. By applying a pulse of heat or humidified air to the region of interest and observing the response of the surface using a thermal camera, it may be possible to resolve fingerprint ridges. This approach is routinely used for defect detection in aerospace materials and has been considered as a fingerprint detection technique, although a practical system has not yet been produced.

3. CAST processes

3.1 IR imaging is not currently (2011) recommended in the *Manual of Fingerprint Development Techniques* 2nd edition because it does not reveal fingerprints in its own right but can aid the visualisation of fingerprints developed using other processes, in particular physical developer. It is likely to be included as a specialist imaging process in the next edition of the manual.

3.2 IR imaging is recommended in the recent HOSDB newsletter on arson [23], where it has been demonstrated that IR imaging can reveal fingerprints treated with physical developer on charred paper exhibits.

Because IR imaging is an essentially non-destructive technique it can be inserted at appropriate stages of any sequential treatment without detriment to subsequent treatments.

3.3 The procedure currently (2011) recommended is to utilise a digital imaging system without an IR blocking filter bonded to the chip. Previously this option was only available in scientific grade, machine vision cameras, but digital single lens reflex (SLR) cameras are now becoming available for forensic imaging applications that are built without UV/IR blocking filters over the sensor. For IR reflection imaging, a light source emitting in the near IR is required. Standard halogen bulbs are appropriate for this purpose. To view the reflected IR radiation and block the visible region of the spectrum, IR cut-on filters are used in front of the camera. A range of Schott glass filters are available giving cut-on wavelengths between 645 and 1000nm. Although the lower wavelength filters do have some use in document examination, those of most use in suppression of patterned/coloured backgrounds and charred substrates in fingerprint imaging are RG715, RG780, RG850 and RG1000.

3.4 The same range of camera filters can be used when imaging in IR fluorescence. However, the light sources and fingerprint development reagents for this application have not yet been optimised.

4. Critical issues

4.1 For near IR imaging to be effective, imaging devices that are sensitive in the IR region of the spectrum must be used. Conventional charge coupled devices (CCD) and complemetary metal oxide semiconductor (CMOS) sensors used in digital cameras are not sensitive in this region because they usually have an UV/IR blocking filter bonded to them. Specialist models of camera are becoming available for IR imaging with this blocking filter removed.

4.2 An appropriate light source must also be used. For IR reflection imaging the light source must output in the near-IR region. Tungsten lamps are suitable for this purpose, fluorescent tubes and light emitting diodes (LEDs), unless specifically produced for IR emission, are not. The most appropriate wavelengths for exciting IR fluorescence are not yet known.

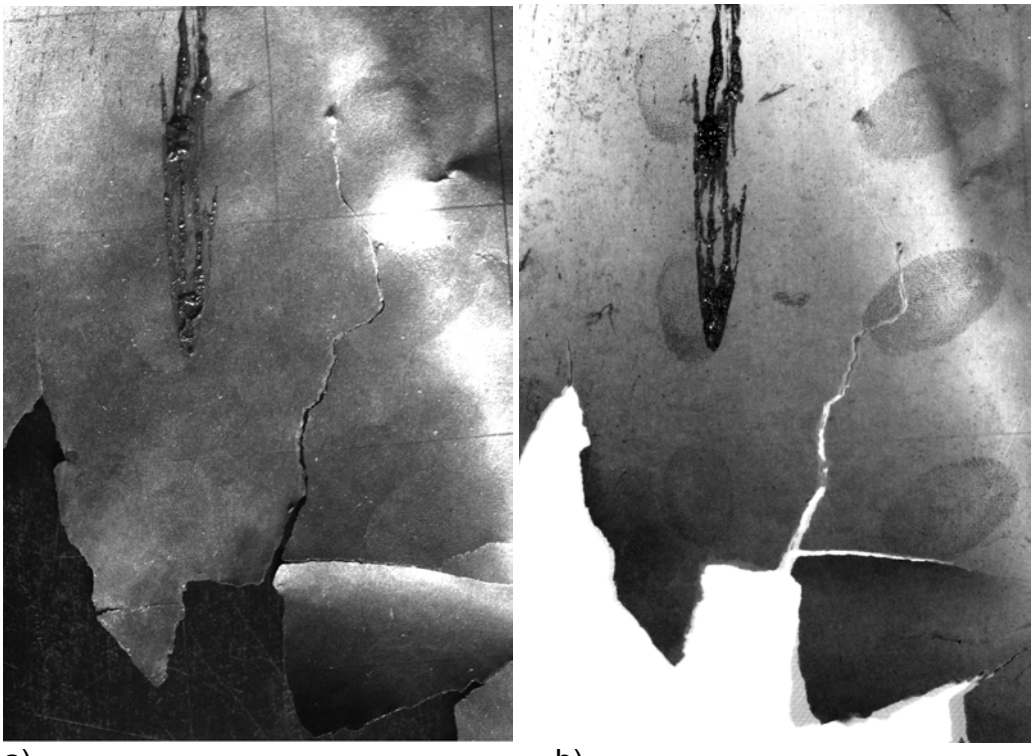
5. Application

5.1 Suitable surfaces: Reflected IR imaging is suitable for use on any coloured, patterned surface provided that the fingerprints present have been developed using a process that leaves metallic or inorganic material on the fingerprint ridges (e.g. powders, vacuum metal deposition, powder suspensions). The fingerprints then remain visible in the IR region of the spectrum and organic dyes and inks are typically

transparent. This has been found to be effective on printed paper, fabrics and printed plastic bags.

5.2 The principal application for IR imaging has been in the suppression of patterned backgrounds on porous substrates where marks have been developed using physical developer. This is of particular benefit on articles such as banknotes, where the printing is multicoloured and patterned. Although regular background patterns can be removed using digital techniques such as fast Fourier transforms, in many regions of banknotes the pattern is not regular and this approach cannot be used. The most commonly used technique for porous surfaces, ninhydrin, produces marks of a similar colour to the £20 note and makes imaging of features difficult. In these cases, using physical developer followed by IR imaging can produce fingerprints that cannot be visualised by other techniques.

5.3 The other application where IR imaging has been proven to be of benefit is on charred articles, again where physical developer has first been used to develop any marks present [23].



a) b)

Photograph of fingerprints developed using physical developer on charred paper a) viewed under tungsten illumination and b) viewed under tungsten illumination using infra-red long-pass filter (Schott glass RG780).

6. Alternative formulations and processes

6.1 There are many regions of the IR spectrum that can be utilised for IR imaging of fingerprints, and the different techniques for imaging fingerprints have been described in the preceding sections.

7. Post-treatments

7.1 There are no post-treatments used with IR imaging.

8. Validation and operational experience

8.1 IR imaging is used as a non-destructive post-treatment to aid in the visualisation of marks developed using other processes and therefore an extensive validation study has not been conducted. Studies have been carried out on a range of UK and European banknotes (one of the principal surfaces where IR imaging could give benefits) to demonstrate which elements of the printed background drop out under IR imaging conditions. A further small-scale study has been carried out by CAST to demonstrate which fingerprint development processes give marks that are still visible when imaged in the near IR [13].

8.2 There are known operational cases where police forces have utilised IR imaging to suppress backgrounds on exhibits where marks have been developed using physical developer. One police force treated a batch of £20 notes with ninhydrin and although several marks were developed these were in patterned regions where it was not possible to resolve minutiae. CAST recommended re-treating the exhibits with physical developer followed by IR imaging and several identifiable marks were produced.

8.3 Another force carrying out a cold case review treated a 25-year-old postal order that had been wetted with physical developer. A mark was developed but some minutiae were obscured by printing. IR imaging successfully suppressed the printing and revealed some additional minutiae. However, there was still insufficient detail for an identification.

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4.3 Multispectral imaging and monochromatic illumination

1. History

1.1 Multispectral imaging is a technology originally developed for aerial photography, and describes a system capable of simultaneously capturing spectral as well as spatial information. The spectral information can be used to distinguish between areas of nominally similar appearance, e.g. identifying different types of crop or vegetation by the differences between their reflected light spectra. More recently, the technique has been applied to other scientific disciplines, in particular medical imaging. In this application, the spectral information captured by multispectral imaging has been used to differentiate between different types of cell/tissue stained with coloured or fluorescent markers. Multiple stains can be used on a single sample and multispectral imaging used to identify the distribution of each in turn.

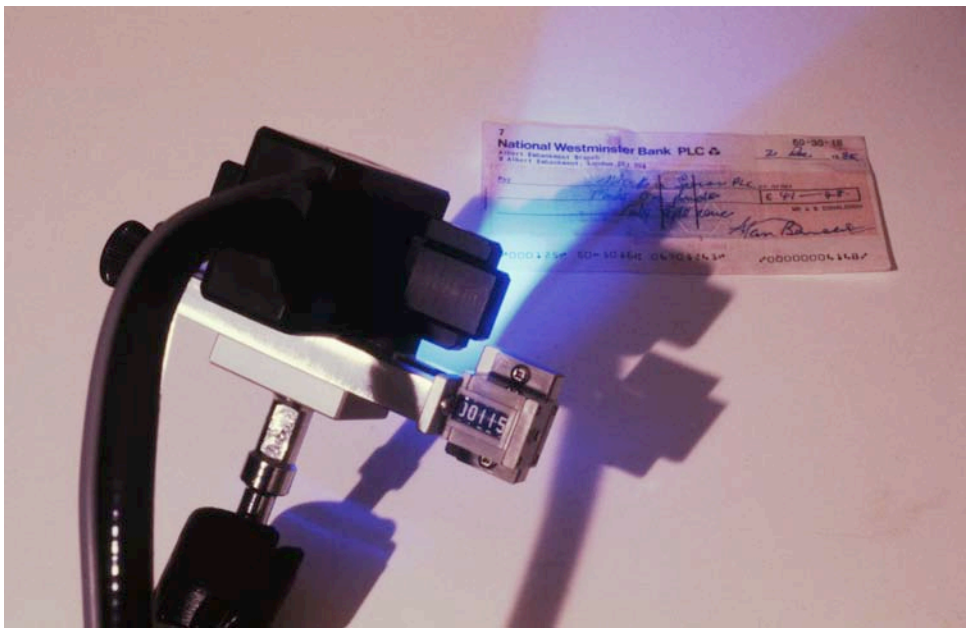
1.2 The potential of the technique for forensic applications became recognised in the late 1990s and Exline *et al* [1] demonstrated that chemically treated fingerprints could be imaged in both absorption and fluorescence modes using multispectral imaging systems, and that the improved spectral resolution obtained revealed more ridge detail than conventional imaging routes. In some cases, latent untreated fingerprints could be detected on coloured paper by multispectral imaging alone. Later studies by the same group demonstrated that the technique could be applied to a wide range of treated fingerprints, and faint ninhydrin marks in particular could be significantly enhanced by this method [2].

1.3 Initial forensic studies utilised multispectral imaging systems operating in the visible/near infra-red (IR) regions of the spectrum although later studies [3,4,5] demonstrated that multispectral imaging systems operating further into the IR region could also be used to resolve fingerprints, in this case using specific chemical vibrations from species present in fingerprint ridges to resolve the print against a patterned background.

1.4 Subsequent studies using both visible and IR multispectral imaging demonstrated that the technique could also be applied to document examination, including ink discrimination, paint analysis, detection of gunshot residue and fibre analysis [6,7,8].

1.5 The Home Office Scientific Development Branch (HOSDB) purchased a multispectral imaging system in 2006 and initially confirmed the results of the Australian researchers for a range of different fingerprint development techniques [9]. The technique has since been applied to some operational cases, demonstrating that fingerprints can be successfully resolved against coloured/patterned backgrounds by means of their characteristic spectral response.

1.6 Monochromatic illumination is closely related to multispectral imaging in terms of using spectral differences to differentiate between chemically treated fingerprints and similarly coloured backgrounds. Monochromators function by splitting white light into narrow spectral bands, and may utilise prisms, variable diffraction gratings or variable interference filters to achieve this. In the fingerprint imaging application, a monochromator is used in conjunction with a white light source to illuminate an exhibit with a narrow portion of the visible spectrum. By choosing a region of the spectrum that matches and suppresses reflected light from the background, fingerprints may be resolved. HOSDB first investigated this approach for the imaging of fingerprints developed using ninhydrin against the patterned backgrounds of cheques in the late 1980s [10] and developed the Quaserchrome monochromator accessory for use with the Quaser 100 and Quaser 40 at about the same time. More recently, monochromators have been provided as an integral part of the Integrated Rapid Imaging System (IRIS) workstation [11] developed and manufactured by HOSDB.

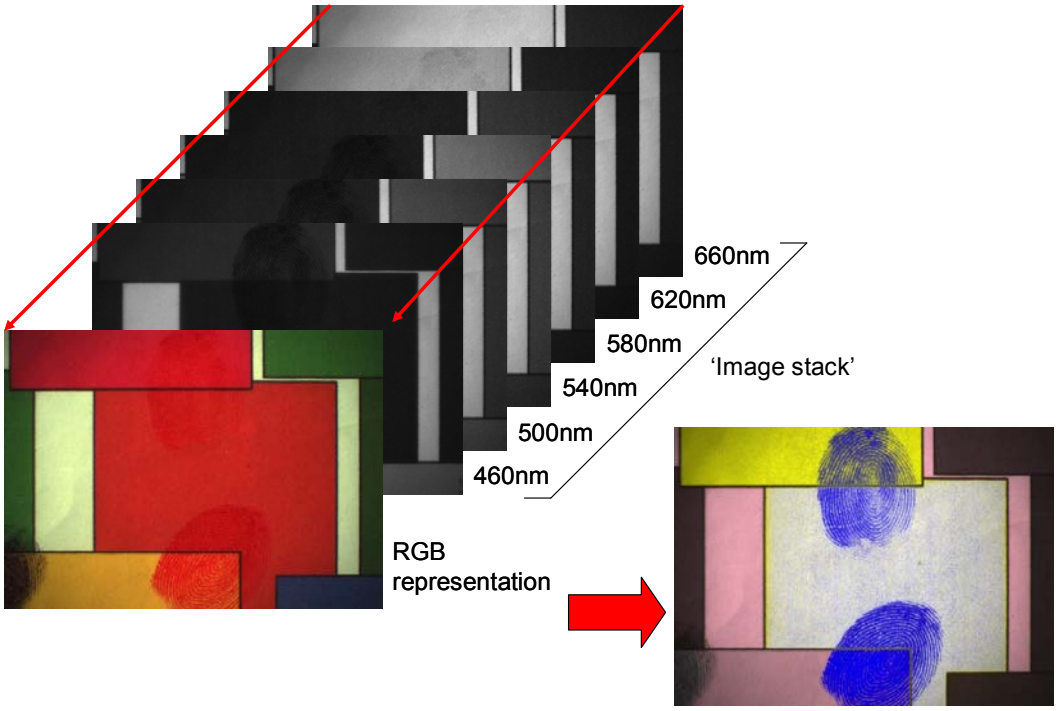


Prototype monochromator under test.

2. Theory

2.1 Multispectral imaging describes a range of techniques that all ultimately result in the capture of a digital image with spectral information associated with each pixel of that image. Such information may be obtained using either a single sensor capturing spectral information, which is then scanned across the area of interest [3], or an array of such sensors capable of capturing spatial and spectral information simultaneously [12-15]. These approaches are most often used for multispectral imaging in the IR region of the spectrum.

2.2 An alternative approach, more commonly used for multispectral imaging in the visible – near-IR – region, is to use a monochrome sensor array in combination with a tunable filter. Different tunable filter technologies are available, including liquid crystal and acousto-optical, but both types operate in essentially the same way. The tunable filter is a narrow bandwidth bandpass filter (typically with bandwidth in the range 2–20nm) for which the centre point of the bandpass can be controlled within the selected wavelength range. When carrying out multispectral imaging, the exhibit is illuminated with an appropriate light source and the tunable filter programmed to capture monochrome images at set wavelength intervals over the selected wavelength range. The series of monochrome images thus collected are known as an 'image cube' (or 'image stack') and can be interpreted by software to give a red-green-blue (RGB) , i.e. colour representation of the exhibit. An example is illustrated below.

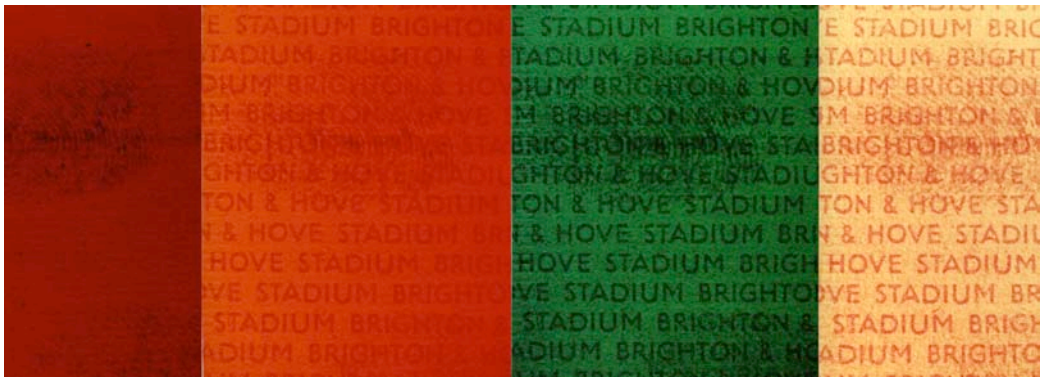


An example of an 'image cube' collected by a multispectral imager, the corresponding red-green-blue representation and unmixed image.

2.3 Once the image cube has been obtained, a range of processing techniques can be applied to the spatial and spectral information to extract the desired information. In the simplest form of analysis, regions with the desired spectrum (e.g. ninhydrin) can be identified, as can regions of unwanted background colour/pattern. These can be assigned false colours and the image unmixed to show the fingerprint in greater contrast. Alternatively, the regions corresponding to each colour channel can be viewed individually to see if any of these show the fingerprint more clearly than the unmixed image.

2.4 For images with multiple colours in the background and the fingerprint crossing several colour boundaries, other approaches such as Principal Component Analysis can be adopted to separate out the major spectral responses from the image, or a pure spectrum can be calculated from a subtraction from regions of background and mixed background/fingerprint spectrum.

2.5 Monochromatic illumination is an older and less versatile technique for revealing fingerprints on coloured backgrounds. In this technique a high intensity white light source is used in combination with a narrow bandwidth (~25nm) variable interference filter (typically a glass filter coated with a progressively thinner metal layer, giving a different transmitted colour along its length, e.g. the Schott glass Veril filter). The colour of the incident light can be controlled by moving the filter in front of a slit in the path of a light guide leading from the white light source, the objective being to match the incident colour with that of the printed background, thus suppressing it. If there is sufficient colour difference between the fingerprint and the background, this technique can be particularly effective.



a) b) c) d)

Mark in ninhydrin developed on patterned background viewed a) with red monochromatic illumination b) with orange monochromatic illumination c) with green monochromatic illumination and d) white light illumination.

2.6 Disadvantages compared with multispectral imaging are that the monochromator can only suppress one colour at a time and on multicoloured surfaces not all of the background will be removed. In addition, the bandwidth of the monochromator is generally broader than that achievable with tunable filters, and spectral differentiation will be correspondingly less.

3. CAST processes

3.1 CAST is in the process of evaluating the use of multispectral imaging for the capture of developed fingerprints and consequently a definitive method has not been devised. In the studies to date (2011), the

Cambridge Research and Instrumentation (CRi) 'Nuance' system has been utilised, consisting of a 1 megapixel digital camera integrated with a CRi 'Varispec' liquid crystal tunable filter with 7nm bandwidth and wavelength range 420–720nm. The 'Nuance' system has been fitted with a C-F mount adaptor and Nikon 105mm macro lens, bringing the camera sufficiently close to the exhibit such that the capture resolution is in excess of 500ppi. The exhibit is illuminated with a tungsten light source, and brought into sharp focus using the lens, viewing the image of the article on screen in the 'live' mode. The wavelength range of interest is selected, and the tunable filter set to collect a spectrum at 10nm intervals throughout the selected range. The filter is then set to calculate automatically the optimum exposure for each wavelength, and finally set to acquire the image cube. The operator can then carry out a variety of analysis tasks on the data contained in the image cube, such as Principal Component Analysis or calculation of pure spectra in order to separate the fingerprint from the background. For evidential purposes, it is recommended that the RGB representation of the exhibit, the unmixed image, the image associated with each spectral channel and the spectral information are retained. The wavelength range and step interval between spectra can be refined to the particular region of interest once the initial image cube has been obtained.

3.2 For monochromatic illumination using the Quaserchrome, the accessory should be fitted to the end of the light guide running from the Quaser light source. The light source should be set to the white light illumination mode, using the appropriate key to override the interlock. The dial on the Quaserchrome can then be rotated to move the filter in front of the slit in the path of the light guide, and the change in colour output can be observed by eye. Because the output is only a small region of the visible spectrum, the power is much reduced from normal Quaser excitation filters and consequently it is not necessary to wear viewing goggles. The mark to be imaged is viewed by eye as the illumination colour is varied, and the colour giving optimum contrast between the fingerprint and the background is selected for any subsequent photography.

3.3 The procedure using the integrated monochromator on IRIS is very similar. The light source selector switches should be set to the Quaser 2000, which should have 'white light' selected as the excitation band. The monochromator dial should then be turned until the orange light on the front of the Quaser 2000 is illuminated. Pressing the orange light illuminates the Quaser in the violet region of the spectrum and the illumination colour can be varied by continuing to turn the monochromator dial. The optimum illumination colour is either determined by eye or by viewing the semi-live image on the computer monitor.

4. Critical issues

4.1 For multispectral imaging, it is essential to ensure that the sample is as evenly lit as possible and that the light source used to illuminate it has a continuous output across the spectral range of interest. Best results for spectral discrimination are obtained from systems with narrow bandwidth filters and by collecting images at many closely spaced wavelengths.

5. Application

5.1 Suitable surfaces: The principal application for multispectral imaging and monochromatic illumination is in revealing developed fingerprints on articles with patterned and/or multicoloured backgrounds, as may be encountered on exhibits such as banknotes. Best results are obtained when the development process itself produces marks of a characteristic colour.

Mark developed using ninhydrin on patterned, multicoloured background of a £20 note.

5.2 Both techniques can be used to exploit differences between the colour spectrum of the developed fingerprint and the background printing. Monochromatic illumination is effective if only one background colour is prevalent, whereas multispectral imaging can be applied where many colours are present.

5.3 Both techniques are applied after chemical treatment to produce a coloured or fluorescent product, and are non-destructive, only involving illumination of the exhibit with a relatively low power light source.

6. Alternative formulations and processes

6.1 It is also possible to remove regular patterned backgrounds by means of fast Fourier transforms, a digital filtering technique. A Fourier transform is taken of the digital image and the features associated with the patterned background are identified. These are then masked and the inverse transform is taken, which suppresses the background pattern in the image and may reveal additional detail in the more irregular fingerprint [16,17]. However, fast Fourier transforms are most effective where the pattern is regular, and this is often not the case for many regions of banknotes. In these situations multispectral imaging or monochromatic illumination may yield better results.

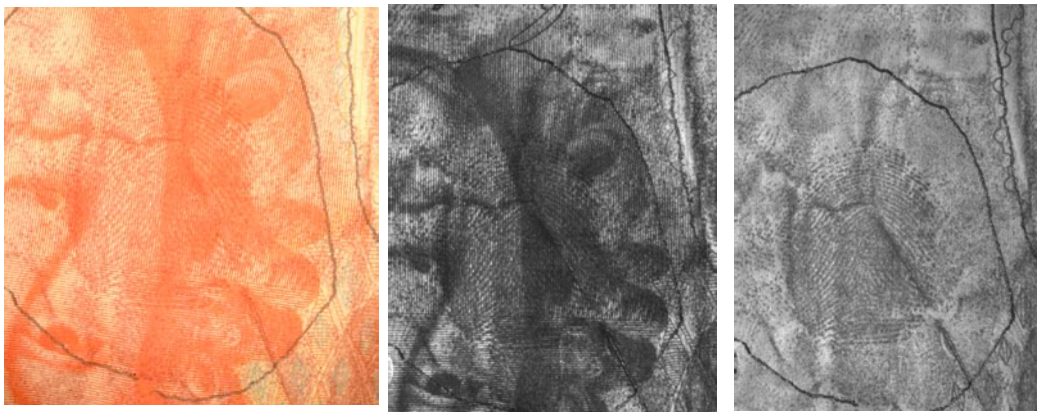
7. Post-treatments

7.1 There are no post-treatments used with monochromatic illumination. The principal post-treatment used with multispectral imaging is the analysis software used to extract the spectrum of the fingerprint reagent from those of the background.

8.Validation and operational experience

8.1 Multispectral imaging and monochromatic illumination are non-destructive techniques and can be used during a sequential process without detriment to subsequent treatments. As a consequence there is less of a requirement to conduct comparative laboratory experiments with other techniques or operational trials before implementing them on operational work.

8.2 Monochromatic illumination has been in use for 20 years on operational work. It is known to work well with ninhydrin marks on the Bank of England £50 note, the former ‘Edward Elgar’ £20 note and on some regions of the £10 note.



a) b) c)

Fingerprint developed using ninhydrin on a £50 note a) colour image illuminated with white light b) monochrome image illuminated with green monochromatic light and c) monochrome image illuminated with red monochromatic light.

8.3 Since 2007 multispectral imaging has been used on selected operational cases where marks have been developed but cannot be resolved by monochromatic illumination, IR imaging or digital filtering techniques such as fast Fourier transforms. In several of these cases entire marks or additional ridge detail have been revealed, leading to successful identifications and convictions.

a) b)

Fingerprint in coloured contaminant found on a £10 note a) red-green-blue image and b) unmixed image showing fingerprint extracted from the background by spectral characteristics (courtesy of Nick Marsh, Metropolitan Police Service).

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Chapter 5: Alternative finger mark development techniques

5.1 Alternative blood enhancement techniques

1. History

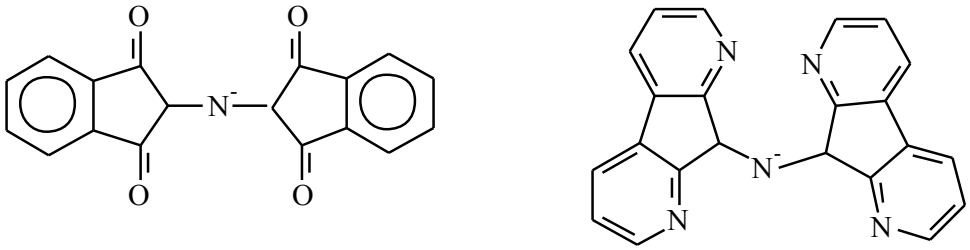
1.1 The history of the development of blood dyes has been outlined in Chapter 3.1, Acid dyes, of this *Fingerprint Source Book*.

2. Theory

2.1 General theory

2.1.1 The theory associated with the action of protein stains (in particular the acid dyes), in enhancing traces of blood is described in Chapter 3.1, Acid dyes (acid black 1, acid violet 17, acid yellow 7).

2.1.2 There are other reagents that react with the amines present in blood to give coloured or fluorescent products, the most well known of these being ninhydrin and 1,8-diazafluoren-9-one (DFO). They both react similarly with amino acids to form products that contain two deoxygenated molecules of the starting product bridged by a nitrogen atom, which is donated from the amine [1,2].



The reaction products with ninhydrin (left) and 1,8-diazafluoren-9-one (right) and amines.

2.1.3 While the reaction mechanisms and products have similarities, the method of their visualisation is entirely different. Ninhydrin, under the right conditions, produces an intensely coloured product called 'Ruhemann's purple' after the discoverer and DFO a pale pink, extremely fluorescent product. Ruhemann's purple can be made to fluoresce by complexing it with metal salts but this additional process is still not as sensitive as DFO [3]. DFO requires heat for the reaction to proceed [4] while ninhydrin will react at room temperature provided moisture is available, although the process proceeds much faster at elevated temperatures and humidities. These techniques are not specific to blood and will detect other amine-containing substances, including latent fingerprint deposits.

2.1.4 There are several ways of positively identifying blood using spectroscopic methods [5,6] but they are all carried out ex situ, so are of no use in the enhancement of blood-contaminated fingerprints.

2.1.5 Haemoglobin strongly absorbs light throughout the ultraviolet, visible and near infra-red parts of spectrum and this property can be utilised to detect and enhance blood, although once again this cannot be regarded as a way of confirming that it is blood that is present. Where deposits of blood are heavy or are present on light coloured surfaces a good white light may suffice to enable enough detail to be observed. However for pale or insubstantial deposits it may be necessary to use high-intensity light sources to enhance the contrast between the blood and the surface.

2.1.6 The use of fluorescence to enhance fingerprints in blood can be extremely effective in these circumstances. There are two ways this may be achieved:

- by exciting fluorescence of the background surface on which the blood is deposited;
- by treatment with a process that either breaks the haem group or turns the blood into a fluorescent species, or does both of these.

2.1.7 Many materials fluoresce when excited by high-intensity light in the ultraviolet and violet regions of the spectrum. This is coincidently where the haem group is most absorbent, with a peak around 421nm (known as the Soret Band) [5,7,8] and why blood-contaminated fingerprints will appear dark against a light background. Fluorescence examination may be used before any other fingerprint enhancement techniques as it is non-destructive and if long-wave ultraviolet or violet/blue light (350–450nm) [9] is used then DNA typing is also unaffected [10]. The use of ninhydrin, acid black 1 or acid violet 17 can further intensify the contrast between the fingerprint and the background by increasing the light absorption properties of the blood.

2.1.8 The use of a strong organic acid in conjunction with hydrogen peroxide [11,12] breaks up the haem group so that it is no longer effective at absorbing light. After such treatment, blood will fluoresce orange when excited by green light (500–550nm). This effect has also been noted as blood ages.

2.1.9 DFO produces fluorescent species with blood, which can be excited by green (510–570nm) light. This can be less effective on heavy deposits of blood as the haem group retains its ability to absorb both the excitation light and that emitted as fluorescence.

2.1.10 There are three kinds of tests for blood detection that use the haem group in haemoglobin: crystal tests; catalytic tests; and antibody tests. The sensitivity of these techniques is limited by their effectiveness to lyse blood cells, so releasing the haem-containing proteins that are only present within the red blood cells.

2.1.11 The Teichmann test [13] results in the formation of brown rhombohedral crystals of haematin and the Takayama test [14] in red-pink crystals of pyridine haemochromogen. Both of these tests have to

be carried out ex situ so are of no use for fingerprint enhancement as the ridge detail is inevitably destroyed as the blood is removed, unless an area containing no ridge detail, such as a smear, alongside the fingermark is used.

2.1.12 There are a number of advantages to the Takayama test, as compared with the Teichmann test. Heating is not required to obtain results within a reasonable amount of time in the Takayama test; and even if heat is applied, the test is not subject to being ruined by over-heating. The test also yields positive results under some of the circumstances where the Teichmann test fails.

2.1.13 The catalytic tests are only presumptive or infer the presence of haem, as they only use the haem to facilitate another reaction and are subject to both false positive and false negative reactions caused by a variety of non-blood substances. Consequently individual results require careful interpretation by experts.

2.1.14 These tests all rely on the 'peroxidase activity' of the haem group. Enzymes that catalyse the peroxide-mediated oxidation of organic compounds in vivo are called peroxidases; haemoglobin and the other compounds that show this catalytic property are thus said to have 'peroxidase activity'. This peroxidase activity may be utilised to cause the oxidation of colourless reduced dyes, such as phenolphthalein, leucocrystal violet, tetramethyl-benzidine and fluorescein, which when oxidised form their coloured, or in the case of the latter, fluorescent, counterparts.

$$H_2O_2 + \text{colourless reduced dye} \rightarrow H_2O + \text{coloured oxidised dye} \quad [15]$$

2.1.15 The luminol test also relies on the peroxidase activity of the haem group, but can be used with either hydrogen peroxide [16] or sodium perborate [17]. Then in the presence of blood a product which chemiluminesces is produced. The bluish-white chemiluminescence is faint and must be viewed in the dark by an operator who is fully dark-adapted to gain the best evidence from this test. However, even with careful application of luminol it is extremely easy to damage the fine detail of the blood-contaminated fingerprint ridges on both porous and non-porous surfaces. Therefore this technique should only be used when fine detail is not required and when other techniques might be compromised by surface type or impracticality, such as dark or patterned carpets [11].

2.1.16 The major concern with the catalytic tests for blood is that they can produce false-positive results in the presence of chemical oxidants and catalysts, salts of heavy metals such as copper, nickel and iron, and plant peroxidases such as those found in horseradish, citrus fruits, and numerous root vegetables [18]. A two-stage test can help to stop false positives from true peroxidases. The reduced colourless dye is applied initially and if no colour change is observed then the hydrogen peroxide

added. A colour change at this point is more likely to indicate the presence of blood rather than a peroxidase, although contamination by metal salts is not distinguished.

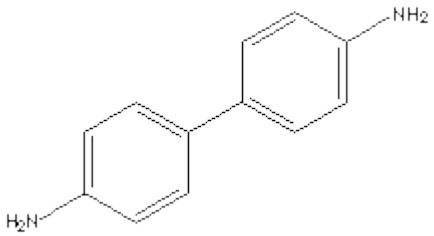
2.1.17 It is generally accepted that a negative result with a catalytic test proves the absence of blood, however strong reducing agents such as ascorbic acid [19] and active oxygen cleaning products [20] may inhibit such tests.

2.1.18 The antibody tests [21, 22] like the crystal tests are confirmatory for blood, but as they use anti-human Hb antibodies they are also specific for human blood. Currently (2011), they have to be used ex situ so are of no use for fingerprint enhancement, and it remains to be seen whether these tests can be used after the more effective enhancement techniques [22] to prove that what is being enhanced is human blood.

2.2 Specific reagents

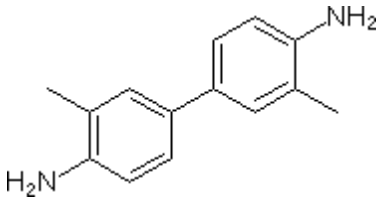
2.2.1 A review of blood enhancement agents has recently been conducted by Powell [23,24] and the relevant information below is extracted from these documents. Although the purpose of the review was for footwear enhancement, there is direct read-across to fingerprints because the contaminant being targeted is the same.

2.2.2 Benzidine: Benzidine was first used in 1904 and was the first reagent that utilised the peroxidase activity of haem. Benzidine is colourless in its reduced form and will turn dark blue when oxidised in the presence of haem or haem derivatives. It caused the entire surface being treated to be stained a light brown colour but was used on a variety of porous and non-porous surfaces. Due to its high sensitivity and dramatic colour change benzidine found widespread operational applications until health and safety concerns curtailed its use.



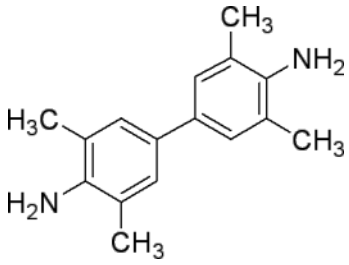
Structure of benzidine.

2.2.3 Ortho-tolidine: Ortho-tolidine is structurally related to benzidine, and is also colourless in its reduced form and dark blue when oxidised. It was first used in 1912 and again was widely employed due to its sensitivity and pronounced colour change. It was initially suggested as a possible alternative to benzidine. A sensitivity comparison of blood enhancement techniques rated ortho-tolidine second only to benzidine and suggested that it could be used providing that all health and safety precautions are taken.



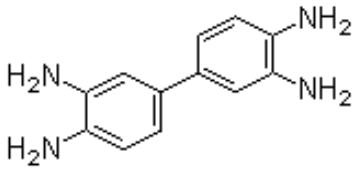
Structure of ortho-tolidine.

2.2.4 Tetramethyl-benzidine: As the commonly used reagents such as benzidine and ortho-tolidine were found to be carcinogenic thoughts were turned to find a new reagent of equal specificity but without the associated health and safety problems. There was some evidence that the issue was the participation of ortho-hydroxy derivatives of aromatic amines in the carcinogenic action, therefore the use of 3,5,3',5-tetramethylbenzidine (TMB) was suggested where ortho-hydroxylation is impossible. A print developed by TMB would turn green/blue.



Structure of 3,5,3',5- tetramethyl-benzidine).

2.2.5 Diaminobenzidine: Diaminobenzidine (DAB) undergoes a chemical polymerase reaction converting blood marks to an insoluble brown product. Its alternative name is tetraamino-biphenyl (TAB).



Structure of diaminobenzidine.

2.2.6 DAB is a derivative of benzidine and was thought to be a suitable substitute reagent for the enhancement of blood marks, as it is used as an aqueous solution and does not employ any organic solvents. The working solution is mixed just prior to use and involves the addition of a phosphate buffer solution to an aqueous solution of DAB. The reaction is initiated by hydrogen peroxide.

2.2.7 A widely used formulation is given below and involves the addition of a phosphate buffer working solution to the aqueous solution of DAB.

Solution A – fixing solution: Dissolve 20g 5-sulphosalicylic acid in 1 litre of distilled water.

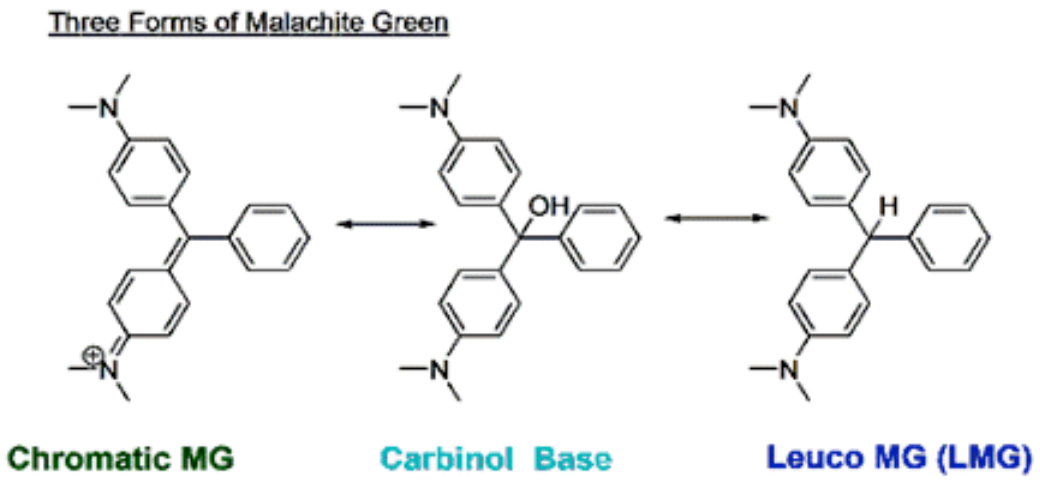
Solution B – buffer solution: Mix 100mL of 1M phosphate buffer (pH 7.4) with 100mLof distilled water.

Solution C – DAB: Dissolve 1g of 3,3'-diaminobenzidine tetrahydrochloride in 100mL of distilled water.

Working solution: Mix 180mL of solution B with 20mL of solution C and add 1mLof 30% hydrogen peroxide. The fixing solution is applied prior to the working solution.

2.2.8 Leuco-dyes: These are catalytic tests for blood and will bind with the proteins found in blood limiting the leaching and running of the developed impression. The hydrogen peroxide solutions will catalyse oxidation of the haemoglobin and its derivatives, producing a blue/green colour for leucomalachite green (LMG) and violet for leucocrystal violet (LCV).

2.2.9 Leucomalachite green: LMG is oxidised to form its coloured product when in contact with the haem group in blood.

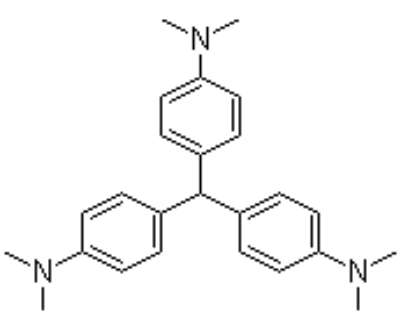


Changes occurring between the leuco- and coloured forms of malachite green

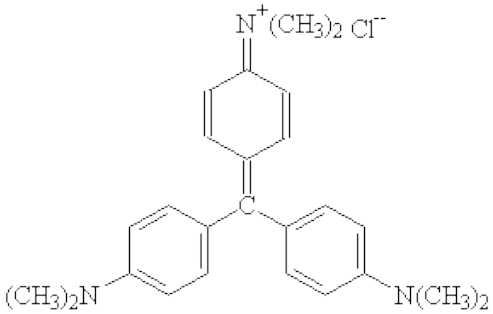
2.2.10 There are several formulations of LMG in the literature; they all contain LMG, diethyl ether, glacial acetic acid and hydrogen peroxide, the only difference being the quantity of each reagent. For optimum results the reagent must be prepared immediately prior to use. A green colour indicates that blood is present. The formulation given below is one used by the Royal Canadian Mounted Police.

Place 0.2g of LMG in a clean glass beaker, and add 67mL of methanol. Once the LMG is dissolved add 33mL of glacial acetic and 0.67g of sodium perborate and stir well until dissolved. Pour into a 1-litre beaker and add 300 ml of 1-methoxynonafluorobutane (HFE 7100). Store in a dark glass bottle until required. The prints can be fixed by submersion in ethanol.

2.2.11 Leucocrystal violet: LCV is the completely reduced form of crystal violet and is colourless. The reaction is initiated by hydrogen peroxide and when LCV comes into contact with the haem in blood the reaction is catalysed and the clear solution is converted to a purple/violet colour.



Crystal violet

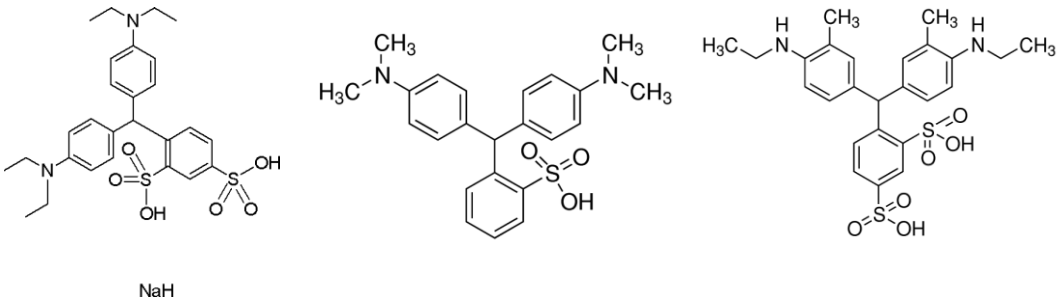


Leucocrystal violet

2.2.12 LCV is applied to the enhancement area via a spray method. The most common formulation is given below.

Dissolve 10g of 5-sulphosalicylic acid in 500mL of 3% hydrogen peroxide. Add and dissolve 3.7g sodium acetate. Add and dissolve 1g of leucocrystal violet with a magnetic stirrer. Store in dark-coloured glassware and refrigerate.

2.2.13 Alternative leuco dyes: Powell [24] studied a range of alternative leuco dyes to investigate whether issues with sensitivity and carcinogenicity of the existing leuco dyes could be overcome. The first alternative dye investigated was leuco patent blue (LPB). LPB is an acidic peroxidase dye compared with LCV, which is basic. As the fixing agent precipitates basic proteins, the acidic peroxidase reagent would then dye the basic proteins in a manner analogous to the protein stains. Two other similar systems, leuco berbelin blue (LBB) and leuco xylene cyanole (LXC) were also evaluated.



Structures of leuco patent blue, leuco berbelin blue , and leuco xylene cyanole.

2.2.14 Formulations for these reagents are given below.

0.1042g of leuco patent blue is dissolved in 10mL of water; 4mL of acetic acid and 1mL of 3% hydrogen peroxide are then added.

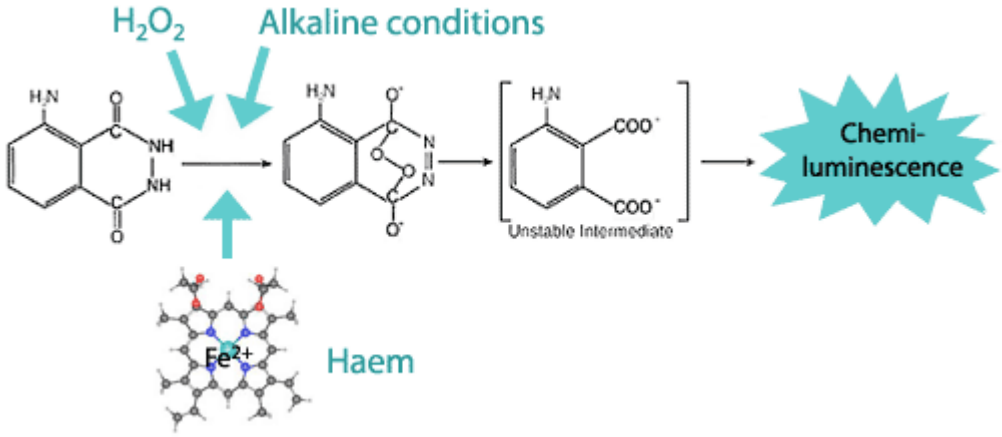
0.072g of leuco berbelin blue is dissolved in 10mL of water; 4mL of acetic acid and 1mL of 3% hydrogen peroxide are then added.

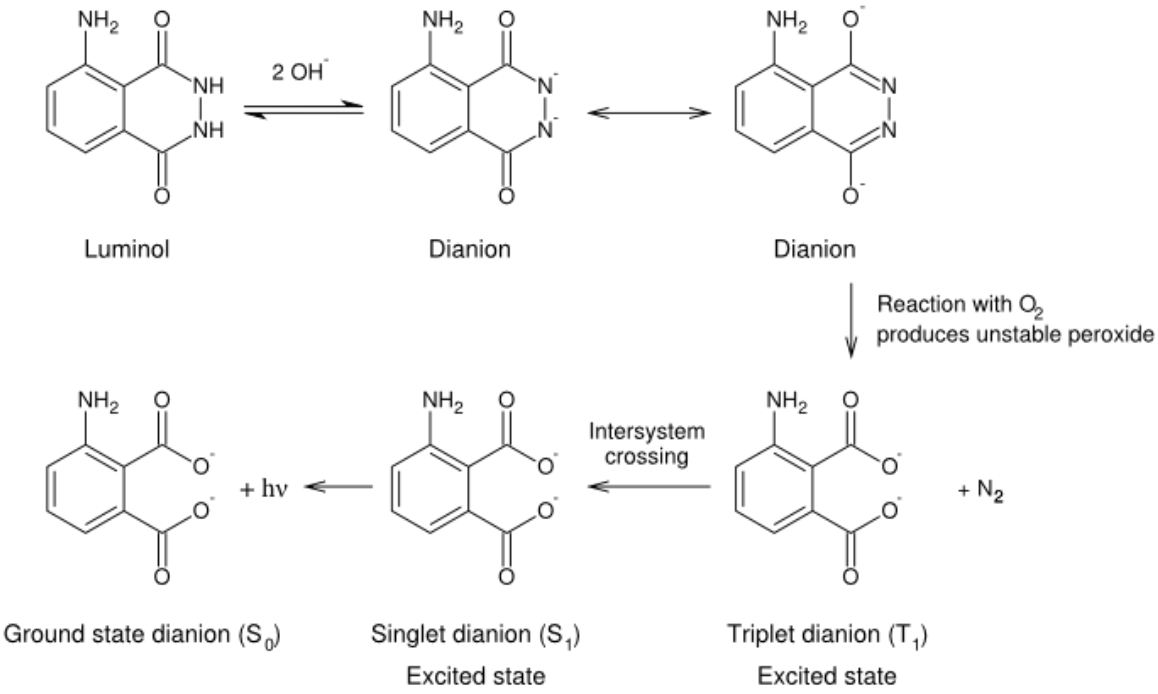
0.091g of leuco xylene cyanole is dissolved in 10mL of water; 10mL of acetic acid with 2mL of hydrogen peroxide are then being added.

2.2.15 Luminol: The active chemicals in this generic class of blood detection reagents are luminol ($C_8H_7O_3N_3$) and hydrogen peroxide (H_2O_2). The hydrogen peroxide and the luminol react in alkaline conditions to produce chemiluminescence (in this case a blue/white glow), with the reaction being catalysed by the iron present in haemoglobin.

2.2.16 In the resultant oxidation reaction, the luminol molecule loses nitrogen and hydrogen atoms and gains oxygen atoms, resulting in a compound called 3-aminophthalate. The reaction leaves the 3-aminophthalate in an excited state with the electrons in the oxygen atoms being promoted to

higher energy levels. The electrons quickly fall back to a lower energy level, emitting the extra energy as a light photon.





Schematic diagrams showing the mechanisms associated with the chemiluminescent reaction between luminol and blood.

2.2.17 This then produces a product that luminesces in the presence of blood. The bluish-white chemiluminescence is faint and must be viewed in the dark by an operator who is fully dark-adapted to gain the best evidence from this test. Even with careful application of luminol it is all too easy to damage the fine detail of blood-contaminated fingerprints. This technique should only be used when fine detail is not required and when other techniques might be compromised by surface type or impracticality, such as dark or patterned carpets. Two published formulations for luminol are

given below, and proprietary pre-prepared products (e.g. Bluestar) are also available.

Grodsky:

3.5g sodium perborate is dissolved in 500mL distilled water, 0.5g luminol and 25g sodium carbonate are added and dissolved. Solution is left to stand for five minutes before being used immediately.

Weber:

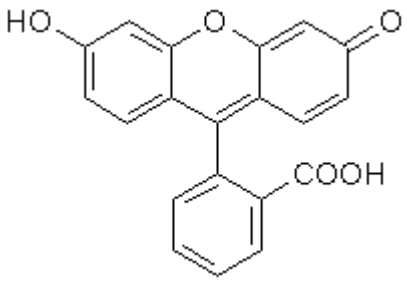
Stock solution A: 8g sodium hydroxide dissolved in 500mL distilled water.

Stock solution B: 10mL 30% hydrogen peroxide in 490mL distilled water.

Stock solution C: 0.354g luminol dissolved in 62.5mL of solution A and made up to final volume of 500mL with water.

Working solution: 10mL solution A + 10mL of solution B + 10mL of solution C + 70mL distilled water.

2.2.18 Fluorescein: Fluorescein is a presumptive test for blood that utilises the peroxidase activity of the haem group. The reduced form of the chemical, fluorescin, is colourless and when sprayed onto the target area it is oxidised to fluroscein, a coloured/fluorescent product, by the presence of blood associated proteins and iron ions found in the haemoglobin molecule. Even minute traces will fluoresce when excited with a light source between 425–485nm and viewed through a yellow to orange barrier filter.



Structure of fluorescein.

2.2.19 Fluorescein is usually applied in a two-step process – the application of fluorescein alone will develop the yellow coloration, however an overspray of hydrogen peroxide is also used to reduce background fluorescence and false-positive reactions.

2.2.20 The preparation of fluorescein is quite a lengthy process and the reduced fluorescin has a very short shelf life – the recommended usage is within 24 hours. The original formulation is as follows.

A 10% sodium hydroxide (NaOH) stock solution is prepared by dissolving 10g NaOH in 100mL deionised water.

1.0g fluorescein is dissolved in 100mLof the 10% NaOH stock solution and placed on a hot plate and heated gently.

10.0g zinc powder is then added and heated to a gentle boil.

The solution is allowed to cool and the un-dissolved zinc to settle.

The cooled solution is then decanted to remove any un-dissolved zinc.

The fluorescein reagent solution is then made by mixing 50mL of the decanted solution with 950mL of deionised water. This reagent must then be kept in dark glassware.

The hydrogen peroxide overspray is made by mixing 100mL of 30% hydrogen peroxide with 200mL deionised water.

3. Reasons technique is not recommended by CAST

3.1 The Home Office Centre for Applied Science and Technology (CAST) does not recommend the use of haem-specific, reactive blood dyes for general use because they are not as sensitive as the protein stains recommended in the *Manual of Fingerprint Development Techniques* [10]. This is intuitive – there is far more proteinaceous material present to interact with the dye than there is haem and therefore the protein stains will remain effective on far smaller quantities of blood residue than reactive dyes. This is supported by the sensitivity testing conducted by Sears *et al.* [11] when developing the formulations for acid black 1, acid yellow 7 and acid violet 17.

3.2 It is recognised that there will be circumstances where the use of haem-specific dyes will be preferable, e.g. where there is other proteinaceous contamination present and a more specific dye will more clearly identify the blood. Reactive dyes are also more suited to speculative searching of scenes, and can be more easily spray applied. However, this approach is more suited to footwear development than to fingerprints. A range of the alternative blood enhancement agents (protein stains and reactive dyes) is outlined below, with some comments on those most commonly proposed for operational use.

3.3 Benzidine: Benzidine was found to be a highly effective blood-enhancing reagent but was later recognised as a known carcinogen and there are reports in the literature stating forensic analysts developed bladder

cancer due to the use of this reagent. It is now known to be extremely hazardous and breathing its vapours or touching the chemical or its salts could cause cancer to develop. It is not recommended for use by CAST and is included in this review for historical purposes only

3.4 Ortho-tolidine: Although ortho-tolidine was originally proposed as a safer alternative to benzidine, there are several reports in literature stating that workers suffered from prolonged headaches and skin burns after using ortho-tolidine when safety precautions were not taken. Ortho-tolidine is now also a known carcinogen and its use is therefore not recommended by CAST.

3.5 3,5,3',5 Tetramethylbenzidine (TMB): Sensitivity studies carried out in comparison with acid black 1 show TMB to be significantly less sensitive. There are also concerns about TMB being a possible carcinogen and mutagen and its use is therefore not recommended by CAST.

3.6 3,3' Diaminobenzidine tetra hydrochloride dehydrate (DAB): Sensitivity studies carried out in comparison with acid black 1 show DAB to be significantly less sensitive. The colour formed during the reaction is light brown, which is similar to dried blood and not ideal for enhancement of bloody fingerprints, whereas a protein dye such as acid black 1 will stain the mark a dark colour, which will aid with contrast against the background. There are also reports on the suspected carcinogenic activity of DAB, and therefore it is not recommended for use by CAST.

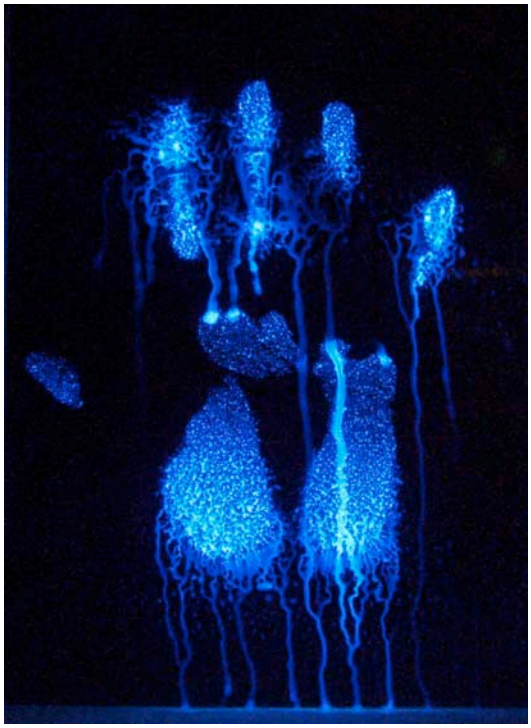
3.7 Leucomalachite green: LMG has been found to be less sensitive than acid black 1 and does not produce as vivid a colour change as some other reagents studied. It was also found to be less consistent in performance than LCV.

3.8 Leucocrystal violet: LCV has been shown to be an effective treatment for marks in blood, albeit less sensitive than protein stains. If a haem-specific reagent were to be recommended by CAST, LCV would be the preferred option but only under controlled conditions in a laboratory. The purple coloured form crystal violet is now classified a known carcinogen which makes large scale spraying at scenes undesirable.

3.9 Alternative leuco dyes: Of the alternative leuco dyes evaluated, LBB gave high background staining and although LPB and LXC were effective in preliminary studies, the cost of the dyes is prohibitive for operational use.

3.10 Luminol: Luminol and related compounds are not recommended for fingerprint detection because they are spray applied and could cause diffusion of marks. Because luminol relies on a chemiluminescent reaction to produce blue fluorescence that fades with time, multiple applications may be required to first locate and then photograph any fingerprints. However, it has been demonstrated that repeat applications

will ultimately cause diffusion of ridge detail and therefore the use of a reagent giving a coloured or conventionally fluorescent mark is preferred.



Palm print in blood on glass, with ridge detail diffused by excessive spraying.

3.11 Fluorescein: Fluorescein has been found to be lower in sensitivity to most of the other dyes outlined here and the acid dyes recommended in the *Manual of Fingerprint Development Techniques* [10].

3.12 Alternative protein stains: In addition to reactive dyes, CAST has considered a wide range of alternative protein stains that were evaluated in comparative studies with acid black 1, acid yellow 7 and acid violet 17 [25,26]. These dyes were rejected on the basis of lack of sensitivity, lack of availability or poor visibility of the developed mark. A summary of those systems evaluated is given in the table below.

Colour Index name	**Colour Index number**	**Comments**
Acid blue 92	13390	Plasma stain
Acid red 88	15620	Plasma stain
Acid red 29	16570	
Acid red 1	18050	Plasma stain
Acid yellow 23	19140	Collagen stain (protein)
Direct yellow 12	24895	Plasma stain (in pathology)
Acid red 71	27165	Cytoplasmic stain
Acid red 112	27195	Stain basic tissue elements

Acid blue 1/acid blue 3	42045/42051	
Basic violet 4	42600	
Acid blue 90	42655	Protein stain
Acid blue 83	42660	Protein stain
Acid violet 19	42685	Plasma stain
Acid dye	43535	
Basic blue 11	44040	
Acid red 87	45380	Plasma stain
Basic dye	51140, 51145	
Direct red 148	52005	
Acid blue 74	73015	
Quinacrine	-	
Lucifer Yellow (CH & VS)	-	
Rivanol	-	

Alternative protein stains evaluated by CAST but not recommended for operational use.

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5.2 4-Dimethylaminocinnamaldehyde (DMAC)

1. History

1.1 4-Dimethylaminocinnamaldehyde (DMAC) was first proposed as a fingerprint development reagent in the UK by Morris *et al.* in 1973 [1] and was believed to react with the urea present in eccrine fingerprint secretions. In the initial work conducted at AWRE, DMAC appeared to be more sensitive than the ninhydrin formulations and processing conditions then in use, and it was decided to proceed to operational trials in 1973. For operational use DMAC was dissolved in a mixed ethanol/ chlorofluorocarbon (CFC) solvent and the articles to be treated immersed in the solution until visible marks developed. When DMAC reacts with urea under acidic conditions it gives a magenta coloured product within two minutes, the developed mark providing good contrast with the background.

Palm print developed using 4-dimethylaminocinnamaldehyde solution.

1.2 The operational trials in the UK were conducted in a limited number of police forces and abandoned after only a few months as the performance of DMAC was found to be poor in terms of finger mark yield compared to ninhydrin. Many of the marks that were developed were also diffuse and lacking in ridge detail. As a consequence the use of DMAC as a solution dipping process was discontinued in the UK by the mid 1970s.

1.3 Van Enckevort [2] found DMAC, when sprayed or dipped, to be useful on a wide range of substrates in laboratory trials, particularly those that showed a high background development with ninhydrin. However, he too

found the reagent to be less successful in operational trials with the prints visualised showing blurred ridge detail, which was attributed to the diffusion of urea. He observed that useful prints were only obtained up to three to ten days after deposition and consequently found little use for the reagent.

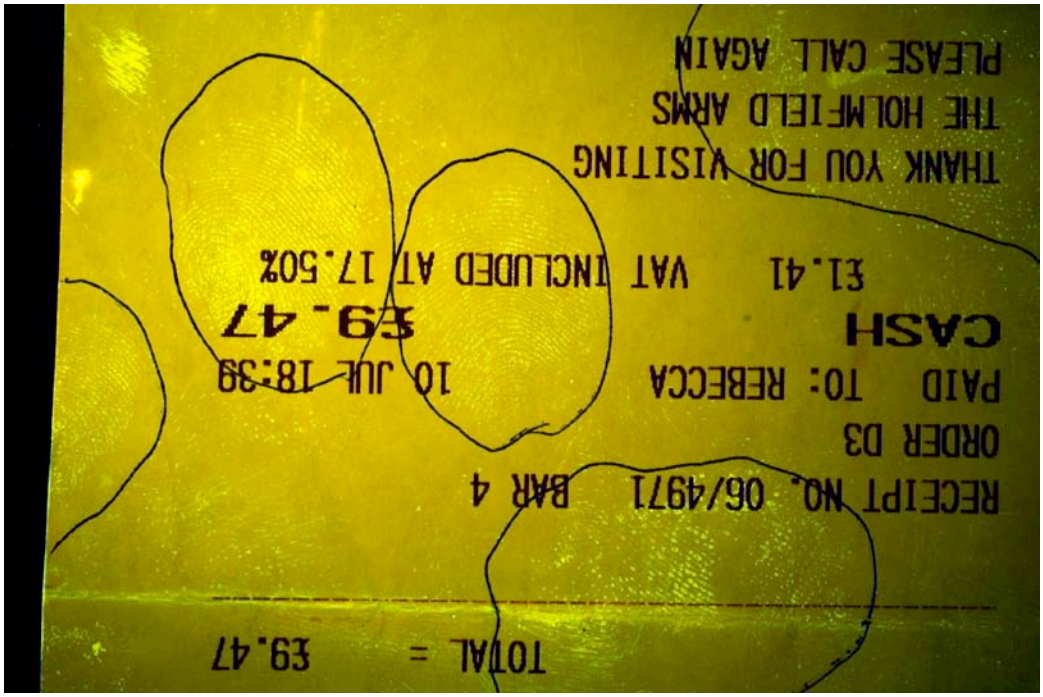
1.4 DMAC was later investigated as a fuming agent and was found by Brennan *et al.* [3] to give good ridge detail visualisation on a wide selection of substrates, with potential to be included in routine sequential examination procedures. Katzung [4] reported that prints developed using DMAC fuming showed yellow fluorescence under excitation using 360nm light sources and that he had managed to detect four-week-old prints using this method.

1.5 Although vapour phase fuming can offer an answer to problems associated with solvent based fingerprint techniques, some researchers have described the limitations and scope of the reagent's ability to produce visible prints. Sasson and Almog [5] concluded that although ninhydrin was a more general and versatile reagent, DMAC was preferable to ninhydrin on fresh prints (up to 72 hours old) in situations where the application of heat is not possible. Brennan [6] reported that for cases involving porous items other than thermal papers, all the prints developed by DMAC were subsequently developed by 1,8-diazafluoren-9-one (DFO), ninhydrin or physical developer and concluded that DMAC fuming was less effective than existing processes on such articles. On thermal papers, however, prints were developed on the thermal surface that would otherwise have been lost using other methods. This study was further reported by the Metropolitan Police Serious Crimes Unit [7] which emphasised the potential of vapour phase fuming with DMAC and subsequent visualisation of the fluorescence using a laser as a powerful non-destructive technique that does not interfere with following sequential treatments. It was regarded as having particular potential for detecting marks on thermal papers.

1.6 In the mid 1990s, the use of DMAC as a 'contact transfer' development process was proposed by Ramotowski [8] for development of fingerprints on paper. This approach involves pressing an exhibit between two sheets of paper that have been soaked with DMAC solution and subsequently dried, resulting in a pale yellow colouration to the paper and barely visible prints that give yellow fluorescence when illuminated with green light.

1.7 Experiments have also been carried out to investigate the use of the contact transfer process on the polymer banknotes used in Australia , looking at different temperatures and exposure times. Results indicated that contact transfer at room temperature was not particularly successful, with results demonstrating poor contrast between the notes and prints treated up to four hours. They also found that heat contact transfer at various temperatures using an ironing press for 20 seconds developed high background luminescence and the contrast between the developed

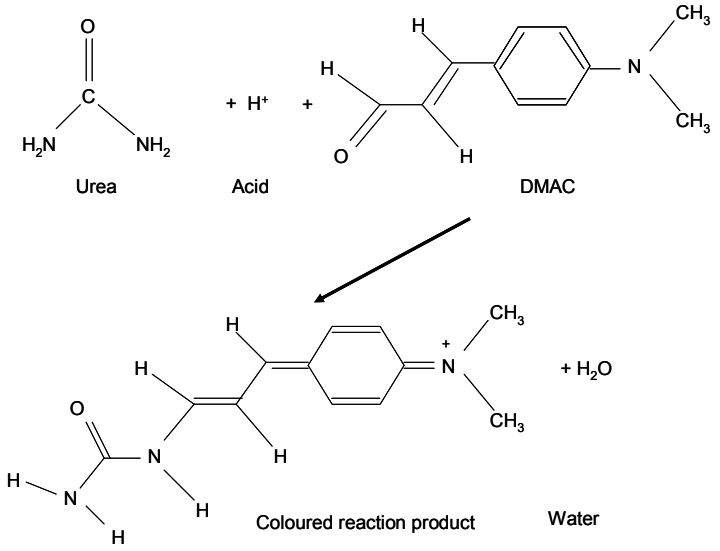
fingerprint and background was very low. The contact transfer technique has since been proposed for development of fingerprints on thermal papers with the stated advantages that it leaves the printed text intact and does not cause the thermal receipt to blacken during processing.



Fingerprints developed using contact transfer 4-dimethylaminocinnamaldehyde process.

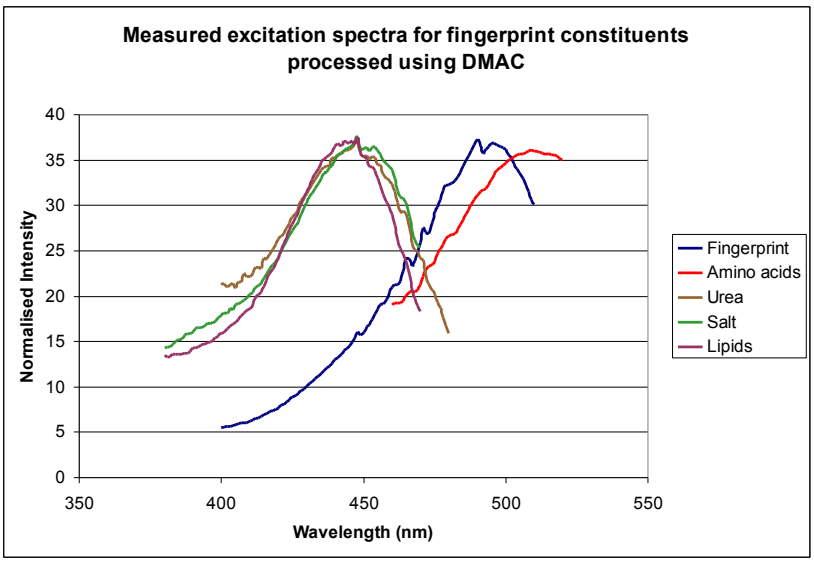
2. Theory

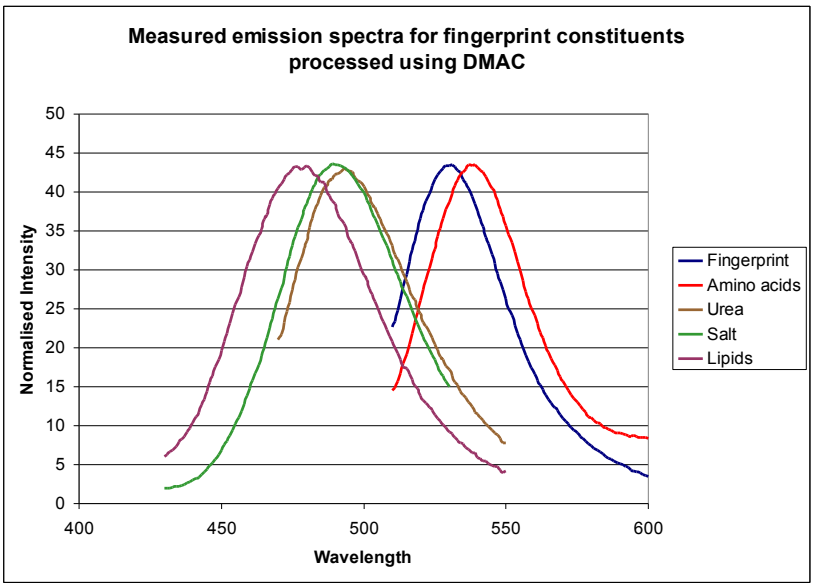
2.1 The reaction mechanism for the original solution treatment form of DMAC was the formation of a coloured Schiff base by the reaction between DMAC and urea under acidic conditions.



Proposed mechanism for formation of coloured product from reaction between 4-dimethylaminocinnamaldehyde and urea under acid conditions.

2.2 The precise mechanism by which fluorescence occurs in the contact transfer process is not known, but spectroscopy has been carried out by the Home Office Centre for Applied Science and Technology (CAST), which indicates that when used as a contact transfer process DMAC interacts with amino acid constituents in the fingerprint rather than urea. The nature of the fluorescent reaction products has not been determined.





Excitation and emission spectra obtained for filter paper pad impregnated with fingerprint deposits and model fingerprint constituents, then treated with the 4-dimethylaminocinnamaldehyde contact transfer process.

a) b)

Reaction products formed between 4- dimethylaminocinnamaldehyde and 0.1M solutions of amino acids and other fingerprint constituents a) visible and b) fluorescence.

2.3 The formulation originally used for solution dipping was a two-part system made up as follows.

Solution A: mix 650mL of 1,1,2-trifluorotrichloroethane (CFC113) with 350mL of absolute ethanol. Take 750mL of the mixed solvent, add 5g of DMAC and stir until dissolved, then make up to 1 litre with remainder of solvent, filter and store in a brown bottle.

Solution B: mix 650mL of CFC113 with 350mL of absolute ethanol. Add 20g of 5-sulphosalicylic acid and stir until dissolved.

2.4 A working solution is made by mixing together equal proportions of solutions A and B, and articles are then dipped. Spray application is possible, but in this case the surface to be treated is first sprayed with solution A, followed by a second spray of solution B.

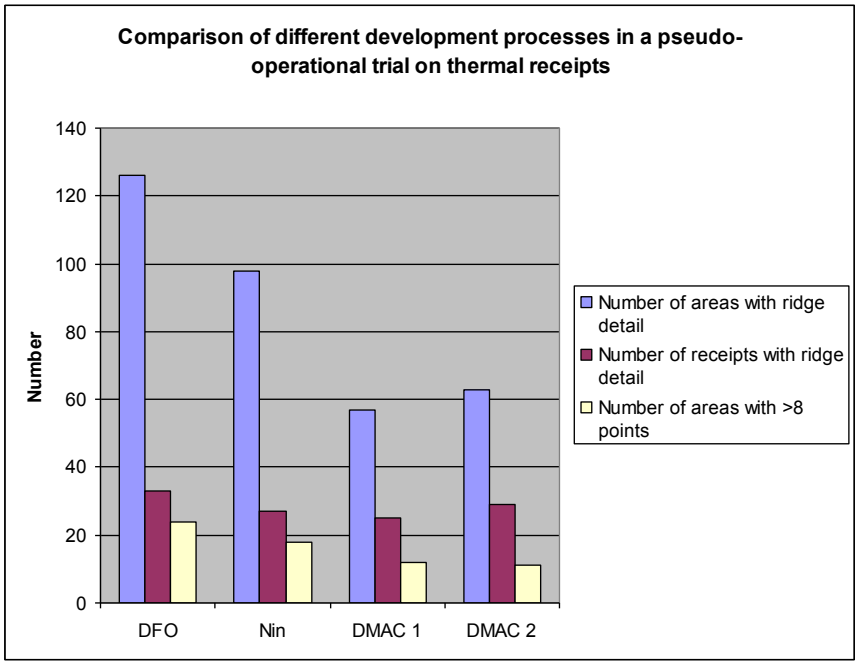
2.5 The contact transfer process utilises sheets of paper immersed in a solution of 0.25g of DMAC dissolved in 100mL of ethanol. The sheets are then allowed to dry. The article to be treated is sandwiched between two sheets of impregnated paper, placed in a press and left overnight.

3. Reasons technique is not recommended by CAST

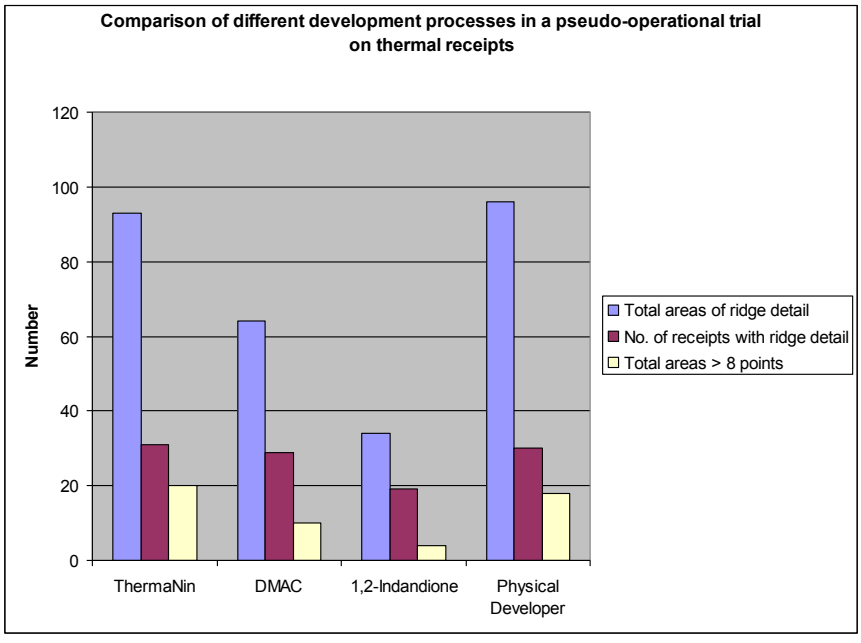
3.1 DMAC is not recommended by CAST in either solution dipping or contact transfer form. Operational experience in the 1970s demonstrated that the solution dipping process was not suitable for marks more than a few days old because of the rapid diffusion of the urea constituent. The solution dipping formulation is based on CFCs and would not be acceptable for use without reformulation to a less ozone-depleting solvent.

3.2 More recently, CAST conducted experiments to compare the effectiveness of DMAC against DFO and ninhydrin for cases where it is not necessary to retain printed text on thermal receipts. A further

comparison was conducted with ThermaNin, 1,2 indandione and physical developer for cases where it is necessary to retain printed text on thermal receipts. In both these cases, pseudo-operational trials confirmed laboratory experiments, and in neither case was DMAC found to be as effective as processes currently recommended by CAST [10,11,12].



a)



b)

Results of pseudo-operational trials conducted on batches of thermal receipts comparing the effectiveness of the contact transfer 4-dimethylaminocinnamaldehyde process with a) techniques removing printed text and b) techniques leaving printed text visible.

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5.3 Electrochemical techniques

5.3.1 Etching and electrodeposition

1. History

1.1 Untreated metal surfaces present an unusual problem for fingerprint development. While the majority of non-porous surfaces received in laboratories are effectively inert, in the case of metals there is the potential for chemical reactions to occur between constituents of the fingerprint (e.g. salts) and the metal surface. In extreme circumstances this can result in a permanent record of the fingerprint being etched into the metal surface. However, the interactions that occur are very dependent on the metals present and the particular constituents in the fingerprint, and reactions will only occur if conditions are favourable. In many cases the metal will be alloyed with other elements to inhibit such corrosion reactions occurring, e.g. 'stainless steel'.

1.2 It is possible to utilise the chemical reactions that can occur between a metal, the fingerprint constituents and a chemical solution to visualise fingerprints on this type of surface. Essentially, there are two generic types of technique that can be applied, etching and electrodeposition. In etching techniques, material is selectively dissolved from the surface and into solution. If the fingerprint constituents either enhance or inhibit the rate of etching at the fingerprint ridge relative to that of the background, there may be sufficient contrast produced to enable the fingerprint to be visualised. In electrodeposition the reverse is true. Metal is deposited from solution onto the surface and if the presence of the fingerprint constituents inhibits or accelerates growth of the deposit on the ridges relative to the rate of growth on the background, contrast will again be produced.

1.3 The primary sources of untreated metal surfaces are cartridge cases, which have always presented a problem for fingerprint development because of the conditions they are exposed to. High temperatures, abrasion and deposition of propellant residue all reduce the chances of recovering fingerprints and a variety of techniques have been considered. Given [1] investigated powdering techniques on brass and nickel-plated cartridges, but also included nitric acid fuming as a technique for selectively etching the metal. It was considered that sebaceous prints would protect the metal surface from corrosion, thus producing contrast.

1.4 Around the same time, Belcher was experimenting with techniques for developing fingerprints of different metals after heating [2,3]. He proposed dipping copper into solutions of brown photographic toner, and steel samples into liquid gun-blueing solution [2], later recommending potassium permanganate solution for cartridge casings with thin copper coatings [3]. In 1977 Belcher wrote to New Scotland Yard to propose the operational use of these techniques on articles recovered from terrorist

incidents and this prompted an investigation by the Police Scientific Development Branch (PSDB) into related techniques [4]. Among the chemicals investigated were: nitric acid, which showed some preferential etching of nickel-based cases; 5% selenic acid, which gave the 'gun blueing' effect on brass with some results on steel and nickel; copper sulphate, which etched nickel; sodium sulphide, which gave reasonable results on brass; and a solution of antimony in hydrochloric acid, which plated antimony onto the metal surfaces. Hydrochloric, sulphuric and hydroiodic acids gave no useful results. Vacuum metal deposition was noted to give reasonable results on most metal surfaces.

1.5 Interest in techniques for development of fingerprints on cartridges revived in the mid-1990s, with several papers on the subject being presented at the International Symposium on Fingerprint Detection and Identification in Israel in 1995. Saunders and Cantu [5] investigated the use of a modified physical developer, acidified silver nitrate and gun blueing for unfired cartridge casings and also compared superglue and gun blueing on a range of fired cases. It was found that the most effective combination was superglue, followed by gun blueing, although success rates on operational work were not as good as those observed experimentally.

1.6 Wiesner *et al.* [6] considered the effects of firing conditions on fingerprint development and compared gun-blueing, silver nitrate and superglue. The effects of gunpowder residue, friction and heating to high temperatures were studied. Of the techniques investigated gun blueing again exhibited most promise.

1.7 Migron *et al*. [7,8] considered the electrodeposition of palladium for the development of latent fingerprints and assessed a range of palladium compounds for this purpose. Good results were obtained for fingerprints on unfired cartridges and in some cases a preliminary etch of the surface using iodine also produced good images of the fingerprint. However, it proved difficult to develop marks on fired cartridges using this technique.

1.8 Bentsen *et al.* [9] tested a variety of electrodeposition techniques on fired cartridge cases using solutions of copper, nickel, chromium and tin sulphate at different concentrations and compared the results with those obtained by other techniques, including 4% selenious acid (the principal constituent of gun blueing solutions). Selenious acid had a higher sensitivity than the other electrodeposition techniques and therefore these were not studied further.

1.9 One issue sometimes experienced with the use of gun blue solutions was the overdevelopment of the blue surface coating formed. Cantu *et al.* [10] demonstrated that acidified hydrogen peroxide could be used to prevent overdevelopment and that the same solution could also be used to visualise sebaceous prints on metal surfaces by selectively etching the background.

1.10 There was a general consensus among researchers that gun blueing, either used singly or in combination with other processes such as superglue, was one of the most effective processes in revealing marks on brass surfaces. For other types of metal surface, such as aluminium, alternative formulations such as aluminium black were investigated [11,12]. These still contain selenious acid as the principal active constituent, but with a range of other chemicals making them more suited for use on aluminium.

1.11 More recent studies involving electrochemical techniques include an extensive comparative investigation conducted by the Bundeskriminalamt (BKA) [13] and an investigation conducted in the laboratories of Strathclyde Police [14]. The conclusions from both these studies indicate that optimum treatments may vary from metal to metal and that there may be some merit in combining techniques such as superglue and palladium deposition.

2. Theory

2.1 The chemical reactions associated with the principal electrochemical techniques are outlined below.

2.2 Silver nitrate: For silver nitrate on brass or copper surfaces, a reaction occurs between the silver in solution and the copper in exposed regions of the surface. This results in deposition of silver (as a grey deposit) on the surface.

$$2Ag^{+} + Cu \leftrightarrow 2Ag + Cu^{2+}$$

2.3 Gun blueing: The principal reaction occurring with gun blueing is associated with the reaction of selenious acid with metals, shown below.

$$H_2SeO_3 + 4H^{+} + 4e^{-} \leftrightarrow Se + 3H_2O \text{ (general reaction)}$$

2.4 Although selenious acid will work on a range of different metals, it is most suited to brass where parallel reactions occur between copper and zinc, and zinc and selenious acid, resulting in the formation of the black CuSe product on the surface.

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$
$$H_2SeO_3 + 4H^{+} + 2Zn \rightarrow Se + 3H_2O + 2Zn^{2+}$$
$$Se + Cu \rightarrow CuSe_{(black)}$$

2.5 Palladium deposition: Several different palladium compounds were investigated for palladium deposition and the reactions of those found most suited for this purpose with brass are shown below. In both cases a coating of grey palladium metal is formed on the surface.

$Zn/Cu + 2Na_2PdCl_4 \rightarrow Pd + ZnCl_2 + CuCl_2 + 4NaCl$
$2Zn/Cu + 2K_2PdCl_6 \rightarrow Pd + 2ZnCl_2 + 2CuCl_2 + 4KCl$

3. Reasons technique is not recommended by CAST

3.1 CAST does not currently (2011) recommend any electrochemical processes for fingerprint detection because their relative effectiveness has not been established. In addition, some of the chemicals used in the processes are highly corrosive and there are health and safety issues associated with their use. However, such processes may prove to be more effective than the techniques currently recommended and it is hoped that a planned comparative study between electrochemical techniques, scanning Kelvin probe and current techniques, such as superglue and vacuum metal deposition, will enable more detailed advice to be given.

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5.3.2 Heating and electrostatic powdering

1. History

1.1 A recent addition to the range of techniques that can be utilised for the visualisation of fingerprints on cartridge casing (and other metals) is the method developed by Dr John Bond at Northamptonshire Police [1-4]. This visualisation technique utilises the fact that salts and other components of fingerprint residue are capable of causing metals and their alloys to corrode. In the technique the metal surface is heated to promote further corrosion and oxidation of the surface, the combination of which may produce sufficient distinction in colour between the fingerprint ridges and the uncorroded metal for the mark to be seen without any further treatment. Further enhancement of the mark can be obtained by applying an electrostatic charge of 2.5kV to the surface, then applying carbon-coated spherical beads, as used in the electrostatic detection apparatus (ESDA) process (see Chapter 5.4), to the surface.

1.2 The technique was shown to work for a range of different metals and alloys [1,2] and to continue to develop marks after surfaces had been cleaned with water and acetone. The technique has attracted much

interest worldwide and has been used on operational casework dating back several years [3]. Research is ongoing to determine the corrosion mechanisms that operate in producing the fingerprint images [2,4], to look at the physical and chemical changes occurring at the surface, and also to measure anion and cation concentrations in eccrine sweat.

2. Theory

2.1 The theory associated with the process is that corrosion is locally initiated on the metal surface by the action of chloride ions in the fingerprint residues. In general, the process operating is:

$$M^{Z+} + ZCl^- + ZH_2O \rightarrow M(OH)_Z + Z(H^+ + Cl^-)$$

2.2 This process results in pitting corrosion penetrating into the metal surface. This localised pitting corrosion is then enhanced by the subsequent exposure to heat, where the colour change of the metal surface caused by oxidation may also aid visualisation of the fingerprint.

2.3 The corroded areas of the metal surface also have a surface potential to the uncorroded metal, and it is these differences that are exploited by electrostatic charging and subsequent powdering.

3. Reasons technique is not recommended by CAST

3.1 The Home Office Centre for Applied Science and Technology (CAST) does not currently (2011) recommend the process because its relative effectiveness has not been compared with both currently recommended processes and processes that are still under development, including the scanning Kelvin probe. Comparative studies are planned in the near future and more informed advice will then be given

3.2 When the process was used on operational casework in the UK, it was observed to cause detrimental effects to the striations in the surface that are used for ballistic analysis. This resulted in the use of the technique being suspended. These detrimental effects were attributed to the high temperature used for 'developing' the corrosion in the surface, and this temperature has subsequently been reduced to overcome this issue.

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5.4 Electrostatic detection apparatus (ESDA)

1. History

1.1 The Police Scientific Development Branch (PSDB) set up a general investigative contract with the London College of Printing in the early 1970s, with the purpose of exploring novel fingerprint detection methods and also methods for taking the fingerprints of prisoners. During this contract the electrostatic detection apparatus (ESDA) was proposed, originally for the detection of finger marks on fabrics [1-3]. In-house work at PSDB had indicated that the decay time for charged fingerprints on most materials was very short and that this precluded the use of direct charging and toning as an effective detection technique. The researchers at the London College of Printing overcame this by covering the surface being examined with a thin layer of Mylar (a polyester) and producing the charge image on this thin polymer film. The thin film was exposed to a corona charging device and then treated with an electrostatic image developer, in this case carrier beads mixed with a cascade toner.

1.2 At around the same time, Japanese researchers also demonstrated that electrostatic images of fingerprints could be transferred to thin polymer films from paper exhibits by sandwiching the paper between the polymer films and holding them in a steel press [4]. Upon separation, the electrostatic image on the polymer sheet was developed by scattering dielectric powders of sulphur, lead oxide and toner over the surface. However, this approach does not appear to have been progressed further and no practical apparatus appeared from this research.

1.3 Further PSDB-sponsored research demonstrated that the process was capable of developing fingerprints on surfaces, including papers and fabrics, but this was confined to fresh marks and those over 24 hours old did not generally produce acceptable images. Attempts to improve sensitivity were unsuccessful and therefore the work on fingerprints was terminated. However, during the course of these studies it had been observed that the technique was capable of revealing indented writing on paper and could give results superior to techniques then available, such as oblique lighting [5,6]. A further contract was placed by PSDB to develop apparatus specifically for enhancement of indenting writing and this was subsequently developed and manufactured as a commercial system by Foster and Freeman in the UK, with other manufacturers taking up the concept worldwide.

1.4 HO SRDB did revisit the electrostatic detection apparatus (ESDA) in the early 1980s to establish whether it was possible to explain some of the phenomena associated with the process and also to see if any advances in technology could be used to improve the speed or sensitivity of the process [7]. An experimental system utilising a scanning probe was developed during the course of these studies but was not progressed further. A large format ESDA system was also built with the intention of investigating the technique to screen large areas of fabric for contact

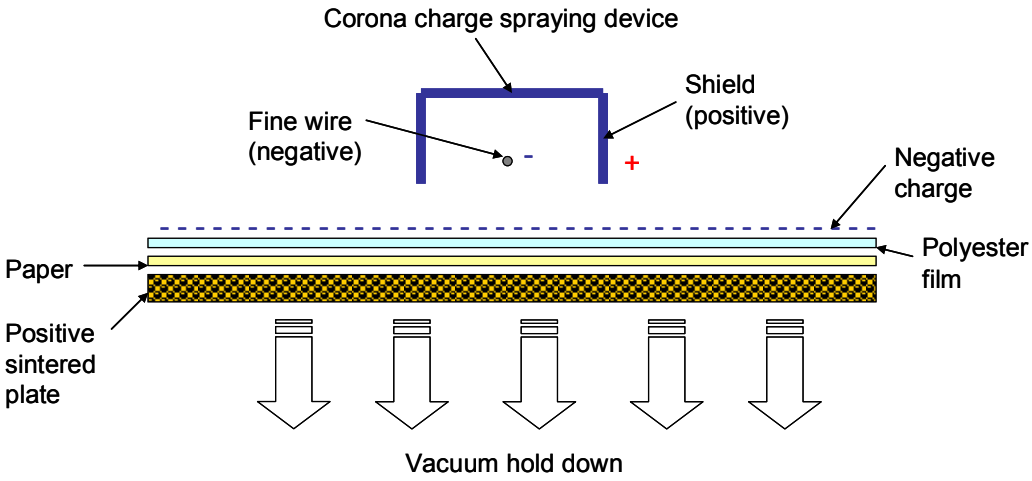
areas that could then be targeted using other, more sensitive techniques such as radioactive sulphur dioxide. This had limited success and was not taken forwards to production.

1.5 Although the ESDA system was primarily adopted for document analysis, research was carried out to establish an integrated forensic approach for document examination by examining whether treatment with ESDA could be detrimental to subsequent development of fingerprints. Initial results by Heath in 1983 [8] appeared to indicate that ESDA in general was detrimental to subsequent treatment with ninhydrin and that pre-humidification for five minutes prior to ESDA and ninhydrin treatment actually improved the quality of the fingerprints. This was contradicted in later studies by Moore [9] who found that pre-humidification of documents was detrimental to the development of fingerprints with ninhydrin, and that exposures for longer than 5–15 minutes were to be avoided. The pre-humidification effect was thought to be cumulative and repeat exposures of documents to pre-humidification and ESDA were to be avoided where possible. When it became known that pre-humidification enhanced the performance of ESDA for indented writing, HO SRDB almost immediately issued warnings that this could be detrimental to the detection of amino acids in fingerprints, particularly on some types of paper. A later study by Azoury *et al.* [10] looked at the effects of pre-humidification on fingerprint development by other amino acid reagents, including 1,8-diazafluoren-9-one (DFO) and 1,2 indandione. The results of Moore were confirmed and it was also shown that pre-humidification was detrimental to subsequent treatment with 1,2 indandione and less so to DFO, although exposures of over 60 minutes also began to degrade DFO development.

1.6 Although ESDA is found today in most UK police fingerprint laboratories, it is primarily used as a document analysis technique and if fingerprints are detected by the technique during document processing this is regarded as a bonus rather than an expected outcome.

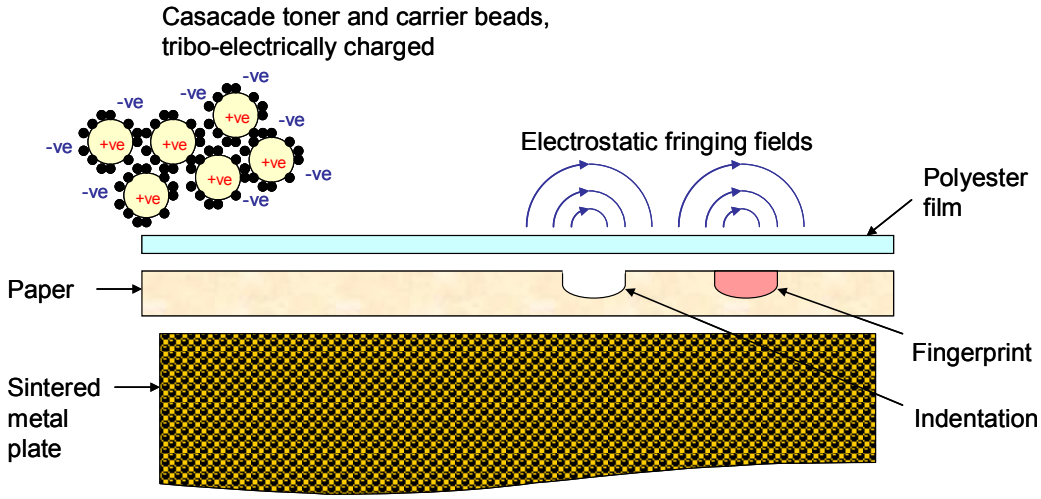
2. Theory

2.1 The mechanism of ESDA has not been conclusively established, but it is possible to describe the stages in the process. The porous exhibit to be treated is first held down on a sintered plate using a vacuum, and a thin (~3.5μm) film of Mylar laid over the top of it. This film is then negatively charged by passing a charge spraying device known as a corotron above the surface.

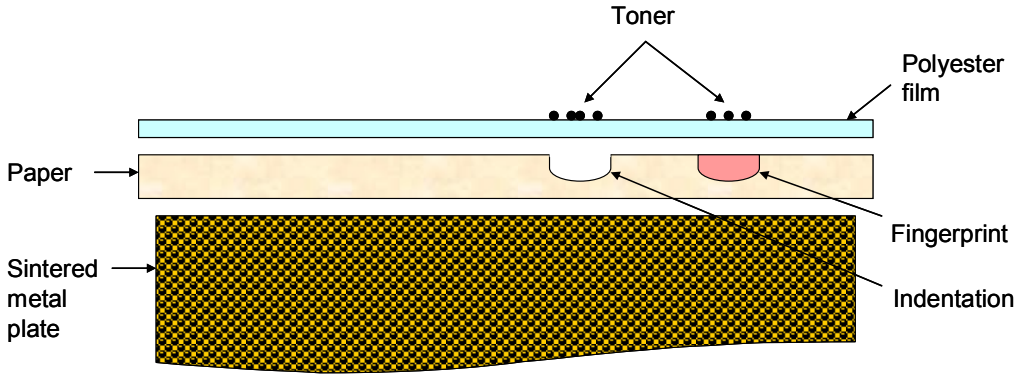


Schematic diagram of the general charging procedure for electrostatic detection apparatus.

2.2 The charging process sets up electrostatic fringing fields around features in the exhibit (the exact mechanisms of which are not precisely known). A mixture of carrier beads (fine glass spheres) and toner particles (carbon black) are cascaded across the surface, and the toner selectively adheres to areas where the fringing fields are present. This is illustrated schematically below.



a)



b)

Schematic diagrams showing toner development of electrostatic images a) development of electrostatic fringing fields on the polymer film and b) selective adherence of toner particles to regions where fields are present.

2.3 It was originally proposed that the fringing fields could be explained by a simple capacitance theory [6]. The indentations cause a local increase in capacitance due to a reduction in the distance between the charged surfaces and fingerprints, causing a local increase in capacitance because of the water in the fingerprint increasing the local dielectric constant. However, capacitance variations cannot be the only mechanism because it is noted that very deep impressions sometimes do not develop with ESDA.

2.4 It was later proposed that the indented writing effect could be explained by damage and abrasion of surface fibres caused by lateral movement between sheets of paper during the writing process [7]. The poor

performance often observed with glossy papers in the ESDA process may be explained by the fact that such papers are sized, calendared or highly loaded with inorganic filler.

2.5 Another theory proposed to explain the improved performance of ESDA often observed after pre-humidification of the article was termed 'surface variation theory' [11], which considered that after humidification the paper no longer behaved as a dielectric but as a conductor. In this theory the variation of electrostatic potential on the polymer film is a function of the degree of close contact between the polymer film and the paper, and also variation in surface features of the paper, such as glossiness and smoothness (which may also be modified by the presence of fingerprint residue). This could explain why deep indentations, where the film does not contact the paper, do not produce results using ESDA. As fingerprint residues are absorbed into the porous surface, their effect on the surface will reduce, which may explain the poor development observed on marks over 24 hours old. However, none of these mechanisms has been conclusively proven.

Fingerprints developed by electrostatic detection apparatus while processing a document.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the ESDA process as a primary fingerprint detection technique because it is less sensitive than other techniques for

developing fingerprints on porous surfaces, and is ineffective on marks more than 24 hours old. However, it may reveal fingerprints when used as part of an integrated strategy for retrieval of forensic evidence, ESDA being mostly non-destructive to fingerprint evidence unless pre-humidification is used. It is referred to as an additional development process in the 'Notes' section of the treatment chart for porous surfaces *Manual of Fingerprint Development Techniques* [12].

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5.5 Fuming techniques

1. History

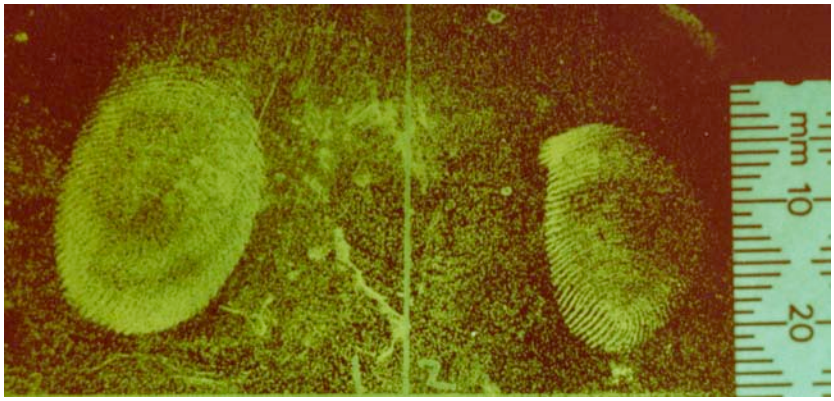
1.1 The development of fingerprints using fuming processes has been utilised since the early days of fingerprint identification. Iodine and osmium tetroxide were already known to develop fingerprints on porous surfaces by the 1920s and the fuming of a range of other substances has been investigated since then.

1.2 Several of the processes described in other chapters either involve fuming, e.g. superglue, or have been investigated as fuming techniques, e.g. 4-dimethylaminocinnamaldehyde (DMAC). Fuming has the potential advantages that it does not wet the article, which may be a benefit if subsequent document analysis is required, will permeate porous exhibits, and impinge upon all available surfaces for non-porous exhibits.

1.3 Fuming can be used to develop fingerprints in several ways, described in more detail in the section below. In a review of techniques for development of latent prints issued in 1974 [1], Micik lists three fuming techniques: iodine; hydrogen fluoride (for etching fingerprints on glass); and the burning of substances, including camphor and magnesium, to produce fumes that selectively deposited particles on fingerprint ridges.

1.4 Almog and Gabay [2] carried out an investigation into the development of fingerprints on paper by fuming several fluorescent chemicals. Good results were reported for anthranilic acid (for fresh marks), anthracene (for older marks) and antimony trichloride. In some cases the fluorescent chemical was selectively deposited on the ridges, in other cases deposition occurred on the background only.

1.5 The Home Office Scientific Research and Development Branch (HO SRDB) conducted a subsequent study into the anthracene fuming process [3], first investigating the optimisation of fuming conditions using fingerprints deposited on glass slides and then applying the optimised process to fingerprints on different types of plastic and metal surfaces. The potential benefits of vacuum deposition of anthracene were also explored. It was found that sublimation in air gave better results than vacuum deposition and although the process did develop fingerprints on plastics, it was not as effective as other processes already available. Results on metals were more promising and anthracene fuming was found to be more effective than iodine over a range of different metal surfaces.



Photograph of fingerprints on metal developed by anthracene fuming.

1.6 Haque [4] considered the fuming of naphthalene and camphor, followed by iodine fuming and dusting with magnetic powder. This multi-step process appeared to give excellent sensitivity on plastic bag substrates. The selective attack of polymer surfaces using the fumes of halogenated hydrocarbons such as dichloromethane and chloroform was also studied. The technique worked well on polystyrene, but was ineffective on vinyl and thermoset plastics, and did not work at all on polyethylene.

1.7 Fuming has also been reported in combination with other processes for the revelation of fingerprints. Meylan *et al.* described the fuming of ammonium hydrogen carbonate after exposure of a paper exhibit to a corona discharge [5]. This combined treatment produced fluorescent fingerprints that could be excited by ultraviolet light. This technique was further investigated by Davies *et al.* [6]; they carried out an analysis of the fluorescent products and suggested that lipid derivatives were responsible for the fluorescence observed.

1.8 In addition to the hydrofluoric acid fuming process mentioned by Micik for developing fingerprints on glass, other acid fuming techniques have been considered. Bentsen *et al*. [7] trialled nitric acid fuming for development of fingerprints on brass cartridge cases and Broniek and Knaap [8] proposed hydrochloric acid fuming as a technique for revealing fingerprints on thermal receipts. The highly corrosive nature of these substances meant that such techniques were not widely adopted for operational use because of the precautions required for their use.

1.9 A novel process that has been recently reported by Kelly *et. al*. is the use of disulphur dinitride, allowed to sublime under a static vacuum [9]. This has been shown to be capable of developing fingerprints on a wide range of surfaces, including paper, fabric, clingfilm and metals, possibly by formation of the blue-black sulphur-nitrogen backbone (SN_x) polymer.

2. Theory

2.1 Because many different types of substance have been used as fuming techniques for the development of fingerprints, there is no single mechanism that applies to all chemicals. A range of mechanisms may operate and some of these are outlined below.

2.2 Absorption of coloured vapours into fingerprint residues – this is the mechanism that occurs for iodine (and other halogens, such as bromine).

2.3 Chemical reaction between fumes and fingerprint residues to form a coloured or fluorescent reaction product, e.g. the black product formed by osmium tetroxide fumes.

2.4 Catalysis of a polymerisation reaction by fingerprint residues, promoting growth of a solid phase from gaseous fumes – this is the case for the superglue process and also possibly the recently reported disulphur dinitride process [9].

2.5 Selective deposition of particulates on fingerprint ridges (or background) – this is observed for fuming of anthracene, camphor and naphthalene.

2.6 Selective etching/attack of ridges (or background) by fumes of acid or other substance – this can be seen for hydrogen fluoride on glass, nitric acid on brass, and chloroform on polystyrene.

3. Reasons technique is not recommended by CAST

3.1 CAST does recommend two fuming processes, iodine and superglue (Chapters 5.10 and 3.10 respectively in this book), in the *Manual of Fingerprint Development Techniques* [10]. Other fuming techniques are not recommended because they are either less effective than other techniques (e.g. anthracene) or there are health and safety issues associated with their use. In particular, there are concerns about the fuming of concentrated acids because they are highly corrosive. In general, all fuming processes need to be well-contained and carried out in areas with good ventilation.

4. References

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5.6 Gelatine lifting

1. History

1.1 Gelatine lifting has been used for the recovery of fingerprints from the early 20th century. The concept was first proposed in 1913 for lifting of marks powdered with lead acetate and subsequently treated with hydrogen sulphide. The lifting medium used in this case was a paper coated with a gelatine/glycerol mix [1]. Gelatine lifting was not widely adopted for fingerprint lifting at that time, but the lifting concept was further investigated for the recovery of footwear marks [2]. By the late 1970s several rubber- and gelatine-based lifters were commercially available for the lifting of footwear marks, including latent marks in dust and dried contaminant, and marks developed by powdering. Experiments conducted by the Police Scientific Development Branch (PSDB) in the early 1970s utilised gelatine films to lift marks developed using vacuum metal deposition from patterned surfaces [3]. Physical developer was then used to intensify the images of the lifted marks. This was reasonably successful, but a high contrast mark developed using vacuum metal deposition was required as a starting point.

1.2 There has been subsequent research into the broader forensic applications of gelatine lifts. The mildly adhesive nature of the gelatine lift combined with a degree of flexibility and compressibility makes them well suited for the lifting of trace evidence from a range of surfaces, without causing significant damage to the surface itself.

1.3 As a consequence of these studies, gelatine lifts are now marketed for the lifting of footwear marks [4,5,6], the lifting of paint and other micro traces [4], recording patterns around bullet holes [4] and the lifting of blood traces from surfaces [4]. They have also been shown to be effective in detecting indented writing, and in comparisons with the electrostatic detection apparatus (ESDA) technique (see Chapter 5.4) have shown better performance than ESDA on thick, glossy paper types, and to be capable of being used sequentially after ESDA on documents [7].

1.4 The principal application of gelatine lifts has remained the lifting of fingerprint and footwear evidence, both latent marks and marks developed using processes such as powders and superglue. Gelatine lifts are currently (2011) available in black, white and clear forms, and because they are flexible and can be compressed against a surface on application, they are better suited to lifting of powdered marks from textured surfaces than some types of tape. The colour of the lift can be selected to give optimum contrast with the powder used, and the lifts are better suited for lifting and subsequent imaging of marks powdered with granular and magnetic powders [4].

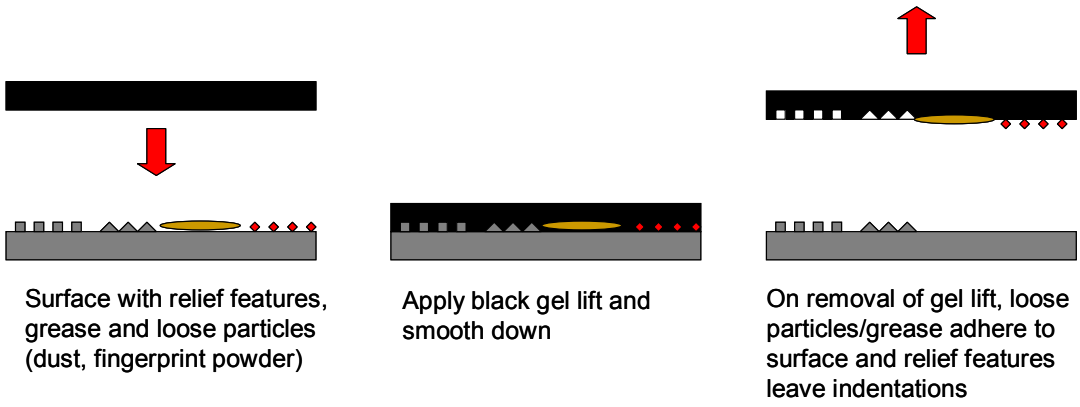
1.5 The gelatine lifting process has also been shown to be a potentially useful technique in recovering marks for subsequent chemical analysis.

The gelatine lift acts as a transfer medium for marks lifted from a scene to be transported back to a laboratory for subsequent compositional analysis [8].

1.6 The recent (circa 2005) development of specialist imaging equipment for the enhancement of marks lifted on black gelatine lifts (GLScan, produced by BVDA, Haarlem, Netherlands) has increased interest in the use of gelatine lifts for the recovery of latent fingerprints prior to chemical development. Several police forces in the UK have proposed the use of the technique as an alternative to powdering. This chapter deals with the application of gelatine lifting as the sole recovery process for latent fingerprints, as opposed to a lifting process for marks developed using other processes, such as powdering or superglue.

2. Theory

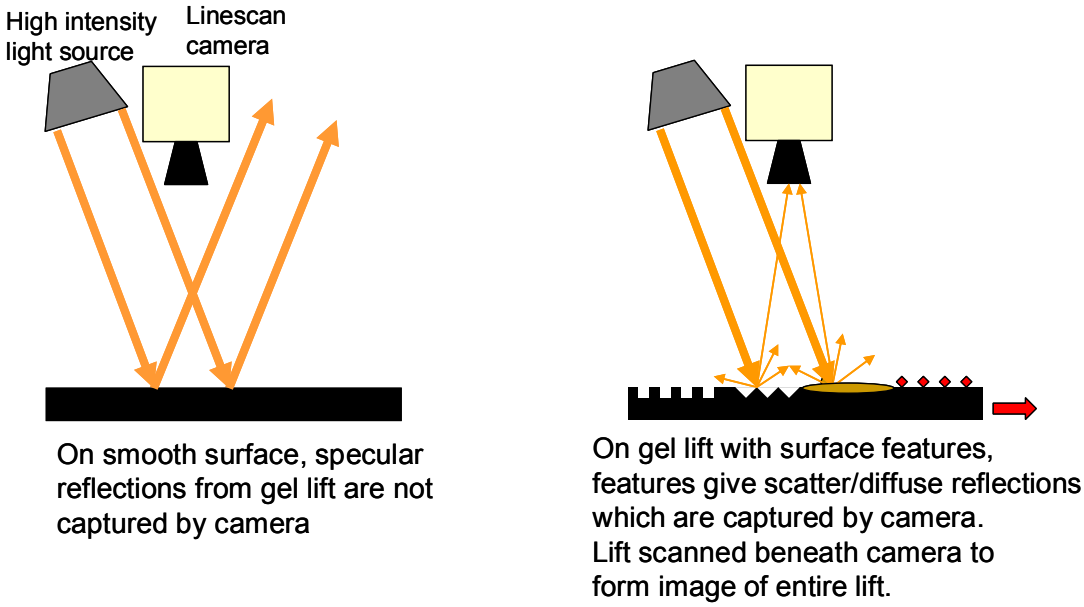
2.1 The theory behind the gelatine-lifting technique is that the gelatine is able to deform to the surface contours during application and smoothing in place. The slight adhesive nature of the surface also means that on removal of the gelatine lift, some of the loose particulate matter and any grease on the surface will be transferred to the surface of the gel. The gel may also retain some impression of the contours of the surface it has been applied to.



Schematic diagram showing how gelatine lifts can lift and reproduce surface features.

2.2 The surface features retained on the lift are then imaged in a way that maximises the contrast between the surface feature and the black background of the lift. This can be carried out using photography in a dark room with the light source perpendicular to the surface and close to the imaging system. Alternatively a specialist imaging system such as the BVDA GLScan may be used. The GLScan system consists of a line scan camera combined with high intensity white light illuminating the gel at an angle close to perpendicular to the surface. The gel itself is mounted on a vacuum stage drawing it flat, and then scanned slowly by moving the vacuum stage underneath the fixed focus position of the line

scan camera. The principle common to both imaging methods is that with nothing on the gel, the specular reflection from the surface means that no light is reflected into the camera and the background appears black. The particulates and grease on the surface scatter light and produce diffuse reflections, meaning that some light reaches the camera and those regions appear lighter.



Schematic diagram showing the way in which images are produced in the GLScan system.

2.3 An example of a section of a gelatine lift taken from a door handle and scanned on GLScan equipment is illustrated below.

Example of a series of latent marks lifted from a door handle using a gelatine lift and imaged on a GLScan system (greyscale inverted).

3. CAST processes

3.1 The Home Office Centre for Applied Science and Technology (CAST) recommends using the process in accord with the gel manufacturer's instructions, peeling the acetate from the gelatine lift and applying it to the surface being treated. The gel is then smoothed in place to remove air bubbles. It may be beneficial to leave the gel in place for several minutes or to warm it slightly, but CAST has no data to conclusively demonstrate the benefit of either of these approaches.

3.2 'Gelatine' lifts can be obtained from more than one manufacturer, the principal supplier being BVDA (Haarlem, Netherlands). A rubber-based lifter is available from Dycem (Bristol, UK) for the same applications and there are other producers of similar products worldwide. It is not possible to recommend a single type of lifter for all applications. In general the BVDA lifts have been found to have higher tack and be more effective than the Dycem lifts, but in some cases the higher tack of the BVDA lift may cause damage to the surface. The ultimate selection of lifter by the user must take these factors into account.

3.3 Once lifted, the gelatine lift should be stored without a cover material, if at all possible, and imaged as soon as it is retrieved to the laboratory. This is because any lifted latent marks will progressively degrade and the reapplication of a cover material exacerbates this.

3.4 Imaging of the lift should be carried out under the conditions outlined in the 'Theory' section above. However, they should also be examined under oblique lighting. This is because any lifted marks in dust are best visualised under oblique light but may not be so prominent under the specular lighting conditions used to capture greasy deposits.

4. Critical issues

4.1 The temperature of the surface to be lifted must be below 40°C otherwise the gelatine lift may melt on the surface.

4.2 The gelatine lift must be smoothed in place to eliminate air bubbles, enabling all parts of the surface to come into contact with the lifting material.

4.3 The lift should ideally be stored without a cover and imaged as soon as possible after lifting, to reduce degradation in the quality of the lifted marks.

5. Application

5.1 Suitable surfaces: Gelatine lifts are suitable for use on all smooth non-porous surfaces where they can be readily formed to the shape of the surface. They can also be used on surfaces where a layer of contaminant is present. It is possible to use gelatine lifts on textured, semi-porous and porous surfaces, but their effectiveness is considerably reduced.

5.2 There are no special application methods for the gelatine lifts other than those recommended by the manufacturer [4]. The lifts may be cut to shape to suit the article or surface they are being applied to.

5.3 Gelatine lifting is recommended for situations where the primary processes in the *Manual of Fingerprint Development Techniques* [9] may not be applicable, primarily as an alternative to powdering. Such circumstances may include the following.

- Heavily contaminated surfaces where marks are visible in the contaminant, but cannot be imaged in situ and chemical development is not feasible.
- Articles that cannot be chemically treated and/or the application of powders may leave permanent traces or have a risk of damage (e.g. electrical equipment such as laptops, valuable antiques, etc.).
- Areas that are not easy to reach using powdering and where any developed marks would be difficult to see (e.g. on the inside of door handles).

6. Alternative formulations and processes

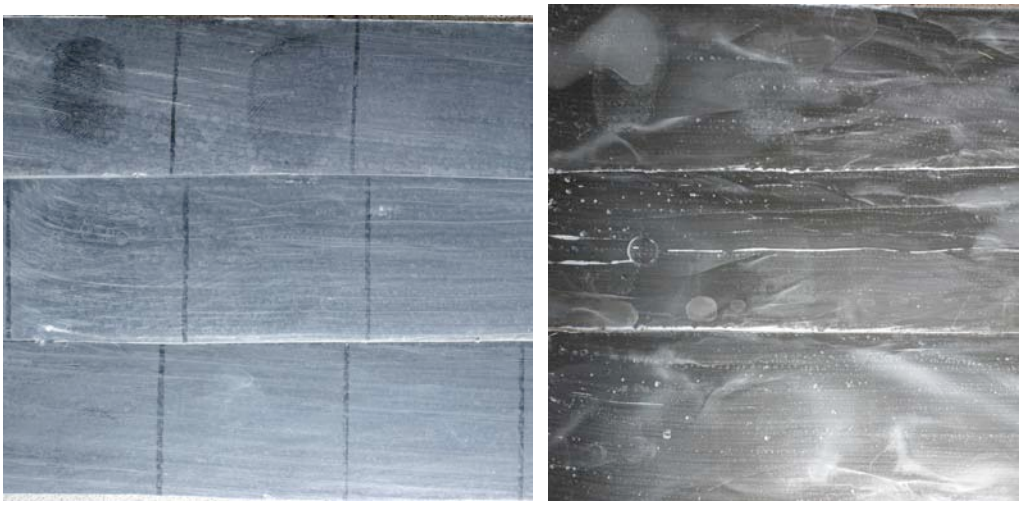
6.1 As alluded to above, there are several different types of gelatine lifter on the market. The only ones evaluated by HOSDB are the BVDA Black Gelatin Lift and the Dycem High Performance Evidence Lifter. Both of these have advantages and disadvantages and the user is encouraged to make a judgement on which lift to use according to the individual circumstances of the scene.

6.2 Silicone casting compounds have also been used to lift latent marks from surfaces, but in this case the lifted marks are not imaged directly on the surface, but are first developed using another enhancement process such as superglue [10].

7. Post-treatments

7.1 In some circumstances it may be able to enhance the latent marks lifted by a secondary chemical process. Attempts have been made to enhance marks lifted on both Dycem and BVDA lifters using white powder suspensions and superglue, which were selected to give maximum contrast with the black lift.

7.2 The results obtained for some donors on post-treated lifts are shown below.



a) b)

c)

d)

Post-recovery enhancement of marks on gelatine lifts a) white powder suspension on BVDA lift b) white powder suspension on Dycem lift c) superglue on BVDA lift and d) superglue on Dycem lift.

7.3 The results suggest that although there is little benefit in applying subsequent chemical treatments to BVDA gels, chemical treatment (superglue in particular) of Dycem gel lifts may improve marks in some cases or even develop additional marks, in particular for superglue treatment. This is in accordance with observations made by other researchers using silicone rubber-based casting compounds [10].

8. Validation and operational experience

8.1 Laboratory trials

8.1.1 CAST has carried out a direct comparison of the effectiveness of gelatine lifting with powdering [11]. This study compared gelatine lifting using black gelatine lifts produced by BVDA with the powdering process found to be most appropriate to the particular surface type being studied, according to guidelines published by CAST [12]. In this study six surfaces, representative of those found at crime scenes, were used:

- glass;
- u-PVC;
- painted metal;
- laminate (fake textured granite);
- laminate (fake ash);
- silk painted plasterboard.

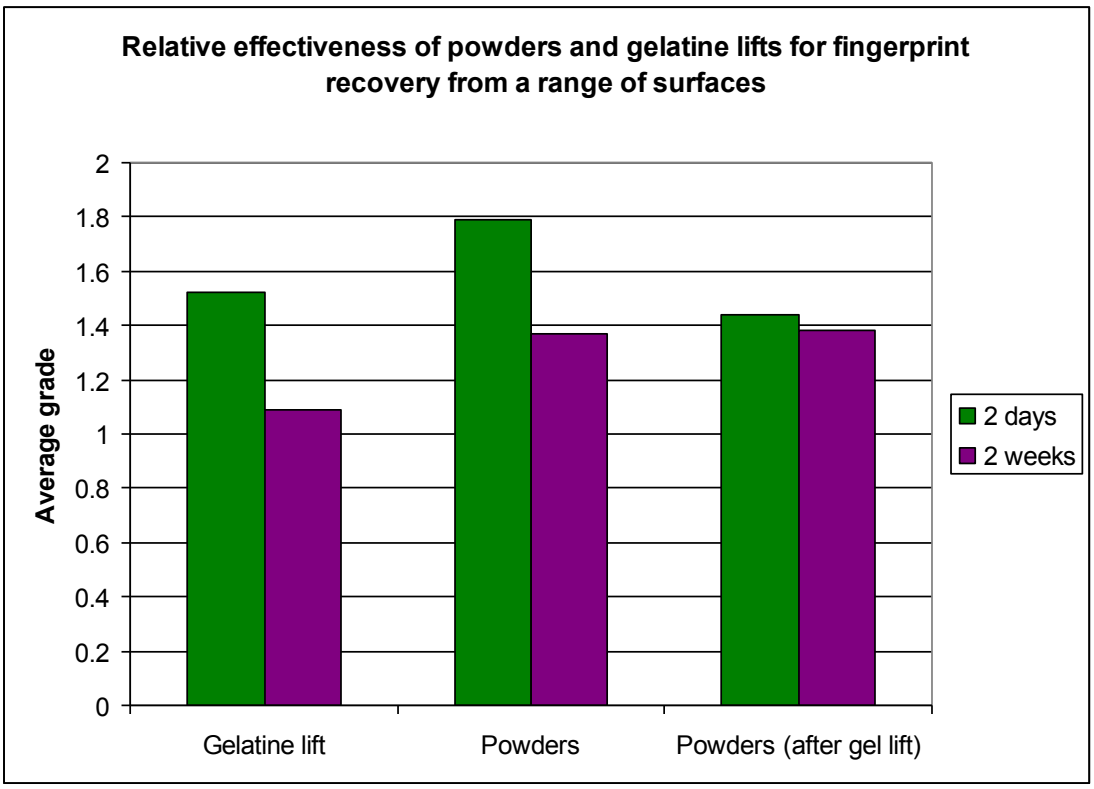
8.1.2 In this trial 70 separate donors were used, each depositing three fingerprints on each of the six surfaces. Donors were asked to wait at least 30 minutes after washing their hands before deposition of the marks, rubbing their hands together before deposition to evenly

distribute the sweat over the entire surface. No 'grooming' of marks (i.e. rubbing fingers on nose or forehead) was permitted.

8.1.3 The surfaces were then aged for periods of two days and two weeks. The marks were processed by three different routes:

- gelatine lift of the latent mark and subsequent imaging on the GLScan;
- application of fingerprint powder according to recommendations of the CAST *Fingerprint Powders Guidelines* [12];
- application of fingerprint powder as above, but on the same surface previously treated with the gelatine lift.

8.1.4 The results of the experiment to compare relative process effectiveness are shown below, with the average grade of developed mark across all 70 donors being compared for powdering and gel lifting.



Results of the experiment to compare the effectiveness of gelatine lifting and powdering for fingerprint recovery.

8.1.5 The information depicted in the graph shows that for both powdering and gelatine lifting used as a single process there is a drop in the average grade of marks developed as the age of the mark increases from two days to two weeks. This is consistent with trends seen in previous studies of the powdering process.

8.1.6 It can also be seen that for both ages of fingerprint, powdering gives superior results to gelatine lifting.

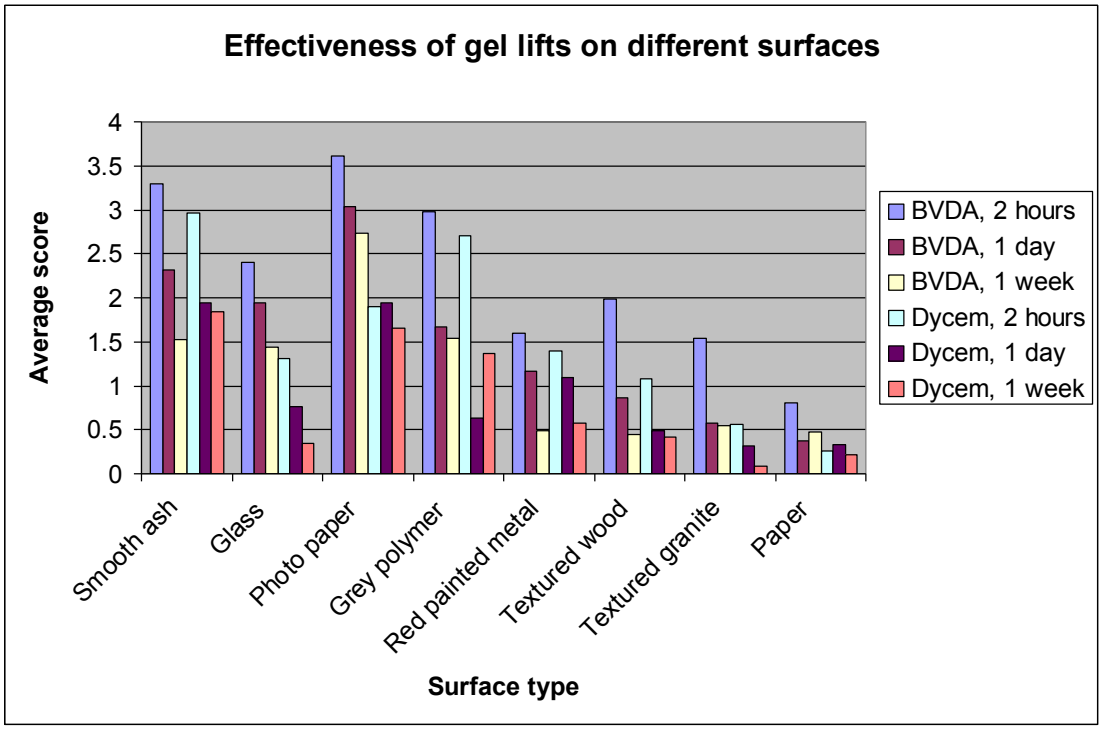
8.1.7 For two-day-old marks, the average grade of powdered marks is reduced by 20% if the gelatine lift is applied prior to powdering. Gelatine lifting transfers some of the residue to the lift, hence reducing the amount of material left on the surface for powders to adhere to. For two-week-old marks, application of the gelatine lift prior to powdering is far less detrimental because the mark has hardened and less residue is transferred.

8.1.8 A second study [13] was carried out to establish the relative effectiveness of two types of lifter (BVDA and Dycem) across surfaces ranging from smooth non-porous through rough non-porous to porous surfaces. The following surfaces were used in the study:

- glass;
- glossy photographic paper;
- laminate (fake smooth ash);
- grey polypropylene polymer;
- red painted metal (car paint scheme);
- laminate (fake textured oak);
- laminate (fake textured granite);
- printer paper.

8.1.9 Depletion series of nine marks were deposited by a range of six to seven donors (depending on the size of the surface used for deposition) using the same process described above. Marks were aged for two hours, one day and one week prior to gel lifting.

8.1.10 The results of this study are summarised in the graph below, which shows the average score across all marks deposited.



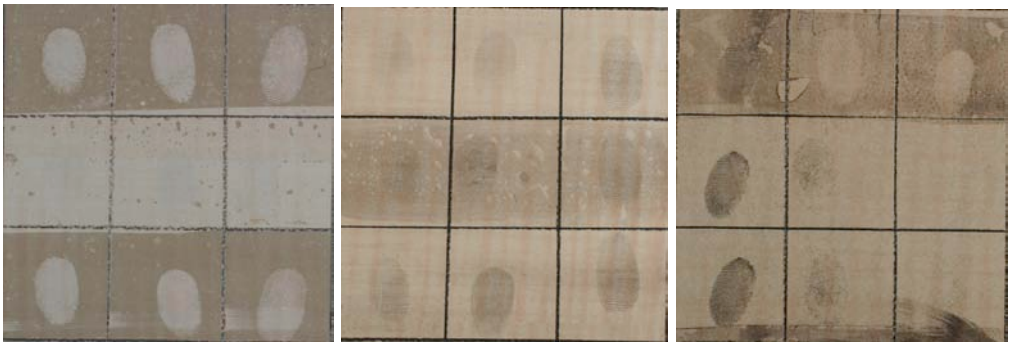
Graph showing the effectiveness of gelatine lifting on different surfaces and on marks of different age.

8.1.11 The BVDA gel lifts were found to be more effective than Dycem lifters on all the surfaces studied to date (2008), and this is consistent with the greater surface tack of the BVDA gel when the protective acetate sheet is removed. However, the potential of the higher tack BVDA lifts to cause surface damage should be recognised.

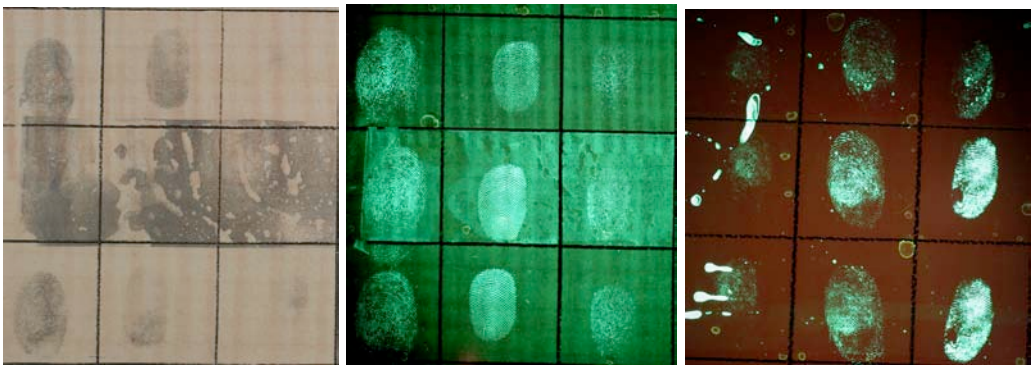
8.1.12 The effectiveness of gel lifts was seen to decrease as surface roughness and porosity increases.

8.1.13 In accordance with the initial study above, it can be seen that the effectiveness of gelatine lifting decreases as the age of the mark increases, and that significant degradation in the average score of lifted marks actually occurs in the period between two hours and one day after deposition.

8.1.14 Further experiments were carried out to establish if gelatine lifting could be used in sequence with other processes. It was shown that both types of lifter could be detrimental to subsequent treatment, but that it was not always possible to tell which combination of lifting material, surface and subsequent development technique would cause problems. The use of gelatine lifting as a development process is therefore not recommended if further treatments are likely to be carried out to the surface.



a) b) c)



d) e) f)

The effects of gelatine lifting on subsequent fingerprint development processes a) vacuum metal deposition on fake ash laminate b) black magnetic powder on fake ash laminate c) black powder suspensions on fake ash laminate d) Magneta flake powder on fake ash laminate e) superglue/basic yellow 40 on fake ash laminate and f) superglue/basic yellow 40 on painted metal. Top row = lifted with BVDA lift, middle row = lifted with Dycem lift and bottom row = control (no lifter applied).

8.2 Pseudo-operational trials and operational experience

8.2.1 No fully recorded pseudo-operational trials have been conducted on gelatine lifting, although small-scale exercises have been conducted on 'real' surfaces by HOSDB to see what types of item the technique can recover marks from. These were articles and surfaces tested during a tour around the laboratories and common areas at HOSDB, without any pre-planting of marks. Surfaces that marks were successfully lifted from included: soft drinks cans, coffee mugs, door handles and push plates, glass windows, wooden pool cue handle, bench top, credit card, pens, guns and glossy magazine covers.

8.2.2 Operationally there are few situations where the process should be used in preference to powdering using the optimum brush/powder combination, but there are some police forces using the technique routinely for lifting of latent marks. One widely publicised success was obtained from gelatine lifting a mark in grease from the ceiling of an

abattoir. This mark could not be powdered because of contamination, could not be chemically treated because of the difficulties in washing chemicals over the ceiling, and was difficult to photograph in situ because of it being on a white background.

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5.7 1,2 Indandione

1. History

1.1 1,2 Indandione was first proposed as a fingerprint development reagent in 1997 [1,2], following observations by researchers at the University of Pennsylvania that it reacted with amino acids to give products that were both coloured (pink) and fluorescent. A range of analogues were also developed in this study, but only 1,2 indandione has been extensively researched since.

1.2 1,2 Indandione is applied in a very similar way to 1,8-diazafluoren-9-one (DFO) and ninhydrin, drawing the exhibit through a bath of solution, allowing it to dry and then placing it in an oven to develop the marks. The initial observations of both coloured and fluorescent reaction products prompted more detailed investigations of the reagent in comparison to the ninhydrin and DFO formulations then in common use [3,4]. Both these studies indicated that 1,2 indandione merited further study, with results equivalent to DFO being obtained in laboratory tests. However, it was also observed that sequential treatments using combinations of ninhydrin and 1,2 indandione were not particularly effective [3].

1.3 Further studies were carried out in both Israel [5] and by the Police Scientific Development Branch (PSDB) in the UK [6] to establish the optimum processing conditions for 1,2 indandione, although these arrived at different conclusions. The Israeli researchers found that a formulation free of acetic acid gave the best results, and suggested processing conditions of 20 minutes at 100ºC and 60% relative humidity, whereas the UK research identified an optimal level of acetic acid to promote fluorescence and suggested processing for 10 minutes at 100ºC and 0% relative humidity. Variable results have since been obtained from 1,2 indandione at different laboratories worldwide and it has been concluded that humidity is very important in the development process and variations in local humidity conditions affect the results obtained.

1.4 However, both the Israeli and UK research provided further evidence that 1,2 indandione justified operational trials, PSDB [6] finding it giving equivalent results to DFO on batches of 75 cheques and a range of representative porous items, and the Israelis [5] reporting an improved performance over DFO on a pseudo-operational trial conducted over batches of 500 cheques per process. Once again it was found that using ninhydrin in sequence after 1,2 indandione developed few, if any, additional marks.

1.5 Based on these results, the process was adopted for operational use in Israel and taken forward into a full operational trial in the UK [7]. In the UK operational trials the performance of 1,2 indandione was the least effective of the formulations under test and was consequently not recommended for operational use. A similar operational trial in Canada

[8] arrived at similar conclusions and in both countries DFO remained the technique of choice.

1.6 1,2 Indandione has become more widely used in Australia and Israel and to some extent in the USA, and further research into the reagent has been conducted in all three countries. Stimac [9] has proposed a formulation of 1,2 indandione for use with thermal papers and Azoury *et al.* [10] have reported that the treatment of exhibits with 1,2 indandione is not detrimental to subsequent DNA profiling. However, a survey conducted into the usage of chemical treatments worldwide demonstrated that 1,2 indandione was still not in widespread use in many countries and in some cases the respondents were not aware of it at all [11].

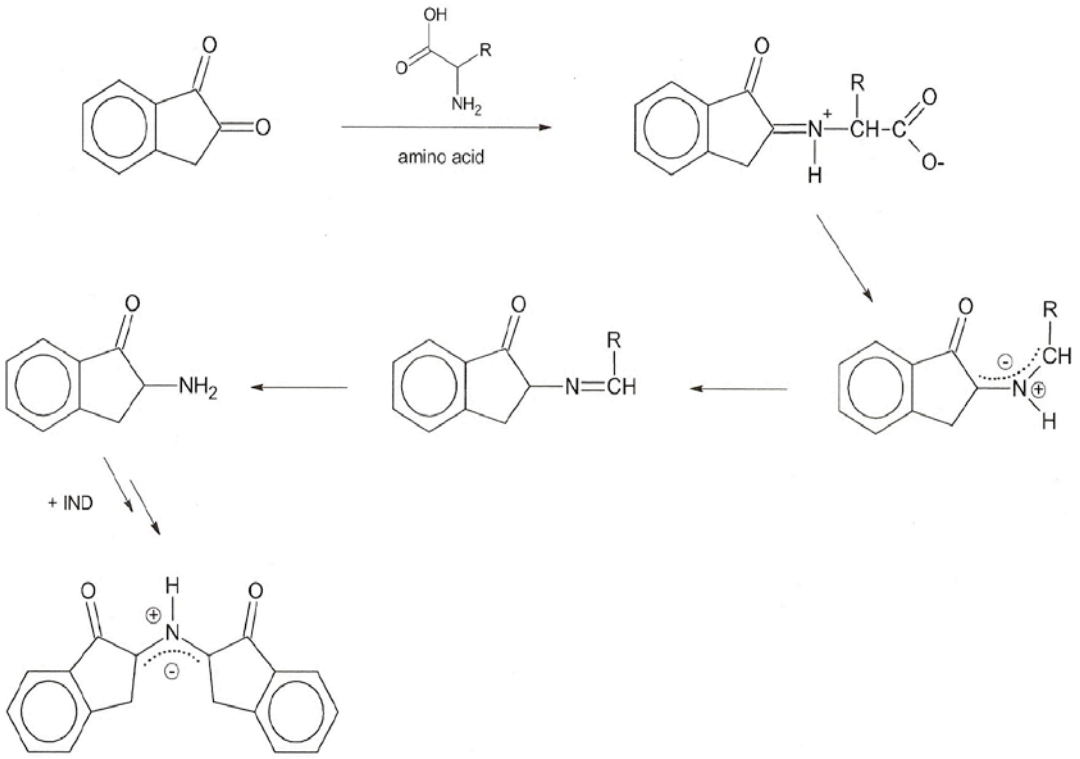
1.7 The lack of widespread use may partly be attributed to the variable results that were obtained worldwide, in some cases different cities in the same country giving very different results according to local weather conditions. As a consequence optimised formulations differed according to local humidity and environment. More recently, a potential solution to this problem has been identified. In early assessments of 1,2 indandione it was noted that the fluorescence may be enhanced by toning with metal salts in a similar manner to ninhydrin [3]. It has recently been shown that by adding zinc salts to the treatment solution the fluorescence of the mark can be enhanced without the need for a post-treatment and the resultant formulation is considerably more resilient to local fluctuations in humidity and environment [12,13]. Optimised formulations were developed for use under Australian conditions, with the best results claimed after hot-pressing at 165ºC for 10 seconds. The development of this formulation prompted further studies by HOSDB to see whether this offered a credible alternative to or replacement for DFO in the UK [14,15]. Comparative studies were carried out of the formulations recommended by Australian and US researchers in 2007 alongside the PSDB formula used in the late 1999 comparison with DFO, with zinc salts added into the formula. In this study the modified HOSDB formulation was found to be most effective and was compared with DFO in a further comparison. The results of this experiment are reported below, and showed the performance of 1,2 indandione-zinc to be closely equivalent to DFO.

1.8 Further work has since been carried out by the Australian and US research teams in further optimising formulations. Bicknell and Ramotowski in the US further refined the reagent formulation and found it to out-perform DFO [16]. They also observed that although the stability of the 1,2 indandione-zinc system to humidity fluctuations was much improved, the humidity level in the paper after dipping did have an influence on the subsequent development route. For papers below a critical humidity level (approximately 70%), treatment in a humidity oven using ninhydrin processing conditions was recommended, whereas for papers with humidity content above this level a dry oven and DFO processing conditions gave best results.

1.9 CAST is aware that the US researchers have produced a further modification to the 1,2 indandione-zinc formulation and have directly observed it to perform better than the HOSDB DFO formulation in small-scale comparative trials. This formulation is based on petroleum ether and would not be recommended for operational use in the UK, but could form the starting point for more reformulation studies. There has also been a further comparative trial between 1,2 indandione-zinc and DFO in Australia, which again reinforces the fact that 1,2 indandione-zinc may need further investigation to see if it could replace DFO. One element of these studies will be to assess whether the DFO-ninhydrin sequence gives more marks than 1,2 indandione-ninhydrin, because sequential processing must be considered in addition to the single most effective process.

2. Theory

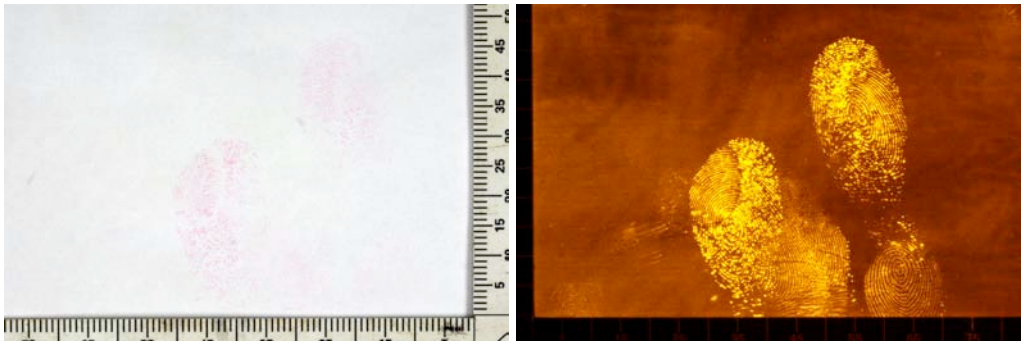
2.1 1,2 Indandione is closely related to ninhydrin and it has been proposed that its reaction with amino acids follows a very similar pathway, one suggested reaction path being illustrated below.



Proposed reaction pathway for 1,2 indandione with amino acids.

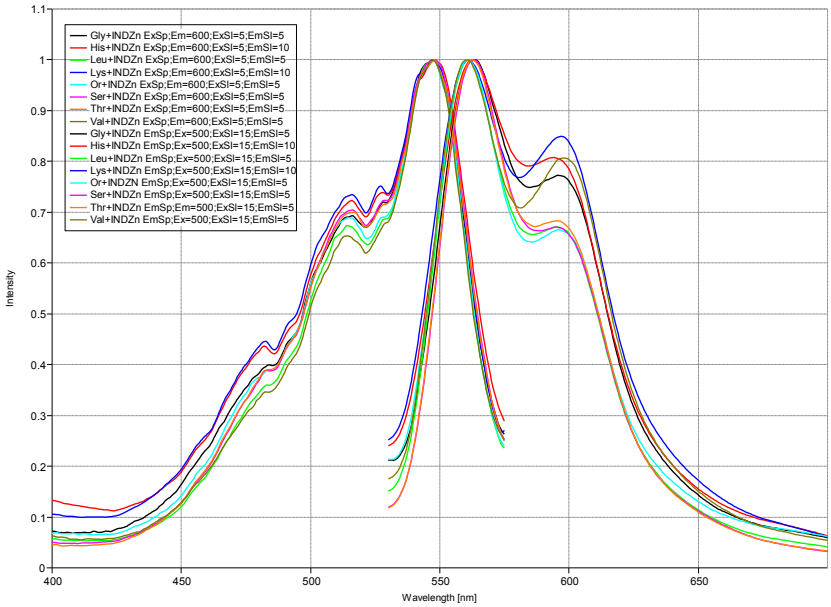
2.2 The proposed formation of a Ruhemann's purple analogue as shown above may account for the pink coloration seen for prints developed from formulations using high 1,2 indandione contents. However the product responsible for the fluorescence has not been conclusively identified.

2.3 Unlike DFO, methanol is not necessary for the reaction to proceed and may in fact inhibit it. This is because 1,2 indandione forms a stable hemiketal with methanol and this prevents the reaction with amino acids taking place.



a) *b)*

Fingerprints on paper developed using 1,2 indandione and imaged in a) reflected light and b) fluorescence mode.



Absorption and emission spectra measured for 1,2 indandione-zinc [17]

2.4 The addition of zinc to the formulation has been shown to give reaction products that are consistent in their excitation and emission spectra across a wide range of amino acids. This was not true of 1,2 indandione formulations without zinc salt additions [17] and it was proposed that the Zn^{2+} present in the solution has a catalytic effect in driving the formation of the fluorescent reaction product.

3. Reasons technique is not recommended by CAST

3.1 CAST does not currently (2011) recommend the use of 1,2 indandione because an extensive research programme including operational trials

has not demonstrated that it gives any improvements in effectiveness over the currently recommended DFO formulation. There have also been suggestions in previous published work that 1,2 indandione may not be as effective as DFO when used as part of sequential treatments [3,5] although other studies indicated that 1,2 indandione may develop more fingerprints than the DFO-ninhydrin sequence [5,12]. However, recent formulations incorporating zinc salts give improved performance and may need further evaluation.

3.2 A summary of the experiments performed and the results on which these conclusions are based is given below.

3.3 In the late 1990s/early 2000s, PSDB began a programme of work to optimise the 1,2 indandione formulation for use in UK conditions [6]. Observations from this work included:

- 0.25g 1,2 indandione per litre of solution gives the optimum fluorescence level in the developed mark. Higher concentrations can give a more intense pink colour, but in common with the DFO formulation, CAST regards fluorescence as the most important characteristic;
- 10 mL of acetic acid per litre of solution gives the optimum fluorescence of fingerprints without increasing undesirable background fluorescence to a level where it begins to obscure marks;
- 90 mL of ethyl acetate per litre of solution is added as a co-solvent;
- the solution is made up to 1 litre with 1-methoxynonafluorobutane (HFE7100), selected as a proven non-flammable, non-toxic solvent for fingerprint formulations.

3.4 It was also determined that the optimum processing conditions for maximum fluorescence were heating for 10 minutes at 100ºC without humidity, and that processed exhibits should be stored in the dark to maximise subsequent development of marks and to retain fluorescence. More recently, other researchers have suggested that equivalent (if not better) performance can be obtained by heating at higher temperatures (~160°C) for shorter times [12], but this has not yet been investigated by CAST.

3.5 Pseudo-operational trials were then conducted on batches of 75 cheques, comparing the optimised 1,2 indandione formulation with DFO. The results are shown in the graphs below.

Chart 1

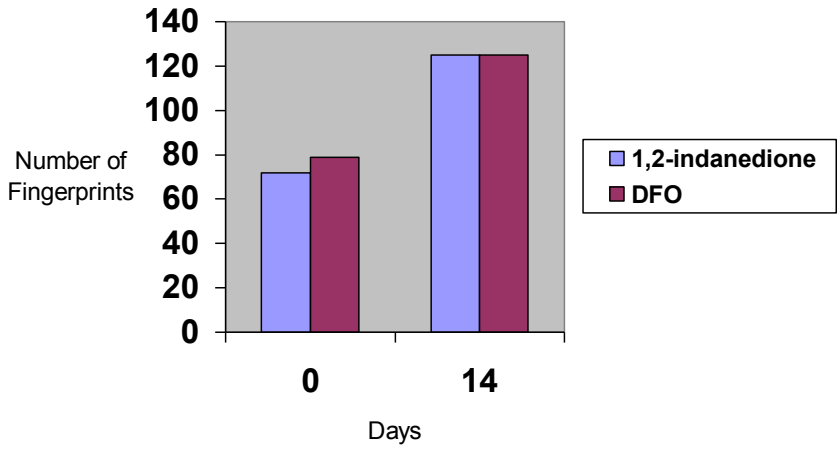
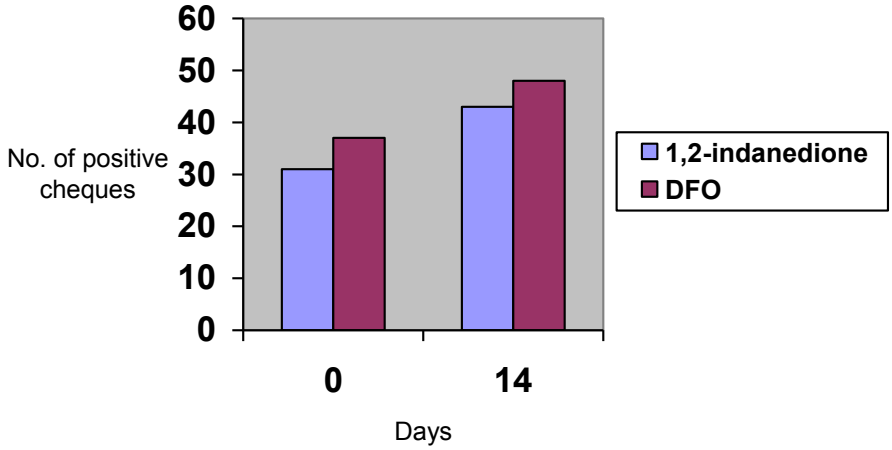


Chart 2



Number of fingerprints detected on cheques developed using 1,2 indandione and 1,8-diazafluoren-9-one processes and number of cheques yielding positive results.

3.6 These results indicated that the two systems were closely equivalent in performance, with DFO developing slightly more marks. A further pseudo-operational trial was conducted on a range of different porous exhibits, the results being tabulated below.

Article	Number of articles	Number of developed fingerprints	
		DFO	1,2 Indandione
White envelopes	20	41	44
Brown envelopes	15	17	33
Photocopy paper	20	92	82
Newspaper	20	2	2
Receipts	20	5	7
Train tickets	19	10	6
Total	**114**	**167**	**174**

Results of pseudo-operational trial on samples typical of porous exhibits encountered in casework.

3.7 These results were sufficiently encouraging to justify inclusion of 1,2 indandione in an operational trial of two ozone-friendly DFO formulations against the chlorofluorocarbon (CFC) 1,1,2-trifluorotrichloroethane (CFC113)-based DFO formulation [7]. In these trials the 1,2 indandione formulation proved least effective on operational work and was not pursued further. Similar results were obtained from an operational trial in Canada [8].

3.8 However, more recent publications from Australia [12,13] suggest stabilisation of the 1,2 indandione system to humidity by additions of zinc salts in solution. This necessitated a re-evaluation of the process and HOSDB carried out a further work programme with the objectives of identifying the optimum formulation with zinc salt additions and carrying out a comparative trial with DFO. In this trial18 different porous substrates were used, covering a range of different paper types.

Substrate	Brand	Size	Weight	Description
1	Tesco value	A4	75gsm	White copier paper
2	Woolworths	A4	80gsm	Multipurpose paper
3	WH Smith	A4	100gsm	Premium inkjet paper
4	XEROX	A4	80gsm	Laser copier paper
5	HP	A4	80gsm	Everyday inkjet paper
6	WH Smith	A5	–	Writing paper
7	PUKKA	A4	80gsm	Premium quality lined writing paper
8	Woolworths	A4	–	Premium pad lined
9	Tesco value	A4	–	Refill pad lined
10	Tesco	C4	–	White envelopes
11	Tesco value	C4	–	Brown envelopes
12	Woolworths	50cm x 5m	–	Brown paper

13	*TV Choice*	–	–	TV magazine
14	*Heat*	–	–	Magazine
15	*Sun*	–	–	Newspaper
16	Ryman	A4	–	Silk finish paper laser printers
17	Ryman	C4	130gsm	White envelopes
18	Ryman	A4	90gsm	Ivory parchment paper

Summary of porous surfaces used in comparative studies.

3.9 This study consisted of over 180 deposited marks per substrate, per condition examined. For experiments using all 18 substrates, greater than 180 x 18 prints were examined. The intensity of the fluorescence for developed marks was measured using a Minolta 100LS spot meter, and marks graded using a 0–4 grading scheme [18]. The fluorescence conditions used were illumination with the 473–548nm excitation band of a Quaser 40, viewed through a 549nm cut-on long-pass filter (Schott glass OG570).

3.10 Initial studies compared the effectiveness of 'optimised' formulations, including zinc salts developed by the Australian Federal Police, HOSDB in the UK, and the US Secret Service in the USA.

UK 1,2 indandione-zinc formulation

0.125g 1,2 indandione

45mL ethyl acetate

5mL acetic acid

0.25mL $ZnCl_2$ stock solution (0.2g $ZnCl_2$ in 5mL absolute ethanol)

500mL HFE7100.

USA 1,2 indandione-zinc formulation

0.5g 1,2 indandione

15mL dichloromethane

30mL ethyl acetate

5mL acetic acid

2mL $ZnCl_2$ stock solution

448mL petroleum ether.

Australia 1,2 indandione-zinc formulation

0.5g 1,2 indandione

15mL dichloromethane

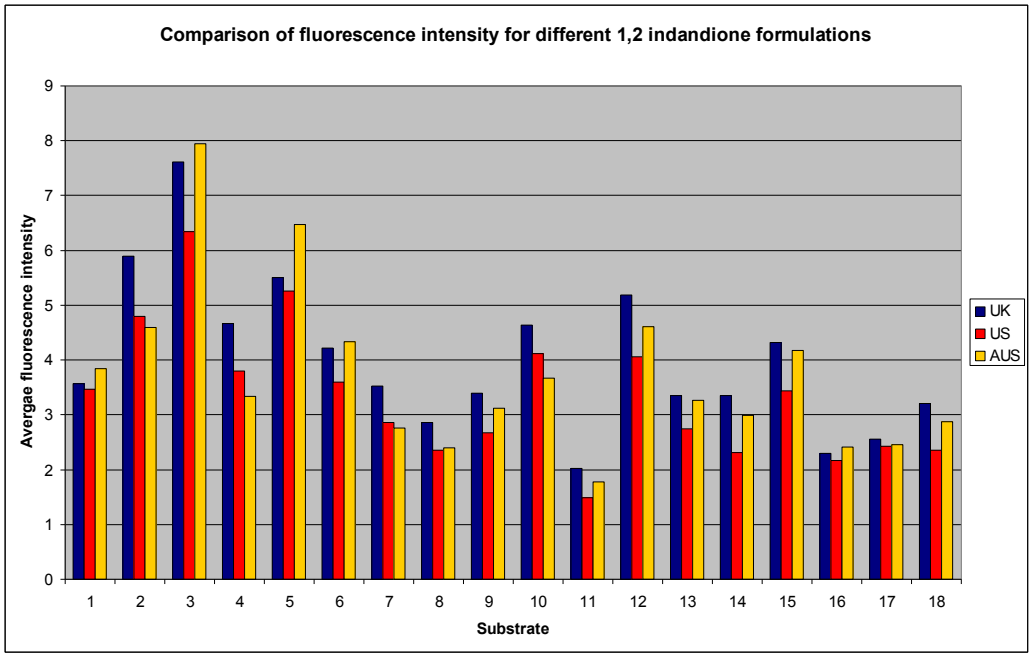
30mL ethyl acetate

5mL acetic acid

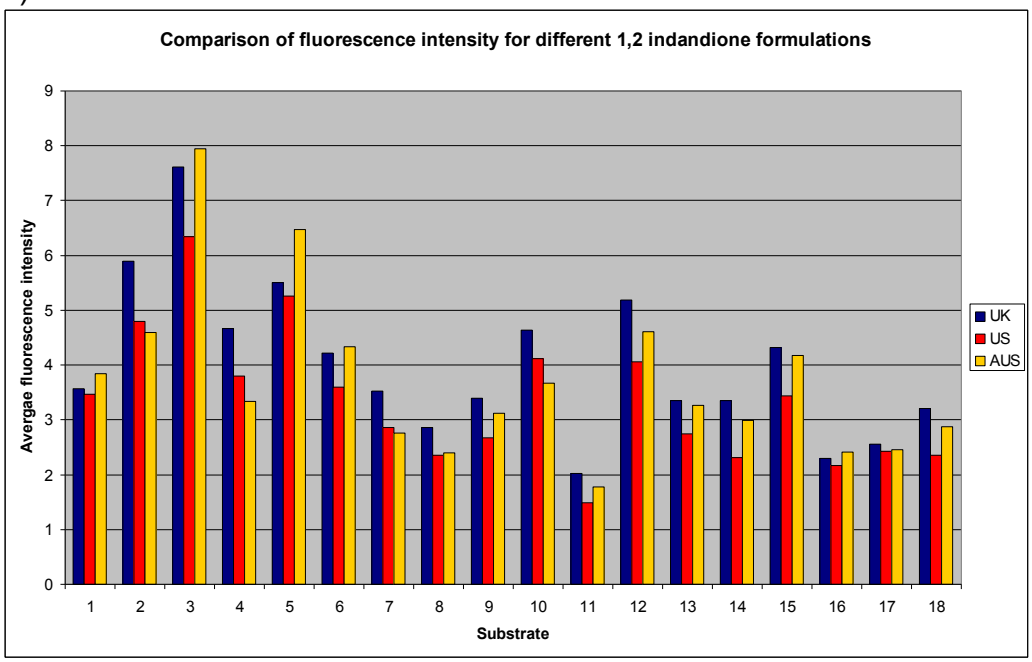
0.5mL $ZnCl_2$ stock solution

450mL HFE-7100.

3.11 The results of this pre-selection exercise are depicted graphically below.



a)



b)

Results of comparative trials between different 1,2 indandione formulations a) fingerprint quality and b) intensity of fluorescence.

3.12 From these trials it appeared that under UK conditions the HOSDB formulation gave the best performance in terms of both quality of fingerprints developed and intensity of fluorescence from the developed mark. The HOSDB formulation with zinc salt additions was therefore compared with the existing HOSDB DFO formulation, both formulations being given below.

UK 1,2 indandione-zinc formulation

0.125g 1,2 indandione

45mL ethyl acetate

5mL acetic acid

0.25mL $ZnCl_2$ stock solution

500mL HFE7100.

DFO formulation

0.25g DFO

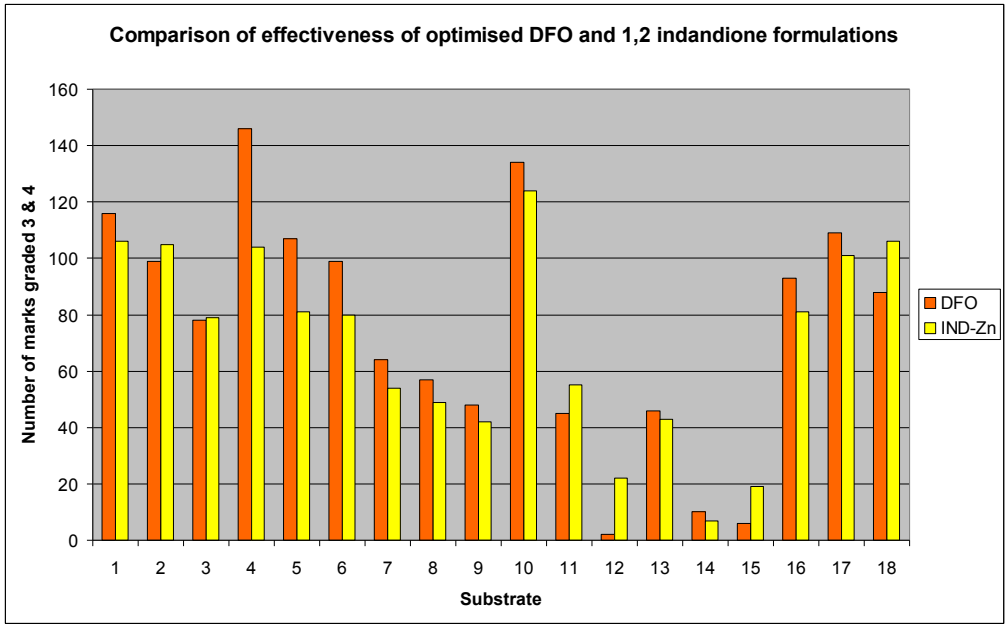
30mL methanol

20mL acetic acid

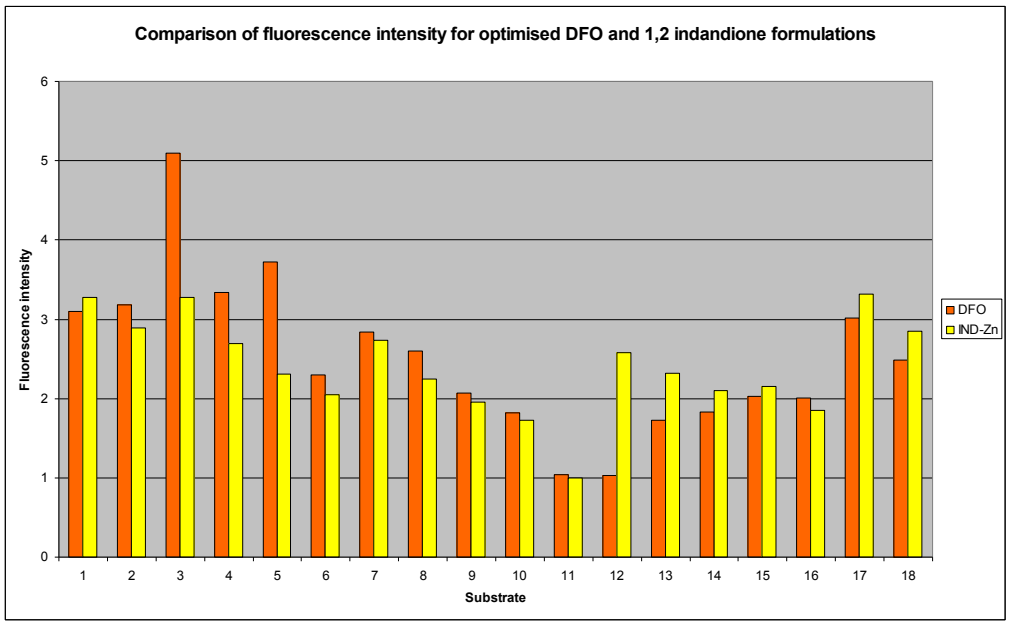
275mL HFE71DE (trans-1,2-dichloroethylene)

725mL HFE7100.

3.13 Once again, comparisons were made between the quality of the developed mark and intensity of fluorescence. Results from this comparison on two-day-old marks are shown in the graphs below.



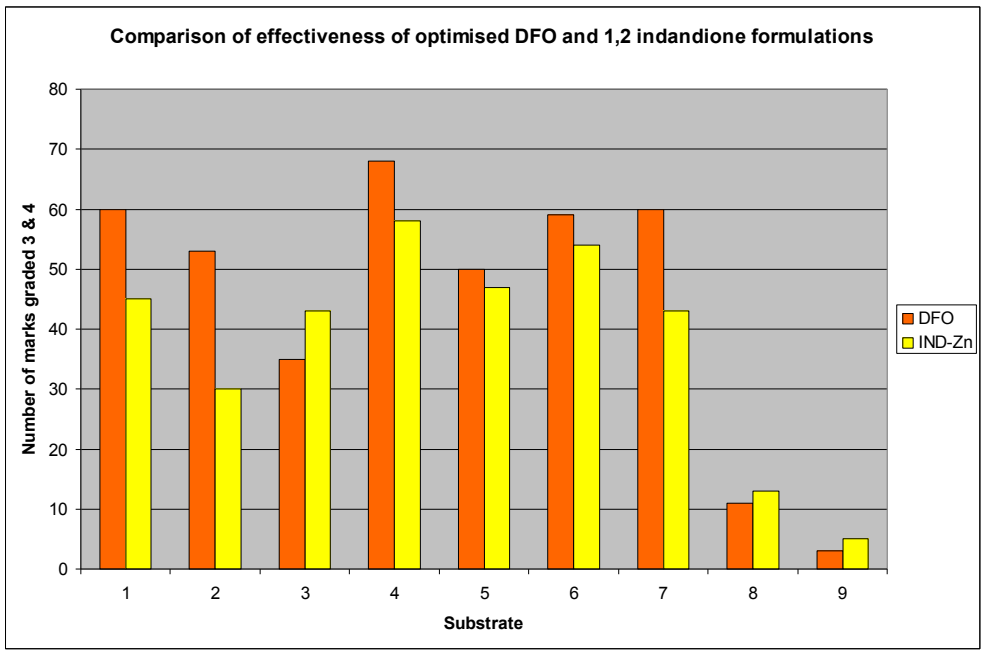
a)



b)

Results of comparative trials between 1,8-diazafluoren-9-one and 1,2 indandione formulations on two-day-old marks a) fingerprint quality and b) intensity of fluorescence.

3.14 In these trials the formulations give closely equivalent performance, with DFO giving marginally better results. An assessment on 14-day-old marks was commenced but it was not possible to complete the study in the time available. However, initial results (illustrated below) suggested a similar trend.



Results of comparative trials between 1,8-diazafluoren-9-one and 1,2 indandione formulations on 14–day-old marks, assessing fingerprint quality alone.

3.15 The results obtained showed no improvement in performance from 1,2 indandione over DFO and this, combined with reports that ninhydrin develops no additional marks after 1,2 indandione, but is known to do so after DFO, resulted in HOSDB recommending no further evaluation of 1,2 indandione. DFO was therefore retained as the recommended HOSDB process and the sequential treatment of DFO-ninhydrin-physical developer remained unchanged.

3.16 However, as outlined in the sections above subsequent studies have been carried out in Australia, which again found that 1,2 indandione-zinc outperformed DFO (in this case the HOSDB DFO formulation) under Australian conditions. Similarly, the US Secret Service has developed a revised 1,2 indandione-zinc formulation, which appears to give improved performance over the HOSDB DFO formulation in a limited study under UK conditions. Clearly, further work is required to see if 1,2 indandione-zinc has potential for replacing DFO in operational use.

4. References

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5.8 Ninhydrin analogues

1. History

1.1 Many ninhydrin analogues have been synthesised, but the first concerted synthesis of such analogues for assessment as fingerprint reagents was carried out by Almog *et al.*[1] in the early 1980s. These studies identified benzo[f]ninhydrin as a reagent with potential for operational use, the reaction product being a dark green in colour.

1.2 Benzo[f]ninhydrin was first assessed in the UK by Jones and Pounds [2], who conducted a comparison of the new reagent with ninhydrin. These studies found that there was little difference in sensitivity between the two reagents, but benzo[f]ninhydrin was less soluble and the increased solvent levels required in the formulation caused ink to run. However, it was noted that benzo[f]ninhydrin may allow better distinction of marks on coloured backgrounds, because of the darker colour of the developed marks.

1.3 It was later found that benzo[f]ninhydrin could be treated with metal salts in a similar manner to ninhydrin to produce a fluorescent reaction product. An examination of zinc chloride ($ZnCl_2$)-toned benzo[f]ninhydrin marks was conducted using a neodymium:yttrium aluminium garnet (Nd:YAG) laser (green, 532nm), and these were found to be well-matched to the absorption spectrum of the toned mark [3].

1.4 In the mid-1980s, a wider range of ninhydrin analogues were synthesised including 5-methoxyninhydrin. These studies included an extensive investigation of the reactions between these analogues and metal salts, and the fluorescence characteristics of the reaction products [4]. The same researchers carried out further studies of the fluorescence produced from metal toning [5] and found that in this respect benzo[f]ninhydrin and 5-methoxyninhydrin were particularly useful. Both these compounds gave reaction products with more intense fluorescence than ninhydrin and fluorescence occurred at longer wavelengths, thus reducing problems associated with background fluorescence.

1.5 A further investigation into reactions of both ninhydrin analogues and related compounds with amino acids was carried out by Almog [6]. It was observed in these studies that only cyclic triketones gave coloured reaction products with amino acids, whereas open chained triketones did not.

1.6 The intense fluorescence from metal-toned 5-methoxyninhydrin was investigated using a copper-vapour laser [7,8]. Marks developed using this reagent had the same visible appearance as ninhydrin but were considerably more fluorescent when illuminated with the copper-vapour laser at 510.6nm. The laser was found to be the most appropriate light source for excitation of this fluorescence.

1.7 An extensive review of ninhydrin, its analogues and reactions was published by Joullie *et al.*[9]. However, the interest in developing ninhydrin analogues for the fluorescent properties of their reaction products did fall off with the introduction of 1,8-diazafluoren-9-one (DFO), which did not require a post-treatment to give fluorescent marks. One final class of ninhydrin analogues that were investigated were the thioninhydrins [10], which were found to give the most intense fluorescence from marks after metal toning than any other ninhydrin analogue.

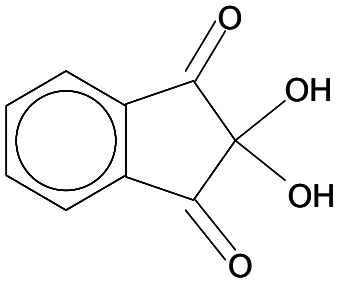
1.8 The Police Scientific Development Branch (PSDB) carried out limited evaluations on some ninhydrin analogues, including 5-methoxyninhydrin and 5-(2-thienyl) ninhydrin. The most comprehensive study was carried out on benzo[f]ninhydrin in collaboration with the Israeli National Police, comparing the effectiveness of the two reagents on bundles of cheques in a pseudo-operational trial [11]. It was found that ninhydrin gave significantly better results and therefore benzo[f]ninhydrin was not recommended for operational use in the UK.

1.9 Recently Israeli researchers have revisited the toning of ninhydrin analogues with metal salts, most notably by incorporating the metal salts into the formulation and eliminating the need for a post-treatment stage [12]. The analogues used in this study were 5-methoxyninhydrin (5-MN) and 5-methylthioninhydrin (5-MTN). It was reported that these 'dual action' reagents gave a more intense colorimetric reaction than ninhydrin, and the zinc toned marks of 5-MTN produced a fluorescent product of intensity equivalent to DFO.

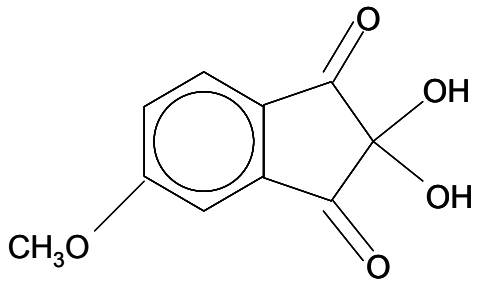
2. Theory

2.1 All ninhydrin analogues essentially follow a similar reaction path with amino acids to ninhydrin itself, and for those analogues that do form complexes with metal salts, the structures of these complexes are similar to those observed for ninhydrin.

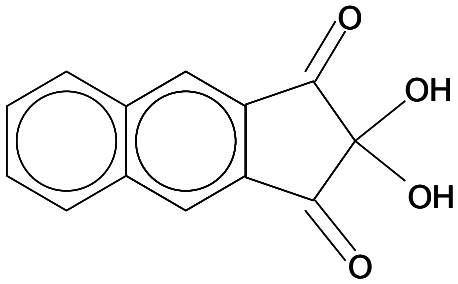
2.2 The structures of ninhydrin and the principal analogues that have been considered for fingerprint development are illustrated below.



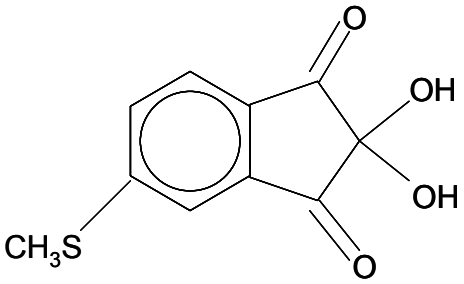
Ninhydrin



5-methoxyninhydrin



Benzo[f]ninhydrin



5-methylthioninhydrin

Structures of some of the principal ninhydrin analogues.

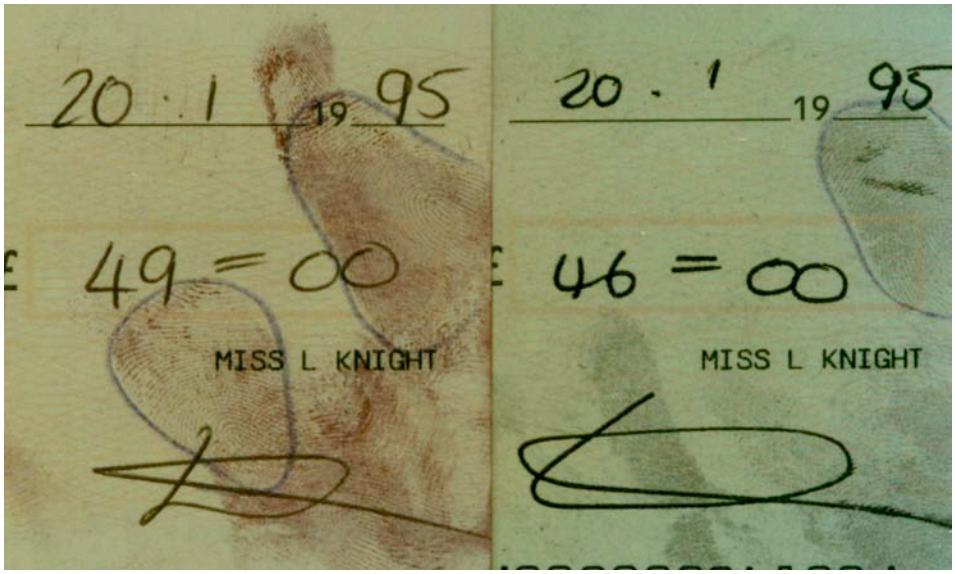
3. Reasons technique is not recommended by CAST

3.1 CAST does not currently (2011) recommend the use of ninhydrin analogues because those studied to date offer no performance benefits over ninhydrin itself. The two analogues that have generated the most interest, benzo[f]ninhydrin and 5-MN, may have niche applications, but in routine use are no more effective. However, the recent development of 5-MN and 5-MTN formulations incorporating metal salts [12] merits further study and may lead to one or both of these analogues being preferred over ninhydrin.

3.2 Both 5-MN (and 5-MTN) are of interest because they produce a more intensely fluorescent reaction product than ninhydrin when post-treated with metal salts. However, they are no more sensitive than ninhydrin and the visible reaction product is almost identical in colour. The requirement for intense fluorescence after metal toning reduced significantly with the introduction of reagents producing fluorescent products such as DFO and therefore it was not considered necessary to change from the currently recommended ninhydrin formulation. As stated above, the recent observation that metal salts can be incorporated into 5-MN and 5-MTN formulations rather than being used as an additional, post-treatment step may revive interest in these compounds. The development of intensely coloured, inherently fluorescent marks may

offer operational advantages and will be studied by CAST in the near future.

3.3 Benzo[f]ninhydrin has been of interest because it produces a grey-green reaction product, which may be easier to distinguish on coloured papers than the purple colour produced by ninhydrin. It also fluoresces at a longer wavelength after metal toning than ninhydrin, which again may be useful in distinguishing developed marks against background fluorescence.



a) b)

Comparison of reaction products produced with a) ninhydrin and b) benzo[f]ninhydrin.

3.4 However, in comparative trials between ninhydrin and benzo[f]ninhydrin, ninhydrin was found to be significantly more effective in terms of the numbers of fingerprints developed on batches of cheques from different banks [11]. A brief summary of this trial is given below.

3.5 The formulations used were as follows:

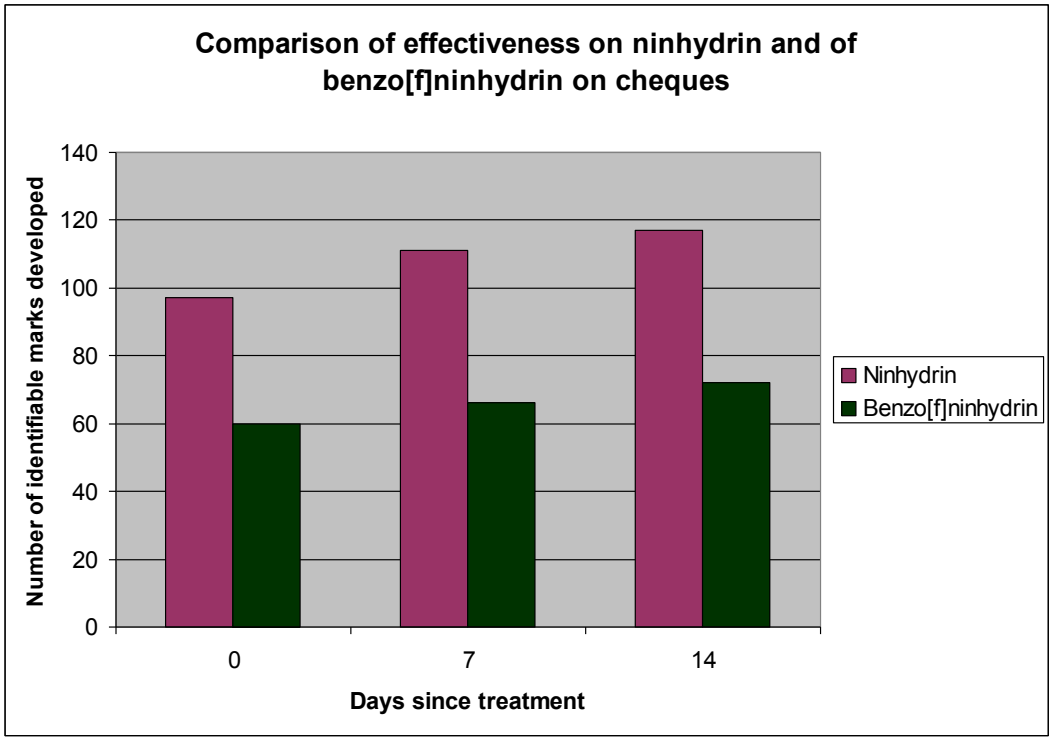
ninhydrin: 5g ninhydrin, 45mL ethanol, 5mL acetic acid, 2mL ethyl acetate, 1 litre 1-methoxynonafluorobutane (HFE7100);

benzo[f]ninhydrin: 6g benzo[f]ninhydrin, 60mL methanol, 30mL acetic acid, 60mL methyl acetate, 850mL 1,1,2-trifluorotrichloroethane (CFC113).

3.6 The numbers of fingerprints containing more than eight points developed using each process is recorded in the table below, and also shown graphically.

Days since treatment	Number of fingerprints							
	Ninhydrin (HFE7100)				Benzo[f]ninhydrin (CFC113)			
	B	M	N	Total	B	M	N	Total
0	22	41	34	97	12	21	27	60
7	28	46	37	111	13	23	30	66
14	30	50	37	117	15	26	31	72

Number of fingerprints developed on bundles of fraudulently passed cheques (B = Barclays, M = Midland, N = Natwest).



Total number of fingerprints developed on bundles of 75 fraudulently passed cheques.

3.7 As can be seen, the results do not justify the operational use of benzo[f]ninhydrin on grounds of effectiveness, although there may be niche applications, such as the development of marks on coloured surfaces.

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5. **Lennard, C. J., Margot, P. A., Stoilovic, M. and Warrener, R. N.** (1988) 'Synthesis and Evaluation of Ninhydrin Analogues as Reagents for the Development of Latent Fingerprints on Paper Surfaces', *J. Forens. Sci. Soc*., vol. 28, pp 3–23.

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7. **Almog, J. and Hirshfield, A.** (1988) '5-Methoxyninhydrin: A Reagent for the Chemical Development of Latent Fingerprints That is Compatible with the Copper-Laser Laser', *J. Forens. Sci*, vol. 33 (4), pp 1027–1030.

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9. **Joullie, M. M., Thompson, T. R. and Nemeroff, N. H.** (1991) 'Ninhydrin and Ninhydrin Analogs. Syntheses and Applications', *Tetra.*, vol. 47 (42), pp 8791–8830.

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5.9 Miscellaneous amino acid reagents:

5.9.1 Fluorescamine

1. History

1.1 Fluorescamine (4-phenylspiro[furan-2(3H), 1'-phthalan]-3,3'-dione) was developed in the early 1970s as a fluorescent reagent for automated assay of amino acids [1,2]. This was based on earlier work showing that fluorescent products could be obtained when treating phenylalanine with ninhydrin and a peptide. By deducing the structure of these fluorescent products, it was possible to identify a novel reagent (fluorescamine) that would react directly with primary amines to give the same fluorescent reaction products. Tests demonstrated that fluorescamine was capable of detecting both amino acids and peptides and had a high level of sensitivity.

1.2 Several studies were carried out to compare the sensitivity of fluorescamine, ninhydrin and o-phthaldialdehyde (another reagent proposed for assay of amino acids). These concluded that for detection of most free amino acids, fluorescamine offered no advantages over ninhydrin. However, for recovery of peptides, fluorescamine did appear to work over a wider range of substances than ninhydrin [3].

1.3 The reagent also became considered as an alternative to ninhydrin for the development of fingerprints on porous surfaces. However, initial tests indicated that the aqueous buffer required to provide the optimal pH environment washed out the fingerprint ridge detail and therefore organic bases were investigated as alternative ways of providing an alkaline environment. A suitable formulation was developed based on fluorescamine dissolved in acetone with addition of triethylamine [4].

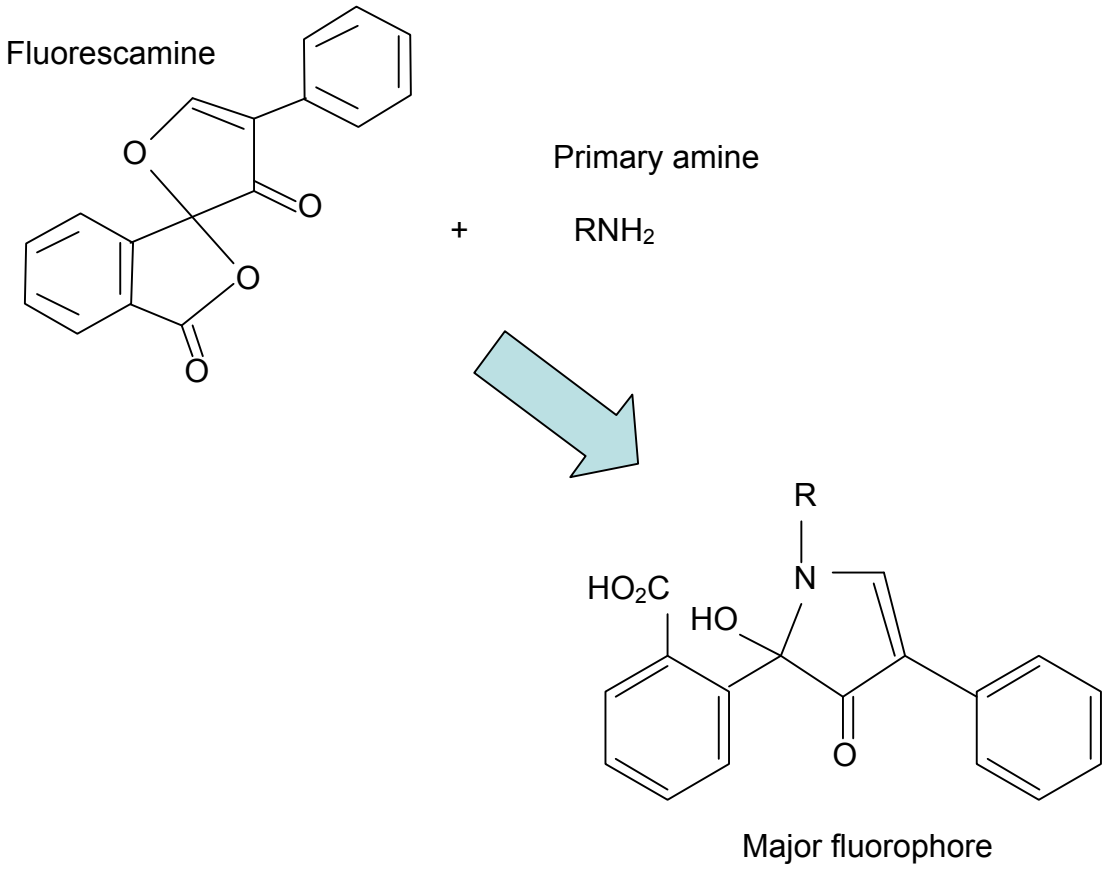
1.4 This formulation was then compared with ninhydrin and an optimised formulation of o-phthaldialdehyde for the detection of fingerprints was deposited on a range of surfaces, all reagents being applied as sprays [5]. These studies indicated that fluorescamine had some advantages over ninhydrin, including greater sensitivity, ability for mark detection on dark and multicoloured surfaces, and the fact that heat is not required for the reaction to occur. However, there were also some disadvantages: the solution does not have long-term stability and water will hydrolyse fluorescamine to a non-fluorescent product; in addition, ultraviolet (UV) light is required to visualise developed marks.

1.5 The reagent does not appear to have become widely used for fingerprint detection, possibly because of the greater ease in visualising the purple marks produced by ninhydrin and the fact that ninhydrin solution is more stable for long-term storage. The increasing use of optical brighteners in papers also means that many such surfaces now fluoresce a bright blue when illuminated with UV light, and this will swamp the weaker, pale blue fluorescence of any marks developed using fluorescamine. The

technique is therefore no longer appropriate for the types of surface that it was originally intended for.

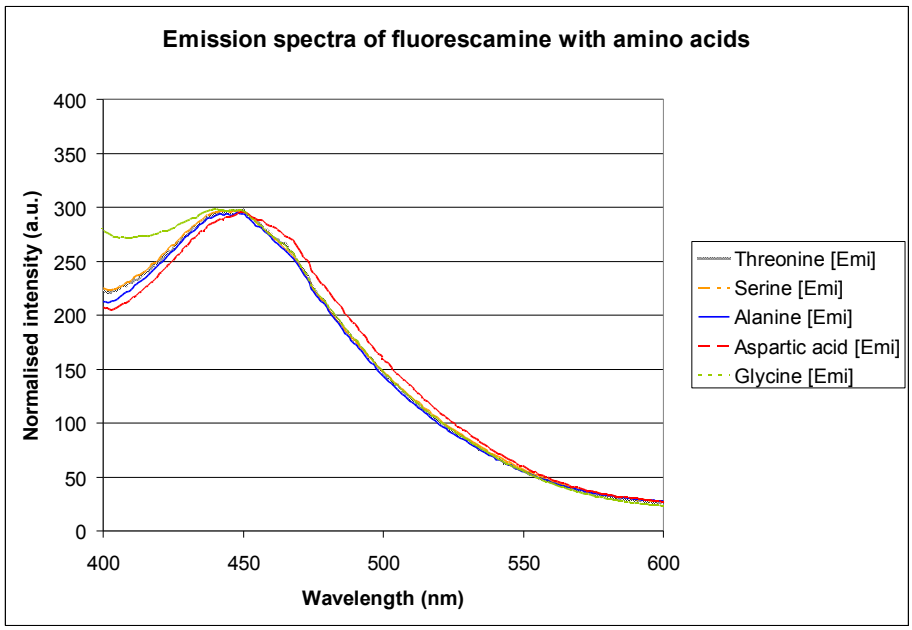
2. Theory

2.1 The way in which fluorescamine works is by a chemical reaction between the fluorescamine molecule and the amine groups present in amino acids and peptides to give a fluorescent reaction product. This is illustrated below:



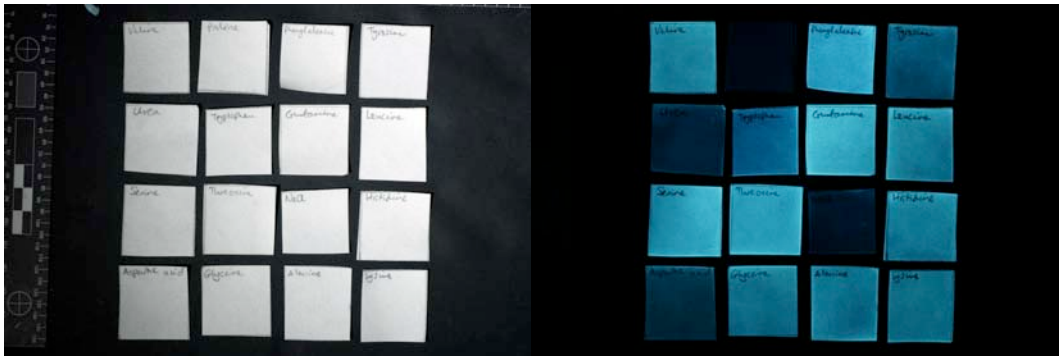
Reaction of fluorescamine with amines to form fluorescent products,

2.2 The major fluorophore produced by this reaction can be best visualised using an excitation wavelength ~390nm (long-wave UV) that produces a visible emission in the region 475–495nm.



Emission spectra of reaction products of fluorescamine with amino acids.

Palm print developed on painted wall using fluorescamine.



a) b)

Reaction products formed between fluorescamine and 0.1M solutions of amino acids and other fingerprint constituents a) visible and b) fluorescence.

2.3 The formulations proposed for use in the late 1970s utilised acetone as the principal solvent, small additions of triethylamine as an organic base, and fluorescamine. One such formulation is given below [6].

15mg fluorescamine
100mL acetone
0.1mL triethylamine.

2.4 These constituents were mixed together and then sprayed using an atomiser onto the surface being treated.

3. Reasons technique is not recommended by CAST

3.1 Although the technique was evaluated in the late 1970s, the Home Office Centre for Applied Science and Technology (CAST) has not recently conducted any extensive trials to compare fluorescamine with ninhydrin and/or 1,8-diazafluoren-9-one (DFO) and therefore it is not known whether there are any operational benefits in its use. However, reformulation work would be required to change the base solvent for fluorescamine from acetone to another less flammable substance less likely to cause ink to run and affect any subsequent document analysis, e.g. 1-methoxynonafluorobutane (HFE7100). Some components of the original formulation (such as dichloromethane) also have health and safety issues associated with them and alternatives would need to be identified. The solution is also unstable in contact with water and is more difficult to store than ninhydrin.

3.2 The fact that long-wave UV is required to visualise the developed fingerprints also makes fluorescamine less attractive for operational use. Extended usage of long-wave UV light sources does have health and safety implications for the operator and many modern papers also contain optical brighteners that are excited by long-wave UV, making developed marks more difficult to see against the fluorescing background.

4. References

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5. **Lee, H. C. and Attard, A. E.** (1979) 'Comparison of Fluorescamine, O-phthalaldehyde, and Ninhydrin for the Detection and Visualization of Latent Fingerprints', *J. Police Sci. & Admin*., vol. 7 (3), pp 333–335.

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5.9.2 O-phthaldialdehyde

1. History

1.1 O-phthaldialdehyde is another reagent originally developed for assay of amino acids in the early 1970s. Initially, o-phthaldialdehyde was not found to be as effective as ninhydrin or fluorescamine for detection of peptides, but by the mid-1970s revised formulations were published that were stated to overcome these issues [1]. The authors suggested that o-phthaldialdehyde was actually preferable to fluorescamine for fingerprint development because it exhibited greater fluorescent quantum yields, was stable in aqueous buffers, and was cheaper.

1.2 Similarly to fluorescamine, work was carried out to adapt the assay formulations for the development of fingerprints. One reported study investigated the use of a Babington nebuliser to provide a means of delivering o-phthaldialdehyde to large areas with saturating the surface [2]. In this formulation boric acid and potassium hydroxide were used as

a buffer solution, with additions of a detergent (Brij 35) and 2-mercaptoethanol.

1.3 O-phthaldialdehyde was also compared with ninhydrin and fluorescamine in spray reagent form. No single reagent out-performed the others in all respects, with o-phthaldialdehyde performing well in terms of sensitivity but suffering from a complex formulation and application procedure coupled with lack of stability in air [3].

1.4 Alternatives to the boric acid/potassium hydroxide buffer solution were investigated, this being found to cause diffusion of ridge detail. Ohki reported a formulation based on chloroform, triethylamine and 2-mercaptoethanol that overcame this problem [4].

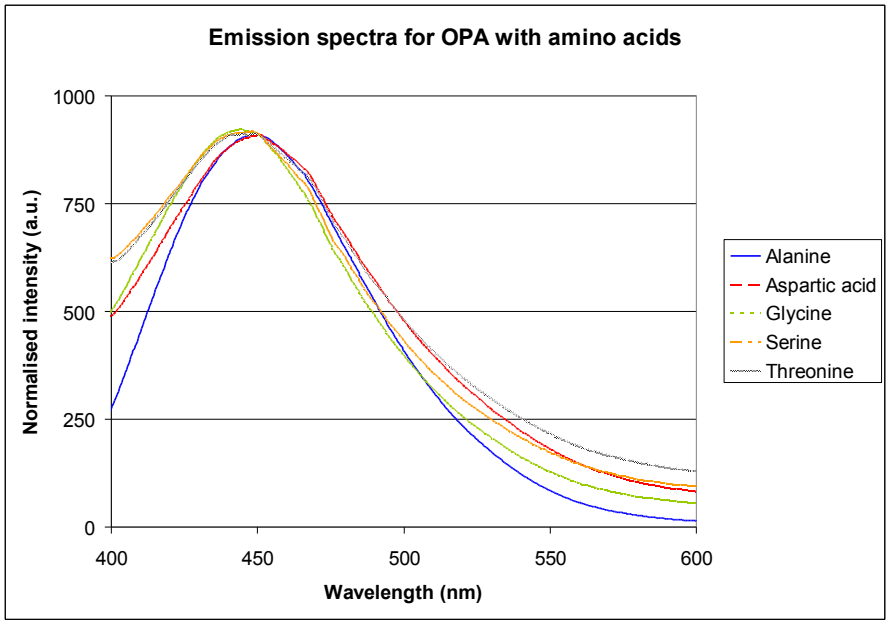
1.5 Subsequently Fischer [5] investigated a simpler and less hazardous formulation that involved dissolving o-phthaldialdehyde in acetone, dipping the exhibit and then lightly spraying with a 1% nitric acid solution in acetone. The fluorescent products produced in this way were excited with blue/green light rather than ultraviolet (UV).

1.6 The reagent does not appear to have become widely used for fingerprint detection, possibly because of the greater ease in visualising the purple marks produced by ninhydrin. The increasing use of optical brighteners in papers also mean that many such surfaces now fluoresce a bright blue when illuminated with UV light, and this will swamp the weaker, pale blue fluorescence of any marks developed using o-phthaldialdehyde. The technique is therefore no longer appropriate for the types of surface it was originally intended for.

2. Theory

2.1 O-phthaldialdehyde undergoes a chemical reaction with primary amines that may be present in fingerprint deposits to form fluorescent reaction products. The reaction products have an optimum excitation wavelength of ~340nm and an emission ~455nm.

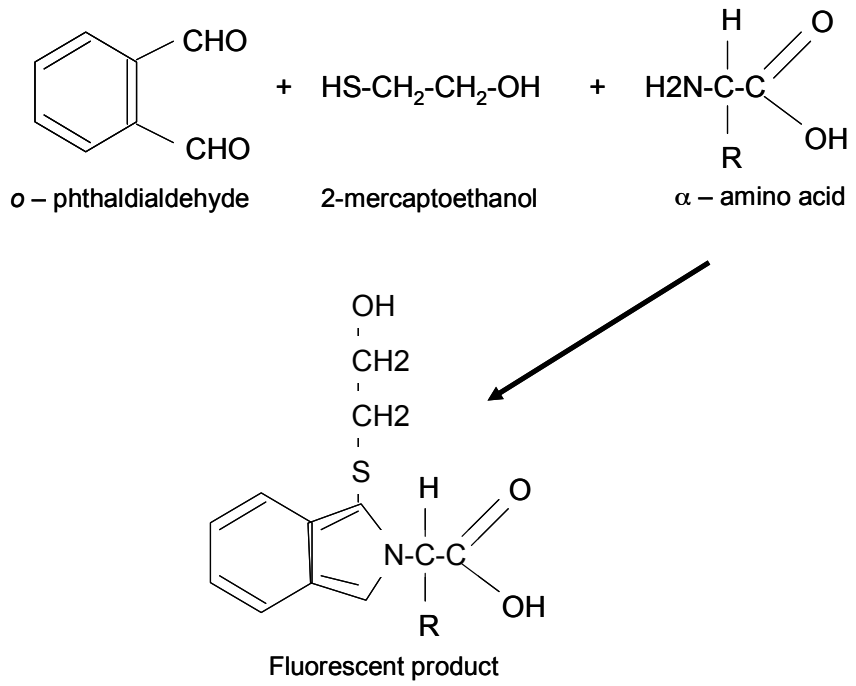
Fingerprint developed on filter paper using o-phthaldialdehyde.



Emission spectra for reaction products of o-phthaldialdehyde (OPA) with amino acids.

2.2 Research has indicated that the fluorescent reaction products are 1-alkylthio-2-alkyl-substituted isoindoles [6,7,8].

2.3 Some of the reactions proposed for o-phthaldialdehyde are given below.



Proposed reaction between o-phthaldialdehyde, 2-mercaptoethanol and α-amino acids [8]

2.4 Lee and Attard [3] proposed a two-part formulation with an aqueous base, where solution A comprised:

2.5g boric acid
95mL distilled water
pH adjusted to 10.40 with additions of 6M potassium hydroxide
0.3mL Brij 35 detergent
0.2mL 2-mercaptoethanol;

and solution B comprised:

0.5g o-phthaldialdehyde
1mL methanol.

The solutions were mixed together and then sprayed.

2.5 Ohki [4] proposed an alternative, one-part solution with an organic base:

40mg o-phthaldialdehyde
1mL 95% ethanol
50mL chloroform
0.5mL triethylamine
0.1mL 2-mercaptoethanol.

Again, the solution was sprayed onto the surface being treated.

3. Reasons technique is not recommended by CAST

3.1 CAST has not recently (since the late 1970s) conducted any extensive trials to compare o-phthaldialdehyde with ninhydrin and/or 1,8-diazafluoren-9-one (DFO) and therefore it is not known whether there are any operational benefits in its use. However, most o-phthaldialdehyde formulations are based on 2-mercaptoethanol, which is toxic, corrosive and dangerous for the environment and therefore it is unlikely that any formulation based on this substance would be recommended for operational use for health and safety reasons. Alternatives are available, but this would require extensive reformulation work for little operational benefit.

3.2 In common with fluorescamine, there is the problem that long-wave UV is required to visualise the developed marks and this brings with it health and safety issues associated with long exposures, and also interference with the developed mark from background paper fluorescence. The solution is also unstable in contact with air and may need to be stored under an inert gas, making it impractical for routine use.

4. References

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5.9.3 Genipin and lawsone

1. History

1.1 Genipin is a natural product that can be extracted from the fruit of Gardenia jasminoides. Since the 1960s it has been recognised that genipin brought into contact with skin produces an indelible blue-violet colour and that the same reaction readily occurs with amino acids [1]. However, the potential of such systems for the development of latent fingerprints was only explored in the mid-2000s when Almog *et. al*. [1] demonstrated that genipin could be mixed into solution with solvents such as 1-methoxynonafluorobutane (HFE7100) and petroleum ether, and the resultant formulations used to develop fingerprints on porous surfaces. It was also noted that in addition to the colorimetric reaction giving developed fingerprints a blue/black colour, the reaction products were also fluorescent with maximum emission at the red end of the spectrum.

1.2 Further experiments were carried out to establish optimum processing conditions for genipin, to compare its sensitivity with both ninhydrin and 1,8-diazafluoren-9-one (DFO) and to look at the reaction products formed between genipin and a range of amino acids [2]. The studies of these exercises identified a formulation based on genipin dissolved in ethanol/ethyl acetate and diluted using HFE7100, which could be used on documents without causing inks to run. It was found that genipin was slightly less sensitive than ninhydrin when considering the coloured reaction product, and less sensitive than DFO when considering the fluorescent reaction product. However, unlike DFO the emission spectra obtained from reaction products with a range of amino acids differed slightly from each other. On some types of paper genipin gave advantages over DFO because the longer wavelength fluorescent product reduced interference from background fluorescence of the paper and/or inks.

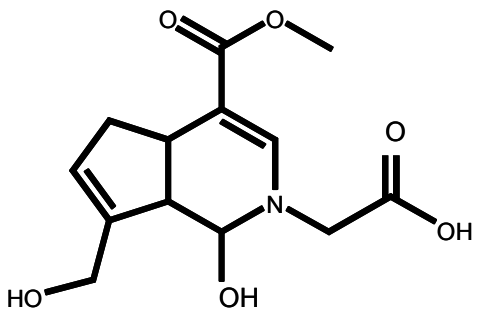
1.3 More rigorous comparative testing against other reagents with dual colorimetric and fluorescent reaction products, e.g. ninhydrin combined with metal salts [3] confirmed that genipin was, on the whole, less sensitive than such reagents, but that this longer wavelength fluorescence could make genipin the reagent of choice on brown paper

articles where background fluorescence may cause problems in imaging developed marks.

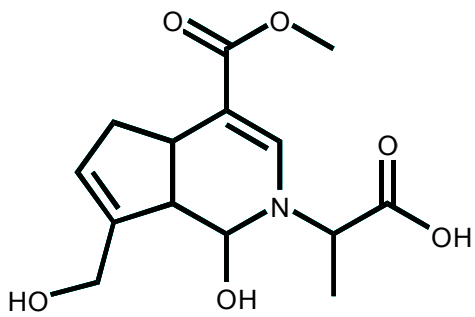
1.4 The research into genipin has since prompted research into other naturally occurring products that could be used as fingerprint development reagents, and information has recently been published on lawsone (2-hydroxy-1,4-napthoquinone), a component of henna [4]. This gives purple-brown marks with a red fluorescence when reacting with the amino acids in fingerprints. Further developments based on naturally occurring products are anticipated.

2. Theory

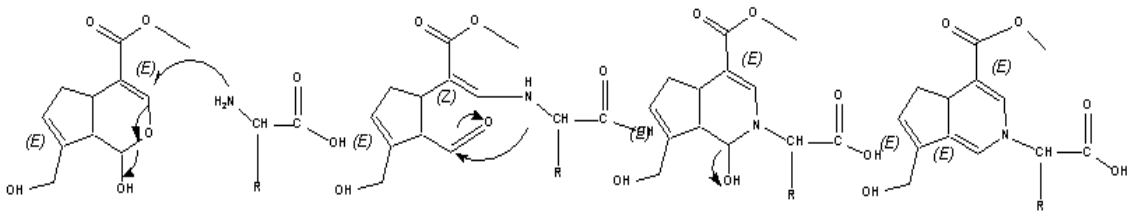
2.1 The mechanism of the reaction between genipin and amino acids and the nature of the coloured and fluorescent reaction products has not yet been established. The studies above [2] have established that slightly different reactions will occur between genipin and the different amino acids present in the fingerprint. Some of the blue reaction products produced with amino acids have been identified and the proposed reaction and structures are shown below.



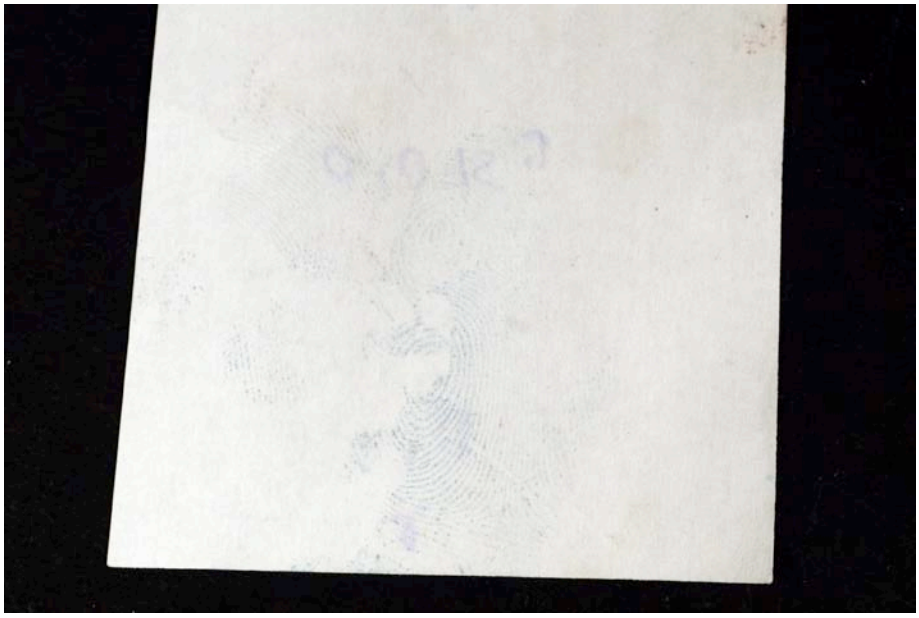
Genipin/Glycine



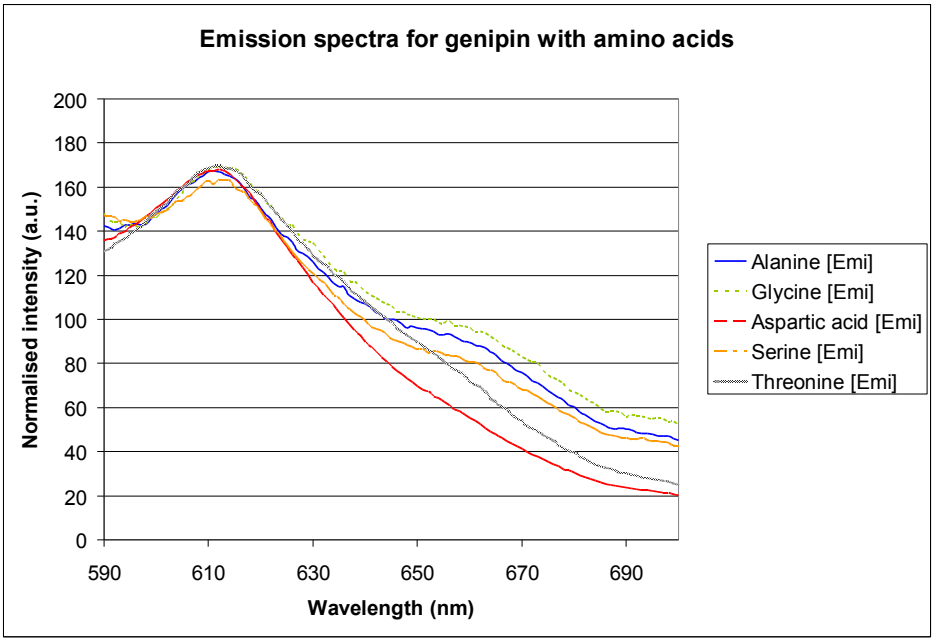
Genipin/L -Alanine



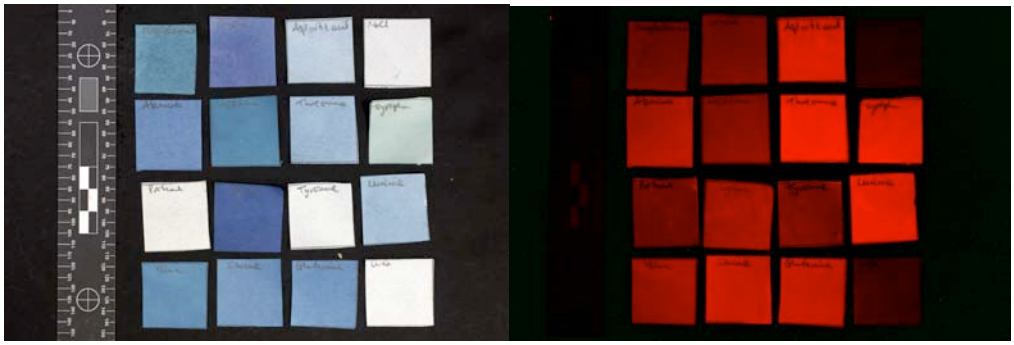
Proposed reaction mechanism for genipin with amino acids and structures of some reaction products [5].



Blue reaction product obtained from genipin.



Emission spectra for reaction products of genipin with amino acids.



a) *b)*

Reaction products formed between genipin and 0.1M solutions of amino acids and other fingerprint constituents a) visible and b) fluorescence.

2.2 The formulation proposed for use by the Israeli National Police (and used in the comparative studies below) comprises:

1.7g genipin
57mL absolute ethanol
86mL ethyl acetate
587mL HFE7100.

3. Reasons technique is not recommended by CAST

3.1 Genipin is not recommended for operational use because it is not as effective as ninhydrin in colorimetric mode, and not as effective as DFO in fluorescence mode.

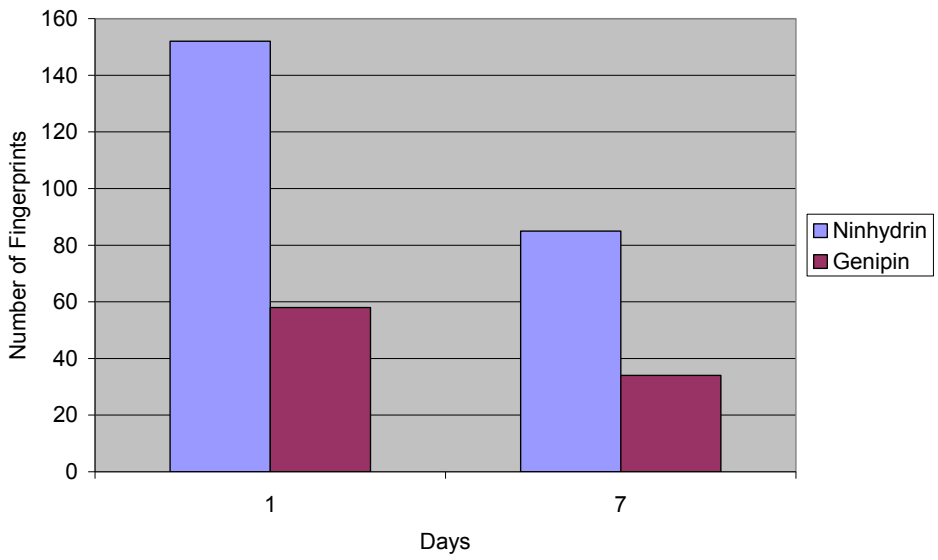
3.2 On certain paper types genipin may give better results than ninhydrin or DFO, but unless a detailed analysis of paper type is carried out prior to chemical treatment it will not be possible to identify when genipin should be used. This is clearly not practical for routine operational work.

3.3 These observations are based on the results of a short study of the effectiveness of genipin conducted by CAST in 2005 [6]. These studies utilised six donors leaving depletion series of six fingerprints on ten different types of paper found in the UK, namely:

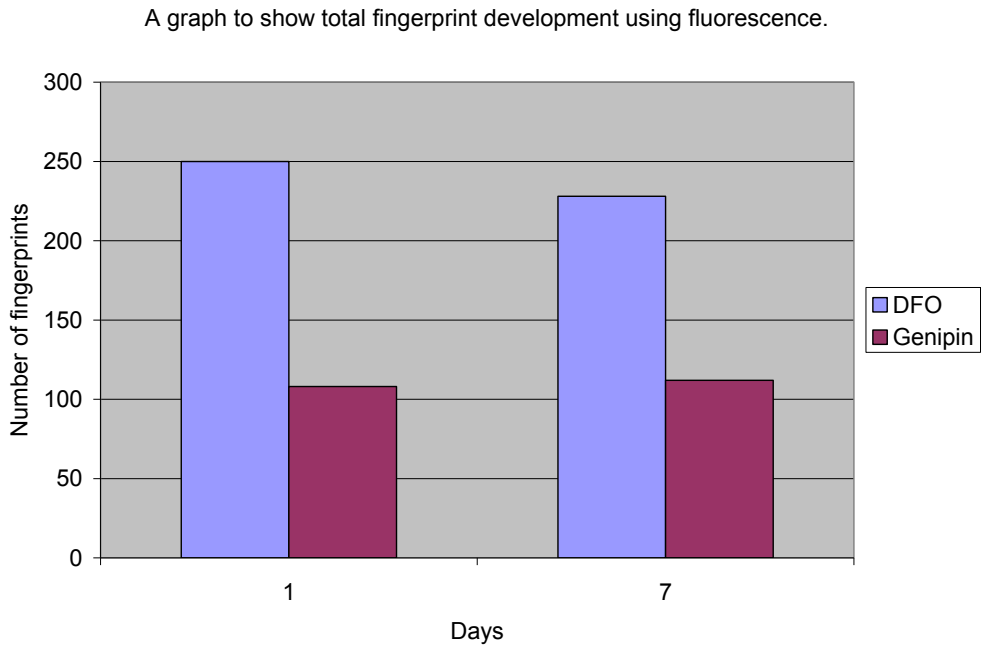
business paper (wove);
parchment paper;
photocopier paper;
writing paper;
white envelope;
brown envelope;
yellow card;
laser printer paper;
newspaper;
magazine.

3.4 The depletion series were split down the middle, one-half being treated with genipin and the other with ninhydrin or DFO. Prints were aged for one day and seven days before processing. The results are illustrated below.

A graph to show fingerprint development using visual examination.



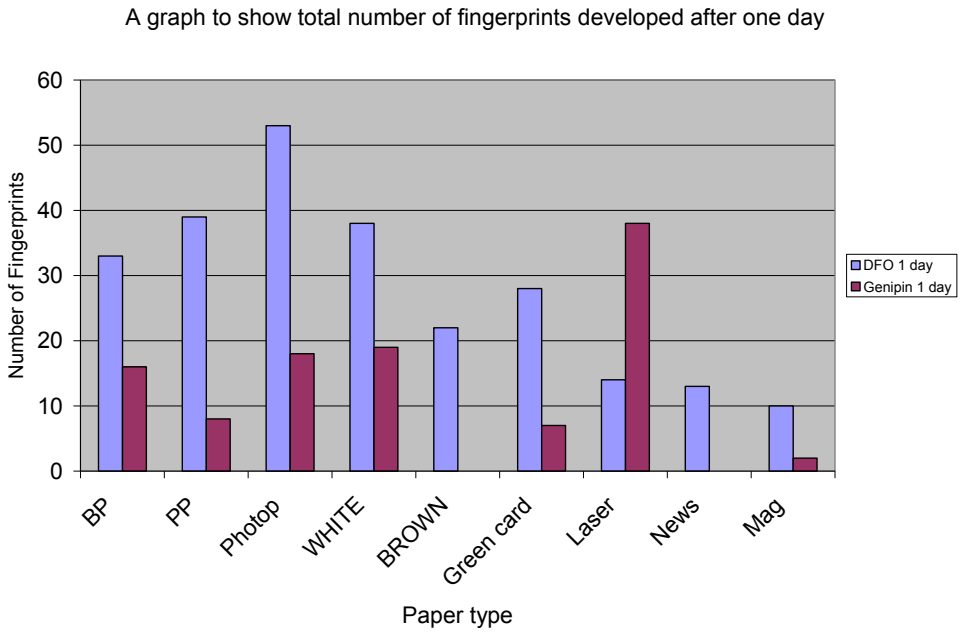
a)



b)

Comparison of the effectiveness of genipin with existing techniques for porous surfaces a) with ninhydrin in colorimetric mode and b) with DFO in fluorescence mode.

3.5 It can be seen that when overall numbers of marks developed on all types of paper are considered, genipin is clearly not as effective as either DFO or ninhydrin. However, a more detailed breakdown by paper type (an example is given below) actually showed that on laser printer paper genipin was the most effective reagent. However, this observation is of no operational benefit unless it is positively known that a particular exhibit is laser printer paper and genipin can be recommended as an alternative treatment.



More detailed comparison of results obtained comparing genipin to DFO on individual paper types

4. References

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5.9.4 Alloxan

1. History

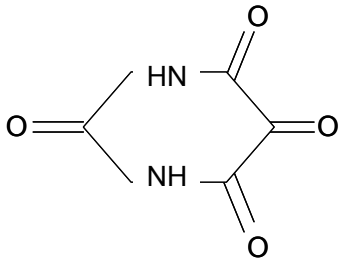
1.1 Reactions of the substance alloxan with amino acids had been observed in the 1860s, and the formation of red reaction products between alloxan and the amino acid glycine were noted at the beginning of the 20th century. After his synthesis of ninhydrin in 1910, Ruhemann conducted a series of experiments that demonstrated that alloxan and ninhydrin must be closely related compounds [1] because of the similar nature of their reactions.

1.2 Alloxan was not investigated as a fingerprint reagent until the discovery that ninhydrin could develop fingerprints on paper in 1954. This led to the re-evaluation of several related compounds in the same role and alloxan formulations for fingerprint development were reported in Japan in the late 1950s [2], the fingerprints thus developed being orange-yellow in colour. However, it was noted that for the majority of surfaces studied ninhydrin gave superior performance.

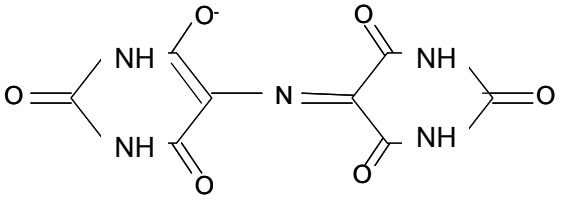
1.3 The use of alloxan for fingerprint development was mentioned in the 1970s [3], although it was still regarded as inferior to ninhydrin, developing fewer fingerprints with lower contrast and higher levels of background staining. The most recent comparative study of alloxan was carried out by Almog [4] in 1987, in an assessment of the reactivity and colour intensity of a range on ninhydrin analogues. It was concluded that alloxan was inferior to ninhydrin as a fingerprint development reagent in all respects.

2. Theory

2.1 The reaction between alloxan and amino acids is directly analogous to that with ninhydrin, and a Ruhemann's purple analogue is formed as a result. The structure of alloxan and the corresponding coloured product is shown below.



Alloxan



Ruhemann's Purple Analogue

Structures of alloxan and the corresponding Ruhemann's purple analogue.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend alloxan because it is significantly less sensitive than the currently (2011) available 1,8-diazafluoren-9-one (DFO) and ninhydrin processes.

4. References

1. **Ruhemann, S.** (1911) 'Triketohydrindene Hydrate. Part III. Its Relation to Alloxan', *J. Chem. Soc*., vol. 23, pp 792–800.

2. **Morris, J. R.** (1974) *An Examination of the Chemical Literature on Fingerprint Technology for the Period 1890 to August 1974*, AWRE SSCD Memorandum 359, October. Aldermaston: Atomic Weapons Research Establishment.

3. **Caton, H. E.** (1974) 'Physical and Chemical Aspects of Latent Print Development', *Proceedings of the Conference on the Science of Fingerprints*, 24–25 September 1974, London, UK.

4. **Almog, J.** (1987) 'Reagents for Chemical Development of Latent Fingerprints: Vicinal Triketones – Their Reaction with Amino Acids and with Latent Fingerprints on Paper', *J. Forens. Sci*, vol. 32 (6), pp 1565–1573.

5.9.5 4-Chloro-7-nitrobenzofurazan (NBD chloride)

1. History

1.1 In the late 1960s and early 1970s, a series of chemicals were developed that gave fluorescent reaction products with amino acids. The primary application of these compounds was in amino acid detection in thin layer chromatography, although it was soon recognised that these could also be applied to fingerprint detection in the same way as ninhydrin. 4-Chloro-7-nitrobenzofurazan (NBD chloride) was one such compound, introduced in the late 1960s with investigations of its effectiveness in amino acid detection under way in the early 1970s [1].

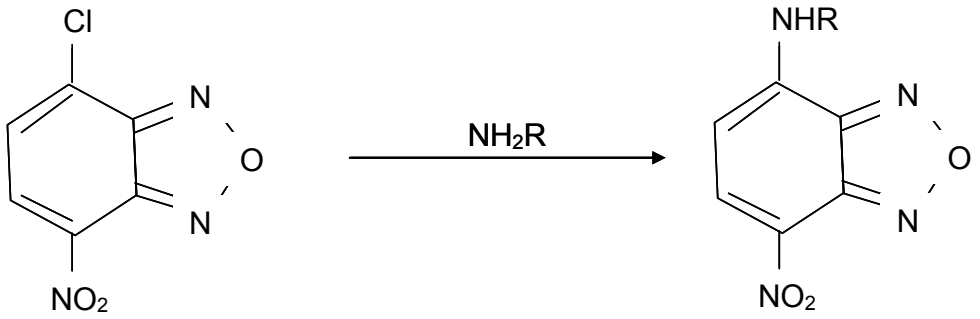
1.2 Initial studies into the use of NBD chloride as a fingerprint reagent were conducted in the late 1970s [2], the results of which suggested that the technique may give improved sensitivity over ninhydrin when developed marks were excited using a laser.

1.3 By the early 1980s, NBD chloride was still being evaluated as a fingerprint reagent for the development of fingerprints on porous surfaces, using blue light (~475nm) from a filtered xenon arc lamp to promote fluorescence in the developed marks [3]. A further, more extensive comparative study with ninhydrin demonstrated similar sensitivity between the two techniques [4]. In some cases the background fluorescence of the paper caused issues and it was recommended that an area of paper be tested to assess the level of background fluorescence prior to treatment of the entire exhibit.

1.4 The process was introduced into operational use in several police forces, including the Metropolitan Police [5] where it was used as part of a sequential treatment routine in serious cases. However, by the late 1980s, concerns were being raised about the fact that NBD chloride was a potential mutagen and its use began to decline. Almog *et al.* investigated the synthesis and properties of a range of NBD chloride derivatives [6] and identified several with potential for further study, but with the introduction of 1,8-diazafluoren-9-one (DFO) this class of compounds does not appear to have been developed further.

2. Theory

2.1 NBD chloride is a non-fluorescent compound that reacts with amino acids to produce a fluorescent reaction product, shown in outline below.



NBD Chloride

Fluorescent product

Fluorescent product formed by reaction between 4-chloro-7-nitrobenzofurazan and amino acids.

2.2 Published NBD chloride formulations utilised chlorofluorocarbon (CFC) 1,1,2-trifluorotrichloroethane (CFC113) as the carrier solvent and either ethanol or acetonitrile as the principal solvent. The formulation used by Salares [2] consisted of:

20mg NBD chloride
2mL absolute ethanol
20mL CFC113.

2.3 The resultant solution was sprayed, the treated article allowed to dry and then heated for 10 minutes at 90°C. Other researchers [3] used the solution as a dip bath, and suggested heating for the same time at the slightly higher temperature of 110°C.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the use of NBD chloride because it is not as effective as DFO, and there are concerns about it being a suspected mutagenic compound.

4. References

1. **Fager, R. S., Kutina, C. B. and Abrahamson, E. W.** (1973) 'The Use of NBD Chloride (4-chloro-7-nitrobenzo-2-oxa-1,3-diazole) in Detecting Amino Acids and as an N-Terminal Reagent', *Anal. Biochem*., vol. 53, pp 290–294.

2. **Salares, V., Eves, C. and Carey, P.** (1979) 'On the Detection of Fingerprints by Laser Excited Luminescence', *Forens. Sci. Int*., vol. 14, pp 229–238.

3. **Warrener, R. N., Kobus, H. J. and Stoilovic, M.** (1983) 'An Evaluation of the Reagent NBD Chloride for the Production of Luminescent Fingerprints on Paper: I. Support for a Xenon Arc Lamp Being a Cheaper and Valuable Alternative to an Argon Ion Laser as an Excitation Source', *Forens. Sci. Int*., vol. 23, pp 179–188.

4. **Stoilovic, M. Warrener, R. N. and Kobus, H. J.** (1984) 'An Evaluation of the Reagent NBD Chloride for the Production of Luminescent Fingerprints on Paper: II. A Comparison with Ninhydrin', *Forens. Sci. Int*., vol. 24, pp 279–284.

5. **Creer, K. E. and Brennan, J. S.** (1987) 'The work of the serious crime unit', *Proceedings of the International Forensic Symposium on Latent Prints,* 7–10 July 1987, pp 91–99. Virginia USA: FBI Academy, Quantico.

6. **Almog, J., Zeichner, A., Shifrina, S. and Scharf, G.** (1987) 'Nitrofurazanyl Ethers – A New Series of Fluorigenic Fingerprint Reagents', *J. Forens. Sci*, vol. 32 (3), pp 585–596.

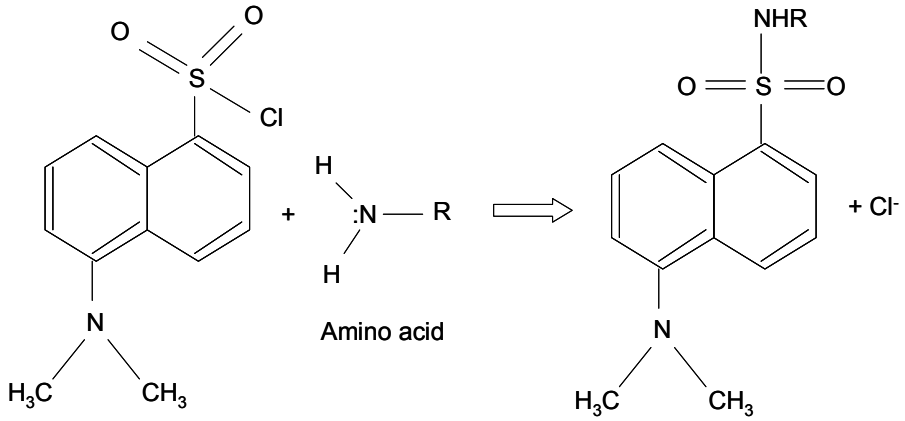
5.9.6 Dansyl chloride

1. History

1.1 Dansyl chloride is another reagent originally developed for the analysis of amino acids [1-3], producing a fluorescent reaction product that is excited by ultraviolet (UV) light. In common with other amino acid detection compounds, it has been investigated as a fingerprint development reagent [4]. In tests where ninhydrin and dansyl chloride were used as spray reagents on brown paper and cardboard, dansyl chloride appeared to give higher sensitivity on weaker marks. However, the process has not been extensively pursued as a practical technique since the mid-1980s.

2. Theory

2.1 The dansylation reaction of amino acids is described in detail elsewhere [1]. The reaction product formed by the reaction of dansyl chloride with fingerprint residues has been shown to absorb at 360nm (UV) and an emission maximum at around 475nm.



Reaction between dansyl chloride and amino acids.

2.2 A formulation given for dansyl chloride is:

0.2g dansyl chloride
100mL acetone
adjust pH to 10 using additions of 8M potassium hydroxide.

The resultant solution was applied by spraying.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the process because no extensive comparative studies have been carried out on its effectiveness. Dansyl chloride is also corrosive and potentially explosive under certain conditions and is therefore not recommended for health and safety reasons.

4. References

1. **Sieiler, N.** (1970) 'Use of the Dansyl Chloride in Biochemical Analysis'. In *Methods of Biochemical Analysis*, Glick, E. J. (ed). J Wiley.

2. **Lee, M. - L. and Safille, A.** (1976) 'Improved Solvent System for Thin-layer Chromatography of Dns-amino acids', *J. Chromatog.*, vol. 116, pp 462–464.

3. **Tapuhi, Y., Schmidt, D. E., Lindner, W. and Karger, B. L.** (1981) 'Dansylation of Amino Acids for High-Performance Liquid Chromatography Analysis', *Anal. Biochem*., vol. 115, pp 123–129.

4. **Burt, J. A. and Menzel, E. R.** (1985) 'Laser Detection of Latent Fingerprints: Difficult Surfaces', *J. Forens. Sci*, vol. 13 (2), pp 364–370.

5.10 Iodine

1. History

1.1 Iodine is one of the earliest chemical processes proposed for the development of latent fingerprints and is still in operational use today. The observation that iodine fumes could be used both to detect handwriting alterations and to develop latent fingerprints was reported by Coulier in 1863 [1]. In a review of early literature relating to fingerprint development conducted by Morris [2] references to the use of iodine fuming are made in 1891 and a procedure for its application given in 1912. It was noted that fumes of iodine directed onto paper produced a yellow colour where the iodine was absorbed by the fingerprint residues. However, this staining was only transitory, fading in minutes, and further experiments were conducted to identify a method of fixing the mark.

1.2 Iodine fuming was in operational use in the UK by 1931 [3] and a method of transferring and fixing developed marks using moist paper carrying rice starch was proposed in 1935 [2]. An alternative means of 'lifting' developed marks by means of a silver foil was being used by the 1960s [4], the iodine selectively reacting with the surface to form silver iodide, which then darkened when exposed to strong light. A refinement to the starch fixing process was proposed at about the same time [5], the proposed method being to brush the mark with finely ground starch powder, blow to remove the excess and then expose the mark to gentle steam for 1–2 seconds. In a summary of methods used to develop fingerprints produced by Scotland Yard in 1970 [6] iodine fuming was among the recommended development techniques, in this case utilising the starch powder fixing method. Iodine fuming was either applied within an enclosure, or could be applied to surfaces using a fuming pipe, the latter approach not now recommended because of health and safety concerns.

1.3 The lifting of fingerprints developed using iodine with silver or tin plates was further investigated as a means of recovering fingerprints from skin [7,8,9]. Experiments demonstrated that marks could be recovered from both live and dead skin using this technique and although marks could be recovered up to 72 hours after deposition on dead skin, the retention time on live skin was significantly shorter. It was also observed that only oil-rich, sebaceous marks were developed in this way, no development being observed for eccrine marks.

1.4 Further work was carried out on iodine fixatives in the 1970s. 'Tetrabase'(4,4-Bis(dimethylamino)diphenylmethane) was investigated as a fixing solution and also as an additive in uncured silicone rubber mixes, which could be moulded over a developed mark to fix it without recourse to solvent dipping or spraying [10]. Other researchers proposed α-naphthoflavone [11], with this method of fixing ultimately being favoured in the UK for operational use [12,13]. Simultaneous fuming of iodine and steam was studied as a means of improving the sensitivity of

iodine fuming on paper and also improving the performance of the reagent on older marks [14]. Iodine fuming was also applied to non-porous surfaces, with successful results on brass being claimed [6].

1.5 It was subsequently proposed that the sensitivity of the technique could be improved by applying the iodine in solution, combined with the a-naphthoflavone fixative [15]. This formulation used cyclohexane as the solvent for iodine, which is highly flammable and not considered appropriate for use at scenes of crime. The Metropolitan Police and Home Office Central Research Establishment (HO CRE), Aldermaston developed a non-flammable, two-part formulation with the objective of treating large areas such as painted and papered walls at scenes [16]. This formulation was based on iodine dissolved in Fluorisol (1,1,2-trichlorotrifluoroethane, also known as CFC113 or Arklone), with the α-naphthoflavone fixative dissolved in dichloromethane applied as a separate solution. Comparative trials were carried out with the chlorofluorocarbon (CFC)-based ninhydrin formulation – known as non-flammable ninhydrin (NFN) – then in operational use, recording the marks developed under ambient conditions [16]. It was shown that the iodine solution was more effective in these conditions, although on paper and paper-based wallpaper ninhydrin gave superior performance if it was exposed to elevated temperature and humidity. Iodine solution was introduced into operational use by some organisations with marks being developed at around one-third of scenes treated [16].

1.6 The iodine solution formulation developed by HO CRE was considered for inclusion in the first edition of the *Manual of Fingerprint Development Techniques*, primarily as a process for application to wall surfaces at crime scenes. However, further comparative testing carried out by the Home Office Scientific Research and Development Branch (HO SRDB) between iodine solution and the CFC-based ninhydrin formulation indicated that ninhydrin was in fact the more effective process and that the sequence of iodine solution and fixative followed by ninhydrin may produce fewer marks than ninhydrin as a single treatment [17]. The principal advantage of iodine solution was that it developed marks instantly, compared with the period of up to ten days required for the development of marks treated with ninhydrin at a scene. Because of the potentially detrimental (albeit slight) effect of iodine solution and fixative on subsequent ninhydrin development, the process was ultimately omitted from the manual. The possibility of applying the reagent as a spray was also investigated [18], and was claimed to be more effective than both ninhydrin and the brush application of iodine solution.

1.7 With the introduction of the Montreal Protocols in 1987 and the banning of the use of CFCs, it became necessary to look at alternative formulations of iodine solution. PSDB initiated a programme of work to revisit the iodine solution formulation and assess alternatives to the solvent, fixing agent and to iodine itself [19]. These studies identified heptane and methyl cyclohexane as possible alternative solvents to CFC113. However, both these solvents are flammable and not suitable

for crime scene use without significant precautions. Alternative non-flammable solvents gave inferior performance in the development of fingerprints. Of the range of fixing agents studied, α-naphthoflavone proved to be the most effective in terms of colour and longevity of the fixed mark.

1.8 Australian researchers also studied the use of formulations based on the non-CFC solvents 1-methoxynonafluorobutane (HFE7100) and 2,3-dihydrodecafluoropentane (HFC4310mee) [20]. Although not as effective as the CFC-based formulation, the HFC4310mee formulation was investigated as a spray reagent on a range of surfaces, including treated wood, glass, wallpaper, vinyl, paint, brick and raw wood, and its performance compared with powdering and a ruthenium tetroxide spray reagent. In these trials, iodine was found to be the most effective treatment of those evaluated for vinyl, wallpaper and brick. Other studies using iodine have looked at α-naphthoflavone as a fixative for marks developed on skin using fuming [21] and fuming as a technique for developing marks on adhesive tape [22].

1.9 More recently, in 2004-2005, HOSDB included a flammable (heptane-based) iodine solution in comparative studies of techniques for developing marks on contaminated surfaces, where it was compared with solvent black 3 and basic violet 3. On certain surfaces iodine did appear to give superior results and it will be necessary to explore this in more detail to see if iodine has a place in some sequential treatment charts.

1.10 A further study has been conducted by HOSDB to compare the flammable, heptane-based iodine solution to ninhydrin on a range of wall coverings representative of those commercially available in 2009 [23]. The materials used to manufacture wallcoverings have changed in the years since the previous studies, and the results demonstrated that the flammable iodine formulation was far more effective than ninhydrin on the surfaces studied, in contrast to previously observed trends. This does raise some operational issues because the flammable formulation should not be applied at scenes and the effectiveness of ninhydrin has evidently declined. Subsequent treatment of these surfaces with powder suspensions has indicated that this process is potentially far more effective than either iodine or ninhydrin and further work is required to optimise advice given for treatment of such surfaces.

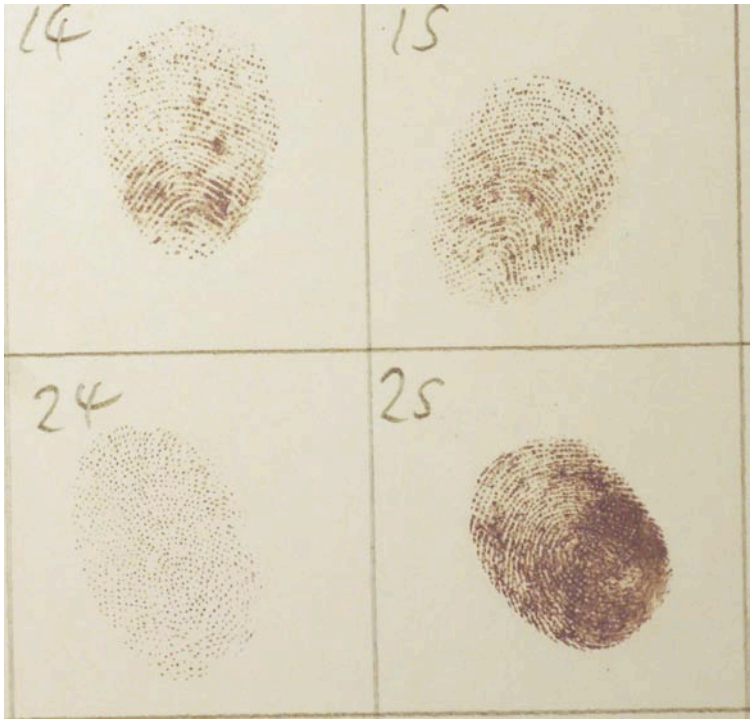
2. Theory

2.1 It has been suggested that the development of fingerprints using iodine occurs by an addition reaction across the carbon double bonds in the unsaturated fatty acid components of the fingerprint residue [24]. The readily reversible nature of this reaction is used to explain the rapid fading of prints developed using iodine.

2.2 However, observations by subsequent researchers indicate that this may not be the sole reaction mechanism [14]. The following reasons for this are cited.

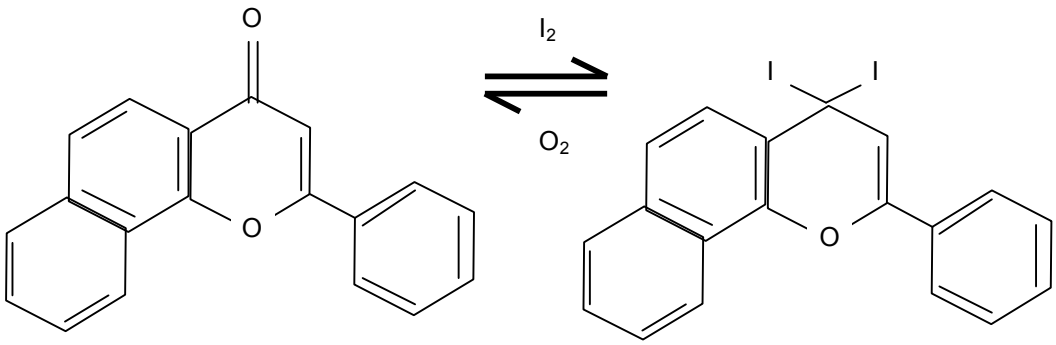
- The addition reaction across the double bonds of unsaturated compounds is known to be slow, whereas the development of prints using iodine is instantaneous and still occurs at sub-zero temperatures.
- The reactions that occur to fix the developed marks would not occur unless free iodine was present; the iodine compounds formed by the saturation reaction would not react in the same way.
- Laboratory trials with chemical compounds representative of other fingerprint constituents, including saturated hydrocarbons, amino acids, inorganic salts and water, also gave visible reaction products on exposure to iodine fumes.

2.3 It was proposed that the principal mechanism binding iodine into the fingerprint deposit and causing its yellow/brown coloration is the attractive interaction between the constant dipole of water molecules in the fingerprint and a dipole induced on the iodine molecule. It is proposed that this effect is enhanced by the presence of inorganic salts in the fingerprint residue [14]. Because the presence of water is necessary, this would account for the observed poor performance of iodine on older marks where water has evaporated.



Fingerprints from different donors developed on glossy paper by iodine fuming.

2.4 The mechanism of the fixing reaction has not been conclusively identified, but Sears [17] suggests a reversible reaction between iodine and α-naphthoflavone, which would account for the fading of the fixed marks with time.

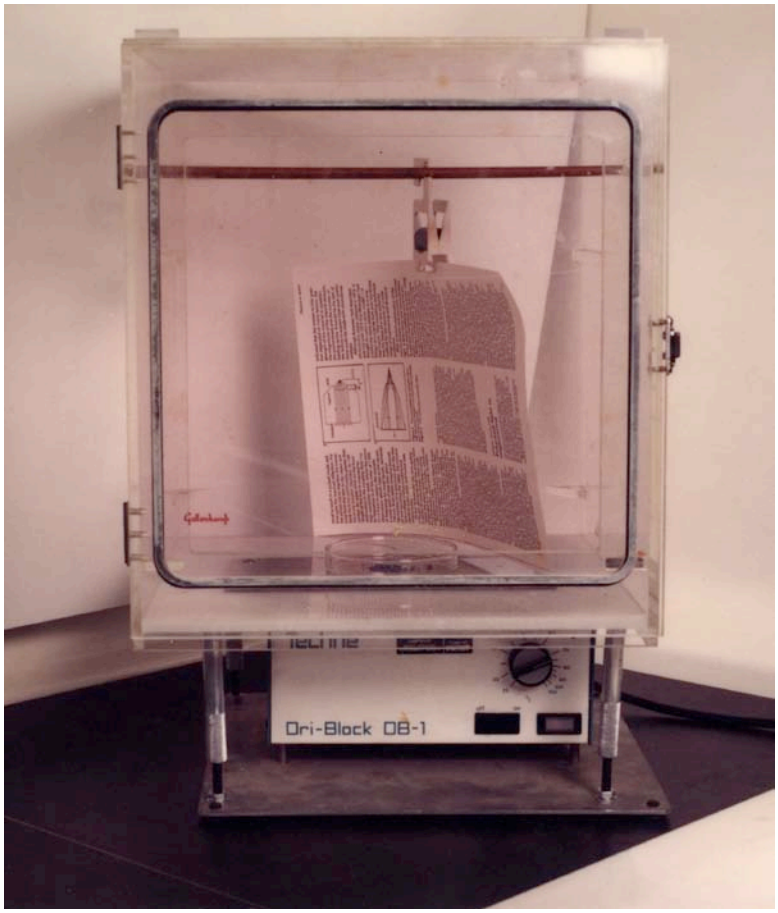


α-Naphthoflavone

Proposed fixing mechanism for iodine using α-naphthoflavone.

3. CAST processes

3.1 The currently (2011) recommended CAST process is iodine fuming rather than solution treatment, although this will be withdrawn from the principal processes recommended in the forthcoming 3rd edition of the *Manual of Fingerprint Development Techniques*. In the fuming process, the article to be treated is supported or suspended within a small chamber, 1g of iodine placed onto a glass dish at the base of the chamber, and the chamber sealed. The iodine is then allowed to sublime (or can be gently heated to 50ºC), producing a violet/brown vapour.



Article being treated by iodine fuming.

3.2 Development of fingerprints is monitored and when the maximum contrast is reached between ridges and the background, the excess iodine vapour is removed from the chamber and the article removed and photographed.

3.3 Fingerprints may then be fixed using a solution based on α-naphthoflavone, but the formulation given in the 2nd edition of the *Manual of Fingerprint Development Techniques* [13] requires review because it is based on CFC113.

4. Critical issues

4.1 Iodine fumes are corrosive and harmful, and iodine solution is harmful and flammable. Neither process should be used outside the controlled environment of a laboratory.

4.2 Marks developed using iodine may fade rapidly and require fixing to make them more visible and more permanent for subsequent imaging.

4.3 Iodine is not effective on marks more than a few days old, and should not be used if older marks are being targeted.

5. Application

5.1 Suitable surfaces: Iodine fuming is suitable for porous surfaces, in particular paper. Performance is best on glossy paper types. It can be used on non-porous surfaces, but is most suited for those where greasy contamination is present. Iodine solution is suitable for all surfaces where iodine fuming is successful, and is also effective in developing fingerprints on painted wall surfaces. However, it is not recommended for use on painted walls because of the flammability of the solution.

5.2 The iodine process does not appear in any of the sequential treatment flow charts in the *Manual of Fingerprint Development Techniques* [13]. This is because there is no surface for which iodine is more effective in developing fingerprints than any of the other recommended processes. Iodine fuming is retained in the manual because it is the only chemical treatment that can be used without leaving visible traces on the treated article. There are specialist applications where the lack of a visible, developed mark is important and iodine fuming is an option in these cases. Because it is not often possible to determine what substances may be present in an article before treatment, iodine should be used with caution because some substances may be capable of temporarily fixing the mark and inhibiting the normally rapid fading process.

5.3 Iodine fuming (and iodine solution) are also capable of detecting fingerprints on contaminated surfaces. Because iodine, basic violet 3 and solvent black 3 all develop marks in slightly different ways and may not target the same constituents, iodine may develop marks where other processes are ineffective. At least one practical case of this is known (see section 8 on validation and operational experience, below). Because it has proved difficult to generate consistent ‘contaminated’ surfaces for laboratory trials, it is not currently (2011) possible to give comprehensive guidance for when (or if) iodine should be considered in either fuming or solution form, or to propose sequences with other reagents for contaminated surfaces.

5.4 In the laboratory, iodine fuming should be carried out in a chamber sited within a fume cupboard. Fuming can be also be carried out on larger items or at scenes of crime using portable glass pipes with heated compartments to start iodine fuming, and desiccant crystals to dry the fumes. Because of the toxic and corrosive nature of iodine vapour, this should only be carried out in well ventilated and/or extracted areas by operators with the appropriate protective equipment.

5.5 Iodine solution can also be applied in a laboratory or at a crime scene by brushing or spraying. The solvents used as carriers for iodine are either flammable or capable of displacing air and should therefore be used with appropriate health and safety measures. CAST does not currently (2011) recommend the use of iodine solution.

6. Alternative formulations and processes

6.1 Several processes have been proposed as alternatives to the fuming technique outlined in the manual [13]. The principal one of these is the iodine solution treatment, until recently (up to around 2008) in regular use in the UK by the Forensic Science Service (FSS). CAST does not recommend this process for a variety of reasons, including effectiveness (although this may need to be reassessed), impact on subsequent treatments, health and safety, and scene clean up considerations. However, it is recognised that the technique does have some potential advantages and may warrant more evaluation.

6.2 Previous assessments of the iodine solution process carried out by CAST in the late 1980s and late 1990s [17,19] have included investigations into alternatives to the solvent, fixing agent and iodine itself.

6.3 In the late 1980s, replacements to cyclohexane as the solvent for iodine were considered [17], with the main consideration being to identify a less or non-flammable formulation. Several candidate systems were rejected on the basis of cost (dichlorocyclohexane, dibromocyclohexane, 1,9-dichlorononane, 1,10-dichlorodecane and 1,7-dibromoheptane). Decahydronaphthalene ('Decalin') was tested as an alternative solvent and found to give fingerprint development equivalent to the cyclohexane formulation. However, evaporation time of the solvent from the treated surface increased from seconds to 20–40 minutes and this was not deemed practical for operational use. Ultimately, the CFC113-based formulation developed by HO CRE provided a non-flammable system that could be used at scenes of crime.

6.4 Replacements for dichloromethane in the α-naphthoflavone fixing solution were also investigated. Ethanol, ether, 2-ethoxyethanol, 1,1,1 trichloroethane did not dissolve α-naphthoflavone and were therefore unsuitable. α-Naphthoflavone did dissolve in acetone and glacial acetic acid, but in both cases the quantity of solvent required was far greater than the amount of dichloromethane and no change to the existing formulation was made.

6.5 After CFCs were withdrawn from regular use, HOSDB reassessed several formulations that included CFC113, including iodine solution. The objective was to produce an all-in-one formulation containing iodine and fixing agent. The CFC formulation was compared with a range of different solvent types, including:

- hydrofluorocarbons (HFCs) – 2,3-dihydrodecafluoropentane (HFC4310mee), 1,1,1,3,3-pentafluorobutane (HFC365mfc), 1-methoxynonafluorobutane (HFE7100) and 1-ethoxynonafluorobutane (HFE7200);

- siloxanes –octylmethylcyclotetrasiloxane (Volasil 244), decamethylcyclopentasiloxane (Volasil 245);
- hydrocarbons – cyclohexane, heptane, methyl cyclohexane.

6.6 Of these, iodine had only limited solubility in the hydrofluorocarbons, as did α-naphthoflavone. This resulted in rapid precipitation of the fixative unless excess dichloromethane was added. Solutions based on the siloxane solvents were more stable, but often took in excess of one hour to evaporate from the surface being treated. Solutions based on siloxanes also developed fewer fingerprints. All hydrocarbon solvents produced solutions that were effective in fingerprint development. However, all are flammable.

6.7 The opportunity was also taken to review alternatives to α-naphthoflavone. The alternatives considered were starch, β-cyclodextrin and the leuco-dyes leuco crystal violet, leuco malachite green, leuco patent blue and leuco berbelin blue.

6.8 The leuco dyes were effective fixing agents but for a variety of reasons, including the cost of the reagent and background staining, were not proposed as replacements for α-naphthoflavone. Starch was the least effective of the fixing agents examined and although β-cyclodextrin did fix marks, the colour contrast was poor and ninhydrin could not be used sequentially after its use.

6.9 The interhalides iodine monobromide and iodine monochloride were considered as replacements for iodine. Solutions formed with these compounds were less stable and the colours of the fixed marks were less strong. As a consequence, these compounds were not pursued further.

6.10 The most effective all-in-one iodine solution was identified as:

part A: 0.4g iodine dissolved in 194mL of heptane or methyl cyclohexane;
part B: 0.6g α-naphthoflavone dissolved in 6mL of dichloromethane.

Part B is added to part A, the resultant solution is filtered and applied with a brush.

6.11 However, there were disadvantages with the formulation (such as flammability) making it difficult to recommend for widespread use, especially at crime scenes. This formulation is used internally by CAST as the standard formulation for comparative laboratory studies of technique effectiveness.

7. Post-treatments

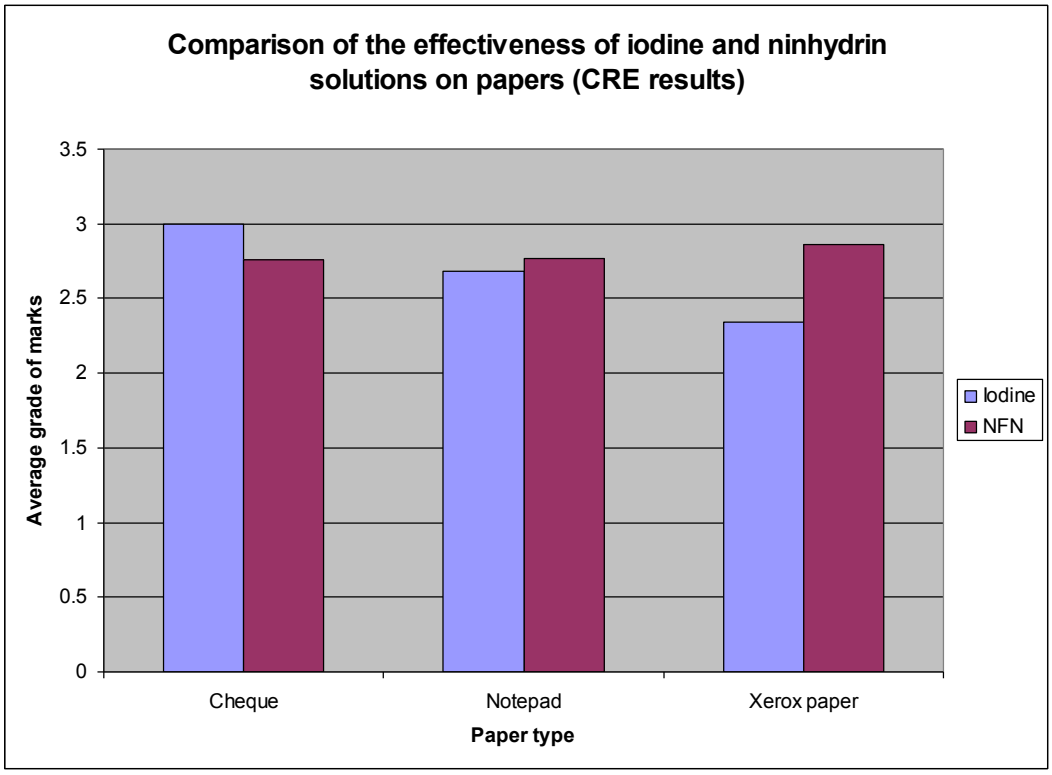
7.1 The principal post-treatment used for iodine is fixing solution, which can be applied to marks developed using both fuming and solution treatments (although the CAST solution contains the fixative in the solution itself). The fixing solution converts the yellow/brown marks into a product with a more highly contrasting colour, and prevents them from rapidly fading. The most commonly used fixing agent for iodine is α-naphthoflavone, which gives a deep blue coloration.

7.2 For fingerprints developed using iodine on skin, lifting using tin or silver plates has been proposed, which involves placing the metal plate in contact with the developed mark. The reactive iodine will form a metal iodide on regions of the metal in contact with the fingerprint ridges, which can then be darkened by illumination with strong light to reveal the ridges.

8. Validation and operational experience

8.1 Laboratory trials

8.1.1 Iodine solution was proposed as one possible treatment for paper samples in a laboratory during the early/mid-1980s. To explore this potential application HO SRDB and HO CRE both carried out laboratory trials on paper exhibits, comparing the effectiveness of iodine solution and the non-flammable ninhydrin formulation then in operational use. The results obtained by HO CRE are tabulated below, being based on the results of developing and assessing single fingerprints deposited by 100 different donors.



Comparative results obtained for iodine and ninhydrin (NFN) on porous surfaces.

8.1.2 The HO SRDB studies consisted of trials using 40 split prints on white card and cheques. Three comparisons were made: iodine versus ninhydrin; the effect of subsequent ninhydrin treatment after iodine; and the iodine/ninhydrin sequence versus ninhydrin. The results are summarised below.

Grading	Iodine = ninhydrin	Iodine > ninhydrin	Iodine < ninhydrin
Percentage	75	10	15

Grading	Iodine = iodine/NFN	Iodine > iodine/NFN	Iodine < iodine/NFN
Percentage	70	25	5

Grading	Iodine/NFN = ninhydrin	Iodine/NFN > ninhydrin	Iodine/NFN < ninhydrin
Percentage	60	10	30

Results of comparative tests between iodine, ninhydrin and iodine/ninhydrin sequences.

8.1.3 The PSDB results were in accordance with the HO CRE results. Iodine solution was, in general, a less effective treatment than ninhydrin for paper samples and the sequential use of ninhydrin after iodine did not yield as many marks as ninhydrin alone. Iodine solution was therefore not recommended for use on paper articles by HO SRDB.

8.1.4 To assess the effectiveness of iodine solution on wall surfaces, Pounds [16] carried out a series of laboratory trials at HO CRE comparing iodine solution and the CFC-based ninhydrin formulation on surfaces representative of wall coverings. Initial tests looked at sheets of substrate stored in a laboratory, and consistently showed the iodine solution to be more effective when marks were developed under ambient conditions. Subsequent tests utilised actual sections of painted wall and added powders to the techniques used in comparative studies. The results of these studies are tabulated below.

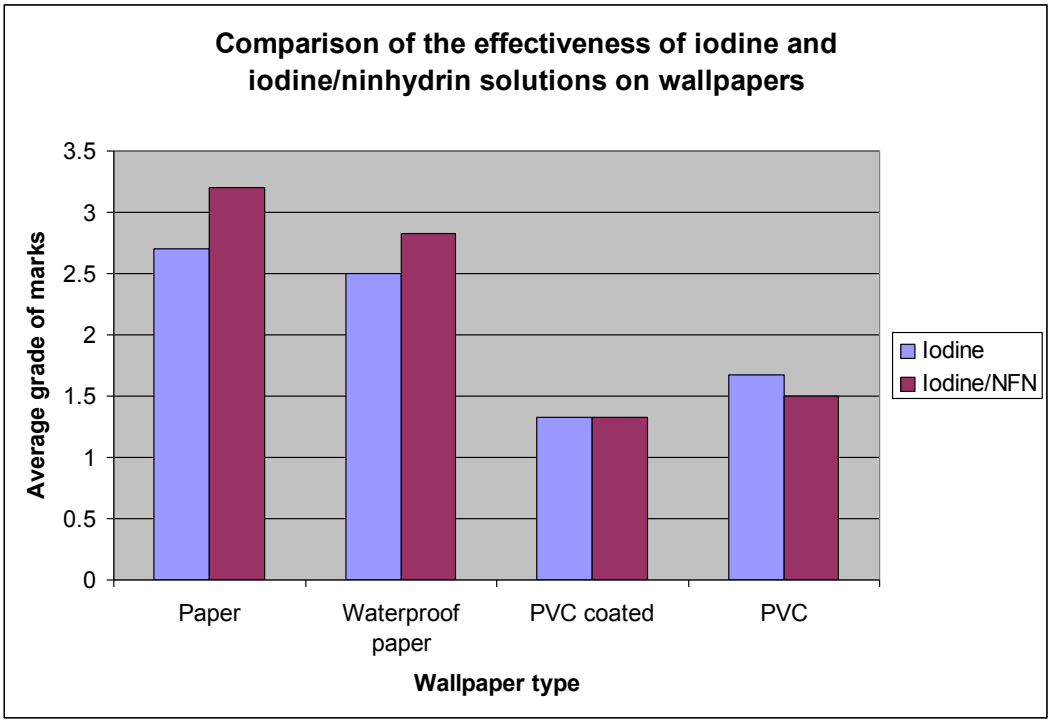
Storage condition	**Development method**	**Days treated and assessed**					
		0	**5**	**12**	**20**	**32**	**53**
Wall by window	Iodine solution	3.1	1.5	1.7	1.5	1.5	1.1
	Ninhydrin (CFC)	2.2	–	–	–	–	1.6
Wall in shade	Iodine solution	2.9	1.7	2.1	1.4	1.4	1.6
	Ninhydrin (CFC)	2.0	–	–	–	–	1.9

Average quality score for fingerprints developed on emulsion painted wall.

Development method	**Days treated and assessed**			
	1	**5**	**12**	**27**
Iodine solution	3.9	3.3	2.9	1.9
Ninhydrin (CFC)	1.0	–	–	–
Magnetic powder	2.9	–	–	–
Aluminium powder	1.0	–	–	–

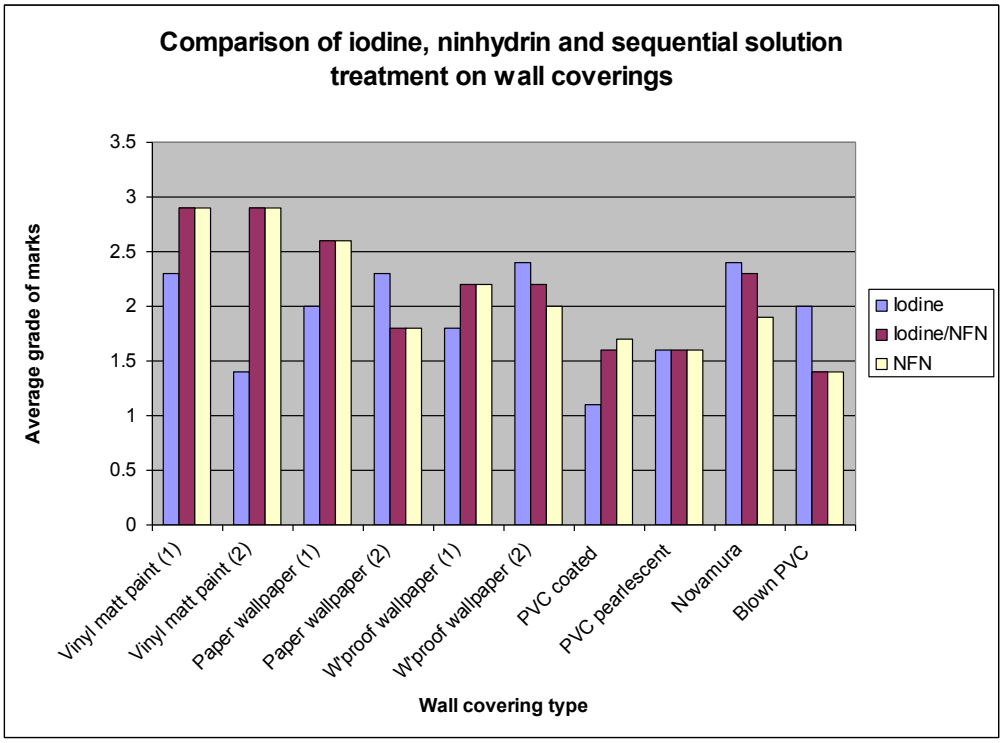
Average quality score for fingerprints developed on emulsion painted wall.

8.1.5 HO SRDB carried out similar studies [17] looking at a wider, more representative range of wall coverings, including painted walls and different types of wallpaper. Two trials were conducted, both involving the grading of over 200 prints. The first looked at aluminium powder, black granular powder, iodine and iodine followed by ninhydrin on the full range of surfaces. In this trial, aluminium powder was found to out-perform iodine solution on vinyl silk painted walls, but apart from this surface both powders produced significant clogging on the surface and were not recommended for use. On matt paint iodine worked well, but additional marks were developed by subsequent ninhydrin treatment. A summary of the results for the wallpaper surfaces is given below.



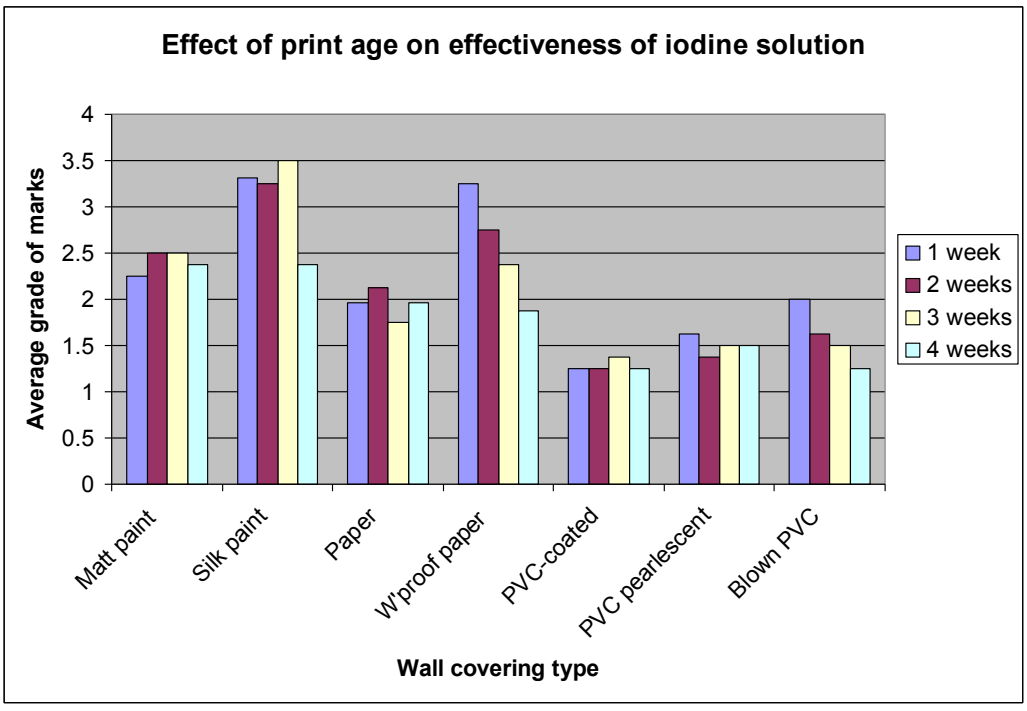
Comparative results obtained for iodine and iodine/ninhydrin on wallpapers.

8.1.6 The results again showed a general trend that ninhydrin developed more marks after iodine solution, but this was not true on every surface examined. This trial was repeated, but now including marks that were treated with ninhydrin alone. The results were similar to those above, showing that in general the iodine solution was less effective than the iodine/ninhydrin sequence and ninhydrin alone. However, there were certain surfaces where iodine solution was the single most effective treatment, although it was not always possible to determine which type of surface was present before commencing treatment.



Comparison of effectiveness of different processes and sequences on different wall coverings.

8.1.7 The effect of the age of the print on development using iodine solution was also studied by HO SRDB, 96 marks being deposited and graded for each age (from one to four weeks). Results are summarised below.



Effect of age of mark on effectiveness of iodine solution.

8.1.8 There is again agreement between the HO SRDB results and those obtained by HO CRE. In general the effectiveness of iodine solution falls with time but on certain surfaces there is a less obvious fall off.

8.1.9 Based on laboratory trials, HO CRE introduced iodine solution into operational use in the late 1980s. The performance of the Fluorisol-(CFC113)-based iodine formulation was found to be equivalent to the cyclohexane-based formulation in laboratory tests, and superseded it in operational use until CFCs were banned by the Montreal Protocols and the formulation reverted to one based on a flammable solvent. Operational performance figures recorded for iodine solution (including results obtained using both formulations) are given below.

Type of case	**Number of scenes**		**Number of iodine marks recorded**
	Examined	**Marks found**	
Murder	71	28	56
Rape	12	3	4
Burglary	9	4	6
Other major crime	11	2	3
Total	**103**	**37**	**69**

Operational results obtained by the use of iodine solution at scenes of crime.

8.1.10 The results presented above were criticised by HO SRDB at the time in that they did not provide a detailed assessment of the types of surface the iodine solution had been applied to (only the crime type), nor did they record the effectiveness of subsequent ninhydrin treatment [25]. In several of these cases, it was known that ninhydrin had developed significant numbers of additional marks. Subsequent development of a spray formulation [18] resulted in further operational trials by HO CRE, the initial results of which are given below.

Surface type	**Number of scenes**		**Number of iodine marks recorded**
	Examined	**Marks found**	
Wallpaper	5	2	15
Emulsion paint	11	6	24
Total	**16**	**8**	**39**

Operational results obtained by the use of iodine spray at scenes of crime.

8.1.11 Subsequent testing of the different application routes for iodine solution by PSDB [19] found that solution dipping was the most effective, followed by brush application, with spray being the least effective. Brush application is the technique that was used at crime scenes up until 2008.

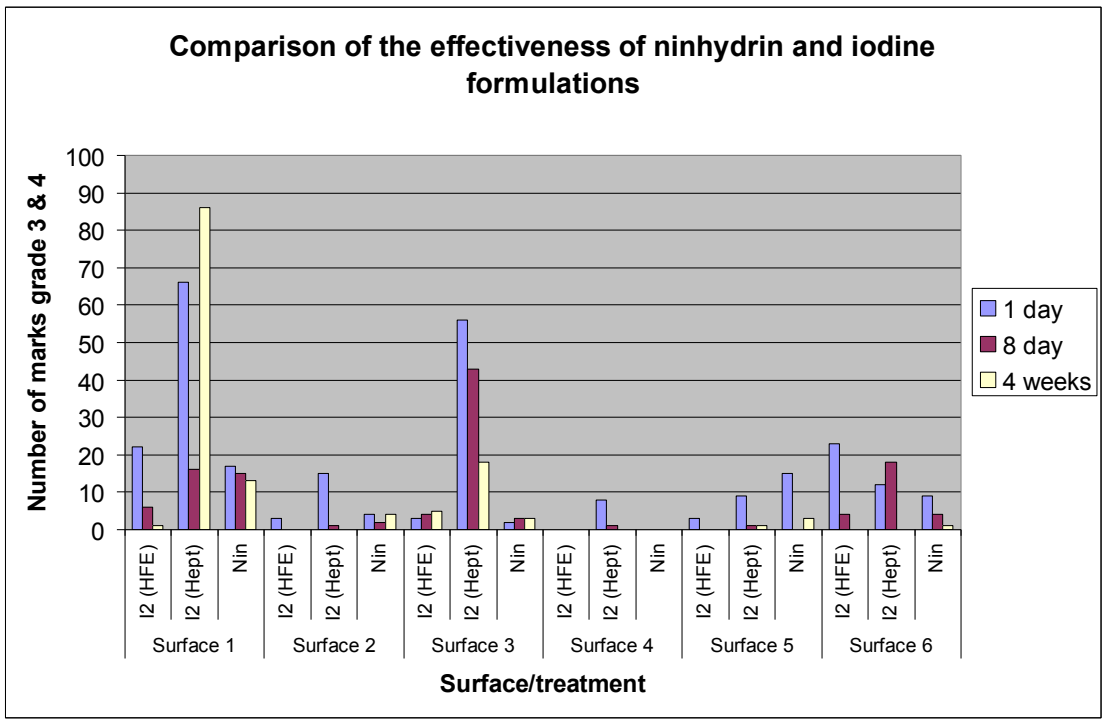
8.1.12 One of the other potential applications of iodine solution (and fuming) is in the development of marks on contaminated surfaces. Comparative laboratory trials were carried out between the CAST iodine solution formulation and solvent black 3. These are more fully reported in Chapter 3.9 Solvent black 3 and demonstrated that in general solvent black 3 was more effective, although there were some surfaces, such as gloss painted wood, where iodine solution was more effective.

8.1.13 In the repeat trials on wallcoverings conducted in 2009 [23], the following surfaces were examined.

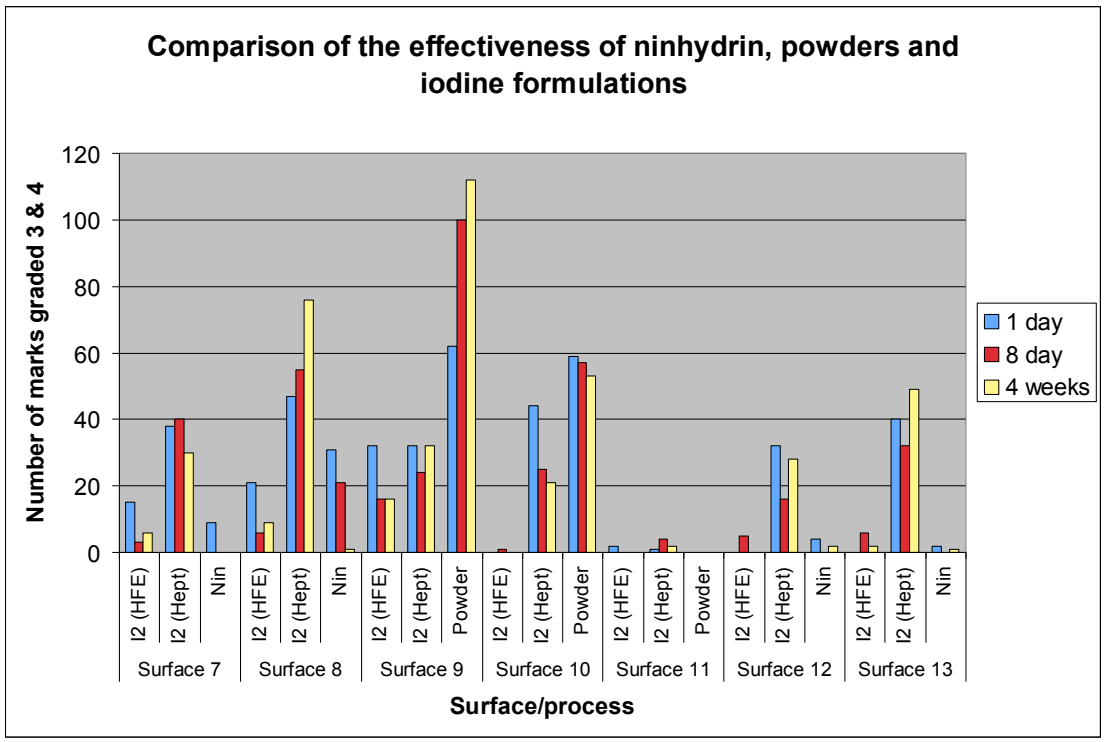
Surface	**Type**	**Porosity**
1	Wickes master washable matt paint	Porous
2	Dulux interior matt paint	Porous
3	Wallpaper – pulp	Porous
4	Wallpaper – vinyl	Non-porous
5	Wickes interior matt emulsion paint	Porous
6	Crown silk emulsion	Non-porous
7	Wallpaper – foamed polyethylene	Semi-porous
8	Wallpaper – washable vinyl coated	Semi-porous
9	Wickes liquid gloss paint	Non-porous
10	Dulux liquid gloss paint	Non-porous
11	Crown non-drip satin paint	Semi-porous
12	Dulux grease and stain resistant, tough matt paint	Porous
13	Wallpaper – vinyl coated	Semi-porous

Description of the surfaces examined in the 2009 study.

8.1.14 For all surfaces except gloss paint, the effectiveness of the heptane-based iodine solution was compared with a low-flammability, HFE71DE-based iodine solution and ninhydrin, whereas on gloss painted surfaces powders were substituted for ninhydrin. Over 4,500 marks were graded in this study.



Results of the 2009 comparative study on surfaces 1–6.



Results of the 2009 comparative study on surfaces 7–13.

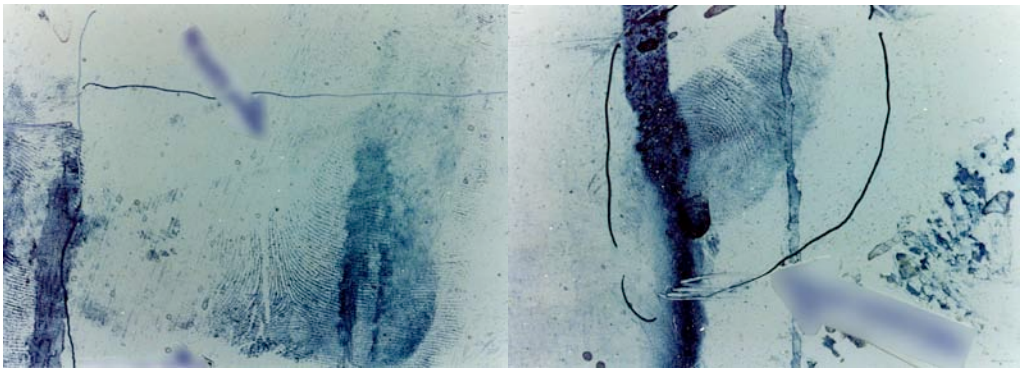
8.1.15 It can be seen that the heptane-based iodine solution out-performed the HFE71DE-based iodine solution and ninhydrin on all almost surfaces, except for 1 day old marks on surface 6. The heptane-based solution gave far less background staining than the HFE71DE-based solution, and marks of greater contrast than ninhydrin. On gloss

surfaces, powdering gave superior performance to both of the iodine solutions. Very few additional marks were found to be developed by leaving surfaces treated with ninhydrin for a further two-week period. Subsequent treatment of the surfaces with powder suspensions produced a significant improvement in the number and quality of developed marks over and above all of the initial treatments. The results of this further study are still (2011) being analysed.

8.2 Pseudo-operational trials and operational experience

8.2.1 The use of iodine fuming on operational work is rare, because it is only recommended in special circumstances, such as where the surface is contaminated or the treatment should ideally leave no trace on the article being examined. However, there are recorded cases where iodine has produced marks of value and the other processes recommended for contaminated surfaces (basic violet 3, solvent black 3) have not. PSDB was involved in the treatment of a contaminated fridge from a fast food outlet in the 1990s where iodine fuming yielded identifiable marks.

Contaminated fridge treated using iodine fuming followed by fixing with α-naphthoflavone.



Marks developed on contaminated fridge using iodine fuming followed by fixing with α-naphthoflavone.

8.2.2 The operational use of iodine solution has been more contentious, with CAST not recommending the process and the FSS until recently (2008) often using it on serious operational cases. One of the reasons CAST has not recommended iodine solution is that previous studies conducted in the late 1980s and again in the late 1990s indicated that it was less effective than ninhydrin across the range of surfaces it was likely to be applied to, and the use of fixative may inhibit subsequent ninhydrin development. However, the most recent studies (2009) have shown that this may no longer be true, with considerably more marks being found by iodine solution than were developed by ninhydrin. In addition, marks are revealed instantly with iodine and may take several days to develop fully with ninhydrin. Some of the background data behind these original recommendations are presented here, although it should be noted that all the early comparisons were between iodine solution and the CFC-based ninhydrin formulation (NFN). The more recently developed HFE7100-based ninhydrin formulation was more effective than the CFC-based formulation on paper (see Chapter 3.4, Ninhydrin) but until the recent study [23] no tests had been carried out on surfaces representative of wall coverings.

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5.11 Multimetal deposition

1. History

1.1 The multimetal deposition (MMD) system for developing fingerprints was first proposed by Saunders [1] in the late 1980s. The system incorporated principles of both small particle reagent and physical developer and provided a universal developing agent capable of producing marks on porous, semi-porous and non-porous surfaces.

1.2 To carry out the MMD process, porous items were immersed in distilled water for 20–30 minutes (treatment of other types of article omitted this immersion stage). Items were then immersed in colloidal gold solution for 30–120 minutes, rinsed in distilled water (for up to 15 minutes in the case of porous items) and then immersed in a silver physical developer solution for 5–15 minutes. After a final rinse in distilled water items were air dried and photographed.

1.3 After the publication of this technique, researchers in the UK and elsewhere began to investigate the capabilities of MMD. In the UK, the Central Research and Support Establishment (CRSE) of the Home Office Forensic Science Service (FSS) carried out a trial comparing MMD with superglue fuming and vacuum metal deposition on a range of surfaces known to be difficult to treat, including clingfilm, plastic shotgun cartridges, masking tape and expanded polystyrene [2]. These results suggested that for some of these surfaces MMD did produce superior results, although it could not be used sequentially after superglue.

1.4 The Police Scientific Development Branch (PSDB) also carried out an assessment of the process and confirmed that it worked on a wide range of substrates, including polythene bags, metal, fabric tape, coated cardboard, masking tape, wax candles, leather and cling film [3]. Tests were carried out on paper, but no results were obtained because the paper blackened. Development of fingerprints on fabrics was also attempted, as was subsequent radioactive toning of any marks developed. Faint ridges were seen during drying but these were not visible when fully dry, although some detail could be seen after radioactive toning and autoradiography. The microstructure of the marks developed was also studied by scanning electron microscopy. HOSDB concluded that MMD was a versatile technique, but gave no better results for any given surface than other techniques already available, and therefore it was not pursued further.

1.5 The process was later extensively re-evaluated by Schnetz and Margot [4]; they proposed an improved formulation offering increased reactivity, improved resolution and greater amplification selectivity (and therefore reduced background interference). Important elements in the revised formulation were the use of an alternative means of producing colloidal gold, giving smaller particle sizes, and the replacement of the silver

nitrate/iron(II), iron(III) redox system in the physical developer stage with silver acetate/hydroquinone.

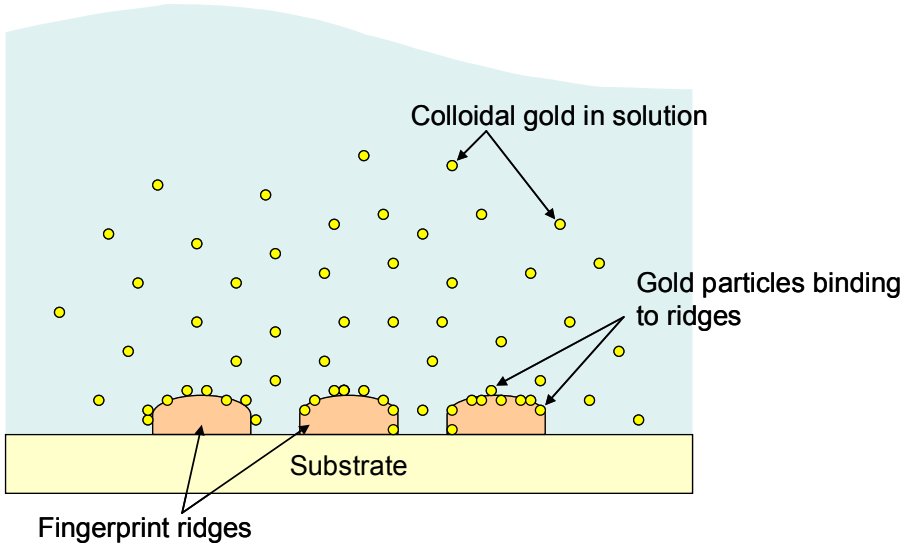
1.6 Jones [5] used the revised MMD formulation in an extensive study of processes for developing fingerprints on semi-porous surfaces. It was found that although not particularly effective on the polymer banknotes used in Australia, MMD did have potential applications for other semi-porous surfaces, including expanded polystyrene, latex and nitrile gloves, and waxed paper.

1.7 More recently Becue *et al.* [6,7] have considered further revisions to the MMD process, trying to simplify the process and to investigate the possibility of functionalising the gold nanoparticles with colorimetric or fluorescent tags. These studies are ongoing and may yield further revised formulations in future.

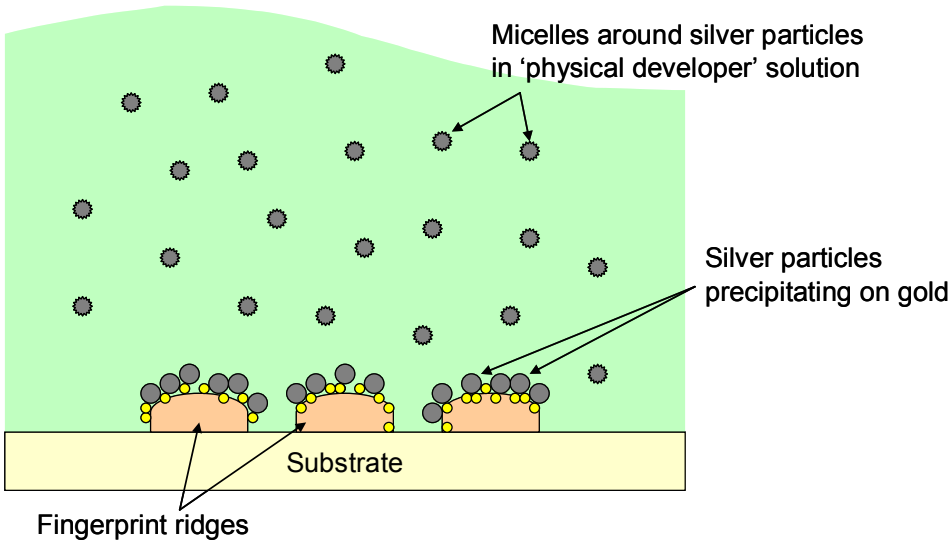
1.8 Other recent refinements have included the development of formulations for single metal deposition (SMD) [8,9] where the two-stage silver and gold deposition is replaced by a single-stage gold deposition process. This is claimed to have the advantages of reducing the number of treatment stages, reducing the number of different reagents and associated costs, and utilising reagents with a longer shelf life.

2. Theory

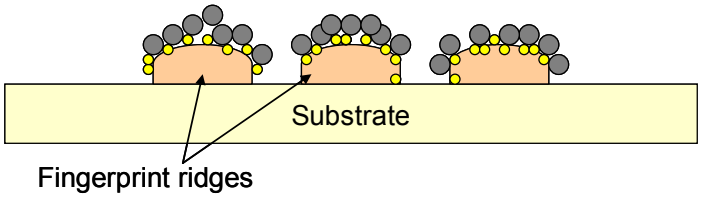
2.1 MMD is essentially a two-phase development process, illustrated schematically in the diagrams below. The exhibit to be treated is immersed in an acidified solution containing colloidal gold particles, which bind preferentially to the amino acid, protein and peptide constituents of the fingerprint. This stage alone generally gives poor contrast of the ridges and therefore a second amplification stage is used. This involves the use of a modified physical developer solution, where surfactant stabilised silver particles preferentially deposit on the colloidal gold, thus turning the ridges dark grey to black in colour.



a)



b)



c)

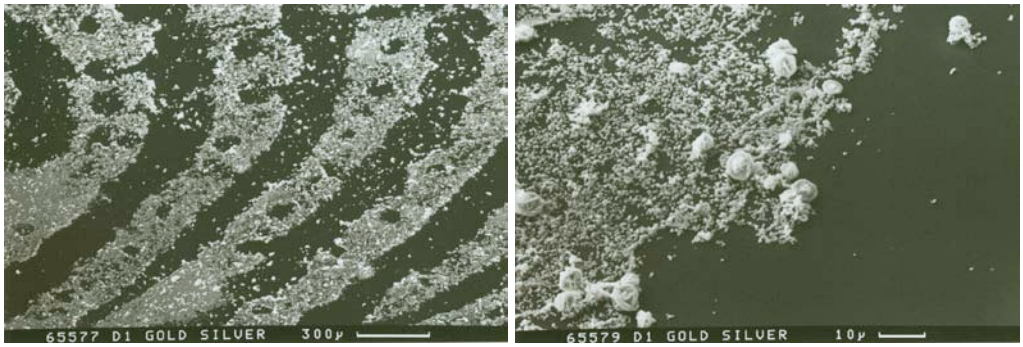
Schematic diagrams illustrating the stages in the multimetal deposition process a) colloidal gold binding to ridges b) preferential deposition of silver particles on pre-existing gold and c) dried mark with contrast provided by silver particles.

2.2 The reason that colloidal gold particles (in the case of MMD formed by the chemical reduction of tetrachloroauric acid) are used is that they are both negatively charged and hydrophobic. Binding between organic compounds and colloidal gold particles can occur by both electrostatic and hydrophobic reactions. The dominant binding mechanism varies with pH, hydrophobic interactions dominating at high pH and electrostatic interactions dominating at low pH. Schnetz and Margot [4] have suggested that it is the electrostatic interactions that are responsible for the reaction with fingerprint deposits and the pH of the treatment solution is kept low (pH 2.5–3) to facilitate this. Mildly acidic compounds such as amino acids, fatty acids and proteins carry a positive charge under these conditions and attract and bind to gold particles from the solution.

2.3 The size of the gold particles is also regarded as important, with smaller particles claimed to result in higher specificity. A size of 5–15nm is recommended, although some researchers claim to have obtained equivalent results with 30nm particles.

2.4 The physical developer solution is effectively a modification of the system used to develop fingerprints on paper, containing silver ions in the presence of a reducing system, the solution being stabilised by surfactants. The silver ions are reduced to silver metal and the gold particles bound to the ridges act as a nucleation site for this to occur. The gold particles also act to catalyse the reduction of the silver.

2.5 Scanning electron micrographs of a mark developed using MMD are shown below [3].



a) b)

Scanning electron micrographs of marks developed using multimetal deposition a) low magnification showing fingerprint ridges and b) higher magnification showing precipitated particles.

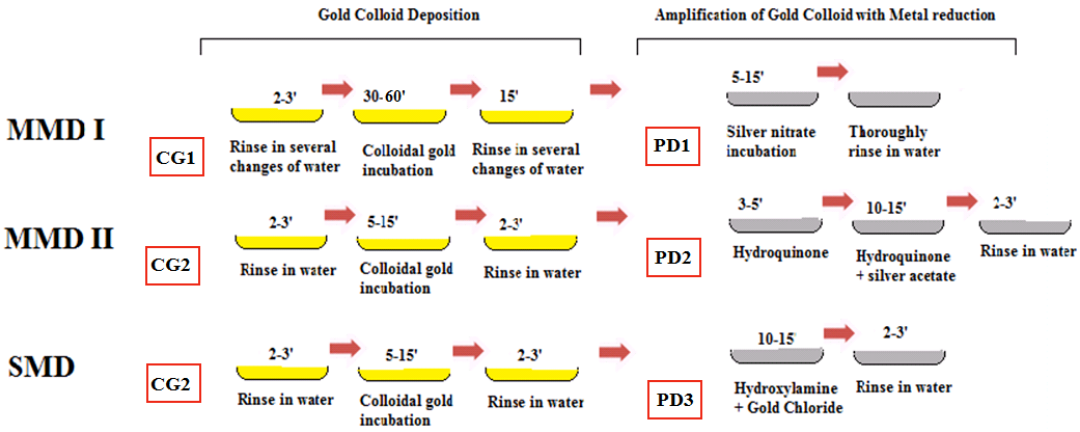
3. Reasons technique is not recommended by CAST

3.1 CAST does not currently (2011) recommend MMD because it has not been shown to give better performance than any other technique currently recommended. MMD does give reasonable results on a wide range of surfaces, but in tests carried out by PSDB in 1992 there was no single surface on which MMD gave better results than any other recommended process.

3.2 In addition to this, the technique is difficult to carry out effectively compared with many other existing processes. It requires siliconised glassware, all items used in the process must be kept scrupulously clean and it is necessary to constantly monitor pH while carrying out initial colloidal gold deposition. There are also many stages to the process and some of these may be time-consuming, even more so than the physical developer process. It has proven difficult to obtain good, reliable results and therefore the process is not recommended for routine use. The more recent SMD process [8,9] utilises fewer stages and offers potential for further study.

3.3 More recently, a further study has been carried out at HOSDB [10] to assess the relative effectiveness of MMD I, MMD II and SMD and to compare an optimised MMD process with currently recommended

processes in the *Manual of Fingerprint Development Techniques* [11]. The essential elements of the two MMD and one SMD processes are shown schematically below.



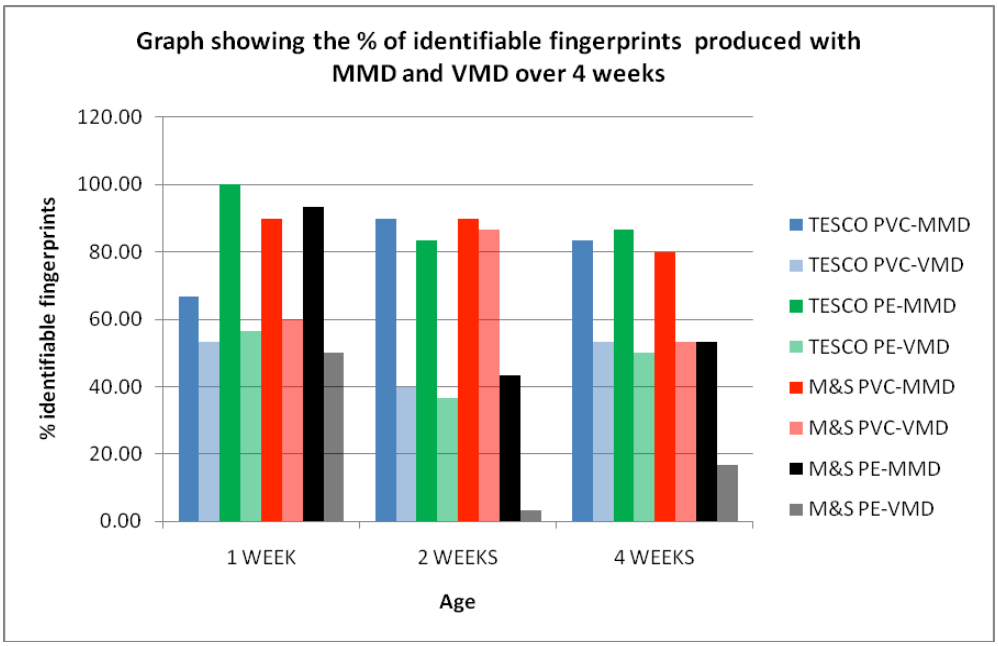
Schematic diagram showing the stages in the multimetal deposition and single metal deposition processes, and their duration.

3.4 Comparative tests confirmed that the MMD II process was the most effective. However, it was felt that this was impractical for routine use and the MMD I technique, with the pH of the colloidal gold solution reduced to pH 2.5–2.8, was chosen as the preferred method for comparative trials. This was compared with the techniques currently (2011) recommended in the CAST manual [11] for the various surfaces, summarised in the table below.

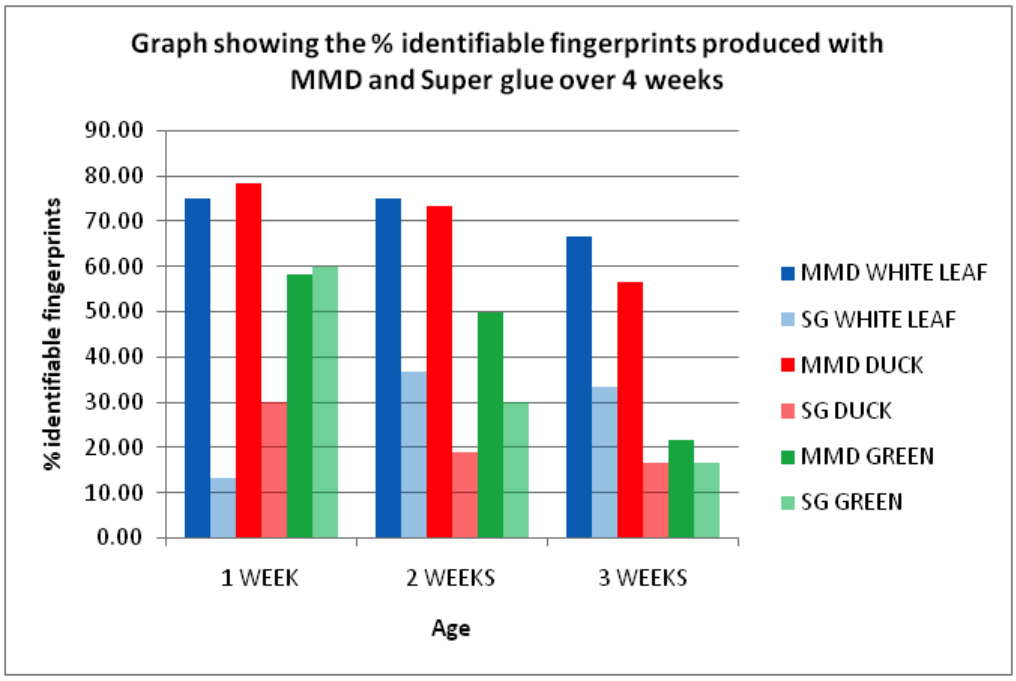
Surface	Current recommendation
Cling film – PVC/PE-based	Silver vacuum metal deposition (VMD)
Shower curtains – vinyl-based	VMD and cyanoacrylate fuming
Leatherette – PVC-based	Powder suspensions – Wet Powder Black/White ™
Leather	Powder suspensions – Wet Powder Black/White ™

Surfaces for which comparative experiments were carried out, and the processes used in the comparisons.

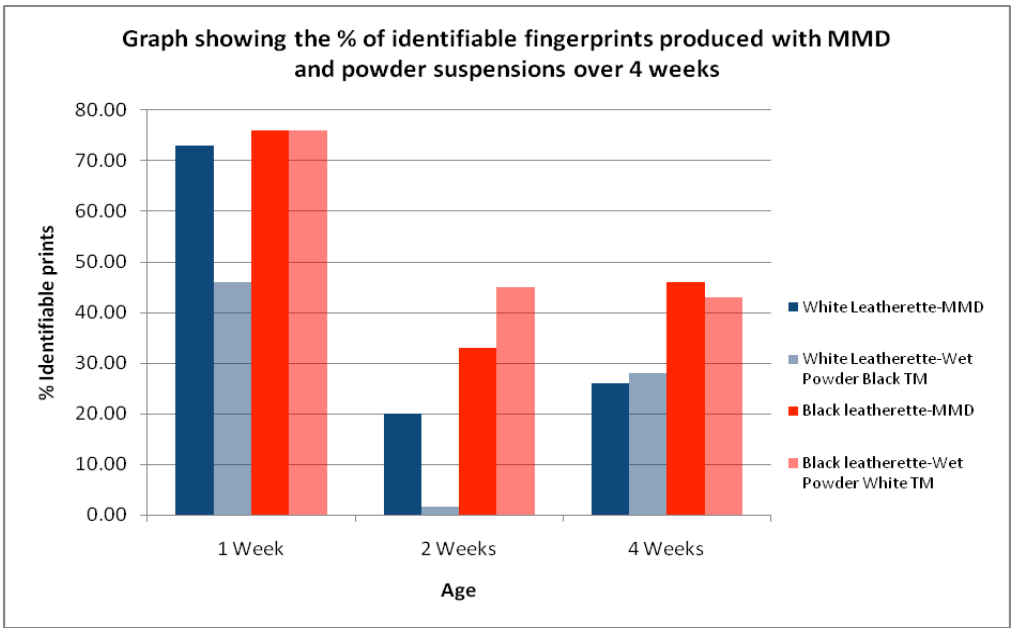
3.5 The results of these comparisons are summarised in the series of graphs and tables below.



Graph showing the proportion of potentially identifiable fingerprints developed on clingfilm over four weeks.



Graph showing the proportion of potentially identifiable fingerprints developed on shower curtains over four weeks.



Graph showing the proportion of potentially identifiable fingerprints developed on leatherette over four weeks.

	Leather white textured	
	MMD	**Wet Powder Black™**
% Identifiable prints	5.00	18.00
Average score	0.57	0.97
Standard deviation	0.89	1.37

The average score, proportion of identifiable prints and standard deviation for marks developed using multimetal deposition and powder suspension on white leather – whole prints.

3.6 MMD did show improved performance over existing techniques for vinyl-based polymer surfaces in general, and on clingfilm in particular. These results suggest there may be operational merit in using MMD on such surfaces and that further research is desirable to see if the process could be incorporated into processing sequences.

4. References

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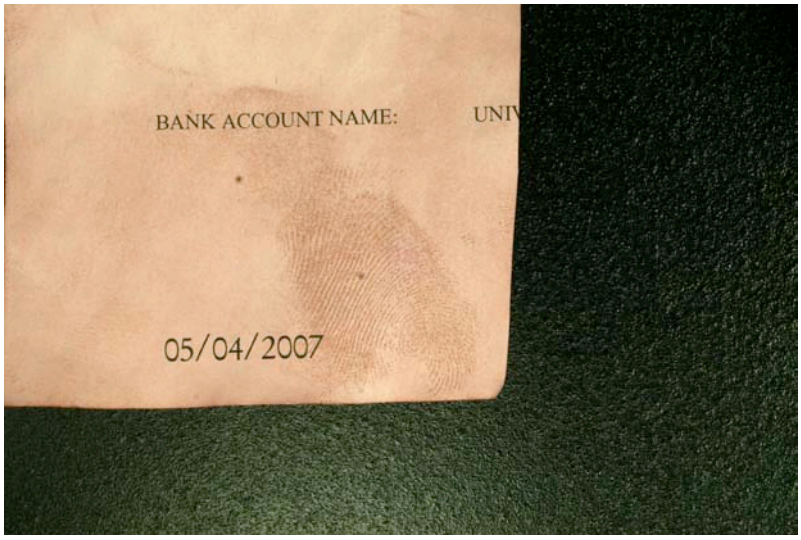
5.12 Oil Red O

1. History

1.1 Oil Red O (also known by its Colour Index name solvent red 27) is a superlipophilic diazo dye and is closely chemically related to Solvent Black 3. It has been used as a fat stain for biological samples and also industrially as a colorant for oils, fats and waxes. As the name suggests, the dye is red in colour and selectively stains lipid components. The Police Scientific Development Branch (PSDB) initially investigated Oil Red O, amongst other lipid dyes, as an alternative to solvent black 3 on non-porous surfaces [1]. These studies indicated that solvent black 3 was a superior dye for the particular range of surfaces being investigated (i.e. non-porous surfaces) and no further work was carried out on Oil Red O at this time.

1.2 The next reported forensic application of Oil Red O was for the development of lip prints [2], with a range of similar dyes including Oil Red O, solvent black 3, solvent red 23 (Sudan III) and solvent red 24 (Sudan IV) being applied, both in powder form and in solution for the staining of lip prints deposited on tissue paper.

1.3 In 2004, Beaudoin [3] reported an Oil Red O formulation for the development of fingerprints on wetted papers. The work was carried out to identify alternatives to the complex and time-consuming physical developer process, and resulted in a two-stage method consisting of a dip bath of Oil Red O in a methanol/sodium hydroxide solvent, followed by immersion of the exhibit in a sodium carbonate/nitric acid buffer solution. Initial tests on wetted surfaces ranging from porous to non-porous in nature indicated that Oil Red O was effective on porous and semi-porous surfaces, but that developed marks were difficult to visualise on non-porous surfaces.



Photograph of fingerprint developed on paper using Oil Red O.

1.4 This was followed by a comparative study looking at the relative effectiveness of Oil Red O and physical developer on thermal papers, white printer paper and brown Kraft paper [4]. In these studies sebum-rich fingerprints were deposited on paper that was wetted, divided in two and then treated using the selected process. For the range of surfaces examined, Oil Red O gave superior results on both thermal papers and white printer paper. On the brown Kraft paper, average scores were similar, but physical developer gave more marks of high quality.

1.5 A further study was conducted to look at the insertion of Oil Red O into sequential treatments on porous surfaces [5]. Again sebum-rich fingerprints were used, and comparisons made between the quality of fingerprints developed in the sequences including Oil Red O and those omitting it. Both wetted and dry papers were considered in these studies. For white paper, results indicated that improved fingerprint quality could be achieved by inserting Oil Red O into standard sequential treatments as the stage before physical developer. For brown papers Oil Red O was found to be detrimental, primarily because of the pink background staining caused by Oil Red O making marks subsequently developed using physical developer more difficult to visualise.

1.6 The promise of these studies has resulted in more detailed studies being carried out in several countries, including Australia, the UK and the USA [6]. These studies have generally used ‘standard’ fingerprints rather than deliberately sebum-rich marks and have tended to indicate that the effectiveness of Oil Red O begins to fall with the increasing age of the mark, and for marks much older than four weeks, the marks are very diffuse with little ridge detail being developed. The same effect is observed for longer immersion times in water. In both these cases, physical developer continues to develop marks with good clarity of ridge detail.

1.7 Further studies have been carried out at universities within the UK [8,9]. These again demonstrated that on groomed, sebum-rich prints Oil Red O gave superior performance to physical developer, but when normally deposited marks were used, the performance was closely equivalent. It was shown that exposing porous surfaces to accelerant was detrimental for both processes, no marks being developed by Oil Red O or physical developer after exposure.

2. Theory

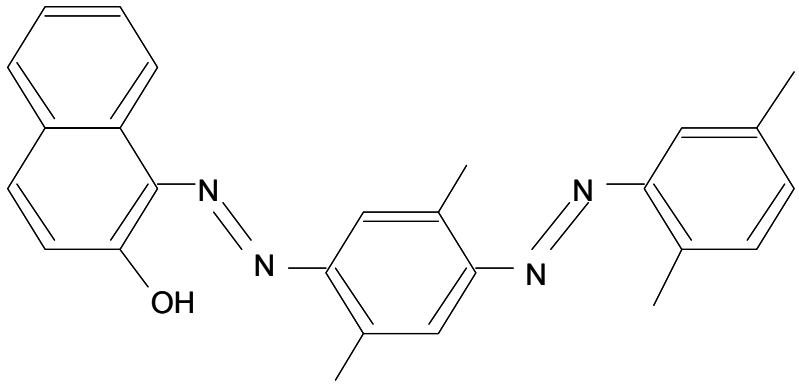
2.1 Oil Red O is a lysochrome, more commonly known as a fat stain. Most lysochromes are azo dyes that, because of their structure, have undergone molecular rearrangement making them incapable of ionising.

2.2 The basis for these dyes colouring fats is that they dissolve into it. From another perspective, the fat is the solvent for the dye. Lysochromes are

mostly insoluble in strongly polar solvents, such as water, and somewhat more so in less polar solvents, such as ethanol. They are quite strongly soluble in non-polar solvents, such as xylene. Triglycerides, being non-polar compounds, dissolve them quite well. Other lipids, having fatty components, may also dissolve them.

2.3 Lysochromes such as Oil Red O are applied from solvents in which they are sparingly soluble. As they come into contact with materials in which they are strongly soluble, they transfer to them significantly, often colouring them more strongly than the original solvent. This process is known as preferential solubility.

2.4 Oil Red O is more strongly hydrophobic than some earlier dyes used for staining lipids, and it is thought that this makes it more effective in staining applications [7]. The structure of Oil Red O is shown below.



Structure of Oil Red O (solvent red 27).

2.5 The formulation proposed by Beaudoin [3] consists of three separate baths, a staining bath to stain the lipid components of the fingerprint, a buffer solution to neutralise the base side of the staining solution and stabilise the developed marks, and finally a water wash. The formulations used are as follows:

stain bath – dissolve 1.54g Oil Red O in 770mL methanol;
dissolve 9.2g of NaOH in 230mL water;
add the two solutions, mix together, filter and store in a brown bottle.

buffer solution – add 26.5g of Na_2CO_3 to 2 litres of water and stir to dissolve;
add 18.3 mL of concentrated HNO_3;
increase volume of solution to 2.5 litres with water.

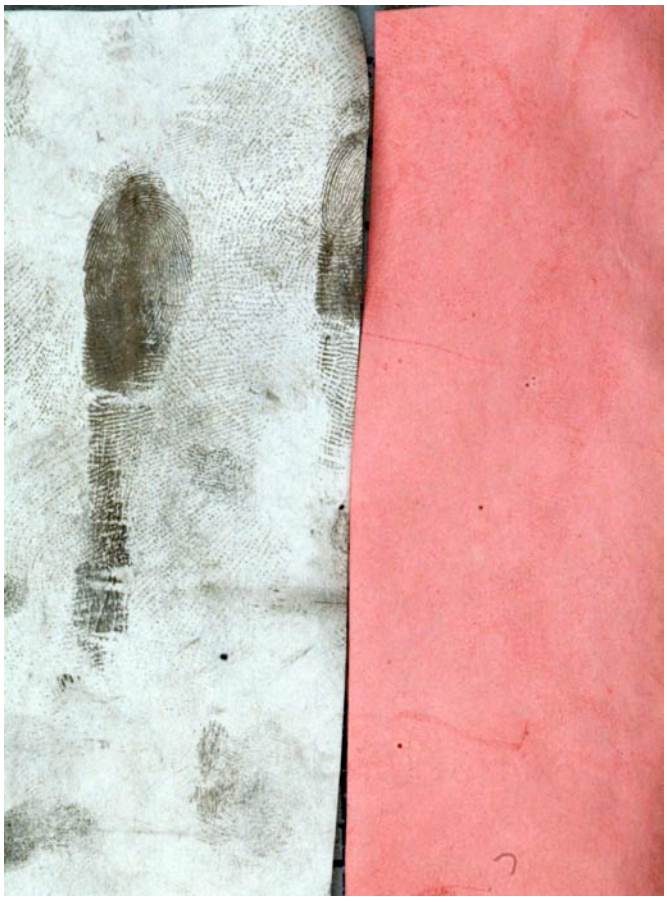
2.6 Articles to be treated are immersed in the stain bath for up to 90 minutes, then removed, drained and placed in the buffer solution. Finally the articles are rinsed in distilled water and allowed to dry.

3. Reasons technique is not recommended by CAST

3.1 The principal reason that Oil Red O is not recommended by CAST is because it is not as effective as physical developer. Although papers referenced above [4,5,8] indicate the reverse to be true, these experiments have been performed using single, sebum-rich marks, which are not truly representative of what may be encountered on real exhibits. Subsequent experiments using 'natural' fingerprints and depletion series of marks [6] are in general accord that:

- Oil Red O is not effective on marks older than four weeks;
- Oil Red O is not effective on marks exposed to prolonged immersion in water;
- some solvents used in ninhydrin and 1,8-diazafluoren-9-one (DFO) formulations outside the UK (e.g. petroleum ether) may dissolve the constituents targeted by Oil Red O and therefore it cannot be used in sequence after these processes.

3.2 A small-scale study carried out by CAST on marks known to be one year old confirmed that physical developer was a far more effective reagent and that Oil Red O developed very few marks on articles of this age.



a) b)

Palm print approximately one year old a) treated with physical developer b) treated with Oil Red O

3.3 In addition to this, although Oil Red O involves fewer processing steps overall than physical developer, it may actually take up to 90 minutes for marks to develop and therefore the whole process may actually be slower in many cases.

3.4 For these reasons, CAST does not currently (2011) see any operational benefit in recommending Oil Red O as a replacement for, or in sequence with, physical developer.

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5.13 Other lipid specific reagents

5.13.1 Ruthenium tetroxide (RTX)

1. History

1.1 The use of ruthenium (and osmium) tetroxide for fingerprint development has been reported since the 1920s [1]. In its early application the process was extremely dangerous to use, requiring ruthenium crystals to be heated in a water bath at temperatures not exceeding 50ºC. Explosions could occur if heating was too rapid or the temperature exceeded 50ºC, making the technique unsuitable for use in most laboratories [2].

1.2 The risk of explosion while fuming ruthenium tetroxide was overcome by the discovery of a chemical method for producing fumes by Mashiko *et al.*[3]. In this technique a solution consisting of 0.1g of ruthenium chloride (III) hydrate in 100mL of water was added to a second solution containing 11.3g of ammonium cerium (IV) nitrate in 100mL of water. The fumes generated in this reaction were circulated with a development chamber using a fan, and the authors demonstrated that sebaceous fingerprints could be developed on both porous and non-porous surfaces. Some work on sequential treatment was carried out, showing that ruthenium tetroxide must be used before ninhydrin and 1,8-diazafluoren-9-one (DFO), but cannot be used in sequence with physical developer. Some interference with superglue and Gentian Violet (basic violet 3) processing was also observed.

1.3 However, it was found difficult to generate sufficient quantities of fumes by the chemical reaction process and Mashiko and Miyamoto [4] later proposed a solution consisting of 0.25g per 100mL of tetradecafluorohexane (C_6F_{14}), which was applied to articles via spraying directly from a glass bottle through a nozzle. Solution dipping was also proposed for exhibits such as adhesive tapes. Wilkinson *et al.* [5] investigated the use of ruthenium tetroxide solution for the development of fingerprints on skin and although the process was found capable of developing marks, these appeared to be of lower contrast than marks produced using other techniques, and could not be lifted.

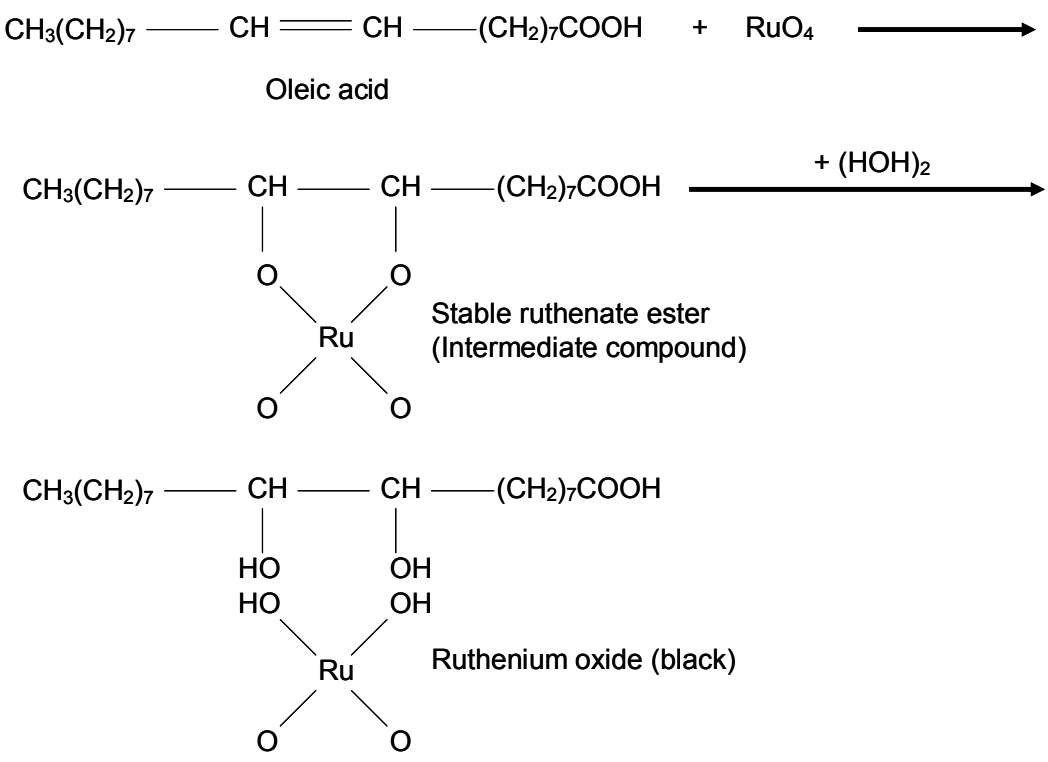
1.4 Mashiko later developed ruthenium tetroxide as a commercial product and has advertised its use in fingerprint journals, [6] although there has been ongoing debate about the safety of the process [7,8].

1.5 In the one comparative study carried out to date, Mashiko's commercial product was not used for cost reasons and the researchers attempted to prepare solutions by dissolving ruthenium tetroxide fumes in carrier solvents of 1-methoxynonafluorobutane (HFE7100) or 2,3-dihydrodecafluoropentane (HFC4310mee). The best results were obtained from HFE7100, which gave a solution of equivalent effectiveness to the commercial formulation. Ruthenium tetroxide

solution was then spray applied and the results obtained compared with those obtained from spray application of iodine solution and powdering. In these trials ruthenium tetroxide was only found to be the best process for very fresh marks on wallpaper and paint. For marks over one day old, performance decreased significantly. Ruthenium tetroxide could not be used in sequence with powders, and inhibited the take-up of fluorescent dye in marks developed using superglue.

2. Theory

2.1 Ruthenium tetroxide (and the closely related process osmium tetroxide) develops fingerprints by reacting across the carbon double bonds present in unsaturated fatty acids in fingerprint residues. The reaction product is a black hydrous oxide that allows the fingerprint to be visualised.



Reduction of ruthenium tetroxide by reaction with unsaturated fatty acids, (adapted from equivalent reaction for osmium tetroxide [2]).

2.2 The same reaction will occur whether ruthenium tetroxide is applied by fuming or in solution.

3. Reasons technique is not recommended by CAST

3.1 The Home Office Centre for Applied Science and Technology (CAST) does not recommend the use of ruthenium tetroxide because it is not as effective as other available processes and there are health and safety concerns about its use.

3.2 HOSDB has not carried out any comparative studies on ruthenium tetroxide because of health and safety concerns raised by other researchers. In the only published comparative study involving ruthenium tetroxide published to date [9], the reagent was found to be less effective than both powders and iodine-benzoflavone spray.

3.3 With regard to the health and safety aspects, there has been published debate about whether ruthenium tetroxide is toxic or not. There is also confusion as to whether the material safety data sheet (MSDS) data referred to in information supplied with the commercial product are for ruthenium dioxide or ruthenium tetroxide. CAST has reviewed the chemical literature available on the toxicity of ruthenium tetroxide and at best the substance has not been fully evaluated. Until this has been satisfactorily resolved CAST does not intend to carry out comparative trials or to recommend the process for operational use.

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5.13.2 Osmium tetroxide

1. History

1.1 Osmium tetroxide was already being proposed as a reagent for developing fingerprints on paper in the early 1900s. By 1920, Mitchell [1] was able to describe two application techniques, namely 'osmic acid', a 1% aqueous solution of osmium tetroxide brushed onto a document, and osmium tetroxide fuming, where the paper exhibit was held over a dish of the boiling 1% aqueous solution. The 'osmic acid' solution treatment was stated to produce black marks if the surface was kept moist whilst exposed to sunlight, whereas the prints produced in the fuming process were grey. A further fuming process was later proposed, involving placing osmium tetroxide crystals in a small, shallow glass dish within a fuming cabinet and adding ethyl ether or carbon tetrachloride [2]. It was essential not to apply heat in this process because of the risk of an explosion.

1.2 Later researchers used pre-prepared ampoules of osmium tetroxide within a fuming cabinet, and used a sensitising chemical called 5-norbornene-2-carbonyl chloride in vapour form as a pre-treatment to produce additional linkages for the osmium tetroxide to react with [3].

1.3 Bones [4] carried out a detailed assessment of the osmium tetroxide fuming process, looking at different environments for the fuming process (air, argon), different development conditions (light, dark, vacuum) and the effects of ageing and humidity on the quality of prints developed. It was concluded that the process was equivalent to ninhydrin in sensitivity, and that the optimum processing conditions were in an air environment and in darkness. It was also shown that osmium tetroxide could develop handprints on fabrics, although there was negligible ridge detail visible.

1.4 Smith Jr [5] later proposed the osmium tetroxide fuming technique for the development of fingerprints on adhesive tapes, including medical

tapes and strapping tapes. The exhibits were processed in air and stored in the dark; progressive darkening of the substrate was observed if exhibits were exposed to the light, and this could obscure marks.

1.5 In the early 1980s the Home Office Scientific Research and Development Branch (HO SRDB) included osmium tetroxide in a comparative study of techniques for development of fingerprints on fabrics [6], which included vacuum metal deposition and radioactive sulphur dioxide. Of these techniques osmium tetroxide, both as a fuming process and in solution, proved significantly less effective than radioactive sulphur dioxide and vacuum metal deposition, and no further work was carried out on this reagent.

2. Theory

2.1 The theory associated with osmium tetroxide is identical to that described for ruthenium tetroxide above. Osmium tetroxide reacts across the carbon double bonds in the unsaturated fatty acids within fingerprint deposits to form intermediate osmate ester compounds that finally produce the black osmium dioxide compound [7].

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the osmium tetroxide process because of the highly toxic nature of the substance. In comparative studies that have been carried out it has not proved to be any more effective than any other process currently (2011) in use.

4. References

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5.13.3 Europium chelate

1. History

1.1 The use of lanthanide series elements in fingerprint detection has been considered in a range of techniques. The attraction of these elements is that they can form fluorescent complexes with large Stokes shifts, meaning that they can be illuminated in the ultraviolet region of the spectrum and emit in the red/infra-red region. The decay time during fluorescence is also longer than many other fluorescent species, making them useful in time-resolved imaging applications and for visualising fingerprints on fluorescing backgrounds.

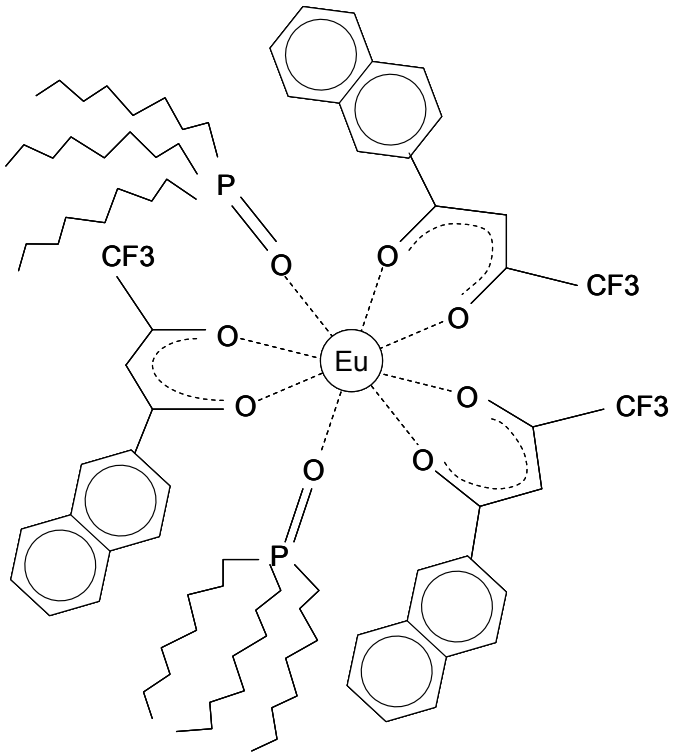
1.2 Initial studies into the potential of these elements for fingerprint detection utilised europium salts as complexing agents for the post-treatment of marks developed using ninhydrin [1]. However, it was recognised that europium complexes also had potential for use as a superglue dye, especially in circumstances where background fluorescence caused problems and a large Stokes shift was desirable [2-4]. The dye was successfully applied to superglue marks developed on multicoloured surfaces and on skin. Dyes were dissolved in methyl ethyl ketone [2,3] or petroleum ether [4].

1.3 Later researchers have considered europium chelates as a fingerprint development reagent in their own right, producing a range of formulations that can either be applied by spraying or as a solution that exhibits can be dipped into [5-9]. Bright, fluorescent marks were successfully developed on both porous and non-porous items in laboratory trials, although these were not replicated when the technique was applied to casework.

2. Theory

2.1 The theory associated with the europium chelate reagent is that the europium complex is in some way attracted by the lipid components of the fingerprint deposit and absorbed into it from solution. Wilkinson [7] suggests that the presence of methanol may aid the transfer process from solution into the fingerprint. Methanol partially dissolves in the lipids of the fingerprint residue, and because the europium complex is water insoluble and prefers the hydrophobic environment of the fingerprint lipids, some of the complex is transferred with the methanol. Once

absorbed by the lipids, the water molecules attached to the europium complex are displaced and replaced by various lipid-based ligands. The resultant structure is a fluorophore and will fluoresce when illuminated with light of an appropriate wavelength.



Structure of biological fluorophore [7].

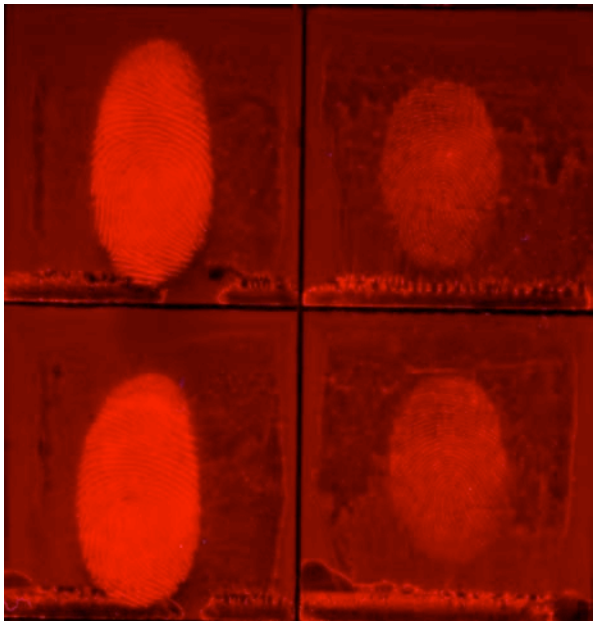
2.2 The bulky fluorophore structure protects the europium from the aqueous environment of the biological medium (in this case the water present in the fingerprint residue). A detergent is added to further isolate the europium ion from the water molecules.

2.3 The formula proposed by Wilkinson [7] is made up as a two- part system and is as follows:

Solution A – 23mg europium chloride hexahydrate;
300mL distilled water;
2mL Tergitol 7.

Solution B – 42mg thenoyltrifluoroacetone;
50mg trioctyl phosphine oxide;
700mL methanol.

2.4 The two solutions are then mixed together for 30 minutes, and articles to be treated are immersed in the resultant solution for 5 seconds then washed in water and allowed to dry.



Sebaceous marks deposited on a ceramic tile and developed using europium chelate.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the process because it has not yet been evaluated. The main reason for this is that reports from other researchers indicate that the performance of the reagent on older marks is poor, therefore it is unlikely to provide advantages over any currently (2011) recommended process. The main solvent used in the existing formulation is methanol, which is not preferred by HOSDB because of its flammability and toxicity. If the process were to be recommended, some reformulation work would be required to see if the methanol content could be reduced or eliminated.

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5.14 Radioactive sulphur dioxide

1. History

1.1 The potential application of radioactive sulphur dioxide ($^{35}SO_2$) for the development of latent fingerprints was first reported by Grant *et al.* in 1963 [1] during the course of investigations into the resistance of paper to attack by atmospheric pollution. They observed that when developing autoradiographs of paper treated with SO_2, spots could be seen on the paper that on closer examination were identified as fingerprints. A further publication by Grant *et al.* [2] gave more background detail on the method used. Radioactive SO_2 was measured into an evacuated flask and the pressure raised to atmospheric by the addition of air at a controlled humidity of 66%. The paper sample was exposed to the gas mixture for 12 hours, then placed against x-ray film for 1 week. Other experiments carried out by the researchers demonstrated that ageing of the marks reduced the chances of fingerprint development. It was also found that alkaline fillers in the paper could give rise to heavy SO_2 take-up by the background and that metal impurities also picked up SO_2.

1.2 The results of further research into the technique were reported by Spedding in 1971 [3]. He suggested that SO_2 was reacting with the lipids present in fingerprint deposits and noted that reactions occurred with oleic and linoleic acids. Prints were also developed on paper that had been wetted. Spedding *et al.* also issued a more detailed report [4], providing details of the apparatus used for development of fingerprints. This consisted of a treatment box within which samples could be hung on a rail. Humidity inside the box was raised to 60%, radioactive SO_2 introduced and the samples exposed for 30 minutes before being removed and placed in contact with x-ray film. Trials were also conducted for a range of paper types, comparing the effectiveness of SO_2 for fingerprint development with that of ninhydrin and iodine. SO_2 was found to be the most effective technique across the range of paper types investigated. Spedding *et al.* also considered the potential effects of the SO_2 technique on subsequent development techniques, in particular the 60% humidity and SO_2 concentration used. It was considered that the humidity could be detrimental to the subsequent use of silver nitrate, but that other techniques should be unaffected. The report also suggested that radioactive SO_2 could prove a useful technique for the development of fingerprints on fabrics.

1.3 The wider application of the technique to substrates other than paper was reported in late 1970 [5]. Excellent results were reported for PVC sheet and initial results on fabrics were encouraging. Further studies into the optimum humidity for treatment were presented, with humidities in excess of 60% giving rise to an increase in the uptake of SO_2 in the substrate compared with that in the fingerprint, and therefore being undesirable.

1.4 The initial results obtained for paper exhibits had been encouraging and the technique was used on operational exhibits of types that had previously given poor results with ninhydrin, iodine and silver nitrate. An early operational success was obtained on forged £5 notes [6].

1.5 Research into the technique continued, with the objectives of establishing optimum processing conditions and the range of substrates that radioactive SO_2 could develop marks on. A more detailed study was carried out into fingerprints deposited on paper [7], investigating the effect of storage time (1–6 days) and storage humidity (31–93% relative humidity) on the quality of fingerprints developed using radioactive SO_2, ninhydrin, iodine, silver nitrate and vacuum metal deposition (VMD), then also in a developmental stage. Across the range of conditions studied VMD gave the best results, followed by ninhydrin. In these trials radioactive SO_2 performed relatively poorly. In contrast, studies conducted on dry paper identified SO_2 as being more effective than ninhydrin, silver nitrate and a sequence of ninhydrin followed by silver nitrate [8]. One advantage of the SO_2 process was that it eliminated much of the printed text that could potentially obscure minutiae. An optimum development sequence of SO_2 > ninhydrin > silver nitrate was proposed for paper exhibits.

1.6 The major area of research for the practical application of radioactive SO_2 was the development of fingerprints on fabrics and a comprehensive report into these studies was issued by Wells in 1975 [9]. The equipment used in these studies consisted of a 150 litre Perspex box into which a mixture of radioactive SO_2 and nitrogen gas (N_2) was introduced. The optimum humidity was identified as 65%, but effectiveness fell rapidly in the range 66–75% and 60% was recommended for operational purposes. The addition of ozone into the gas mixture was found to increase SO_2 uptake by the fingerprint and thus reduce autoradiography times. An autoradiography guide was developed for a range of substrates including fabrics, plastic wrappings and banknotes, outlining optimum development times. The use of a dark, sealed enclosure containing desiccant was recommended for storage of exhibits prior to treatment. Fingerprints were successfully developed on a wide range of fabrics, although the quality and number of marks were significantly reduced when ageing conditions involving any degree of high humidity were used. Extended exposure to atmospheric, non-radioactive SO_2 was also thought to desensitise the print. Prints on Melinex film were least affected by these conditions, followed by prints on fabrics, with paper being the most affected. Throughout the studies operational work was performed to see if marks could be developed on real fabric exhibits and parallel studies were also performed on fabrics worn for different periods of time, both next to the skin and as outer garments. It was concluded that for operational work on fabrics, exhibits needed to be dry, of fine weave and not worn next to the skin.

1.7 In the mid-1970s an Atomic Weapons Research Establishment (AWRE) system using compressed SO_2 cylinders was used on adhesive tape

from Irish Republican Army (IRA) improvised explosive devices (IEDs) and numerous fingerprints were found. The rise of Republican terrorism and the planting of IEDs on the mainland led to a need for a method of processing adhesive tape from unexploded devices. The Police Scientific Development Branch (PSDB) worked closely with the anti-terrorist unit and eventually trained members of the unit to use the radioactive SO_2 system. A number of identifications from the terrorists fingerprints on adhesive tape were found. The main reason for the use of SO_2 was that most of the tape was black and a non-destructive method was required in order to carry out other forensic examinations for fibres, hair and mechanical fit. The equipment using a pressurised gaseous source of SO_2 was potentially hazardous and PSDB designed and built a metal-free reaction chamber and control system, and a simple Perspex chamber was developed for treatment of exhibits [10]. The source of SO_2 was changed from pressurised gas cylinders to paper impregnated with radioactive thiourea, which was ignited to release radioactive SO_2 gas. This became the standard system introduced in the UK for operational work although only two other systems were built, one for the Metropolitan Police Forensic Science Laboratory Serious Crimes Unit (MPFSL SCU) and one for the Birmingham Forensic Science Service (FSS). PSDB also developed light-tight sachets based on aluminised Melinex for autoradiography of non-flat items in daylight [11] and further research was carried out to investigate methods for developing marks on curved surfaces [12]. The development of the basic violet 3 (Gentian Violet) transfer technique subsequently reduced the need for SO_2 on tapes.

1.8 Initial studies to investigate the relative effectiveness of SO_2 on adhesive tapes established that marks could be detected on both sides of the tape using this technique. Marks were shown to survive for 64 days on the adhesive side, although survival times were shorter on the non-adhesive side and dependent on whether the tape was stored indoors or outdoors [13]. The technique was found to give excellent operational results on adhesive tapes in several terrorism-related cases in the 1970s, and became regarded as an essential treatment for this type of exhibit in serious and terrorist-related cases [14]. A further comparative trial was carried out on fabrics in the early 1980s, investigating the relative effectiveness of several techniques including SO_2, VMD and osmium tetroxide fuming [15,16]. This study looked at ageing fingerprints on a range of fabrics and types of weave. These studies showed that SO_2 was the most effective of the three techniques, developing appreciably more high quality marks than VMD, the next most effective technique.

1.9 A small operational trial was also carried out with some ridge detail being developed in at least two operational cases on fine synthetic outer garments. A small scale evaluation of SO_2 as an enhancement technique for superglue on synthetic substrates was also carried out and an identifiable, policeman's fingerprints were found on one nylon outer garment. With this operational work showing limited success, thetechnique became mainly limited to use on adhesive tapes. However, the complexity of equipment required to carry out the processing, and the

health and safety issues associated with the use of radioactive isotopes, led to a gradual decline in the operational use of the technique The last operational equipment was decommissioned by the FSS, Lambeth in 2005. CAST holds the equipment in storage in case there is a future requirement to re-investigate the technique, but at present it is unlikely to be restored to operational use at the Sandridge laboratories.

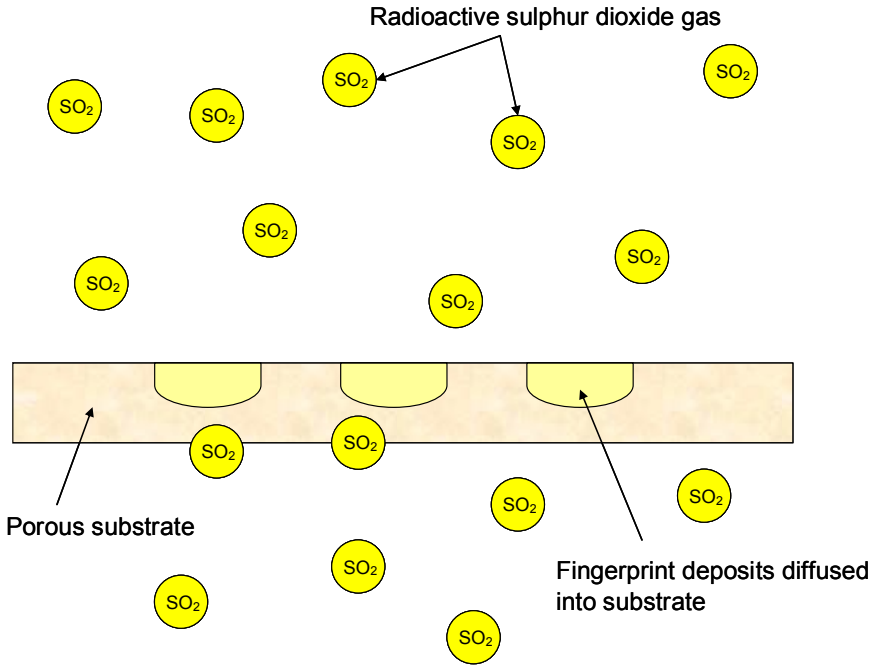
2. Theory

2.1 Wells [9] in his comprehensive report of the radioactive SO_2 process, suggested that several reactions with fingerprint deposits were possible and that a complex combination of these contributed to the fingerprint development process. The mechanisms processed by Wells included the following.

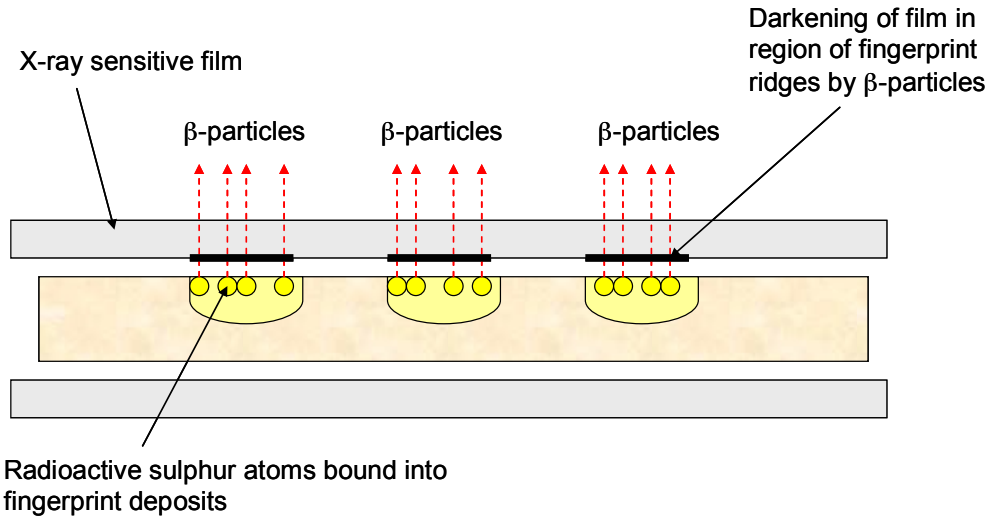
- The fixation of SO_2 as SO_4^{2-} in the water phase associated with sebum and in water adsorbed from the atmosphere due to the hygroscopic nature of the deposit.
- The sensitisation of wettable substrates (e.g. paper, fabric) by adsorbed layers of water molecules directly as a result of contact by fingerprint ridges.
- Reaction(s) with lipids, which may involve the double-bonds of unsaturated free fatty acids, etc.

2.2 The strong dependence of the SO_2 reaction on the relative humidity during treatment tends to support the theory that the main reaction occurring is the water phase fixation mechanism.

2.3 The development of fingerprints by the radioactive SO_2 process and subsequent autoradiography is illustrated schematically below.



a)



b)

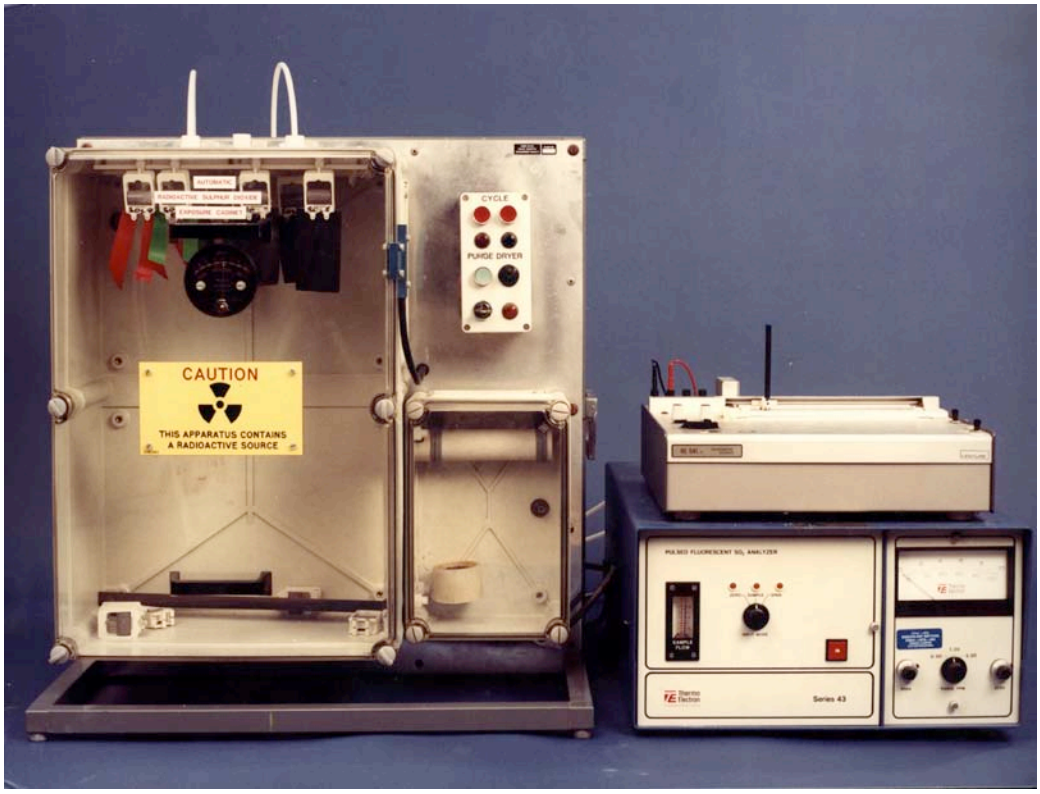
Schematic diagram illustrating the radioactive sulphur dioxide process a) sulphur dioxide gas diffusing through porous substrate and b) autoradiography of sample with radioactive sulphur bound into fingerprint ridges.

3. CAST processes

3.1 The technique ultimately recommended by the Home Office Centre for Applied Science and Technology (CAST) was the combustion of filter paper impregnated with radioactive thiourea in a humidity-controlled cabinet.

3.2 The SO_2 sources were prepared by dissolving radioactive thiourea in water and decanting small aliquots of solution onto discs of filter paper. It is essential to use readily combustible cellulose-based filter papers for this purpose. The concentration of the solution was adjusted to give a concentration of 1mCi (milliCurie) per 50μL, with 5μL being impregnated into each disc to give a disc content of 0.1mCi of thiourea.

3.3 The impregnated disc was then loaded into the crucible chamber of the radioactive SO_2 apparatus. The system used activated charcoal to remove the SO_2. After the normal treatment time of 20 minutes, the gas content of the chamber was passed through the charcoal scrubbing system. A separate chamber containing water was used in the initial humidification phase, which was manually controlled.



Photograph of the radioactive sulphur dioxide apparatus.

3.4 Samples were then suspended in the main chamber, which was sealed and brought to a relative humidity of 55%. The impregnated disc was then ignited and allowed to fill the chamber with the pre-determined concentration of radioactive SO_2 released by combustion. Once the cycle had completed and the SO_2 level had returned to the value before commencing treatment, articles were removed from the chamber, sandwiched between two sheets of x-ray film and then placed in a press. Activity was monitored with a Geiger counter to calculate exposure times, typically seven to ten days.

3.5 The humidity level in the chamber and concentration of radioactive thiourea used in the process were chosen to give the optimum conditions identified in early experimental work. The role of the thiourea in the process was to release SO_2 as a combustion product.

3.6 The process involved constant monitoring of all items of laboratory equipment, clothing and exhibits that came into contact with radioactive material, and the disposal of contaminated articles in an approved fashion.

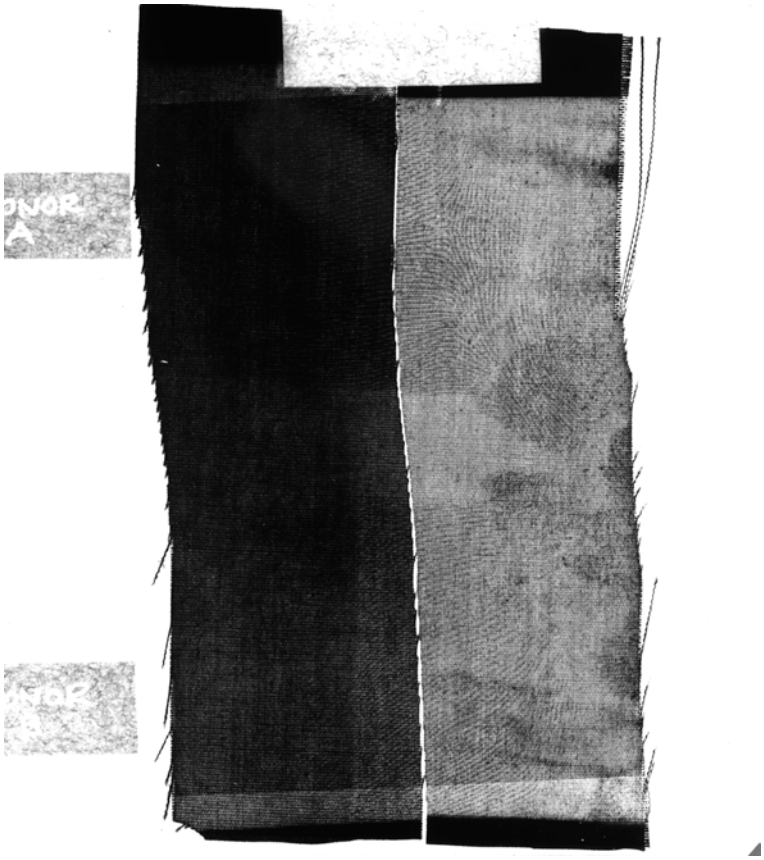
4. Critical issues

4.1 The technique is no longer used operationally and therefore there are no critical issues associated with its use. However, continuous monitoring of radioactivity levels was required when carrying out processing.

5. Application

5.1 Suitable surfaces: Radioactive SO_2 was suitable for use on both sides of adhesive tape and on fabrics. In practice it could be used on both porous and non-porous surfaces, but was restricted to articles small enough to fit inside the reaction chamber.

5.2 The two applications for which radioactive SO_2 is suggested in the *Manual of Fingerprint Development Techniques* [17] are as part of a sequential treatment process for adhesive tapes, and as the principal treatment for fabrics. In theory it was a versatile technique and could be applied to both porous and non-porous surfaces, a potential advantage being that patterned backgrounds that could obscure the developed mark were not visible in the autoradiograph.



Autoradiograph of fabric sample exposed to different environments and treated with radioactive sulphur dioxide.

5.3 When applied to adhesive tapes, the technique was capable of developing marks on both sides of the tape simultaneously, and was also effective on vinyl tapes where techniques such as VMD performed poorly. During the 1970s this type of tape was often found on explosive devices and radioactive SO_2 gave good results, resulting in its continued use on terrorist-related cases until the mid-2000s.

5.4 The technique was shown to be the most effective process for development of marks on fabrics, although in practice no marks with sufficient detail for a positive identification were obtained from operational work.

6. Alternative formulations and processes

6.1 Other vapour phase materials labelled with radioactive isotopes have been considered for the development of fingerprints using autoradiographic methods. Goode *et al*. [10, 18] considered the use of radioactive bromine in two forms, ^{80}Br and ^{82}Br. Bromine was considered for its potential reaction with unsaturated fats in the fingerprint deposit and for the fact that this reaction is rapid. Both isotopes also have a shorter half life than radioactive SO_2, which is advantageous. Fingerprints were successfully developed on a range of paper substrates using radioactive Br_2 and the process shown to be quicker than SO_2 [18]. The quality of the developed prints was shown to be similar to those produced by SO_2, although the contrast of the marks was significantly degraded by exposure to ultraviolet radiation. The technique as originally applied utilised vacuum equipment and this was thought to be clumsy compared with the apparatus used for the more established SO_2 technique. As a consequence, radioactive Br_2 was not pursued further.

6.2 Higgins also reported the use of radioactive iodine (^{128}I) in iodine vapour and in radioactive iodine monochloride (ICl) [19] for the development of fingerprints on paper and again a reduced processing time was achieved compared with SO_2. Although initial trials were successful, the technique was not progressed further.

7. Post-treatments

7.1 No post-treatments are used with the radioactive SO_2 technique other than autoradiography for developing the marks on photographic paper.

8.Validation and operational experience

8.1 <u>Laboratory trials</u>

8.1.1 The largest recorded laboratory trial for radioactive SO_2 was a comparison with VMD on a range of different fabrics representative of over- and undergarments [16]. This trial used six donors, each placing one mark that was split and aged for one day prior to processing. The results are outlined below in terms of individual fabric type, and further summarised in the second table.

Material	**Process**	**Grade of mark**			
		1	**2**	**3**	**4**
Brown, 100% Nylon Warp knit, 1.5 stitches x 3 rows	SO_2	0	2	3	1
	VMD	1	5	0	0
Cream, 100% Silk Standard weave, 3 weft x 3 warp	SO_2	0	3	1	2
	VMD	0	5	1	0
White, 100% Acetate Standard weave, 3 weft x 3.5 warp	SO_2	0	1	4	1
	VMD	4	2	0	0
Grey, 100% Polyester Standard weave, 3.5 weft x 4 warp	SO_2	6	0	0	0
	VMD	5	1	0	0
Cream, 65/35% Polyester/Cotton Standard weave, 3 weft x 4 warp (well worn)	SO_2	6	0	0	0
	VMD	6	0	0	0
White, 65/35% Polyester/Cotton Standard weave, 3 weft x 4 warp	SO_2	3	3	0	0
	VMD	0	4	2	0
White/blue stripe, 65/35% Polyester/ Cotton, Standard weave, 3 weft x 4 warp (well worn)	SO_2	3	3	0	0
	VMD	2	4	0	0
Yellow, 65/35% Polyester/Cotton Standard weave, 3 weft x 4.5 warp (well worn)	SO_2	0	6	0	0
	VMD	2	4	0	0
Red, 80/20% Polyester/Cotton Standard weave, 3 weft x 3.5 warp	SO_2	2	3	1	0
	VMD	3	3	0	0
White, 100% Nylon 'antistat' Warp knit, 1.25 stitches x 2 rows (well worn)	SO_2	0	5	1	0
	VMD	0	6	0	0
White, 100% Nylon Kayser 'antistat', warp knit, 1.5 stitches x 2 rows	SO_2	0	5	1	0
	VMD	0	6	0	0
White, 100% Nylon	SO_2	0	5	1	0

Fine Fare, Warp knit, 2 stitches x 2 rows	VMD	0	6	0	0
White, 100% Nylon 'counterstat', Warp knit, 2 stitches x 2.5 rows	SO_2	1	4	1	0
	VMD	0	4	2	0
White, 100% Nylon Kayser, Warp knit, 2 stitches x 2.5 rows	SO_2	0	6	0	0
	VMD	0	5	1	0
White, 100% Polyester, 4 Float satin weave, 4 weft x 4 warp	SO_2	0	1	2	3
	VMD	0	3	3	0

Material	**Process**	**Grade of mark**			
		1	**2**	**3**	**4**
All fabrics	SO_2	21	47	15	7
	VMD	23	58	9	0

Summary of comparative study carried out between radioactive sulphur dioxide and vacuum metal deposition on fabrics.

8.1.2 The results indicate that that radioactive SO_2 produced about 50% more marks with ridge detail worth initiating a search against (grades 3 and 4) than VMD, and hence radioactive SO_2 was the principal technique recommended for treatment of fabrics. It should be noted that when this trial was conducted in 1984, an optimised superglue technique was not available.

8.1.3 A similar comparison was carried out between radioactive ICl and SO_2, again using six donors, each placing one mark that was split and aged for one day prior to processing. ICl did not develop any marks in this study, but radioactive SO_2 was found to give similar results to the initial trial against VMD.

Material	**Process**	**Grade of mark**			
		1	**2**	**3**	**4**
All fabrics (one-day-old marks)	SO_2	33	34	14	3
	ICl	84	0	0	0
All fabrics (one-week-old marks)	SO_2	45	27	8	4
	ICl	84	0	0	0

Results of further comparative studies between radioactive sulphur dioxide and iodine monochloride on fabrics.

8.1.4 Further comparative trials against osmium tetroxide as a fuming process and as a spray also showed SO_2 to be the most effective process on fabrics.

8.2 Pseudo-operational trials and operational experience

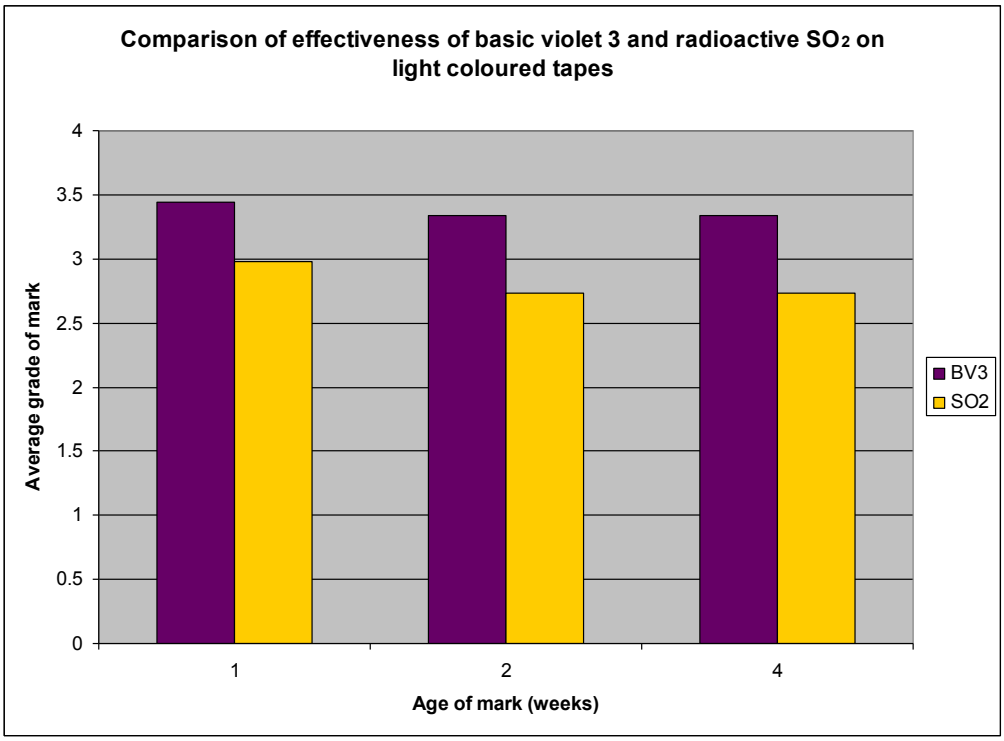
8.2.1 Operational figures for the first years that radioactive SO_2 was used are summarised below.

Period	Number of cases	Number of articles	Marks developed (cases)	Comments
01/01/1975 – 01/05/1975	4	118	4	Mainly PVC tapes
02/05/1975 – 02/05/1976	28	677	12	Mainly tapes and plastic bags
03/05/1976 – 31/03/1977	49	754	9 + 7 with fragmentary marks	Mainly tapes

Results of casework using radioactive sulphur dioxide in the mid-1970s.

8.2.2 The main successes of the technique were on dark and coloured PVC tape, where none of the techniques then available (basic violet 3, VMD) were capable of yielding marks. Many of these successes were in high-profile cases involving explosive devices.

8.2.3 A laboratory comparison was carried out by PSDB in the late 1970s, comparing basic violet 3 and radioactive SO_2 on a range of light coloured adhesive tapes. The results from approximately 300 graded marks are illustrated below.



Comparison of the relative effectiveness of radioactive sulphur dioxide and basic violet 3 on a range of light coloured adhesive tapes

8.2.4 These results indicate that basic violet 3 is the more effective process, but the processes do not target the same constituents and may be used in sequence. In 1983 HO SRDB treated a series of tape exhibits using radioactive SO_2 and developed 11 marks, only one of which was subsequently detected by basic violet 3.

8.2.5 A further operational case in 1984 gave a further opportunity to assess the sequential processing of tapes from 18 separate exhibits, using basic violet 3 after radioactive SO_2. Results of this exercise are summarised below.

Side of tape	Both processes negative	Both processes developed same ridge detail	SO_2 developed more ridge detail	Basic violet 3 developed more ridge detail
Adhesive	28	0	2	11
Non-adhesive	18	12	10	1

Results of casework using radioactive sulphur dioxide and basic violet 3 on adhesive tape in 1984.

8.2.6 Again, basic violet 3 appeared the more effective process on the adhesive side but it was apparent that the two processes could be used sequentially.

8.2.7 The laboratory trials conducted by HO SRDB and reported above indicated that radioactive SO_2 was the most effective technique for development of marks on fabrics, and selected operational exhibits were treated between 1980 and 1984.

Period	Number of cases	Number of articles	Marks developed (cases)	Comments
01/09/1980 – 01/10/1984	12	13	4	No marks with sufficient ridge detail for identification

Results of casework using radioactive sulphur dioxide on fabrics from 1980 to 1984.

8.2.8 The factors affecting the recovery of identifiable marks were the time lapse before receipt of the exhibit (in many cases greater than one week) and the pattern of the fabric warp/weft obscuring ridge detail. At the present time (2011), the number of points of detail required for identification of a fingerprint are less than they were in the 1980s (when a minimum 16-point standard was in place), and there are digital filtering techniques that can remove the patterned background from the image (such as fast Fourier transforms). Both these factors may have made the marks developed more operationally significant if developed in the current environment.

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5.15 Silver nitrate

1. History

1.1 The use of silver nitrate for the development of latent fingerprints on porous surfaces was first reported at the end of the 19th century, and together with iodine offered the only effective techniques for this type of surface until the use of ninhydrin was proposed in 1954. In the process silver nitrate reacts with the chlorides in the fingerprint to give silver chloride, which is converted to silver metal on exposure to light.

1.2 Various formulations had been reported, utilising both water and alcohol as solvents. The concentration of silver nitrate in these formulations typically varied from 3–10%, often with small additions of nitric acid to the aqueous solutions. In 1969 Cuthbertson carried out an extensive investigation of fingerprint chemistry and utilised the silver nitrate reaction to determine chloride contents in fingerprint deposits [1] and as a consequence of these studies proposed that the optimum silver nitrate concentration was 1%. Below this level there was insufficient reagent to react with the chloride available in the fingerprint and above 10% the background coloration began to become excessive [2]. It was also noted by Cuthbertson that under conditions of high humidity the chlorides in the fingerprint migrated and ultimately the mark became diffuse and undetectable. The operational implications of this study were published by Godsell [3] who recommended that UK police forces adopt the 1% silver nitrate formulation for operational use and ensure that exhibits for treatment were stored in low humidity environments.

1.3 The principal issue with the use of silver nitrate as a fingerprint development reagent was the progressive darkening of the background after treatment and research was carried out in the late 1960s and early 1970s in an effort to overcome this. Green [4] investigated the use of alternative silver salts with greater stability to light, and also explored the use of a sodium thiosulphate-acetic acid solution as a fixing process. Morris and Goode [5,6] developed a modified silver nitrate process to overcome both the background darkening and the lack of control over the photochemical development step. The preferred method ultimately proposed by Morris and Goode was to convert the silver chloride to silver sulphide using thiourea, giving a more stable final product. A complexing agent, disodiumethylenediaminetracetic acid (Na_2EDTA), was used in the silver nitrate solution to form complexes with unreacted silver so that it could be washed from the surface more easily. This was found to significantly reduce background darkening [2].

1.4 During the assessment of experimental techniques in the UK in the early 1970s, silver nitrate was used in comparative trials with other processes, including iodine, ninhydrin, radioactive sulphur dioxide and vacuum metal deposition. These trials showed that silver nitrate was the process most adversely affected by storage conditions of high humidity or exposure to moisture [7]. However, if dry storage conditions were used silver nitrate

developed a higher proportion of marks than ninhydrin, although not as many as radioactive sulphur dioxide. However, it must be noted that these experiments were conducted before the heat and humidification protocols were introduced for ninhydrin. Using silver nitrate after ninhydrin was found to produce more marks than either process alone [8]. These results were also confirmed by Caton in 1974, who reported the results of an assessment on over 6,000 paper and cardboard items; 1,617 marks were developed by ninhydrin, with a further 170 developed by subsequent silver nitrate treatment [9].

1.5 Although development of marks was typically carried out using light (ultraviolet or photoflood lighting being recommended), chemical developers could also be used [10]. Products typically used for photographic development were suggested, although the use of an additional immersion stage was not considered desirable because of the potential damage to some types of paper.

1.6 Silver nitrate was also considered as a technique for the intensification of faint ninhydrin marks, using a modified formulation using ethanol instead of water as the solvent [11]. This prevented the diffusion of the amino acids that occurred when the water-based formulation was used and meant that any marks developed using silver nitrate enhanced the existing ninhydrin marks and did not degrade any ridge detail already present. Other researchers have also considered non-aqueous alternatives to silver nitrate, one published formulation consisting of 3% silver perchlorate in toluene [12].

1.7 Other approaches to make the silver nitrate technique more practical were considered, including the use of stopping solutions based on methanol, acetic acid, glycerol and water [13]. This slowed the background darkening effect and negated some of the need for immediate photography and storage of exhibits in the dark. However, the technique was rarely used on paper after the mid-1970s, and although recommended as a reagent for raw wood its use in the UK declined after it was withdrawn from the second edition of the *Manual of Fingerprint Development Techniques* [14]. No further developments have been reported since 1998.

2. Theory

2.1 The theory of the silver nitrate process is that the silver nitrate in solution reacts with the chloride constituents of fingerprint deposits to produce insoluble silver chloride.

$$AgNO_3\ (aq) + NaCl\ (aq) \rightarrow AgCl\ (s) + NaNO_3\ (aq)$$

2.2 Silver chloride is light sensitive and when exposed to ultraviolet light darkens rapidly as metallic silver is formed.

$$AgCl\ (s) + hv \rightarrow Ag\ (s) + \tfrac{1}{2}Cl_2\ (g)$$

2.3 The treated exhibit is therefore exposed to ultraviolet (or white) light to promote development although the optimum exposure time will vary from surface to surface and is not always easy to establish because both the print and the background progressively darken with time. In the case of the background this occurs due to gradual breakdown of unreacted silver nitrate in the porous substrate, and treated exhibits should be stored in the dark to reduce the speed at which this occurs.

2.4 The formulation formerly published by the Home Office Scientific Research and Development Branch (HO SRDB) for operational use on raw wood [15] was as follows.

2.5 Mix 10g of silver nitrate with 500mL of methanol. Immerse article in solution for a maximum of 5 seconds and allow to dry in the dark. Illuminate article and continue exposure until the background starts to darken.

SILVER NITRATE developed fingerprint. Inset: illuminating to develop fingerprints

Development of fingerprints using silver nitrate.

3. Reasons technique is not recommended by CAST

3.1 CAST did recommend and issue the silver nitrate process in the first edition of the *Manual of Fingerprint Development Techniques* [15],

primarily as a process for the development of fingerprints on light coloured, raw wood. It was withdrawn from the manual in subsequent editions [14] because it was considered that physical developer was equally as effective in this application and had no issues associated with progressive darkening of the background on exposure to light.

3.2 On paper items, silver nitrate can develop additional marks if used sequentially after ninhydrin because it is targeting different constituents in the fingerprint deposits. However, chlorides are more affected by moisture and high humidity conditions than many other fingerprint constituents and silver nitrate cannot be used on items that have been wetted. For this reason, physical developer is the preferred method for sequential treatment after ninhydrin because it targets different constituents and can be used on wetted items.

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Chapter 6: Specialist imaging techniques

6.1 Scanning electron microscopy

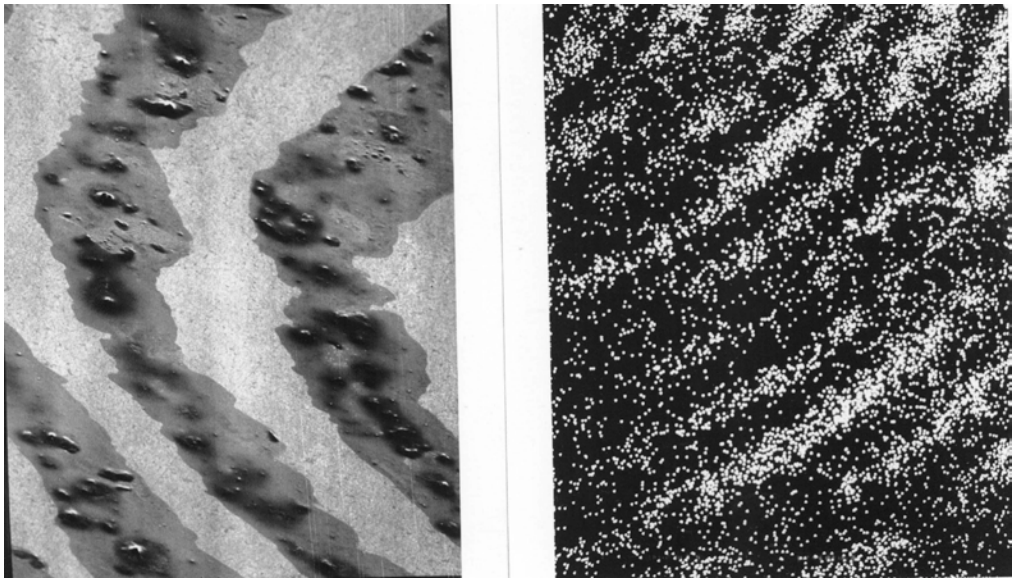
1. History

1.1 As early as the 1920s it was recognised that beams of electrons could be focused by means of electrostatic or magnetic fields and that the short wavelength of electron beams offered significant improvements in both resolution and depth of field compared with light microscopy [1].

1.2 It was not until the 1950s and 1960s that practical electron microscopes began to emerge, utilising both transmission and scanning modes to provide images of materials. The potential applications of electron microscopy (in particular the scanning electron microscope) in forensic science were first explored in the late 1960s. Van Essen [2] reported the use of scanning electron microscopy in combination with energy dispersive x-ray spectroscopy for the analysis of paint and metal fragments, ink composition and for studying hair and fibres.

1.3 It was also recognised that scanning electron microscopy could be used for imaging of fingerprints, and Garner *et al.* [3] demonstrated that latent fingerprints could be detected on both glass and metal substrates. On the non-conductive, glass surface a gold coating was required to prevent charging and it was also observed that older marks were more difficult to image than freshly deposited marks.

1.4 The Police Scientific Development Branch (PSDB) began studies into the use of electron microscopy in the late 1970s [4,5], and installed a JEOL scanning electron microscope with an energy dispersive x-ray spectrometer specifically to explore imaging of fingerprints. Various imaging modes were investigated [4] including specimen current imaging of latent marks and mapping of silver distribution in marks developed using physical developer. The microscope was also used as a research tool to study the secondary electron escape depth from fingerprints [5]. Both latent and treated fingerprints were used in these studies, the differences in elemental deposition occurring using vacuum metal deposition being utilised to reveal fingerprint ridges crossing print boundaries.



a) b)

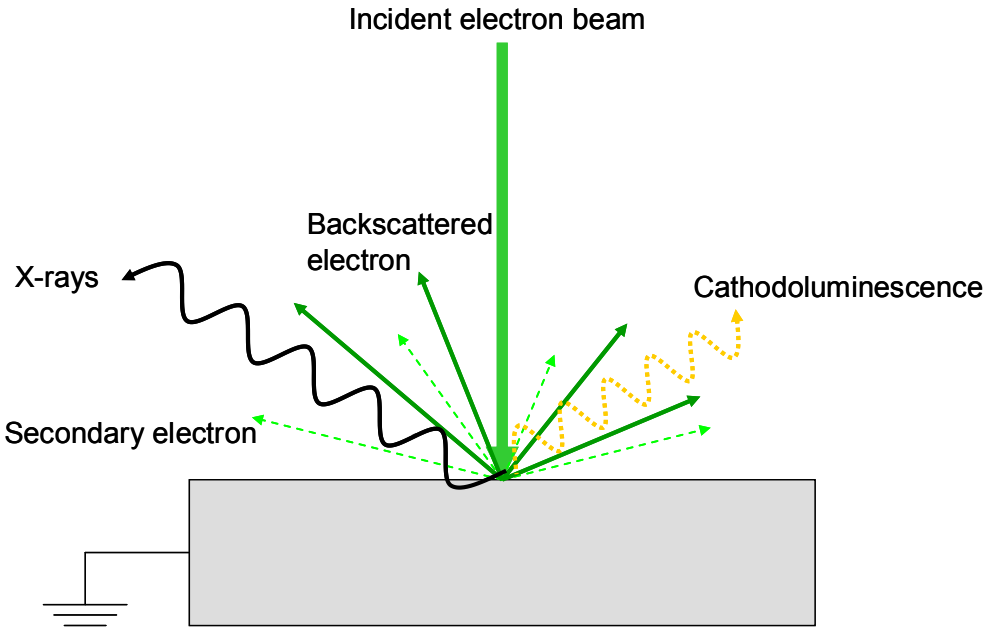
Early scanning electron microscopy images of fingerprints a) latent fingerprint in secondary electron imaging mode and b) mark developed using vacuum metal deposition in elemental mapping mode

1.5 Although potentially effective for distinguishing fingerprint ridges against obscuring backgrounds, scanning electron microscopy and its associated analytical modes have been more useful in providing information about the mechanisms of other development processes and the composition of powders and reaction products. Scanning electron microscopy has been extensively used by PSDB in the characterisation of fingerprint powders and brushes [6-9] and has also provided useful images of the reaction products from the superglue and physical developer processes.

1.6 In practical terms, scanning electron microscopy is little used for casework because its application often requires a small area to be cut from the exhibit and coated with a conductive material to prevent the sample charging. However, there are situations where it may provide additional information and it remains an invaluable tool for understanding the interactions between fingerprints and the surfaces they are deposited onto.

2. Theory

2.1 When an energetic beam of electrons is focused onto a surface there are a number of interactions that can occur [1]. These include transmission and diffraction, which are of most interest for transmission electron microscopy and are therefore not discussed further here. The interactions of principal interest for scanning electron microscopy are illustrated schematically below.



Principal interactions between electron beam and sample in scanning electron microscopy.

2.2 Discussing each mechanism in turn, backscattered electrons occur where the incident electron undergoes a series of inelastic collisions with atoms in the sample and are scattered backwards out of the surface and towards the detector. These electrons are relatively high energy and the number of them occurring will be related to the atomic density of the surface being examined.

2.3 Secondary electrons occur during the inelastic collisions between the primary electrons and the atoms and some have sufficient energy to escape the surface towards the detector. They are of lower energy than backscattered electrons.

2.4 X-rays are also emitted, in a process analogous to fluorescence in the visible region of the spectrum. Electrons promoted into excited states by the interaction with the electron beam decay into their ground states, with the emission of an x-ray of energy/wavelength characteristic of the element present.

2.5 For certain materials, the emission of energy as the electrons decay back into their ground state occurs at an energy/wavelength corresponding to the visible region of the spectrum. This is known as cathodoluminescence.

2.6 Of all these mechanisms, secondary electron imaging is most useful for examining the morphology of powders, brushes and reaction products. In secondary imaging, a positive charge is applied to the detector, which

attracts most of the negatively charged electrons emitted from the surface. As a result, the signal received at the detector is relatively high and the image is not 'noisy'. The electron beam is scanned across the surface in a series of lines known as a raster, and the signal level recorded at each pixel represented on a screen.

2.7 Backscattered electron imaging is most useful where the elemental composition of the fingerprint ridge and the background differs, especially if one contains an element of a significantly higher atomic number. Because the number of backscattered electrons is a function of atomic density, areas of high atomic density will produce more backscattered electrons and appear brighter. Backscattered electron imaging can be carried out by biasing the detector with a slight positive charge, thus repelling the low energy secondary electrons and only allowing the higher energy backscattered electrons to reach the detector. Because fewer electrons reach the detector, backscattered images may be more noisy, but may be capable of resolving fingerprints developed using techniques such as vacuum metal deposition and iodine.

2.8 X-ray spectroscopy can be carried out in a static mode, to determine the elemental composition of a particular location on the sample. X-rays can be separated and analysed according to their characteristic wavelength or energy. In practice the energy dispersive detectors are more compact (although not as suitable for quantitative analysis) and are more commonly fitted to electron microscopes. Energy dispersive x-ray spectroscopy can also be used in mapping mode, scanning the beam across the surface and recording the types of x-rays emitted at each point. If a characteristic element is present in the fingerprint ridges, it is possible to resolve the ridges from the background in this way.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the process for routine operational work because it will normally be destructive to the exhibit, involving cutting an area small enough to fit inside the chamber of a scanning electron microscope and coating with a conductive element to prevent charging. These processes may be detrimental to subsequent analysis for other types of forensic evidence. However, recent advances in electron microscope design may mean that larger samples can be examined and a conductive coating may not always be required. In some circumstances scanning electron microscopy and associated analytical techniques may be capable of providing additional information about a fingerprint and its use should not be discounted. Suitable microscopes can be found in most universities.

3.2 Scanning electron microscopy is a useful research tool for investigating fingerprint development techniques and has primarily been used for this purpose in recent years, in some cases augmented by transmission

electron microscopy and atomic force microscopy for cases where very high magnifications are required.

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6.2 X-ray imaging

1. History

1.1 The properties of the x-ray were first observed by Wilhelm Roentgen in 1895, during experiments into the effect of passing electricity through bottles containing gas. Roentgen observed that rays emitted from the bottles had the ability to take pictures of objects hidden under or within other objects, and took a picture of his wife's hand that revealed her bones and her wedding ring.

1.2 Although rapidly adopted for medical applications such as the imaging of the interior bones, x-rays were not seriously considered for forensic imaging until the mid-1960s, when Graham and Gray at the Victoria Infirmary, Glasgow, began experimenting with the technique of electronography [1,2], initially with the intention of revealing the watermark of stamps attached to documents. In the electronography technique a metal irradiated with a high energy, monochromatic x-ray beam emits its own characteristic x-rays, which cause a photographic film in intimate contact with the sample to darken. This is outlined in more detail in the 'Theory' section below.

1.3 Graham [2,3] next considered using powdered lead to reveal indented writing, carrying out electronography to enhance the indentations the lead had preferentially settled into. Graham and Gray considered that fingerprints could be developed in a similar way [4], powders already being extensively used for fingerprint development. Magnetic powders with the Magna-brush were considered, but the emission from iron was not found as effective as that from lead and subsequent studies utilised lead powdering in combination with electronography. The first application proposed for electronography was the revelation of fingerprints deposited on patterned backgrounds. Once the fingerprint had been developed using the lead powder, only the developed areas emitted during subsequent electronography and the resultant fingerprint image was free of background. Test fingerprints were resolved on magazine covers and postage stamps.

1.4 Electronography was also proposed to image fingerprints on dead human skin, again using lead powdering to develop the mark and electronography to enhance the image and remove the background of skin texture, hairs, etc. [5]. There was reasonable interest in the technique for this purpose, with no satisfactory development technique being available at that time. The Police Scientific Development Branch (PSDB) placed a contract with Graham in the early 1970s to investigate the development of fingerprints on limbs using lead powder and electronography. The technique was adopted in some laboratories in the USA [6,7], and refinements were proposed to make the technique easier to apply both in the laboratory and in the field [6]. Later adaptations were proposed within the UK [8], and the use of lead powder with electronography was proposed as an alternative to vacuum metal

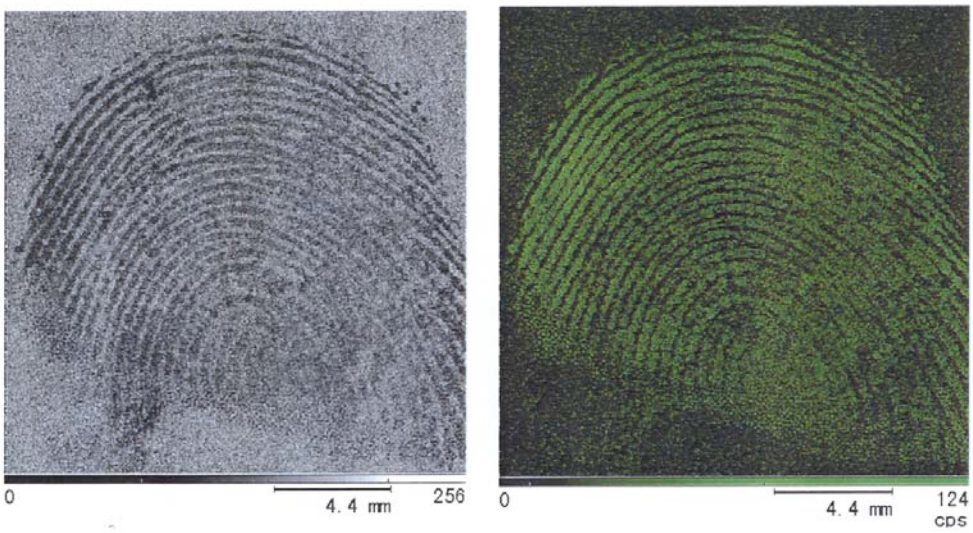
deposition (VMD) for developing marks on polythene [9]. VMD was found to be far more effective than lead powdering for this purpose, and after the late 1970s the technique seems to have gradually faded from use.

1.5 X-rays can also be used to image fingerprints in other ways. X-rays are also emitted from samples bombarded by electron beams in electron microscopes, and the characteristic x-rays thus emitted can be used to build elemental maps of a surface. This is described in greater detail in Chapter 6.1, Scanning electron microscopy.

1.6 Another way in which x-rays can be emitted is by x-ray fluorescence, irradiating a sample with monochromatic x-rays and causing characteristic x-rays to be emitted in a process directly analogous to fluorescence in the visible region of the spectrum. More recently, researchers have used an x-ray fluorescence instrument to scan surfaces and detect fingerprints by mapping characteristic elements within latent fingerprints and within contaminants that may be present on fingers such as sun cream [10]. Potential advantages of x-ray fluorescence over x-ray mapping within a scanning electron microscope are that larger areas can be examined, the sample does not have to be under a vacuum and the sample does not have to be coated with a conductive coating to prevent charging.

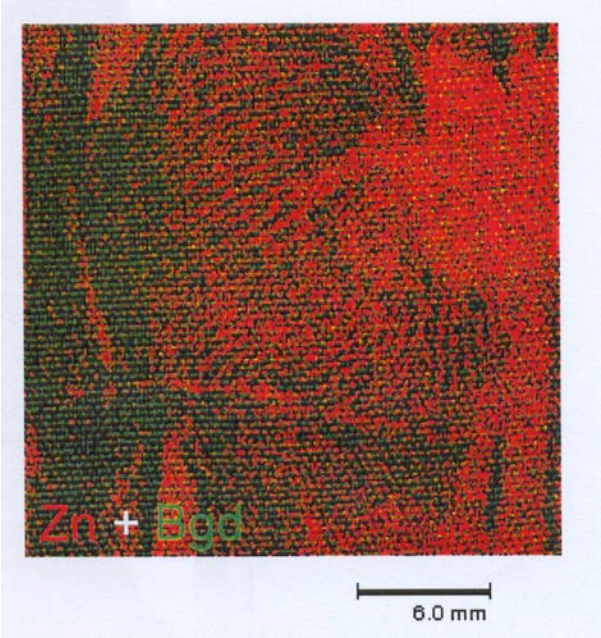
1.7 The Home Office Scientific Development Branch (HOSDB) has also carried out some initial studies into the x-ray fluorescence technique, in this case looking at fingerprints developed using techniques that result in characteristic elements being present in fingerprints ridges, such as physical developer, vacuum metal deposition and metal toning of ninhydrin [11]. It was shown that the technique had potential for revealing fingerprints on patterned backgrounds, such as magazines, and also on fabrics. The instrument used in these studies also had a transmitted x-ray mode and for fingerprints containing heavy elements, such as iodine, this was also found to be effective for distinguishing ridges from the background.

Overview of fingerprint treated with physical developer on magazine page, subsequently toned with potassium iodide.



a) b)

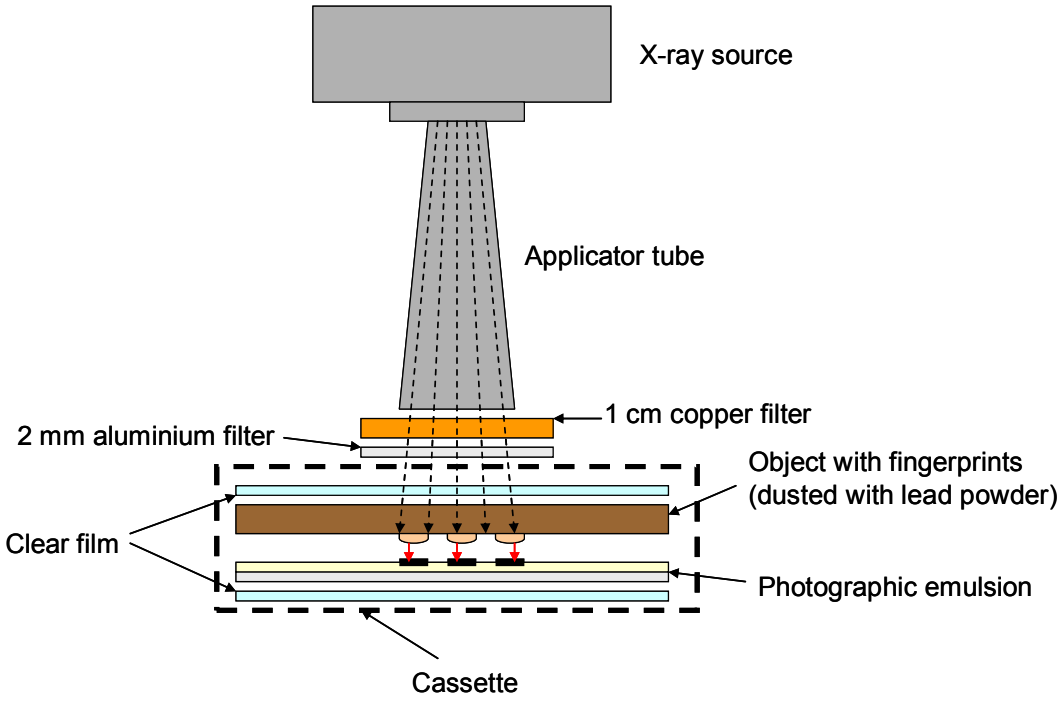
Closer view of x-ray images a) image of mark in x-ray transmission mode and b) image formed from characteristic x-rays from iodine.



X-ray image from mark developed on fabric using vacuum metal deposition, red signal = zinc from metal deposition, green signal = fabric background.

2. Theory

2.1 The practical apparatus used by Graham and Gray is illustrated schematically below, and the theory of electronography outlined subsequently.

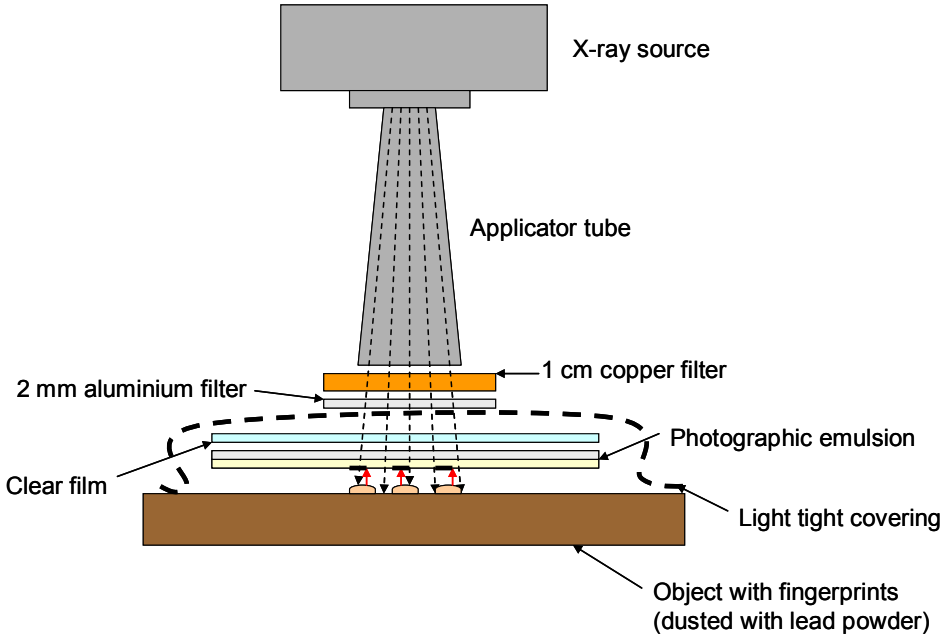


Electronography apparatus proposed for thin exhibits such as documents.

2.2 All metallic elements, when irradiated by a high kilovoltage beam, emit both electrons and x-rays characteristic to that element. These characteristic x-rays and electrons cause the silver halides of a photographic film emulsion to convert to silver, leaving a black image of the areas containing the characteristic metal element.

2.3 For this to be effective, the original, incident x-rays must have a negligible effect on the photographic emulsion and it is therefore necessary to filter the original broad spectrum of wavelengths emitted by the x-ray source. The longer wavelength x-rays that cause film fogging are filtered out by passing the beam through a 1cm block of copper. The characteristic copper x-rays emitted as the primary beam passes through the copper filter are in turn removed by a further 2mm aluminium filter, and the x-rays emitted from the aluminium filtered out by a clear plastic film. The short-wave x-rays pass through the object under examination and hit the lead particles adhering to the fingerprint ridges, promoting emission of x-rays and electrons that develop an image of the fingerprint on the photographic film in intimate contact with the surface. A further clear film is used below the photographic film to absorb scatter and emission from other areas within the cassette.

2.4 For articles that were not flat or could not be fitted inside a cassette, an adaptation of the method was proposed.



Electronography apparatus proposed for solid exhibits such as bodies.

2.5 In this adaptation, x-rays are allowed to pass through the photographic film and fall upon the surface being examined. The x-rays from the surface are emitted backwards onto the film and the clear film, film and surface are enclosed within a light-tight covering.

2.6 The theory of x-ray fluorescence is exactly analogous to fluorescence in the visible region of the spectrum. A short wavelength beam of x-rays is used to irradiate a surface, promoting electrons into excited states. As these electrons decay back to ground states, they emit x-rays at longer wavelengths with an energy characteristic to the particular elements present in the surface. By scanning the x-ray probe across the surface, a map can be produced of all locations where a particular characteristic element is present. If such an element is known to be specific to the ridges of the fingerprint, x-ray fluorescence can be used to reveal fingerprint detail.

2.7 X-ray imaging can also be carried out in transmission mode. In this mode it is the atomic density of an area that determines the intensity of x-rays transmitted through a sample. If a high atomic number element is present, fewer x-rays are transmitted and the area appears dark in the developed/collected image. If fingerprint ridges (or the background) can be preferentially doped with a high atomic number element, it may be possible to obtain contrast between the fingerprint and its background. This has been demonstrated using potassium iodide toning of a mark treated with physical developer and to a lesser extent with a mark powdered with bismuth salts.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend electronography for operational use in police force fingerprint laboratories because of the hazards associated with the use of x-rays and the harmful nature of lead powder. In addition, no comparative studies have been carried out to demonstrate that electronography is more effective than other techniques for any of the applications for which it has been proposed.

3.2 X-ray fluorescence and x-ray transmission may be useful for practical application and the development of fingerprint reagents designed for x-ray functionality is feasible. However, the cost of analytical equipment is high and beyond the reach of most police forces. If the technique is to be used operationally it is likely that it will be confined to special cases, utilising equipment at establishments such as universities.

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6.3 Other specialised imaging techniques

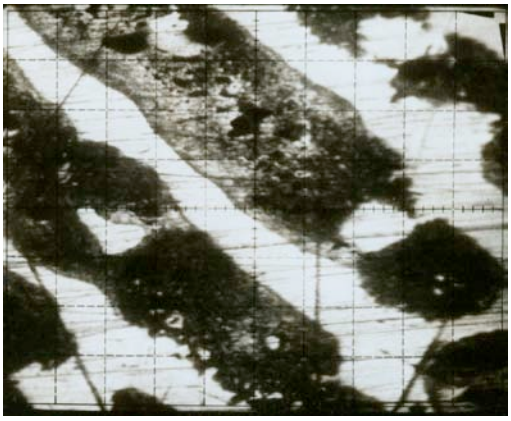
6.3.1 Secondary ion mass spectrometry (SIMS)

1. History

1.1 Secondary ion mass spectrometry (SIMS) has been used for many years as a technique for performing high sensitivity elemental analysis and operates by bombarding a surface with a high energy beam of particles and analysing the mass of the secondary ions emitted. The process was originally not suitable for surface analysis because the high energy beam progressively removed layers of material, but by the 1980s higher sensitivity detection systems were available that allowed the use of lower energy primary beam currents, and hence caused considerably less damage to the surface. Researchers began to explore the applications of SIMS for surface analysis, utilising the technique to identify the composition of surface coatings and small surface features [1]. SIMS was also used in an imaging mode, scanning the surface and detecting positions that specific molecular fragments were emitted from.

1.2 Bentz [2] applied SIMS to the analysis of fingerprint residues, in particular to the detection of traces of contaminants in the fingerprint. Many 'natural' fingerprints contained traces of silicones, and it was also demonstrated that small traces (nanograms) of illicit substances could theoretically be detected by the technique.

1.3 The Home Office Scientific Research and Development Branch (HO SRDB) funded an investigation of the use of the SIMS technique for both analysing fingerprint residues and mapping their distribution using the scanning mode [3]. These studies used fingerprints from six different donors, and confirmed the presence of sodium (Na^+) and chloride (Cl^-) ions in varying quantities. Spectra from all donors contained peaks indicative of the presence of both long- and short-chain aliphatic materials, and also peaks characteristic of silicones. Fragments representative of alkoxy and phenoxy groups were detected and, more specifically, spectra from all donors contained the main negative ion from myristic, palmitic and oleic acids. One donor also gave the stearate ion. The imaging mode was also successful in distinguishing between the composition of fingerprint ridges and that of the background.



a)

b)

c)

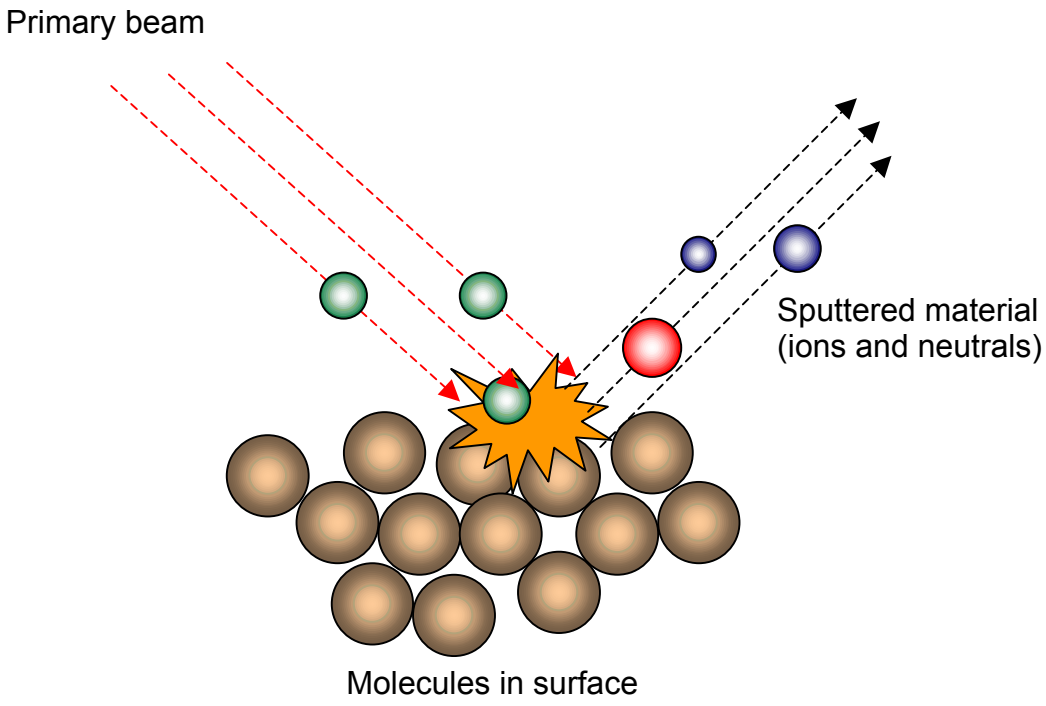
Images obtained using scanning secondary ion mass spectrometry for surface analysis a) ion induced secondary electron image, b) Na^+ secondary ion image and c) $C_3H_5^+$ secondary ion image.

1.4 As the instrumentation available for SIMS has advanced, other researchers have also reported the use of the technique for fingerprint imaging and determining the distribution of principal constituents [4-6]. SIMS has also been used for depth profiling, examining the penetration depth of fingerprints into porous surfaces and determining whether printing or fingerprints were present first. The size of the instrument has also reduced and desktop systems are now available. It is unlikely that SIMS will become a primary fingerprint detection and/or imaging technique, but it can provide valuable information about fingerprint composition, contamination present in the fingerprint and contextual data. It may therefore be appropriate to use the technique in special cases.

2. Theory

2.1 The theory of SIMS is that an energetic beam of particles is used to bombard a surface in a vacuum. The collisions between the incident particles and the molecules in the surface layer produce a number of charged atoms, molecules and molecular fragments, which are ejected from the surface. This process is known as sputtering, and the ejected

species are known as secondary ions. The secondary ions may be positively or negatively charged.



Schematic diagram showing secondary ions ejected from surface by the action of the primary beam.

2.2 The secondary ions ejected from the surface can be focused into a mass spectrometer where they are separated and identified according to their mass to charge ratio. Under appropriate conditions, minimal fragmentation of the surface molecules occurs and the molecular ions present can be more readily identified.

3. Reasons technique is not recommended by CAST

3.1 CAST does not recommend the process for routine operational work because it will normally be destructive to the exhibit, involving cutting an area small enough to fit inside the chamber of a SIMS instrument. In some circumstances SIMS may be capable of providing additional information about a fingerprint and its use should not be discounted. Suitable instruments can be found in some universities.

4. References

1. **Brown, A. and Vickerman, J. C.** (1984) 'Static SIMS, FABMS and SIMS Imaging in Applied Surface Analysis', *Anal.*, vol. 109, pp 851–857.

2. **Bentz, B.** (undated) *Characterisation of Human Fingerprint Residues on Surfaces using a Neutral-Beam Organic Secondary Ion Mass Spectrometry (Organic SIMS)*, paper from unknown source

3. **Brown, A.** (1986) *Characterisation of Fingerprints by Static SIMS and SIMS Imaging*, Analysis Report, Surface Analysis Industrial Unit, 22 March. University of Manchester Institute of Science and Technology.

4. **Koch, C. H., Augustine, M. R. and Marcus, H. L.** (2001) 'Forensic Applications of Ion-beam Mixing and Surface Spectroscopy of Latent Fingerprints'*, Proc. SPIE* vol. 4468. 'Engineering Thin Films with Ion Beams', *Nanoscale Diagnostics, and Molecular Manufacturing*, pp 65–77.

5. **Williams, G. and McMurray, N.** (2007) 'Latent Fingerprint Visualisation Using a Scanning Kelvin Probe', *Forens. Sci. Int*., vol. 167, pp 102–109.

6. **Szynkowska, M. I., Czerski, K., Grams, J., Paryjczak, T. and Parczewski, A.** (2007) 'Preliminary Studies Using Imaging Mass Spectrometry TOF-SIMS in Detection and Analysis of Fingerprints', *Imag. Sci J.,* vol. 55 (3), p180–187.

6.3.2 Scanning Kelvin probe

1. History

1.1 The scanning Kelvin probe technique was developed for the detection of corrosion occurring on metal surfaces. However, it was noted by Williams *et al*. [1] that electrochemical interactions may also occur between fingerprint deposits and metal surfaces and they subsequently investigated the application of the scanning Kelvin probe technique to fingerprint detection. Initial results were promising, with fingerprints being imaged on metal surfaces heated to 600ºC and beneath layers of insulating films.

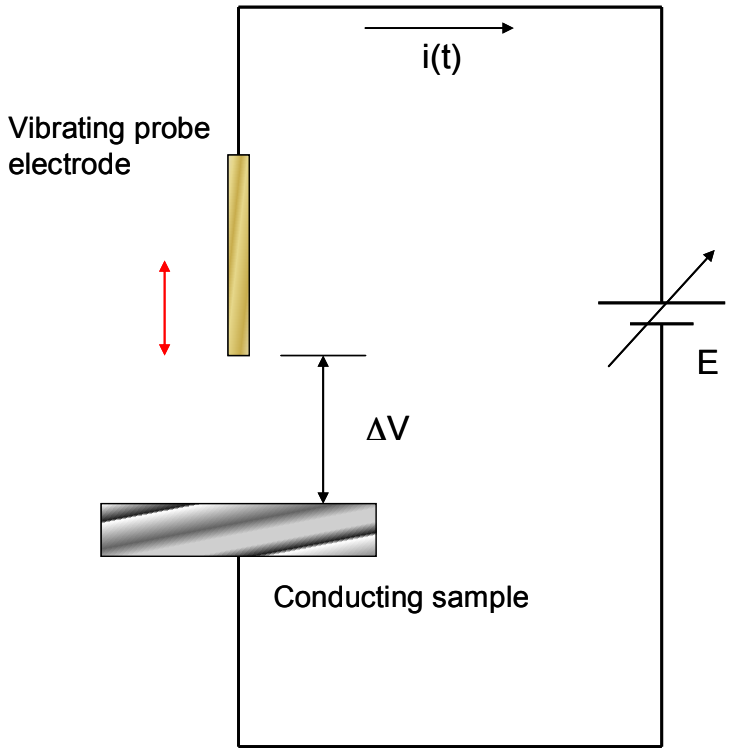
1.2 Subsequent research by the same authors showed that the process was applicable to a range of metal surfaces and could still detect traces of fingerprints on surfaces where the residue had been rubbed away with a tissue. The technique was also applied to practical situations and apparatus was constructed for the scanning of cylindrical items such as cartridge casings [2].

1.3 The technique has the advantage that it is non-contact and non-destructive. It could, in theory, be used as the initial stage in a sequential treatment process. However, it has not yet been compared with existing processes in terms of sensitivity or effectiveness and the Home Office Centre for Applied Science and Technology (CAST) is currently (2011)

funding a research programme to carry out this study with the University of Swansea.

2. Theory

2.1 The scanning Kelvin probe consists of a fine, vibrating gold electrode brought into close proximity to the surface being examined. The vibrating probe tip and conducting sample surface form the two plates of a parallel plate capacitor, with the space between them (predominantly air but possibly including any non-conducting layers on the surface) forming the dielectric. If there is a Volta potential difference (ΔV) between the probe and sample surface, the periodic capacitance change caused by the vibrating probe generates an alternating current, i(t), in the external circuit. The Kelvin probe measurement is made by applying a d.c. bias voltage E until the value of ΔV, and hence i(t). is zero. The circuit is illustrated below.



Schematic diagram showing principle of operation of the scanning Kelvin probe.

2.2 It can therefore be seen that any slight changes to the conducting sample or the dielectric between the probe tip and sample surface will result in changes to ΔV and therefore the resultant Kelvin probe measurement. Both eccrine and sebaceous fingerprints can change the surface and dielectric sufficiently for changes in ΔV to be detected, giving contrast between areas of ridge and background when the probe is scanned across the surface. In the case of eccrine prints there may be

an electrochemical reaction between the print residue and the metal that changes surface potential, whereas in the case of sebaceous prints an additional layer of dielectric material is deposited on the surface.

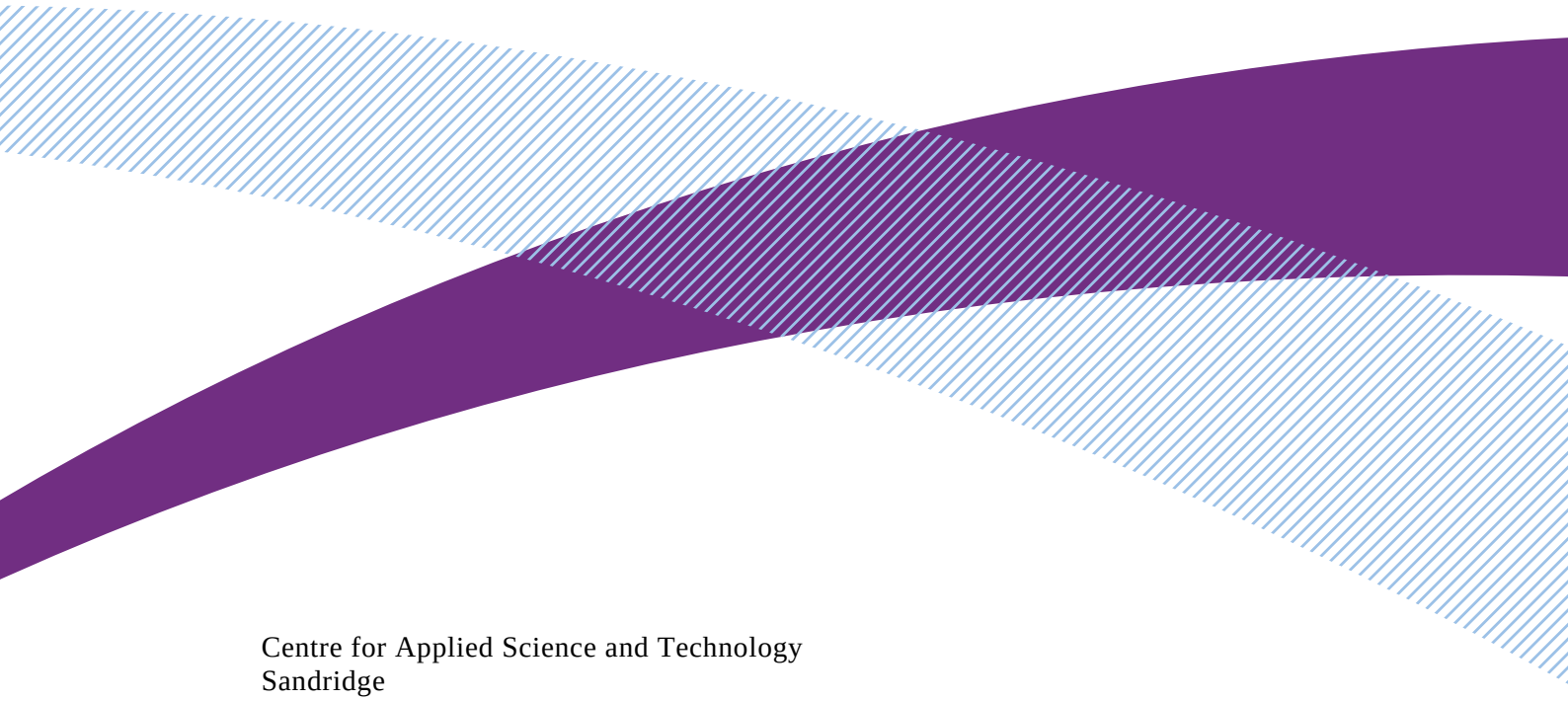
3. Reasons technique is not recommended by CAST

3.1 CAST does not currently (2011) recommend the scanning Kelvin probe process for fingerprint detection because its relative effectiveness has not been established. However, the process is non-destructive, both for subsequent fingerprint development techniques, DNA recovery and examination of firing and rifling marks and there is no reason why it should not be utilised if the situation warrants it. The process is relatively slow, taking several hours to scan a single cartridge casing at high resolution, but for serious cases may provide valuable information. It is hoped that the planned comparative study will enable more detailed advice to be given on the use of this technique.

4. References

1. **Williams, G., McMurray, H. N. and Worsley, D. A.** (2001) 'Latent Fingerprint Detection Using a Scanning Kelvin Microprobe', *J. Forens. Sci.*, vol. 46 (5), pp 1085–1092

2. **Williams, G. and McMurray, H. N.** (2007) 'Latent Fingerprint Visualisation Using a Scanning Kelvin Probe', *Forens. Sci. Int*., vol. 167, pp 102–109.



Centre for Applied Science and Technology
Sandridge
St Albans
AL4 9HQ
United Kingdom

Telephone: +44 (0)1727 865051
Fax: +44 (0)1727 816233
E-mail: CASTenquiries@homeoffice.gsi.gov.uk
Website: http://www.homeoffice.gov.uk/science-research/