Novel Techniques for the Development of Latent Fingermarks

By

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A Doctoral Thesis

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“…to my mother, my dog, and clowns”

“If we knew what it was we were doing, it would not be called research, would it?”

- Albert Einstein (1879 – 1955)

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Declaration

I, Lloyd William Laidlow Davis, declare that the interim report entitled “Novel Techniques for the Development of Latent Fingermarks” submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University is my own work. Work undertaken by other people has been identified and referenced accordingly.

Lloyd Davis

Abstract

The scientific study of fingerprints/fingermarks; dactyloscopy, is one of the most important fields in forensic science today. Fingermarks are amongst the most common type of evidence recovered from crime scenes and are arguably the most valued due to the fact that they are, unlike deoxyribonucleic acid (DNA), completely unique to an individual. Fingermarks recovery techniques are constantly evolving and new reagents are always being sought. This project aims to develop and access new fingermark enhancement procedures.

The efficacy of an ethanoic solution of phosphomolybdic acid, has been investigated as a latent fingermark enhancement reagent, primarily on porous substrates. After treating samples and exposing them to ultraviolet radiation, the phosphomolybdic acid solution was shown to develop fingermarks to a high quality. Unlike the common amino acid reagents used for the enhancement of fingermarks on porous substrates, ninhydrin and 1,8-diazafluoren-9-one, phosphomolybdic acid stains a range of other compounds found within fingermark deposits, including lipids. The lysochrome diazo dye Oil Red O was used for comparative purposes due to its application in staining some of the same components of fingermark residues that phosphomolybdic acid would be proposed for. Initial results indicate that phosphomolybdic acid is comparable to Oil Red O at developing fingermarks on porous surfaces and may also have applications on non-porous surfaces.

A systematic evaluation of solvent carriers was conducted, and whilst many solvents were insufficient, others did show some potential. Primary alcohols such as ethanol, methanol and propan-1-ol all developed fingermarks with identifiable ridge detail. Attempts to mix phosphomolybdic acid with other reagents which react with different fingermark constituents than those phosphomolybdic acid targets were, for the most part unsuccessful. However, not entirely ruled out. Many substrates were tested to observe which developed fingermarks when treated with the phosphomolybdic acid solution. Whilst marks were detected on numerous substrates, paper proved to be the most receptive. Similar stains to the phosphomolybdic acid were tested under the same conditions, however, none were as effective as the phosphomolybdic acid.

A non-destructive, non-invasive technique was developed, utilising cuprous metals and their reactions with rubeanic acid. By bringing substrates with fingermarks deposited upon their surface into contact with a copper or copper alloyed plate, it was possible to transfer the fingermark residues to the plate. Forensic gelatin lifters could then be used to lift the marks from the metal plates, these lifted marks could subsequently be treated with a rubeanic acid solution to visualise the fingermarks. The rubeanic acid reacted with the Cu(II) which had been transferred to the fingermark residues to produce a dark product in the pattern of fingermark ridges. The technique was successful at developing fingerprints on semi-porous substrates. The technique was as effective on non-porous substrates, such as glass, but an investigation into the process on porous surfaces was less positive.

Attempts to reuse the cuprous metals for the transference of fingermarks after an initial lift resulted in double or ghosted marks being developed, after a thorough wash with soap and water. This was overcome by cleaning with the metal cleaner Brasso. Copper cleaned with Brasso was reused 5 times to show its effectiveness, and adverse effects were minimal.

The UK's recent move to polymer banknotes has seen some of the currently used fingermark enhancement techniques for currency potentially become redundant, due to the substrate characteristics of the polymer surfaces. Possessing a non-porous surface with some semi-porous properties, alternate processes are required for polymer banknotes. A preliminary investigation was conducted in to the recovery of fingermarks from polymer notes *via* vacuum metal deposition using elemental copper. The study successfully demonstrated that fresh latent fingermarks, from an individual donor, could be clearly developed and imaged in the near infrared. By varying the deposition thickness of the copper, the contrast between the fingermark minutiae and the substrate could be readily optimised. Where the deposition thickness was thin enough to be visually indistinguishable, forensic gelatin lifters could be used to lift the fingermarks. These lifts could then be treated with rubeanic acid to produce a visually distinguishable mark. The technique has shown enough promise that it could be effectively utilised on other semi- and non-porous substrates.

A follow up group study was less effective than the aforementioned initial study. Many samples were processed using the vacuum metal deposition; incorporating a comparison study between copper and the gold/zinc standard and a depletion trial. However, when imaging was attempted a week after treatment, the results experienced before were unable to be replicated.

Attempts to recover samples of radioactive nickel isotope from metal substrates using forensic gel lifters were initially unexceptional. Wipe tests were more successful at recovering the isotope. Experimentation using some non-metallic substrates was more fruitful, the gel lifters were able to recover the radioisotope more readily. Autoradiography showed that, although a weak beta emitter, nickel could be imaged when in sufficient quantities. By using nickel and a short half-life isotope of phosphorus in conjunction with patterned stamps and patterned deposits it was possible to image these patterns by autoradiography of the gels used to lift from the substrates these were deposited upon. These autoradiography images showed enough detail to warrant attempts with a synthetic finger, however, the imaging was insufficient to image the fine details of the friction ridges.

Fingermarks deposited on the surface of agar gels showed bacterial growth after incubation for 24 hours. Aseptic transfer of bacterial colonies to fresh agar plates in a typical streak pattern were fruitful. Further transference to a nutrient broth were effective, however, attempts to seed bacterial agar plates for use in inhibition tests were unsuccessful.

Overall, phosphomolybdic acid proved to be relatively effective, being able to develop fingermarks on a number of substrates. The copper transfer method, although, less fruitful than PMA showed promise. This lead to the idea of gel lifting from copper VMD treated polymer banknotes which was much more effective. Although, the radioactive and biological techniques showed promise, they were unfortunately unsuccessful at developing fingermarks. A number of the techniques evaluated and developed were successful enough to be published in forensic journals.

Abbreviations and Acronyms

AB1	-	Acid Black 1
Au/Zn	-	Gold/Zinc
AV17	-	Acid Violet 17
AY7	-	Acid Yellow 7
BCE	-	Before the Common/Current/Christian Era
BY40	-	Basic Yellow 40
CAF	-	Cyanoacrylate Fuming
CAM	-	Cerium Ammonium Molybdate
CAST	-	Centre for Applied Science and Technology
DIPN	-	Di-Isopropylnaphthalene
DFO	-	Diazafluorenone
DNA	-	Deoxyribonucleic Acid
HFE	-	Hydrofluoroethers
HOSDB	-	Home Office Scientific Development Branch
IR	-	Infrared
ORO	-	Oil Red O
PD	-	Physical Developer
PMA	-	Phosphomolybdic Acid
PTA	-	Phosphotungstic Acid
SWGFAST	-	Scientific Working Group on Friction Ridge Analysis, Study and Technology
UV	-	Ultraviolet
VMD	-	Vacuum Metal Deposition

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1.0 Introduction

1.1 Friction Ridge Skin Formation

The largest organ of the human body; and arguably the most crucial is the skin. It helps protect the internal organs from damage, helps regulate the body's temperature and protects the body from the outside world [1]. Friction ridge skin is a type of skin that is situated on the palmar side of the hands and the plantar side of the feet, its main purpose being to increase the owner's gripping ability. The palmer and plantar friction ridge skin take on a variety of shapes and forms, and it is these formations that have led to the belief that the patterns are unique to the individual. The friction ridge skin on the distal phalanges is widely referred to as fingerprints [2].

Seven to eight weeks after fertilisation, the newly forming foetus starts to develop volar pads on its palms and distal phalanges. Epidermal ridge development occurs at the location of these volar pads [3]. This area of study is known as Dermatoglyphics, from the ancient Greek *derma* meaning skin and *glyphe* meaning carve [4]. Kollman (1883) was the first to propose that growth stresses and compressions exerted during the development of the skin significantly influenced epidermal ridge direction. It was later suggested that the developing friction ridges grow at right angles to these growth stresses and compressions acting on the growing volar pads cause [5]. Hale (1952) went on to state that as developing foetal hands and feet formed, the continual growth caused the forming ridges to be pulled apart. It was widely believed that ridge skin formed as a consequence of mechanical folding, it was later discovered that ridge skin actually forms as a result of cell proliferation [6].

The friction ridge skin of an individual never changes throughout their life; it can, however, through injury be either temporarily altered or permanently destroyed. The upper layers of the epidermis can be temporarily damaged and when the skin repairs itself the original ridge pattern eventually returns. Conversely, should the ridge skin of the dermis be subjected to extreme injury which extends deeper into the dermal papillae, it will result in scarring. Dermal layers which are scarred permanently alter the original pattern of the ridge skin.

Friction ridge skin found on the volar pads of an adult's fingers is in the region of one to two twenty-fifths of an inch thick and the fingerprint ridges themselves are on average approximately one-fiftieth of an inch wide on a male's finger. Women and children's fingerprint ridges are usually less [8].

When fingers come into contact with a surface, fingermarks or fingerprints are left behind. This occurs due to sweat glands in the basal dermis layer of the skin; these sweat glands produce sweat which deposit an oily residue that produce a mirror image of the fingerprint pattern, these deposits are commonly referred to as latent fingermarks. Of the sweat producing glands in the human body; there are three types which play a role in the depositing of fingerprints upon touched surfaces, these are the eccrine, apocrine and sebaceous glands. The eccrine glands are most numerous on the palms of the hands and soles of the feet [9], the secretions from these glands are composed mostly of water, with a small quantity of organic and inorganic components. Sebaceous glands are located in hair follicles and are not found on the palmar or plantar surfaces; their secretions, however, can be transferred to the hands through the touching of skin containing sebaceous glands, such as that located along the hairline of the forehead. The third type of gland, apocrine, is most prevalent in the armpit and genital regions of the body. Secretions from these glands are rarely found within the deposits of fingermarks [8].

1.2 Fingerprint Persistency and Uniqueness

Despite there being certain variation in the patterns of ridges on the palms of the hands and the soles of the feet, the variation is limited by the general growth stresses experienced during foetal growth. However, these patterns cannot form geometric patterns of ridges since there is no foetal hand structure that would allow such a pattern. Within the general ridge flow patterns, the specific shapes and paths of the ridges show infinite variability. These variabilities exist due to the fact that the shape and path of each ridge is not dictated during foetal development. When an organism is developing, the genetic code is responsible for ensuring that the organism has the proper body plan, that the limbs and organs have the correct form and functionality. The finer details of an organism such as the friction ridge formations and crease lines are not programmed in the genetic code, these instead are left up to chance events which take place during development [10].

This is most notable in identical twins, they share the same genetic code yet have different finger-, palm- and footprints [6, 11, 12]. Articles by Jain *et al.* (2002) and Kong *et al.* (2006) published in Pattern Recognition investigated the (dis)similarities between identical twin fingerprints and palmprints in relation to biometric verification. Since identical twins are the result of a single fertilised egg splitting into two embryos they share the same DNA, however, since the foetuses occupy different areas of the womb, they have different intrauterine forces acting upon them resulting in similar level 1 detail but very different level 2 and level 3 detail [13, 14]. This means if one twin has a certain pattern type on their index finger, there is a high possibility that their twin also has that pattern type on their index finger, however, the minutiae on the fingers will not be the same.

The configuration of friction ridge skin persists through an individual's lifetime due to multiple factors; physical attachments and the constant regulation of basal cell division within the epidermis. The basal keratinocytes are a template for the ridges and furrows of the surface of the epidermis, these proliferate in unison to faithfully reproduce the surface ridge detail. There are some conditions and diseases which can cause changes to occur to friction ridge skin; psoriasis, eczema, scleroderma and adermatoglyphia can lead to the loss of fingerprints. The cancer treatment, chemotherapy, can cause acral erythema which can lead to the skin sloughing off, or swelling so much that the friction ridges appear to smooth out [15, 16]. Adermatoglyphia is a condition which causes the skin to lack epidermal friction ridges, causing the fingertips to be smooth, this condition exists from birth. It is due to the lack of expression of the SMARCAD1 gene, and is a rare condition noted only in a handful of families [17, 18].

The quality of fingermarks left are subject to many factors; these include cuts, scars, contaminants on the skin, and even dryness of skin, but the effect of age is a major factor. Friction ridges can also be reduced due to accidents, the effects of an individual's job, as well as wrinkles caused by ageing. These factors can cause false minutiae, these may be temporary or they can become permanent, which can affect the overall print and the ability to obtain an identification from it. The prints will still be unique to the individual despite the fact that they have changed in the sense that they have an increase or decrease in ridge detail [19, 20].

Criminals over the years have tried many techniques to try and alter their fingerprints in order to evade detection; these include adding silicone, nail varnish, glues or latex to the fingerprints in order to smooth out the ridge detail. Others have gone even further in this pursuit and tried to alter their fingerprints more permanently by cutting or burning them. In the 1930s, famous bank robber John Dillinger dipped his fingers in acid in order to obliterate his fingerprints; however, the faint ridge detail began to return once the fingertips healed. Another criminal Robert Philipps was slightly more successful when he grafted skin from his chest on to his fingertips. He managed to alter his fingerprints enough so as to be unidentifiable; however, he neglected to cover the friction ridge skin along the length of the phalanges as well as the areas around the grafts.

Criminals are still trying to destroy their prints to this day, with drug dealer Marc George grafting sections of the soles of his feet to his fingertips, and Jose Izquierdo who cut triangular patches from his fingerprints and swapped them around. And although these methods are successful in changing the individual's fingerprints, the methods which they have chosen to do so involve more friction ridge skin, which means their fingerprints become more unique, therefore identification is still possible. Many of those seeking to alter their fingerprints are doing so in order to avoid identification during border patrol checks, however, the unusual appearance of the prints often draws more suspicion and further investigation [21-23].

1.3 History of Fingerprinting

Of all the types of forensically relevant evidence recovered from scenes of crimes, fingerprints are arguably the most important and have become the cornerstone of modern criminal identification [24]. The science of fingerprinting, known as dactyloscopy [25], has developed in to the best established of the forensic science disciplines used for individual identification [8]. However, evidence suggests that the Chinese were utilising friction ridge skin for identification as far back as 300 B.C.E. [26].

Archaeologists in the northwest of China discovered pottery, estimated at approximately six thousand years old, which had clearly distinguishable fingermarks upon their surface. Whether these impressions were part of elaborate designs or simply accidental marks left by the manufacturers is not known, nevertheless, these fingerprints are considered to be the oldest examples of friction ridge skin impressions that have been found to date. Throughout China's history ridge skin impressions were used on the seals on official and private letters as well as legal documents; including deeds, wills and contracts. Chinese manuscripts of sales and loans have been found in China with ridge skin impressions dated as recently as 1911 [27]. Through trading with China, it is believed that other Asian countries adopted similar fingerprint systems, however, in India the use of friction ridge impressions were usually reserved for royalty [26].

In the late seventeenth European scholars began documenting their findings on friction ridge skin. The first scientist to publish a study on the characteristics of friction ridge skin was Dr Nehemiah Grew; in this paper, Grew describes sweat pores, furrows and epidermal ridges [28]. Dr Grew is often cited as being the pioneer of study into the ridge skin formations of the fingers [29].

In 1687, using the newly invented microscope, Marcello Malpighi an Italian professor began studying the palmar surfaces, a subject on which he wrote numerous discourses. Malpighi's treatise *Concerning the External Tactile Organs* concentrated on the structure, function and form of the friction ridge skin; he also noted how it provided enhanced traction for gripping and walking [26]. In recognition of his work and the discoveries he had made, Malpighi had a layer of the skin named after him, however, he failed to pursue research in the area of friction ridge skin and the advances that he had made would remain unexplored for over a century [29].

In 1788 J.C.A. Mayer, a German scientist, was the first to document the uniqueness of friction ridge skin. Mayer commented on the similarities as well as their differences [30]. In 1823 a significant contribution was made to the field of fingerprinting by Czech, Dr Johannes E. Purkinje. Purkinje classified the friction ridge skin formations into nine different categories [31]. This classification system would be invaluable to future investigators.

Sir William Herschel is credited as the first European to use friction ridge skin in an official capacity. Whilst serving in India as a British Administrator in 1858, Herschel used handprints in lieu of signature whilst dealing with the locals. Herschel demonstrated the persistence of fingerprints by publishing his own prints at varying points throughout his life [32].

A Scottish medical missionary, Dr Henry Faulds observed fingermarks on ancient Japanese pottery in the 1870's. It was this discovery that prompted Dr Faulds to conduct independent research in to the creation of the furrows and ridges normally found on the human palmar surfaces. Through these studies Faulds sought assistance from Charles Darwin regarding his findings, however, Darwin was in ill health and passed Faulds' letter on to his cousin Francis Galton [33]. When Faulds failed to hear from Galton, he chose to publish his findings on the subject in the prominent journal Nature. In his article, Faulds expressed his belief that the science could be used to both identify criminals and exonerate the innocent.

A sentence within Faulds' article *On the Skin-furrows of the Hand* published in Nature would help propel fingerprinting into the world of crime investigation:

> *"...when bloody finger marks or impressions on clay, glass, etc., exist, they may lead to the scientific identification of criminals..."* [34]

This single statement highlighted Dr Faulds as being the first person to emphasise the value that friction ridge skin could have for individualisation, specifically when used as evidence.

Despite receiving the letter written by Dr Henry Faulds to Charles Darwin in 1880, Sir Francis Galton's interest into the science of dactyloscopy did not peak until 1888. Sir Galton's experience lay in hereditary issues, specialising in the scientific and biometric individualisation system of Bertillonage. Any visitors to Galton's anthropometric laboratory were measured in accordance with Bertillon's anthropometric system. Galton started deviating from the specified criteria and began adding to the usual measurements the fingerprints of his subjects [26]. Galton went on to write a number of papers which described fingerprints and their persistence [35], he subsequently wrote the first book on fingerprints, and as such was the first to name and characterise the minutiae which are the specific ridge skin characteristics [36].

Sir Galton took Purkinje's classification system and expanded upon it, classifying the fingerprint patterns into the categories of: loops, arches and whorls. As a result of the contributions Galton made to the science of fingerprinting he was honoured by having the minutiae characteristics named after him, the "Galton" details are known as such to this day [29]. Galton estimated, with the use of statistics, that the likelihood of any two humans possessing fingerprints which were identical to one another were 1 in 64 billion [36].

Whilst stationed in India, Sir Edward Henry started experimenting with Bertillon's anthropometric system, later moving on to study fingerprints. Seeking to increase his knowledge of fingerprints, Henry opened communications with Galton and later visited him in 1894. Upon returning to India, he began devising a classification system with the assistance of a select number of his staff, who included Rai Bahadur Hem Chandra Bose and Khan Bahadur Azizul Haque. The system was completed by late 1896, early 1897. Come mid 1897 the Surveyor General for India, having examined Henry's system, deemed it sufficient to replace Bertillon's anthropometric system where it became the sole method of identification of prisoners [26]. By 1898 in Bengal alone, 345 offenders were identified through the use of fingerprints; that number rose to 569 the following year [37]. Despite Henry being credited with the creation of the system, it later emerged that Bose and Haque contributed more to its inception than initially believed [38].

Henry's first book on the classification and uses of fingerprints was published in 1900, and consequently, the Henry Classification System [39] was introduced at Scotland Yard in 1901. Henry was hired as Assistant Commissioner of Scotland Yard in 1901. It was whilst employed in this role that he started the first fingerprint bureau. By 1903 he had been appointed Commissioner. As word of the system spread, police forces from around the world sent officers to learn Henry's classification system, the system is still used in a number of countries including Australia and the United States, albeit in a modified form [40].

1.4 Galton Details - Ridge Characteristics (Minutiae)

Bifurcation

Bifurcations happen when a ridge splits/forks into two separate ridges.

Core

The core is estimated to be the centre of the fingerprint pattern.

Delta

The delta is the point on which ridges converge from three separate directions.

Deltas are not present in arches and some tented arches.

Ridge Ending

Ridge endings are the abrupt termination of any ridge.

Lake (Enclosure)

A lake occurs when a single ridge, bifurcates, then quickly re-joins and continues on as a single ridge.

Island

Islands are short ridges which simply start and stop. They do not connect to any other ridges.

Dot

A very short island which is approximately the same length as it is wide.

Crossover (Bridge)

A crossover is a short ridge which runs between two parallel ridges.

Spur

A spur is a variation on a bifurcation in which one of the subsequent ridges is significantly shorter than the other, ending close to the originating fork.

Each fingerprint pattern contains varying numbers of each of these minutiae features (Figure 1)[41, 42].

Figure 1: Fingerprint Minutiae

1.5 Fingerprint Pattern Types

Fingerprint patterns can fall in to three broad categories which can then be divided into subcategories by the variances that occur between the patterns within the common categories. These groups of patterns are:

1.5.1 Loops

Loop patterns are a type in which one or more ridges enter from one side, curve back upon themselves, and exit out the same side from which they originated. Loops are further sub-categorised into **Radial** and **Ulnar Loops** (Figure 2 and Figure 3), these terms originate from the radius and ulna bones of the forearm. Loops that flow towards the little finger, in the direction of the ulna bone are called an ulnar loop. Conversely, a loop which flows in the direction of the radius bone, towards the thumb is termed radial loops. To avoid confusion these classifications are based on the way the loops flow on the hand and not as they appear printed on a fingerprint card. Loop patterns contain one delta and are considered the most common of the fingerprint categories, comprising approximately 60 to 65 percent of fingerprint patterns [29].

Figure 2: Loop (Radial on Left Hand, Ulnar on Right Hand)*

Figure 3: Loop (Ulnar on Left Hand, Radial on Right Hand)*

* Pictures referenced from Wisconsin DOJ Identification Manual [44]

1.5.2 Arches

The arch pattern can be sub-grouped into Plain Arches and Tented Arches. **Plain Arches** (Figure 4) display a pattern of ridges which come in from one side, rise or wave in the centre, and continue out the opposite side. **Tented Arches** (Figure 5) show a ridge or formation of ridges near the core which show an upward thrust at an angle of 90° or less, giving the appearance of a tent outline. Arch patterns contain no delta and account for around 5 percent of all fingerprint patterns [43].

Figure 4: Plain Arch*

Figure 5: Tented Arch*

* Pictures referenced from Wisconsin DOJ Identification Manual [44]

1.5.3 Whorls

A whorl pattern comprises 30 to 35 percent of all fingerprints encountered. Whorl patterns contain ridges which turn through at least one circuit, and they possess two or more deltas. Whorl patterns fall into four sub-categories; the **Plain Whorl** (Figure 6) which comprises one or more ridges which make a complete circuit and contains two deltas, the **Central Pocket Loop Whorl** (Figure 7) contains at least one ridge which recurves or an obstruction at a right angle to the line of flow, and contains two deltas. The **Double Loop Whorl** (Figure 8) is comprised of two separate loop patterns which encompass two distinct and separate sets of shoulders and deltas. Finally, the **Accidental Whorl** (Figure 9) is the term given to patterns which contain an amalgamation of two different categories of patterns, with the exception of the plain arch; accidental patterns contain two or more deltas.

Figure 6: Plain Whorl*

Figure 7: Central Pocket Loop Whorl*

Figure 8: Double Loop Whorl*

Figure 9: Accidental Whorl*

* Pictures referenced from Wisconsin DOJ Identification Manual [44]

1.6 Types of Fingermarks

Fingerprint evidence uncovered at crime scenes or upon items associated with a crime can be divided into three general groups; latent, visible (or patent) and plastic fingermarks.

1.6.1 Latent Fingermarks

It is believed that the term “latent” is derived from the Latin *latēns* from the present principle *latēo* meaning to lie hidden [45]. Because these marks are “invisible” to the naked eye, they require an appropriate method to visualise the latent mark. Application of an optical light source (ultraviolet imaging), chemical (ninhydrin), or physical treatments (powdering) can be utilised to make the fingermarks visible [46].

1.6.2 Visible Fingermarks

As the term suggests visible fingermarks are those which can be observed with the naked eye without any treatment, so long as there is sufficient contrast between the mark and the substrate upon which it has been deposited on [47]. These marks can be subdivided into positive; where the fingerprint ridges have been contaminated with a foreign material such as ink, paint, blood, *et cetera*. Conversely, negative marks, occur when the fingerprint ridges remove surface material, such as with dust covered or sooty surfaces [46]. Some metal surfaces, such as aluminium and brass can be susceptible to corrosion due to the salt and acid content within the fingerprint residues, such corrosion can present as a visible fingermark [48].

1.6.3 Plastic Fingermarks

Plastic or indented marks occur when the finger comes in contact with an acquiescent substance; like candle wax, wet paint, soap or putty, that consequently retains a three-dimensional representation of the print [47].

1.7 Friction Ridge Details

When comparing an exemplar fingerprint to that of a fingermark recovered from a crime scene, there are three basic levels of comparison; first, second and third level (or level 1, 2 and 3) detail.

1.7.1 First Level Detail

First level detail is the overall ridge flow and general pattern of the latent fingermark, although this is will not include sufficient detail to allow an identification, it can be used for exclusion purposes and thereby narrowing the number of possible donors. Level 1 detail will allow the examiner to gather information such as orientation, delta and core location, and will allow them to differentiate between a fingermark and a palm mark. When these pattern configurations are found to be dissimilar, the exemplar print is eliminated, this will continue until the examiner needs to move to second level detail to obtain an identification [49, 50] (Figure 10).

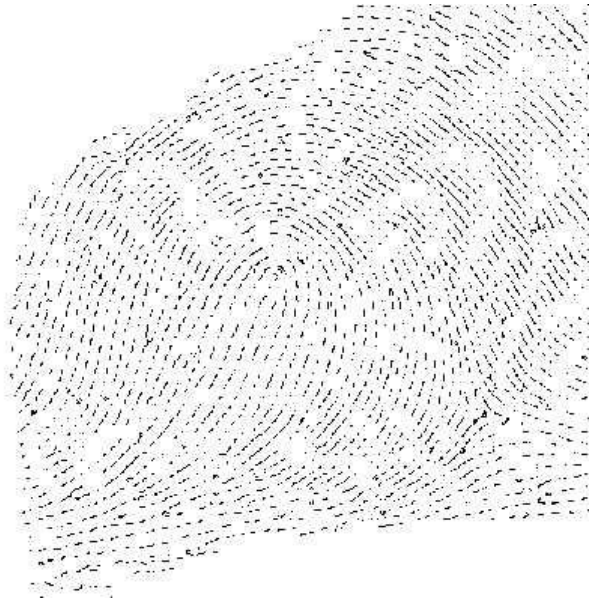


Figure 10: Level 1 Detail (Ridge Flow)

1.7.2 Second Level Detail

Level 2 detail concerns specific friction ridge minutiae for example; ridge endings, islands, bifurcations, or combinations thereof. It also takes into account accidental features such as scars and flexion creases[*]. The locations of these friction ridge pathways, as well as scars, are random and the combinations for the ridge characteristics which the examiner looks for in the exemplar print. Comparisons usually start with a ridge feature which is common to both the latent mark and the exemplar print. Each ridge pathway would be compared to one another moving out from the centre. Using this methodology, the examiner can move from one ridge path to the next sequentially working their way through the whole fingermark. Like a maze, it is as important to ascertain where a pathway goes as much as it is to where it starts, stops or bifurcates. Since ridges flow in concert to one another, there are rarely areas where there are empty areas on the volar surface. When one ridge path ends, other paths divert to fill the void. It is these relationships between the second level details enable the examiner to make an identification [49, 51] (Figure 11).

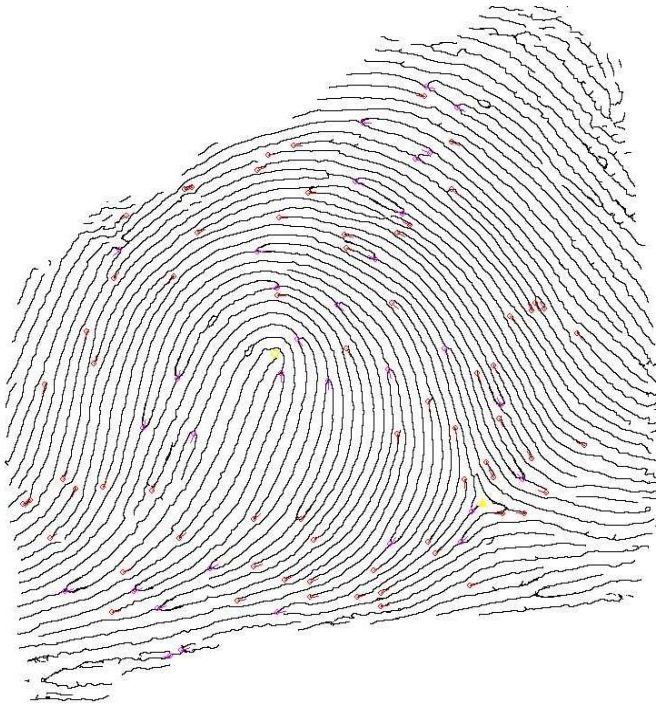


Figure 11: Level 2 Detail (Specific Minutiae)

[*] Flexion creases are areas of skin where the underlying attachment to structures is firmer. Although they are not strictly part of the dermatoglyphic system, flexion creases are included in comparisons because they too develop randomly. On the hand flexion creases are found between the phalanges as well as on the palmar surface, these aid in allowing the skin to fold when the hand is closed.

1.7.3 Third Level Detail

Third level details incorporate all the small shapes on the ridge, as well as the relative location of pores, and the small details which occur due to accidental damage to the friction ridges. These shapes are created by variances in growth or random damage at the ridge unit level. The alignment or misalignment of ridge units, ridge unit thinness or thickness, ridge unit shape and the relative pore locations are all caused by differential growth. Scars cause twisting and creasing to the surrounding ridges, as can certain genetic conditions. These are all examples of third level detail which can be used to match fingermarks to exemplar prints, however, these details are always used in conjunction with second level details. These small intrinsic details are tremendously discriminating and the more of these found to be in agreement the more certain the identification is. The comparison is complete when all available areas of the latent mark which are in the exemplar print have been compared [52] (Figure 12).

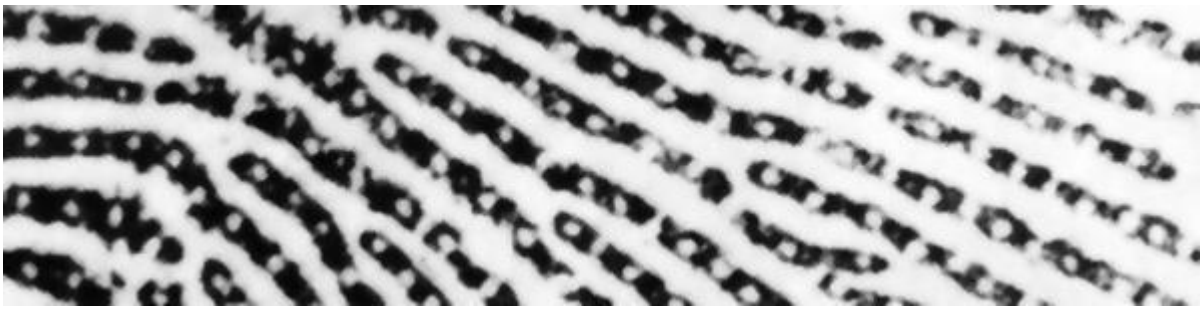


Figure 12: Level 3 Detail (Pore Detail)

1.8 ACE-V Examination Method

The acronym ACE-V stands for Analysis, Comparison, Evaluation and Verification, which are the four main stages of the protocol used by examiners when identifying fingermarks. ACE-V is not too dissimilar to the stages used to describe scientific method; observation, hypothesis, testing, analysis and conclusion. The ACE-V method for comparing fingermark details sees the examiner observe the mark, form a hypothesis about the mark's origin, they then test the recovered mark against their known mark to ascertain if there is agreement between the two, next they analyse the amount of agreement or disagreement between the marks, they then conclude whether the marks match before retesting to determine if the conclusion can be repeated [53].

1.8.1 Analysis

Analysis refers to the assessment of the fingermark as it appears on the substrate. During analysis, the examiner assesses; the substrate the mark is deposited upon, the development enhancement, the deposition pressure and any motion distortion to determine the variations in appearance. The examiner uses experience and knowledge to determine whether the fingermark has sufficient information to compare with their known mark. If the mark is deemed to be insufficient, the examination is concluded and judged that the print is inadequate for purpose of comparison [52].

1.8.2 Comparison

Comparison looks at comparing friction ridge details and flexion creases to determine if the various aspects of the mark; ridge similarity, sequence and spatial relationship are in agreement [54]. The examiner makes a comparative assessment of all these details and their configurations and sequences. The comparative measurements take into consideration any variations in appearance which may have been caused by distortion. First, second and third level detail are also examined in conjunction with the comparison of the sequences and configurations of the friction ridge pathways. Ultimately, the comparison stage is where the examiner seeks to determine whether there is agreement or disagreement between the similar details in the sequences and configurations between two fingermarks [53].

1.8.3 Evaluation

Evaluations happen when the examiner formulates a conclusion based on their analysis and comparison of the friction ridge marks. The conclusions the examiner can make are: identification, exclusion or inconclusive. Identification occurs when the examiner can find agreement between the quality and quantity of ridge detail within a mark found at a crime scene and that of an exemplar fingerprint. Exclusion occurs when the examiner determines that the comparison of two marks with sufficient quality and quantity of friction ridge details are not in agreement, thus finding the marks originated from different sources. An inconclusive determination occurs when the examiner is unable to identify or exclude the source of a friction ridge mark [54, 55].

1.8.4 Verification

"Verification is the independent examination by another qualified examiner resulting in the same conclusion." [54]. The second examiner, using the same ACE methodology, must examine the known and unknown fingermarks without prior knowledge of the initial examiners conclusions. This way the second examiner is not unduly influenced by the initial findings. Since the comparison of two fingermarks is objective, other examiners must be capable of seeing the sequences and configurations the original examiner sees. The verifying examiner must be able to reach an unbiased conclusion [52]. Should the two examiners reach different conclusions, both must assess their examinations and determine why the difference in findings has occurred [56].

1.9 Composition of Fingermark Residues

When a fingerprint comes in to contact with a surface the initial fingermark secretion contains a mixture of many substances which originate from three separate sources; (1) the epidermis, (2) secretory glands within the dermis and (3) external contaminants.

1.9.1 Compounds from the Epidermis

The epidermis forms the outermost layer of the skin, which is composed of very densely packed cells called epithelium, this tissue is divided into distinct layers called strata (Figure 13).

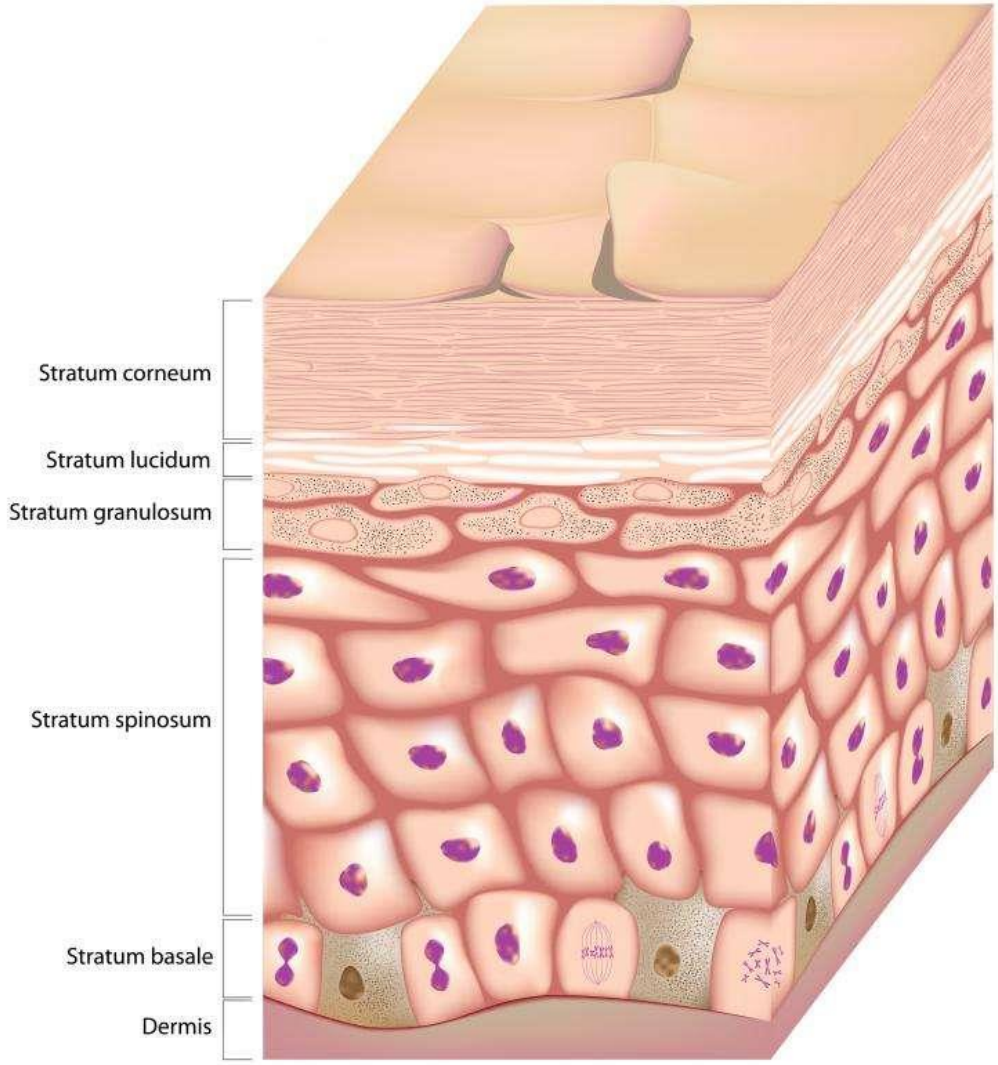


Figure 13: The Structure of the Skin (Adapted from Atherton [57])

The most external layer of the epidermis, the stratum corneum, is comprised of dead cells which are continually shed through the desquamation required for skin renewal, during which cells migrate through the strata from the stratum basale layer towards the surface over a period of approximately 4 weeks [58]. Proteins and peptides from these shed cells are believed to be present within fingermark residues [59].

1.9.2 Compounds from the Dermis

The dermis is the bottom layer of the skin which contains over five million secretory glands; apocrine, eccrine and sebaceous. The secretions from these glands (Figure 14) make their way to the skin surface *via* epidermal pores situated along the ridges of the friction ridge skin.

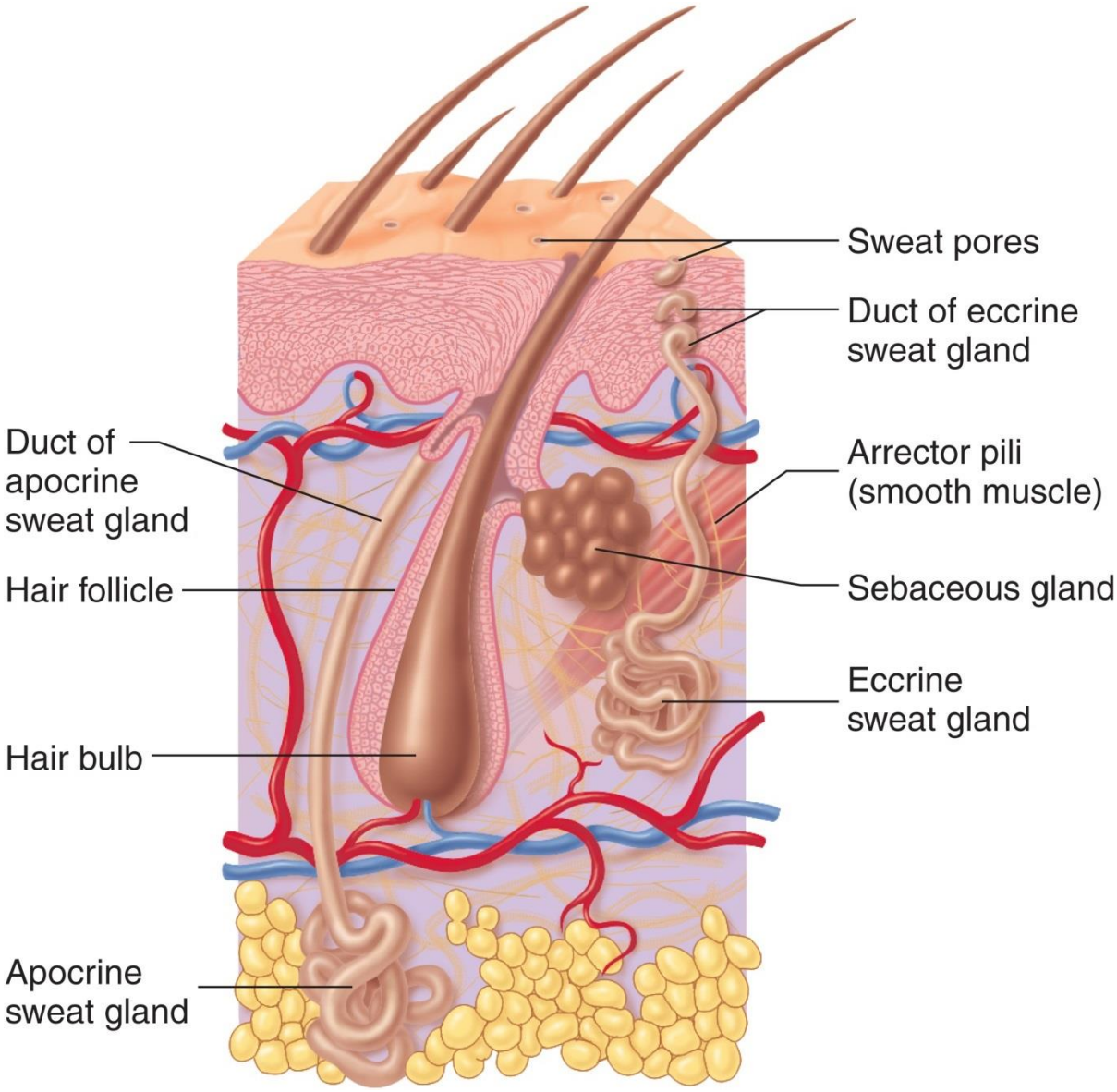


Figure 14: Sweat Glands [60]

The latent fingermark deposits which are the foundation of all fingerprint enhancement techniques are comprised of perspiration secreted from sweat pores. This perspiration is composed of water and various organic and inorganic constituents (Table 1) [61]. In 2000, Bernier *et alii* conducted a study in which they discovered nearly 350 compounds within the surface skin residues, 300 of which were positively identified [62].

Source	Constituents of Fingermark Residues	
	Inorganic	Organic
Eccrine glands	Chlorides	Amino acids
	Metal ions	Urea
	Ammonia	Lactic acid
	Sulphates	Sugars
	Phosphates	Creatinine
		Choline
		Uric acid
		Vitamins
Sebaceous glands		Fatty acids
		Glycerides
		Hydrocarbons
		Alcohols
Apocrine glands	Iron	Proteins
		Carbohydrates
		Cholesterol

Table 1: Fingermark Constituents

Compounds from Eccrine Glands

Although these glands are found throughout the body, the largest concentrations are found on the palmer and plantar surfaces. Eccrine secretions contain; inorganic salts, the most abundant of which being sodium chloride. Organic substances include amino acids, fatty acids, lactic acid, ammonia and urea [63].

Up until recently, the general opinion was that water content within eccrine fingermark residues was in the vicinity of up to 98 per cent [47], with the remaining 2 per cent of the residue being made up of organic and inorganic constituents. Kent (2016) published a review article which views the water content in a new light. Although Kent conducted no analytical measurements, he examined many articles currently in forensic literature and used deductive reasoning coupled with scientific formulae to deduce that due to a number of factors including re-absorption and evaporation this amount was just not logical. He showed, although theoretical, that the organic and inorganic components of fingermark deposits would far exceed the 2% stated in multiple references, with a typical fingermark deposit having the potential to contain around 5µg of non-aqueous material present. Kent concluded that the typical maximum water content of an eccrine mark was more likely to be in the region of 20% with the possibility of being considerably less [64].

Compounds from Sebaceous Glands

Sebaceous glands are located in areas containing hair follicles, most abundantly around the face and scalp. The palmer surfaces contain no sebaceous glands, however, sebaceous secretions (sebum) are found in latent fingermarks due to the propensity to the face, on average two to four times per minute. Sebum contains; saturated fats, wax esters, phospholipids, glycerides, sterols and squalene [65].

Fatty acids are the most abundant group of compounds found within the sebum, these along with alcohols react to form wax esters *via* esterification. The fatty acids involved in these reactions are linear and often have double bonds, whereas the alcohols are generally saturated. Triglycerides found in fingermark residues are the product of glycerol and fatty acids. Cholesterol is also present in sebum, although not secreted by the sebaceous glands, it is thought to be there as a result of entering into the sebum *via* blood circulation and through the plasma [66]. Squalene, a cholesterol precursor has also been identified within sebaceous secretions [61].

Compounds from Apocrine Glands

The apocrine glands are mainly found in the axillary and perineal regions of the body. Unlike its counterparts, there have been very few studies conducted in to the secretions of the apocrine gland, mostly due to their location. Since the apocrine gland lies further in to the dermis, attempts to analysis the secretions emanating from it are complicated due to contamination from the eccrine and sebaceous glands [61].

1.9.3 Contaminants

As well as compounds found intrinsically there are frequently compounds which are found extrinsically from the body present in fingermark residues. These compounds are contaminants and can come from numerous different sources. Food residues, bacterial spores, dust, drugs, cosmetics; face/body creams, perfume and hair products have all been identified during the course of fingermark residue analysis [66]. Some cosmetics contain the same lipid compounds which are present within fingermark residues, making it difficult to differentiate between them [61].

1.10 Factors Affecting Fingermark Residues

1.10.1 Aged Fingermark Composition

Numerous chemical and physical factors influence the rate of aging of deposited fingermarks. These can follow many different pathways such as evaporation, migration, oxidation, drying, degradation, diffusion or polymerisation [66, 67].

Eccrine Fingermarks

Mong *et al.* reported that 85% of a fingermark's weight had been lost over a 2 week period and presumed this was primarily due to water loss [68]. However, reports suggest amino acids are stable over time, especially when fingermarks are deposited on paper due to their affinity for cellulose. This means that the amino acids do not tend to bleed when on the paper's surface, instead, they remain for extended periods of time which allows for the retrieval of sharp, defined fingermarks using suitable reagents [69]. A study by Reinholz using plasma proteins to develop fingermarks showed that the antibody reaction taking place was stable on older fingermarks up to 130 days old on "real world" porous substrates [70].

Sebaceous Fingermarks

Compounds within the sebaceous secretions; primarily squalene, cholesterol and fatty acids undergo degradation as a function of time, producing new compounds, generally smaller oxidised molecules [68]. Old fingermarks were shown to contain small short chain fatty acids while long chain fatty acids were present more in fresher fingermarks, it was surmised that short chain fatty acids were derived from the longer chain fatty acids as the fingermark aged [71].

Inorganic Fractions

Silver nitrate has been used to enhance fingermarks on porous substrates *via* the chlorides present in eccrine residues, however, it has been found to be less effective on older marks. Angst (1962) attributed this to the diffusion of the chlorides into the substrate over time [46].

1.10.2 Substrate Surface Characteristics

The porosity of the substrate a fingermark has been deposited upon and its ability to retain compounds are the main factors the substrate has in influencing the fingermark's composition. The more porous the substrate, the greater the physio-chemical processes are that are occurring on the surface and within the substrate. This means that the adhesion forces are stronger and more of the fingermark components will migrate in to the substrate [48]. Residue penetration in to a substrate is proportionate to the substrates porosity; porous substrates experience significant penetration of residues, whereas non-porous substrates encounter little in the way of residue penetration.

The fingerprint enhancement technique employed depends on the print-receptive surface upon which the friction ridge skin has come into contact with. There are three basic surface characteristic types (Table 2) [61].

Substrate Type	Substrate Residue Mechanics	Examples
Porous	Eccrine compounds rapidly absorbed. Sebaceous compounds absorbed more slowly.	Paper, cotton, wood
Semi-Porous	Eccrine compounds absorbed but at a slower rate than porous substrates. Sebaceous compounds absorbed very slowly, need more time than eccrine counterparts.	Varnished wood, waxy surfaces, some plastics, glossy papers
Non-Porous	Both eccrine and sebaceous compounds stay on substrate surface until degradation occurs (physical, chemical or biological).	Glass, metal, paint, some plastics

Table 2: Substrate Surface Characteristics

Porous Surfaces

Porous surfaces are those which tend to absorb latent fingermark deposits quickly. Surfaces such as paper will absorb the water soluble components of the fingermark within seconds of deposition. The urea and salt components seep the deepest into the porous surface, with the amino acids staying near the surface. The fats, waxes and other water insoluble components of the deposit [65], however, remain on the surface. Penetration depth depends on a number of factors: the porosity level of the substrate, the relative size of each constituent, molecular properties, and environmental conditions such as humidity and temperature. Since amino acids are larger molecules than urea, they tend not to penetrate as far into the substrate [48]. When the relative humidity is higher (>80%), migration of the water soluble deposits is faster. The mobility of non-soluble water deposits at normal temperatures (20°C) is generally slow, however, when temperatures increase above 35°C the mobility of these deposits increase significantly and they are quickly diffused into the substrate surface [46]. Once the mark deposits are absorbed into the porous surface the water soluble components are fairly well preserved, they cannot be rubbed away, but they can be washed away easily with water. Small amounts of the water insoluble components can remain on the substrate surface for years if appropriately preserved (Figure 15) [72].

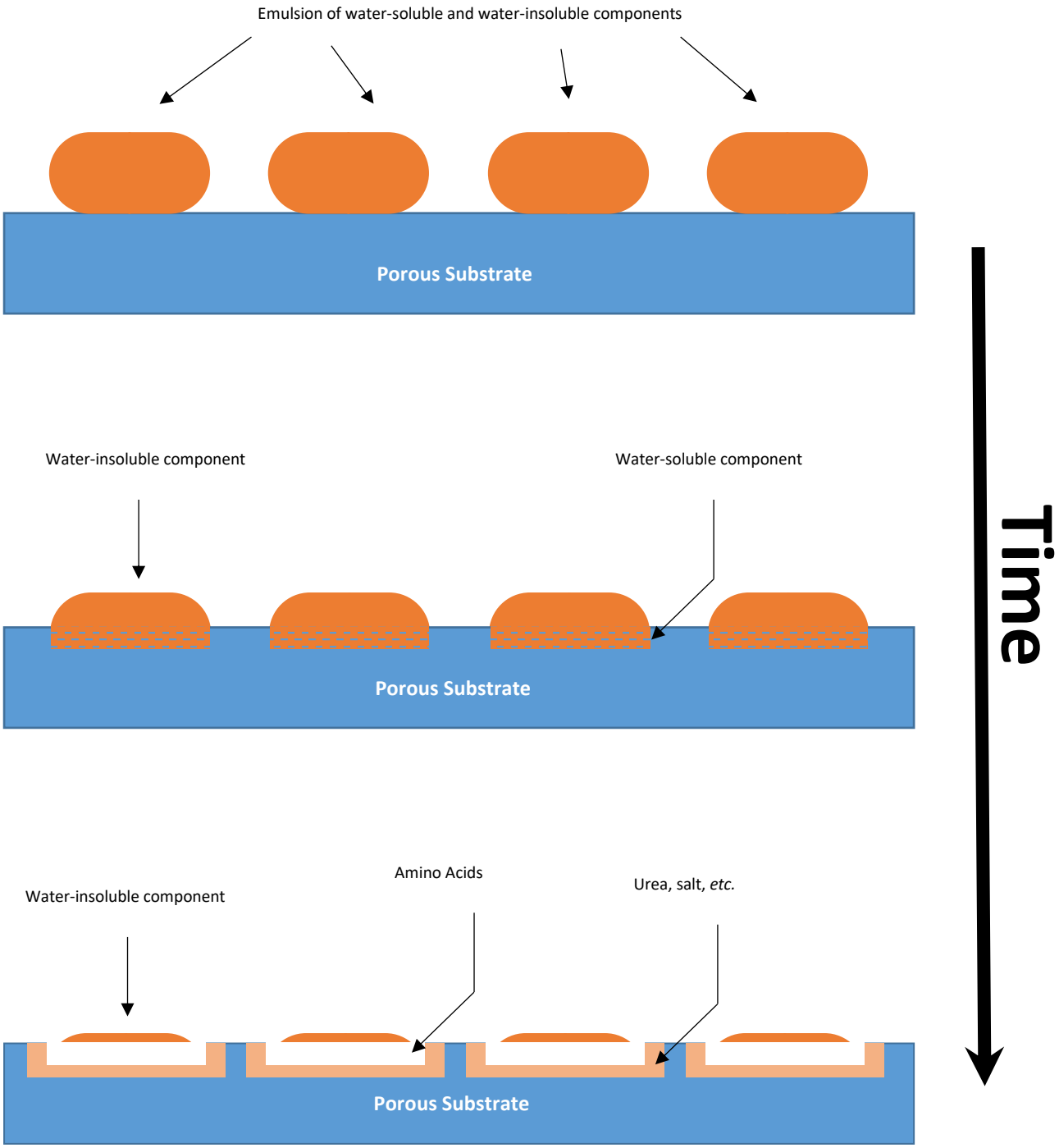


Figure 15: Cross-section: Aging of Latent Fingermark Deposit on a Porous Substrate (e.g. paper) (A) Immediately after being deposited, (B) Seconds/minutes after deposition, and (C) Days/weeks after being deposited (Adapted from Champod *et al.* [72])

Semi-porous Surfaces

Surfaces which have characteristics which are not entirely consistent with those of porous or non-porous surfaces are called semi-porous. Waxed paper, polymer banknotes and certain types of painted surfaces are typical examples of semi-porous surfaces. These types of surface, as with porous surfaces, absorb the water soluble components of the fingermark deposit, albeit at a slower rate.

Non-porous Surfaces

Conversely, substrates which do not absorb any of the fingermark components are classified as non-porous. Glass, plastic bags and shiny metal are all examples of non-porous surfaces [73]. When a fingermark is deposited upon such surfaces all of the fingermark residues, water soluble and insoluble alike, remain upon the surface of the substrate. Since all of the deposit sits on the non-porous surface, the latent fingermark is very fragile and can be rubbed off the surface. Water will remove the water soluble materials, leaving the water insoluble behind, these can be removed by the use of organic solvents (Figure 16) [72].

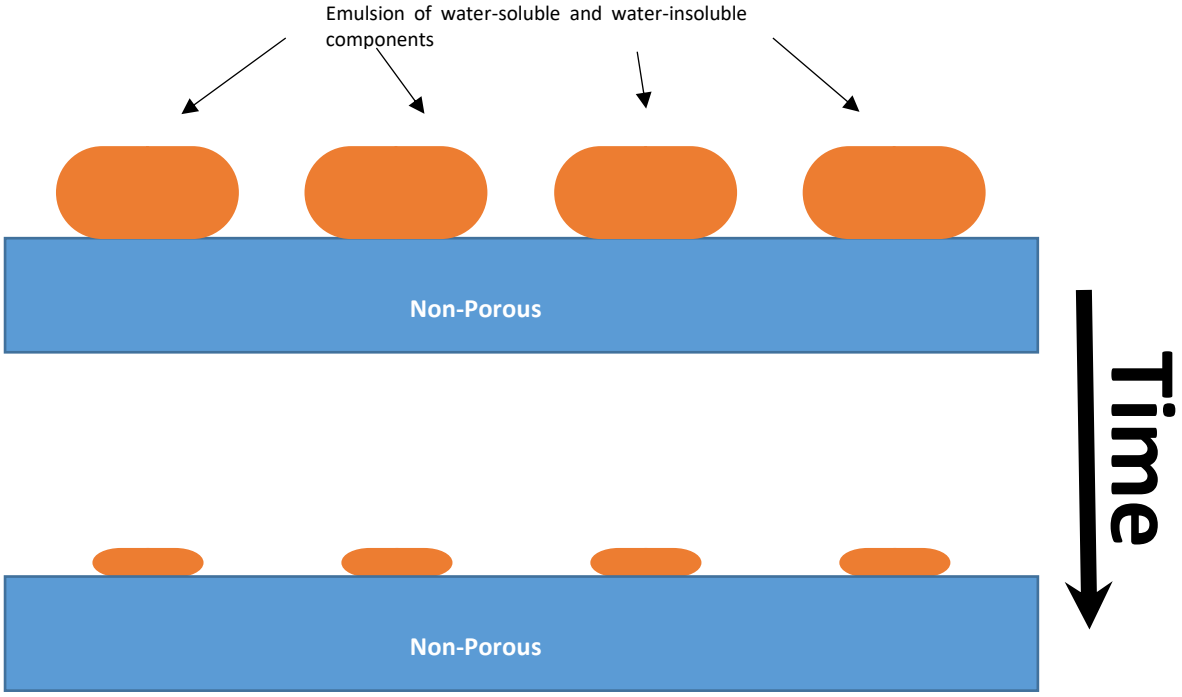


Figure 16: Cross-section: Aging of Latent Fingermark Deposit on a Non-Porous Substrate (e.g. glass) (A) Immediately after deposition and (B) Weeks/months after being deposited (Adapted from Champod *et al.* [72])

1.11 Terminology - Fingerprint or Fingermark?

More recently the term ‘fingermark’ has begun to make its way in to scientific research literature. But what is the difference between ‘fingerprint’ and ‘fingermark’? The term ‘fingerprint’ is now being employed to describe the pattern on the tips of the finger and to impressions taken under controlled conditions; such as inked elimination prints or Livescan images taken when a suspect is in custody.

‘Fingermark’ on the other hand refers to marks left by uncontrolled contact between the fingers and surfaces at a crime scene. These marks will generally need enhancement to make them visible. The deposits examined in a laboratory setting, it could be argued, should be termed ‘fingerprints’ since this is a controlled environment. However, since they are a representation of latent marks that would be needing to be developed at a crime scene, it could also be reasoned that they should be termed ‘fingermarks’ [74, 75].

Throughout this report, both terms will be utilised, since, in these instances, both terms are technically correct.

1.12 Project Aims

This work builds upon previous forensic activities within the Kelly group by utilising close contacts with the Home Office labs at the Centre for Applied Science and Technology in order to develop new forensic methodologies and reagents. By way of example, these include the identification of new chemical reagents for fingermark development and new methods of utilising autoradiography to identify traces of radioactive materials (and to employ radiolabelling in fingermark imaging). Work will extend to biological samples, assessing the role of bacteria in providing forensic information from fingermarks.

2.0 Fingermark Enhancement Techniques

2.1 Established Techniques

The method of development used depends greatly on the surface type upon which the mark has been deposited. When enhancing a fingermark, be it *via* a physical or a chemical process, it always begins with the least destructive technique first. After the use of some enhancement methods, marks can occasionally be subsequently treated with another development technique if required [76].

2.1.1 Porous Surfaces

Ninhydrin

2,2-Dihydroxyindane-1,3-dione or ninhydrin (Figure 17) as it has come to be known was first discovered, serendipitously, by the chemist Siegfried Ruhemann. He found that the solution would stain the amino acids contained within the sweat on the hand, producing a purple coloured product [77], referred to nowadays as Ruhemann's Purple. Ninhydrin was routinely used as a stain for thin layer chromatographic amino acid assays, to allow the visualisation of the separated amino acids. Surprisingly, it would be another four decades until ninhydrin's true potential would be realised when it was proposed as a reagent for the detection of fingermarks [78], exploiting the amino acid content within the eccrine component of the latent mark.

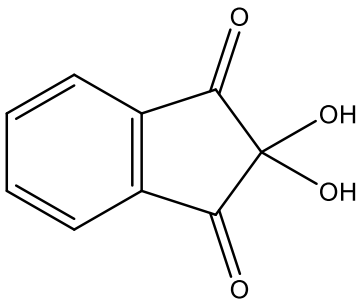


Figure 17: Structure of Ninhydrin

Ninhydrin has been through numerous formulations since its inception as a latent fingermark enhancement reagent by Oden and von Hofsten (1954). Of the many solvent systems experimented with by Oden and von Hofsten, they discovered that acetone or ether had the highest sensitivity to amino acids [79]. Petroleum ether was introduced, in 1969, as an alternative to the acetone/ether solvent, and although highly flammable it worked well with paper being subjected to document analysis due to its ability to cause less ink running than previous solvents [80].

In the Seventies, with its increased usage, an effort was made to improve the safety of the ninhydrin reagent. CFC-113 (1,1,2-trichlorotrifluoroethane) was introduced as a new solvent for ninhydrin, its implementation increased performance on many levels; it was non-toxic as well as non-flammable, it reduced damage to handwritten documents and most importantly, it increased the overall number of fingermarks developed [81]. The late Eighties saw the advent of a reasonably priced humidity oven which the Police Scientific Development Branch used as a catalyst to optimise the ninhydrin process. They managed to both increase the number of marks detected as well as decrease development time from days to minutes.

By the end of 1995 another solvent carrier was being sought, after the banning of CFC-113 under the 1992 Brussels Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer. Several research studies were conducted [82] using 3M Novec™'s HFE-7100 which was found to satisfy the requirements devised for use in fingermark work [83]. ninhydrin is currently the most utilised technique for fingermark detection on porous surfaces [46].

There have been a vast number of studies conducted in to the reaction mechanisms and colour formation of Ruhemann's purple *via* reactions of ninhydrin with amino acids [84-87]. The reaction pathway between ninhydrin and amino acids is generally accepted as detailed in Figure 18 [72, 88]. Ninhydrin reacts with the amine group of the amino acid to form Ruhemann's purple. Other compounds can react anomalously, however, these do not proceed all the way to the formation of the purple product.

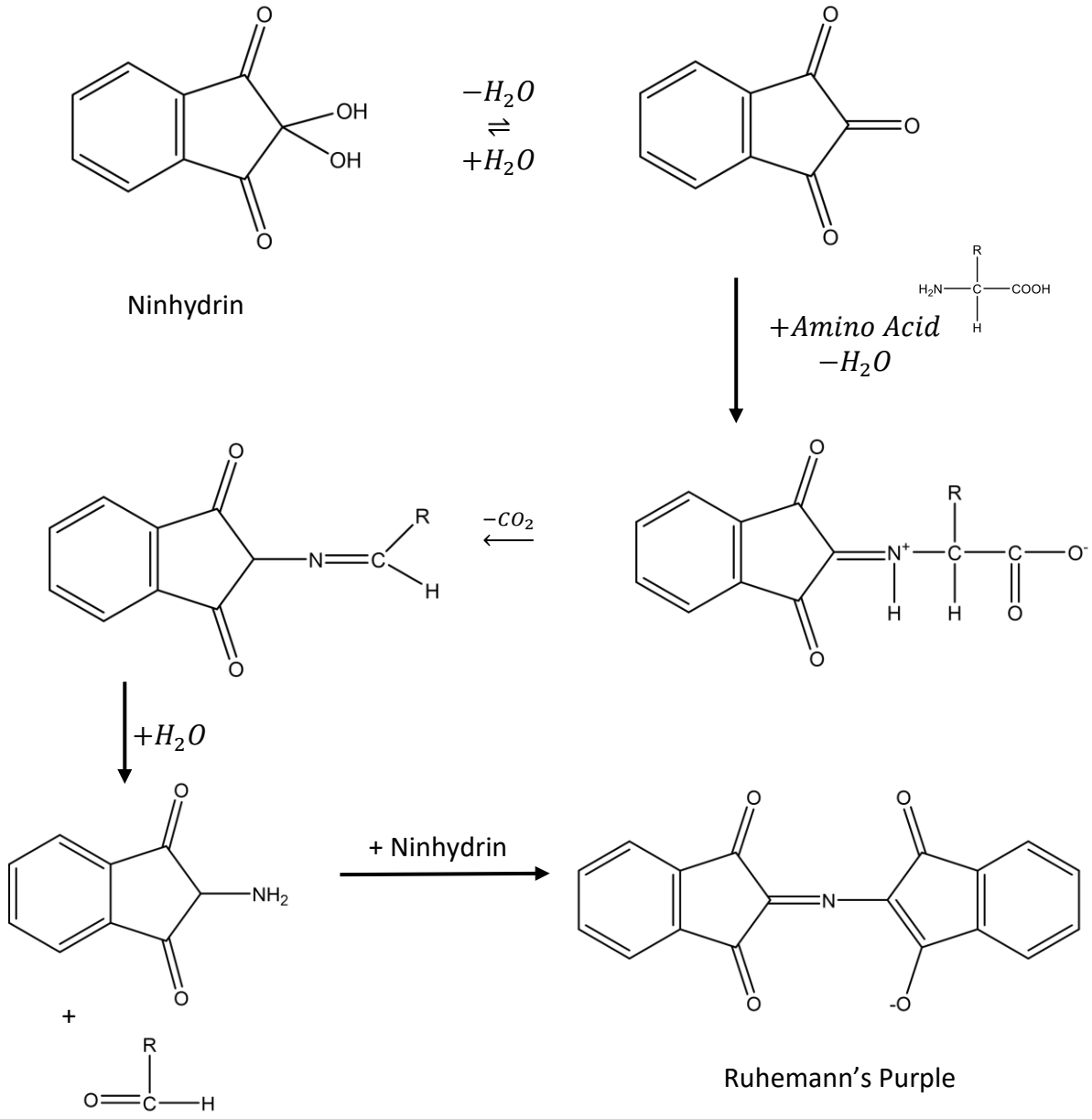


Figure 18: Reaction Mechanism of Ninhydrin with Amino Acids

Although the ninhydrin reaction will commence under normal room temperature and humidity conditions, the process is greatly accelerated when treated articles are at a higher temperature (80°C) and humidity (65%) environment such as those found in specialist humidity ovens [88]. The Centre for Applied Science and Technology (CAST) recommend using ninhydrin as a standalone technique or in a sequence of enhancement techniques as it gives quick results that can be easily captured using a range of equipment.

Diazafluorenone (DFO)

DFO (1,8-diazafluoren-9-one) (Figure 19) was discovered in the early 1950s [89], and like ninhydrin it was not utilised as a fingermark reagent until several decades later. The DFO treatment process differs from that of the ninhydrin process in that it requires a dry heated environment to develop rather than a humid one [90], it reacts with the amino acids in the fingermark residue to produce a similar but lighter coloured complex to the "Ruhemann's Purple" of ninhydrin [91]. The faint red/pink coloured product of DFO treated fingermarks fluoresce brightly under high intensity green light in the 473 – 548 nm wavelength range [92].

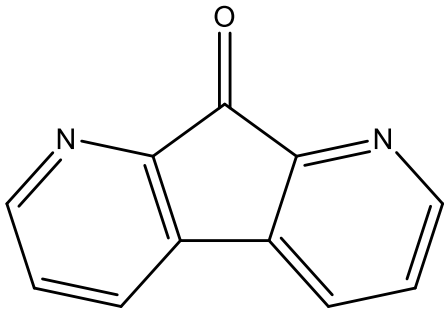


Figure 19: Structure of DFO

DFO has been the subject of many studies investigating its sensitivity as a fingerprint reagent, these studies determined that DFO was more sensitive than ninhydrin, producing superior numbers of identifiable latent fingermarks [93]. One study found that DFO does not react with every amino acid with the fingermark residue, this leaves amino acids free to react with ninhydrin [94]. On porous surfaces such as paper, DFO is considered the best fluorogenic fingerprint reagent, and when utilised before ninhydrin more latent marks are developed than when either enhancement method is used independently [95].

Like ninhydrin, DFO has had many formulations including; petroleum ether [96] as its solvent carrier and HFE-7100 [97] which is the solvent carrier which is used operationally to this day. As ninhydrin and DFO are, by nature protein stains, they can also be used to develop fingermarks contaminated with blood. They achieve this by reacting with the proteins found in the blood [98].

Grigg *et al.* and Wilkinson were amongst the most active groups studying the reaction mechanism for DFO [91, 94], with Wilkinson suggesting that the DFO mechanism follows a similar path to that of the ninhydrin with amino acid reaction. The proposed reaction pathway between 1,8-diazafluoren-9-one (DFO) with amino acids is detailed in Figure 20 [72, 94], this pathway was closely related to Grigg *et al.*'s original predictions ten years prior [91].

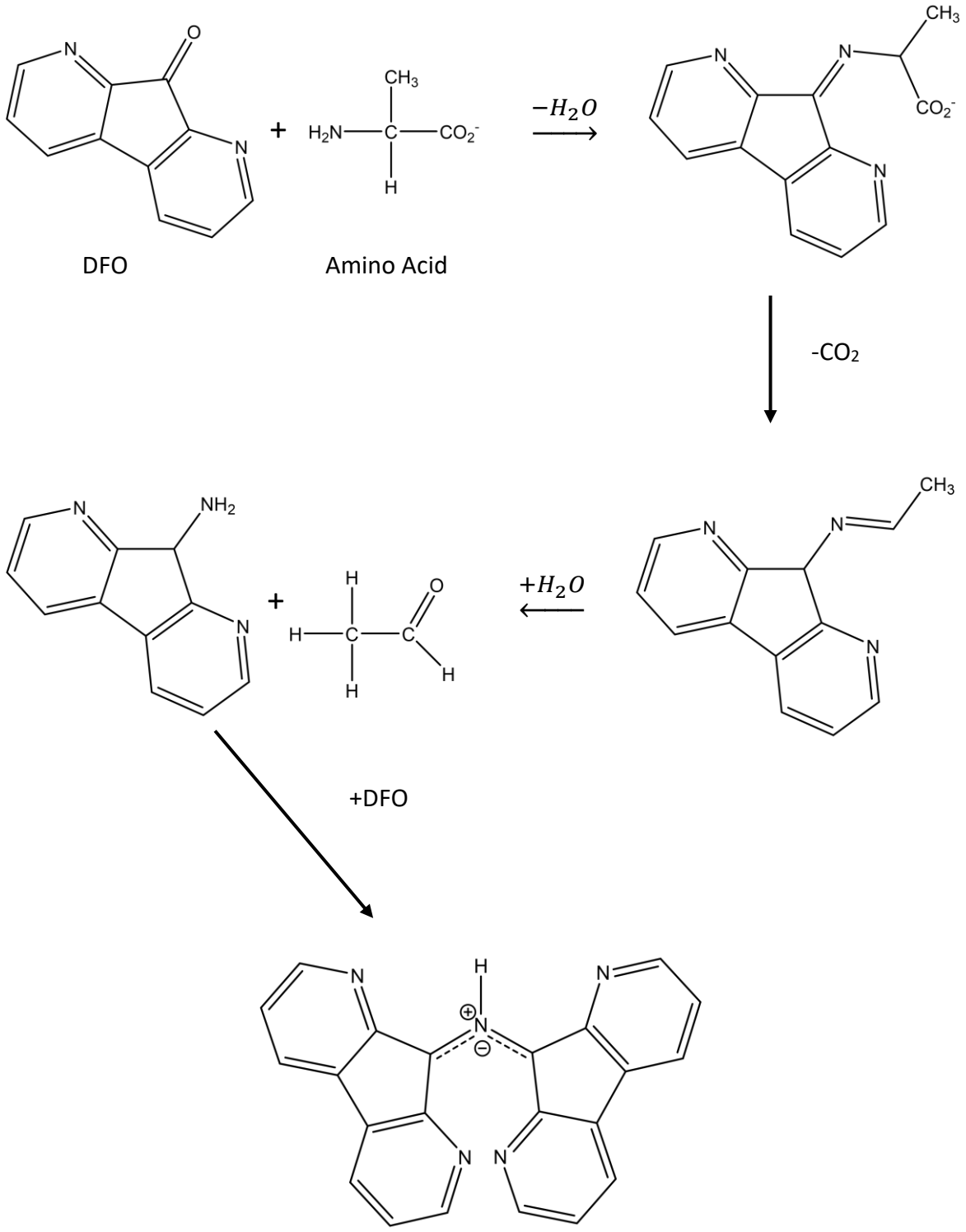


Figure 20: Proposed Mechanism of 1,8-diazafluoren-9-one (DFO) with Amino Acids [93]

Iodine Fuming

Iodine is one of the earliest chemical processes for the development of latent fingermarks. In 1863, while using iodine fuming to detect alterations made to questioned documents, Coulier observed enough friction ridge detail on the documents that could lead to the identification of the author [99, 100]. However, the staining was found to be short-lived as the marks would fade within minutes; *ergo*, a method of prolonging this period or fixing the stain indefinitely was sought. Iodine fuming was in use operationally in the UK from 1931 [88], with a lifting method involving moist paper infused with rice starch being proposed in 1935 [101]. By the early 1960s, silver foil was suggested as a means of lifting the iodine fumed marks, with the iodine selectively reacting with the foil to produce silver iodide, this then darkened when exposed to strong light [102] cited in [88]. Shortly after this, Larsen (1962) proposed a new starch fixing process which involved brushing the marks with a fine starch powder, blowing the excess away, and then exposing the mark to a light steam for up to 2 minutes [103]. Silver and tin plates were investigated as a method of recovering iodine fumed fingermarks which had been developed on human skin [104-106]. Fingermarks were shown to be recoverable from both live and dead skin; however, despite demonstrating that marks could be lifted from dead skin up to 72 hours after deposition, recovery from live skin was considerably shorter. The technique was observed to be ineffective on eccrine marks, instead only developing sebaceous marks.

A lot of investigatory work was conducted in to fixative solutions for the iodine fuming process in the 1970s. Investigators experimented with using uncured silicone rubber mixes impregnated with fixing solutions that could be moulded over developed marks with the aim to moving away from solvent dipping or spraying [107]. Mashiko and Ishizaki (1977) proposed α-naphthoflavone [108] as a fixative method which the UK favours for operational use [109]. Almog *et al*. found that by simultaneously fuming iodine with steam on paper substrates, improved results could be observed on older marks as well as on marks left by poor donors. Latent fingermarks up to 110 days old could be made visible using the iodine and water vapour method [110]. In the wake of this, Haque *et al*. suggested iodine in a solution mixed with α-naphthoflavone, however, the formulation also used cyclohexane which was considered inappropriate for use at crime scenes due to its flammability [111].

The Metropolitan Police in conjunction with the Home Office Central Research Establishment (HOCRE) worked to develop a non-flammable solution, what was produced was a two-part formulation comprising of iodine dissolved in 1, 1, 2-trichlorotrifluoroethane (CFC113) and the α-naphthoflavone in a separate solution. The aim was to enable the treatment of large scale areas at crime scenes, however, upon comparison with a non-flammable ninhydrin (NFN) solution, the iodine solution performed better in ambient temperatures whereas the NFN performed better at increased temperature and humidity ([112] as cited in [88]). Although the iodine solution was adopted for operational use by some organisations, it was only successful in developing marks at approximately a third of crime scenes treated.

Radioactive Techniques

Takeuchi *et al*. (1958) described a process which utilised ^{14}C-labelled stearic acid as a fingermark enhancement technique. The stearic acid was absorbed by the fats present in latent fingermark deposits. They successfully obtained positive results on fabric, paper, wood and metal [113]. Gel'fman *et al*. (1964) used ^{14}C-labelled formaldehyde to develop latent fingermarks on mosaic patterned surfaces and those with heavy typewriter print. The radiolabelled formaldehyde was believed to react with either the amino acids or the fatty constituents of the fingermark residue. After treatment the sample could be imaged using contact radiography. Gel'fman found this to be useful on substrates where the pattern of the substrate interfered with the visualisation of the fingermark, and further stated that the technique was capable of developing marks which had previously been processed with other reagents which failed to reveal any ridge detail [114].

Prokopowicz *et al*. (1966) reported using radioactive silver (^{110}Ag) to react with the latent fingermark residue. Prokopowicz *et al*. had a number of donors deposit their fingermarks on a variety of paper substrates; including newspaper. Samples were treated by dipping into a radiolabelled silver nitrate solution for a variety of times ranging from around 0.05 – 0.1 minute (3 – 6 seconds) to 2 minutes, the samples were then washed with distilled water for anywhere between a fraction of a minute to 2 minutes.

It was found that the immersion and washing times had no effect on the autoradiography images obtained, therefore different exposure times were examined in order to determine the timeframe at which the contrast was at its clearest. The exposure time was found to be dependent on the activity of the $^{110}AgNO_3$. The radioactive silver nitrate solution was found to react with the chlorides in the latent fingermark residues to produce radioactive silver chloride [115].

Radioactive sulphur dioxide ($^{35}SO_2$) was first proposed as a latent fingermark development process by Grant *et al*. while they were investigating paper's resistance to attacks *via* atmospheric pollution. While developing autoradiographs which had been subjected to sulphur dioxide treated paper, they noticed marks that were later identified as fingermarks were present. Paper was exposed to a radioactive SO_2 gas for 12 hours then placed against an autoradiography plate for a week. The sulphur dioxide was found to be picked up preferentially in the areas contaminated with fingermarks, causing the x-ray film to appear darker in these areas [116]. Further work conducted by Grant *et al*. showed that aged fingermarks had a reduced chance of developing, they also found that paper with alkaline fillers within the paper took up heavy amounts of radioactive sulphur dioxide uniformly across the substrate making the detection of fingermark ridges difficult [117].

This lead to research by Spedding (1971), in which he proposed that the radioactive SO_2 was reacting with the lipids present in the fingermark residues, highlighting oleic and linoleic acids as being reactive. Spedding and his team also conducted a series of experiments comparing the effectiveness of $^{35}SO_2$ against ninhydrin and iodine for the development of fingermarks on paper. The investigation found the radioactive SO_2 to be the superior technique over a variety of different paper types. The report also suggested that the technique could prove effective at recovering fingermarks from fabrics, and initial results were promising [118].

Ganson (1973) reported success using radioactive sulphur dioxide in an operational application. The case involved the recovery of fingermarks from forged £5 notes which had proved resistant to traditional fingermark recovery techniques (i.e. ninhydrin and silver nitrate). Four notes were treated with $^{35}SO_2$, three marks were developed, two marks on one note and a single mark on another. Two of the marks recovered were from the individual who turned the counterfeit in and the third mark was from an unknown donor. This process achieved positive results where other, well established techniques fell flat, but Ganson stressed that despite the compelling results, radioactive sulphur dioxide was not likely to be an all-encompassing, one-stop reagent. The article went on to detail the use of the radioactive sulphur dioxide for the development of fingermarks on fabric.

In order to simulate realistic grab patterns, fabric swatches were placed around the biceps of donors, who were instructed to grasp the fabric with their opposite hand. Another experimental set involved strangulation simulation by tying and knotting a piece of fabric. The bicep grasping experiment resulted in uneven clarity over the impression area, some areas showed considerable ridge bleeding, however, other areas showed clearly defined ridge detail. They found that the knot tying experiment resulted in mainly useless impressions, with a few fragments of clear ridge detail. Overall Ganson found that radioactive sulphur dioxide does not inhibit further processing with other fingermark enhancement reagents [119].

In 1978 Goode *et al*. reported their preliminary findings using vapour phase radioactive bromine isotopes on paper and plastic substrates. They found the technique to show promise and showed that it offered some advantages over $^{35}SO_2$, mainly its speed and its effectiveness with regards to the rate of degradation [120].

Oil Red O

Oil Red O (ORO) is a lysochrome, or lipid stain similar to Sudan Black used for staining fatty acids, lipoproteins and triglycerides. Initially, Oil Red O was investigated as an azo-dye (Figure 21) for the staining of lip prints deposited on tissue paper [88]. Alexandre Baeudoin reported a formulation of Oil Red O which was capable of developing fingermarks not just on dry porous surfaces but also porous surfaces which had been wetted. It was also found to work on semi-porous and soiled paper. The process is completed in two stages, first, an Oil Red O dip bath for up to 90 minutes followed by immersion in a buffer solution [121].

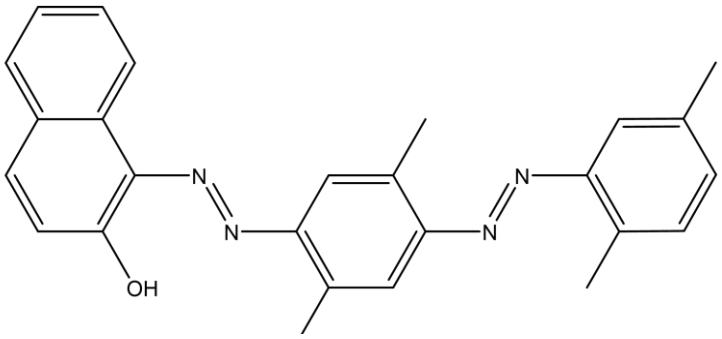


Figure 21: Oil Red O Structure

Other studies have looked at Oil Red O as an alternative to Physical Developer (PD) as well as how it performs in sequence with other fingermark development techniques. In the comparison trial with PD, the two techniques were tested on three different types of wetted paper; thermal, white and brown Kraft papers. ORO was found to be more effective on fresh sebum rich fingermarks on thermal papers. The white and brown papers were tested using aged fingermarks, up to 30 days old. Oil Red O produced more marks on wetted white paper than the physical developer [122], however, it performed to a lesser degree on brown paper [123]. Further study revealed that ORO outperformed PD on fingermarks under 4 weeks old, than on those older. However, due to this ORO performance issue with time, the report recommended that ORO not completely replace physical developer but rather be considered over it for fingermarks less than 4 weeks old [124]. Oil Red O is not currently recommended for use in the UK due to it being less effective than physical developer, ineffective on older marks, and not effective on marks which have been immersed in water for a prolonged period of time [88].

2.1.2 Non-Porous Surfaces

Cyanoacrylate Fuming

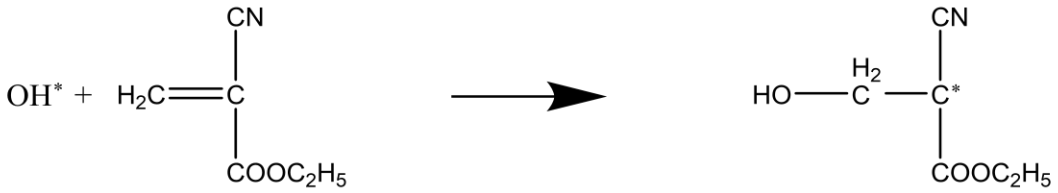
Cyanoacrylate or superglue as it is more commonly known was accidentally developed in the fifties during researcher's attempts to create an acrylic polymer for use in the aircraft industry [88]. It eventually ended up being a successful liquid adhesive for use on non-porous surfaces. Unconventionally, it also found use as an impromptu field dressing during the Vietnam War [125].

It would be the late seventies before its forensic potential would be realised, when the British and the Japanese working independently of each other discovered, almost simultaneously, the effects that superglue fumes had on latent fingermarks [88, 125, 126].

Initial investigations into the technique had researchers using large fish tanks sealed with tape to create a superglue chamber. The samples being developed were then suspended within, with aluminium foil placed on the base. A number of drops of cyanoacrylate ester, usually ethyl cyanoacrylate, containing glue would then be placed on the bottom of the tank. This technique could take up to several days to develop any latent marks [127]. Not surprisingly, much research has gone into the technique over the last three decades, which resulted in many acceleration techniques being investigated. Catalysts [128, 129] and heat [130, 131] were the two main methods investigated, however, results were still mixed and the technique unreliable. In 1982 in the UK the Police Scientific Development Branch (now Centre for Applied Science and Technology) began investigating the superglue technique and subsequently discovered that humidity played a major role in both speed and sensitivity.

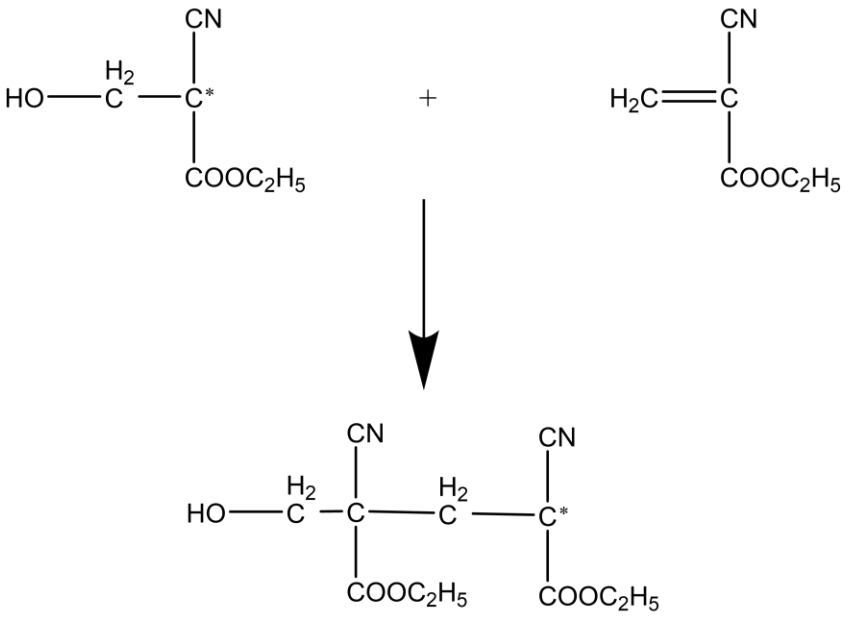
Superglue treatment produces a white coloured deposit upon the fingermark residue, this white deposit is polycyanoacrylate. Polycyanoacrylate is formed *via* the polymerisation of cyanoacrylate monomers (Figure 22). Sebaceous marks are especially susceptible to the cyanoacrylate vapour, however, the vapour also reacts with water soluble components in eccrine deposits in conjunction with moisture from its 80% relative humidity environment [46].

Initiation



Polymerisation

Ethyl Cyanoacrylate



Polycyanoacrylate

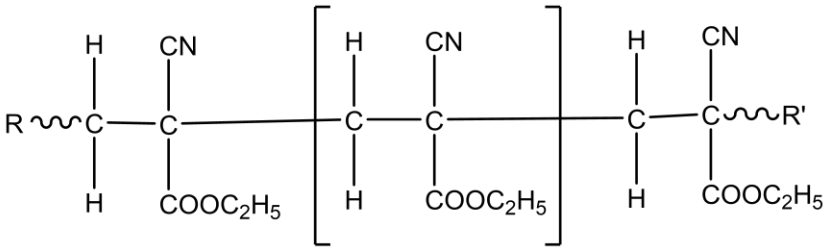


Figure 22: Polymerisation Reaction of Ethyl Cyanoacrylate

The white deposit of superglue fuming process can be a challenge to visualise on a light coloured surface. Many attempts were made to increase the contrast of the enhanced mark through powdering and ultimately through fluorescent dyes. Initially, Rhodamine 6G (also known as Basic Red 1) was the dye used [132], however, this was quickly replaced due to the use of methanol as its solvent and the suspected carcinogenetic effects of Rhodamine. Ultimately it was Vaughn Sears at the Police Scientific Development Branch who discovered the Basic Yellow 40 dye in 1985, a dye which is still used sequentially with cyanoacrylate fuming to this day (Figure 23) [88].

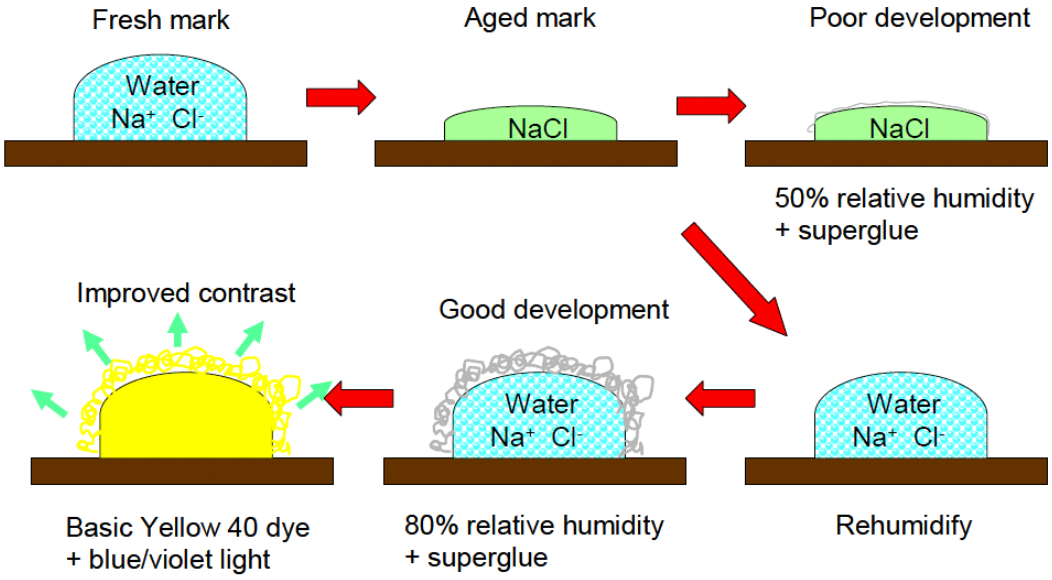


Figure 23: Cyanoacrylate Development and Dyeing Process [88]

Fingerprint Powders

Fingerprint powders are one of the oldest and most widely used physical development techniques for the enhancement of latent fingermarks on non-porous surfaces. The earliest reports of powders being used to enhance fingermarks was in 1891 in a report by Forgeot [125]. Faulds soon began conducting his own studies using both black (soot) and white (magnesium carbonate) powders for enhancement on different coloured substrates [133].

Since their inception, there have been scores of different fingerprint powder formulations which have been tried and tested. Fingerprint powders fall into the general subcategories of regular, metallic and luminescent. Regular powders are a mixture of a resinous polymer for binding to the latent mark residues, and a colour pigment for enhanced visualisation. The most common of this type is carbon black, which produces dark grey/black enhanced marks that can be visualised on a variety of different coloured substrates [134]. Metallic powders include magnetic flake powders which are applied with a magnetic applicator and are extremely successful at recovering latent marks on substrates such as plastics and leather. Aluminium powder is regarded as the most commonly used metallic powder and is considered the most effective for use in fingermark detection [46]. Luminescent powders contain a combination of organic and/or synthetic compounds that are able to fluoresce or phosphoresce under UV or high energy light sources. Luminescent powders are used to visualise marks that have been deposited on multi-coloured surfaces where regular powders would be ineffective [88].

Vacuum Metal Deposition

Vacuum metal deposition (VMD) is a thin-film deposition technique in which source metal is evaporated in a vacuum in order to coat a substrate. The technique, which was long established in industry for the application of a metal coating to glass for making mirrors, was proposed for use as a fingermark development technique in 1964. After accidentally developing latent fingermarks on a glass surface during the deposition of silver in a vacuum, Professor Tolansky contacted the Home Office to report his findings. However, due to cheaper and easier techniques being used, the Home Office decided not to follow up on the technique [125].

By 1968 French researchers were reporting latent marks being developed on paper whilst using zinc *via* VMD, this lead to a revival of interest in the UK. Investigations into single metal and multiple metal coatings were conducted, in which the current operational preference of gold followed by zinc was found. In the mid-1970s VMD was being attempted on fabric, the idea was soon abandoned due to the opinion that fingermarks surviving washed and worn fabrics were miniscule [88].

VMD has been successful in treating a wide range of substrates including; plastic bags and bottles, glass, firearms, glossy card, photographic paper, magazine covers and clean leather. However, many of these substrates now have alternate enhancement processes as VMD is less effective, although, the deposition of silver is one of the few techniques which are successful on Clingfilm.

The vacuum chamber used for VMD needs to be able to pumped down to high levels of vacuum, typically $<3 \times 10^{-4}$ mbar. The chamber also has filaments for the evaporation of the chosen metal, and a window for viewing the deposition. Substrates are affixed to the workholder, which runs around the perimeter of the chamber, above the filaments (or boats) (Figure 24) [98]. The filaments are usually made from thin sheets of molybdenum, formed to have shallow dimples or troughs.

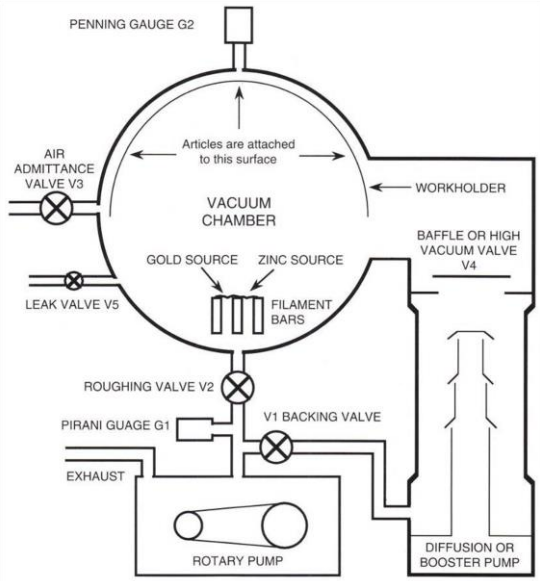


Figure 24: Vacuum Metal Deposition Schematic Illustration [98]

When treating samples with the Au/Zn technique, gold is applied first followed by the zinc. Samples are attached to the workholder, gold and zinc samples are placed in their respective boats, the chamber door is then closed and the pump engaged. Once the chamber has reached a pressure of approximately 3 x 10^{-4} mbar, gold deposition takes place. The current to the filament is increased until it glows with a yellow/white heat, it is held here until the gold has evaporated, typically around ten seconds. Once the gold has completely dispersed the chamber pressure is increased to ~5 x 10^{-4} mbar, whereby the zinc filaments are engaged and the current increased until the filament glows a cherry red/dull orange colour. At this point, the operator should be able to visualise the deposition of the zinc on the substrate, and as fingermarks become visible the current should be ceased to avoid overdevelopment. After development is completed, the gold filaments are usually briefly engaged to burn off any zinc contamination [88].

Alternate Light Sources

Ultraviolet (UV) Imaging

Ultraviolet Absorption

The fatty acids within fingermark residues are known to absorb strongly at the 277nm wavelength. In instances where a fingermark has been deposited upon a surface which reflects UV or fluoresces, this absorption can help provide enough contrast to make the fingermark visible (Figure 25).

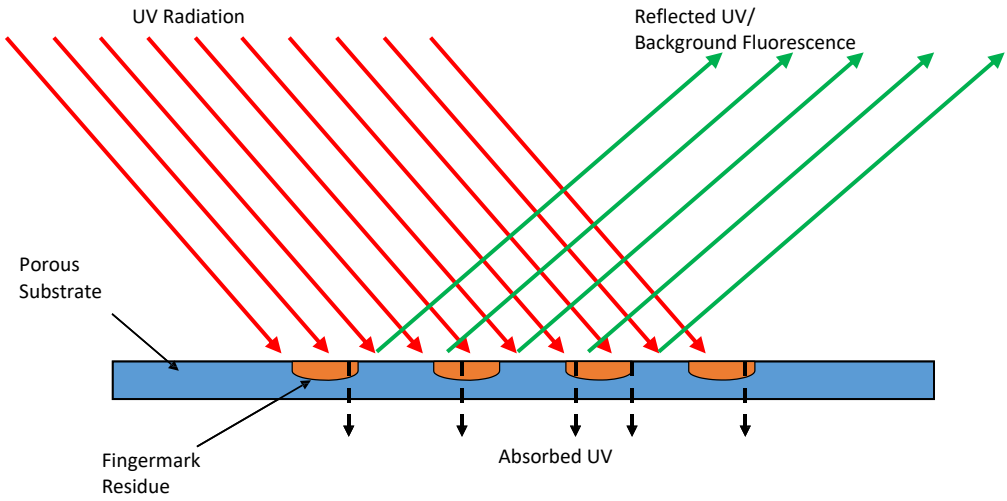


Figure 25: Schematic Diagram Showing UV Reflection/Absorption vs Ridge Contrast of Latent Fingermarks [88]

This works particularly well on white paper since it contains optical brighteners which fluoresce in the presence of UV radiation. This fluorescence provides a strong contrast with the absorbing fingermark ridges, this usually presents as dark ridges against a light background [88].

Ultraviolet Reflection

Ultraviolet reflection offers a contrast between the fingermark ridges and the substrate background by a greater means of scattering from the fingermark residues rather than the background as with UV absorption. This occurs in cases where the background absorbs the UV radiation more strongly than the fingermark residues or when the fingermark residues scatter more UV radiation back to the detection system (Figure 26). By placing a short-wave UV filter on to a camera, fluorescence and reflected light from the light source can be cut out. UV reflection works best in revealing latent fingermarks on smooth surfaces and in the further improvement of fingermarks enhanced using cyanoacrylate fuming. This is due to the strong scattering of the noodle-like structures created during the superglue fuming process [88].

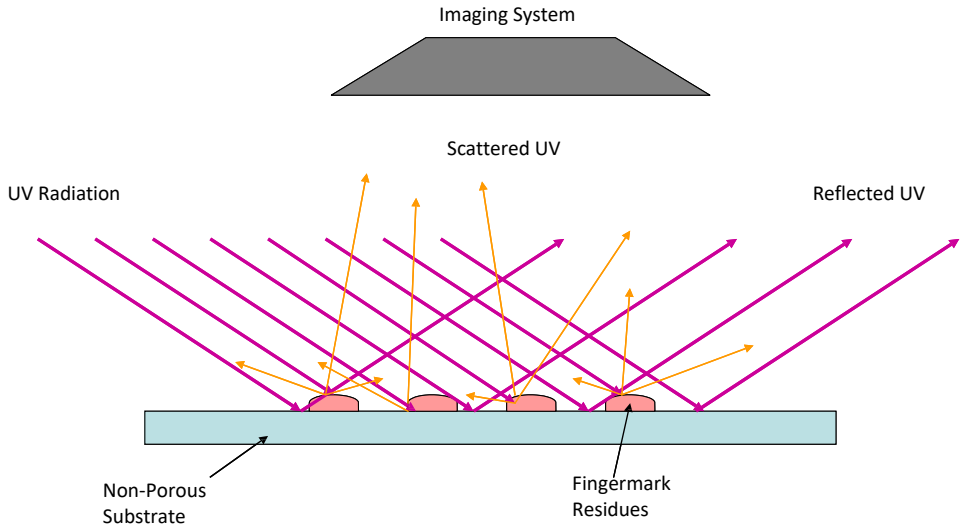


Figure 26: Schematic Diagram Showing UV Reflection/Scattering vs Ridge Contrast of Latent/Superglue Treated Fingermarks [88]

Infrared (IR) Imaging

In the near infrared (700 - 1,100 nm) region of the spectrum, fluorescence and absorption/reflection mechanisms used in the visible and UV regions to image, are primarily the same and as a result can be used in a similar manner. One of the fundamental differences between imaging in the visible region of the spectrum and imaging in IR is that man-made printing inks have been found to be IR transparent. This means that a highly patterned substrate can appear devoid of printing when viewed in near infrared conditions.

Unfortunately, latent marks cannot be detected with IR alone; they require staining with dyes or powders in order to become visible in this region of the spectrum. Basic violet 3 and acid violet 17 fluoresce in the IR region when green/yellow and yellow high intensity light sources are utilised. Many of the inorganic or metallic development processes; such as powders, powder suspensions and vacuum metal deposition either scatter or absorb IR to a higher degree than the substrate background. This allows developed marks to be visualised when using IR light sources [88].

Coaxial Lighting Imaging

Episcopic coaxial illumination is a diffused reflection mode for use on flat, shiny surfaces. Incident light is directed along the same axis as the camera lens, perpendicular to the surface to be photographed. This is achieved by mounting a semi-transparent mirror at 45° angle in front of the camera facing towards the lens and light path (Figure 27). The incident light beam is directed at a 45° angle onto the mirror through a diffuser. Some of the incident beam is reflected by the semi-transparent mirror and travels along the lens axis towards the exhibit substrate. The rest of the incident beam passes through the mirror and is absorbed by the black surface behind it. The flat substrate surface reflects more of the incident light (specular reflection) than the friction ridge deposits do (diffused reflection). This produces the opposite effect to the usual reflection mode, *id est* it produces a dark image on a light background. Episcopic coaxial illumination has been shown to successfully photograph latent fingermarks, cyanoacrylate developed fingermarks, and fingermarks in blood on smooth shiny surfaces such as metal, plastic and glass ([135] cited in [72, 136]). To gain optimum results, the substrate surface must be as flat as possible.

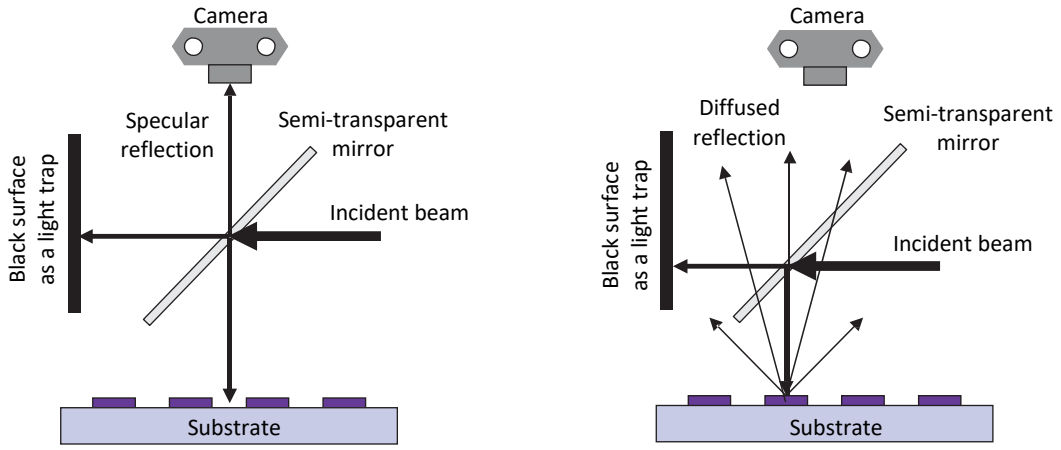


Figure 27: Episcopic Coaxial Illumination. (a) The reflected light beam strikes the shiny surface, specular reflection moves back in the same direction, toward the camera. (b) Light hitting the fingermark is diffusely reflected. The surface reflects more light than the fingermark, so the fingermark ridges present dark against the lighter background when photographed. [72]

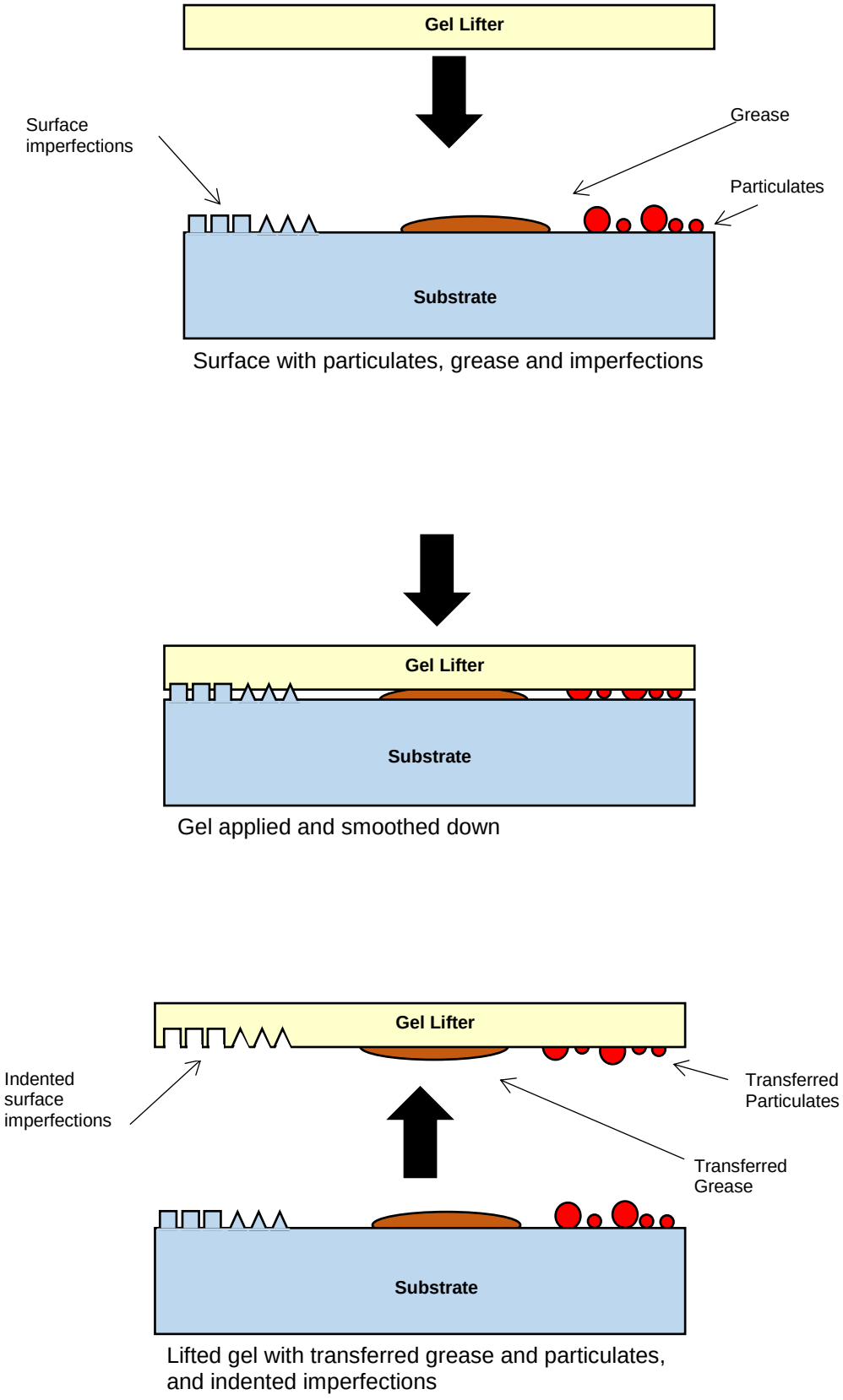
Gelatine Lifting

Gelatine lifting to recover fingermarks from surfaces is by no means a new concept, Bleay *et al.* highlight in ***The Fingerprint Sourcebook*** that it was first proposed by Crispo in 1913 for the recovery of powdered marks using paper coated with a gelatine/glycerol mixture. The technique was not investigated again until the 1970s when it was evaluated for the recovery of footwear marks [137]. Commercially available rubber and gelatine for lifting footwear marks were common by the late 1970s, since then gelatine lifters have been researched to access the adhesive coating, flexibility and compressibility and found to be well suited for the purpose of lifting trace evidence from multiple surfaces without causing damage to the surface [88].

Through these studies, gelatine lifters are now marketed for the lifting of a variety of forensic evidence; footwear marks [138, 139], micro trace evidence [140], the recording around bullet holes in glass [141], blood traces from surfaces and ear prints [140] amongst others. Research has also shown that gelatine lifters are effective at detecting writing on a variety of different paper types, and in some instances the gel lifting was shown to be superior to the gold standard ESDA (Electrostatic Detection Apparatus) technique [142]. Despite these other proven uses, the principle use for gelatine lifters has remained the recovery of fingermark and footwear evidence; both latent and developed marks. Since gelatine lifting sheets are flexible, they can be compressed against a surface on application, this makes them better suited to recovering powdered marks from textured surfaces than some conventional lifting tapes. The gelatine lifting sheets themselves come in black, white and transparent forms which can give optimum contrast depending on what is being lifted [140]. The gel lifting process was successfully shown to be of use for recovering latent fingermarks for the subsequent treatment with chemical enhancement techniques, this means gels can be used at the scene to lift marks to be transported back to the lab for analysis [143].

Due to their pliable nature, gelatine lifting sheets are able to deform to the surface contours during the application to the substrate being lifted from. The adhesive has a light tackiness meaning that upon removal from the sample substrate the loose particulates such as dirt and grease are transferred to the gel without adverse effect to the substrate itself. The gel lifter may also retain some impressions from the contours of the substrate it has been applied to (Scheme 1).

Gelatine lifters are suitable for use on smooth non-porous surfaces, however, they can be used on textured, semi-porous and porous substrates, with reduced effectiveness. They can also be used in instances where there are fingermarks visible on a contaminated surface and other enhancement techniques are not feasible or where treating an article may cause damage to the article. Bleay *et al*. (2011) showed that the subsequent chemical treatment of gels used to lift latent fingermarks could in some instances improve marks and even develop additional marks [144].



Scheme 1: Diagram Showing How Gelatine Lifters Can Lift and Reproduce Surface Features (Adapted from [88])

2.2 Emerging Techniques

2.2.1 Fingermark Recovery from Metals

Bond reported that by heating metal samples deposited with eccrine containing fingermarks, the chloride ions present in the sodium chloride secretions deposited from the papillary ridge pores caused pitting corrosion on the metal's surface. Where continuous ridges were formed, it was posited that was due to the joining of discrete pools of chloride ion rich sweat deposits. Further to this discovery, it was observed that after corrosion had taken place, granular powder was still able to adhere to the fingermark ridges despite being heated to 600°C, although to no evidentiary gain. It was discovered that the heat-induced corrosion enhancement of fingermarks was possible when the deposit was in either a hydrous or anhydrous state. Successful trials were conducted with arson samples, where finger marks were able to be recovered from under layers of soot. Bond also reported that fingermark enhancement *via* corrosion was also found to occur when eccrine deposits were left on metal substrates at normal room temperature [145].

Bond conducted additional studies in to a number of metals and alloys including; brass, copper, aluminium, gold, silver and nickel amongst others. By cleaning the alloy substrates abrasively, Bond was able to remove an oxide layer which allowed for a greater amount of corrosion to occur. Of the alloys tested in this manner, brass developed fingerprints at grade 3 or 4 (Table 3) on 60% of the samples, from the previous 11% obtained from alloys which were cleaned non-abrasively. Nickel silver behaved in a similar fashion, showing an increase from 22% to 55%. However, silver and gold alloys cleaned in the same abrasive manner showed no increase in grade 3 or 4 marks [146].

Realising the potential for recovering problematic fingermarks on spent bullet casing, typically made of brass, Bond conducted a case study utilising a shell casing from a 14 year old homicide [147]. The casing was re-examined, where visual examination offered no ridge marks, the case was then heated to 700°C which had two effects. Firstly, it removed the cyanoacrylate deposits from previous attempts to develop fingermarks; secondly, it induced the corrosive effect detailed above.

After this treatment, another visual examination was conducted and faint ridge details were visible. The ridge detail was further enhanced by applying a small electrostatic current to the shell casing (2.5 kV) and carefully applying Cascade Developer [148] typically used for document analysis to the surface [145]. This coated the faint ridges in a carbon powder to allow enhanced visualisation of the ridges.

In recent years, researchers at Loughborough University working in conjunction with The Home Office, used rubeanic acid in a novel way to help combat heritage crime. In 2011 figures showed that in excess of 1,000 metal theft offences were being carried out each week in Britain. The metal theft is viewed as the 'biggest single threat' to the country's landmarks [149]. The Loughborough research found that by simply having contact with copper or lead for a few seconds, left enough trace residues present on the skin and on fabric. This residue could then be lifted using a gelatine sheet, for subsequent treatment with rubeanic acid.

The gelatine sheet can be treated with rubeanic acid immediately or many days later. The copper appears almost immediately, whereas the lead requires a UV light source to develop [150]. This technique is practical in a forensic context, as it would allow for the testing of skin (hands) and clothing of suspected heritage metal thieves in situations where they have disposed of stolen metal for fear of being caught 'red handed'. The detail obtained from the gelatine lifters is so precise that ridge detail and fingermark minutiae are discernible. More importantly, the whole process is non-invasive and can still generate results after light washing of the hands.

In 2008, Kelly and King of Loughborough University reported that they observed an unexpected effect of their disulphur dinitride work. They found that the polymerisation of the S_2N_2 caused latent fingermarks to become visible as blue/black marks. The enhancement of fingermarks was observed on a number of substrates; pottery, cling film, aluminium foil, glass, cotton and paper. Interestingly, the technique still performed on paper that had been wetted and subsequently dried. The technique was also able to react with latent inkjet ink trace transfers which occurred when a printed sheet had come in contact with another clean paper surface [151].

Further research by Kelly and King explored the use of disulphur dinitride on stainless steel and brass surfaces. They found that the S_2N_2 process was able to image fingermarks which had been washed from the surface of the metal substrate. They postulate that this was possible due to the corrosive nature of the fingermark residues on the metal. Marks started to become visible within 10 minutes, with full development taking up to 1 hour. The technique appears to be so sensitive that third level details are easily visible. Kelly and King highlight that since this process takes place in the gaseous phase, it would be advantageous on large, contorted surfaces. The only real disadvantage to this process is the fact that S_2N_2 is a friction sensitive explosive, meaning that extreme caution must be undertaken when proceeding in this area of work [152].

2.2.2 Fingerprint Powders

King went on, in 2015, to develop a new fingerprint enhancement powder. King focussed on an ongoing problem encountered in fingermark enhancement; the poor contrast between fingermark ridges and the background substrate. White powders applied to fingermarks on a black background, and vice versa, provide excellent contrast. However, highly patterned backgrounds can often cause problems, as multiple colours can make selecting a suitable coloured contrast powder difficult. King developed the powder by exploiting the naturally occurring *spirulina platensis* and its derivatives. The compounds used were chosen for their high levels of chlorophyll and anthocyanin because of their known ability to fluoresce in the IR region of the spectrum *via* blue/red excitation. The compounds were milled to reduce particle size from up to 120µm to a particle size of under 30µm. The milled product was used in the same manner as traditional fingerprint powders, by applying to the fingermarks *via* a zephyr brush. The resulting powder provided considerable contrast on black, white and grey backgrounds due to its green colour. The powder's true promise comes when viewing dusted marks on multi-coloured and highly patterned substrates *via* IR and near IR imaging. The advantage is two-fold; busy backgrounds often 'drop-out' while the developed fingermark is highly fluorescent giving excellent contrast[153].

King *et al.* also developed a tailored cuprorivaite fingerprint powder which exhibits NIR – NIR fluorescence when illuminated with a 780 nm narrowband lighting array, suppressing nearly all background interference. Given that its excitation wavelength is essentially invisible as it lies outside the visible spectrum, the cuprorivaite powder can be imaged under typical lighting conditions, without the need to blackout the environment by using an NIR sensitive camera coupled with an 810 nm long-pass filter [154].

Chadwick *et al.* looked to develop a magnetic fingerprint powder which would luminesce in the NIR region of the spectrum. They experimented with coating a number of powders of varying particle size; aluminium, titanium and zinc oxide with a styryl dye. These powders were then mixed with a variety of magnetic fingerprint powders. The study showed that while their powder was found to be comparable to commercially available alternatives on marks up to 2 weeks old, it was superior on marks up to one month old [155].

A recent study conducted by the University of Abertay Dundee has provided positive results in the fight against wildlife crime. McMorris *et al* evaluated a number of fingermark enhancement techniques on six species of bird of prey feathers and seven species of bird of prey eggs. They utilised 5 different donors of varying deposition quality, ranging in age from 19 – 45 years old. They assessed seven enhancement techniques, including fluorescent techniques on deposited on marks over a 3 week period; at intervals of 1, 3, 7, 14 and 21 days.

The Abertay team reported that their most successful techniques; the magneta flake powder gave 48% positive marks, the red fluorescent powder tested furnished 89% positive marks and the green fluorescent powder provided 84% positive marks, all on the bird of prey feathers. However, the marks were evaluated using the "CAST Fingermark Grading Scale" (Table 3, Page 82) and many of the marks were grade a "1" meaning that there was evidence of contact but no ridge detail; which means that they had little to no evidentiary value. Looking at the results in a forensic context, the magneta flake powder actually only gave 28% positive marks, the red fluorescent powder gave 17% positive marks and the green fluorescent powder, 25% positive marks. Cyanoacrylate fuming followed by basic yellow 40 staining and black magnetic powder were also reported as giving 60% and 66.7% positive marks, how many of these were useable forensically is unknown.

They evaluated the development of marks on the bird of prey eggs in a similar fashion; grading positive marks as opposed to grading as forensically viable. Their most effective techniques on the bird of prey eggs provided results as follows (percentage of marks with forensic potential are in brackets); black magnetic powder showed 96% (83%) positive marks, magnetic bi-chromatic powder gave 81% (56%) positive marks, magneta flake powder provided 60% (40%) positive marks and the green fluorescent powder 78% (66%) positive marks [156].

2.2.3 Vacuum Metal Deposition

Fraser *et al.* (2011) described using the CAST recommended Vacuum Metal Deposition (VMD) process (Chapter 2.1.2 – Vacuum Metal Deposition, Page 48) using gold and zinc on white fabrics, Although the process of using VMD to image fingermarks on fabric is not new, it did fall out of favour when other more reliable techniques became available. Using gold (0.002 g) and zinc (1 g) Fraser's group tested four fabric types: cotton, nylon, poly-cotton and polyester; nylon performed the best, this was attributed to its smooth, shiny, tight weave. The report shows that age of the mark affects the recovery, however, fingermarks with no ridge detail were still able to have DNA taken from them [157].

Further to this work, Knighting *et al* conducted a similar experiment using VMD on dark fabrics with silver in place of the gold/zinc previously discussed. The fabrics used in this study were; poly-cotton, polyester, satin and cotton. Of the fabrics tested in this experiment, polyester consistently outperformed the other fabrics. Again, this was credited to its smooth, shiny, less porous weave. The use of the silver over the previously used gold and zinc made ridge detail easier to visualise on the dark fabrics [158].

Recently Fraser *et al* (2014) conducted a comparison study between gold/zinc vacuum metal deposition and Cyanoacrylate Fuming (CAF) followed by Basic Yellow 40 (BY40) staining. The study used the same white fabrics previously used (2011); polyester, poly-cotton, cotton and nylon. The cotton samples showed limited results using Au/Zn-VMD and no results utilising CAF/BY40. The nylon samples treated with Au/Zn-VMD again performed very well, developing marks ranging from no development up to excellent development, however, the same fabric treated using CAF/BY40 only managed to produce finger marks graded fair. The other fabrics; polyester and poly-cotton performed between the cotton and nylon in terms of successfulness. The success of the Au/Zn-VMD was not unexpected given the previous study, however, it was suggested that the reason the CAF/BY40 showed limited enhancement was due to excessive background staining of the substrates [159].

2.2.4 Cyanoacrylate Fuming

A study by Prete *et al.* (2013) investigated a new cyanoacrylate fuming process that does away with the traditional two-step process (Figure 22 on page 45) in favour of a new one-step process called Lumicyano™ developed *via* collaboration between Laboratoire de Photophysique et Photochimie Supramoléculaire et Macromoléculaire based in Paris and the forensic supply company Crime Scene Technology. Lumicyano is a cyanoacrylate which contains a fluorophore of low molecular weight which sublimes easily, allowing latent fingermarks to be observed *via* fluorescence under UV (315-340 nm) light. The report indicates that Lumicyano produces readily fluorescent fingermarks with good contrast, and although some poorly developed marks are less intense than when enhanced by the traditional method, they can still be enhanced further *via* the use of a fluorescent dye such as BY40. The study also showed that Lumicyano can also develop fluorescent marks on semi-porous surfaces which are often problematic using the traditional two-step process [160].

Farrugia, Deacon and Fraser (2014) conducted an operational comparative trial to test the effectiveness of Lumicyano, CAF/BY40 and powder suspensions when compared against each other. Their study found that all three techniques detected a similar number of fingermarks. Of the finger marks developed with CAF/BY40, the majority could be seen with the naked eye in daylight conditions, 7.54% could only be visualised *via* fluorescence. The Lumicyano was similar, in that 8.78% needed fluorescence to be seen. Furthermore, subsequent dyeing of the Lumicyano samples with BY40 yielded an additional 43 new fingermarks an increase of 14.53%. This was in line with discoveries made by Prete *et al* (2013). The study reiterated the advantage of Lumicyano being a one-step process over and above CAF/BY40 and requires no dyeing or drying before visualisation can commence. The trial also demonstrated that Lumicyano treated fingermarks still fluoresced after a period of six months when stored in dry, dark conditions [161].

2.2.5 Multi-Metal Deposition

Saunders (1989) first proposed multi-metal deposition (MMD) as an enhancement technique for fingermarks. The method combined aspects of physical developer and small particle reagent to provide a versatile development reagent which was adept at enhancing fingermarks on surfaces of varying porosity; non-, semi- and porous alike. The process involved immersing the item to be treated in a colloidal gold solution for between 30 – 120 minutes; porous substrates such as paper required a pre-treatment by soaking in multiple changes of distilled water over a 20 – 30 minute period. The item was then rinsed in distilled water; paper was rinsed in multiple changes of distilled water for up to 15 minutes. Items were then submerged in a modified physical developer solution containing silver, for 5 – 15 minutes. Items were then subject to a final rinse in distilled water before being left to air dry then photographed [162].

This technique was based on a method used to stain proteins, antibodies and other macromolecules, which had been separated on gels or membranes. The method involved using colloidal gold to stain the macromolecule, and then enhancing the gold stained protein with a silver developer. Kausche and Ruska (1939) were amongst the first to observe this binding of colloidal gold to proteins [163]. Holgate *et al*. (1983) went on to show that the gold staining could be further enhanced by using a silver stain. They highlight that the gold colloids were highly negatively charged particles that bound to a great number of macromolecules and that they acted as activation sites for the silver staining reagent [164].

Through his knowledge of fingermark residues, Saunders theorised that the colloidal gold and silver physical developer staining method should be capable of staining many of the macromolecules, such as proteins and lipoproteins, contained therein. Using the Frens method [165], Saunders formulated his own colloidal gold solution and silver physical developer, and since he formulated these he was able to optimise them for latent fingermark detection. The technique was found to be effective on non-porous and porous surfaces alike regardless of whether they were light or dark [166].

Schnetz and Margot (2001) optimised the technique *via* an improved formulation. The new formulation offered an increase in reactivity between the gold and the fingermark residues, an improvement in resolution and a greater amplification selectivity which allowed for a reduction in background interference [167]. Becue *et al*. (2007/8) tried to further revise the MMD process by attempting to functionalise the gold nanoparticles with fluorescent tags increasing the technique's sensitivity whilst helping to eliminate background colours which was one of the main disadvantages of the traditional MMD process [168, 169]. Other research has looked at simplifying the process further by developing formulations for a single metal deposition (SMD) technique, whereby the two-step gold and silver deposition was replaced by a single-step gold deposition process. This SMD method has a number of advantages over its two-step predecessor such as; reducing the number of treatment stages making it less labour-intensive, the inclusion of reagents with a longer shelf life and reducing the number of reagents used which in turn reduces the associated costs [170, 171].

Multi-Metal Deposition is a two-step process, with the sample to be treated initially being immersed in an acidified colloidal gold solution. The colloidal gold particles, both negatively charged and hydrophobic, preferentially bind to the protein, amino acid and peptide constituents of the fingermark residue. This stage enhances fingermarks; however, the enhancement is light in colour which generally gives weak contrast (Figure 28).

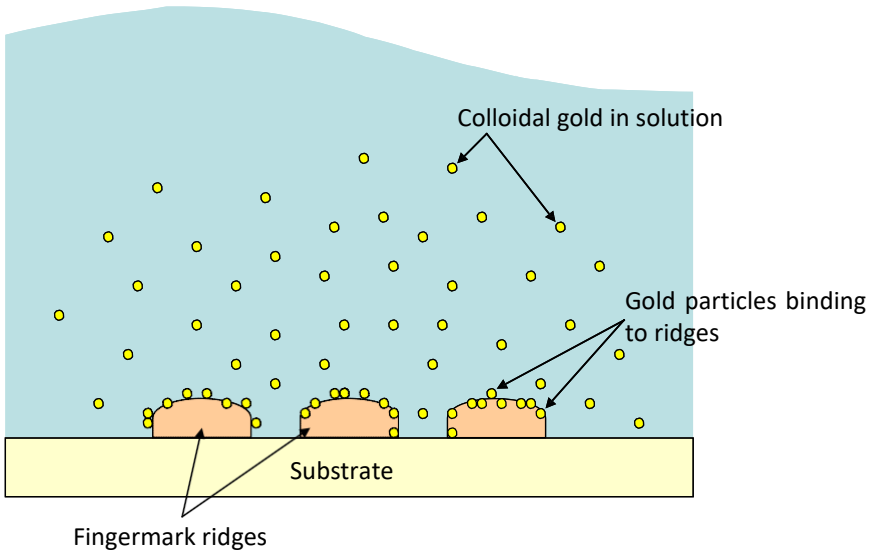


Figure 28: Multi-Metal Deposition Stage 1 [88]

Therefore, a second stage is required to further amplify this development; this is achieved using the modified physical developer solution. The physical developer solution contains silver particles stabilised in a surfactant (Figure 29), it is these silver particles which preferentially deposit upon the already deposited colloidal gold turning the light coloured ridges to a dark grey/black colour (Figure 30).

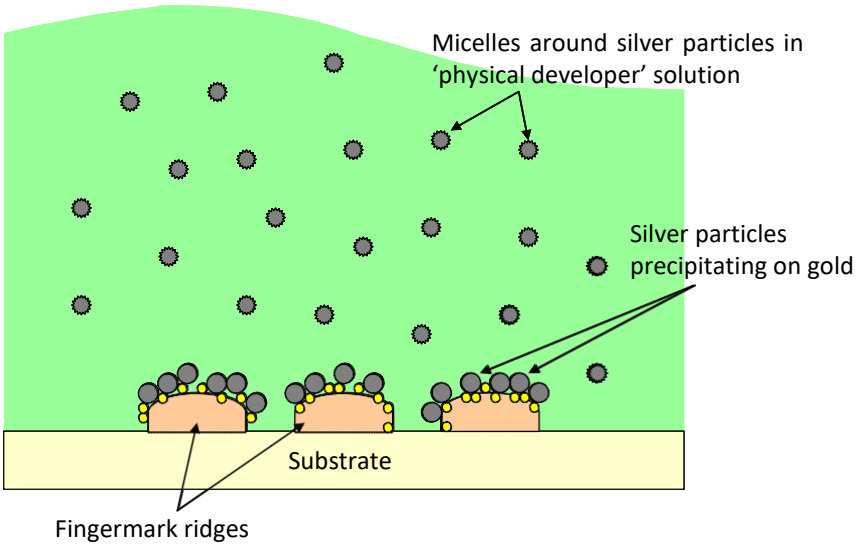


Figure 29: Multi-Metal Deposition Stage 2 [88]

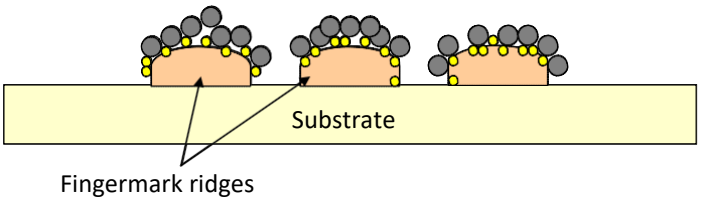


Figure 30: Multi-Metal Deposition Fully Treated Marks [88]

3.0 Phosphomolybdic Acid

3.1 Introduction

J.J. Berzelius discovered the first heteropoly species in 1826 by acidifying solutions that contained phosphate and molybdate producing the yellow crystalline precipitate, ammonium phosphomolybdate [172] $(NH_4)_3PMo_{12}O_{40}$, which contained the heteropolyanion $[PMo_{12}O_{40}]^{3-}$ (Figure 31). For over a hundred years the structure of these compounds, collectively called polyoxometalates, was a mystery. It was not until 1933 that the mystery was solved by J.F. Keggin [173]. Keggin described a 1:12 tetrahedral structure for phosphotungstic acid ($H_3PW_{12}O_{40}$) which is structurally identical to its species counterparts with the formula $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (P^V, As^V, Si^V or Ge^{IV} amongst others) and M is the addenda atom (usually Mo^{VI} or W^{VI}).

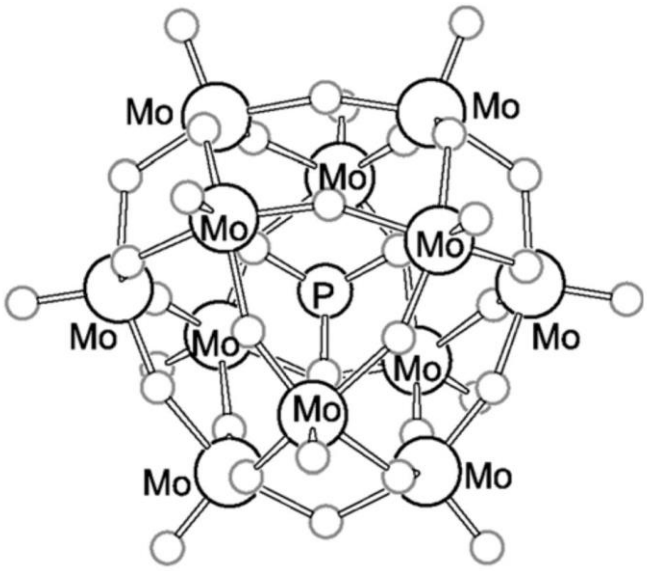


Figure 31: Phosphomolybdate Anion [171]. Cations Omitted for Clarity

The heteropolyanions with the general formula $[XM_{12}O_{40}]^{n-}$ have a structural form known as The Keggin Structure. The Keggin structure comprises of a single heteroatom (X), in this instance phosphorus, which is surrounded by a group of four oxygen atoms which form a tetrahedron. The addenda atom is caged within a group of six oxygen atoms forming a slightly distorted octahedral. The heteroatom tetrahedron unit, XO_4 is caged within twelve of the addenda octahedron MO_6 units, which are linked *via* neighbouring oxygen atoms. These MO_6 octahedra are arranged in four groups, each group consists of three MO_6 octahedra which share edges (M_3O_{13}) and have an oxygen atom which is shared with the central XO_4 tetrahedron heteroatom. In total there are forty closely packed oxygen atoms.

These oxygen atoms have four differing natures: twelve terminal M=O, twelve bridging angular M-O-M linking the edges of the octahedra within each M_3O_{13} structure, twelve corner bridging M-O-M which connect the different M_3O_{13} groups, and four internal X-O-M. The metal centres within the twelve addenda octahedra are arranged almost equidistantly from each other in a sphere, giving the overall structure a tetrahedral symmetry.

The phosphomolybdic acid is reduced to molybdenum blue in the presence of conjugated, unsaturated compounds. The phosphomolybdate anion $PMo_{12}O_{40}^{3-}$ is reduced to $PMo^{V}_4Mo^{VI}_8O_{40}^{7-}$ (Equation 1).

$$PMo_{12}^{VI}O_{40}{}^{3-} + 4e^- \rightleftharpoons PMo_4^{V}Mo_8^{VI}O_{40}{}^{7-}$$

Equation 1: PMA Reduction Reaction

Molybdenum blue takes the form of a 'Giant-Wheel' cluster which is made up from various molybdenum building blocks. From the building block pool (Figure 32) a bipyramidal MoO_7 pentagonal unit shares edges with five MoO_6 octahedra units forming {(Mo)Mo_5} groups [175].

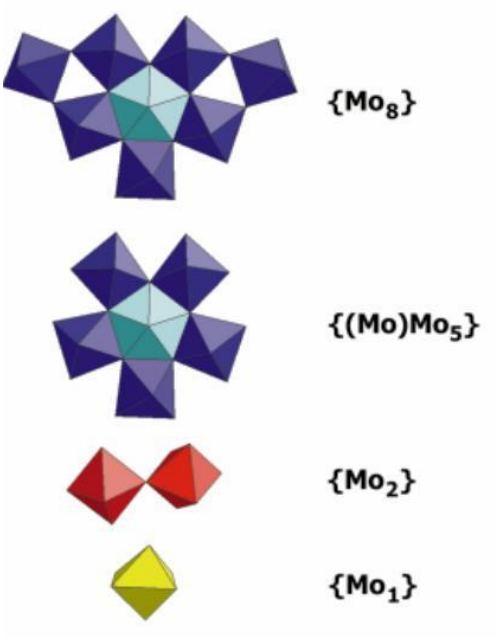


Figure 32: Molybdenum Blue Building Blocks [176]

This {(Mo)Mo_5} is a constituent of the {Mo_8}-type unit which is found in abundance in giant polyoxometalate molecules. An additional two MoO_6 octahedra are loosely bound to the {(Mo)Mo_5} unit to complete the {Mo8} building block [176]. The overall molybdenum blue ring (Figure 33) structure contains 140 MoO_6 octahedra and 14 pentagonal MoO_7 bipyramidal units [177]. Using the different building blocks the formula for molybdenum blue can be looked at thus [172, 178];

$$[\{Mo_2\}_{14}\{Mo_8\}_{14}\{Mo_1\}_{14}]^{14-} \equiv [Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-} \equiv [Mo_{126}^{VI}Mo_{28}^{V}] \equiv \{Mo_{154}\}$$

Equation 2: Molybdenum Blue Formula

Burstein found that the blue colour becomes more intense with an increase in the number of double bonds in the molecule being stained [179].

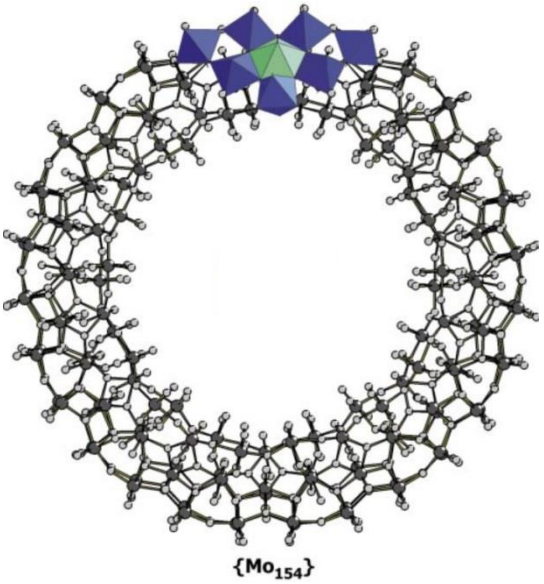


Figure 33: Molybdenum Blue Molecule [176]

Phosphomolybdic acid (PMA) was originally used for quantitative determination of blood glucose and other such reducing sugars [180]. It is commonly used in histology as a component of Masson's Trichrome Stain and as an indicator in thin layer chromatography, where it is used to visualise a great many compounds including; steroids [181] and sterols [182], lipids [183], fatty acids and triglycerides as well as many others. It was the PMA's versatility in identifying the aforementioned compounds that lead to its investigation as a possible fingerprint enhancement reagent in 1973 [184], although this had not been pursued further in the following decades. Vincent originally considered PMA as a spray reagent for use on porous surfaces including fabrics and paper.

3.1.1 Aims

To assess the effectiveness of phosphomolybdic acid as a reagent for the enhancement of latent fingermark ridge detail on a variety of different substrate types. A number of donors were used to deposit fingermarks which were aged up to 28 days. Secondary aims involved optimising the technique through refining the formulation and experimental processes.

3.2 Experimental

3.2.1 Assumptions

Throughout the experimental section, the following assumptions are made;

- Where not specified, the author's fingermarks were used for enhancement purposes.
- Whenever the phosphomolybdic acid solution had to be stored, it was stored in a refrigerator, in a brown bottle.
- With respect to the solutions, application was achieved *via* an Ecospray atomiser (Labo Chimie France).
- Fingermark deposition types:
    - Natural series: A series of marks where the donor deposits their fingermarks with no additional "grooming" involved, and having not washed their hands for at least 30 minutes prior to deposition.
    - Sebaceous loaded series: A fingermark where the person depositing the mark intentionally rubs their fingertips on or around their forehead and nose areas, and then presses their finger onto the sample medium.
    - Depletion series: A series of marks where the initial mark is loaded then deposited, the same finger is used for deposition repeatedly until the desired number of marks is achieved. Each fingermark then has less sebaceous residue than the previous mark.
    - Eccrine loaded series: The donor would initially wash their hands then don nitrile gloves for a period of 30 minutes. After removing the gloves, fingermarks were then deposited onto the selected sample substrate.
- Unless otherwise stated the sample substrate used was paper; the paper used was:
  Brand: Polaroid Copier Paper
  Weight: 80gsm

3.2.2 Substrate Preparation

The substrates used in these studies were paper, acetate, aluminium and stainless steel. The stainless steel used in the studies was a 316 grade with a plain 2B finish; it was smooth, shiny and non-porous. The aluminium was grade 1050, with a natural semi-bright finish; it was also smooth and non-porous. The acetate used was LabelHeaven OHP Film, it had a smooth, non-porous finish. The only substrate that was not non-porous was the paper, which was an 80 gsm A4 copier paper made by Polaroid. These substrates were used as representations of common everyday items frequently found at crime scenes.

Paper

Loaded and Depletion Series

An A4 sheet paper was cut into sections measuring approximately 15 cm by 5 cm, a size that would allow a row of five fingermarks to be deposited. Either a depletion series of five natural marks or five loaded marks were deposited onto the substrate (Figure 34). A depletion series entails depositing a natural or loaded mark, then continuing to deposit from the same finger. This allows for the examination of how sensitive a technique is due to being able to observe at which point the fingermarks stop being developed.

Figure 34: Substrate Template (Depletion Series)

Split Series

Samples of the cut 15 cm by 5 cm paper were orientated vertically and a line drawn in pencil down the middle of the sample, a series depletion of five marks was deposited in a down the centre of the drawn line. The substrates were cut along the pencil lines, creating two sections. The left hand section was treated with one process, *Process X*, and the right hand section treated with an alternate process, *Process Y*. Once each half had been treated the matching sections were recombined, by the use of tape on the underside. This allowed various treatments to be directly compared on fingermarks with the same chemical composition, quantity of material and pressure, at time of donation (Figure 35) [185].

Metals

Sheets of stainless steel and brass were obtained (www.metaloffcuts.co.uk) and cut to 12 cm by 3 cm sections *via* an industrial guillotine, which allowed for five marks to be laid onto each sample substrate. Aluminium foil was cut to into 15 cm by 5 cm sections, marks were laid onto both the shiny and the dull sides of the foil.

Polyethylene

Clear polyethylene food bags were cut in to sections of 15 cm by 5 cm, large enough for the deposition of five fingermarks.

Cotton

A white cotton t-shirt was cut into sections much the same as the other substrates. Sections measuring 15cm by 5 cm were prepared, ready for the deposition of fingermarks.

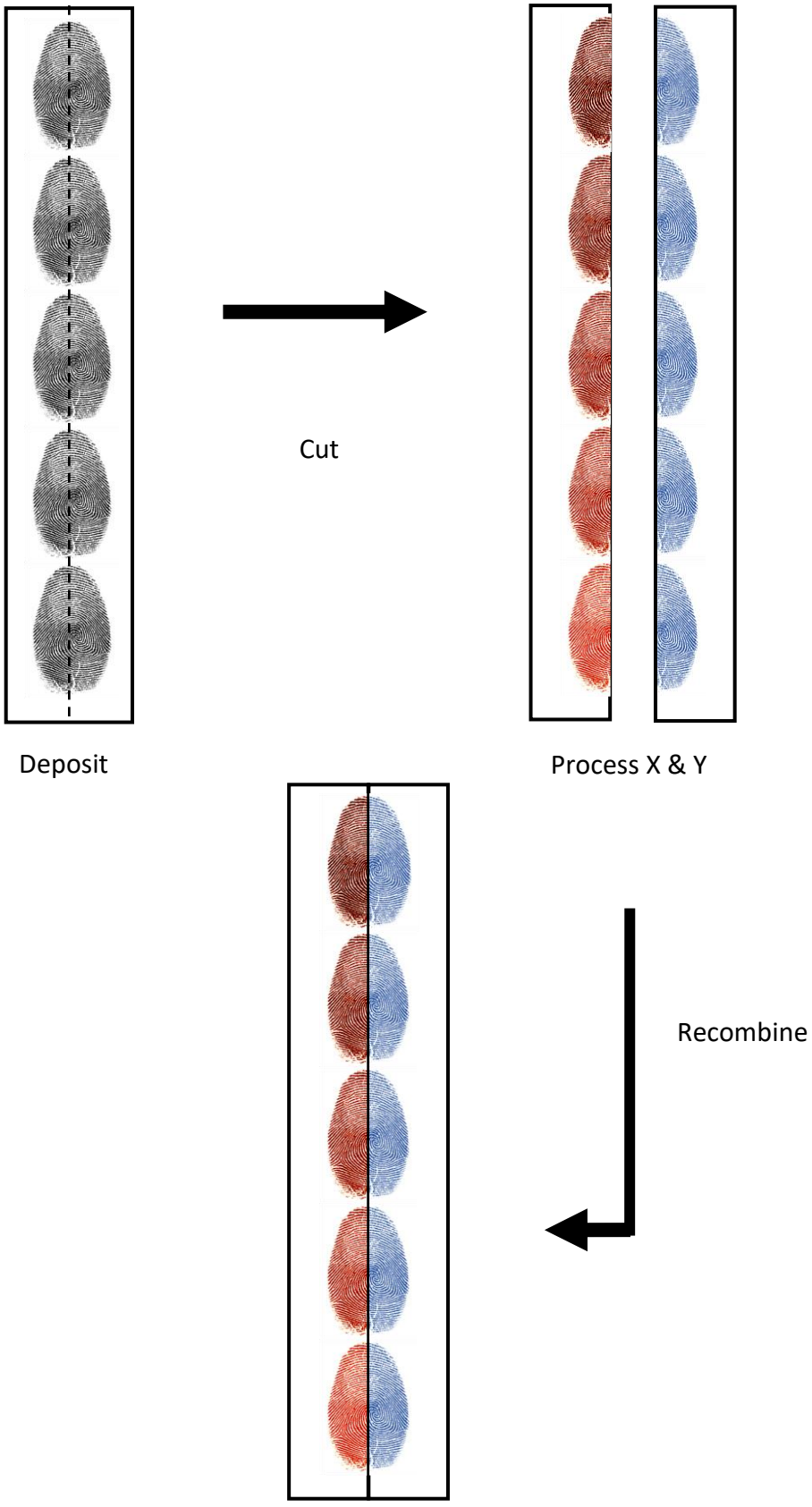


Figure 35: Split Series Sequence

Materials Used

Paper Type 1 – Evolution Value 75% Recycled 80gsm

Paper Type 2 – Polaroid A4 Copier Paper 80 gsm

Photo Paper – Polaroid Photo Paper 220 gsm

Aluminium Foil – Tesco Strong Kitchen Foil

Polyethylene – Tesco Zip Slide Food & Freezer Bags

Brass – CZ 108 Grade Brass (0.3 mm thick)

Stainless Steel – 316 Grade Stainless Steel, 2B Finish (0.5 mm thick)

Copper Type 1 – Verve Copper Slug Tape

Copper Type 2 – Grade C106 Copper (0.4 mm thick)

Gel Lifter – BVDA Gel lifters: Footprint Lifters – White, Polyester Backing 18x36cm

3.2.3 Reagent Preparation

Phosphomolybdic Acid

10% Phosphomolybdic Acid Solution

A 10% (w/v) phosphomolybdic acid solution was made by either:

1. Adding 3.000 g of phosphomolybdic acid hydrate (Sigma Aldrich – 221856) to 30 ml of absolute ethanol in a 100 ml beaker and mixing until fully dissolved, or
2. By measuring out 15 ml of supplier bought stock 20% (w/v) phosphomolybdic acid solution (Sigma Aldrich - 319279) and adding 15ml absolute ethanol giving a dilution factor of a half.

5% Phosphomolybdic Acid Solution

A 5% (w/v) solution was prepared by adding 1.000 g of phosphomolybdic acid hydrate to 20 ml of absolute ethanol in a 100 ml beaker.

7.5% Phosphomolybdic Acid Solution

A 7.5% (w/v) solution was prepared by adding 1.500 g of phosphomolybdic acid hydrate to 20 ml of absolute ethanol in a 100 ml beaker.

Phosphotungstic Acid Solution

A 10% (w/v) phosphotungstic acid solution was made by either:

1. Adding 3.000 g of phosphotungstic acid hydrate (Sigma Aldrich – 455970) to 30 ml of absolute ethanol in a 100 ml beaker and mixing until fully dissolved, or
2. Measuring out 30 ml of supplier bought stock 10% (w/v) phosphotungstic acid (Sigma Aldrich – HT152).

Phosphomolybdic-Phosphotungstic Acid Solution

A 10% (w/v) solution was prepared by adding 2.000 g of phosphomolybdic acid hydrate and 2.000 g of phosphotungstic acid hydrate to 40 ml of absolute ethanol in a 100ml beaker and mixing until fully dissolved.

Phosphomolybdic Acid in Petroleum Ether Solution

A 10% (w/v) solution was attempted by adding 2.500 g of phosphomolybdic acid hydrate to 25 ml of 40-60 petroleum ether in a 100 ml beaker and mixing. Unfortunately the PMA failed to dissolve so 15ml of absolute ethanol was added to encourage it to fully dissolve.

Phosphomolybdic Acid in Propan-1-ol Solution

A 10% (w/v) solution was made by adding 2.000 g of phosphomolybdic acid hydrate to 20 ml of propan-1-ol in a 100 ml beaker and mixing until fully dissolved.

Phosphomolybdic Acid in Methanol Solution

A 10% (w/v) solution was made by adding 2.000 g of phosphomolybdic acid hydrate to 20 ml of methanol in a 100 ml beaker and mixing until fully dissolved.

Phosphomolybdic Acid in Diethyl Ether

A 10% (w/v) solution was made by adding 2.000 g of phosphomolybdic acid hydrate to 20 ml of diethyl ether in a 100 ml beaker and mixing, the mixture however, failed to dissolve. The mixture was discarded.

Ninhydrin Solution 1

A formulation for ninhydrin as a thin layer chromatography stain was found which detailed adding 20.000 g of ninhydrin to 600 ml of ethanol [186], since this amount was excessive the amounts were scaled down to suit the needs. 1.000 g of ninhydrin (Sigma Aldrich - 72491) was added to a clean dry beaker, to which 30 ml of absolute ethanol was added, the solution (3.33% w/v) was stirred until all of the ninhydrin was dissolved.

Ninhydrin Solution 2

0.100 g of ninhydrin was added to 30 ml of absolute ethanol in a 100 ml beaker and stirred until dissolved to produce a 0.33% (w/v) solution.

Ninhydrin Solution 3

0.500 g of ninhydrin was added to 30 ml of absolute ethanol in a 100 ml beaker and stirred until dissolved to make a 1.67% (w/v) solution.

Ninhydrin Solution 4

0.250 g of ninhydrin was added to 40 ml of acetone in a 100 ml beaker and stirred until dissolved to produce a 0.62% (w/v) solution [187].

Phosphomolybdic Acid and Ninhydrin Solution 1

15 ml of supplier bought stock 20% (w/v) phosphomolybdic acid solution was diluted to 10% (w/v) by adding 15 ml absolute ethanol in a 100 ml beaker. 0.100 g of ninhydrin was added to 30 ml of absolute ethanol in a separate 100 ml beaker and stirred until dissolved, this was a new recommended ninhydrin formulation [188]. The ninhydrin solution was then added to the phosphomolybdic acid solution and mixed thoroughly.

Phosphomolybdic Acid and Ninhydrin Solution 2

A 10% (w/v) solution was made by adding 3.000 g of phosphomolybdic acid hydrate to 30 ml of absolute ethanol in a 100 ml beaker. In a separate 100 ml beaker 1.000 g of ninhydrin was added to 30 ml of absolute ethanol and stirred until dissolved. The ninhydrin solution was then added to the phosphomolybdic acid solution and mixed thoroughly.

Cerium Ammonium Molybdate

2.500 g of ammonium molybdate tetrahydrate (Sigma Aldrich – 431346) and 1.000 g of cerium ammonium (IV) sulfate (Sigma Aldrich – 221759) were weighed accurately and then added to 90 ml of distilled water in a 250 ml beaker. The mixture was stirred whilst heating until dissolved, 10 ml of sulphuric acid was then carefully added a little at a time until completely mixed [189, 190].

Seebach's Stain

2.500 g phosphomolybdic acid hydrate and 1.000 g of cerium (IV) sulphate (Sigma Aldrich – 359009) were weighed out and added to 94 ml of distilled water. The solution was stirred until dissolved and 6 ml of concentrated sulphuric acid was added slowly a small amount at a time.

Oil Red O

Stain Solution

0.770 g of Oil Red O (Sigma Aldrich – O0625) was weighed out and added to 385 ml of methanol in a 500 ml beaker. The mixture was stirred until fully dissolved. Separately 4.600 g of sodium hydroxide (Fisher Scientific – S/4880/60) was added to 115 ml of water in a 200 ml beaker and stirred until fully dissolved. This solution was then added to the Oil Red O solution and mixed thoroughly. The new Oil Red O solution was then filtered into a brown Winchester bottle and stored away from the light.

Buffer Solution

13.250 g of sodium carbonate (Fisher Scientific – S/4200/63) was added to 1 Ltr of water in a 1 Ltr beaker and stirred until fully dissolved. 9.15 ml of concentrated nitric acid was added carefully and slowly to the solution.

3.2.4 Sample Treatment

After reviewing work previously undertaken involving phosphomolybdic acid being utilised as a fingerprint development reagent [184, 191] and conducting a few tests, the decision was made not to dip the samples into the solution of phosphomolybdic acid but to spray them.

Ecospray Atomiser

The Ecospray Forensic Atomiser was the spray chosen for this purpose, as it is able to produce a very fine mist [192] which allows for a more even covering when spraying.

Development Sources

When developing the samples, after treating them with the reagent of choice the samples were either placed in a bench-top oven; a Carbolite PF60 [193] or placed into a shallow box and covered by a UV light. The UV light source used was a Phillips 75W facial tanner [194] (Appendix).

3.2.5 Sample Evaluation

The samples were examined, and the results tabulated. Each sample was evaluated and the enhancement techniques that performed poorly were omitted from future experimentation.

Sample Grading

The visualised marks were then graded using the "CAST" grading scale (Table 3). Where multiple marks were contained within the same sample subset, the average of the fingermark grades were used.

Grade	Comment
0	No development.
1	No continuous ridges. All discontinuous or dotty.
2	One third of mark continuous ridges. (Rest no development, dotty, smudge or infill).
3	Two thirds of mark continuous ridges. (Rest no development, dotty, smudge or infill).
4	Full development. Whole mark continuous ridges.

Table 3: CAST Fingermark Grading Scale [195]

3.2.6 Treated Sample Recording

Following the various enhancement techniques, the substrates were either photographed or scanned to record the enhancement. Enhanced substrates were photographed using a Nikon D5200 digital SLR camera, or scanned using an Epson Stylus Photo RX585 scanner. The camera was set to manual focus, and placed upon a tripod to keep movement to a minimum and the distance from the substrates consistent.

3.2.7 Group Studies

After corresponding with Stephen Bleay of CAST regarding study protocols, an initial group study was devised [196].

Group Study 1

Substrate samples were cut to a size which would allow tem fingermarks to be deposited in a depletion series. The group was comprised of six individuals, four male and two female, ranging in age from 21 - 40. The ten marks were deposited from the same finger, using fingermarks containing either natural or eccrine only deposits. For the deposition of the natural marks, donors were asked not to wash their hands for at least 30 minutes prior to depositing their marks, and no additional sebaceous materials were applied to the hands prior to deposition. In the case of the eccrine marks, donors donned nitrile gloves and kept them on for a minimum period of 30 minutes to allow their hands to sufficiently sweat. Each donor deposited all their marks at the same time, from different fingers. Sample substrates were to be treated and developed at various time intervals; immediately, after one week, after two weeks and after one month.

Group Study 2

The substrates were prepared for fingermark deposition by cutting 12 cm by 3 cm sized samples, these were labelled using photographic twin check labels with the twinned label being logged with details of sample type, fingermark deposition method, donor number and development day. The thirteen donors used in this study were a mix of males and females ranging in age from 22 – 40, and whose potential to leave fingermark deposits was unknown. Donors had not washed their hands for at least 30 minutes prior to depositing their fingermarks, no extra sebaceous deposits were loaded on to the hands, therefore providing more natural deposits from the donor's hands. However, it was unknown how much the donors had touched their faces prior to donating.

Fingermark deposition was carried out by having the donor deposit their marks either by depositing a mark from each finger or *via* a depletion series from one finger, each donor deposited all their marks at the same time. This, however, meant that due to the sheer number of samples, donors had to reuse fingers. In an effort to try and maintain the amount of sweat containing materials on the fingers, the hands were rubbed together to try and keep an even coating of material on the fingertips. After the fingermarks had been deposited, the samples were stored in cardboard boxes, in the dark, at room temperature for 1, 2, 4, 8, 14, 21 or 28 days before being processed. In total 182 samples of each substrate (13 donors, 7 different ages, 2 deposition methods) were used, 728 samples in total.

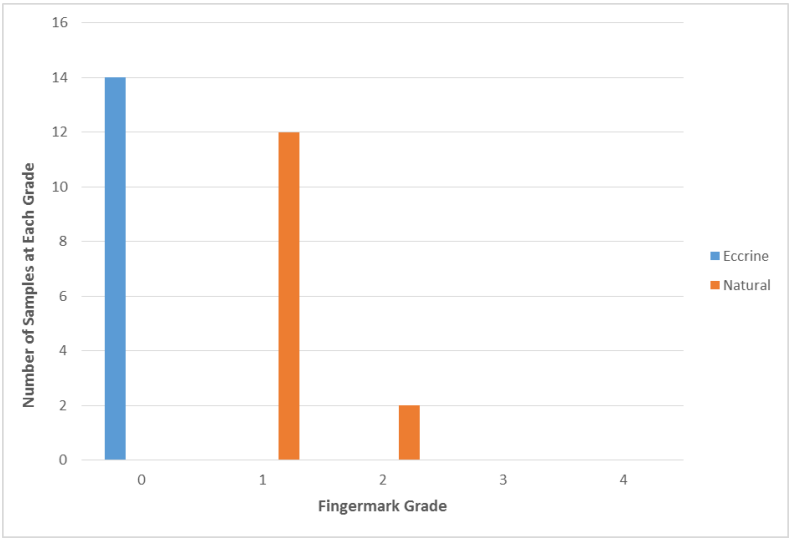
The prepared samples were treated with a 10% (w/v) phosphomolybdic acid (PMA) solution, prepared from phosphomolybdic acid hydrate (Sigma Aldrich – 221856) in absolute ethanol. The samples were sprayed with the PMA solution using an Ecospray and developed for 15 minutes under a UV lamp. Treated samples were then photographed using a Nikon D5200 digital camera.

3.3 Results and Discussion

3.3.1 Initial Tests

A small test was undertaken in order to access how samples looked when treated with PMA using the dipping method. A small amount of PMA was poured into the dipping tray to form a shallow pool. Paper samples with fingermarks deposited upon them were dipped into this solution briefly, in a similar method to that used for ninhydrin. The samples soaked up a lot of the PMA and the paper turned a yellow/green colour. Once developed using an oven the sample background was heavily stained and the contrast between the fingermarks and the substrate was poor.

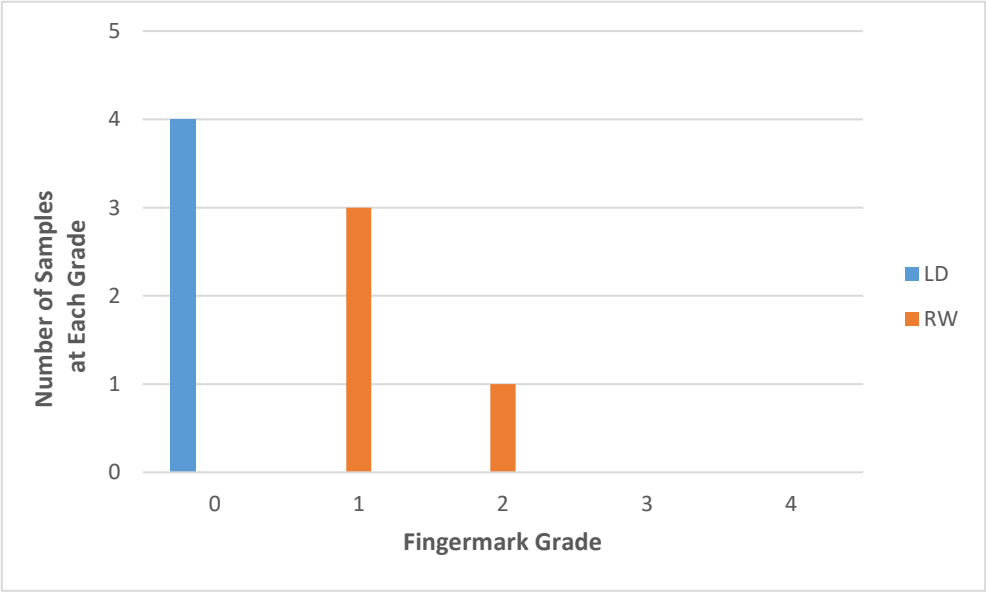
The first samples to be spray treated were fingermarks containing natural deposits (**Error! Reference source not found.**). These samples were sprayed with a 10% solution of phosphomolybdic acid which was prepared from a supplier bought 20% solution. When sprayed the samples could be observed to take on a slight yellow/green colour as the PMA solution coated them. Even passes were required so that a sample was fully coated in PMA, but also helped eliminate untreated areas as well as over treated areas. The samples were then transferred to an oven and heated at 100°C for 5 minutes. When the samples were removed from the oven and examined, the results were very poor (Figure 36). From previous work conducted [191], the sample substrates were expected to be a yellow/green colour with dark blue mark deposits.



Graph 1: Phosphomolybdic Acid on Eccrine and Natural Fingermarks

Figure 36: Initial Sample Development

The most noticeable point from the initial tests was that the fingermarks with sebaceous and eccrine deposits show some dark marks in the stereotypical fingerprint shape. The fingermark deposits that contained only eccrine secretions, showed no such development. This was an observation that warranted further investigation. This same pattern was also shown when another donor's fingermarks (Donor RW) were treated with the phosphomolybdic acid (Graph 2). The substrates for samples 0769 through 0804 all showed a speckled stained background, it was surmised that this was due to the type of paper used for these samples (Evolution Value 75% Recycled 80 gsm), and the fillers used therein.



Graph 2: Phosphomolybdic Acid on Samples from Multiple Donors

3.3.2 Paper Comparison

To test if this theory about the fillers in the paper was correct, two additional types of paper were introduced; Polaroid A4 Copier Paper 80 gsm and Polaroid Photo Paper 220 gsm. The copier paper samples showed none of the speckling experienced in the previous recycled paper samples, however, the development of the marks remained just as poor. The photo paper reacted very poorly with the phosphomolybdic acid, leaving the surface spotted with blue dots on the white background, there were however, small areas where ridges could be visualised (Figure 37).

Figure 37: Photo Paper Trial*

The decision was made to vary the amount of time the samples spent in the oven in an effort to ascertain if this had an effect on the developed marks. Adjusting the heating period did in fact increase the fingermark enhancement. The longer the marks were heated, the more development there seemed to be. Development increased with the heating duration, to the point where there was a good amount of visible ridge detail on some of the fingermarks (Appendix Table 27, Figure 38).

* Contrast and brightness adjusted to allow better visualisation on page. Original image on Appendix CD unaltered

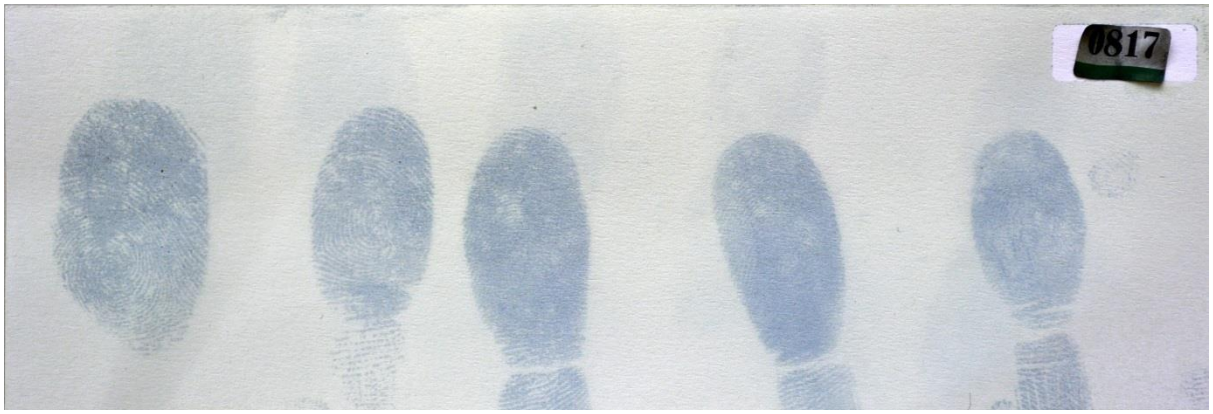


Figure 38: Heating Trial*

The colour of the fingermarks on these samples is more in line with observations made by Vincent [184], Shah [197] and Nickolson [191]. The blue is indicative of the molybdenum blue product which is formed when a portion of the Mo(VI) in the phosphomolybdic acid is reduced to Mo(IV) in the presence of conjugated, unsaturated compounds [198].

Since the process was showing some promise, it was decided to compare the recycled paper against the copier paper. The decision was also taken to adjust the heating time from 10 – 20 minutes to 15 – 30 minutes, to see if this would help further enhance samples. Although some of the samples showed some increased level of development, a ghosting effect was noticed on most of the samples, this effect overlapped some of the other marks and made an unreadable mess (Appendix Table 28 and Table 29). It was unknown why this phenomenon had occurred, however, it was hypothesised that it had been the result of the samples sitting stacked upon each other before and after treatment. This would have allowed the fingermark residues to mix and interfere with each other in the manner that had occurred.

* Contrast and brightness adjusted to allow better visualisation on page. Original image on Appendix CD unaltered

The experiment was repeated (Appendix Table 30 and Table 31), taking care not to replicate what had happened previously, this time however, the results were less impressive than those previously obtained (Appendix Table 27). The only useful information gained from this particular experiment, was that the recycled paper once again performed poorer than the copier paper.

Attempts to replicate previous success returned average results; showing some ridge detail, although faded and often showing a phenomenon called “leaching”. Leaching arises when the developed ridges diffuse and bleed out into neighbouring ridges (Figure 39) [199, 200], this causes problems following ridge flow. Continued experimentation started to return consistent positive results, although these were often muddied in places (Graph 3) (Appendix Table 32 - Table 36), however, enough ridge detail was present that an experienced Fingerprint Identification Officer could likely make an identification.

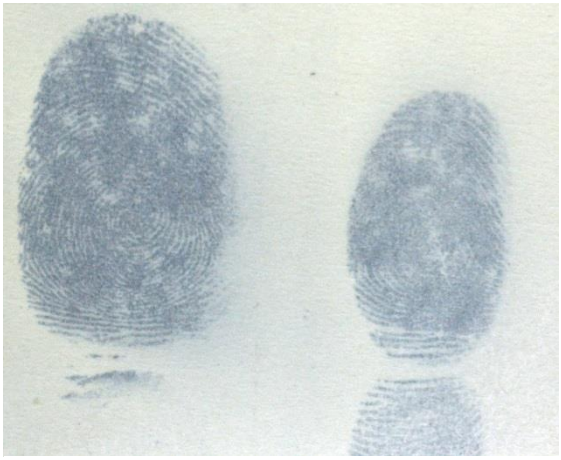
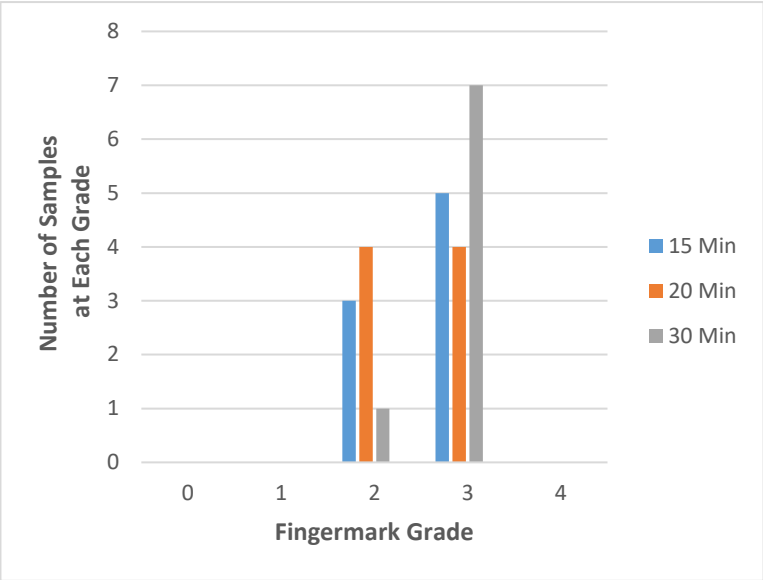


Figure 39: Leaching Effect

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.



Graph 3: Phosphomolybdic Acid Treated Samples with Varying Development Times

At this point an alternative method for the preparation of the phosphomolybdic acid solution was explored. 2.004 g of solid phosphomolybdic acid hydrate was added to 20 ml of ethanol to produce a 10% (w/v) solution. The initial results obtained were poor, and through repetition they only improved slightly. To investigate the new solution further, various concentrations were tested; a 5% w/v solution, a 7.5% solution, and the already used 10%. No concentration greater than 10% was attempted, mostly in part due to the reports made by Nickolson who stated that their attempts to utilise a 20% w/v solution failed to produce any development [191].

All the solutions tested developed fingermarks with some good ridge development. The 7.5% solution performed the worst of the three solutions tested (Appendix Table 42). The majority of the fingermarks developed exhibited some leaching; it was assumed that this was due to too much sebaceous material present on the finger at the time of deposition. With that assumption in mind, the hands were washed to remove all sebaceous secretions that may have been present; they were then lightly and minimally touched around the nose and scalp area before depositing the marks. The results obtained were very poor (Appendix Table 43), which led to the belief that the solution made with the solid phosphomolybdic acid hydrate was not performing as well as the diluted premade phosphomolybdic acid.

3.3.3 Phosphotungstic Acid

Since phosphomolybdic acid and phosphotungstic acid are both Keggin structure heteropolyacids [173], it seemed logical to assume that both acids would perform similarly. In the first instance 30 ml of supplier bought phosphotungstic acid was placed in to the Ecospray for the use on sebaceous containing fingermark deposits. Upon spraying the samples (Appendix Table 44) fingermarks were visibly noticeable, however, the premade solution was made up in water which made the paper samples curl up. After heating in the oven further examination revealed that no marks were present. It was decided that phosphotungstic acid hydrate should be used to prepare a solution with ethanol so that the samples would not curl up as witnessed with the premade solution. This experimentation branch was postponed until the solid phosphotungstic acid hydrate could be sourced.

After obtaining solid phosphotungstic acid hydrate, the decision was made to try mixing it with the phosphomolybdic acid to see if the combination of the two would yield more results than either solution on its own (Appendix Table 61). The results revealed that the combination of the two solutions offered no benefit over that of phosphomolybdic acid on its own. Interestingly, while one of the samples was awaiting transfer to the oven for development it was observed to have begun developing in the sunlight. This lead to the decision to investigate ultraviolet light as a means to develop the phosphomolybdic acid treated fingermarks. A UV light source was obtained and used in place of the previously used oven. Initial experimentation (Appendix Table 55) showed a greater level of enhancement than had previously been obtained (Figure 40).

Figure 40: Initial UV Trial*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.3.4 Non-Porous Substrates

Since the results for using phosphomolybdic acid on paper were relatively consistent, other substrates were studied to determine if the phosphomolybdic acid worked as well on those. The first substrate to be tested was aluminium baking foil. Each side of the foil looked slightly different; one side was shiny whereas the other looked duller. That being said, once fingermarks were deposited on each surface, the oily residue made the mark visible in oblique lighting. After treatment and subsequent development the foil substrates demonstrated an adverse reaction to the phosphomolybdic acid, the solution stained the foil a yellow/green colour while the fingermark residues were stained blue (Figure 41). The fingermarks showed some ridge detail in places, however, a lot of the marks displayed a broken, dotty effect.

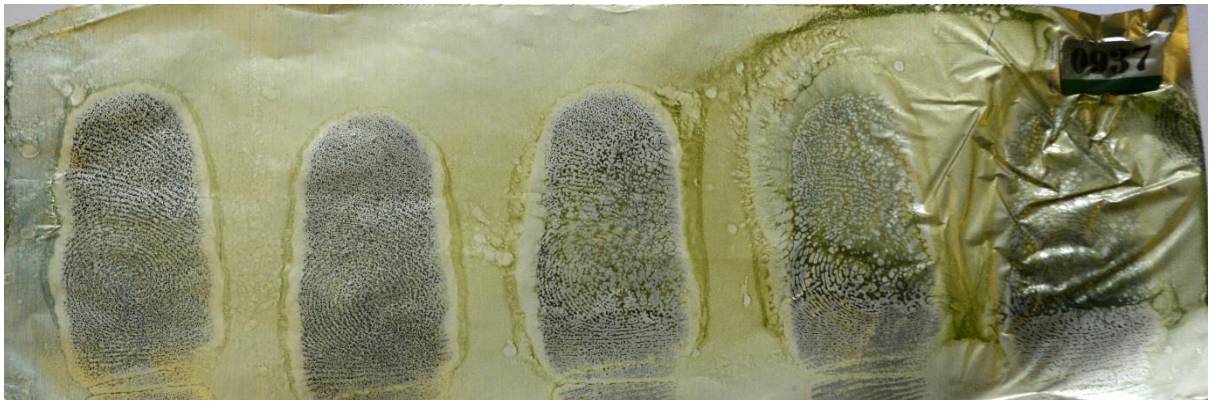


Figure 41: Aluminium Foil Trial*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

After increasing the distance that the solution was applied from, the staining effect witnessed previously seemed to be less prominent. The marks on the dull side of the foil still showed the dotted effect around the stained ridges (Appendix Table 48), conversely, the shiny side showed the marks had developed to a higher quality than before (Appendix Table 49). The solution reacted in such a way that the yellow/green staining previously observed was not present; the surface had instead gone from shiny to a matte with the area where the fingermark ridges occupied remaining shiny. Some of the shiny side samples showed some good ridge detail (Sample 0965, Appendix CD), however, the staining made photographing the samples difficult. Repetition of the experiment on the foil, demonstrated consistency (Appendix Table 51 - Table 54).

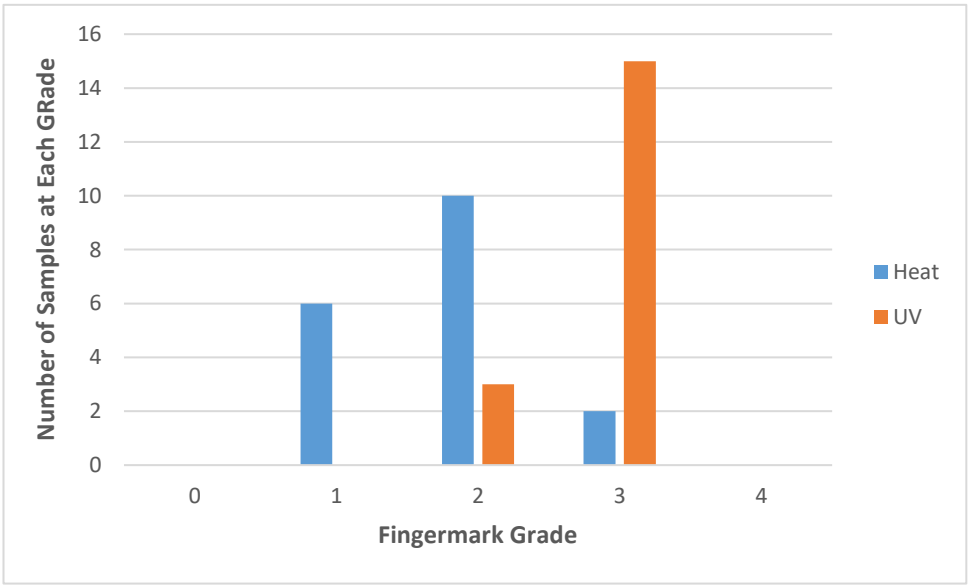
Figure 42: Stainless Steel*

Other metal samples were tested to see how they reacted to the phosphomolybdic acid solution. Stainless steel and brass were selected for experimentation. The steel and brass were treated in the same manner as the aluminium foil. The stainless steel reacted similarly to the shiny side of the foil samples, minimal staining of the substrate and a dark/black staining of the fingermark ridges (Appendix Table 59, Figure 42). The brass on the other hand, reacted badly with the phosphomolybdic acid as soon as it came in contact with it. The surface of the brass started turning blue, with the solution starting to bead. Once the brass had finished developing in the oven, it showed a mottled effect on its surface. Although some ridges could be visualised, they were broken and for the most part, unidentifiable (Appendix Table 60, Figure 43).

Figure 43: Brass*

3.3.5 UV Light Development

The new UV light development technique was used in conjunction with a phosphomolybdic acid solution diluted from a premade 20% supplier solution. These samples developed slightly better than when the same type of solution was used in combination with the oven (Appendix Table 65). Since initial investigation in to the UV light seemed promising, a comparison study between UV and the oven techniques was conducted (Appendix Table 71, Graph 4).



Graph 4: Phosphomolybdic Acid Development Comparing Heat vs UV

After the treated halves of the samples were recombined it became apparent that the enhanced fingermark ridges on the oven half were less prominent in comparison to the UV half (Figure 44).

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

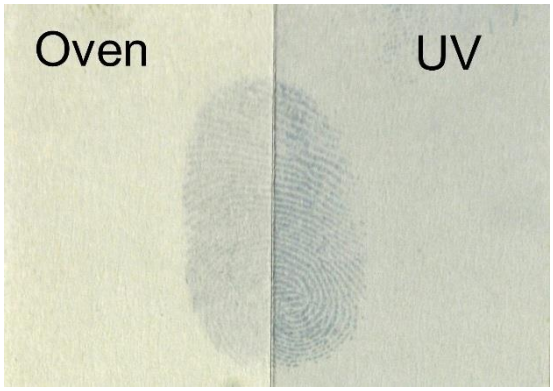


Figure 44: Split Comparison*

Since the UV lamp was obtained late in to the experimentation, it was felt that some of the substrates already tested may benefit from development with the UV lamp. Aluminium foil was tested again, however, the staining issue persisted on the dull side, and the shiny side still enhanced in the same manner (Appendix Table 73).

3.3.6 Destaining

In an effort to eliminate the background staining present on the previous samples, it was theorised that a wash protocol could help minimise this. Much like the protein staining protocols devised by Sears and Prizeman [200], it was decided to attempt a similar washing technique. Acetone was chosen as the solvent to wash the samples in, however, it was unknown if washing should occur after the development or between treatment and development, so washing was attempted at both points in the process. In the first instance, the samples were developed in the oven and provided poor enhancement before the wash was applied. After the washing process, which involved passing acetone over the surface of the sample, any development which had occurred was completely removed (Appendix Table 78). The samples washed before development provided no enhancement at all. The experiment was repeated using the UV lamp as the development source. With these samples (Appendix Table 80), the initial development was better, but unfortunately the acetone still washed these marks away. The assumption is that the acetone removed the sebaceous materials present leaving nothing to be enhanced. Acetone as a suitable solvent for the wash process was deemed ineffective; however, other solvents would be tried instead.

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.3.7 Alternate Formulations

Other solvents were explored as a carrier for the phosphomolybdic acid hydrate, the first tried was Propan-1-ol. The hydrate and solvent were mixed in the same quantities as used for the 10% ethanol solution. The samples were sprayed with the new solution and developed *via* the UV light source. The enhancement on the samples was very faint, but ridges were visible (Appendix Table 82). Some of the samples exhibited higher background staining making the ridges hard to distinguish due to the contrast (Samples 0163/0164, Appendix CD).

Methanol was assessed next; again a 10% solution was used with UV light development (Appendix Table 83). The methanol solution provided good enhancement with visible ridge detail (Figure 45). The background staining was less than that experienced with the propan-1-ol.

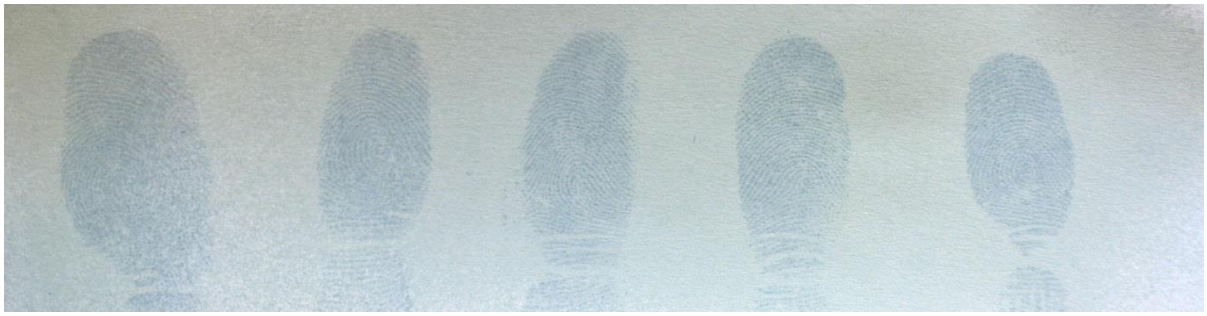


Figure 45: Methanol Trial*

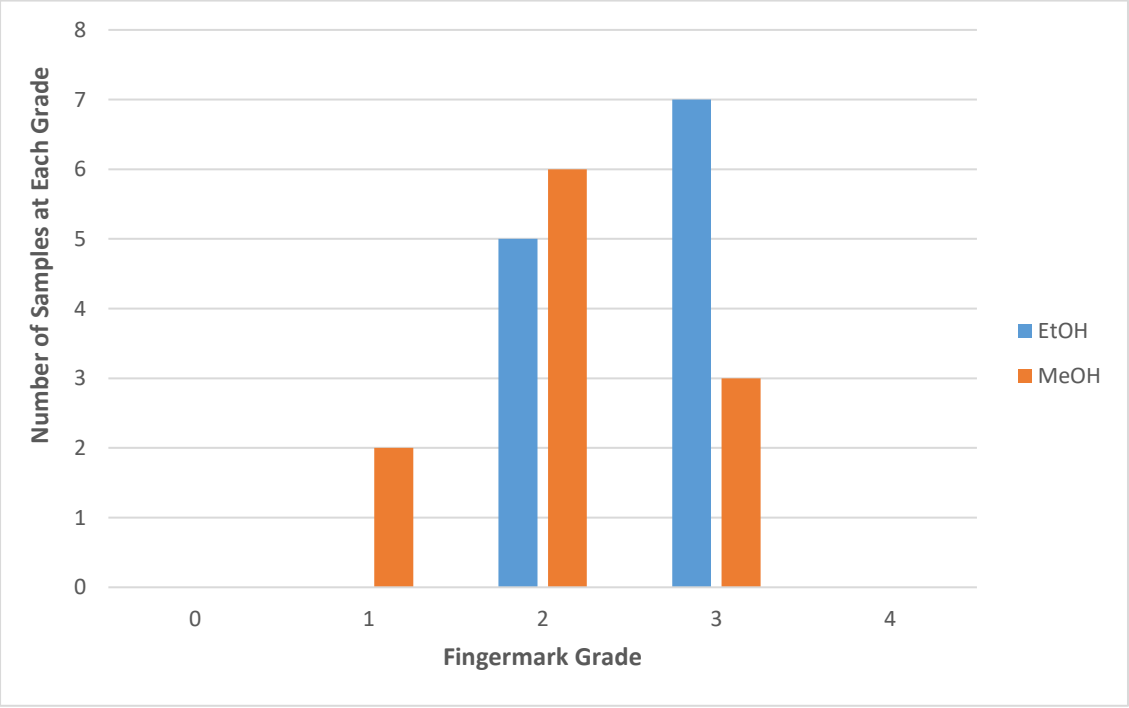
Other solvents were trialled with little success. The phosphomolybdic acid hydrate failed to dissolve in the petroleum ether 40/60, so some ethanol was added to encourage dissolution. The solution had some moderate success at developing latent marks, although this is attributed to the ethanol in the solution since the petroleum ether failed to dissolve the phosphomolybdic acid hydrate (Appendix Table 74). Diethyl ether was also tried, but again the phosphomolybdic acid hydrate failed to dissolve, therefore the solvent was discounted for further experimentation. It was decided to continue experimentation with the methanol solution.

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

A time trial was conducted using the methanol solution. Fingermarks were deposited on paper substrates and developed at intervals of three days, one week, two weeks and three weeks (Appendix Table 85 – Table 88). Fresh solutions were prepared before the development of each batch of samples. The results throughout this section of the experimental were poor, some faint ridge detail was present, although not as defined as had been previously observed.

With methanol performing as well as it had been, it was decided to do a split test between methanol and ethanol. If this technique was used operationally for fingermark enhancement, the use of methanol is avoided for health and safety reasons due to its toxicity [201-203], so establishing whether or not methanol outperformed ethanol was felt to be advantageous.

Development was conducted *via* both an oven and UV light, various development times were also investigated; five minutes, fifteen minutes and thirty minutes. Overall, the samples developed in the oven produced inferior results compared to those developed using the UV lamp (Appendix Table 97). Of the two phosphomolybdic acid solutions, the ethanol solution developed fingermarks which were darker than those developed with the methanol, and of a higher quality more consistently (Graph 5).



Graph 5: Phosphomolybdic Acid Development Comparing Ethanol vs Methanol Formulations

The background staining of the ethanol solution was a yellow/green which provided good contrast, whereas the methanol solution stained the substrate background a blue colour which made for poorer contrast against the blue colour of the stained ridges (Figure 46).

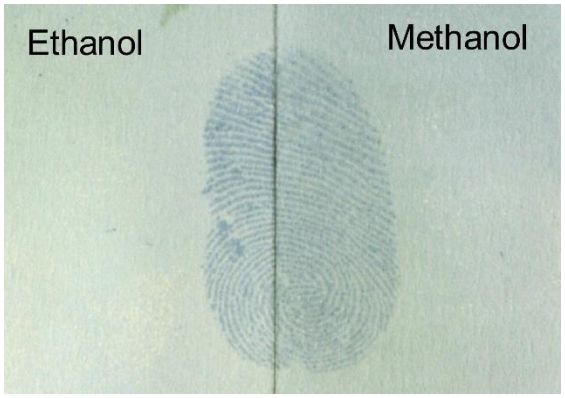


Figure 46: Ethanol/Methanol Split Trial*

The decision was made to stick with the ethanol phosphomolybdic acid solution, due to the contrast. It is also safer from a health and safety perspective.

3.3.8 Destaining Part 2

The washing process was revisited using methanol as the wash solvent. Again the wash was applied either after development or between treatment and development. In addition to this, development was conducted by UV and separately by oven. In both instances, the methanol, as with the acetone, washed the developed fingermarks away. This left nothing in the way of identifiable fingermarks (Appendix Table 92).

Other work being conducted within the chemistry department alluded to sodium hydroxide as being a suitable wash medium. This was investigated using a 2M solution (Appendix Table 95) and a 0.2M solution (Appendix Table 96) of sodium hydroxide. Upon application of the solutions to the treated samples, the sample substrates began to curl up, presumably due to the water content of the sodium hydroxide. After being developed *via* oven and UV, the 2M solution treated samples were totally wiped clean, and the 0.2M treated samples revealed a less stained background, the fingermarks were also less prominent than they had been prior to the application of the sodium hydroxide.

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.3.9 UV Light Development Part 2

There was speculation that due to the phosphomolybdic acid solution developing in heat, that was the only reason that the UV lamp worked, was due to its proximity to the sample substrate. In the UV light box set up (Appendix – Ultraviolet Light Box Set Up), the lamps were approximately 7.7 cm (~3 inches) from the substrate being developed. This closeness meant that it was fair to assume that the heat from the lamps was developing the treated samples. An experiment was set up where the distance between the lamps and the substrate was increased to almost 24 cm (~9.5 inches), more than three times the distance previously used (Appendix Table 98). This distance would allow for the UV element to still be tested, with the heat factor being eliminated. The results obtained were as good as the results obtained previously using the UV light box (Figure 47).

Figure 47: UV Distance Trial*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.3.10 Non-Porous Substrates Part 2

Various other media were chosen to be used in experimentation, some that had been previously used and some new substrates. The substrates used were; aluminium foil, polyethylene plastic bag, stainless steel, brass, cotton swatches, cardboard and thermal paper (Appendix Table 99 and Table 100). Throughout the entire sample pool, the enhancement was relatively poor, with the exception of two of the stainless steel samples (Samples 0281 and 0282, Appendix CD). It is unknown why the samples developed so poorly, though the current thinking is that the amount of sebaceous material within the fingermark was insufficient to allow development.

Forensic lifting gels, typically used for lifting dusted fingermarks or footwear marks, were used to lift sebaceous fingermarks from a laminated desktop. The gel lifter was then treated with the phosphomolybdic acid solution, and exposed to UV light (Appendix Table 101). The gel surface reacted adversely, causing it to have a speckled blue marbled effect (Figure 48). However, ridge flow could be seen, it was just lost amongst the extreme staining the phosphomolybdic acid caused.

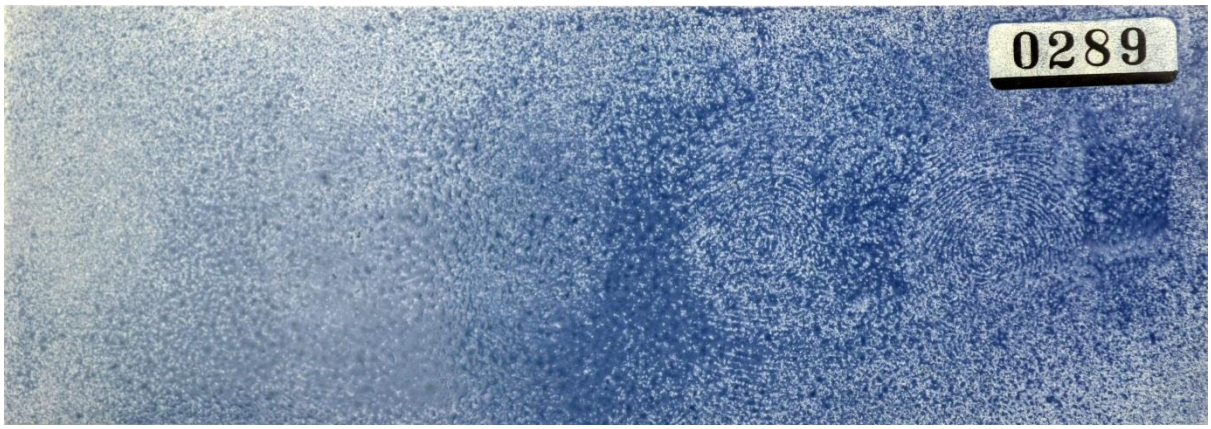


Figure 48: Gel Lifter Trial*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

Throughout the experimental process thus far, the paper substrate was the most rewarding in terms of developing fingermarks. The vast majority of experiments conducted on the paper substrates, were done so using sebaceous secretions. To show that this is where the phosphomolybdic acid is limited, paper samples were prepared with eccrine marks (Appendix Table 102). These samples produced absolutely no enhancement whatsoever, showing that this treatment does not work with eccrine deposits.

3.3.11 Sequential and Combined Treatments

Often in forensics, fingerprint enhancement treatments can be performed sequentially to each other; ninhydrin after DFO, acid violet 17 after acid yellow 7. However, rather than try to find another technique to work sequentially with the phosphomolybdic acid, the decision was made to try and find one that could work in conjunction with it. Since ninhydrin reacts with amino acids on porous substrates, it was chosen to be trialled in a solution with phosphomolybdic acid to try to encourage further enhancement.

Ninhydrin

With ninhydrin needing a humid environment in order to develop the latent fingermarks, and no humidity oven being available, another method was investigated. After some research, it was found that some forensic departments that do not possess a humidity oven use a steam iron and a towel in order to develop ninhydrin treated fingermarks. Before the combination was attempted, a ninhydrin solution had to be tested. Since the reagents for the CAST (Centre for Applied Science and Technology) recommended solution were not available, alternate thin layer chromatography ninhydrin solutions were trialled (on page 78).

Results gained from the first series of experiments with the ninhydrin solution 1 were, for the most part, poor (Appendix Table 75). Although some ridge details were visible on some samples, they were broken and dotty (Figure 49). This made positively identifying the fingermark impossible.

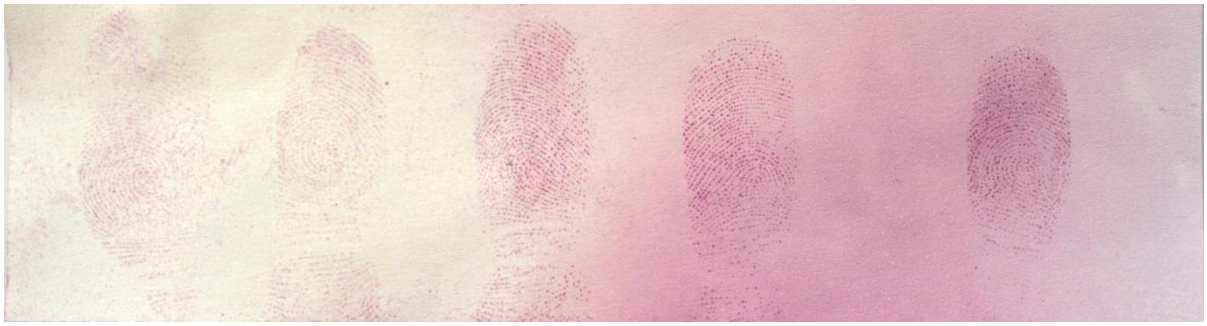


Figure 49: Ninhydrin Solution 1 Trial*

In a bid to eliminate the vast background staining, the amount of ninhydrin dissolved in ethanol was reduced to examine if this had any effect. At first, the amount of ninhydrin was reduced to 10% of the original amount 1.0 g used. The new 0.1g ninhydrin solution, ninhydrin solution 2, showed no signs of development on the substrate (Appendix Table 104). With this in mind, the next solution had 0.5 g ninhydrin in 30 ml of ethanol (ninhydrin solution 3), this solution showed some minor development around the edges if the marks (Appendix Table 105). A further attempt at the original 1.0 g in 30 ml solution was made, this time the development was more apparent, however the ridges were broken and dotty (Appendix Table 106).

Ninhydrin solution 1 was trialled this time it was compared directly with PMA, using the split trial method. The paper substrates were prepared by depositing fingermarks down the centre of the sample, this was then cut in two down the centre line. One half was treated with the ninhydrin solution, and the other with a PMA solution. Both halves were then brought back together in order to compare the development of each solution. The PMA samples were developed using a UV lamp as described before. The steam iron was utilised again in lieu of the humidity oven.

The PMA/Ninhydrin split sample, showed faint fingermarks on the PMA side of the sample, with little useable detail (Appendix Figure 155). The ninhydrin side had a light pink stained background, with darker pink/purple fingermarks. The fingermarks presented as broken ridges with no detail whatsoever. As previously noted, the ideal environment for ninhydrin to develop fingermarks is at 80°C and 65% relative humidity. Unfortunately, a humidity oven was not available at the time of this series of experimentation.

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

To try and remedy this, a makeshift humidity chamber was constructed using a Tupperware box, which could withstand heats up to 120°C, with a beaker containing a saturated solution of sodium chloride in water. Once placed in an over at 80°C, the inside of the box would reach 75% relative humidity. Although this was not the ideal conditions, it was the best that could be achieved utilising the equipment at hand.

The humidity box was placed in the oven for a few hours to acclimatise, numerous samples were treated using this method. The results gained were far better than previously obtained using the steam iron (Figure 50).

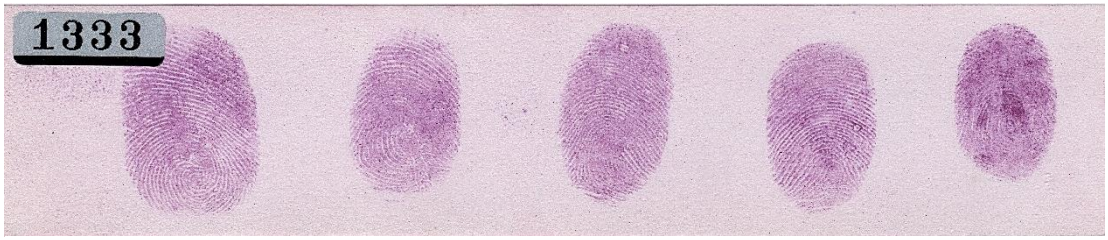


Figure 50: Ninhydrin Development *via* Humidity Chamber

Another attempt was made to use the ninhydrin in conjunction with PMA, with the ninhydrin solution being changed for an alternative solution. The ninhydrin formulation used for this series of experiments was ninhydrin solution 4.

Samples were first treated with PMA then graded, after which they were treated with ninhydrin and developed in the humidity chamber. The initial PMS treatment developed good quality fingermarks, however, when dipped into the ninhydrin the blue background staining of the PMA began to run and streak. The original marks the PMA developed could be seen to start fading, even before being put in the humidity chamber. Once developed in the chamber, the samples presented with a darkened background with some faint pinkish finger mark shapes, often with broken ridges (Appendix Figure 156).

Phosphomolybdic Acid/Ninhydrin Mixture

Research turned up an abundant supply of ninhydrin formulations, and many used ethanol as the carrier solvent. Since PMA is also dissolved in ethanol, the hope was that the two could be combined *and* remain in solution. With both solutions staining different constituents of the fingermark residue, it was theorised that both together should give better enhancement.

For the phosphomolybdic acid/ninhydrin mixture, the best performing individual solutions were used. In the case of the phosphomolybdic acid, the 10% solution using the hydrate was used. For the ninhydrin, the 1 g in 30 ml of ethanol was used. These were mixed together in a 1:1 (v/v) solution, this meant the individual core solution concentrations were reduced by 50% (5% PMA and 1g ninhydrin in 60 ml of ethanol). Despite these reduced concentrations, both solutions have proven to be effective at these levels.

The samples were treated with the solution and placed into a large plastic container with a beaker of hot water, then a locking lid was attached. The lid was transparent, and the UV lamp was laid on top so that the sample substrates would be exposed to humidity as well as UV light. The developed samples were noticeably more stained than when the phosphomolybdic acid was used on its own (Appendix Table 107). On the longer developed samples, there are some pink/purple marks around the finger mark edge, but the marks are faint and hard to distinguish (Figure 51).

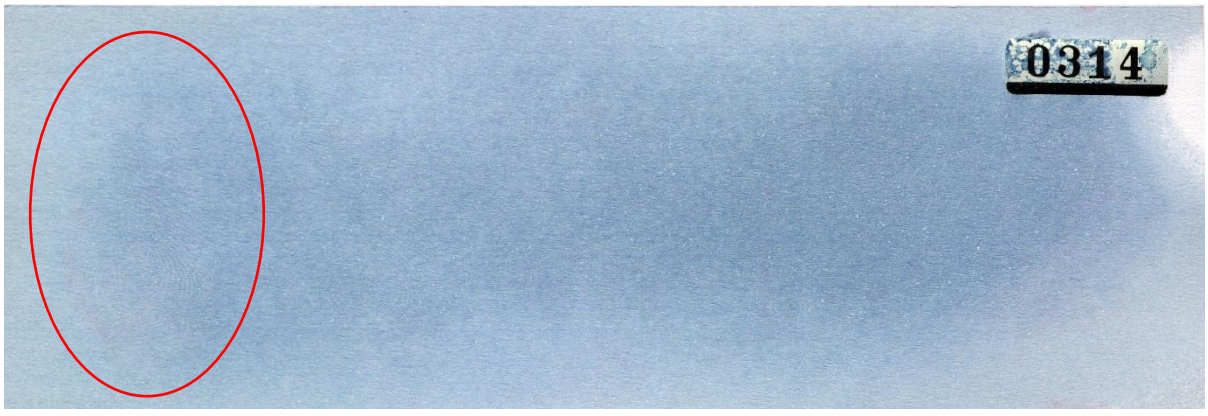


Figure 51: Phosphomolybdic Acid/Ninhydrin Solution Trial*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

It was speculated that the phosphomolybdic acid was reacting with the double bonds of the ninhydrin aromatic rings to form molybdenum blue [179] before the PMA was getting a chance to interact with the fingermarks; this was causing the dark blue staining across the substrate. It was determined that although these solutions were developing marks successfully when used alone and in more dilute forms, they reacted too adversely when used together to be of any use in the enhancement of fingermarks.

Oil Red O

Oil Red O is another fingerprint enhancement technique that is used on porous substrates. It stains lipids and triglycerides of which there are plentiful supplies of in sebaceous deposits. Since PMA only works with fingermarks containing sebaceous materials, it seems logical that these two solutions should work in conjunction with each other. Treating fingermarks with Oil Red O is a three part process; the Oil Red O stain bath, a buffer solution and, finally a water bath.

Oil Red O is dissolved in methanol, which from an operational standpoint is not ideal, due to its toxicity. This, coupled with the fact that it is a multistage process, makes it impractical for mixing with phosphomolybdic acid. It, can however, be used in sequence with PMA. The Oil Red O formulation on page 80 was used for all Oil Red O staining trials. The samples can take up to 90 minutes to be treated in the stain bath. The samples are then placed in the buffer solution for approximately five minutes than rinsed in the water bath and left to dry. In the initial experiment, the paper substrates had fingermarks deposited upon their surface, they were then cut down the centre so that half the mark was on each half of the separated sample, as with previous experiments. One half was treated with Oil Red O and the other with PMA followed by Oil Red O. Once treatments were complete, the two halves were brought back together to be compared.

The initial PMA development produced grade 2 fingermarks; however, once treated with the Oil Red O the marks became fainter. The Oil Red O treated half, developed faint marks with little detail (Appendix Figure 157).

To test if the donor was the issue of the poor quality fingermarks that were developed, an additional two donors were enlisted. The three donors all deposited fingermarks as detailed before, development was conducted as before. Donor 1's developed marks had some good ridge detail within them, although there are areas where ridge leaching has begun. The side which was treated with PMA prior to the Oil Red O, shows very little difference from the side treated solely with Oil Red O. Donor 2's marks show heavy leaching throughout, mostly likely due to depositing their marks too hard on to the surface. Some ridge feathering can be seen around the edges, however, this has very little evidentiary value. The last mark donor 2 deposited, which looks like their thumb, has some good ridge detail within it. The PMA/Oil Red O side of donor 3's developed fingermarks look leached and overloaded; the comparable Oil Red O only treated side looks to be better developed. Again, the last mark in this series is the only overall mark which has great detail throughout (Figure 52).

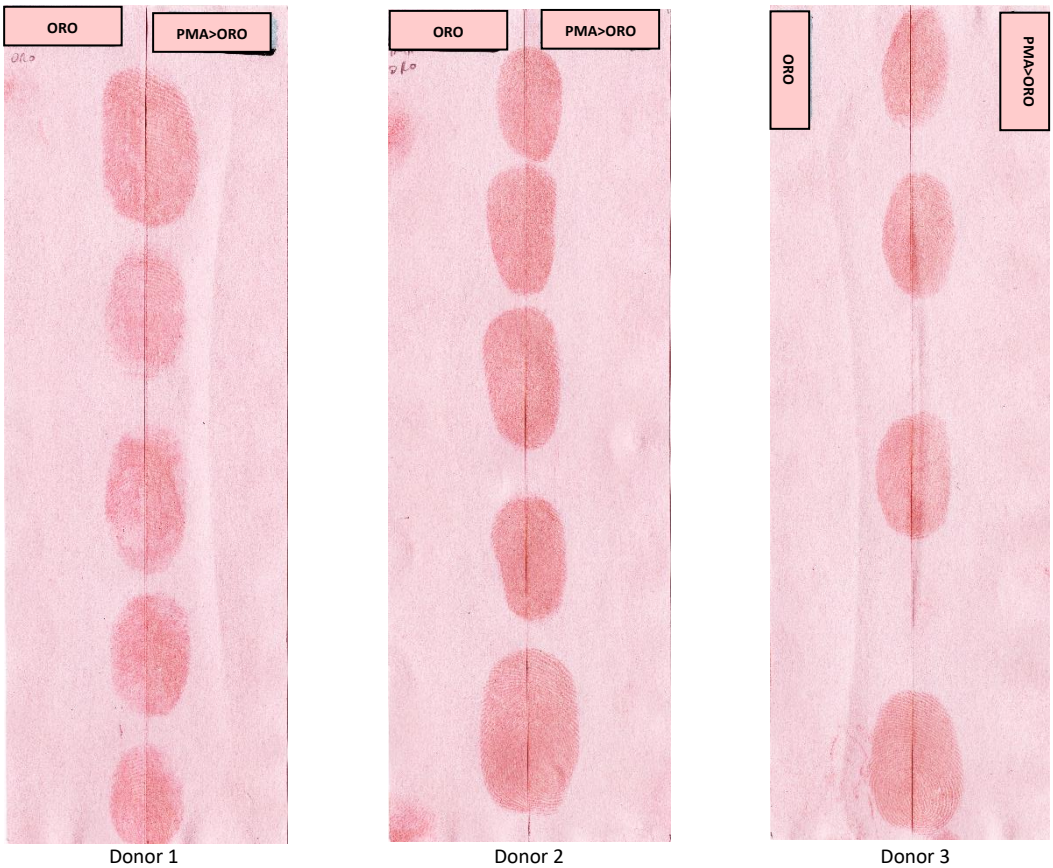


Figure 52: PMA/Oil Red O Comparison Results From 3 Donors (ORO *vs*. PMA>ORO)

Since good results were starting to come more readily, it was decided to try and test whether ethanol could be substituted for the methanol component of the Oil Red O stain recipe. The methanol and ethanol solutions would then be treated and compared in a split trial. The buffer solution was left the same. The protocol as before was used; fingermarks deposited, paper cut, separate halves treated, have reunited then overall examination.

Straight away it could be seen that the ethanol solution was much darker. The methanol halves had developed some faint fingermarks, the ethanol solution had reacted completely differently though. The complimentary ethanol halves had completely stained the paper substrate to the stage of nothing else being visible (Appendix Figure 158). This line of investigation was deemed fruitless and thus abandoned.

Some work conducted by Kelly Group undergraduates suggested that treating paper substrates with phosphomolybdic acid before Oil Red O helped develop better marks when the Oil Red O treatment was done several weeks later [204, 205]. Literature states that Oil Red O has problems developing fingermarks that are over four weeks old [124]. If this claim is true it may provide investigators with a sequence of techniques that allows for fingermarks to be speculatively searched for using the PMA, then any found marks can be developed at a later date with no worry that marks are going to fade.

The same procedures were used for these experiments as used before. Marks were laid, samples were split, one half treated with PMA and developed. All samples were then left for two weeks, after which time they were all treated with Oil Red O. Once dried, all corresponding halves were unified and examined.

The halves treated just with Oil Red O displayed some faint marks, some of which did show some ridge detail. The matching halves pre-treated with PMA showed darker marks, with better definition on the ridge detail. Many of the fingermarks on the PMA half, show specific minutiae which would aid in the identification of the marks (Figure 53). It appears that the PMA has acted in a way so as to lock the fingermark residues in place, much like 5-sulphosalicylic acid locks blooded fingermarks in place for the treatment with certain protein stains [200, 206, 207].

Although this process is in its infancy, the initial results show promise. The use of phosphomolybdic acid as a precursor may just help lock the fingermark residues to the substrate. If this is the case, then the limitation of Oil Red O only working on marks no older than four weeks may be moved one step closer to being solved. Since PMA is a quick technique, it could easily be adapted to work in the field as a speculative technique, showing investigators where to focus their efforts when attempting to recover fingermarks at crime scenes.

Further work will be needed in order to see just how long the PMA can hold the mark in order to give improved Oil Red O results.

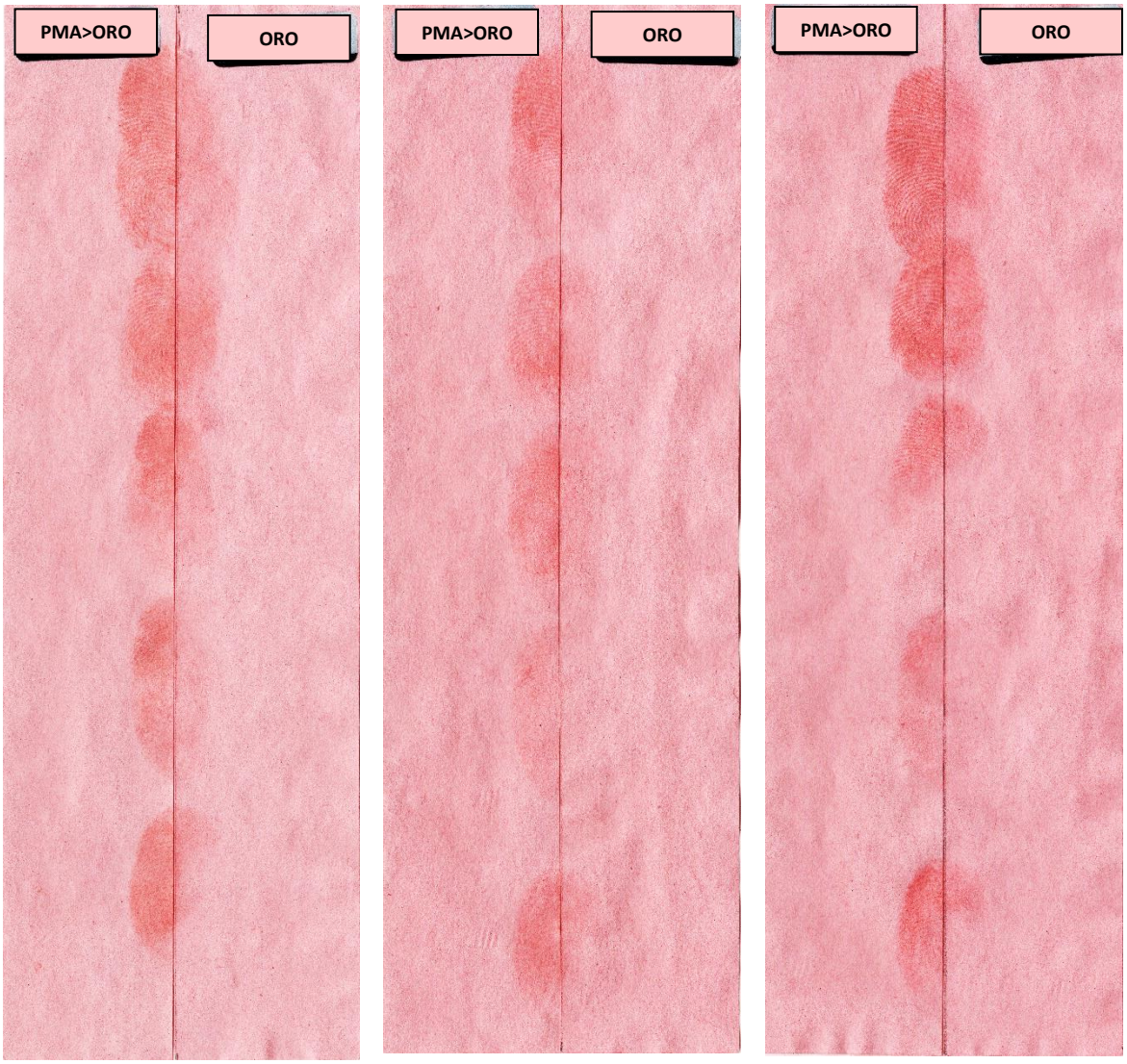


Figure 53: PMA/Oil Red O Sequential Experiment Results

Cerium Ammonium Molybdate

After conducting additional research on phosphomolybdic acid online, another similar stain came to light. Cerium ammonium molybdate (CAM) a derivative of ammonium molybdate [189] was synthesised by the El Khadem group and despite no literature being published, it managed to propagate its way around the world [190]. Using the formulation on page 79, 100 ml of the yellow/green CAM was produced.

Paper substrates were prepared with sebaceous loaded fingermarks. The substrates were sprayed with the cerium ammonium molybdate solution using the Ecospray. Upon the application of the solution, the paper substrate became waterlogged and curled up. The body of the mark became visible as a dark blue/black mark which promptly faded. After development in the oven and under UV no marks were visible (Appendix Table 116).

After discussions with supervisor Dr Kelly, it was hoped that preparing the cerium ammonium molybdate in a volatile solvent such as ethanol may offer a solution more akin to the phosphomolybdic acid, and since there was no water in the preparation it was hoped this would eliminate the waterlogging issue. An attempt was made to produce the cerium ammonium molybdate solution with ethanol in lieu of the water. The ammonium molybdate and cerium ammonium sulfate failed to fully dissolve in the solvent, and the addition of the sulfuric acid turned the solution a muddy dark blue colour. The solution was filtered to remove the excess solids; however it developed no fingermarks when used.

An alternate method was tried to create the ethanol based CAM solution. It was thought that by evaporating the original water based cerium ammonium molybdate solution down, that the resulting solid could be dissolved in ethanol to give the desired solution. Unfortunately, the water based CAM failed to evaporate after several weeks in an evaporation bowl. In an effort to accelerate the process, heat was added to the bowl and the solution brought to a boil. What was left was a tacky paste, this was placed in a vacuum desiccator in a bid to remove the remaining liquid constituent. A hard crystalline substance was left to which some ethanol was added to this in order to dissolve it, however, it failed to dissolve. This solution was deemed ineffective and further examination was discontinued.

Seebach's Stain

After researching numerous thin layer chromatography stains, Seebach's [208] stood out; firstly due to the fact it contains phosphomolybdic acid and secondly, since it is often touted as "Seebach's 'Magic' Stain" due to its ability to stain almost any substance being examined [209]. It was hoped that this stain would provide a better contrast between the fingermark ridges and the substrate background.

Following the formulation on page 80 a Seebach's stain solution was prepared. When mixed, not all of the solid dissolved, therefore the decision was made to filter the solution and use it as it was. It was assumed that the water content may be an issue when dealing with paper substrates, therefore another solution was prepared using ethanol as a substitute for the water.

A series of fingermarks were deposited down the centre of a paper substrate then split in two; one half developed using an over at 100°C, and the other half developed using a UV lamp. Multiple samples were treated, some with the water based solution, and the rest with the ethanol based solution. Once developed, the two halves were reunited so that a comparison of the two solutions could be made.

The water based solution shows a spotty/blotchy appearance over the surface of the substrate (Figure 54). Some fingermark shaped blobs appear down the centre of the sample; however, no ridge detail has developed. The half developed in the oven appears a black colour, whereas the UV developed side is a cyan blue colour.

The ethanol solution has a smoother, more uniform appearance (Figure 55). Some faint ridges can be seen amongst faint fingerprint shaped marks. The halves of the substrate are the same colours as with the water based solution.

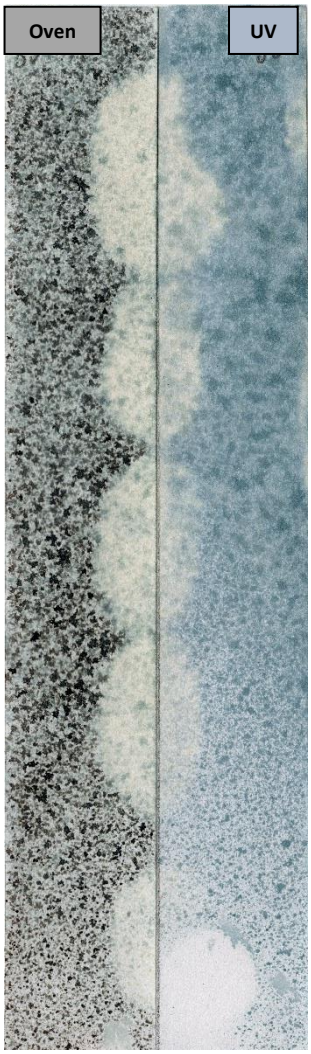


Figure 54: Water-Based Seebach's Stain (Oven *versus* UV)

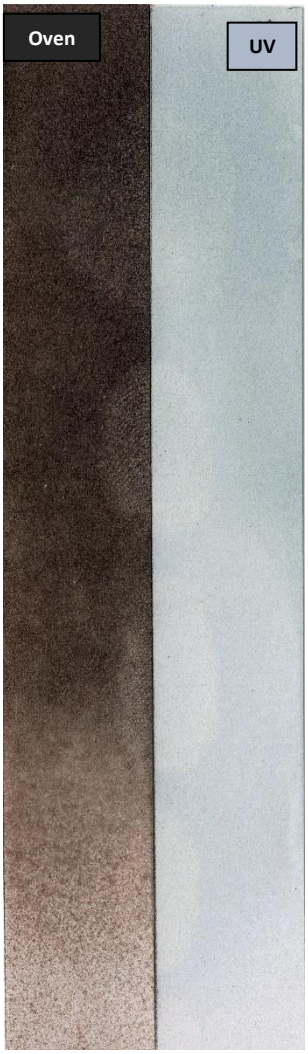


Figure 55: Ethanol-Based Seebach's Stain (Oven *versus* UV)

Due to the lack of any positive results, this area of investigation was not explored any further.

3.3.12 Group Study 1

Of the samples provided by the six donors (Appendix Table 108), the eccrine deposited marks provided no development whatsoever, with the exception of sample 0318 (Appendix CD), which showed a finger shaped mark (Appendix Table 109). It was assumed that this was due to contamination rather than the phosphomolybdic acid reacting with the eccrine constituents.

The samples containing natural secretions developed some marks; however, these were present as dark fingerprint shaped marks which contained no detail at all (Appendix Table 110). Since the study involved a number of participants, the pressure at which the marks were deposited varied and was presumed to be the reason the finger marks were so muddied and lacking in detail.

Despite being less successful than hoped, the group study was felt to be an important factor in defining the capabilities of the process and was deemed to be worth repeating in order to try to gain more reliable results.

3.3.13 Wetted Samples

The next stage of the experimentation was to test the phosphomolybdic acid on wet and wetted paper. Fingermarks were deposited on to the sample substrates then submerged in water from ten minutes to an hour. The samples were then either allowed to air dry or were placed in an oven for ten minutes at 100°C.

The samples which were air dried, showed some minor development (Appendix Table 111). The oven dried samples were warped, and extremely stained upon development (Figure 56). This staining obscured any development that may have occurred. In order to try and eliminate the blue staining, the temperature of the oven was reduced to 65°C and the heating time was increased to twenty minutes. The oven dried samples still showed mild warping; however, the intense staining was not present. There was faint finger marks visible, though no ridge detail was evident. The air dried samples also showed some faint development, but again the marks were faint and not identifiable.

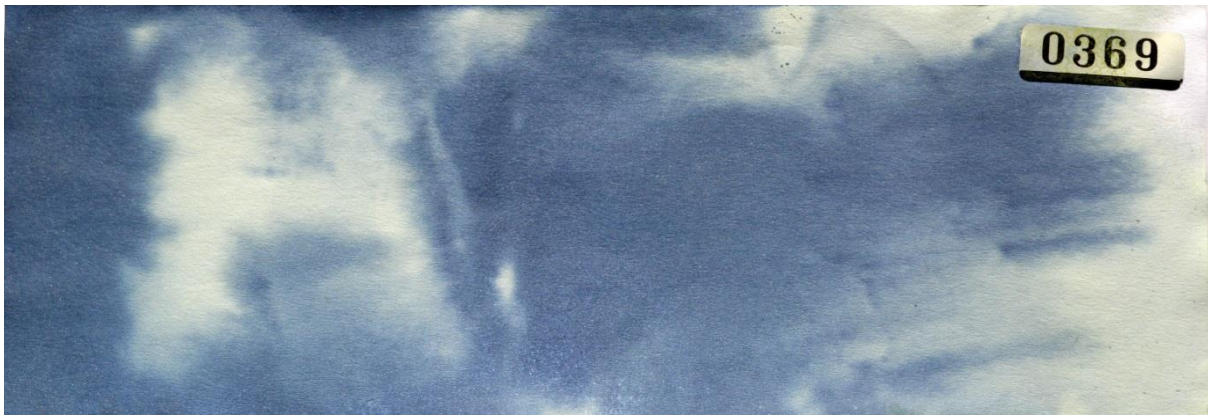


Figure 56: Failed Development on Wetted Paper*

To examine if there was any difference to development, a set of samples were treated while wet. Upon placing the samples in to water bath, the finger marks became visible. The body of the mark appear slightly darker than the rest of the sample substrate. Once removed from the water bath, the samples were sprayed with the phosphomolybdic acid solution and subjected to the UV light for fifteen minutes. After development, the samples were allowed to air dry. Since the samples were wet when the phosphomolybdic acid was applied, it just ran off the sample and created a blue streaky mess. Nothing was developed, and it was decided to continue with the previous method of allowing the samples to dry before applying the development reagent (Appendix Table 113).

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

To try to eliminate the warping on the sample substrates dried in the oven, the temperature was further reduced to 50°C and samples were still dried for twenty minutes. Samples again showed the image of the finger mark when placed in the water bath (Figure 57), however, once developed the level of ridge detail that had been visible on the wetted surface, was not present. The marks were faded, and not identifiable (Figure 58).

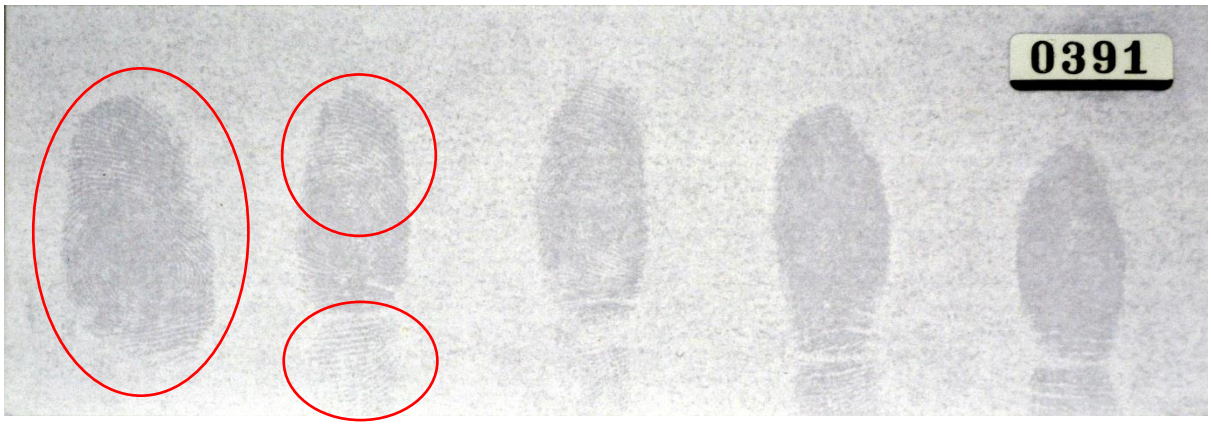


Figure 57: Finger Marks on Wet Paper*

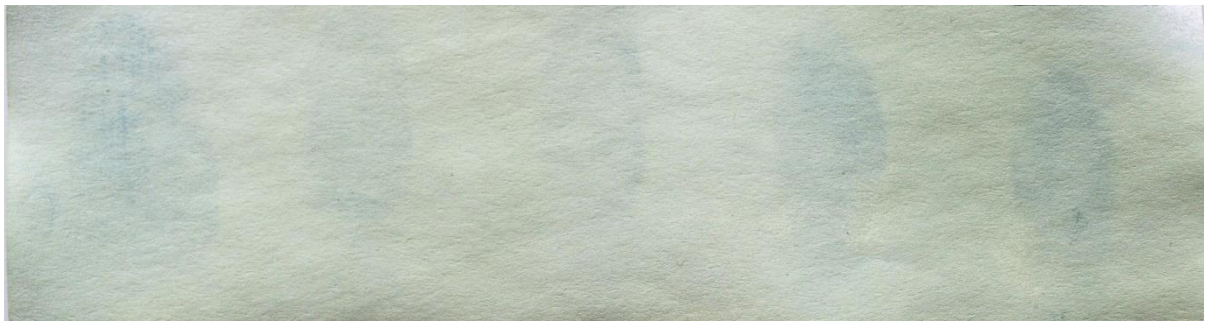


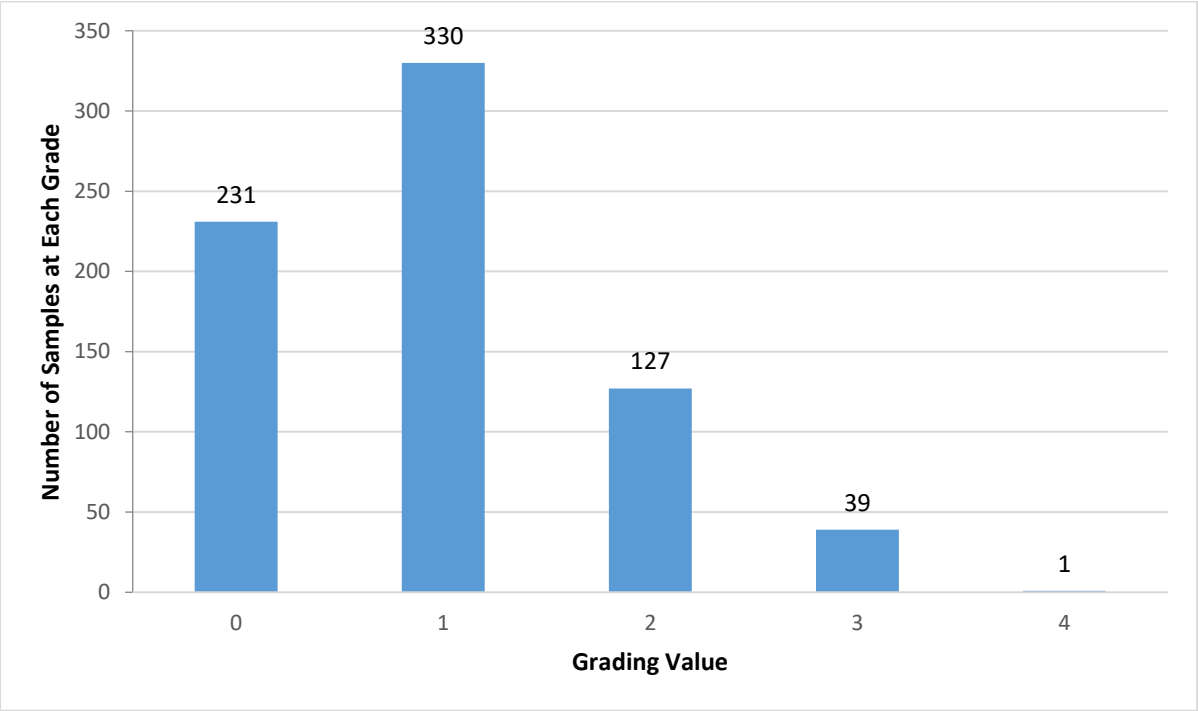
Figure 58: Phosphomolybdic Acid Development on Wetted Paper*

Since there was a lack of development on wetted surfaces, it was posited that this development technique was best suited for dry substrates that had not been subjected to moisture.

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.3.14 Group Study 2

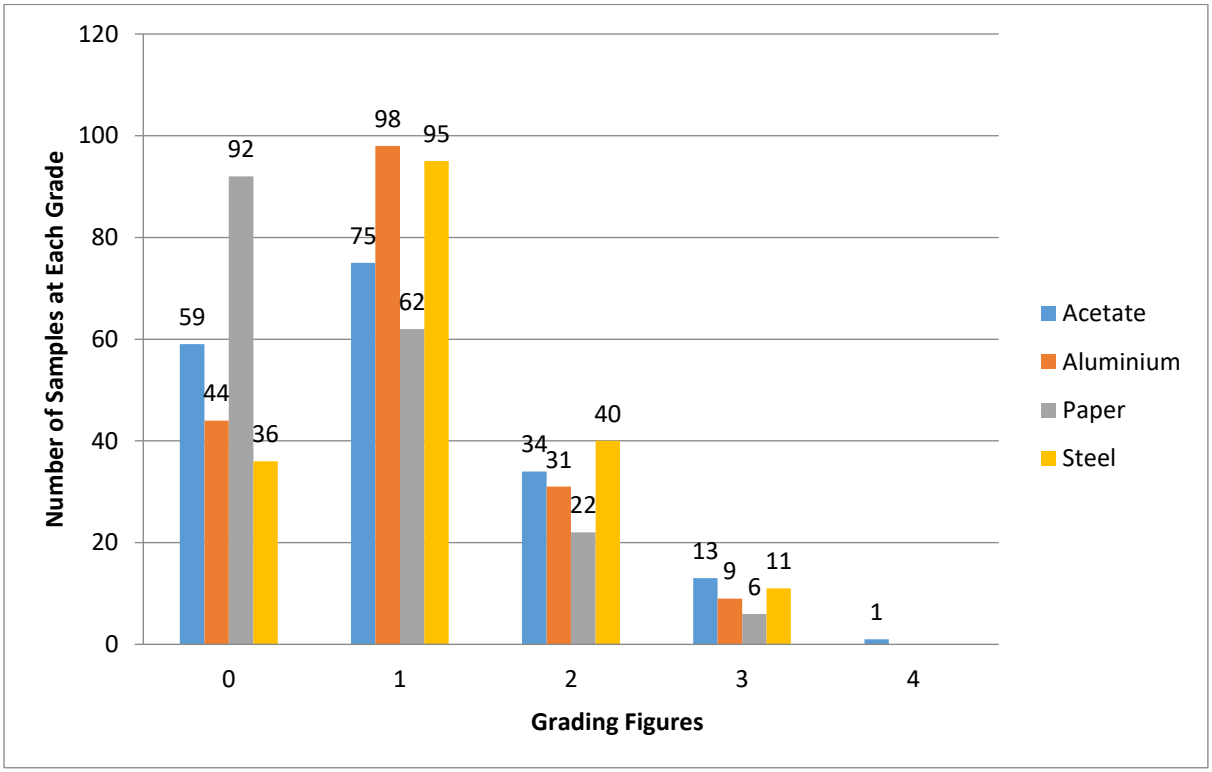
There were 728 total samples (13 donors, 7 different fingermark ages, 4 substrate types and 2 fingermark deposition methods) treated, the developed fingermarks were graded from 0 to 4 after a visual examination. Of the 728 samples, 45% grades as 1, 17% were graded 2 and 6% were graded 3 and above (Graph 6).



Graph 6: Group Study Distribution of Grading Values

Paper provided the most 0 graded marks (those containing no development); double the amount of some of the other substrates. The number of paper samples within each individual grading value was markedly less than those of the other substrates (Graph 7). The metal samples; aluminium and stainless steel both performed very similarly despite having slightly different finishes, slightly brushed compared with a clean smooth finish respectively. Performing slightly behind the metals were the acetate samples which encountered problems due to high instances of background staining.

The paper's poorer performance was thought to be due to the fingermark residues being absorbed into the paper's porous surface, this is also consistent with the recommended use of fingermark reagents (ninhydrin, DFO, Oil Red O) on this type of surface because of the higher proportion of fingermark deposits being drawn into the porous surface. Conversely, all constituents of the fingermark residue sit on the surface of the non-porous metal and acetate substrates and are available to interact with the PMA.



Graph 7: Group Study Results

The differences in the finishes of the metals made a difference in the visualisation of any finger marks present on the surface. The slight brushed finish on the aluminium caused some marks to only be visible at an oblique angle, especially with faint marks. There were some instances where the phosphomolybdic acid caused high background staining on the substrate, leaving the surface awash with blue staining, although some did show signs of ridge detail which was broken and spotty in places (Figure 59). Many of the samples which garnished useable marks were observed to have little in the way of background staining and the ridge detail appeared to be lighter than the background (Figure 60).

This suggests for the metal surfaces used in this study, the primary interaction occurring is between the PMA and the metal substrate.

Figure 59: Aluminium Stained Background

Figure 60: Aluminium with Ridge Detail

The steel had the greatest number of grade 2 and grade 3 marks, however, it also suffered from the background issues that the aluminium had. The finger marks on the steel substrates developed much the same as the aluminium, with ridges presenting as a dark blue/black and in some cases with some yellow staining between the ridges. The acetate substrates performed better in terms of fingermark development than the aluminium samples, but to a lesser degree than the steel samples. When applying the phosphomolybdic acid to the acetate surface it would often tend to produce a 'halo' where a mark was situated, most probably due to the solution being repelled by the oils within the fingermark residues. Out with these haloes the phosphomolybdic acid would sit in pools and stain the acetate a similar yellow/green colour to the original solution (Figure 61). The marks and marks within the voids however, were visible as the characteristic dark blue/black of the molybdenum blue. The background staining observed is similar to that that occurs when using cyanoacrylate fuming and Basic Yellow 40 dye on certain substrates, e.g. tin foil [88]. The enhanced marks on the acetate surface were very fragile and easily destroyed by light touches (Figure 62). Despite this fragility and the instances of high background staining, the acetate did produce high instances of grade 2 to 4 marks (Figure 63).

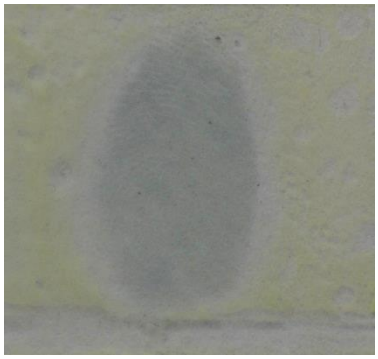


Figure 61: Acetate Background Staining

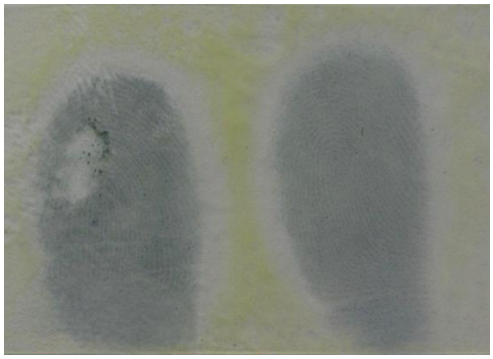


Figure 62: Damaged Mark on Acetate

As mentioned previously the paper substrates did not perform to the same level as the other samples. Over fifty percent of the paper samples returned no enhancement whatsoever, with only fifteen percent giving marks of grade 2 and above. Background staining was also noted with the paper samples, albeit to a lesser degree than the other substrates tested. The staining was observed to be of a variety of colours ranging from the aforementioned yellow/green through to a pale blue. Grade 2 and 3 marks present were often faint; however, some good ridge detail was observed (Figure 64).

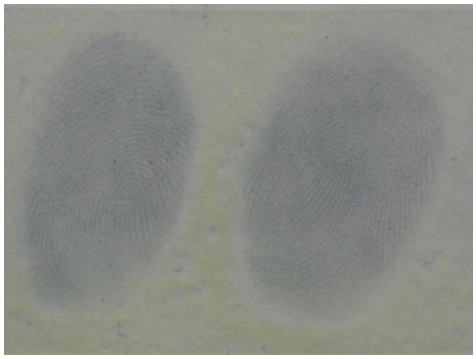


Figure 63: Ridge Detail on Acetate

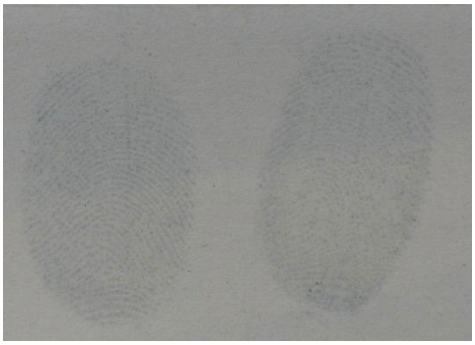
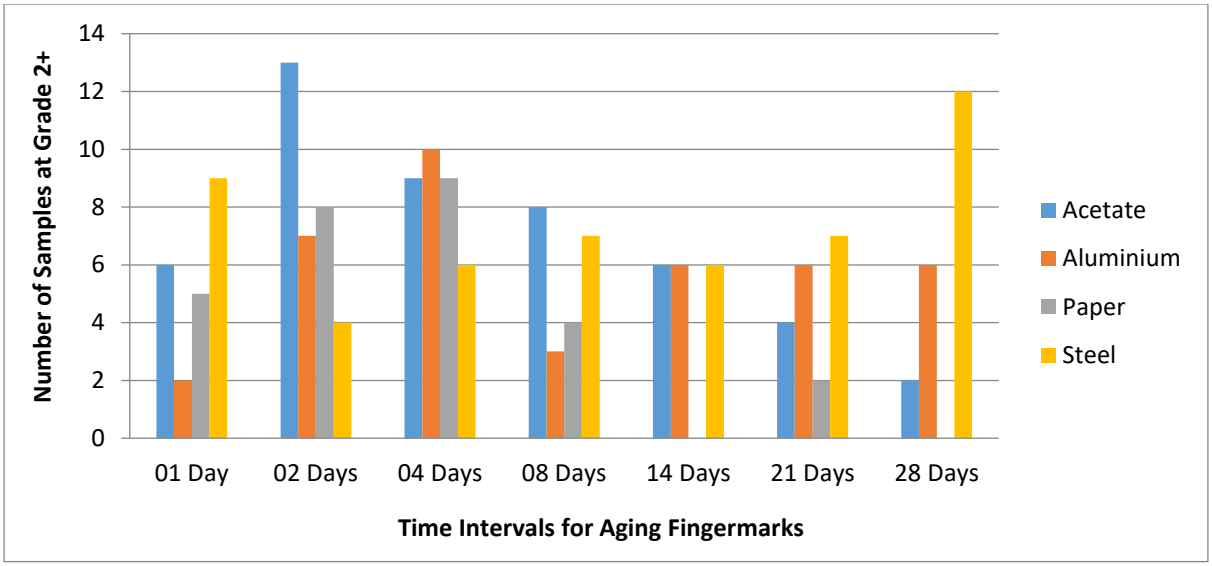


Figure 64: Ridge Detail on Paper

Unlike various other research undertaken over the past years, the enhancement of finger marks on the chosen substrates only diminishes with age on some substrates and others perform consistently [156, 157]. The aluminium and steel are relatively consistent in the numbers of positive marks grade 2 and above through the one to twenty-eight day aging process, whereas the paper and acetate figures show diminishing returns (Graph 8).



Graph 8: Grading Figures per Day at Grade 2 and Above

When looking at the results by day, the number of acetate samples with grade 2 and above marks can be seen to peak at day 2, and then they begin to decline through the rest of the aging series. Aluminium samples showed little ridge detail development to start with on day 1, this quickly increased over days 2 and 4 where it peaked then dropped dramatically again at day 8. There was a small increase on day 14 where the number of developed samples plateaued through till day 28. Paper was the only substrate that did not develop any marks of grade 2 and above on all days of the trial. The development of marks on paper slowly increased from day 1 to day 4 where it suddenly drops off eventually developing no grade 2 or above marks at all on day 14. Although some development occurred on day 21, day 28 did not produce any results either. The steel samples started with a good number of grade 2 and above marks then peaked and dipped throughout the age series peaking again at day 28.

Since there was no clear pattern established within the results of the finger mark aging series it was theorised that the inconsistencies could be the result of too little fingermark residue present within the marks deposited. To test this theory two further, shorter studies were conducted. A study where eccrine only finger mark deposits (sweat from the hands only) and another study where sebaceous sweat deposits were introduced artificially. The number of donors was dropped from thirteen to four and the age of the finger mark deposits was lowered from twenty-eight days to eight (1, 2, 4 and 8 Days). The number of sample substrates remained the same at four.

For the eccrine study, the donors washed their hands then donned nitrile gloves for up to thirty minutes in order to allow the hands to sweat. Marks were then deposited upon the sample substrates. When conducting the sebaceous study, donors were asked to rub their fingertips around their hairline and nose areas where sebaceous sweat glands are abundant. Marks were then deposited upon the sample substrates.

Eccrine Study

The eccrine study failed to yield any positive mark enhancement. This occurred across all the substrate materials. Some showed signs of background staining due to the phosphomolybdic acid, but no signs of any ridge detail staining.

Sebaceous Study

	Acetate	Aluminium	Paper	Steel
Grade 0	3	4	2	3
Grade 1	3	4	3	3
Grade 2	5	3	5	4
Grade 3	5	5	4	4
Grade 4	2	1	2	2
Total	16	16	16	16
% of Grade 2+ Marks	75%	56.25%	68.75%	62.5%

Table 4: Sebaceous Study Results

The sebaceous study provided many positive marks, and high instances of fingermark enhancement that could be used in an operational capacity to identify the depositor of the marks (Table 4). The acetate substrate showed the most grade 2 and above marks, although they still suffered from the delicacy mentioned before. The paper samples also showed a noticeable improvement in the amount of grade 2 and above marks developed (Figure 65).

Figure 65: Sebaceous Study (Paper)*

* Contrast and brightness adjusted to allow visualisation on page. Original image on Appendix CD unaltered.

3.4 Conclusions

Overall this study in to phosphomolybdic acid as a latent fingermark reagent was successful, demonstrating that not only could latent marks be obtained, but that in most cases they could be easily recorded. An array of solvent carriers were examined, with a range of surface substrates being investigated as well the effect deposition time had on the quality of the fingermarks developed.

Assessment of the initial samples showed that the sebaceous loaded marks were the most successful at being enhanced, whereas the eccrine loaded marks showed no signs of development. It was found that the paper type had an effect on how well the phosphomolybdic acid developed fingermarks.

Many aspects of the phosphomolybdic acid formula were investigated. Solvent carriers were investigated and indicated that the solid phosphomolybdic acid hydrate solutions performed to a higher degree than the diluted supplier purchased 20% solution. While investigating alternate solvent carriers, many solvents were found to be wholly inadequate for the job, whilst others showed promise. While temperature was being explored as a development factor, another development method was discovered. Sunlight was found to develop fingermarks; leading to the realisation that ultraviolet light was an effective alternate development source. In a comparison test conducted in order to assess oven heating versus ultraviolet light exposure, UV light was found to be the superior development route, providing darker ridge detail with a background that provided better contrast.

In an effort to increase the contrast between the enhanced friction ridges and the substrate background, a de-staining method was attempted. Numerous solvents were employed to achieve this; unfortunately none of them were successful. Despite this outcome, a washing technique was not completely ruled out.

Of the various substrates tested, most proved unsuited to receive phosphomolybdic acid. The only substrates which developed decent fingermarks when subjected to the PMA were stainless steel and ordinary copier paper. While the stainless steel developed extremely dark blue/black marks against the steel background, the paper substrate cultivated blue marks on a yellow/green background.

Although, ninhydrin, another development technique for porous substrates was investigated, it was done so in order to develop a solution that could combine two successful techniques into one which would be more sensitive than either separately. Unfortunately, this proved a futile endeavour as the PMA and ninhydrin reacted adversely with each other.

Other stains similar to phosphomolybdic acid; phosphotungstic acid, cerium ammonium molybdate and Seebach's stain were all tested under the same conditions as the phosphomolybdic acid. Unfortunately, none of the solutions were successful at developing any fingermarks.

When comparing the efficacy of phosphomolybdic acid against Oil Red O, the two seemed to be comparable on newer marks. However, PMA appeared to outperform ORO on older marks, possibly because it targets a wider range of constituents, some of which may be more persistent than the constituents targeted by ORO. Phosphomolybdic acid could be considered as a cheaper, faster alternative to Oil Red O for the same type of development. By using the phosphomolybdic acid as a precursor to Oil Red O, fingermarks were able to be developed long past the point where Oil Red O normally falls down as a development reagent.

A group study showed that of the substrates tested the non-porous substrates provided more positive results than the porous substrates, which was contrary to the results obtained previously. The paper substrate performed the worst achieving 49.5% positive mark enhancements, only 31% of which were grade 2 and above. An addendum trial found that marks containing only eccrine sweat deposits returned no positive mark enhancements whatsoever, whereas marks with exaggerated sebaceous sweat deposits produced up to 75% positive mark enhancements with greater ridge detail present, this confirmed what was already known about phosphomolybdic acid targeting only the constituents of sebaceous materials. There may well be merit in using PMA in sequence with DFO/Indandione and ninhydrin, much in the same way ORO is proposed for use at present.

PMA has a potentially broad application across porous and non-porous surfaces; it is quicker and potentially more effective than ORO on porous surfaces. However, it is unlikely to outperform an amino acid reagent and there are some health and safety issues in its flammability and corrosive nature, which would need to be addressed. Overall, PMA has shown some promise and would merit further research, especially in regards to working in concert with amino acid reagents and also against other lipid reagents on non-porous surfaces.

4.0 Cuprous Surfaces and Rubeanic Acid

4.1 Introduction

Rubeanic acid, or dithiooxamide as it is also known is the sulphur analogue of oxamide which acts as a chelating agent which is used in the detection of numerous metals including but not limited to lead, copper, silver, zinc, gold, and palladium [210, 211].

Discovered in the early 1800s cyanomethanethioamide (Gay-Lussac, 1815) and dithiooxamide (Wöhler and Liebig, 1825) are thought to be amongst the earliest organosulphur compounds synthesised. They would later be named *Flaveanwasserstoff* (flaveanic acid) and *Rubeanwasserstoff* (rubeanic acid) by Berzelius (1843) on account of their colour, yellow and red respectively. However, it was Völckel's work with dithiooxamide that highlighted its parallels with oxamide, and ultimately lead him to be the first to provide structural proof to the class of thioamides (Figure 66) [212].

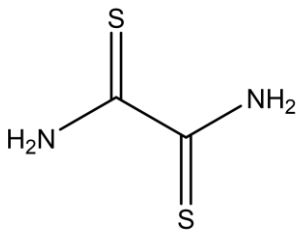


Figure 66: Rubeanic Acid Structure

Through the years many chemists have discussed various uses for rubeanic acid, highlighting the different coloured precipitates obtained when adding it to metal solutions. This was due to the rubeanic acid's ability to exchange protons of the NH_2 groups with metal ions to form metal salts. It would be almost a hundred years before the chemistry of rubeanic acid would progress any further, when in 1926 Ray and Ray pointed out the usefulness of rubeanic acid as a test for copper [213].

Ray and Ray and subsequently Ray and Xavier reported on rubeanic acid's ability to detect copper immediately and went on to describe its ability to detect other metals such as nickel and cobalt with the help of ammonia or sodium acetate. The work conducted by Ray, Ray and Xavier also made note of the differing colours the metal rubeanates produced. Copper rubeanate gave a blue/black coloured precipitate, while a blue/violet precipitate was obtained from nickel rubeanate. The precipitate obtained from cobalt rubeanate was a reddish brown colour [211, 213]. Nillson (1939) added to this metal rubeanate colour palette with his experimentation with rubeanic acid and ferrous and ferric salts, in which he noticed that the colour of the precipitate was dependant on whether the dithiooxamide was in an alcoholic or alkali solution. Nillson further noted that blue precipitate obtained is unstable and changes colour after some time, this he attributed to either oxidation or decomposition [214]. These different colours in the complexes are indicative of transition metal ligands and the electron transitions between non-degenerate *d* orbitals.

Despite being reported that Wöhler reacted lead with rubeanic acid, the interaction has been studied less than other metals over the last century and a half. Ray and Xavier stated that a yellow precipitate forms initially, which decomposes to lead sulphide [211], however, Mikhailov (2001) reported a black precipitation when reacting lead (II) hexacyanoferrate with an alkaline rubeanic acid solution in a gelatine matrix [215].

Since its discovery dithiooxamide has been used for the detection of trace metals; whether it be as a spot test for detecting minute amounts of copper (as little as 1ppm) [216, 217], trace amounts of metal in the environment [218] or in the estimation of copper within other metal alloys [219]. However, most of the work conducted using rubeanic acid focuses on using it to detect copper, as it is a '*rapid, accurate and direct*' [219] method. The interaction between copper and rubeanic acid was studied by Abboudi *et al*. (1985) where they proposed the ligand formed a polymeric complex (Figure 67). Rubeanic acid is a bidentate ligand whose sulphur atoms form a chelate complex with the copper ions present, resulting in the formation of a five-membered CuC_2SN ring structure [220]. These co-ordination schemes combine to form the polymeric copper rubeanate.

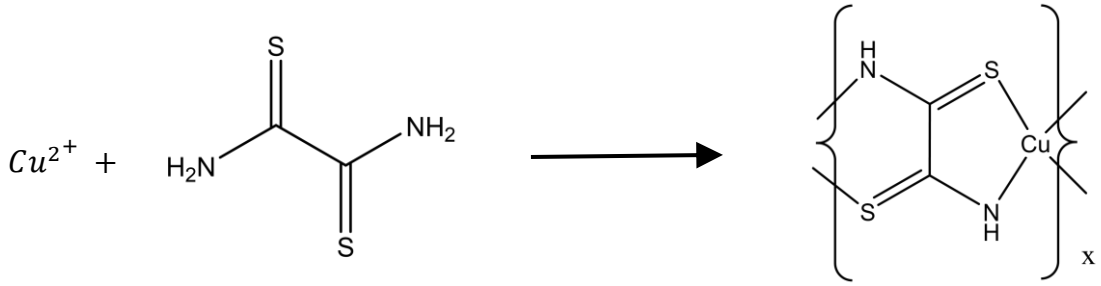


Figure 67: Polymeric Complex of Copper Rubeanate

More recently researchers at Loughborough University used rubeanic acid in a novel way to help combat heritage crime. In 2011 figures showed that in excess of 1,000 metal theft offences were being carried out each week in Britain. The metal theft is viewed as the 'biggest single threat' to the country's landmarks [149]. The Loughborough research found that by simply being in contact with copper or lead for a few seconds, enough trace amounts we left on the skin and on fabric to subsequently be lifted *via* a gelatine sheet to be treated with rubeanic acid. The gelatine sheet can be treated with rubeanic acid immediately or many days later. The copper appears almost immediately, whereas the lead requires a UV light source to develop [150]. This technique is practical in a forensic context as it would allow for the testing of skin (hands) and clothing of suspected heritage metal thieves in situations where they have disposed of stolen metal for fear of being caught 'red handed'. The detail obtained from the gelatine lifters is so precise that ridge detail and fingermark minutiae are discernible. More importantly, the whole process is non-invasive and can still generate results after light washing of the hands.

4.1.1 Aims

After observing the transference of fingermarks from one porous substrate to another when using PMA, it was decided to evaluate rubeanic acid as a latent fingermark enhancement reagent. After observing a colleague using rubeanic acid in conjunction with plates containing copper and forensic gelatine lifting sheets, it was felt this could be applied to a non-destructive fingermark development technique. A variety of substrates will be examined over a number of days to simulate the aging of the fingermarks.

4.2 Experimental

4.2.1 Assumptions

Throughout the experimental section, the following assumptions are made;

- Where not specified, the author's fingermarks were used for enhancement purposes.
- Whenever the rubeanic acid solution had to be stored, it was stored in at room temperature, in a clear bottle.
- With respect to the rubeanic acid solution, application was achieved *via* an Ecospray atomiser (Labo Chimie France).
- Fingermark deposition types:
    - Natural series: A series of marks where the donor deposits their fingermarks with no additional "grooming" involved, and having not washed their hands for at least 30 minutes prior to deposition.
    - Sebaceous loaded series: A fingermark where the person depositing the mark intentionally rubs their fingertips on or around their forehead and nose areas, and then presses their finger onto the sample medium.
    - Depletion series: A series of marks where the initial mark is loaded then deposited, the same finger is used for deposition repeatedly until the desired number of marks is achieved. Each fingermark then has less sebaceous residue than the previous mark.
    - Eccrine loaded series: The donor would initially wash their hands then don nitrile gloves for a period of 30 minutes. After removing the gloves, fingermarks were then deposited onto the selected sample substrate.
- Unless otherwise stated the sample substrate used was paper; the paper used was:
  Brand: Polaroid Copier Paper
  Weight: 80gsm

4.2.2 Substrate Preparation

The substrates used in these studies were paper, polymer banknotes and a variety of fabrics. The paper was an 80gsm A4 copier paper made by Polaroid. The polymer bank notes used were clean, new Vietnamese bank notes in the 10,000 Dong denomination. The fabrics used were; cotton, poly-cotton, nylon and two types of polyester, all were brand new "off the roll" and unwashed. These substrates were used as representations of common everyday items which can be found at crime scenes.

Paper

Loaded Series

An A4 sheet paper was cut into sections measuring approximately 12 cm by 3 cm, a size that would allow a row of five natural or sebaceous-loaded fingermarks to be deposited (Figure 68). These were labelled using photographic twin check labels with the twinned label being logged with the experimentation details. Fingermark deposition was carried out by depositing marks from each finger in a row of four or five marks. After the fingermarks had been deposited, a similar sized piece of copper or brass plate was placed over the fingermarks and secured in place with sticky tape. A lead block was then placed on top of the paper and copper/brass plate and left at room temperature for a period time ranging from 3 hours to 3 days.

Figure 68: Substrate Template

Split Series

Samples of paper were cut to 12 cm by 6 cm and orientated vertically and a line drawn in pencil down the middle of the sample, five marks were deposited in a row down the centre of the drawn line, the fingermarks were single deposits from five separate fingers. A combination of copper and/or brass plates of size 12 cm by 3 cm were then positioned so that they each covered half the fingermark along the pencil line. These plates were then taped together to discourage separation and both were secured to the paper with tape. The lead weight was then placed atop the paper and copper/brass construct and left for up to 3 days (Figure 69).

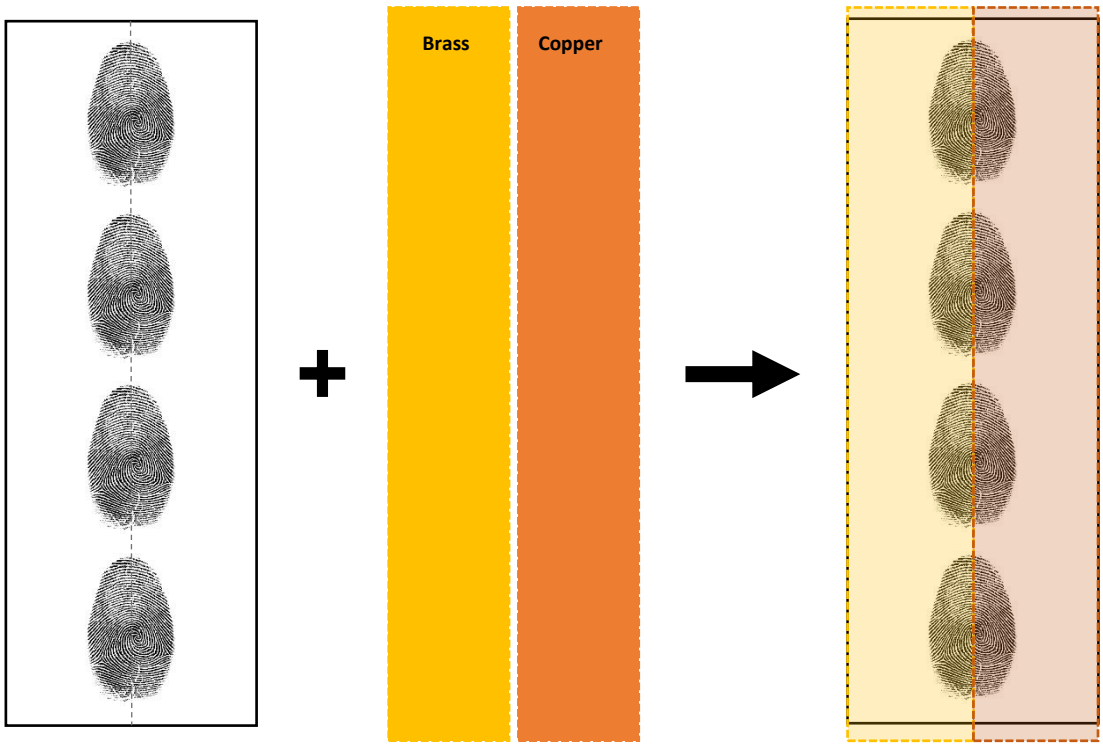


Figure 69: Split Series Sequence

Polymer Banknote

The polymer note substrates were prepared in a similar manner to the paper, with the exception of not being cut to size. The note had fingermarks deposited in two rows, with each note having eight to ten marks deposited. Similarly, a brass or copper plate was applied to the area, and in some cases one of each type (Figure 70). Again, these constructs were left for up to 3 days.

Figure 70: Copper/Brass Transfer from Vietnamese Dong

It was possible to reuse the polymer notes by washing them with liquid detergent and water, then wiping down with acetone and finally washing with liquid detergent again.

Fabrics

The fabrics; cotton, poly-cotton, nylon and polyester (cashmere and Lycra) were procured from a local material shop in 1 metre sections. These were cut into sections much the same as the other substrates. Sections measuring 15cm by 5 cm were prepared, ready for the deposition of fingermarks.

Metals

Sheets of copper and brass were obtained (www.metaloffcuts.co.uk) and cut to 12 cm by 3 cm sections *via* an industrial guillotine, which allowed for up to five marks to be laid onto each sample substrate.

Acetate

Clear overhead projector sheets were cut in to sections of 12 cm by 3 cm, large enough for the deposition of five fingermarks.

Materials Used

Paper – Polaroid A4 Copier Paper 80gsm

Polymer Banknote – 1000 Vietnamese Dong

Traditional Banknote - £1 Royal Bank of Scotland note

Acetate – LabelHeaven OHP Film

Brass – CZ 108 Grade Brass (0.3 mm thick)

Stainless Steel – 316 Grade Stainless Steel, 2B Finish (0.5 mm thick)

Copper – Grade C106 Copper (0.4 mm thick)

Gel Lifter – BVDA Gel lifters: Footprint Lifters – White, Polyester Backing, 18x36cm

Glass – Sailing Boat Microscope Slides

4.2.3 Reagent Preparation

Rubeanic Acid

A 0.1% (w/v) rubeanic acid solution was made by adding 0.05g of dithiooxamide (Sigma Aldrich – 379387) to 50ml of absolute ethanol in a 100ml beaker and stirring until all the solid is fully dissolved.

4.2.4 Sample Treatment

After reviewing work previously undertaken involving rubeanic acid being utilised as a fingermark development reagent [150], the decision was made not to dip the samples into the solution of rubeanic acid but to spray them.

Ecospray Atomiser

The Ecospray Forensic Atomiser (Labo Chimie France) was the spray chosen for the distribution of the rubeanic acid, as it is able to produce a very fine mist [192] which allows for a more uniform coating when dispersing.

Gelatine Lifters

After the time allotted the chosen substrate was removed from the brass or copper plate (4.2.2 Substrate Preparation), a white gelatine lifter (BVDA – B155000) [140, 141] was then applied to the plate for a period of time up to five minutes. Once removed from the plate, the gel lifter was then treated with rubeanic acid solution and left to develop by drying in a drip tray. Treated samples were then recorded and the visualised marks were then graded. In instances where split trials were undertaken each half that had been treated was reunited with its partner and recombined by the use of tape on the underside. This allowed varying treatments to be directly compared on fingermarks with the same chemical composition, quantity of material and pressure at time of donation.

4.2.5 Sample Evaluation

The samples were examined, and the results graded. Each sample was evaluated and the methodology was amended for future experimentation.

Sample Grading

The visualised marks were graded using the “CAST” grading scale (Table 3, page 82).

4.2.6 Treated Sample Recording

Subsequent to being enhanced, the substrates were either photographed or scanned to record the enhancement. The photographs were taken using a Nikon D5200 digital SLR camera set to manual focus, and placed upon a tripod to keep movement to a minimum and the distance from the substrates consistent. The scanning was performed using an Epson Stylus Photo RX585 scanner. The samples were labelled using photographic twin check labels with the twinned label being logged with details of experimentation details, making it easier to correlate the experiment results with the particular images.

4.3 Results and Discussion

The theory behind this series of experiments was the hopes of exploiting the sodium chloride content in the sweat within the fingermark residues to cause a corrosive reaction on the surface of the metal it came in contact with. This would allow mobilised copper to be easily lifted *via* a sheet of gelatine.

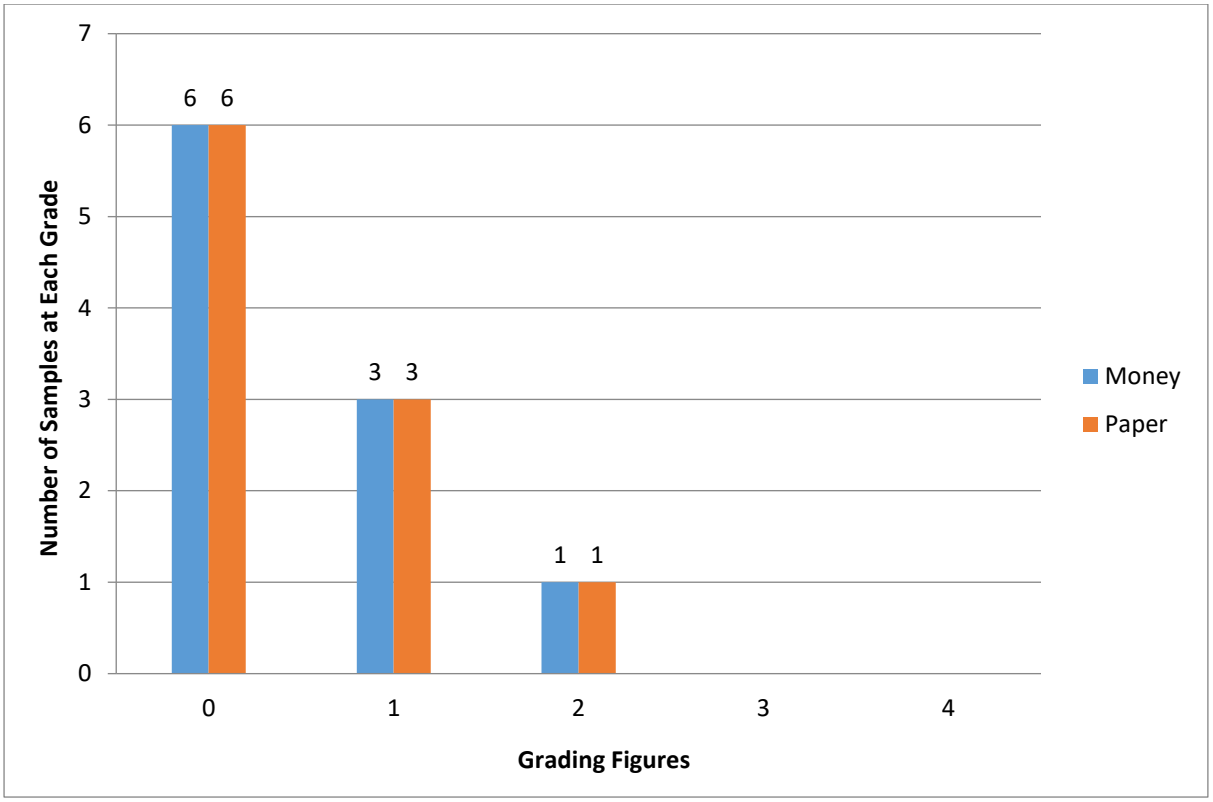
4.3.1 Initial Tests

Initially tests were conducted on paper (Polaroid 80gsm copier), paper banknotes (£1 Royal Bank of Scotland denomination) and a few fabrics (cotton, poly-cotton, nylon and two types of polyester) over the course of one month.

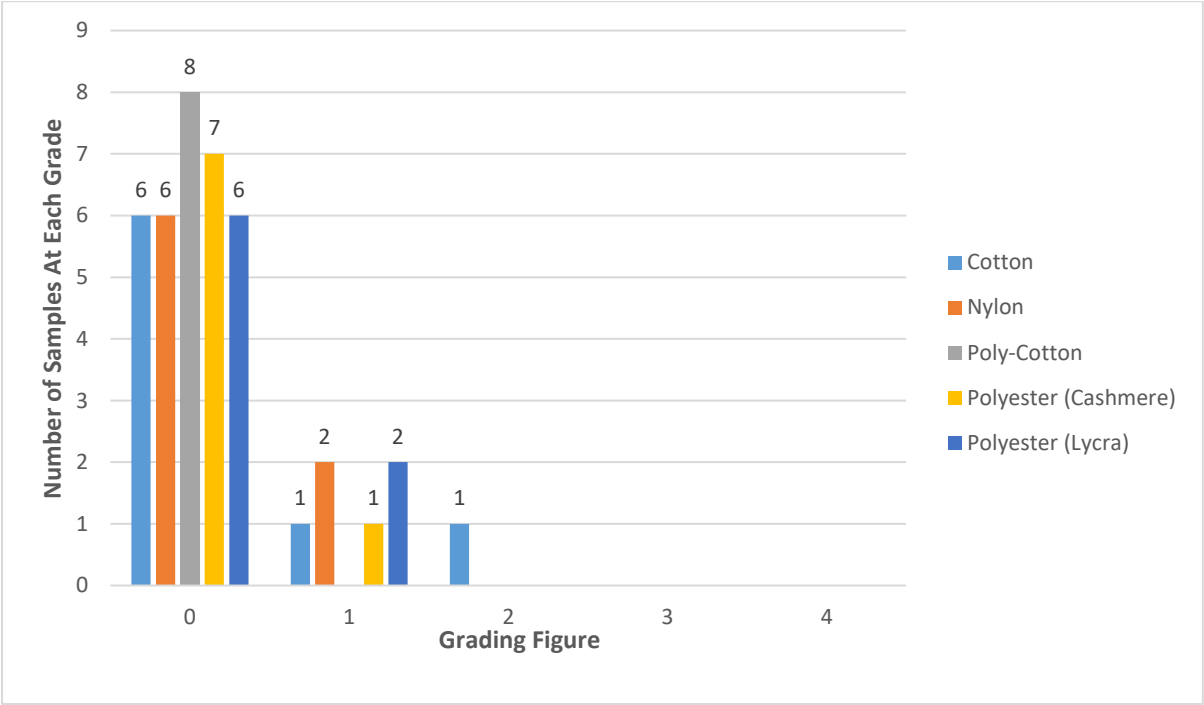
There were 60 total samples (10 paper, 10 money and 8 of each fabric) treated, the developed fingermarks were graded from 0 to 4 after a visual examination. Of the 60 samples, 20% were graded as a 1, 5% were graded 2, there were no samples graded at 3 or above, there was, however, a massive 75% that failed to develop any marks at all.

Of the paper type substrates both performed similarly; producing the same number of results in each grading category. A mere 10% of the substrates had enough ridge detail that might lead to an identification. 30% of the samples had unidentifiable marks and the other 60% did not have any development whatsoever (Graph 9).

The fabric samples performed in a similar manner to the paper substrates, producing mostly grade 0 results. The least successful fabric type was the poly-cotton, which delivered 100% grade 0 marks. Cotton was the only fabric that produced any marks above a grade 1, 12.5% in the grade 2 category (Graph 10).



Graph 9: Development Comparison Between paper and Paper Banknotes



Graph 10: Grading Figures per Fabric Type

Although some ridge detail was visible on the lift from the cotton substrate, it was overshadowed by the fabric's weave (Figure 71 and Figure 72).

Figure 71: Cotton Lift Weave within Ridge Detail

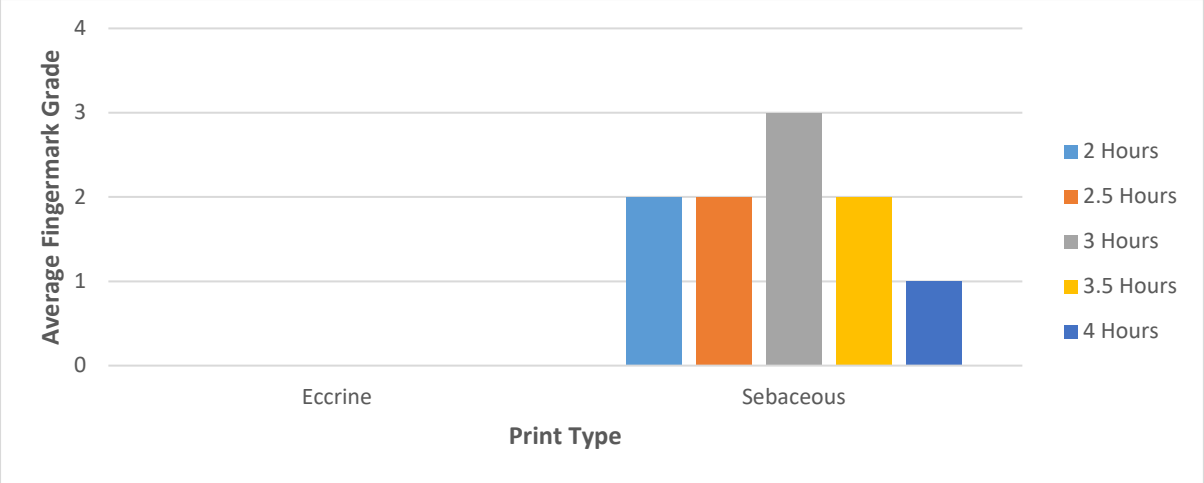
Figure 72: Cotton Lift Weave Pattern

Despite the poor performance on these porous type substrates, this technique did show potential. The information gathered from this series of experiments did allow for the experimental procedure to be adjusted.

4.3.2 Temperature Trial

The first variable to be adjusted was the temperature, paper samples were prepared in the same way as the previous experiments. Natural fingermarks were deposited on separate paper substrates and placed atop brass plates. Brass was chosen to test whether the alloy would perform in the same manner as the copper. The prepared substrates were placed in an oven at 70°C for time periods of 2 – 4 hours.

This experiment looked at five eccrine and five sebaceous samples; of these samples the sebaceous marks developed all samples to varying degrees, whereas the eccrine marks failed to develop any marks. The sebaceous marks developed 20% grade 1, 60% grade 2 and 20% grade 3 marks (Graph 11).



Graph 11: Metal Contact: Eccrine vs Sebaceous Deposits

The results gained from this trial were not as anticipated; the sodium chloride content in the eccrine mark was expected to react with the metal substrate, this however was not the case. This was perhaps due to the salt content diffusing too far into the substrate to make contact with the brass plate.

The sebaceous samples performed fairly well considering the eccrine marks failed to develop at all. Since the non-water-soluble components of fingermark residues stay on the surface of the porous substrate for a longer period than the water-soluble [46], it was theorised that one or more components of the sebaceous residues; glycerides, fatty acids and/or wax esters have reacted with the metal's surface to corrode and mobilise the copper ions in order for the rubeanic acid to detect it on the gel's surface.

The experiment was repeated under the same conditions, and the results were consistent with the previous experiment.

4.3.3 Eccrine Trial

To test whether the eccrine deposits were too far diffused in to the paper substrates to work, a test was set up using acetate as the substrate. Eccrine rich fingermarks were placed on the acetate surface and a brass plate applied to the surface. To this a weight was placed atop and the whole construct was left for two days. After removal of the brass plate, a section of forensic gel lifter was applied to it and left for two minutes. Once the gel was lifted, it was sprayed with rubeanic acid and left to develop. Unfortunately, nothing developed. The hope was that there would be at least a faint fingermark visible, as with when the mark was applied directly to the brass. This could have been due to an insufficient amount of eccrine deposits present.

The hope was that with enough eccrine material, fingermarks could be lifted from paper substrates. With this in mind, the initial experiment was attempted again. To obtain fingermarks with sufficient eccrine material, the hands were washed then immediately placed in latex gloves. The hands remained in the gloves for thirty minutes, the fingermarks were deposited once the gloves were removed. The hands at this point were completely soaked in sweat. The marks were deposited and brass plates affixed, then a weight laid on top for 24 – 96 hours.

Four samples were treated after 24 hours, by removing the paper substrate from the brass and applying a gel lifter for two minutes. After two minutes, the gel lifter was treated with rubeanic acid and left to develop. These four samples failed to develop any fingermark details at all. The four samples weighted down for ninety-six hours were treated in the same fashion as the twenty-four hour samples. Of the four gels treated, only three showed any signs of a transfer, and of those three only one showed any sign of ridge detail. The detail was faint, the ridges were broken and overall the mark would be useless as evidence.

Despite knowing that eccrine marks *can* develop marks *via* gels and rubeanic acid [221], it did not seem possible to coax fingermarks into transferring *via* a porous substrate. This is most likely due to the fact that the component or components responsible for mobilising the copper ions diffuse too far into the porous substrate.

4.3.4 Polymer Banknote Trial

With the introduction of polymer banknotes in the UK; Scotland (2015) and England/Wales (2016), the focus was moved to encompass a similar type substrate. A Vietnamese polymer note (10,000 Dong denomination) was chosen due to its similar characteristics (Figure 73).

Figure 73: Vietnamese 10,000 Dong

Initial tests on the polymer note using the transfer method detailed previously yielded promising results. The experiment was set up in the same manner as had been used with paper substrates. After spraying the gel which had been in contact with the brass plate (for two days), a number of enhanced fingermarks were visible (Figure 74). The quality of the marks enhanced varied throughout. Some marks were overloaded and ridges were leaching together (here), others showed excellent ridge detail albeit faint (Figure 75).

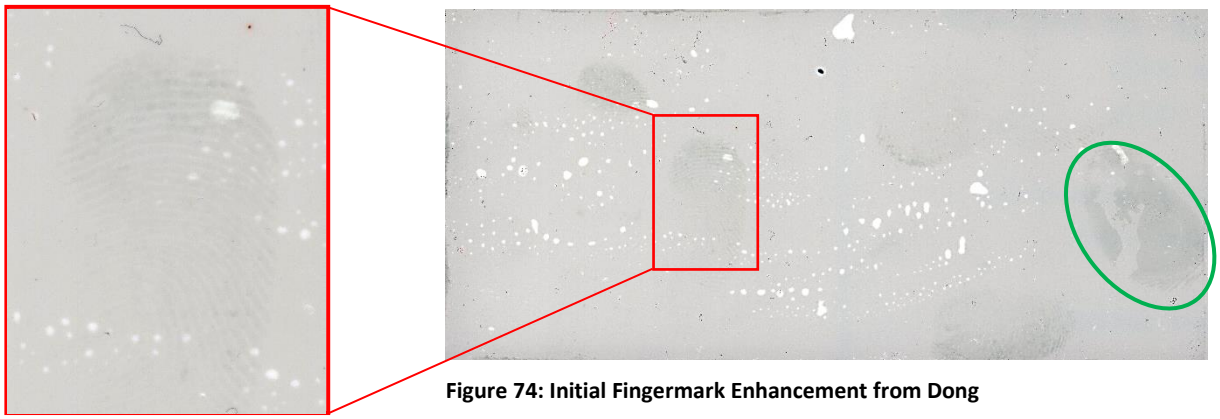


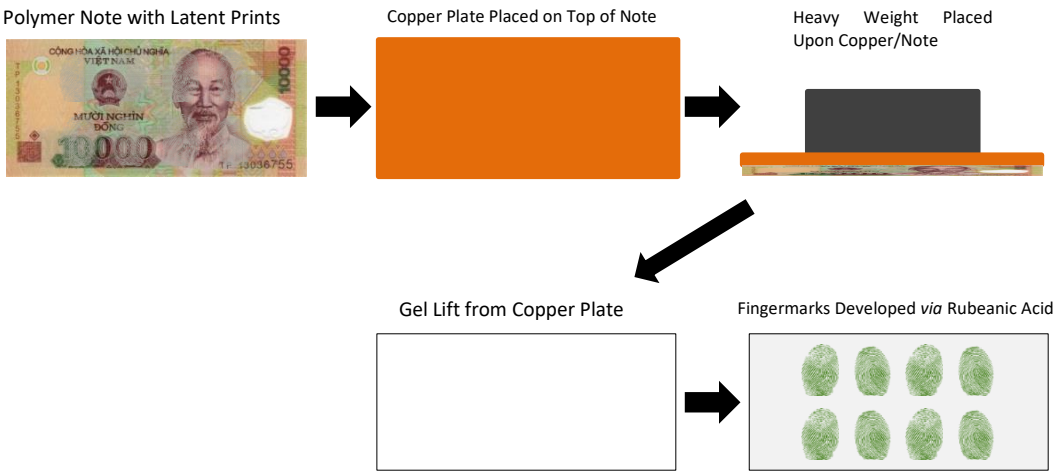
Figure 74: Initial Fingermark Enhancement from Dong

Figure 75: Enhanced Section

The results gained from this experiment were promising, so the technique was repeated a number of times to try to gain the best quality results. After many trials, the process was giving good quality results with both brass and copper plates. The technique was conducted in the same manner as before; natural fingermarks were deposited in two rows across the face of the polymer note, four in each row, and eight marks in total. A copper plate was placed over one row and a brass plate over the other (Figure 76). This was repeated on the back of the note, and a weight placed atop the whole construct for up to forty-eight hours.

Figure 76: Copper/Brass Transfer from Vietnamese Dong

After twenty-four hours, the plates from one side of the note were removed and forensic gel lifters applied to the metal's surface. The gel was removed after two minutes and sprayed with rubeanic acid, then left to develop. This was later repeated for the metal plates left in contact with the polymer note for forty-eight hours (Scheme 2).



Scheme 2: Process of Treatments Used on Paper and Polymer Banknotes

<u>24 Hours</u>

The gel lift from the copper plate exhibited good development, some of the ridges were showing signs of ridge leaching. Other areas of the marks had haloes where air bubbles had formed when the gel was placed on the plate (Figure 77). The lift from the brass plate looked very similar, however, the ridges looked slightly fainter. The detail was still of very good quality (Figure 78).

Figure 77: Copper Plate 24 Hours

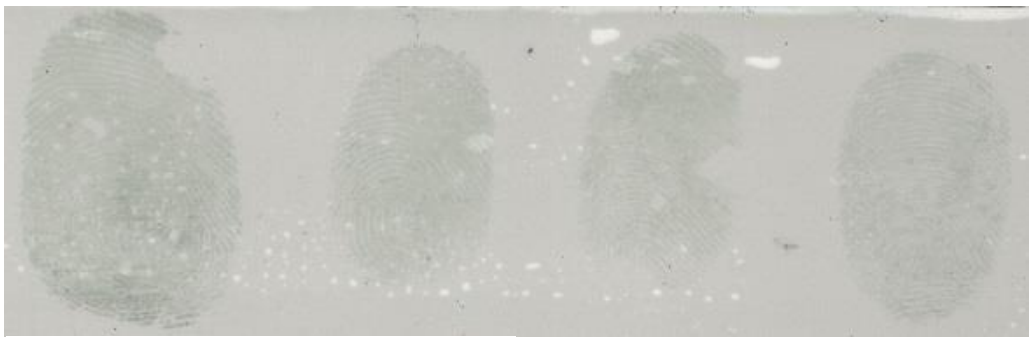


Figure 78: Brass Plate 24 Hours

48 Hours

The gel lift from the copper plate showed some development, some of the ridge detail were visible. Where the ridges were not faint, they were fragmented. Some fingermarks were showing haloes where text from the polymer note had failed to take the fingermark. A few of the developed marks were showing some spotty contamination throughout the fingermark (Figure 79). The lift from the brass plate showed, this time, darker ridges; however, these marks also showed haloes where the mark from the note had come through (Figure 80).

Figure 79: Copper Plate 48 Hours

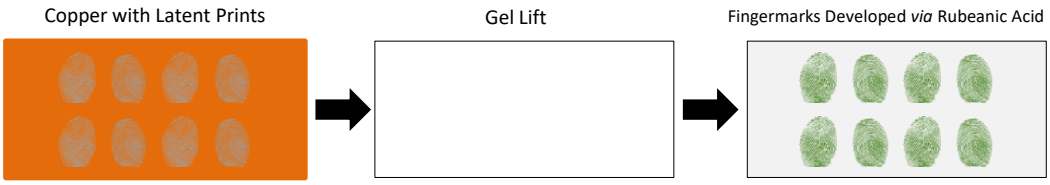
Figure 80: Brass Plate 48 Hours

Although the ridge detail obtained from these lifts is good, the text transfer is an issue. This is most likely due to the note being in contact with the metal plate for too long, as imprint was also on the metal plate. Reducing the contact time from 48 hours to somewhere in between 24 and 48 hours would most likely eliminate this issue.

4.3.5 Direct Lifts from Metal

In order to check whether eccrine deposits can produce good quality marks when utilising copper or one of its alloys with rubeanic acid, a new experimental procedure was set out based on work being conducted by a colleague who was utilising rubeanic acid to investigate Heritage Crime [221]. The procedure involved fingermarks being directly deposited on to metal surfaces.

A number of sections of brass were cut to 3cm x 3cm squares, big enough for a single fingermark to be deposited. A number of these squares had eccrine fingermark deposited upon them, and others had sebaceous rich fingermarks placed on them. These squares were left over the course of a weekend (Fri-Mon), before being treated (Scheme 3).



Scheme 3: Process of Treatments Used on Cupric Surfaces

The samples were treated by applying forensic gel lifters, cut to size, to the brass surface for two – five minutes. The gel was then sprayed with rubeanic acid and left to develop. The sebaceous sample produced a full fingermark with rich, dark ridges, however, the eccrine marks contained haloes, were fainter, and the ridges were more broken and fragmented (Figure 81). Since the quality of the marks are different depending on the type of mark, this may be a factor of how the eccrine deposit reacts with the metal substrate. This may explain why the eccrine fingermarks on the paper failed to react as well as the sebaceous marks.

The gels which had been in contact with the brass for five minutes exhibited a higher degree of background staining than the gels left in contact with the metal for two minutes (Figure 82).

Figure 81: Lift from Brass - 5 Minutes

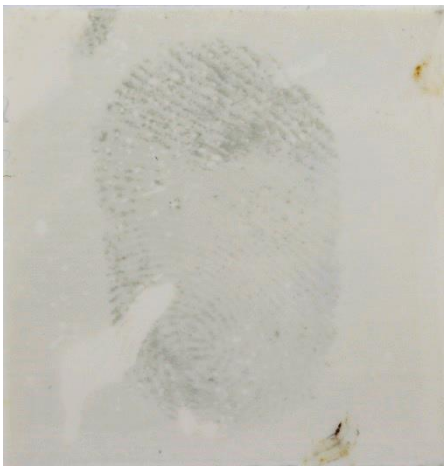


Figure 82: Lift from Brass - 2 Minutes

4.3.6 Optimisation Trials

In order to recover a fingermark with the best contrast between the copper rubeanate and the gelatine lifter being used, the optimum amount of time the gelatine lifter needed to be in contact with the fingermark residue coated copper had to be found. In order to ascertain this, a series of experiments were conducted involving depositing a number of fingermarks on pieces of copper and brass, then subsequently applying a piece of gelatine to the metal in order to lift the fingermark for development. These experiments were again a collaboration with Richard Wilson as part of his Heritage Crime project [221].

Eight samples each of copper and brass were cut to size to allow a single fingermark to be deposited upon them. Natural fingermarks were deposited upon the samples, the samples were subsequently placed in a desiccator for 24 hours. Once removed from the desiccator all the samples had a gel, cut to size, applied to their surface, the gel was left in place between 30 seconds and 30 minutes. Once removed, the gels were sprayed with rubeanic acid and allowed to develop (Figure 83).

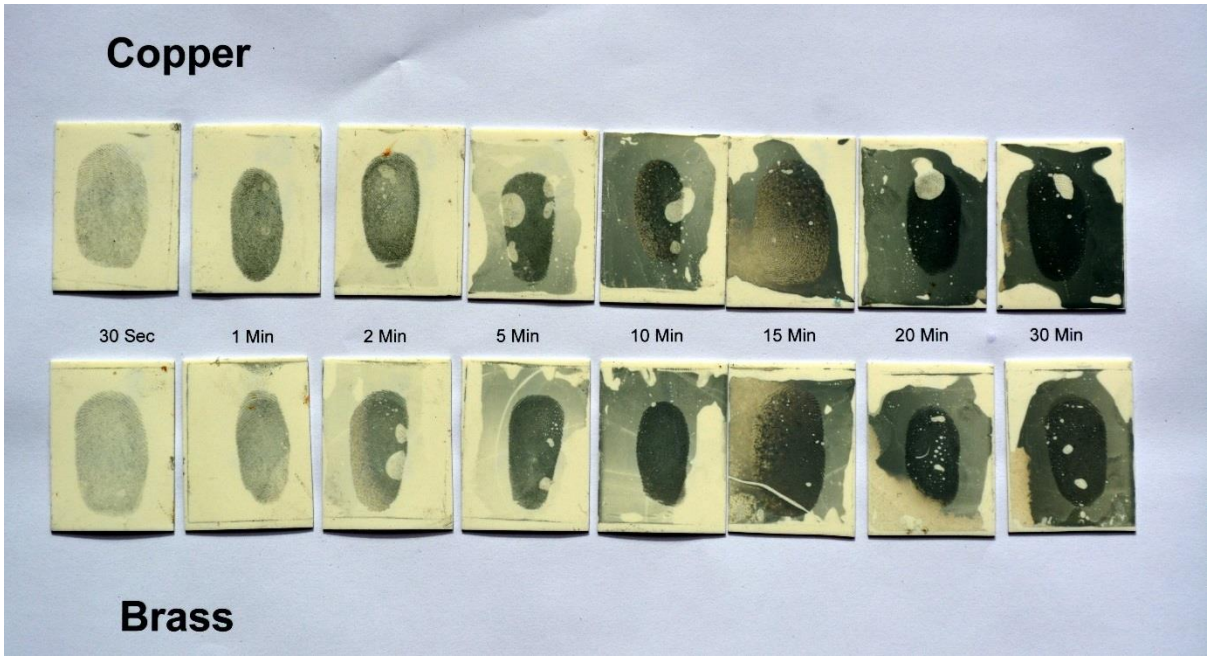


Figure 83: Copper/Brass Optimisation *via* Time

The copper and brass have performed almost identically, meaning that the amount of copper within the brass is sufficient enough to promote the polymerisation of copper rubeanate. As can be observed, the fingermark ridges become darker as the contact time increases, however, this is also true in regards to the background staining. While at the 5 minute mark it is a minor annoyance which only slightly hampers the contrast between the gel and the fingermark ridges, by the time the 30 minute mark is reached it almost completely obscures the fingermark ridges.

4.3.7 Direct Lifts from Metal Part 2

A split comparison trail was designed to compare the effects of desiccation directly against ambient conditions. Three copper plates were placed in a desiccator for 24 hours. After 24 hours, the plates were removed; one section had a gel lifter applied immediately after removal from the desiccator, one section was left in the desiccator for a further 24 hours before being removed and gel lifted. The final section was left in the open ambient laboratory atmosphere for an additional 24 hours before having the gel lifter applied (Scheme 4). The gels were applied for up to 2 minutes, and subsequently treated with rubeanic acid and left to develop before being photographed.

On occasion the results gained showed a minimal difference between the results obtained using the desiccator and those gained when metal was left in the ambient environment of the laboratory. The contrast between sections B and A is visibly improved. Section C marks show some pore detail over and above their section B counterparts (Figure 84). This would confirm that the desiccation of the samples can help improve the quality of the fingermarks recovered from the copper substrate. The colour of the fingermark ridges on section A differs from those of sections B & C, this was thought to be due to the fact that it was left after treatment for 24 hours prior to being photographed.

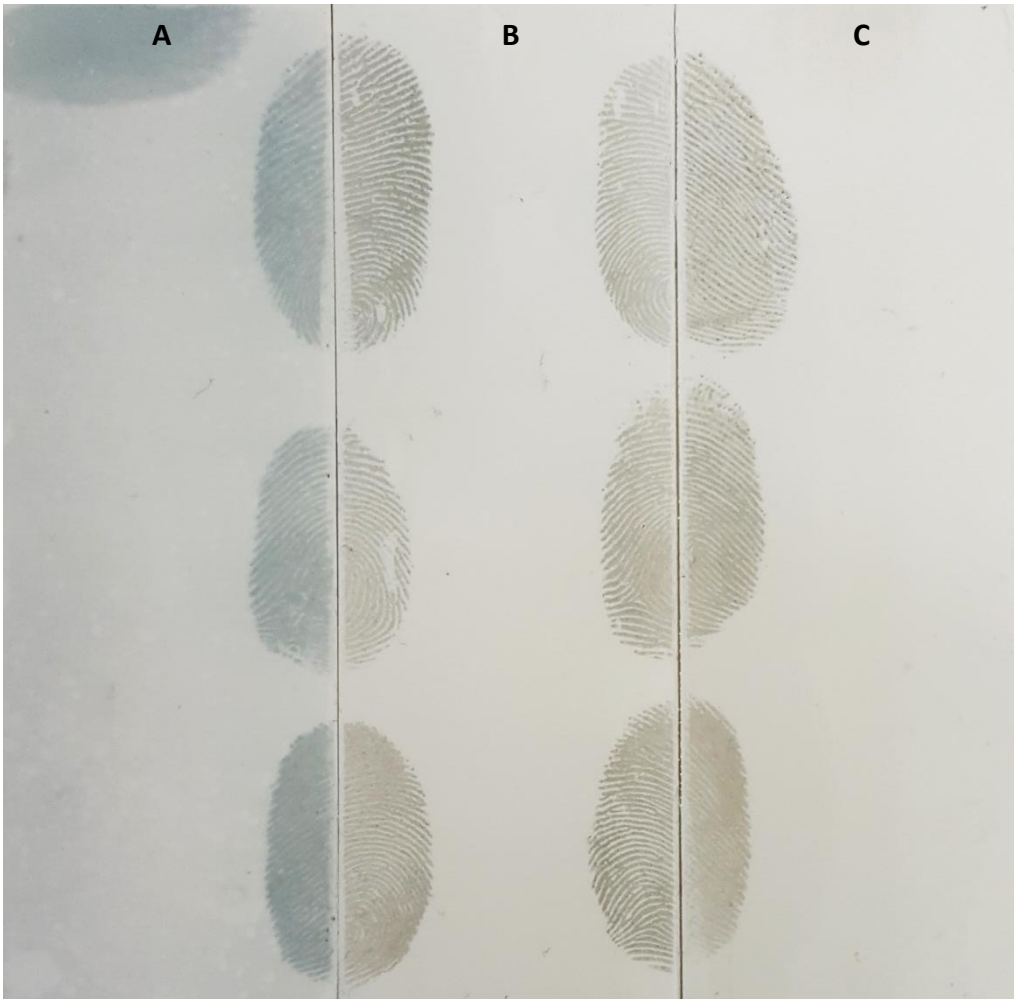
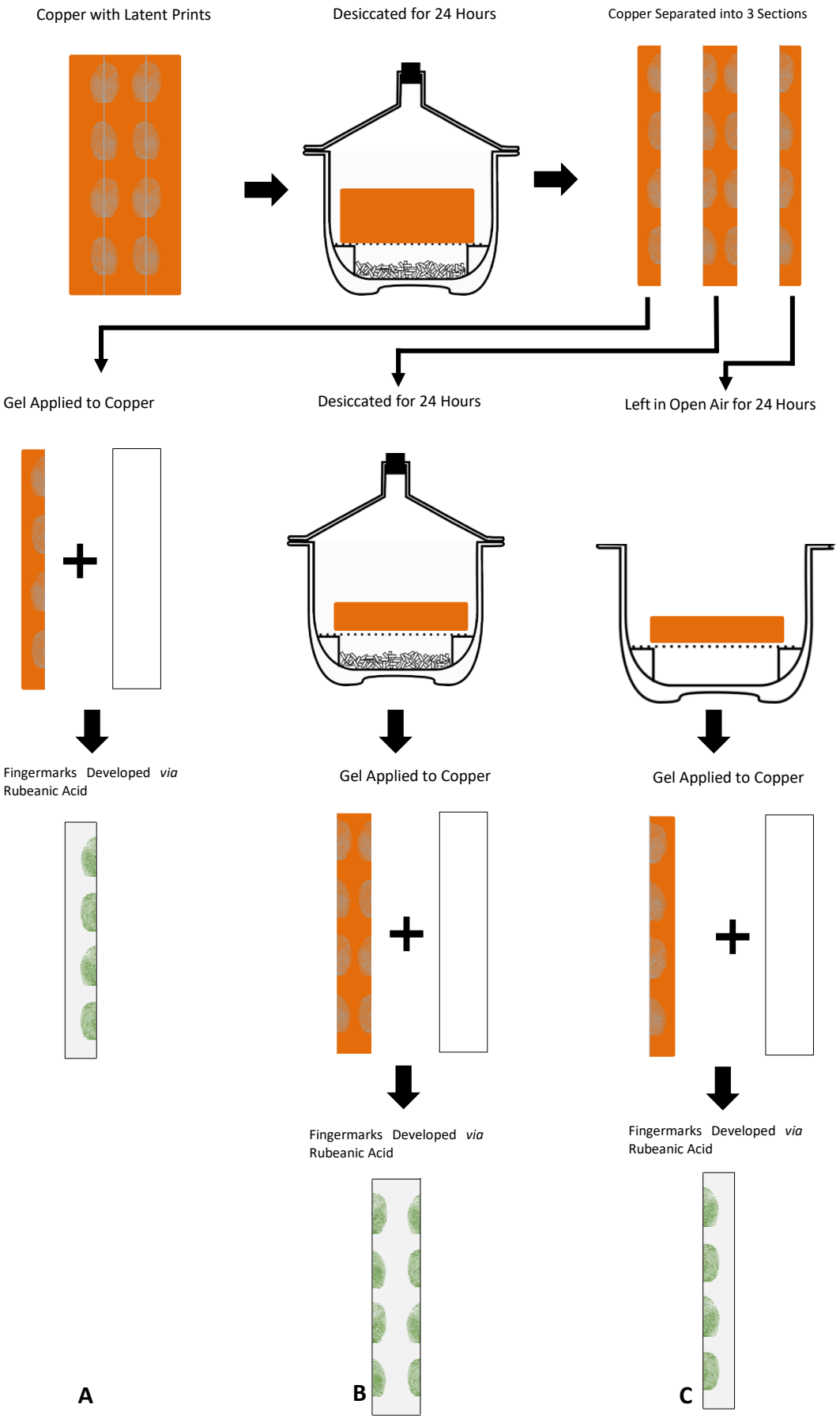


Figure 84: Split Fingermarks Treated *via* Gel Lift and Rubeanic Acid; A) Lift after 24 Hours in Desiccator, B) Lift after 24 Hours in Desiccator and 24 Hours in Open Air, and C) Gel Lift after 48 Hours in Desiccator



Scheme 4: Process of Treatments Used on Cupric Surfaces (Desiccated *vs*. Ambient Air)

4.3.8 Alternate Methodologies

A series of experiments were designed to see whether the gel lifting from the metal plate was necessary or not. This was done by eliminating and rearranging certain steps at certain points in the procedure, such as removing the gel lifting portion of the process.

Method 1

A polymer banknote had a series of fingermarks deposited over its surface, in the same manner as previously described. A brass plate was brought into contact with the polymer note and weighed down for forty-eight hours. Once removed the brass plate was sprayed directly with rubeanic acid to see if the fingermarks would react. Unfortunately, the rubeanic acid began to pool over the surface of the plate, but once it had dried, faint ridge detail could be observed (Appendix Figure 162). However, this might just have been some surface corrosion that had started to develop. As an addendum experiment, a section of forensic lifting gel was applied to the area of the polymer note where the brass plate had been in contact. The gel was applied for two minutes the removed and sprayed with rubeanic acid. The gel developed some dark marks that had some broken ridge detail within them (Appendix Figure 163). The developed gel, however, was in no way comparable to the alternate method.

Method 2

Another experiment was set up to see if the metal plate *had* to be in contact with the polymer note in order to develop the fingermarks. Fingermarks were deposited on the polymer note, instead of bringing the note into contact with the metal plate, it had a gel lifter applied to it instead. The gel was in place for twenty-four hours before being removed. Since the rubeanic acid requires copper ions to develop, the gel was brought into contact with a brass plate. The plate and gel were touching for thirty minutes before the gel was removed and sprayed with rubeanic acid. The reaction happened almost immediately, where the gel began to turn very dark. Once the gel had dried and was able to be examined, a few ridges could be seen, but only a fraction of what had been deposited (Appendix Figure 164). More noticeable was an inverted "100" which was an imprint from the numbers on the Vietnamese 10,000 Dong note. The ridges that were visible appeared to be like haloes in the stained background. With the gel background staining so excessively, it was obvious that thirty minutes is far too long for the gel to be in contact with the copper or brass surface. The brass plate that had been in contact with the gel for thirty minutes had, when tilted at an oblique angle, a corresponding "100" imprinted on its surface. A second gel lift was taken directly from the plate, with the gel being in contact for only two minutes. Once sprayed the second gel lift revealed absolutely nothing, so the brass plate was sprayed again to see if that would help promote any development. Only the "100" and a few faint fingermarks were visible. One fingermark had some good ridge detail within it, but again, in comparison to what was deposited, the return was poor.

4.3.9 Reuse of Metal Plates

Experiments were conducted to explore whether or not the brass or copper plates could be reused.

Method 1

Sebum rich fingermarks were deposited on to the surface of a polymer banknote, a brass plate was placed on top of it, weighted down and left for forty-eight hours. After that period of time, the plate was removed from the polymer note, a gel lifter was applied to it for two minutes, after which the gel was sprayed with rubeanic acid. The developed marks ranged in quality, some had broken ridges, one had an air bubble from when the gel was applied to the plate, and another had leached ridges. However, from the features that did develop, you can see some pore detail within the ridges (Figure 85).

Figure 85: 1st Gel Lift from Polymer Note *via* Brass Plate

After the gel lift had been completed, sebum rich marks were once again deposited on a clean polymer note. The brass plate was washed first with soap and water, then rubbed down with ethanol. It was then scoured with soap and water again to make sure it was clean. The experimental procedure was repeated as outlined above. Once sprayed with rubeanic acid, the resulting developed marks were examined. Fingermarks could be easily observed, however, upon closer inspection, they looked to have a ghosting effect to them. This meant that any ridges observed were hard to differentiate with the second set or fingermarks. There was also some mark transferred from the note visible within some of the marks which hampered quality (Figure 86).

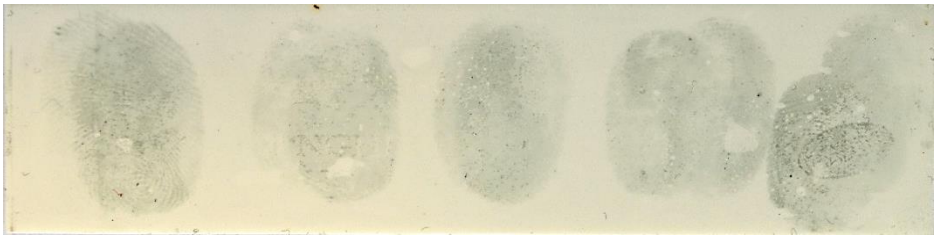


Figure 86: 2nd Gel Lift from Polymer Note *via* Brass Plate

It appears, despite rigorous washing numerous times, that the brass retained the previous set of marks, which ended up being superimposed on the new set of marks. This lead to the conclusion that the recycling of the metals in this manner was not advisable, if good quality marks were a priority.

Method 2

Another attempt was made to clean the surface of the copper plates using the Brasso [222] brand of metal polish (Figure 87). This experiment initially involved taking lifts direct from copper plates before moving on to lifting using the transfer method.

Figure 87: Brasso Metal Polish

Two pieces of copper which had previously been used to lift split fingermarks (Figure 88) were subjected to a rigorous clean using the Brasso and cotton wool. The cleaning regime left the copper completely free of visible fingermarks and other blemishes, and to a high shine (Figure 89). Further polishing with a clean cloth was performed to remove any excess residues. Brasso contains a very fine abrasive powder in a liquid solution containing NH_4OH [222]. The cleaning process works by forming ammonia complexes with the oxidation material, the abrasive additive removes this material easier than it would the pure corrosion, finally a water soluble oil fills in the micro scratches to prevent oxidation from beginning immediately after cleaning.

Figure 88: Used Copper with Fingermarks

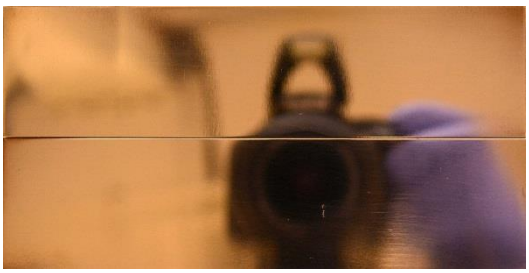


Figure 89: Used Copper after Cleaning

The two pieces were then placed side-by-side and secured using tape on their underside. Fingermarks were then deposited along the split and the tape removed. One half was left in the open air laboratory environment and the other half was left in a desiccator, both were left for 48 hours. After the 48 hours had elapsed, the pieces of copper had a gel lifting sheet, cut to the same size as the copper plate, applied to their surface for 2 minutes. Once removed, the gel was sprayed with rubeanic acid and left to develop.

The developed gels had visible fingermarks from only one set of deposits, unlike the previous attempt. Some background staining was visible on both halves, however, this was more prominent on the half which had been left in the open air environment. The staining did not hamper the quality of the developed marks (Figure 90).

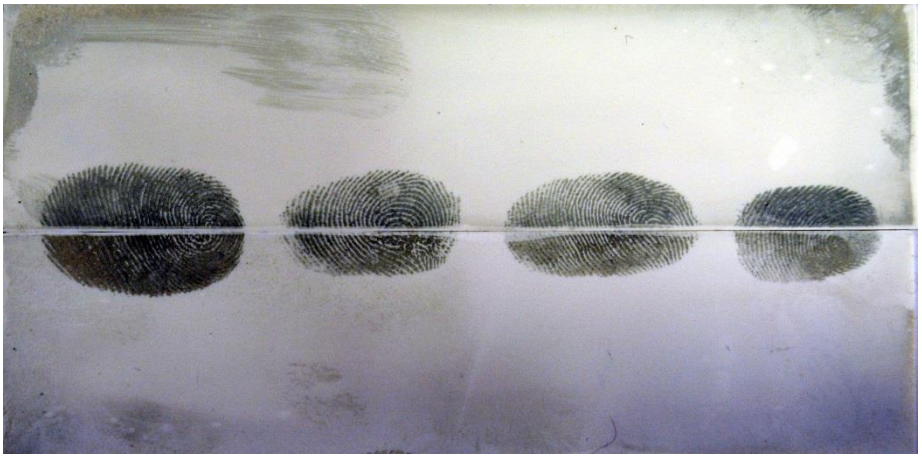


Figure 90: Gel Lift from Copper 2nd Use after 1st Clean

The copper plates were cleaned again and the same process of depositing, storing, lifting, and developing were employed again, with the desiccation time reduced to 24 hours. Again, the treated gels showed only one set of fingermarks as having been developed (Figure 91). However, the background staining was more intense on both halves of the gels. The recovered fingermarks appear darker on the gel which was lifted from the half of copper which was desiccated, that being said, the developed fingermarks were less prominent across the board than the previous marks developed after cleaning the copper with Brasso. Meaning, that it could be possible that the more the metal is cleaned using the Brasso metal polish, the less defined the developed fingermarks will be.

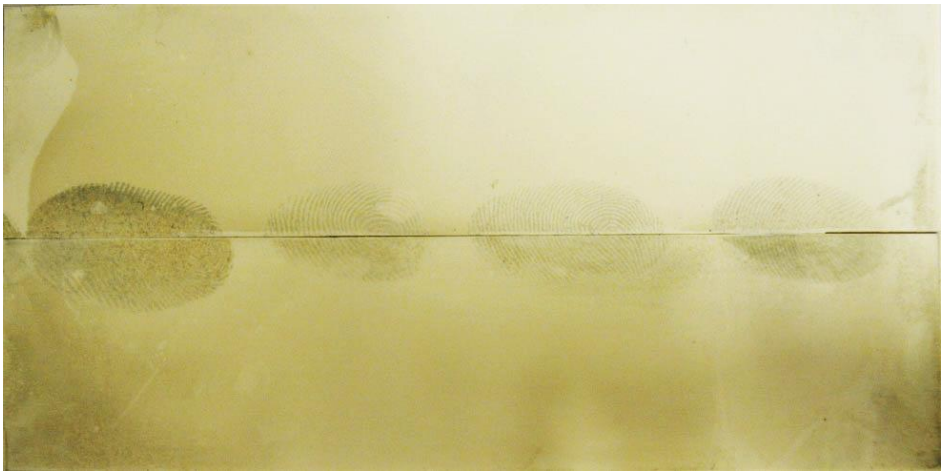


Figure 91: Gel Lift from Copper 3rd Use after 2nd Clean*

The copper was cleaned again, and the process repeated. As witnessed previously, only one set of fingermarks were present, and again they were fainter than previously obtained. The marks on the open air sample have little in the way of ridge detail visible, conversely the desiccated sample again, shows darker ridges. Additionally, background staining can be observed as being more severe than in the previous two attempts (Figure 92).

* Colour difference due to sample being photographed under fluorescent lighting rather than with the camera flash.

Figure 92: Gel Lift from Copper 4th Use after 3rd Clean

The cleaning protocol was employed for a 4th clean, this meant the copper was being utilised for the 5th time. A few of the parameters were adjusted to try and combat both the faintness of the developed marks and the intensity of the background staining. In order to achieve this, the fingermark laden copper plates were left in the open environment and in the desiccator for 48 hours, back up from the previous 24 hours in the hopes that the additional time would allow darker marks to be developed. When applying the gel sheets to the copper, they were left applied for 1 minute, down from the previous 2 minutes.

The adjustments appear to have made a difference as fingermarks are visible on both gel halves. Although friction ridge detail can be observed on both samples, the gel sample containing the fingermarks lifted from the half which was desiccated are, again, darker than its counterpart. The background staining on the 'open air' sample was again darker than the sample from the desiccator (Figure 93).

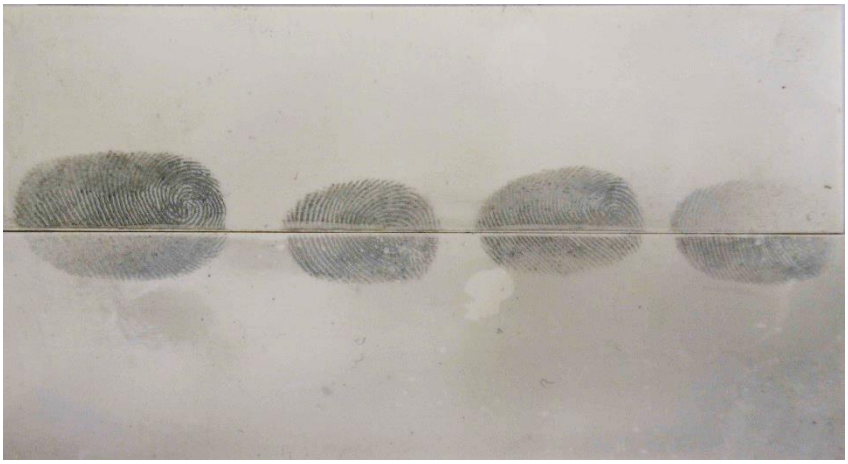


Figure 93: Gel Lift from Copper 5th Use after 4th Clean

The copper plates were cleaned once again (5th clean) and reused for a 6th time. The amended parameters used with the previous attempt were employed again for this trail. The gel lifts continued the patterns witnessed with the previous experiments using these protocols (Figure 94). Reusing the same piece of metal 6 times seemed ample to demonstrate the Brasso's ability to clean the metal well enough to effectively remove previously deposited marks. This technique is not without issues though, as it appears using the Brasso also hastens the ability to develop background staining.

Figure 94: Gel Lift from Copper 6th Use after 5th Clean

4.3.10 Fingermark Transfer *via* Copper from Non-Porous Substrates

Acetate sheets and glass were also tried using the metal transfer method, both substrates were examples of everyday non-porous substrates which contrasted the paper (porous) and the polymer banknote (semi- and non-porous combination) already trialled. The same protocol as was used before was utilised, with sebaceous and natural fingermarks being deposited. Samples spent 48 hours in a desiccator before being brought into contact with elemental copper for a further 48 hours before being lifted and treated.

The results gained from these substrates were mixed, with the sebaceous marks developing the better quality fingermarks, as previously witnessed. The fingermark ridges gained from both substrates appeared broken and fragmented in places, however, those gained from the glass (Figure 95) were superior to those obtained from the acetate (Figure 96).

Figure 95: Fingermarks Lifted from Glass *via* Copper

Figure 96: Fingermarks Lifted from Acetate *via* Copper

After the initial lifts, the copper plates which had been in contact with the sample substrates were placed back into the desiccator for a further 48 hours. A second lift was performed on the copper samples upon removal from the desiccator. Few of these lifts developed any fingermark detail, but those that did had fainter ridges. It is not known at this time whether some fingermark residues were left behind after the initial lift or if the surface corrosion was sufficient enough that the initial lift left some behind for the second lift to pick up. The lift from the glass sample showed the best quality ridges after the second lift (Figure 97).

Figure 97: 2nd Lift from Glass *via* Copper

The same experiment was repeated using all the same parameters with the exception of not placing the sample substrates in the desiccator prior to applying the copper plate. The samples were again secured to the elemental copper for 48 hours before being lifted and treated.

Again results gained from these substrates were varied and the sebaceous marks were darker and better contrasted than the natural fingermarks. There was some ridge detail visible, but little more than would allow the visualisation of ridge flow as opposed to individual minutiae. This time the acetate (Figure 98) developed marks of a higher quality than the glass.

Figure 98: Fingermarks Transferred to Copper *via* Acetate

Brasso was used to clean the surface of previously used copper and the same experiment was repeated using the cleaned copper plate. Natural and sebaceous fingermarks were used on the substrates, the substrates were immediately brought into contact with the copper plates before having a weight placed upon them. The weight was left for 24 hours and once removed the copper plates were separated from the sample substrates before either being left in the open air, or placed in a desiccator. After 24 hours gel lifters were used to lift from the copper plates.

Some of the results obtained through this experiment show that the desiccation of samples does not always improve the fingermarks recovered (Figure 99 and Figure 100).

Figure 99: Gel Lift from Acetate Left in Ambient Conditions *via* Copper

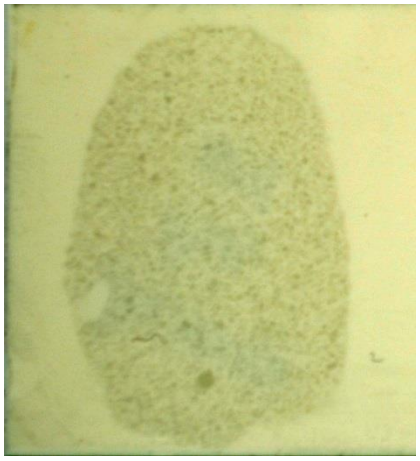


Figure 100: Gel Lift from Acetate *via* Copper Left in Desiccator

4.4 Conclusions

Initial tests conducted on copier paper and banknotes were only partially successful in transferring fingermarks to copper and brass substrates in order to be lifted with gels and imaged *via* the use of rubeanic acid. These porous substrates only managed to develop 10% of the marks treated to a level where ridge detail could be observed. The same experimentation was attempted with five different fabric types, these results were similar, with only 12.5% of the marks treated reaching a grade where ridge detail was observed.

Additional experimentation revealed that fingermarks with purely eccrine content had trouble transferring from the paper substrates to the metal surface, a problem that sebaceous rich marks did not encounter. The paper contact experiment was repeated with both eccrine and natural fingermark deposit, as it was surmised that the sodium chloride content in eccrine marks should elicit a corrosive reaction from the metal's surface. This however, was not the case. It was assumed that the eccrine mark's failure to interact with the metal surface whilst on paper was due to it having diffused too far in to the substrate to make contact with the metal to initiate any reaction with the copper.

The same experimentation conducted on the surface of a semi-porous polymer banknote were much more successful. Utilising the same protocol as used with the previous substrates, the developed fingermarks were of a grade where they could be easily identified in an operational setting.

Temperature was explored as a development factor, with copper samples with fingermarks deposited upon their surface being heated in an over at 70°C. The eccrine marks still failed to provide any useable marks, however the natural marks were better quality than when the oven was not used. The heat definitely helped improve the quality of the marks over what had been achieved prior to this step.

Since the eccrine deposits were failing to be transferred from the paper substrates to the copper, direct lifts were conducted to ensure that the eccrine marks *could* be lifted as well as marks containing sebaceous material. Having been left in ambient conditions for a few days, the eccrine marks did indeed develop, however, they provided fainter less defined marks than the natural fingermarks developed at the same time. It appears that even although the materials contained in the eccrine residues, most likely the chlorides, are reacting with the copper to oxidise it, it is not being as readily oxidised as it is with the materials within the sebaceous deposits.

In order to improve the quality of the fingermarks recovered from directly lifting from copper, an optimisation trial was undertaken. The trial demonstrated that the contact time with the gel lifter was paramount if background interference and poor contrast were to be avoided.

To show the difference in the quality of fingermarks lifted from copper after being left in different environments, a triple split experiment was conducted. Three lengths of copper were placed next to each other length ways and two rows of fingermarks were deposited down each of the two joins. The three separate copper lengths were initially kept under three different environmental conditions including desiccated and ambient. The experiment showed that drying the marks out appears to improve the darkness of the fingermark ridges developed over and above not drying them out.

Alternate methods were explored for the recovery of fingermarks using copper and rubeanic acid. The first of which was to explore if the gel lifter *had* to be applied to the copper plate, or if ridge detail could be enhanced directly on the copper surface. Rubeanic acid was sprayed directly on to the copper after it had been brought into contact with fingermark residues on a polymer banknote. This failed due to the rubeanic reacting with the entire area of copper as opposed to the areas of fingermark ridge detail. Direct lifts from the polymer banknote proved more successful, proving that small amounts of copper transfer into the fingermark residues. The results gained using this method were far inferior to when the gel is applied to the copper plate in order to lift. Finally, an attempt was made to develop fingermarks by lifting mark residues directly from the surface of a polymer banknote using lifting gels. The gel was then placed on copper in an attempt to coax copper ions into the residues on the gel. Unfortunately this was unsuccessful due to the gel absorbing copper across its entire surface, much the same as when heavy background staining is observed.

A method for reusing the copper plates was investigated in the hopes of cutting down on the consumable materials being used. A washing protocol was employed in the first instance, however, despite the copper looking clean and free from fingermarks on a second use the lifts from the copper plates showed a ghosting effect with the fingermarks. The metal cleaning product Brasso was attempted next, and was able to bring the copper plate back to a bright shine. The only drawback was, that as the number of times the copper was cleaned increased, the background staining also increased. The same piece of copper was used six times to recover fingermarks, this was deemed sufficient enough to show that the process was a success.

Since fingermark residues have been able to be transferred from paper and polymer banknotes to copper plates, other substrates were attempted. Glass and acetate were chosen as non-porous alternates to the porous and semi-/non-porous substrates already used. Both substrates had varied results, and through this series of experiments it was observed that the desiccation process does not always improve the quality of the fingermarks recovered when lifting.

This technique shows much promise and is an excellent example of a non-invasive, non-destructive fingermark enhancement procedure. Once perfected this technique could be used to develop fingermarks on items of either great value or of historical importance without causing them any damage.

5.0 Vacuum Metal Deposition

5.1 Introduction

The vacuum metal deposition technique, normally produces what are referred to as negative marks. This occurs due to the zinc not being able to be deposited on areas of the substrate where fingermark residues are located, but only on areas where the precursor gold has been deposited. When gold is evaporated and deposited upon a substrate containing fingermarks, the gold coats the surface almost uniformly with a coating which is nanometres thick. The exception is the area where the fingermark is situated; the gold diffuses into the fats from the residues, leaving no nuclei near the surface, as a result when zinc is subsequently deposited it condenses on the areas where the gold nuclei are deposited and ignores the areas where the fingermark ridges are situated (Figure 101) [88].

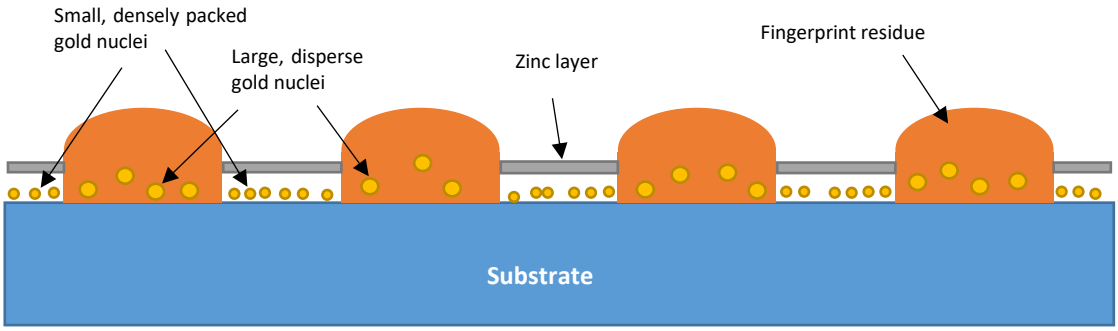


Figure 101: Gold/Zinc Schematic Diagram of Normal VMD Development (Adapted from Philipson & Bleay)

A phenomenon known as reverse development occurs when the zinc deposits onto the fingermark ridges and not onto the background. This has been reported by a number of authors, although its exact cause was a mystery to them [223-225]. It was not until Jones *et al*. conducted extensive studies into the VMD development of latent fingermarks on various polymer substrates [226-229], that they were able to conclude that reverse development only occurred on certain polymer types, such as low-density polyethylene (LDPE), and only under certain VMD conditions. The VMD development quality was found to be dependent largely on both the polymer type as well as the amount of gold deposited on the initial step of the gold/zinc VMD process.

Therefore, the amount of gold being deposited needs to be accurately controlled, however, despite this, no one set of VMD conditions results in good quality fingermark development in all situations [72]. Jones and co-workers confirmed that cyanoacrylate fuming (CAF) was an effective pre-treatment which improved the quality of VMD development [230-232], particularly beneficial on certain polymer types; polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Jones *et al*. developed guidelines for optimising the VMD development of latent fingermarks on polymer substrates [226].

VMD was found to develop ridge detail where other techniques had failed. In 1992 while working with The Royal Canadian Mounted Police, Misner compared the performance of CAF and VMD for detecting latent marks on LDPE. Although the sample size employed was relatively small, the study suggested that vacuum metal deposition was the more sensitive fingermark detection technique, this was particularly notable with older marks; 79% success rate for VMD versus 62% for CAF [233]. Masters and DeHaan (1996) completed a study comparing VMD with CAF for the detection of aged latent fingermarks which had been deposited upon glass slides. They found VMD was more sensitive on marks older than 24 months, whereas, both techniques were similarly sensitive on latent marks less than two months old. The authors suggested that the use of VMD subsequent to CAF may develop more identifiable ridge detail than either technique alone, however, care had to be taken as to avoid losing ridge detail which had already been developed [225].

In 1999 Australian team Flynn *et al.* concluded that vacuum metal deposition was one of a few techniques which could reliably enhance aged latent fingermarks on Australian polymer banknotes [234]. These results were confirmed in further studies completed in 2002 and 2003, as well as establishing an optimised fingermark detection sequence [229, 235]. Polymer banknotes possess a semi-porous surface which does not respond well to the fingermark detection techniques employed on such substrates. Canada introduced polymer banknotes into circulation in 2011 and researchers subsequently began to evaluate the performances of CAF, VMD and various sequences thereof in developing fingermarks on the new currency [236]. They determined that the combination of CAF, VMD and dye staining produced the most fingermarks with visible ridge detail.

An additional study by Lam (2014), optimised lighting, photography and digital enhancement techniques used to record the developed fingermarks on Canadian polymer banknotes using the sequence of CAF → VMD → Rhodamine 6G luminescent staining [237].

In 2002 Suzuki *et al*. found that VMD was superior to the techniques usually applied to the recovery of fingermarks from ferromagnetic-coated substrates, such as those used for Japanese train tickets [238]. They also reported that VMD was more sensitive than the traditional techniques used on polystyrene substrates, however, Jones *et al*. found that Multi-metal Deposition II (MMD II) was better suited to these substrate types than VMD [239]. Researchers at the University of Strathclyde in Scotland compared VMD with Wet Powder Suspension (WPS) on dark, non-porous substrates which had been wetted. The wet powder suspension was found to be akin to vacuum metal deposition across the substrates tested. The authors came to the conclusion that WPS was straightforward, effective, rapid and cost-effective alternative to VMD in these circumstances. The powder suspension can also be used recover marks from non-porous substrates subsequent to a failed VMD treatment [240].

Gunaratne *et al*. (2007) compared a one-step aluminium process with the traditional two-step gold/zinc process. A variety of common plastic substrates were used test the sensitivity of the aluminium for latent fingermark detection. Their results showed that Al VMD developed significantly more useable fingermarks than Au/Zn VMD on fresh articles (<48 hours), but the process showed that the effectiveness dropped for aged samples (>90 days). The conclusion made was that this was a viable alternative to the traditional two-step VMD process for the detection of fingermarks on plastic substrates [241]. Subsequently, CAST (Centre for Applied Science and Technology) assessed the Al VMD technique and found it to have no benefit over the currently used processes [88].

In recent years, the conventional Au/Zn VMD process has been observed to have a decline in performance when attempting to recover fingermarks from plastic substrates. It is theorised that this is due to the change in polymer substrates being encountered in operational casework. Manufacturers are recycling materials, are using a wider range of base polymers, and are including various additives (such as plasticisers and antimicrobial treatments) in their plastics. These factors contribute to changes to the surface characteristics which have culminated in a reduction in the sensitivity of the traditional VMD process in terms of the development of latent fingermarks [72]. Downham *et al.* (2012) reported that the efficiency of the vacuum metal deposition technique when used on plastics had diminished comparative to cyanoacrylate fuming followed by luminescent staining. They did, however, highlight that VMD may still develop additional fingermarks when used after the CAF procedure [242].

5.1.1 Aims

Using the knowledge gained from using copper and rubeanic acid in conjunction with forensic gel lifters. The hope was that rubeanic acid could be used with gels which had been used in combination with thin films of copper applied to various substrates with latent fingermarks upon them. A range of thicknesses of copper films were evaluated, and lifted using gelatine lifting sheets before being treated with the rubeanic acid. Fingermarks used will include fresh and aged samples.

5.2 Experimental

5.2.1 Assumptions

Throughout the experimental section, the following assumptions are made;

- Where not specified, the author's fingermarks were used for enhancement purposes.
- Whenever the vacuum metal deposition process was completed, a West Technology Systems Limited VMD560CX Vacuum Metal Deposition chamber was used [243].
- With respect to measuring the thickness of the deposited metals, an Intellemetrics IL150 Quartz Crystal Growth Rate Monitor was employed [244].
- Fingermark deposition types:
    - Natural series: A series of marks where the donor deposits their fingermarks with no additional "grooming" involved, and having not washed their hands for at least 30 minutes prior to deposition.
    - Sebaceous loaded series: A fingermark where the person depositing the mark intentionally rubs their fingertips on or around their forehead and nose areas, and then presses their finger onto the sample medium.
    - Depletion series: A series of marks where the initial mark is loaded then deposited, the same finger is used for deposition repeatedly until the desired number of marks is achieved. Each fingermark then has less sebaceous residue than the previous mark.
    - Eccrine loaded series: The donor would initially wash their hands then don nitrile gloves for a period of 30 minutes. After removing the gloves, fingermarks were then deposited onto the selected sample substrate.
- Unless otherwise stated the sample substrate used was polymer currency; the banknotes used were:
    - Vietnamese 10,000 Dong notes
    - Bank of England "Chaloner" prototype £50 notes

5.2.2 Substrate Preparation

The substrates used in this study were; glossy magazine pages, glossy magazine cover, plastic carrier bags and polymer bank notes. The magazine was a common type available in any newsagents and the carrier bags were standard supermarket bags. The polymer bank notes used were clean new Vietnamese bank notes in 10,000 Dong denomination and Bank of England "Chaloner" prototype polymer notes.

Magazine & Carrier Bags

The magazine and plastic bag substrates were prepared for fingermark deposition by cutting in to approximately 13 cm by 7.5 cm sized samples. Fingermark deposition was carried out by depositing marks from each finger in a two rows of four or five marks. The top row had 'loaded' sebaceous marks, and the bottom row had natural marks deposited separately (Figure 102).

Figure 102: VMD Substrate Preparation

Some of the substrates had fingermarks deposited fresh, within an hour or two of treatment, others had the marks deposited and left for up to a number of weeks before being treated

Polymer Banknote

The polymer note substrates were prepared in a similar manner to Chapter 4.2.2. The notes had fingermarks deposited in two rows, with each note having eight to ten marks deposited. In some instances, a row of natural marks and a separate row of groomed marks were deposited in order to test sensitivity. Once deposited upon, the banknotes were ready for deposition of the chosen metal (Figure 103).

Figure 103: Vietnamese Dong Polymer Banknote Preparation

Polymer Banknote Split Series

"Chaloner" polymer banknotes had two pencil lines drawn across the note to produce approximate thirds, fingermarks were deposited along both lines. One line had natural fingermarks deposited along it, the other had sebaceous groomed marks deposited. The samples were cut along the lines, creating three sections. The outside sections were treated with one metal, *Process X*, and the inside section was treated with an alternative metal, *Process Y*. Once all the sections were treated, the matching sections were recombined by the use of tape on the underside of the banknote. This recombination allowed the various metal deposition treatments to be directly compared on fingermarks with the same chemical composition, quantity of material and pressure at time of donation (Figure 104).

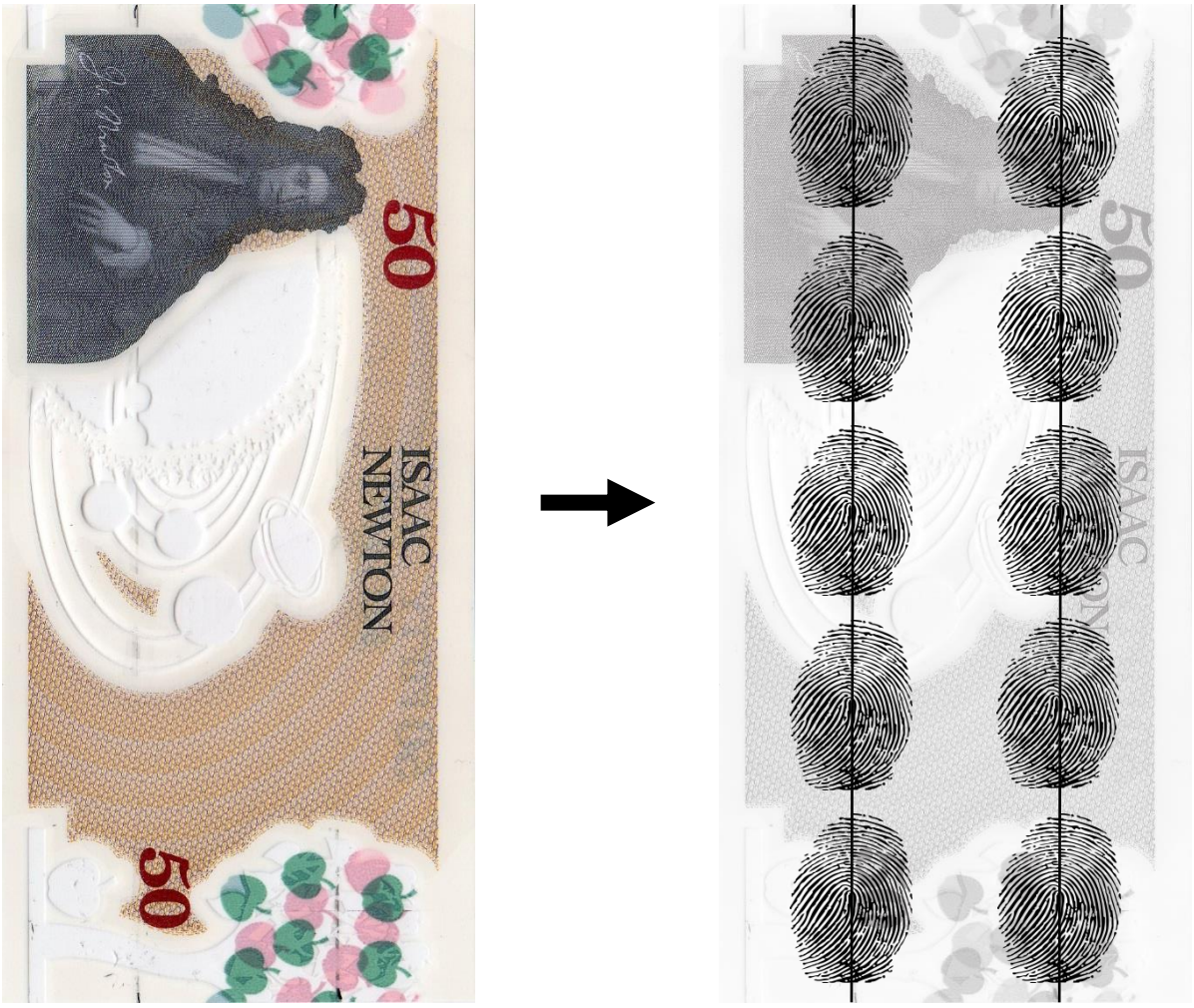


Figure 104: "Chaloner" Prototype Polymer Banknote Split Process Preparation

5.2.3 Reagent Preparation

Deposition Metals

A number of metals were used for evaporation during the vacuum metal deposition process. The metals took the form of wire which was cut into sections as required. The metals used were:

- Gold (9ct., 0.5 mm thickness, www.cooksongold.com)
- Zinc (0.5 mm thickness, www.wires.co.uk)
- Silver (Stirling Silver, 0.5 mm thickness, www.cooksongold.com)
- Copper (1.0 mm thickness, www.scientificwire.com)
    - Bare – Completely bare
    - Non Tarnish (NT) - Has an ultra-thin coating to protect from tarnishing

Rubeanic Acid

A 0.1% (w/v) rubeanic acid solution was used as described in Chapter 4.2.3.

5.2.4 Sample Treatment

VMD Chamber

The prepared samples were placed into the vacuum chamber of a West Technology VMD560CX (Figure 105) [243], held in place *via* magnets. The metal sample being deposited was placed in the source boat and the chamber was pumped down to ≤3 x 10^{-4} mbar. The source boat temperature was increased to in excess of 1000°C, until the filament was glowing to allow evaporation of metal. Throughout the experiments most of the metal samples evaporated were completely consumed during each treatment, with the exception of the copper.

Figure 105: West Technology VMD560CX Forensic Vacuum Chamber

Film Thickness Monitor

The film thickness of the deposited metals varied throughout the investigation. An Intellemetrics IL150 Quartz Growth Rate Monitor (Figure 106) was used to accurately monitor and measure the thickness of the metals being deposited [244].

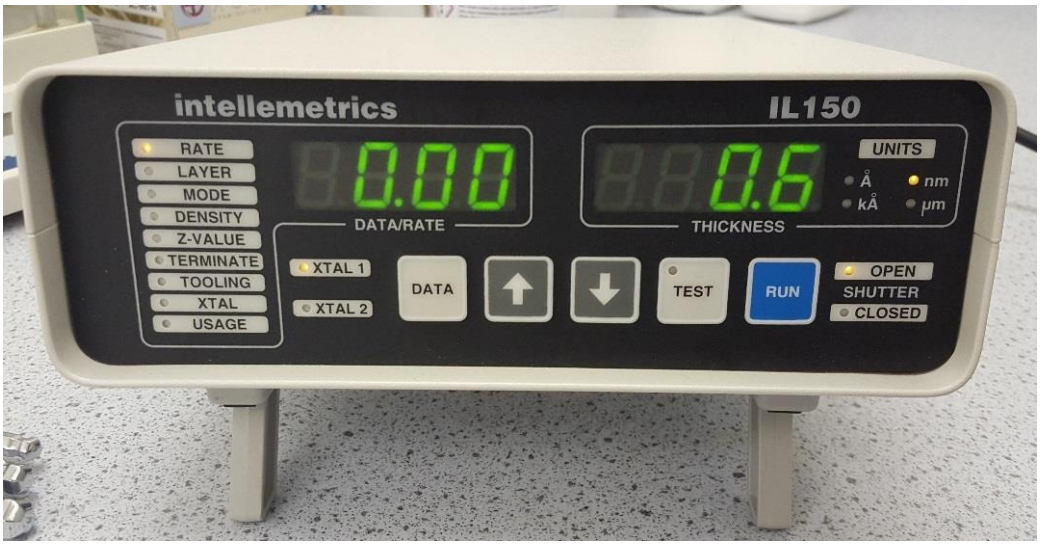


Figure 106: Intellemetrics IL150 Quartz Growth Rate Monitor

Ecospray Atomiser

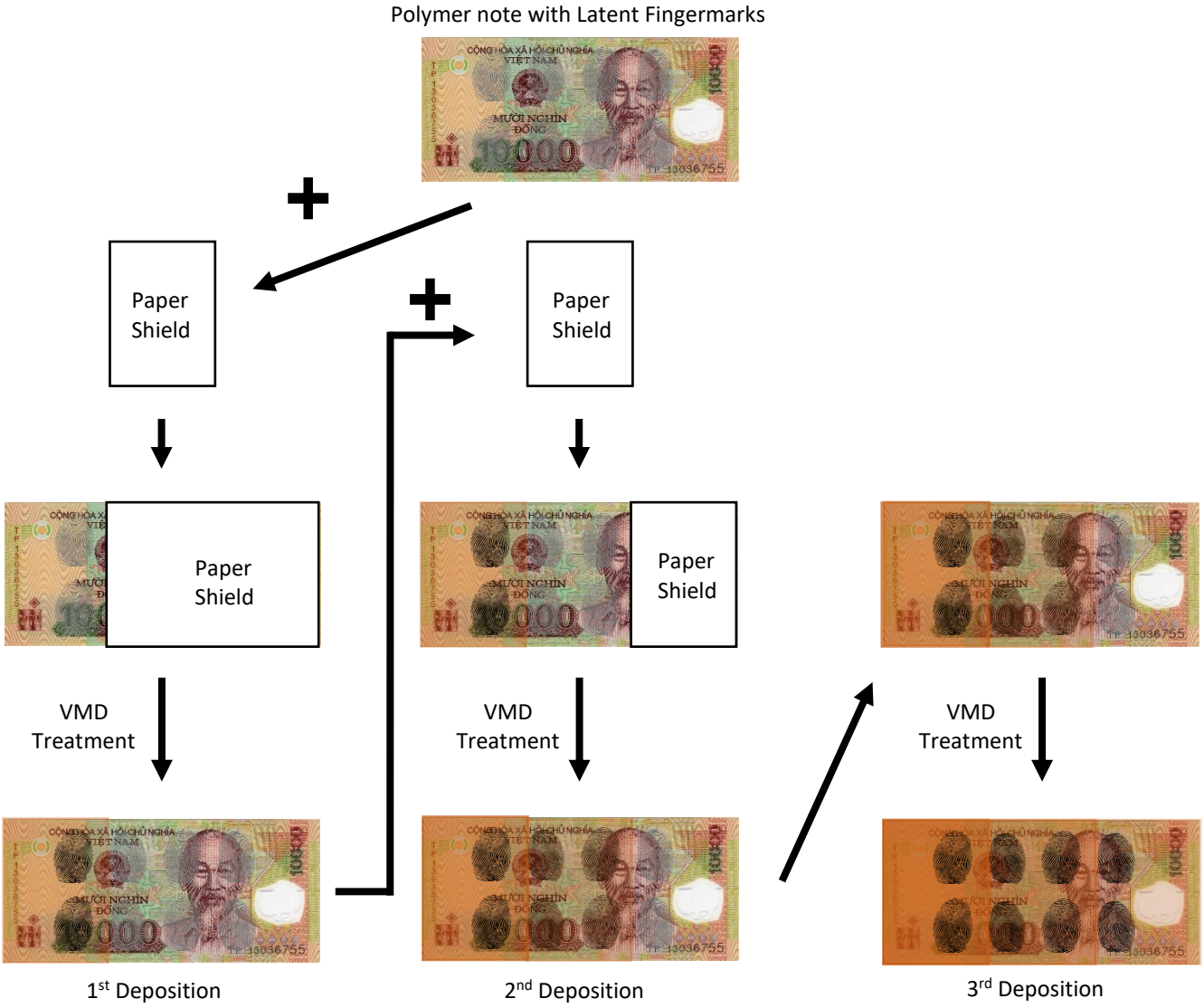
The Ecospray Forensic Atomiser was again chosen for the distribution of the rubeanic acid (Chapter 4.2.4).

Gelatine Lifters

White BVDA Gel Lifters (BVDA – B15500) [140, 141] were used for lifting from the copper vacuum metal deposition (Cu VMD) treated surfaces. The gel lifter was applied to the surface of the treated polymer banknote for up to two minutes. Upon removal from the note, the gel was sprayed with rubeanic acid and allowed to dry before being recorded and graded.

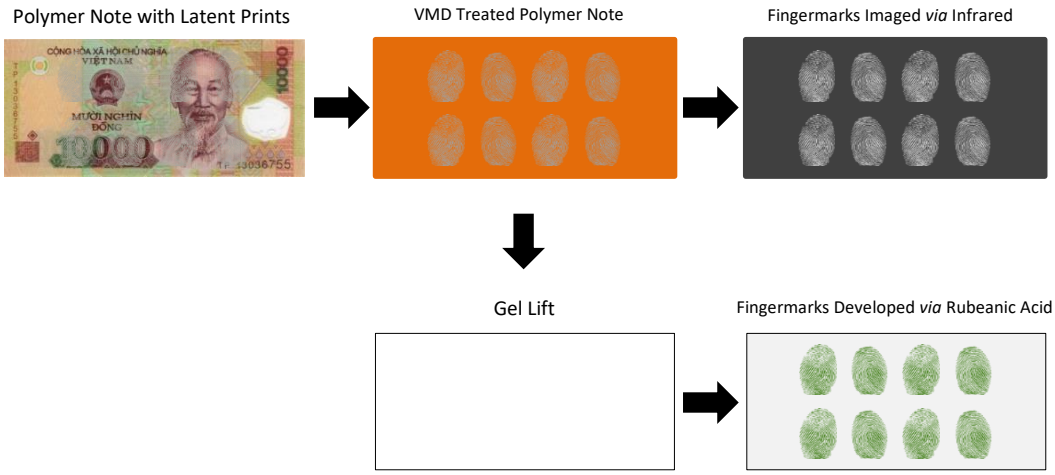
Process of Treatment Steps

In order to make the most of substrates, a few polymer banknotes were treated multiple times in order to ascertain at what deposition thickness the copper was most effective at. This was achieved by covering sections of the note and treating and re-treating the areas so that the note had three distinct areas representing single, double and triple deposition treatments (Scheme 5).



Scheme 5: Schematic of Multiple Deposition Process

In order to try and maximise the chances of recovering fingermarks from the polymer banknote substrates, two routes were followed after the copper VMD process. The first was imaging using infrared, the second was lifting *via* a gel lifter and subsequent treatment with rubeanic acid (Scheme 6).



Scheme 6: Process of Treatments Used on Polymer Banknotes

5.2.5 Sample Evaluation

The samples were examined, and the results were graded. Each sample was evaluated and the methodology was amended as required for future experimentation.

Sample Grading

The visualised marks were graded using the "CAST" grading scale (Table 3, Page 82).

5.2.6 Treated Sample Recording

After the enhancement process, the treated substrates were either photographed or scanned to record the enhancement. The camera used to take the photographs was a Nikon D5200 digital SLR camera set to manual focus. The camera was placed atop a tripod to keep movement to a minimum and the distance from the substrates consistent. When scanning was performed it was completed using an Epson Stylus Photo RX585 scanner. Where possible the samples were labelled using photographic twin check labels. One label being attached to the sample or to the acetate cover of the gel lifter and the other being placed in a laboratory book, logged with the experimentation details, making it easier to correlate the experiment results with the particular images.

Specialist Equipment

Two specialist imaging systems were also used: a desktop Crime-lite Imager [245] fitted with either 25 mm or 35 mm lens. Vis/IR illumination was provided *via* an integrated 80W halogen light source which outputs light over a broad spectral range (400-1000nm), including the near infrared. Imaging was achieved using 780nm or 850nm long-pass camera filters directly in front of a 5MP vis/IR monochromatic camera. A DCS-5 [246] was also employed which comprised a modified Nikon D810 camera fitted with a 105mm macro lens and similar long-pass filters. Illumination on this system was achieved using either a Polytec 150W halogen bright field fibre optic ring light or a Crime-lite 82S IR (800-900nm) [247]. All these products are manufactured by Foster + Freeman Ltd, Evesham, UK.

5.3 Results and Discussion

With the relative degree of success the metal transfer method showed, it was felt that a fine layer of the copper over the prints surface may provide improved results. The polymer notes would be treated using the VMD process then subsequently lifted with a forensic gel and sprayed with rubeanic to develop. Although the gold/zinc method is the process of choice, copper as a source for vacuum metal deposition had been investigated on polymer surfaces in the past, to a degree of success [248]. It was assumed that once treated, the developed substrate could have a gel applied and once lifted the gel would contain copper over the entire surface with the exception of the areas where the fingermarks were present, thus recovering a negative mark.

5.3.1 Initial Tests

The first tests conducted with vacuum metal deposition were conducted during a visit to the Centre for Applied Science and Technology (CAST) in St. Albans. The vacuum metal deposition equipment there did not possess a sensor to measure the thickness of the metal deposited, so it had to be gauged by eye *via* the viewing window. The deposition was done a total of three times on each note, different sections of the note were covered the first two times so as to give three sections of varying metal thickness (Scheme 5).

Figure 107: VMD Treated Polymer Banknote

Fingerprint ridges can easily be observed upon the surface of the polymer note (Figure 107). Despite the thinness of the single deposition section, fingermarks are still easily identifiable. The single deposition section is difficult to observe unless viewing in oblique lighting. A forensic lifting gel was cut to the size of the note, this gel was cut in half along the horizontal. Both halves were placed on the surface of the note, one for one minute and the other for two minutes. Both halves were treated with rubeanic acid and allowed to develop.

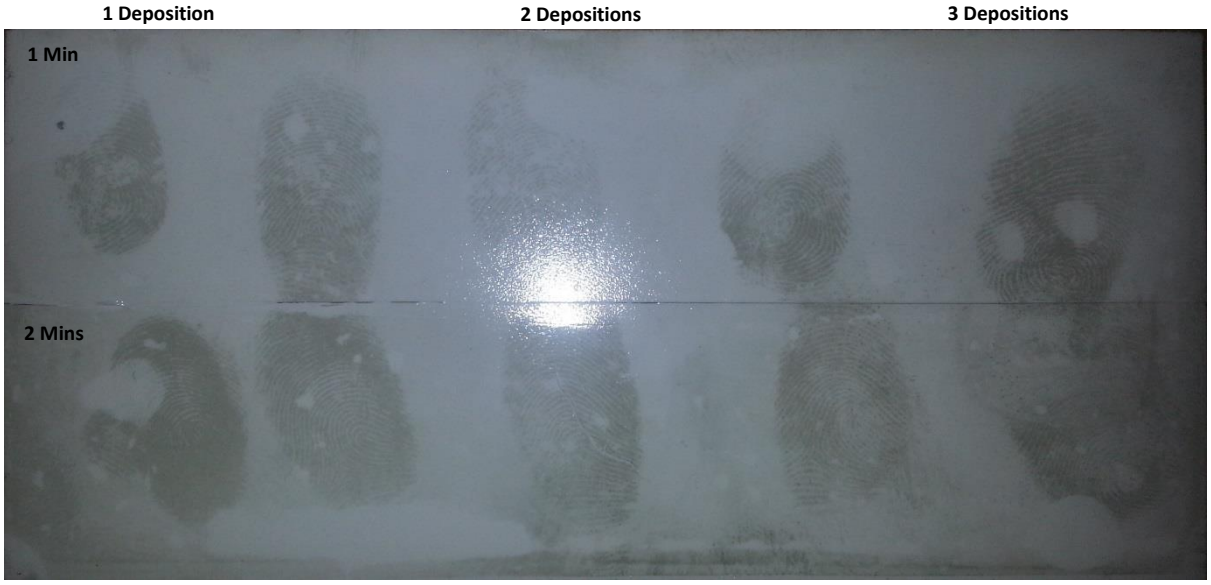


Figure 108: Rubeanic Treated Lift from Polymer Banknote

As can be seen from the treated gel lift (Figure 108), there are many fingermarks developed. Even the area where there was only one, almost indistinguishable, deposition, fingermarks can be observed. The level of detail is so great that individual minutiae can be seen; fingerprint cores, bifurcations and deltas. Some prints show some ridge leaching, other prints are incomplete due to air bubbles when applying the gel and other fingermarks still, have contamination which were obscuring the print. The gel section applied to the note for two minutes shows more background staining than the section applied for one minute. However, the level of ridge detail obtained from both is comparable, so the background staining could be eliminated simply by reducing the gel contact time to one minute.

There was a great deal of detail recoverable using this technique. Unfortunately, unlike the copper contact method, this method is not non-destructive. However, if this technique was to be used on polymer notes from circulation, a thin enough deposition would allow imaging *via* a lift and still allow the note to be put back into circulation with no detrimental effect to the currency.

Serendipitously, during this visit to CAST, Dr Bleay demonstrated imaging equipment produced by the forensic equipment manufacturer Foster + Freeman. Whilst demonstrating the infrared capabilities of the equipment, the copper VMD treated polymer note was viewed. The resulting image showed the note's background drop out and the prints become more readily observed due to enhanced contrast. This lead to a new line of inquiry, examining the effects of infrared and ultraviolet light sources on the VMD treated samples.

5.3.2 Infrared and Ultraviolet Imaging

The number of Vietnamese polymer banknotes that had fingermarks deposited on their back side were imaged under various lighting conditions.

On one of the polymer notes, fingermarks could be seen in normal light but it was hard to distinguish any ridge detail due to the patterned background of the note (Figure 107). The contrast between fingermarks and their background can often be improved by simply converting the image to black and white. In this case however, the patterned background of the note is too busy, and causes interference with the ridge detail of the mark. By using an infrared light source, the busy background could be seen to become more solid, giving much better contrast. Many ridge bifurcations could be observed, and this gave enough detail that there would be no problem matching this fingermark to that of a suspect's. One downside to the infrared imaging is that the image and serial number from the front side of the banknote can be seen in reverse form through the note.

Another note that was adorned with fingermarks across the back surface, marks could be observed in normal oblique light after treatment, as well as the three distinct thickness layers. Again, however, the pattern made it hard to pick out the ridge detail from the background. By using ultraviolet light sources, the background is almost completely eliminated (Figure 109 and Figure 110). Ridge detail becomes very apparent and specific minutiae can be observed. However, within this detail of some of the fingermarks, some of the text and imagery on the surface of the note are also visible. These cause small interferences with the print itself, but are still detrimental to the evidentiary value of the mark developed. By changing the light source to reflected UV (Figure 111), these interferences disappear. The surface of the banknote looks more metallic, and the distinctive thickness layers are very visible here. The fingermarks appear dark on a silvery surface, and when the image is inverted to a negative the contrast can be adjusted to show the prints as light on a darker background.

The reflected ultraviolet light source seems to give the most optimal contrast for the imaging of the fingermarks developed using the copper vacuum metal deposition technique. The process itself is able to image fingermarks leaps and bounds beyond what has been observed with the copper transfer method. Although, as previously mentioned, it is more invasive.

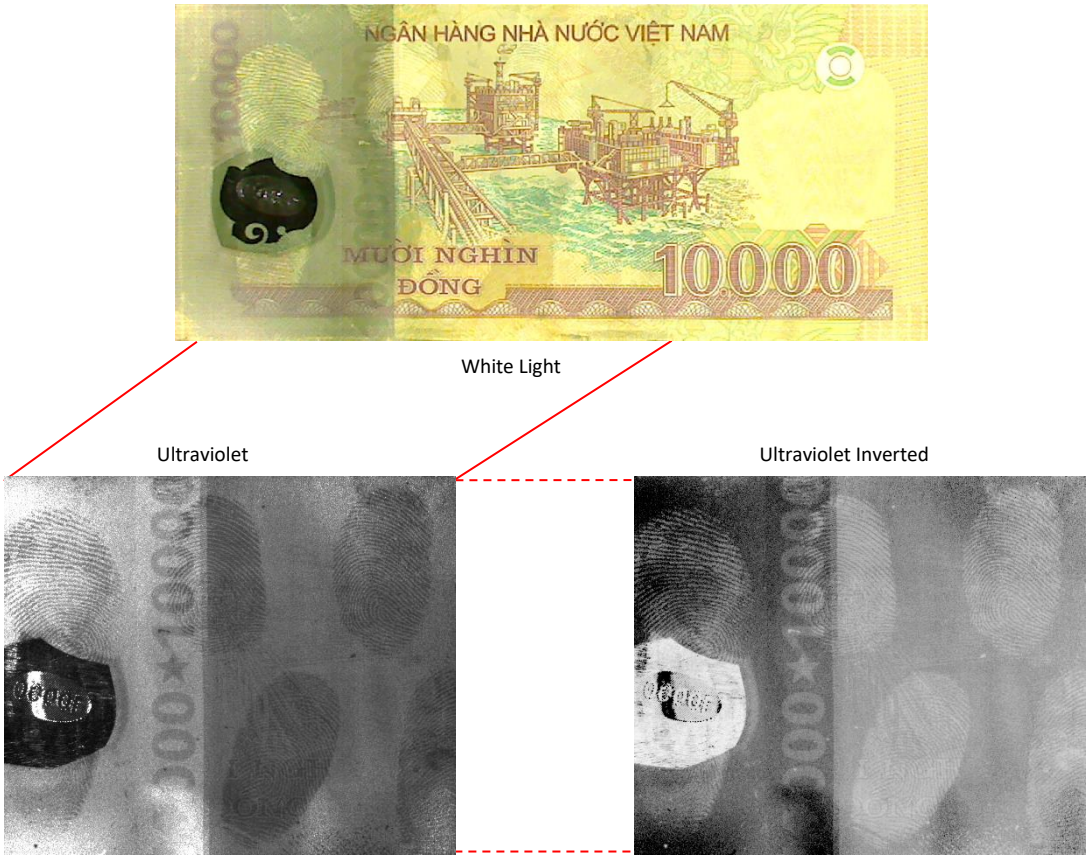


Figure 109: Polymer Banknote with Ultraviolet Enhancement

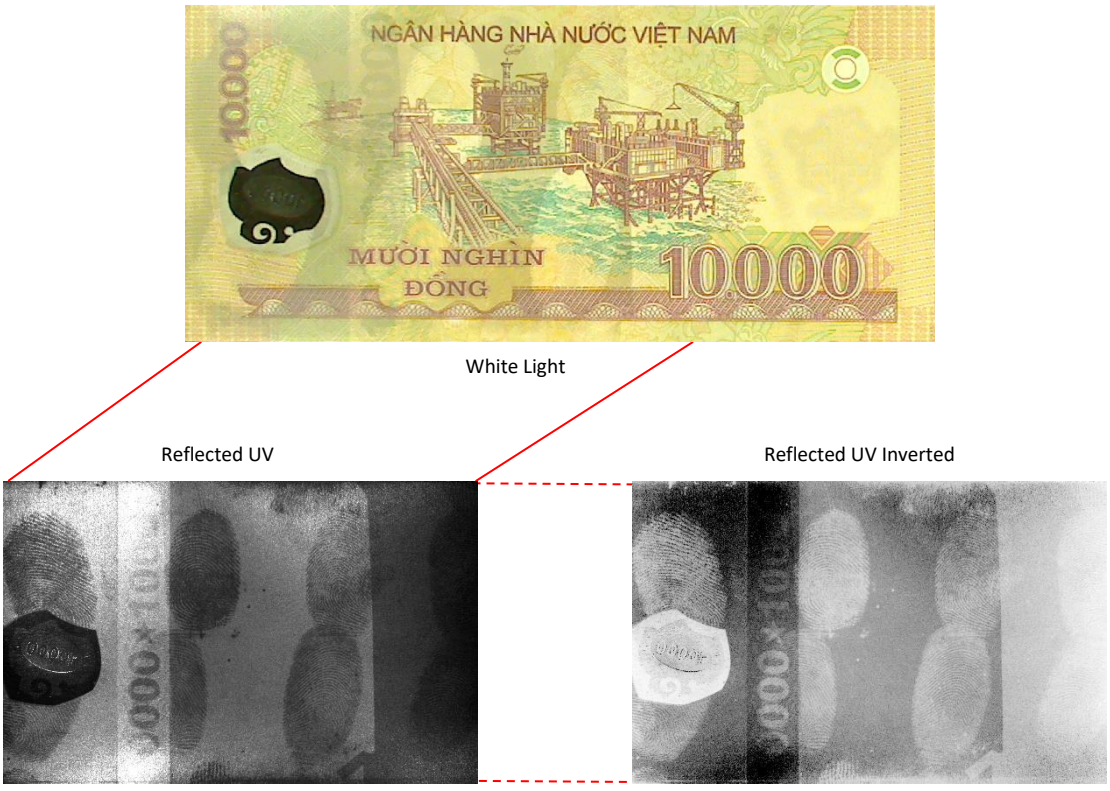


Figure 110: Polymer Banknote with Reflected Ultraviolet Enhancement

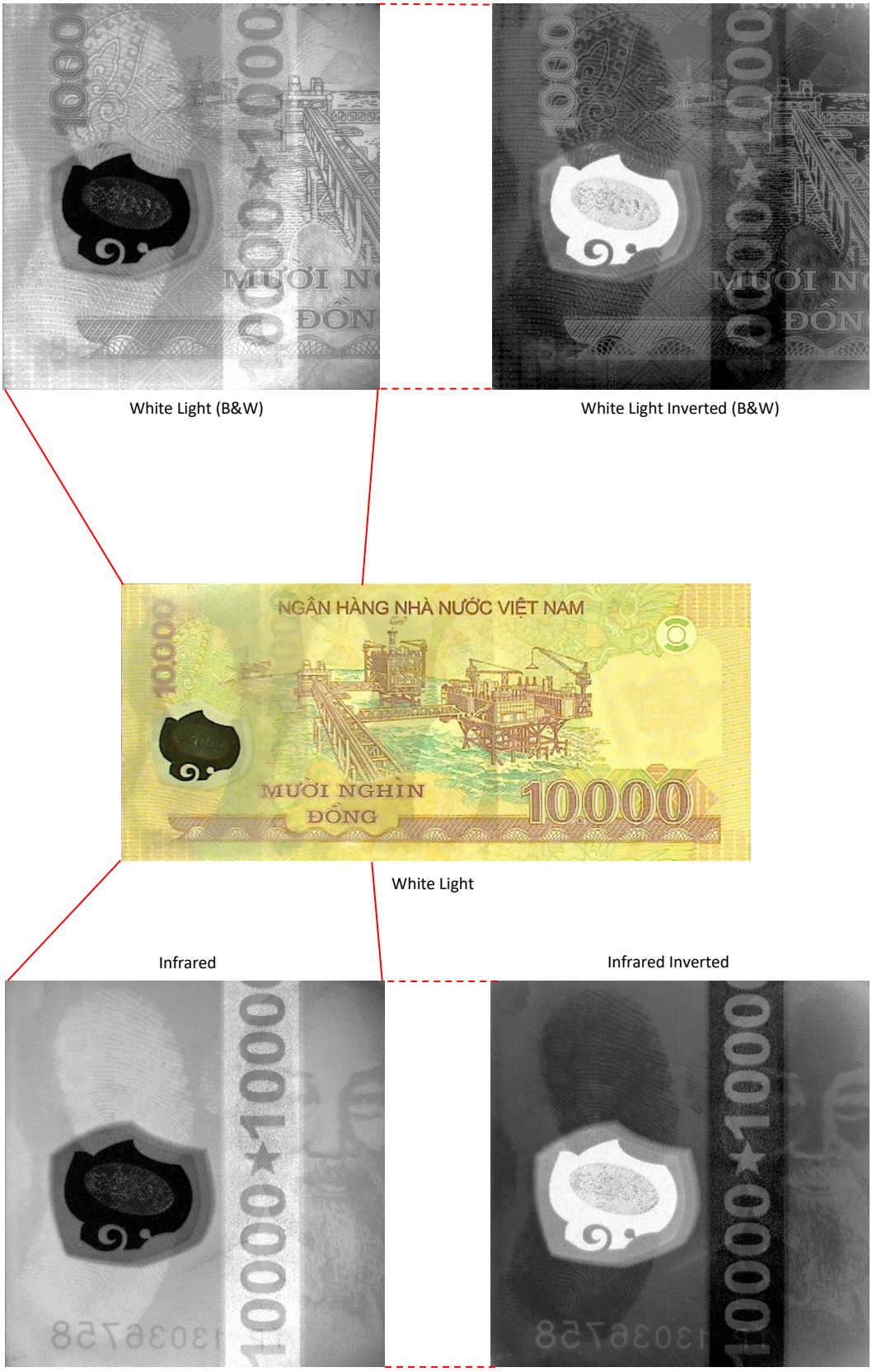


Figure 111: Polymer Banknote with Infrared Enhancement

5.3.3 Magazine & Carrier Bag Trials

To check the alternative light sources in conjunction with VMD further, other forensically pertinent substrates were used for the development of deposited fingermarks. Sections of supermarket carrier bags; low density polyethylene (LDPE) and magazines; glossy cover and pages, were cut to a size to allow the deposition of 4 or 5 fingermarks. Instead of using copper as the metal for evaporation on the substrates, the traditional gold/zinc combination was attempted.

Carrier Bags

Gold was deposited first, at a thickness of 0.6 nm. This was followed by zinc, as per the established protocol for Au/Zn development of fingermarks. The zinc was deposited at a thickness of 2.0 nm.

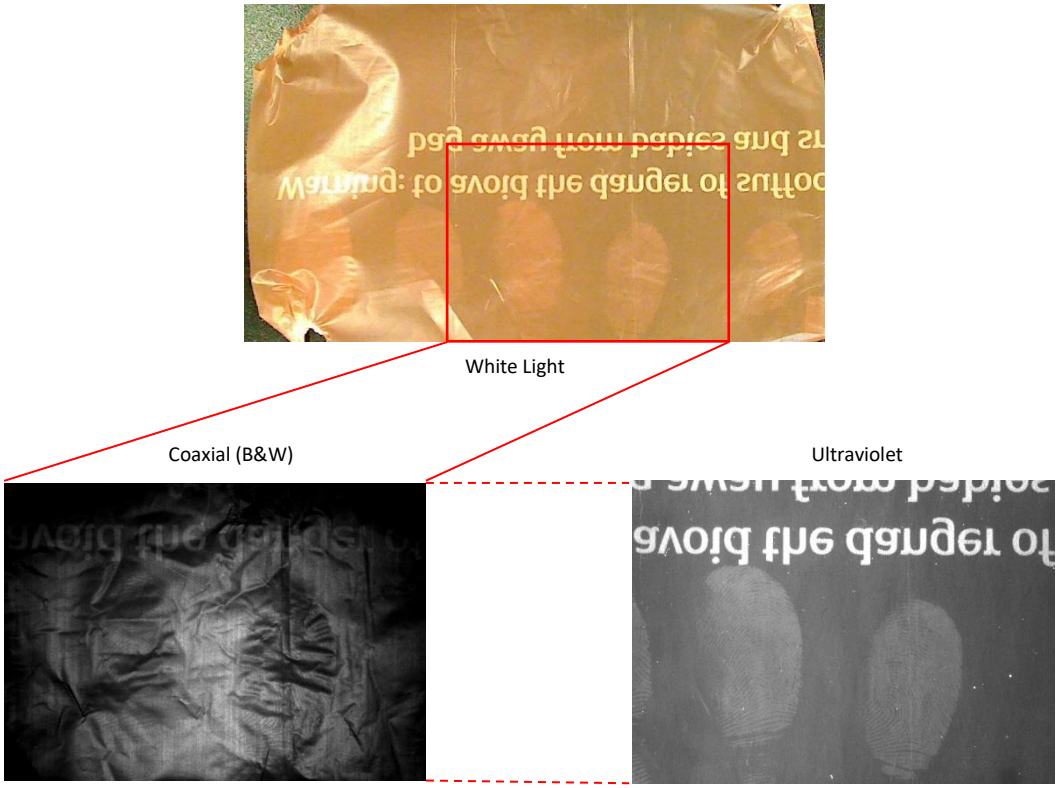


Figure 112: Carrier Bag with Coaxial and Ultraviolet Enhancements

Under normal white light conditions fingermarks can clearly be seen, however, the contrast between the ridges and the substrate background is poor. Viewing the fingermarks under coaxial lighting conditions, some ridge detail is visible, however, there are numerous creases in the substrate which hamper visualisation. These creases disappear when the substrate is viewed using an ultraviolet light source, providing clear contrast between the background and the friction ridge detail (Figure 112).

Magazine

The glossy magazine cover had gold deposited to a thickness of 0.7 nm and the zinc was deposited at 1.2 nm. The zinc was deposited until fingermarks could be visualised through the observation window of the vacuum chamber.

Figure 113: Glossy Magazine Cover with Reflected Ultraviolet Enhancement

When viewing the glossy magazine cover under white light conditions the surface looks free from fingermarks. When viewed using reflected UV marks begin to become visible, however, the ridge detail is somewhat lost within the pattern of the substrate background. When the image is inverted, the contrast between the ridges and the magazine cover become more favourable (Figure 113).

Using the gold/zinc for deposition provided images which appeared to be inferior to those acquired when using copper as the metal for deposition. Further studies into which of these two deposition methods provide the best quality images is required.

5.3.3 Copper Deposition Thickness Trials

This series of tests were conducted with a vacuum metal deposition chamber located at the Chemistry Department at the University of West England in Bristol.

The main objective of the study was to evaluate at what deposition thickness the copper was most effective at revealing fingermarks. Using the filament temperature dial on the VMD, it was possible to control the amount of copper deposited on the polymer note surface. The amount deposited was regulated using the Intellemetrics IL150 Quartz Crystal Growth Rate Monitor. The starting thickness was 0.2nm, increasing in 0.2 - 0.3nm increments to 2.1nm at which point the increments increased to 0.5nm to a maximum thickness of 3.0nm per test sample.

When copper is deposited over the surface it begins to form nuclei, the morphology of which is largely dependent on the nature of the surface on which they are being deposited on to. Areas where the substrate is clean and free from contaminants they form small tightly packed nuclei. However, areas that have fatty residues such as those present from latent fingermarks, act differently. The copper diffuses into the fat and forms larger nuclei that are more disperse (Figure 114), in a similar way as it does with gold [249] & [250] as cited in [88].

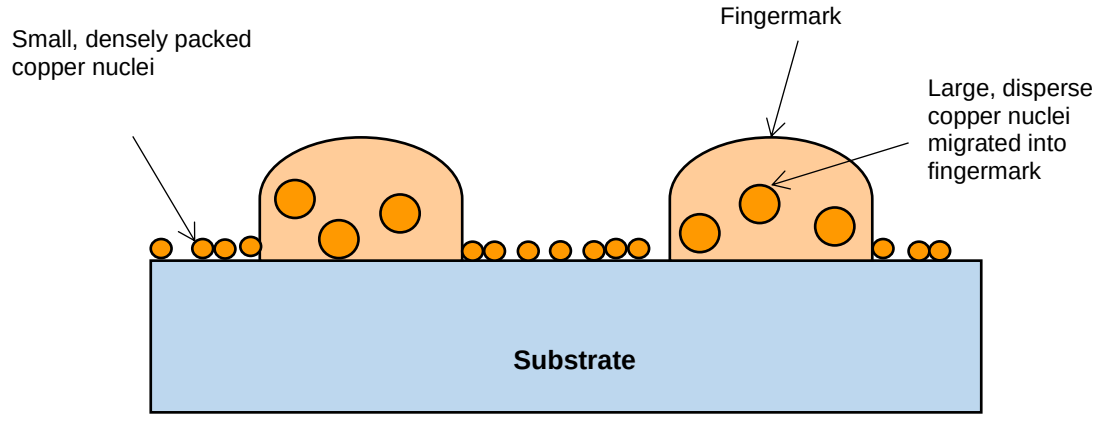


Figure 114: Schematic Diagram of Copper Deposition on Polymer Banknote Surface

A number of "Chaloner" prototype banknotes had two rows of fingermarks placed upon them (Figure 103, page 169). An Intellemetrics IL150 was used to accurately monitor the thickness of the copper being deposited. Two types of copper wire were used to evaporate copper on to the surface of the polymer notes being treated. The non-tasnish copper wire was used to deposit copper in thicknesses of from 0.2 – 3.0nm and bare copper wire was used to deposit thicknesses from 0.6 – 2.1nm. By varying the deposition thickness of the copper, it was possible to observe differences in the substrate's surfaces and their interactions with the deposited fingermarks. Although these interactions could be observed with the naked eye, the substrate background had a busy pattern which made observing specific minutiae difficult. This was overcome by using an infrared sensitive camera.

As the thickness of the copper layer increases, the areas where the nuclei are more densely packed reflect the infrared radiation. Conversely, the areas where the copper nuclei have moved into the fingermark residue, and are more disperse, are more transmissive and thus reflect the IR radiation *via* the original substrate beneath. These differences in the infrared radiation absorption and reflection mechanisms provide a clear, enhanced contrast between the fingermark region and the substrate itself.

Non-Tarnish Copper

At the thinner deposition thicknesses, those up to 1.5 nm, poor contrast was observed due to the amount of copper deposited on the note's surfaces. The less copper deposited, the less it reflects the infrared radiation, making it more difficult to discern the fingermarks against the background of the substrate.

1.7 nm Deposition Thickness

At this thickness of deposited copper, fingermarks can be observed by eye, most notably around the clear window areas (**here**), although some ridge detail can be observed, the background makes it difficult to see all the minutiae (**here**). Some areas, only show a faint fingermark shape (**here**), these marks are the artificially groomed fingermarks (Figure 115). The banknote itself has a very noticeable metallic sheen to it.

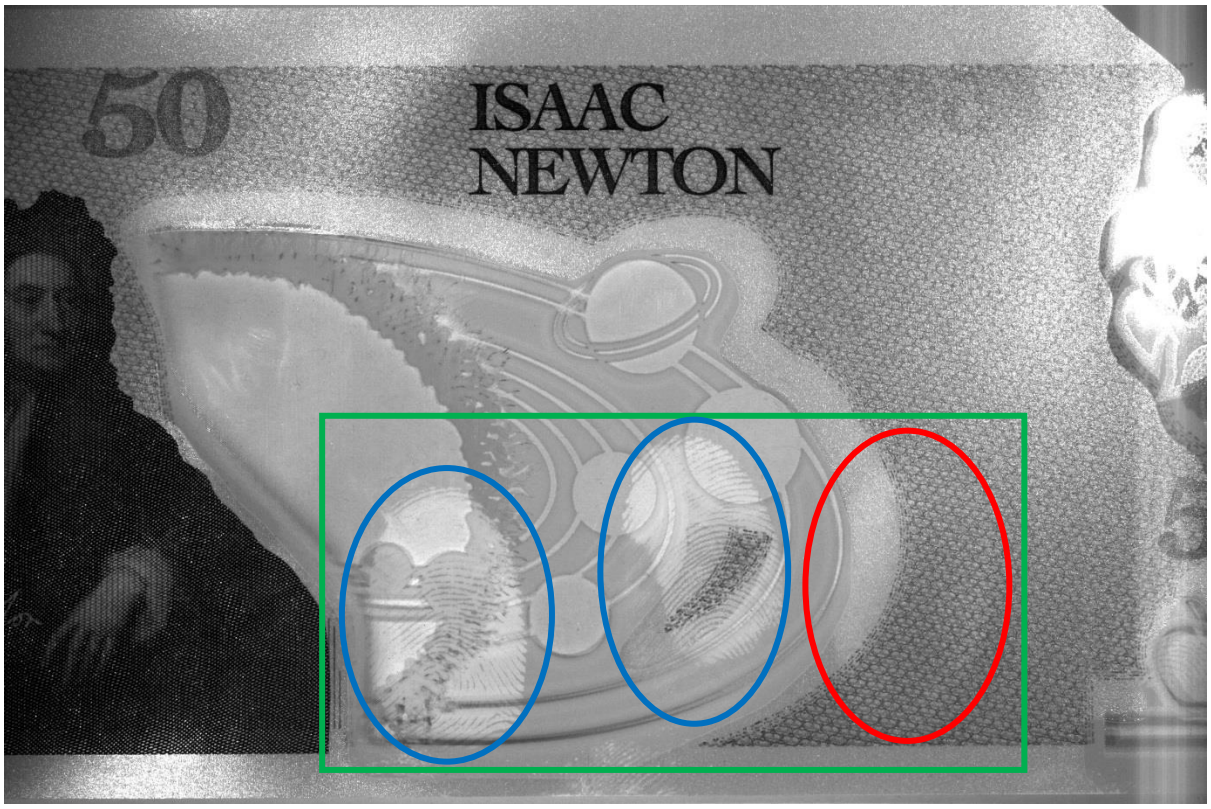


Figure 115: NT Cu VMD (1.7 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W)

When the same image is observed using a 780 nm long pass filter, a number of aspects appear differently.

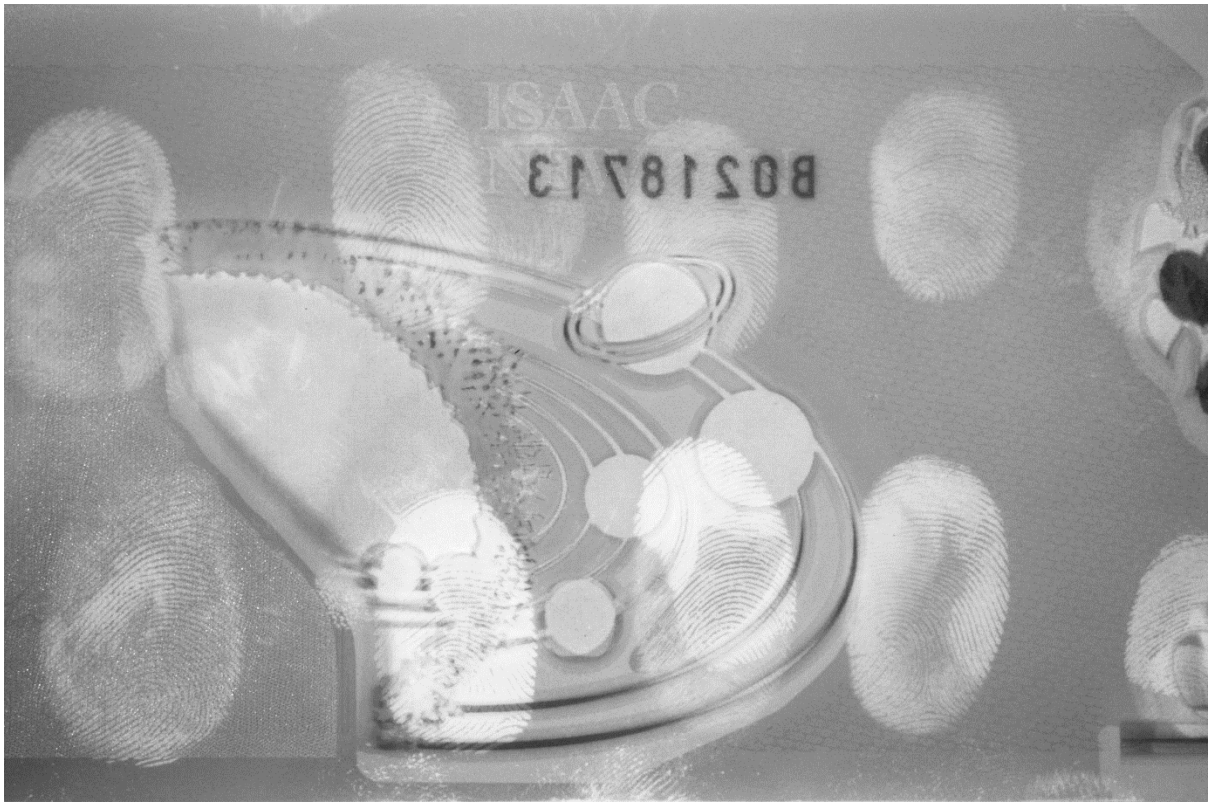


Figure 116: NT Cu VMD (1.7 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR (B&W)

The first noticeable change is the appearance of a large number of additional fingermarks, within which a great deal of ridge detail can be seen. The busy fish scale background is massively reduced, and Sir Isaac Newton has almost completely disappeared. Conversely, the serial number from the other side of the banknote has become visible in reverse form, and the window area where the fingermarks were partially visible under white light appear to be more illuminated (Figure 116). Although, this could also be a function of how heavily the fingermark was deposited.

When the image is inverted, essentially creating a negative, the fingermarks appear to have slightly better contrast against the background. The black fingermarks on the lighter background are easier to read. The fingermarks around the window area are still a bit heavy in areas, however, the darker underlying substrate observed through the window is less distracting. Despite the fish scale background being slightly more visible in this view, the image of Sir Isaac Newton is less noticeable (Figure 117). Both positive and negative views have their merits, and either or both could be used to compare to a suspect fingermark in the process of making an identification.

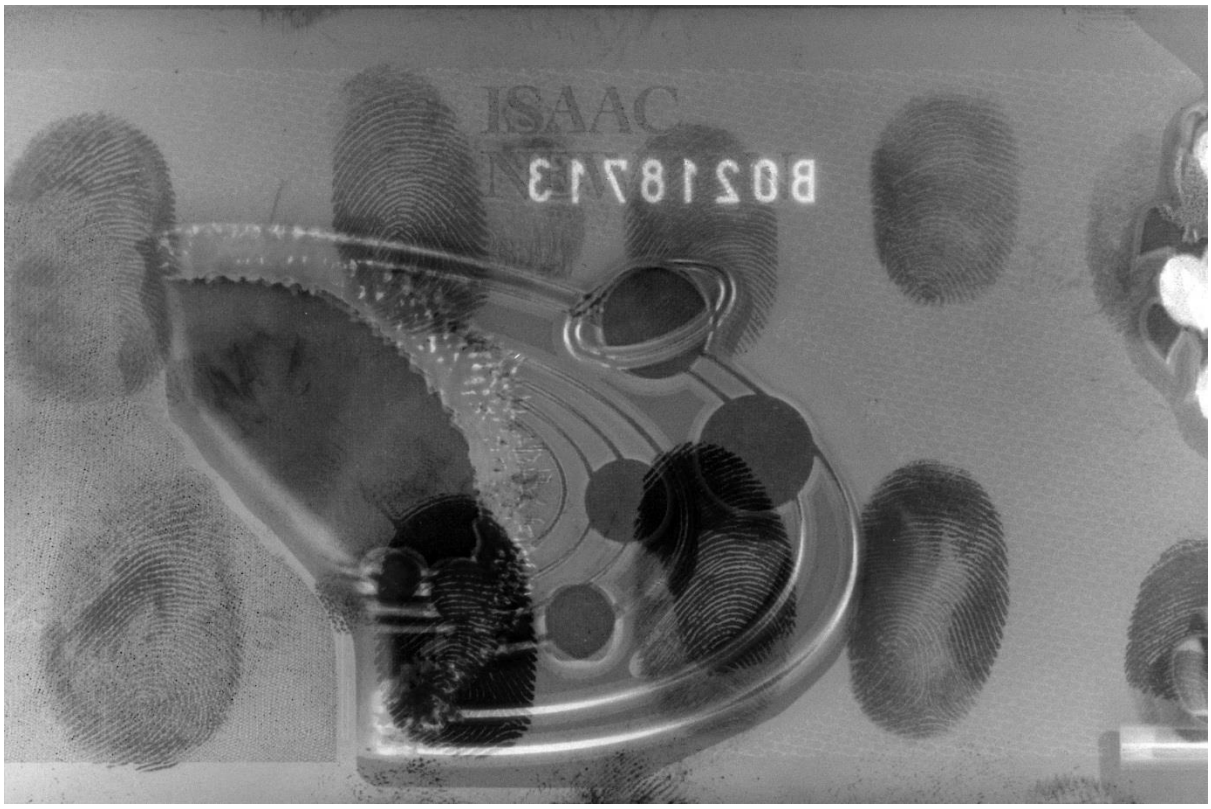


Figure 117: NT Cu VMD (1.7 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W)

2.1 nm Deposition Thickness

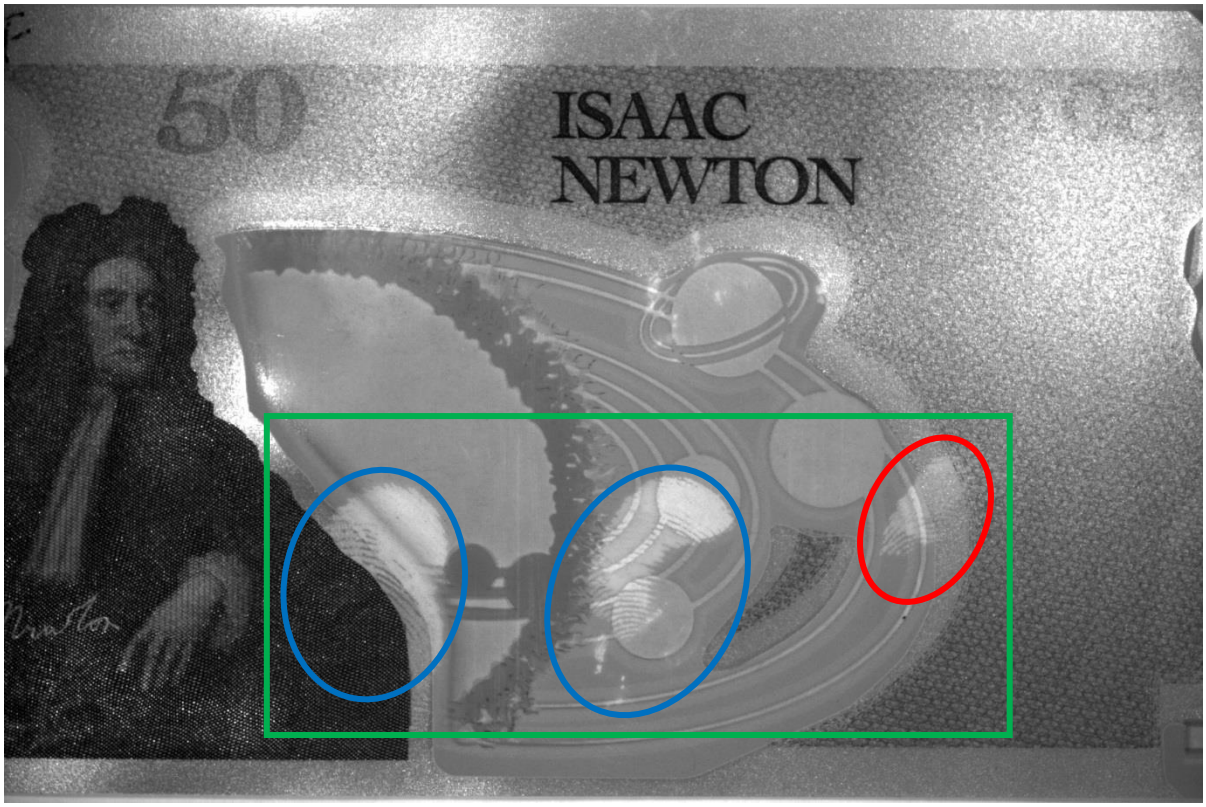


Figure 118: NT Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W)

By increasing the amount of copper deposited by 0.4 nm, the image viewed under white light shows very little difference from its 1.7 nm counterpart (Figure 118). Again some of the heavier groomed fingermarks could be seen around the clear window areas (**here**). There are a few partial marks with some visible ridge detail, however, these are only visible on the clear window area (**here**). Without this area the busy fish scale pattern makes it hard to discern any fingermark ridges (**here**).

When viewed in infrared, fingermarks can again be observed over the banknote's surface. The busy fish scale background is still partially visible, although it is extremely faint. The deposited copper has created a more solid background, which appears darker than the 1.7 nm sample. The serial number from the reverse side of the banknote, although still visible, is less prominent than before. Since the window area has a greater covering of copper, the underlying substrate reflects less, thus appearing less illuminated. The groomed fingermarks appear more leached, but this could again be a function of the deposition process. There are areas of the note where some damage has occurred to the copper coating, this is presenting as scuffs on the surface of the note (**here**) (Figure 119).

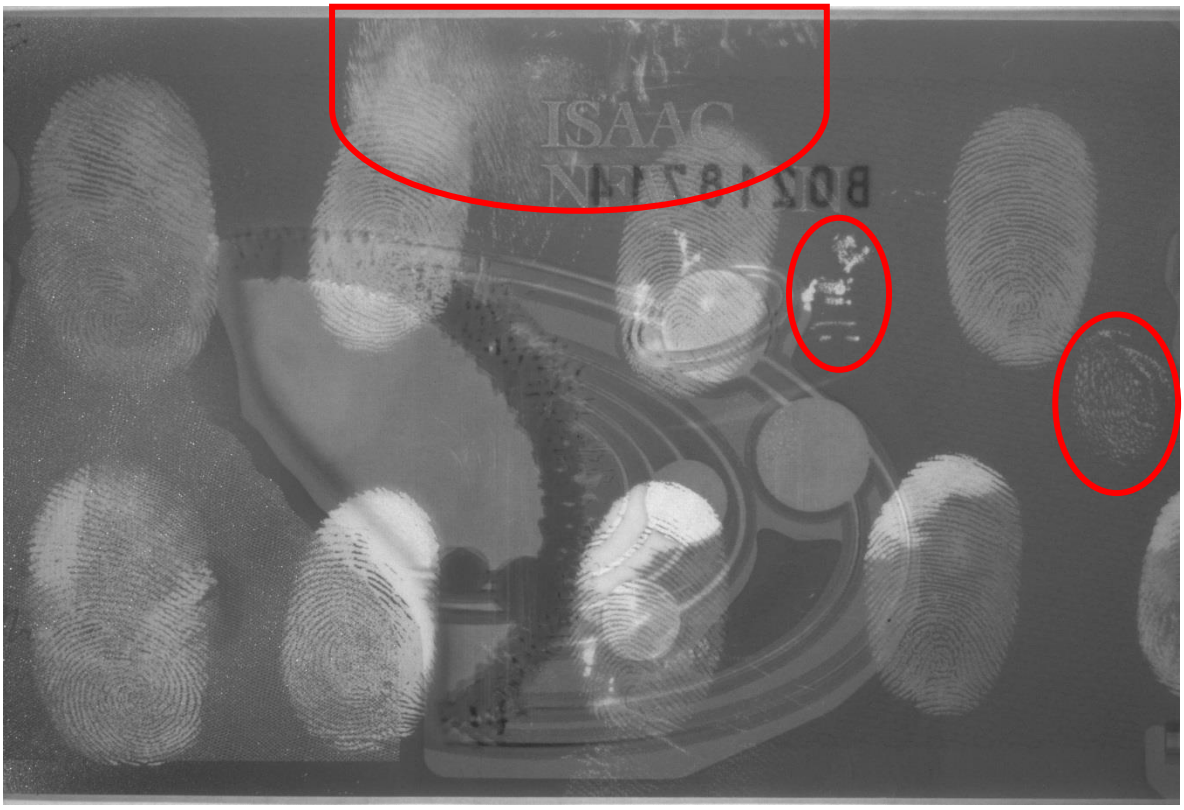


Figure 119: NT Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR (B&W)

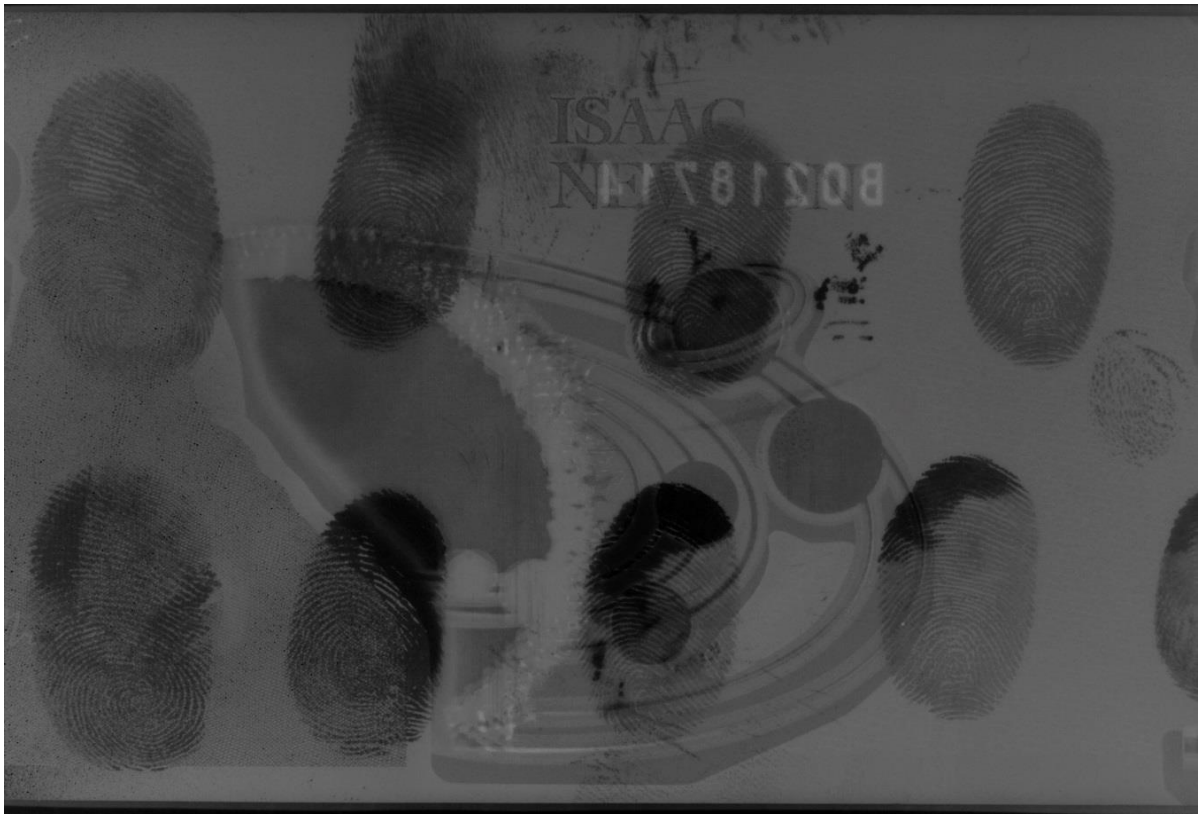


Figure 120: NT Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W)

The inverted infrared image again shows improved contrast. The lighter background is smoother, more solid with less of the fish scale pattern (Figure 120).

2.5 nm Deposition Thickness

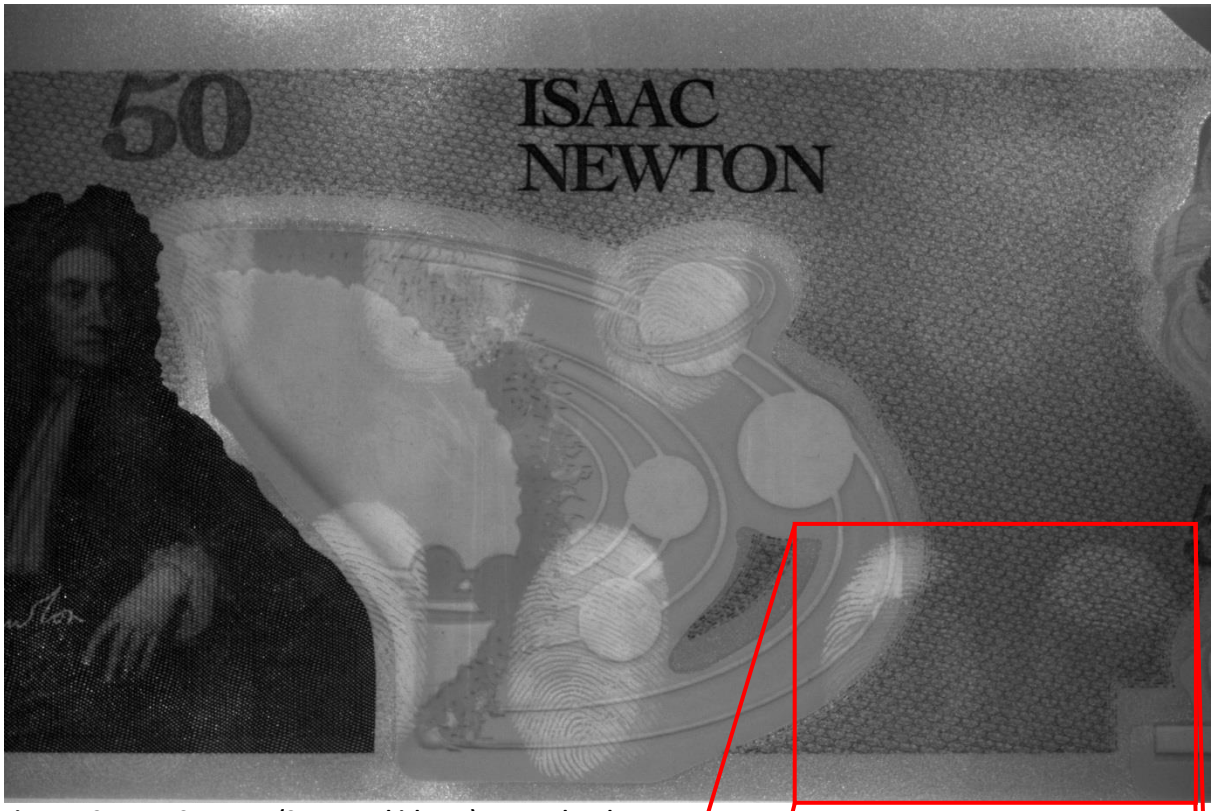


Figure 121: NT Cu VMD (2.5 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W) *

At the 2.5 nm copper deposition thickness, fingermarks can be observed in both rows of the deposited marks. However, as observed in the previously treated notes, the fingermarks are primarily noticeable on the areas where the clear, unprinted portions are. Some faint marks are visible in the printed areas. This is a marked improvement on the thinner deposition treated banknotes. In the zoomed image ridge detail can be observed in the clear areas, but the patterned background obscures the rest of the fingermark (Figure 122 & Figure 122).

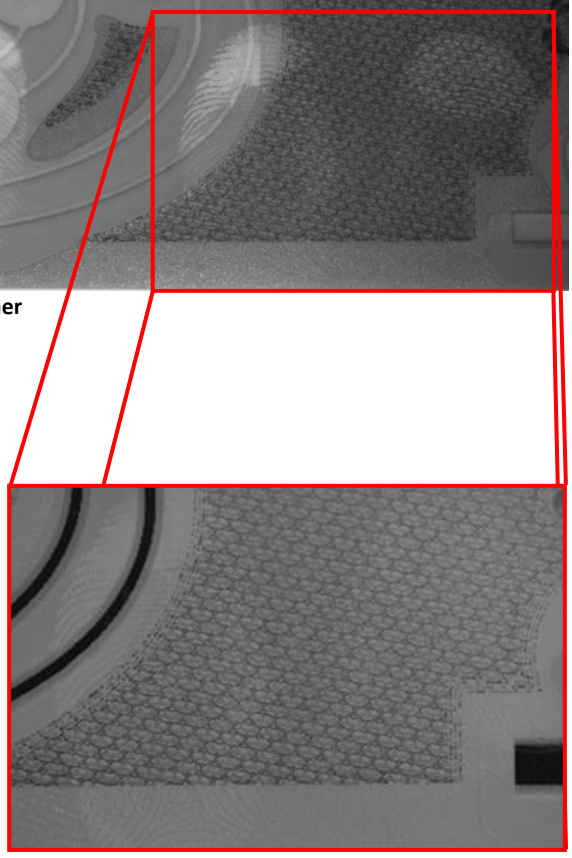


Figure 122: NT Cu VMD (2.5 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W) - Expanded†

* Photographed using Foster + Freeman Crime-lite™ under white light
† Photographed using Foster + Freeman DCS5™ under white light

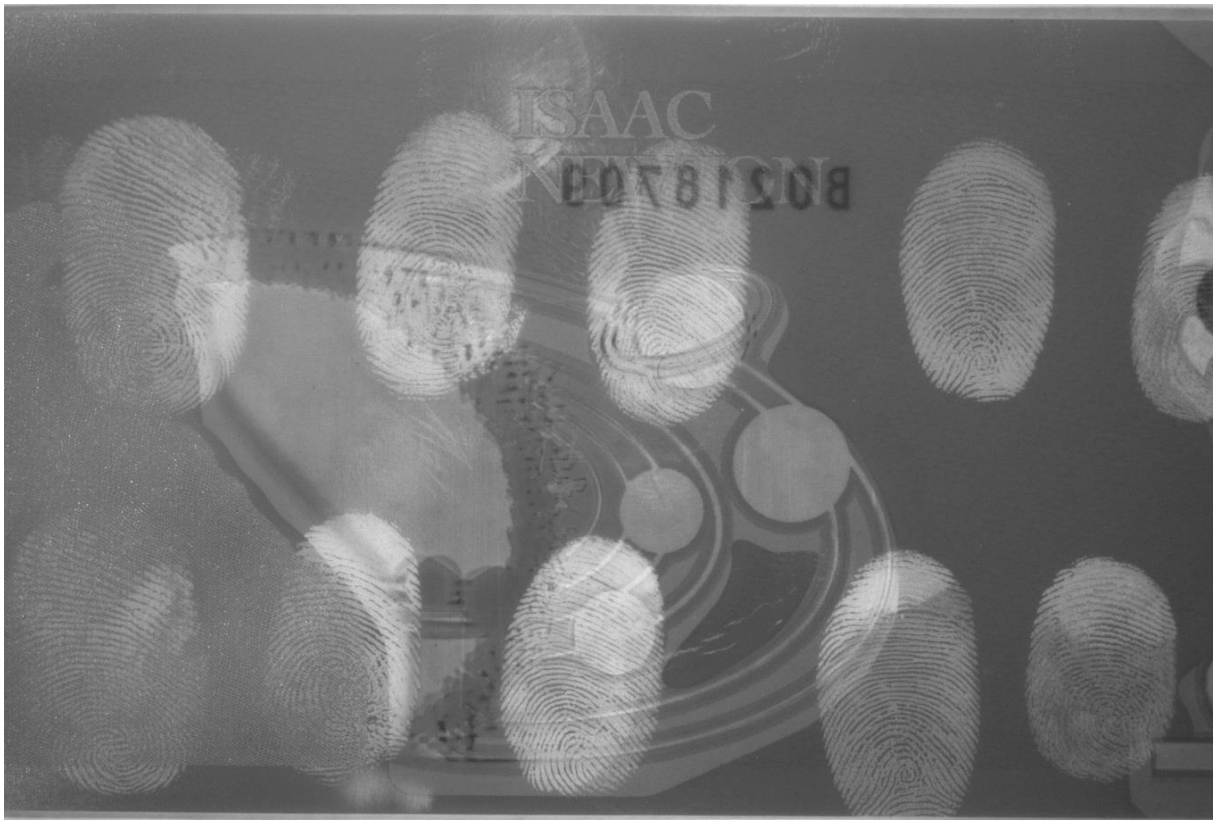


Figure 123: NT Cu VMD (2.5 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR (B&W)

The infrared image shows all the fingermarks present under white light and those not visible. The fish scale pattern is faintly appearing through the almost uniform copper layer, and the background appears slightly darker than the substrates which proceeded it. The treated note is following the same trends as observed with its predecessors (Figure 123).

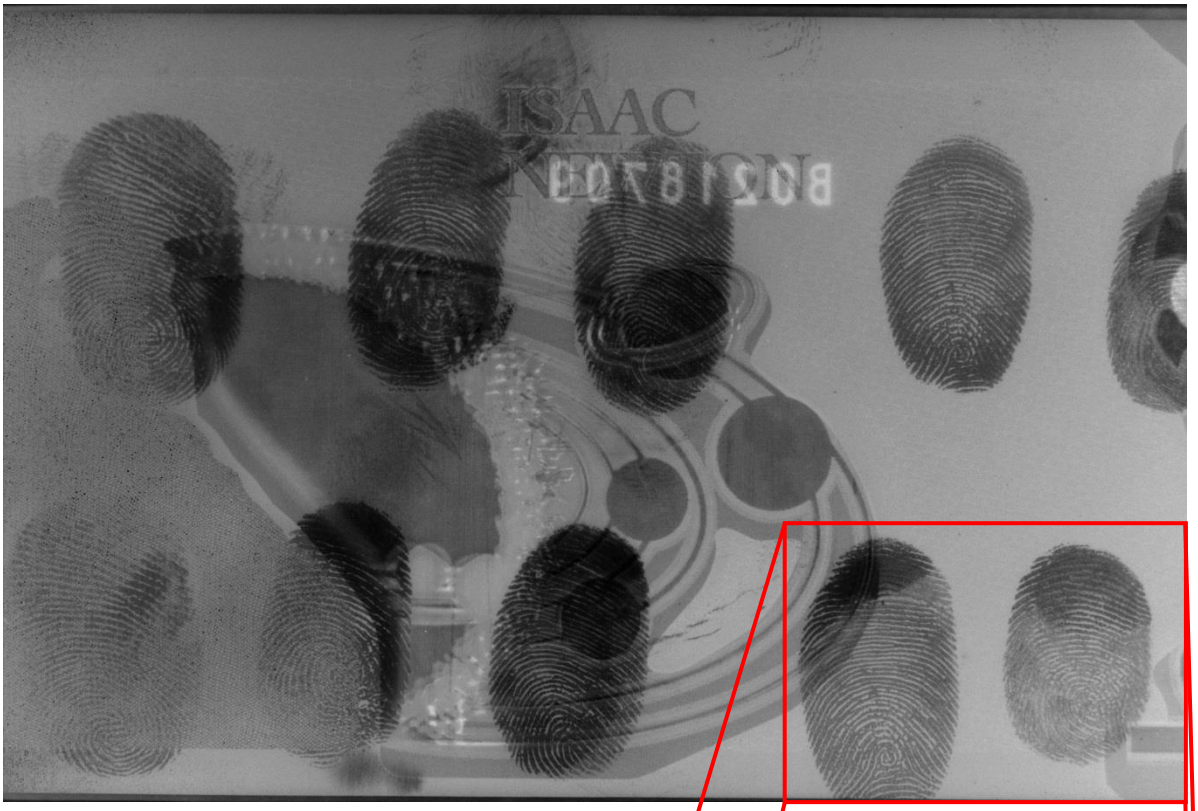


Figure 124: NT Cu VMD (2.5 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W)[*]

The reverse infrared image shows the black fingermarks against a light coloured background. All the fingermarks visible, present with a good degree of discernible ridge detail. Again some surface scuffing is present, and some of the fingermarks are showing leaching (Figure 124 & Figure 125).

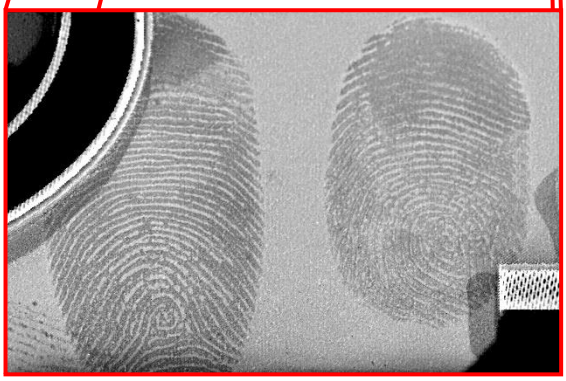


Figure 125: NT Cu VMD (2.5 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W) - Expanded[†]

[*] Photographed using Foster + Freeman Crime-lite™ under reflected infrared
[†] Photographed using Foster + Freeman DCS5™ under reflected infrared

3.0 nm Deposition Thickness

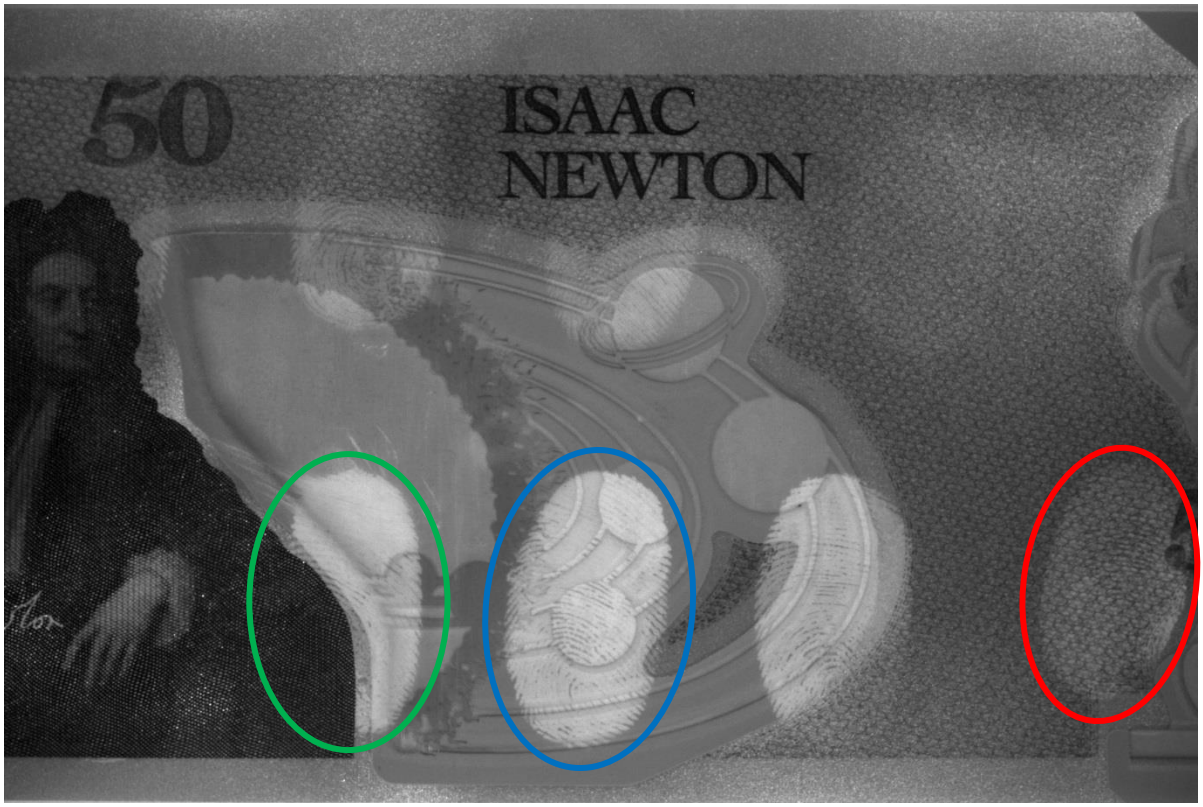


Figure 126: NT Cu VMD (3.0 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W)

As with the 2.5 nm thickness treated banknote, the 3.0 nm copper deposited note shows visible fingermarks in both rows of the deposited fingermarks when viewed under white light conditions (Figure 126). As has been the trend, fingermarks are most visible around the window areas (**here**). However, again some fingermarks are visible on the printed area, although, as previously stated the, the background print interferes considerably when trying to pick out specific minutiae (**here**). Some of the groomed marks show significant leaching, this is most likely a combination of too much material being deposited and slight overdevelopment. These factors make ridge detail difficult to discern (**here**).

Under infrared conditions, most of the fingermarks observed show some degree of leaching, though the groomed marks show the leaching to a higher degree. The background, again, appears darker with less interference from the busy fish scale pattern. The serial number visible from the reverse side, is also appears duller. The area where Newton appears to be retaining the deposited copper to a point where it is sparkling like glitter (**here**) (Figure 127).

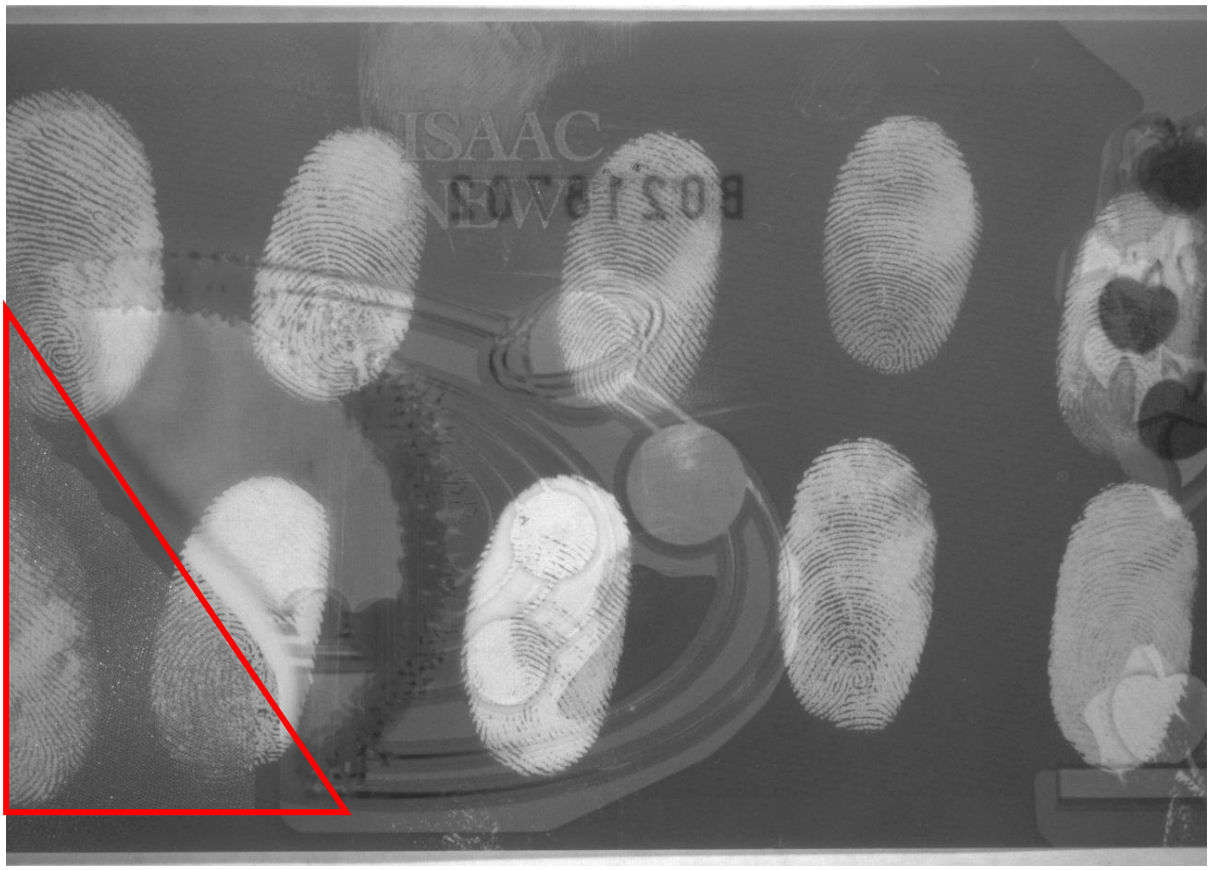


Figure 127: NT Cu VMD (3.0 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR (B&W)

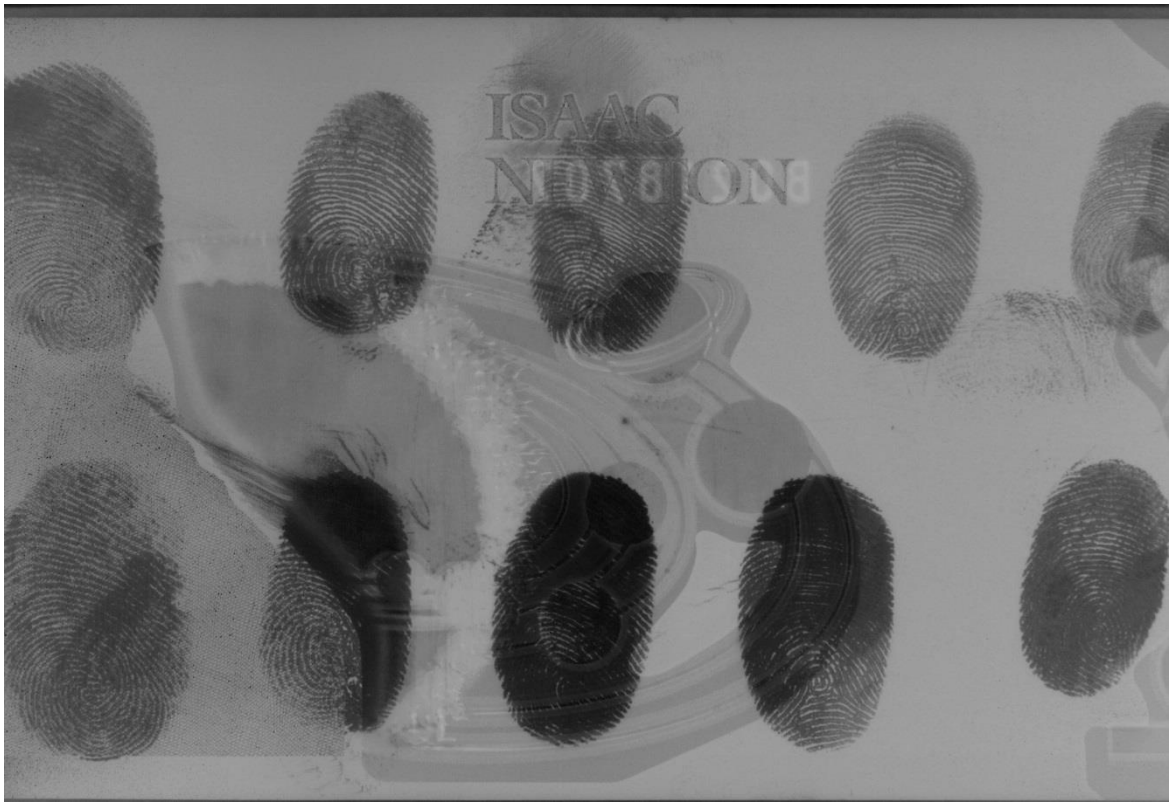


Figure 128: NT Cu VMD (3.0 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W)

When the infrared image is inverted, the background becomes more solid with no sign of the fish scale pattern. The row of natural fingermarks show a great deal of clear ridge detail, the groomed marks, although mostly overdeveloped, show some good ridge detail. The small amount of sparkling observed in the Newton area was not visible in this image (Figure 128).

Bare Copper

Only a few deposition thicknesses were attempted with the bare copper wire; 0.7 nm, 1.3 nm and 2.1 nm. As with the NT copper the banknotes with the thinner copper layers provided poor contrast when imaged. One noticeable difference between the NT and bare copper from the outset, was that the bare copper required a higher temperature in order to evaporate.

2.1 nm Deposition Thickness

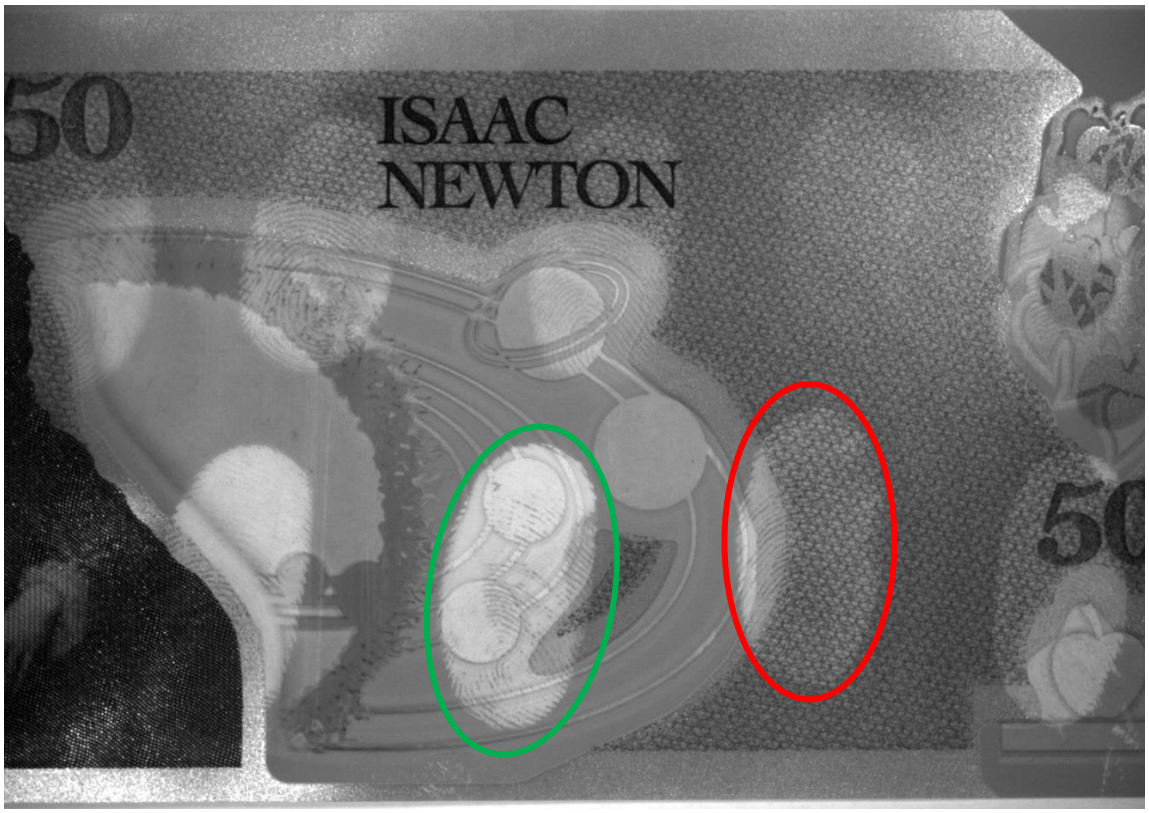


Figure 129: Bare Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with White Light (B&W)

The bare copper showed fingermarks in both rows, where the NT copper counterpart showed less development (Figure 129). As with the NT copper, some of the heavier groomed marks could be observed around the windowed area, although they show leaching (**here**). Other fingermarks were visible in the printed area, although they showed no ridge detail due to the busy background pattern. A few marks pass over from the clear area to the printed area, good clear ridge detail can be observed in the window area, but again become muddied when the ridges pass into the printed area (**here**).

When viewed in infrared, the bare copper developed fingermarks can again be observed over the entire banknote's surface. Like the 2.1 nm insulted copper sample, the fish scale background is partially visible, albeit extremely faint. The deposited bare copper appears darker than its NT copper equivalent, giving improved contrast. The groomed fingermarks that are leached, appear brightly illuminated. The bare copper also appears to be susceptible to the scuffing which causes some damage to the developed note's surface (**here**) (Figure 130).

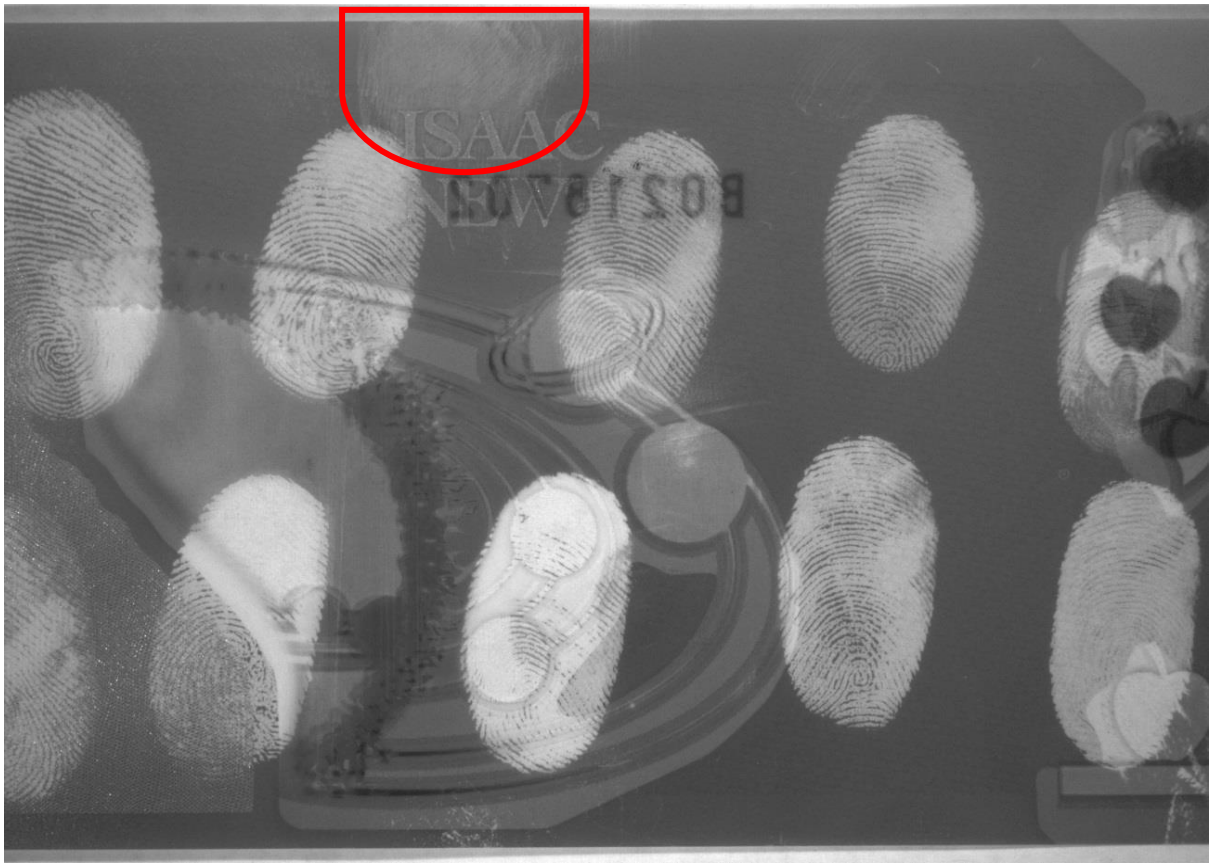


Figure 130: Bare Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR (B&W)

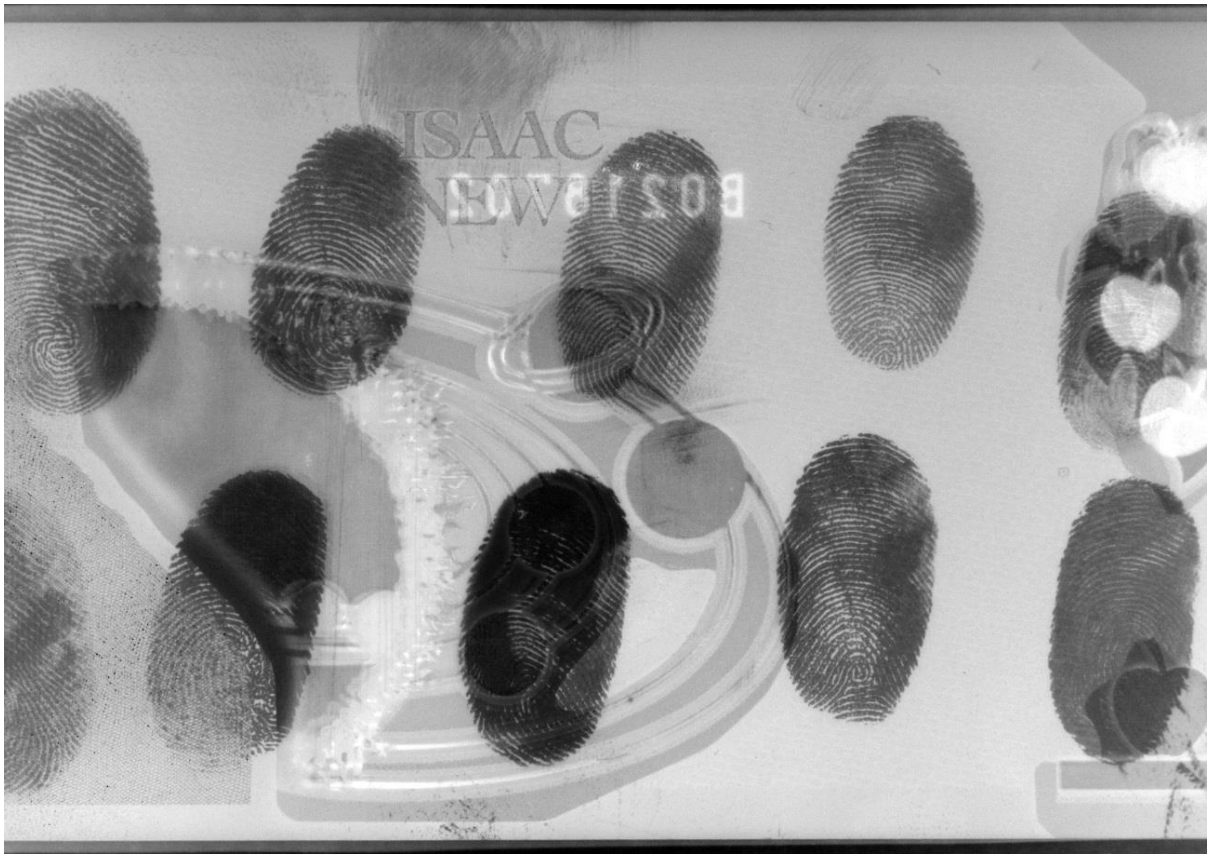


Figure 131: Bare Cu VMD (2.1 nm Thickness) Treated Polymer Banknote Viewed with Reflected IR - Inverted (B&W)

When the image is inverted, the background appears considerably lighter than on its corresponding NT copper sample. The black marks on the lighter background make visualisation easier, especially on the natural marks. The groomed marks show, some shape and flow, but some of the leaching is so pronounced, identification would be extremely difficult (Figure 131).

The tests undertaken highlighted that while the deposition thickness of the copper impacted visual observation of the fingermarks on the substrate surface, certain aspects were improved when viewed under reflected infrared conditions. The thicker the copper deposition layer, the better the contrast between the ridge detail and the substrate to an extent. Samples with 3.0nm of copper deposited upon their surface began to exhibit overdevelopment which presented as the ridges leaching into each other. This technique is of particular use when developing marks on a substrate with a highly patterned background.

5.3.4 Group Study 1

A group study was developed to assess the VMD and infrared technique against samples which have different aged fingermarks from multiple donors. The group was comprised of ten individuals, five male and five female (Appendix Table 117). A series of ten fingermarks were deposited across the surface of each polymer banknote; five natural and five artificially groomed. The samples were to be treated and developed with a 2.5 nm coating of copper *via* vacuum metal deposition at a number of different time intervals. Two different split trials were included; bare copper vs NT copper and bare copper vs gold/zinc (Table 5 and Table 6).

Time Intervals	Thickness	Donors	Metal
1, 2, 4, 8, 14, 28 Days	2.5 nm	10	Cu (Bare)
			Cu (NT)
6	1	10	2
6	10		2
60 Total Samples			2
120 Samples (Splits)			

Table 5: Group Study 1 - Sample Breakdown - Cu (Bare vs NT)

Time Intervals	Thickness	Donors	Metal
1, 2, 4, 8, 14, 28 Days	2.5 nm	10	Cu (Bare)
			Au/Zn
6	1	10	2
6	10		2
60 Total Samples			2
120 Samples (Splits)			

Table 6: Group Study 1 - Sample Breakdown - Cu vs Au/Zn

Due to conflicts in scheduling between the outside organisations being worked with, treatment and imaging of the notes had to be conducted on separate days. West Technology were visited first to utilise their VMD system and Foster + Freeman were visited almost a week later to use their imaging facilities.

Upon initial inspection after the split notes had been reunited, it was easier to observe some fingermark haloes on the sections treated with gold/zinc (Figure 132), this was of no real concern as areas with light copper layers have shown excellent ridge detail in previous experiments. 28 day old samples also showed visible fingermark ridge details when viewed obliquely in normal white light conditions (Figure 133). The notes with the two types of copper were also lacking when examined by eye.

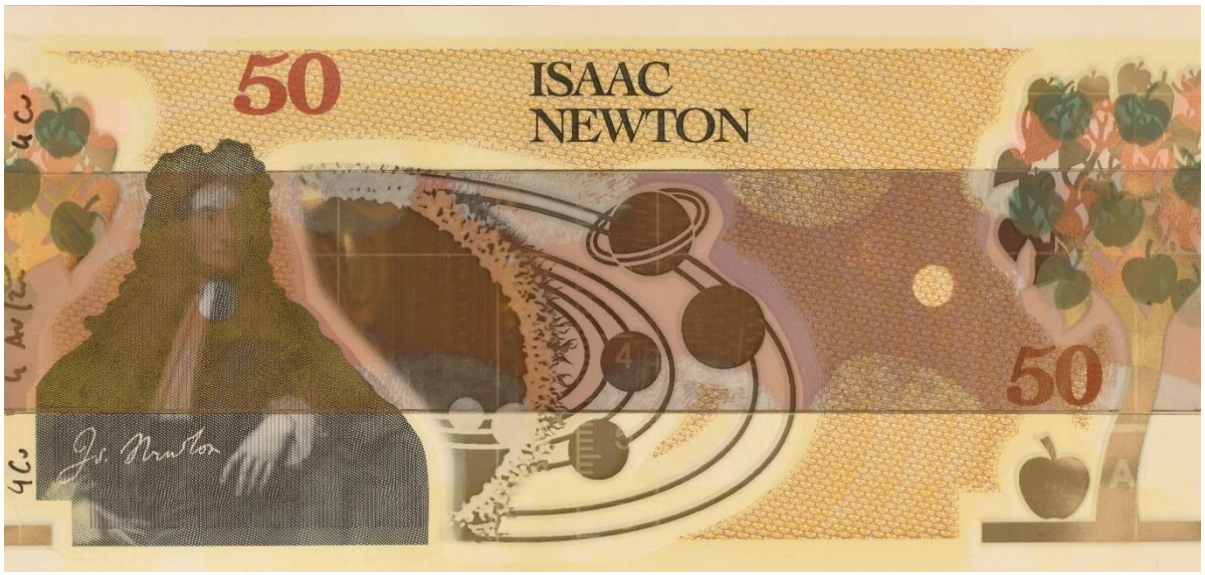


Figure 132: Cu vs Au/Zn - 1 Day Aged - Donor 4 – White Light

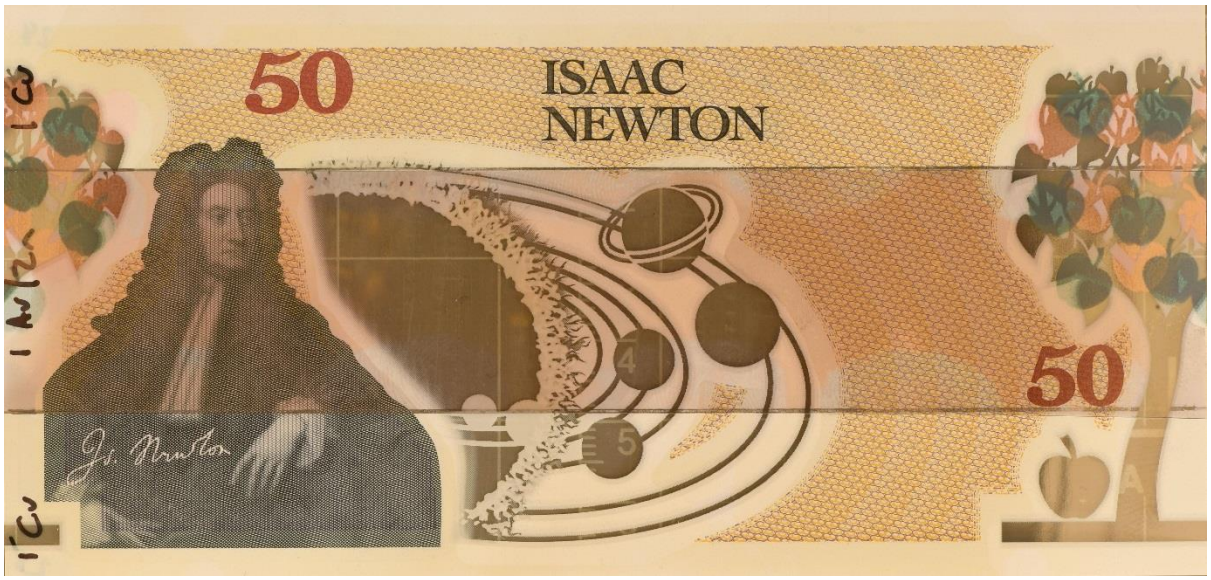


Figure 133: Cu vs Au/Zn - 28 Days Aged - Donor 1 – White Light

Problems became apparent when imaging was attempted. The copper was not appearing to react the same way it had previously, and no fingermarks were visible at all when trying to photograph the banknote. The only indication that fingermarks should have been expected was the presence of the counter halves visible on the Au/Zn sections of the banknotes (Figure 134).

Figure 134: Cu vs Au/Zn - 1 Day Aged - Donor 2 – Infrared

This phenomena was consistent across the whole study, and prompted many questions.

- Were the copper samples even treated?
- Was there a problem with the VMD equipment?
- Did the thickness monitor record the wrong thickness of copper deposition?
- Had something happened in the time between treatment and imaging?

Were the copper samples even treated?

As an initial thought, this does not seem out of the realms of possibility. However, looking at the notes, it is clear to see, in most cases, that the copper did coat the banknotes. This is easier to observe on some notes than others (**here**) (Figure 135).

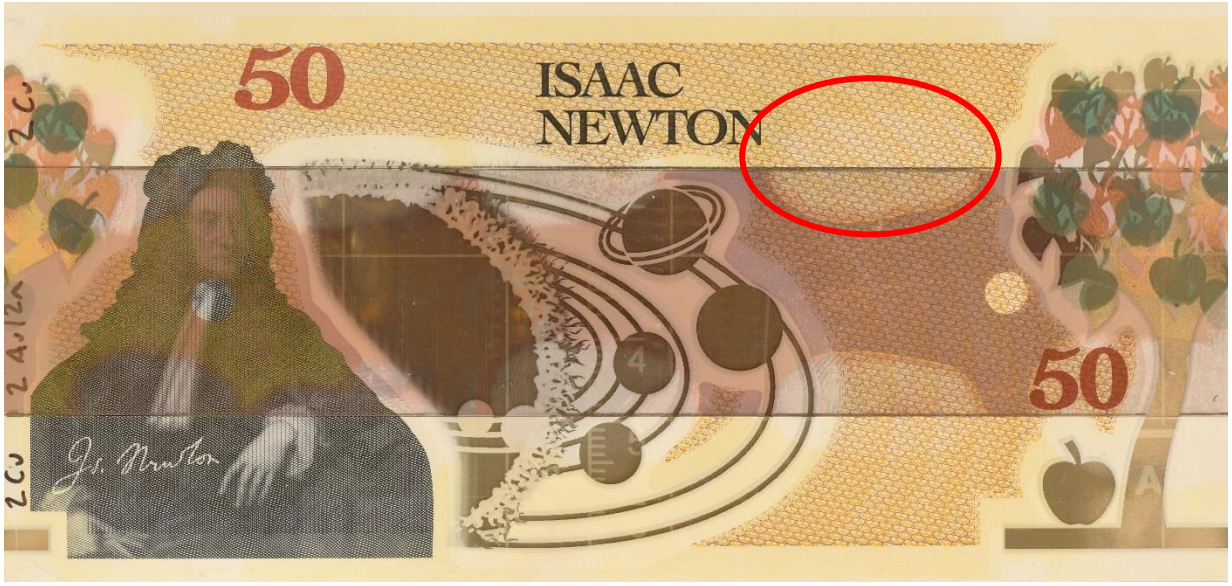


Figure 135: Cu vs Au/Zn - 1 Day Aged - Donor 2 – White Light

Was there a problem with the VMD equipment?

Having already ascertained that the copper had been deposited, the possibility that the VMD equipment was at fault seemed improbable, especially since the gold/zinc deposition had imaged to a degree where ridge detail could be observed.

Did the thickness monitor record the wrong thickness of copper deposition?

Unless the amount of copper that had been deposited was extremely thin, this question is moot. Results obtained from previous experiments (Chapter 5.3.3) have shown that imaging is still highly effective on samples which have been treated with as little as a 1.6 nm coating of copper.

Had something happened in the time between treatment and imaging?

This seems like the most plausible explanation for the apparent change in the copper's behaviour. It is theorised that the thin layer of copper oxidised between the time of deposition and the time of imaging, thus altering the infrared absorption/reflection dynamics witnessed previously.

With the oxidation of the copper being the only rational explanation as to why these samples failed to develop in a similar manner as they had in the past, it seemed only logical to repeat the study with the difference of imaging the same day. This would allow for the exclusion of the variable believed to be hampering the process and the delivery of more consistent results. However, if this resulted in the same poor results being obtained, further exploration into the root cause would be warranted.

5.3.5 Split Depletion Series

Ten “Chanoler” polymer banknotes had a series of 100 fingermarks deposited on them in series of ten marks per note. The notes were each cut along the horizontal twice, producing three sections (Figure 136). The two outer sections had one metal deposited upon them, the inner sections had another. Once recombined, the two metal techniques could be compared.

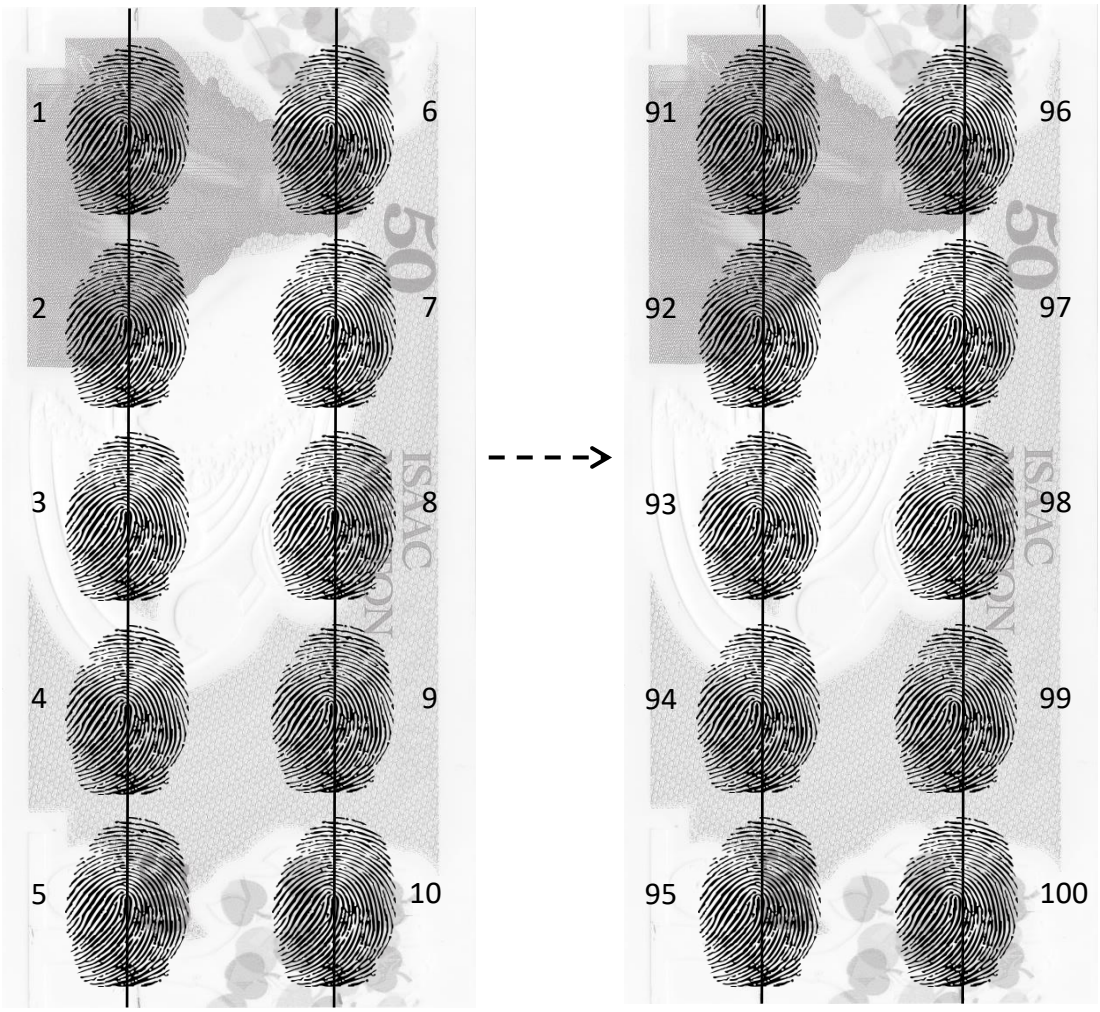


Figure 136: Polymer Banknote Split Series Preparation

This series was designed to ascertain how sensitive the copper VMD could be, in imaging as well as lifting and treating with rubeanic acid.

Unfortunately, these samples were treated and imaged with the failed samples in the Group Study 1. This study would have to be attempted again at a later date.

5.4 Conclusions

Preliminary tests on the polymer banknotes using vacuum metal deposition showed that very little copper had to be deposited, in order to react with the fingermarks. Although, three distinct thicknesses of copper were deposited, only the thickest and intermediate layers were visible to the naked eye. The thinnest layer was hard to observe, however, when a gel lifter was applied to the banknote, all sections produced visible fingermarks after treatment with the rubeanic acid.

The most interesting aspect of this series of experimentation was the interactions between the treated surface and ultraviolet and infrared light sources. Where VMD developed fingermarks give poor contrast against a busy background, the infrared light source helps eliminate the background to provide a much enhanced contrast between the fingermark ridges and the background substrate. The IR illumination does however, have the drawback of showing the some aspects of the image on the inverse side (to that having been treated) in reverse.

The use of ultraviolet light almost eliminates the background, but still leave some of the background imagery and text, which can interfere with flow of the fingermark ridges. When the light source was changed to reflected UV, all background drops out, no imagery leaks through and the fingermark ridges appear as dark lines on a silvery background. This light source also allowed for the distinguishing of the different thickness layers of copper used in this particular experiment.

A study looking at VMD on plastic carrier bags and magazine covers and pages was initially conducted using gold/zinc. When viewing these samples using white light, coaxial imaging, ultraviolet, and reflected UV the results obtained were less than impressive. Copper was not attempted on these substrates as the polymer banknotes took priority, however, it may be worth revisiting these substrates and treating with copper at a later date.

Further studies looking at copper being deposited in different thicknesses showed that while it was possible to deposit a layer of copper 0.2 nm thick, it was at approximately 1.6 nm thick that the imaging, using reflected IR, really came showed exceptional results. At 3.0 nm thickness of deposited copper, the fingermarks begin to leach into each other, making some areas of the fingermark ridge detail difficult to read. A copper thickness of 2.5 nm was found to give the best contrast between the developed fingermark ridges and the substrate background. This study was conducted using a single donor, given the high amount of quality fingermarks recovered, additional studies with multiple donors would be beneficial.

A group study using the same technique as with the single donor study was undertaken, thickness of deposition was set at 2.5 nm as that was observed to give the best contrast between the background and the deposited mark. 10 donors were used, male and female, and multiple time frames were used for aging the fingermarks on the banknotes, ranging from 1 day to 28 days old. The banknotes were also split in order to easily compare gold/zinc with the copper deposition technique. Unfortunately, the copper failed to react in the same way when it came to imaging. This was believed to be due to oxidation of the copper layer due to a prolonged period between treatment and imaging.

A split depletion series was prepared using 100 fingermarks from a single donor across ten polymer banknotes. These notes were to be treated with Au/Zn and Cu as the comparison metal. These were treated and imaged with the failed group study, and therefore also failed to image. This would be well worthwhile attempting again as it would allow for an indication as to how sensitive the Cu VMD is, as well as showing to what level the fingermarks can be lifted and imaged *via* rubeanic acid.

Although still in its infancy, this technique shows the potential to be a very effective protocol for the imaging of fingermarks on polymer surfaces, as well as the possibility of being transferable to other substrates.

6.0 Miscellaneous Techniques

6.1 Introduction

Radioactive Techniques

In 1958, Takeuchi *et al.* described the use of a radiographic technique for developing latent fingermarks on paper, glass and metal foil, their technique involved the use of ^{14}C-labeled stearic acid [113]. In 1963, Grant *et al.* used ^{35}S-labeled sulphur dioxide to develop latent prints on paper [117], Spedding refined the process for application to a wider variety of papers and fabrics [118]. Gel'fman *et al.* (1964) reported using ^{14}C-labeled formaldehyde to develop latent prints, which could then be imaged using contact radiography [114]. Once exposed to $^{35}SO_2$ gas, the latent print material was found to be selectively labelled and could subsequently be imaged using autoradiography. They found that typical exposure time required to obtain a print of satisfactory quality was approximately 40 hours. Ganson went on to describe some successful operational applications of the method to actual casework [65, 119].

Morgan *et al.* (1974) described using radioactive halogens, bromine (^{82}Br) and iodine monochloride (^{133}ICl), were reported to develop latent prints [251] cited in [252]. In 1976, Knowles *et al.* found that the use of a ^{35}S-labeled thiourea solution could be used to image physically developed prints on patterned backgrounds [253] cited in [134]. Fingermarks were developed using silver physical developer, and subsequently tagged with ^{35}S before being imaged by autoradiography. Akerman [254] and Stverak *et al*. [255], cited in [134], reported using radioactive silver (^{110}Ag) to react with latent print residue. The silver reacted with the chlorides in the fingermark residue to produce a radioactive silver chloride. The marks could then be imaged using autoradiography, and was reported to be effective at developing latent fingermarks on polyethylene, ungrained leather and several types of paper.

Biological Techniques

O'Neill (1941) was the first to report the use of bacteria to develop latent fingermarks [256]. Numerous different approaches have been reported over the years, however, none of these techniques are used in casework today. In 1987, Mason reported the use of the gram-negative bacterium *Acinetobacter calciacaticus* in a nutrient gel that could be pasted over latent fingermarks. Growth would then occur preferentially along the friction ridge marks after incubation for 24 hours [257]. Harper *et al.* went on to demonstrate this technique's success on fingermarks on polyethylene. The technique, however, required 48 hours to incubate and required staining with amido black [258].

Many other aspects of biology have been explored in order to enhance latent fingermarks. Enzymes were used by Everse *et al*. sequentially before and after the ninhydrin process [259]. The technique was found to be successful on fresh marks, but not older marks. A further study found that the particle size of the enzyme was a major factor in the quality of the marks developed [260]. Plant materials such as lectin obtained from *Ulex europeus*, was found to bind with sugars located on the surface of red blood cells [261]. More recently King *et al*. found that *Spirulina platensis* mixed with a fingerprint powder demonstrated near-infrared fluorescence which helped background interference on busy substrates [153].

Protein antibodies were reported by Drapel *et al*. to successfully develop fingermarks. Good quality friction ridge detail was obtained from membranes of polyvinylidene fluoride (PVDF), however, fingermarks on paper showed weaker results [59]. Other biological components that have been exploited include; antigens [262], drug metabolites [263-265] and the detection of morphine [266].

6.1.1 Aims

Radioactive Techniques

To determine the feasibility of using gel lifters to lift radioactive material in order to use radioactive techniques to enhance and image latent fingermarks.

Biological Techniques

To investigate the use of bacteria colonies as an enhancement technique to visualise latent fingermarks.

6.2 Experimental

6.2.1 Assumptions

Throughout the experimental sections, the following assumptions are made;

- Where not specified, the author's fingermarks were used for enhancement purposes.
- Fingermark deposition types:
    - Natural series: A series of marks were the donor deposits their prints with no additional "grooming" involved.
    - Loaded series: A fingermark where the person depositing the print intentionally rubs their fingertips on or around their forehead and nose areas, and then presses their finger onto the sample medium.
- Unless otherwise stated the sample substrate used was paper; the paper used was:
  Brand: Polaroid Copier Paper
  Weight: 80gsm

Radioactive Techniques

- Whenever a radioisotope was being deposited, it was done so with an auto pipette set to a volume of 100 µl.
- Liquid Scintillation Counting was conducted on a Packard: Tri-Carb 1900TR or 2100TR Liquid Scintillation Analyser
- Unless otherwise stated, the Liquid Scintillation Cocktail used was Gold Star: Multipurpose Liquid Scintillation Cocktail by Meridian Biotechnologies Ltd.
- Autoradiography was carried out on a Perkin Elmer Cyclone Phosphor system

Biological Techniques

- Where not specified, agar plates and nutrient broths are incubated in incubation ovens at 37°C

6.2.2 Substrate Preparation

Radioactive Techniques

Metals

Sheets of stainless steel (316 Grade Stainless Steel, 2B Finish, 0.5 mm thick) and brass (CZ 108 Grade Brass, 0.3 mm thick) were obtained (www.metaloffcuts.co.uk) and cut to 12 cm by 3 cm sections. The sections were covered with a plastic protective coating. By cutting the protective coating with a razor, sections could be exposed whenever necessary without the risk of contaminating the entire sample.

Plastic

Plastic Petri dishes had their lips removed and the remaining circular disc was cut to 3-4 cm square samples.

Ceramic Tile

White ceramic tiles were obtained and cleaned down with acetone, to ensure a clean surface area to work on.

Gelatine Lifter

Black silicone forensic gel lifters (High Performance Evidence Lifters: Black Footprint Lifters 18x36cm, BVDA – B12500) [141] were cut to the required sample size dependant on the experimental procedure being undertaken.

Biological Techniques

Agar Preparation

The agar was prepared by technician Tim Coles prior to arrival in the lab, and new agar plates were prepared for subsequent experiments. Nutrient broth was also prepared before arrival in the laboratory.

6.2.3 Reagent Preparation

Radioactive Techniques

Nickel-63 isotopes were decanted from a premade aqueous stock solutions.

Stock 1

Activity – 1087.74kBq/100ml

Stock 2

Activity - 1087.74kBq/100ml

Phosphorus-32 isotopes were decanted from a premade aqueous stock solutions.

Stock 1

Activity – 4kBq/2ml

Biological Techniques

No special reagents were required over and above the agarose gels and nutrient broths.

6.2.4 Sample Treatment

Radioactive Techniques

Samples were impregnated with the Nickel-63 or Phosphorus-32 isotope *via* an auto-pipette, the deposited ^{63}Ni or ^{32}P was then allowed to evaporate over the space of a few hours or overnight. The dried ^{63}Ni or ^{32}P was then used for the various experimental techniques that were being utilised.

Liquid Scintillation Counter

Since ^{63}Ni is a weak beta emitter, liquid scintillation counting was the most logical detection method to use. A Tri-Carb 1900TR/2100TR Liquid Scintillation Analyser was used to determine the activity in the samples tested. Liquid scintillation counting detects radioactivity *via* light emission events, this takes place in a solvent cocktail, for example toluene or di-isopropylnaphthalene (DIPN) which contain scintillators, such as phosphors. The scintillation cocktail allows for close interactions between the isotope atoms and the scintillator. Energy released by β-emitting radioisotopes is absorbed *via* the aromatic ring of the solvent in the cocktail. This energy is re-emitted *via* the phosphor as flashes of light. It is these light flashes that are counted by the scintillation counter [267].

Autoradiography

In order to assess the transfer of radioisotopes, autoradiography was employed. A Perkin Elmer Cyclone Phosphor system was used. The Cyclone system allows for the imaging of flat radioactive samples, *via* reusable autoradiography plates. The process involves; erasing the phosphor autoradiography plate shortly before exposure to the radioactive sample, the sample is then placed on the plate in dark conditions for an appropriate amount of time (this could be from hours to days depending on the radioisotope). After exposure, the plate is then secured in the scanning carousel of the Cyclone, in darkened conditions. The carousel with plate attached are then inserted in to the Cyclone scanner and analysed using OptiQuant™ software. The plate is scanned by a laser which is focused to less than 50 µm, it reflects off the latent radioactive material and detected *via* optics to produce a digital image [268].

Biological Techniques

Fingermark Deposition on Gels

When fingermarks had to be deposited on to the agar gels, the fingertips were rubbed over the palms to ensure an equal distribution of materials on them. Fingers then had the volar pads lightly pressed directly on to the gels (Figure 137) before having the lids to the gel plates replaced and the plate placed in an incubation oven.

Figure 137: Fingermark on Agar Gel

Colony Transfer to Agar Plate

Where bacterial colonies were transferred from one agar plate to another, this was done aseptically using an inoculating loop and a Bunsen burner. Using the following procedure:

1. The inoculation loop was sterilised by passing it through the flame of the Bunsen burner, at an angle, until it glowed red hot.
2. The lid of the plate to be sampled was opened enough to allow access to the loop.
    a. The loop was touched to an area with no bacterial growth, in order to cool it down.
3. The loop was used to scrape off a small amount of an isolated colony.
    a. The lid was closed immediately after this in order to keep it from being contaminated by the outside air.
4. The lid from the new plate was removed and the loop containing the bacterial colony was streaked over the surface in three strokes, the plate was then turned some 60-90° and streaked again from the tail end of the initial streaks. This was repeated until almost a complete revolution was obtained then the streaks were brought in to the centre of the plate (Figure 138).
    a. The lid was replaced to avoid further contamination from the air.
5. The loop was then sterilised again *via* the Bunsen burner.
6. The sample was then incubated at 37°C for 24 hours.

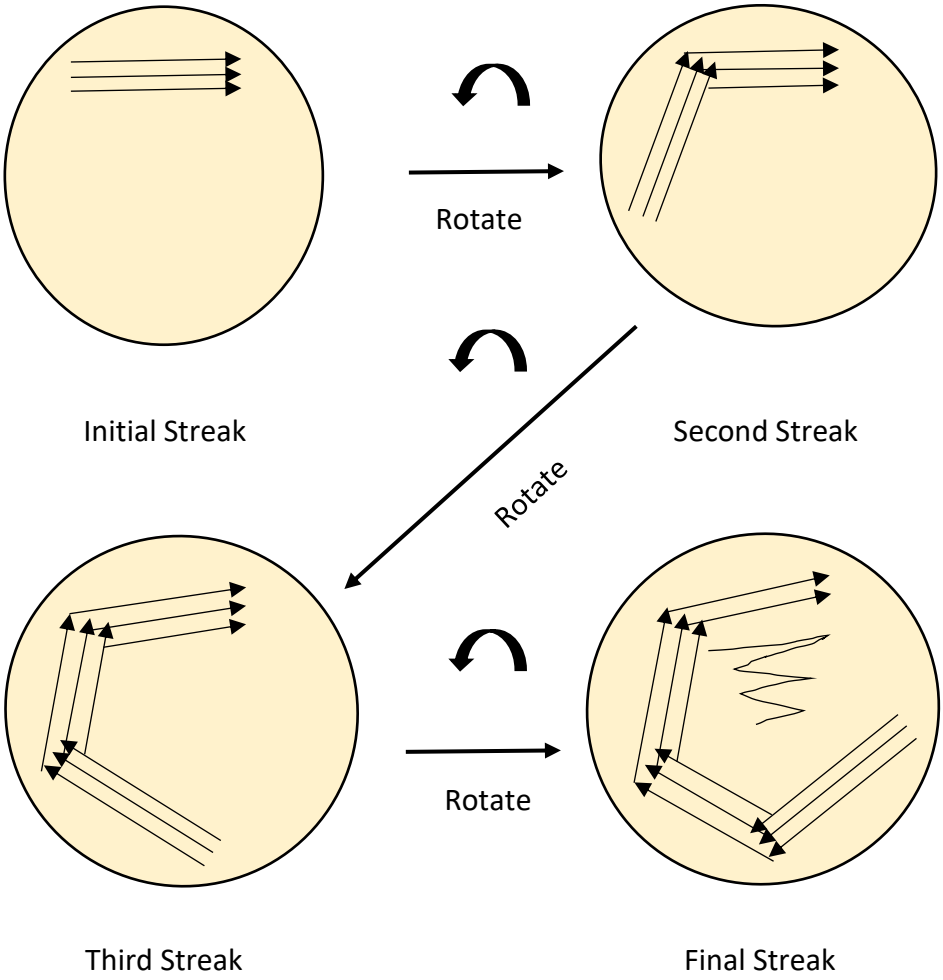


Figure 138: Streak Plate Procedure

Colony Transfer to Nutrient Broth

When the requirement was to transfer from an agar plate to a nutrient broth, the procedure followed the same process as above, however, deviation occurred after step 3. As follows:

4. The vial of nutrient broth was then picked with the free hand, the cap was removed using the palm of the hand holding the loop, and the mouth of the vial was passed through the flame.
5. The vial was held at a 45° angle and the loop was inserted in to the vial, the loop was spread over the wall of the vial at an exposed area which would lie below the surface level when the vial was in an upright position (Figure 139).
6. The loop was then removed from the vial, and the mouth of the vial was flamed again *via* the Bunsen burner.
7. The loop was then sterilised again *via* the Bunsen burner.
8. The sample was then incubated at 37°C for 24 hours.

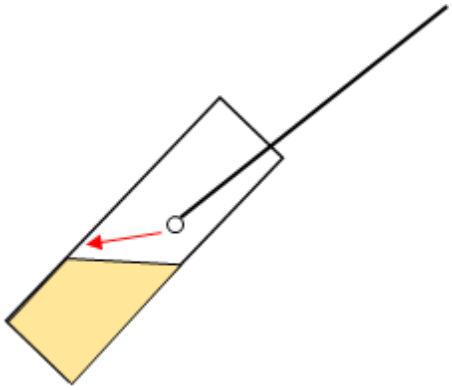


Figure 139: Broth Inoculation

6.2.5 Sample Evaluation

Radioactive Techniques

Following the liquid scintillation counting process, the results from the subsequent printouts were tabulated and calculations performed in order to ascertain the efficiency.

Biological Techniques

After the agar plates had been incubated, they were examined visually for bacterial growth. Any plates that had no growth, were not carried forward into the next stage of the experimentation.

6.2.6 Treated Sample Recording

Once the substrates had been treated, they were photographed to record the enhancement. Photographs were taken using a Nikon D5200 digital SLR camera with the focus set to manual. The camera was placed upon a tripod to minimise movement and to keep the distance from the sample constant.

Specialist Equipment

After the autoradiography procedure was completed and a digital image was procured, the image was processed through another piece of software. There were two very similar pieces of software used to analyse, edit and enhance the autoradiography images; these were ImageJ (NIH2004) and Fiji. Both are very similar in interface and usage, however, Fiji offers more filters and flexibility for the enhancement of the images.

6.3 Results and Discussion

6.3.1 Radioactive Techniques

Working with Nickel-63 (Stock 955X), the first point that had to be established was its activity. The stock solution had an activity of 1087.74 kBq per 100 ml, however, the amounts being used were multiples of 100 µl. This equated to an activity of approximately 1 kBq. 100 µl of ^{63}Ni was then added to a liquid scintillation cocktail and examined multiple times on a liquid scintillation counter (Table 10), the 1 kBq of activity equated to around **46597.4** counts per minute.

Sample	CPMA
Blank	23.0
Standard 1	46543.2
Standard 2	46180.4
Standard 3	46577.6
Standard Av	**46433.7**

Table 7: Standard Counting 1

Sample	CPMA
Blank	18.4
Standard 1	46752.2
Standard 2	46900.8
Standard 3	46406.6
Standard Av	**46686.5**

Table 8: Standard Counting 2

Sample	CPMA
Blank	21.0
Standard 1	46772.2
Standard 2	46446.6
Standard 3	46797.6
Standard Av	**46672.1**

Table 9: Standard Counting 3

Sample	CPMA
Average 1	**46433.7**
Average 2	**46686.5**
Average 3	**46672.1**
Average of Averages	**46597.4**

Table 10: Average of Standard Counting

A stainless steel sample was prepared by removing a couple of strips of the protective plastic (Figure 140), then applying a 100 µl of ^{63}Ni directly to the metal. Nickel was allowed to evaporate overnight. A piece of forensic lifting gel was cut to the size of the sample area. The gel was applied to the surface where the nickel had been applied, and was then placed in to a liquid scintillation vial with the scintillation cocktail and passed through the scintillation counter to see how much activity had been lifted.

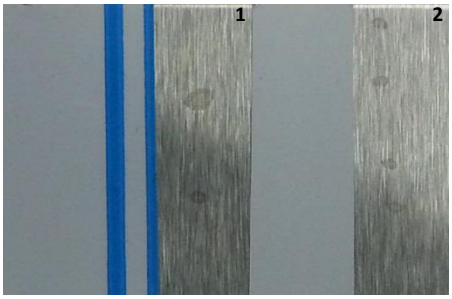


Figure 140: Stainless Steel Sample

Three gel sections per exposed area of metal were used in succession (area 1 – 1st gel, area 2 – 2nd gel), and placed in to separate scintillation vials. This would allow for the calculation of how much nickel was recovered versus how much was deposited. The initial results gained for all three gels combined was very poor (Table 11); **1063.6** counts per minute, a mere **2.28%** recovery from what had been deposited. This was repeated for a second metal sample surface (Table 12).

Sample	CPMA	% Standard
1st Gel: 1st Lift	884.6	
1st Gel: 2nd Lift	113.4	
1st Gel: 3rd Lift	65.6	
1st Gel: Total	1063.6	2.28%
2nd Gel: 1st Lift	1285.4	
2nd Gel: 2nd Lift	90.6	
2nd Gel: 3rd Lift	70.8	
2nd Gel: Total	1446.8	3.10%

Table 11: Gel Counting 1

Sample	CPMA	% Standard
1st Gel: 1st Lift	1158.0	
1st Gel: 2nd Lift	150.0	
1st Gel: 3rd Lift	66.2	
1st Gel: Total Lift	1374.2	2.94%
2nd Gel: 1st Lift	1493.6	
2nd Gel: 2nd Lift	131.8	
2nd Gel: 3rd Lift	88.4	
2nd Gel: Total Lift	1713.8	3.67%

Table 12: Gel Counting 2

Sample	CPMA
1st Gel: Average 1	1063.6
1st Gel: Average 2	1374.2
1st Gel: Average of Averages	1218.9
2nd Gel: Average 1	1446.8
2nd Gel: Average 2	1713.8
2nd Gel: Average of Averages	1580.3

Table 13: Average of Gel Counting

It was decided to do wipe tests on the metal to explore if more nickel could be recovered, this was done by dipping a cotton bud in a 40% acetone solution and rubbing it over the test area. This was done a total of six times per sample area, and each cotton bud was cut from its stick and placed in a separate scintillation vial. Each vial was tested (Table 14) and a much greater amount of nickel was recovered. When these figures were added to the figures from the gel recoveries, the amount recovered looked much higher. The first sample area returned **16739.1** counts per minute, a **35.92%** recovery and the second; **21715.5** counts per minute, a **46.6%** recovery (Table 15). Although these were a massive improvement from what was obtained from using the gels alone, they were still below 50% recovery. It was thought that the gels were retaining the nickel, and quenching the scintillation counting, which would provide erroneous results.

Sample	Cumulative CPMA
1st Gel: 1st Wipe	4550.4
1st Gel: 2nd Wipe	8541.2
1st Gel: 3rd Wipe	11655.4
1st Gel: 4th Wipe	13556.6
1st Gel: 5th Wipe	13993.0
1st Gel: 6th Wipe	**15520.2**
2nd Gel: 1st Wipe	4436.8
2nd Gel: 2nd Wipe	13010.4
2nd Gel: 3rd Wipe	17337.2
2nd Gel: 4th Wipe	18034.6
2nd Gel: 5th Wipe	18539.8
2nd Gel: 6th Wipe	**20135.2**

Table 14: Wipe Tests

Sample	CPMA	% of Standard
1st Gel: Average of Averages	**1218.9**	
1st Gel: 6th Wipe	**15520.2**	
1st Gel: Total	**16739.1**	**35.92%**
2nd Gel: Average of Averages	**1580.3**	
2nd Gel: 6th Wipe	**20135.2**	
2nd Gel: Total	**21715.5**	**46.60%**

Table 15: Overall Nickel Recovery

To test if the gels were retaining the nickel isotope, five gel samples were each impregnated with 100 µl of ^{63}Ni. The nickel was allowed to evaporate, then they were placed in to separate scintillation vials and processed through the scintillation counter (Table 16).

Sample	CPMA
Gel 1	30801.5
Gel 2	31398.7
Gel 3	32755.5
Gel 4	26798.7
Gel 5	24750.0
Gel Av	**29300.9**

Table 16: Recovery from Gel

The average value for the gels was **29300.9** counts per minute, a 62.88% recovery from the **46597.4** counts per minute standard. This showed that the gel does quench/retain some of the nickel.

Other substrates were tested to see how well the gel was able to recover the nickel isotope from them. The substrates used were; ceramic tile, brass and plastic. 100 µl of ^{63}Ni were deposited on the surface of each substrate. Three pieces of gel were used in to lift from the substrates, one after the other. A wipe test was conducted after the gels were used.

Sample	% Recovery Count 1	% Recovery Count 2	% Recovery Average
Standard Average	**46597.4**	**46597.4**	**46597.4**
Tile 1	**83.72%**	**79.11%**	**81.42%**
Brass 1	**56.99%**	**62.29%**	**59.64%**
Plastic 1	**86.81%**	**81.27%**	**84.04%**

Table 17: Percentage Recovery 1

Sample	% Recovery Count 1	% Recovery Count 2	% Recovery Average
Standard Average	**46597.4**	**46597.4**	**46597.4**
Tile 2	**79.25%**	**80.34%**	**79.80%**
Brass 2	**67.26%**	**71.87%**	**69.57%**
Plastic 2	**80.05%**	**78.46%**	**79.26%**

Table 18: Percentage Recovery 2

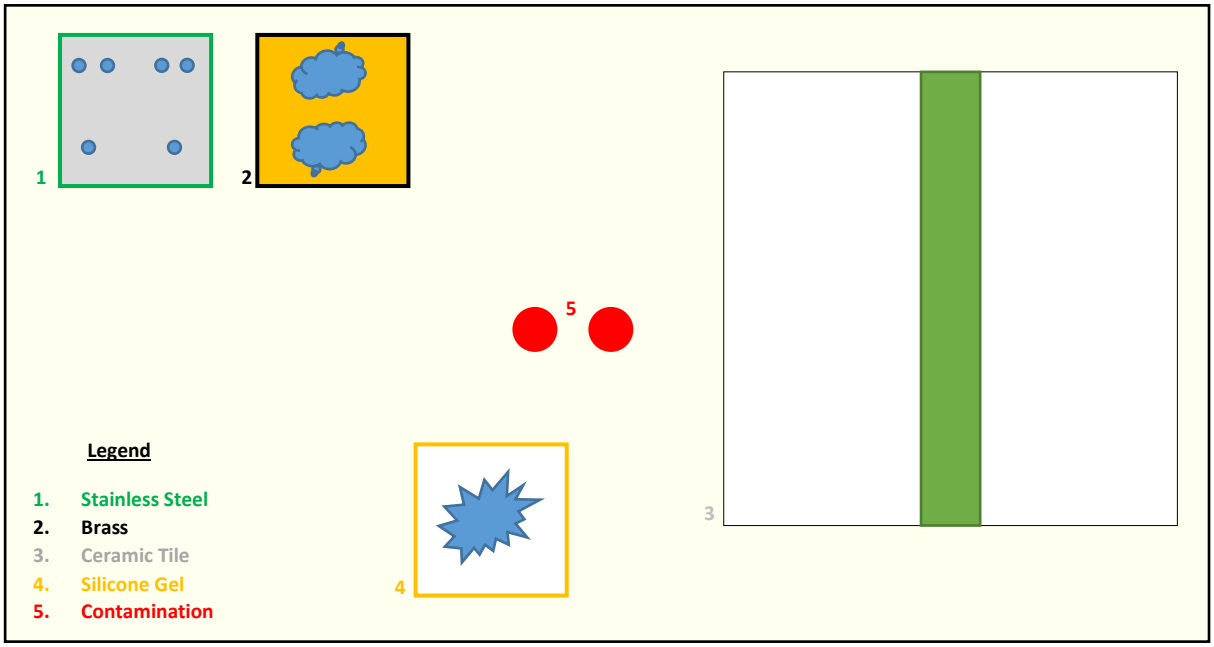
Sample	% Recovery
Standard Average	**46597.4**
Tile Overall Average	**80.61%**
Brass Overall Average	**64.61%**
Plastic Overall Average	**81.65%**

Table 19: Average Percentage Overall Recovery

The gels used on the brass samples recovered very little nickel, but the wipe tests recovered a lot more. On the brass samples the overall recoveries ranged from **26554.4** to **33489.2** counts per minute, **59.64%** to **69.57%** respectively (Appendix Table 122 - Table 125). The plastic samples yielded recoveries from **36559.8** to **40452.4** counts per minute, equating to a range of **79.46%** to **86.81%** of the standard (Appendix Table 126 - Table 129). The final substrate, the ceramic tile, gave overall recoveries in the range of **36862.8** and **39012.2** counts per minute, which were **79.11%** and **83.72%** of the initial standard (Appendix Table 118 - Table 121). Both the tile and plastic provided much higher recovery yields for the nickel *via* the gel lifters, and less recovery with the wipe test. This lead to the realisation that the nickel was reacting differently with the brass and stainless steel. Since nickel is present in stainless steel and can be present in brass, it was assumed that the nickel was leaching in to the metals and remaining there. This was more evident since the average recovery from the plastic and tile surfaces was over 80% in each case (Table 19).

With the aforementioned recovery data in mind, it was felt that the forensic gel lifter could in theory be used to lift radioactive isotope contaminated fingerprints, depending on the surface, and autoradiography of the gel to produce an identifiable fingerprint. In order to test the validity of this assumption, various test were conducted using autoradiography plates and utilising Nickel-63 as the radioactive isotope source.

Since ^{63}Ni is a weak emitting beta, an experimental protocol using previously utilised substrates was devised. The autoradiography plate was activated using a light box, then in almost dark conditions, a previously used ceramic tile, piece of brass, stainless steel and section of silicone gel were placed upon the surface of the autoradiography plate (Scheme 7).



Scheme 7: Layout of Samples on Autoradiography Plate

The plate with the samples on was placed into a box with a tight fitting lid to ensure no light got to the plate. After one day, the plate was removed from the box, again in almost dark conditions, and placed in the Cyclone scanner to be read. The scanned image looked blank until loaded in to the Fiji software, where it was manipulated with various filters which allowed the visualisation of the radioactivity present on the sample substrates (Figure 141).

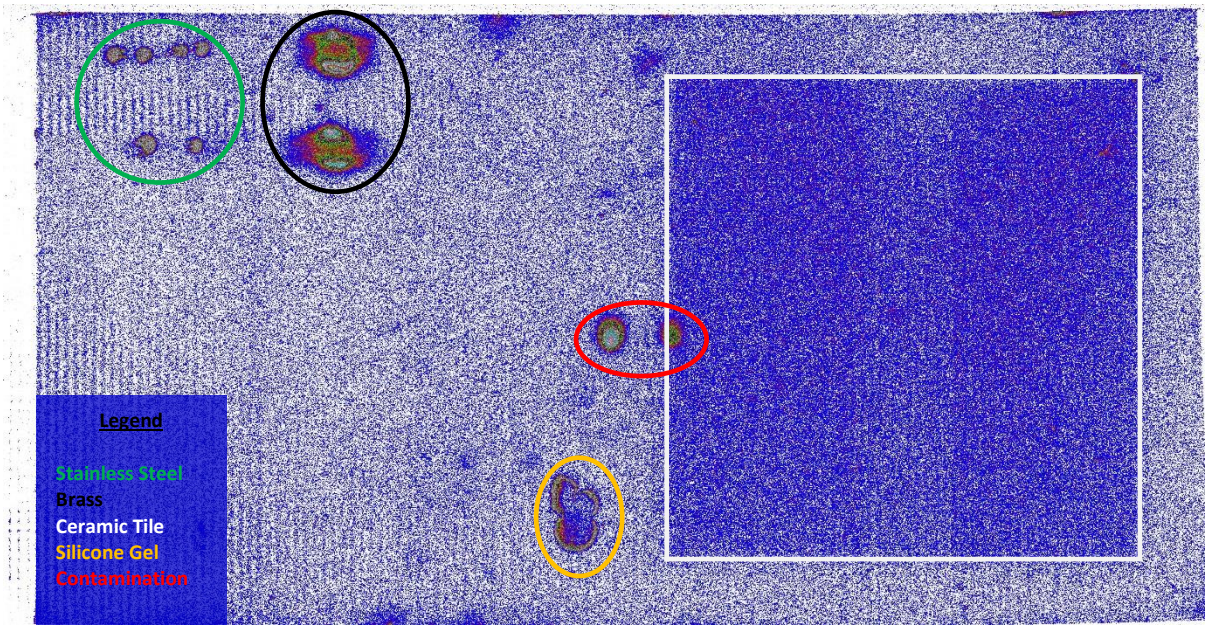


Figure 141: Full Autoradiography Test Plate Using Fiji and Glasbey Filter

The area marked off in white, is where the ceramic tile was placed on the plate, other than the faint shadow of the tile, no radioactivity was observed. The **green** circled area was from the stainless steel (Figure 140), where the nickel isotope had dried in four dots on the top section and two on the bottom. The area circled in **black** was the brass sample, which had been subjected to a wipe test and had varying levels of radioactivity intensity throughout the imaged mark.

Since the wipe test had been conducted using a cotton bud, the wiping had focused mainly on the centre of the mark, where it appears to have ploughed through it, leaving a small amount of radioactivity in the middle, with a lot more on the two outer edges which had not been subjected to the wiping (Appendix Figure 165 and Figure 166). The area with the **orange** circle was where the silicone gel was positioned, as the nickel dried on the gel, it left more of the isotope around the outer edges and less in the middle (Appendix Figure 167 and Figure 168). The two dots circled in **red** were a contaminant present on the autoradiography plate used and had nothing to do with the experiment at hand.

Having experienced moderate success using the autoradiography plate, the next step was to test whether or not a pattern could be laid down in a radioactive isotope and subsequently imaged. In order to achieve the patterns a children's stamp set was used (Figure 142).

Figure 142: Stamp Set

A piece of tissue was doped with 300 µl of ^{63}Ni and the stamps were pressed into the wet tissue to ensure an even coating. The stamp was then pressed on to a variety of substrates; plastic, brass and sections of silicone gel lifter. The same process as described on the previous page was used for the preparation and development of the autoradiography plate. Fourteen samples in total were placed on the plate, of the fourteen three were plastic, two brass, two stainless steel, four gel and the three stamps. The dragonfly stamp was applied to both plastic samples, one was left, and the other was lifted using a section of gel. The butterfly stamp was applied to the brass samples, again one was lift with the lifting gel. The stainless steel samples had the last stamp, the ladybug, applied, and one had the gel applied. The last remaining gel sample had the dragonfly stamp applied directly, and the last plastic sample had a sebaceous loaded fingerprint applied, to test if any of the natural deposits provided any visualisation on the autoradiography plate. The three stamps were laid on the plate as well, as they had residual nickel isotope on them.

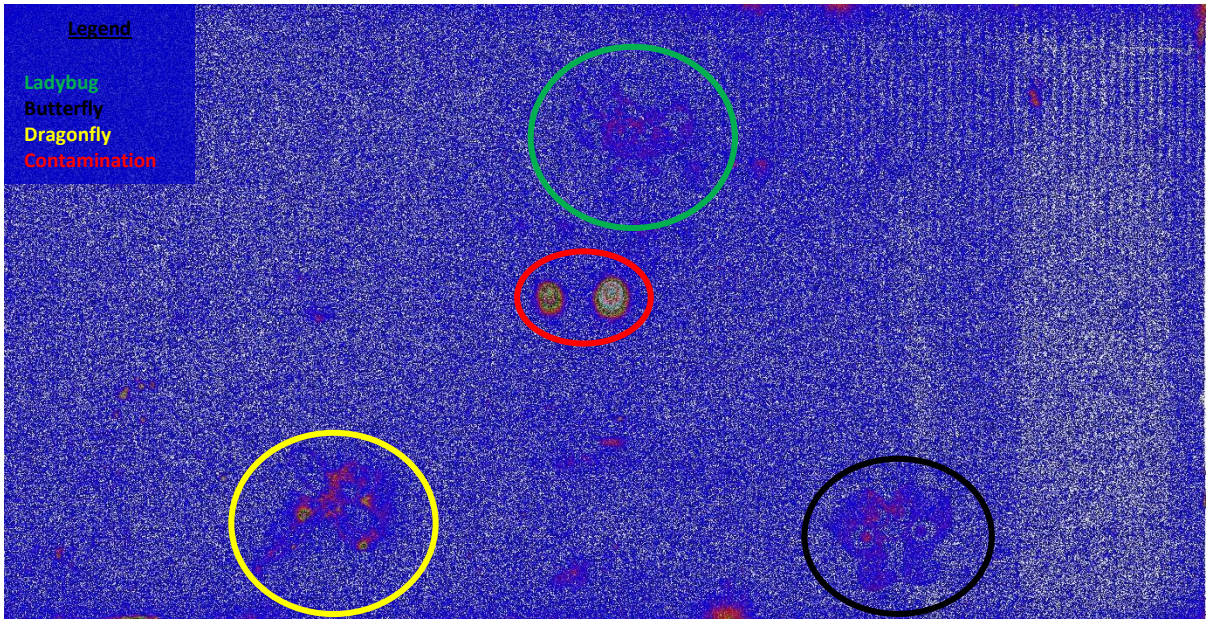


Figure 143: Full Autoradiography Plate of Stamps Using Fiji and Glasbey Filter

The development on the plate was less than expected (Figure 143). The only test samples that were picked up were the stamps. The images on the plate are faint and hard to make out. The images circled are the stamps, the red circle is the contaminant mentioned before. By adjusting the filters used in Fiji, the images were enhanced further.

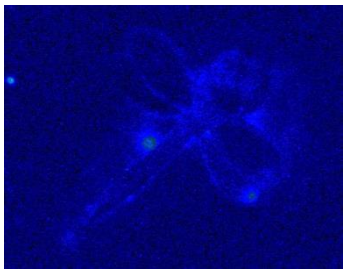


Figure 144: Dragonfly Stamp

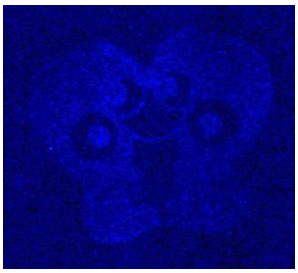


Figure 145: Butterfly Stamp

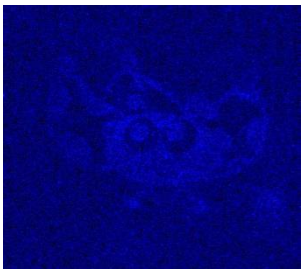


Figure 146: Ladybug Stamp

By adjusting the Fiji filter to 3-3-2 RGB, it was possible to enhance the images to where the stamp patterns could easily be discerned (Figure 144 - Figure 146). Since only the stamps were visualised on the autoradiography plate, it is assumed that the material the stamp is made out of is retaining the nickel isotope and not transferring it on to the substrates tested. In order to test this hypothesis, another method to lay down a pattern will have to be devised.

Since the gel lifters appeared to be lifting radioactive isotope for imaging, another similar series of experiments were conducted. 100 µl of ^{32}P was placed on to the same surfaces as used before; plastic and tile, in distinct patterns. The phosphorus was deposited dropwise using a pipette to form the patterns. The drops were placed in such a manner as to create easily recognisable patterns when the autoradiography imaging took place.

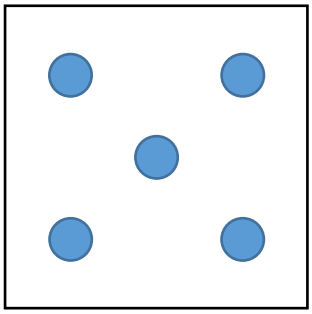


Figure 147: "X" Pattern

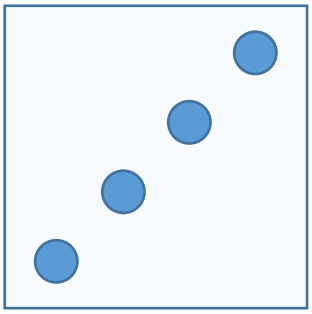


Figure 148: "/" Pattern

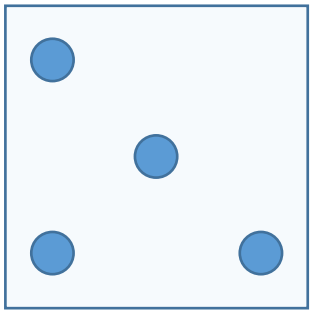


Figure 149: "λ" Pattern

Once the radioactive phosphorus solution had dried, a forensic gel lifter was applied to the surface of the sample substrates for approximately 10 minutes. The gels were the removed and placed on the autoradiography plate for 1 day.

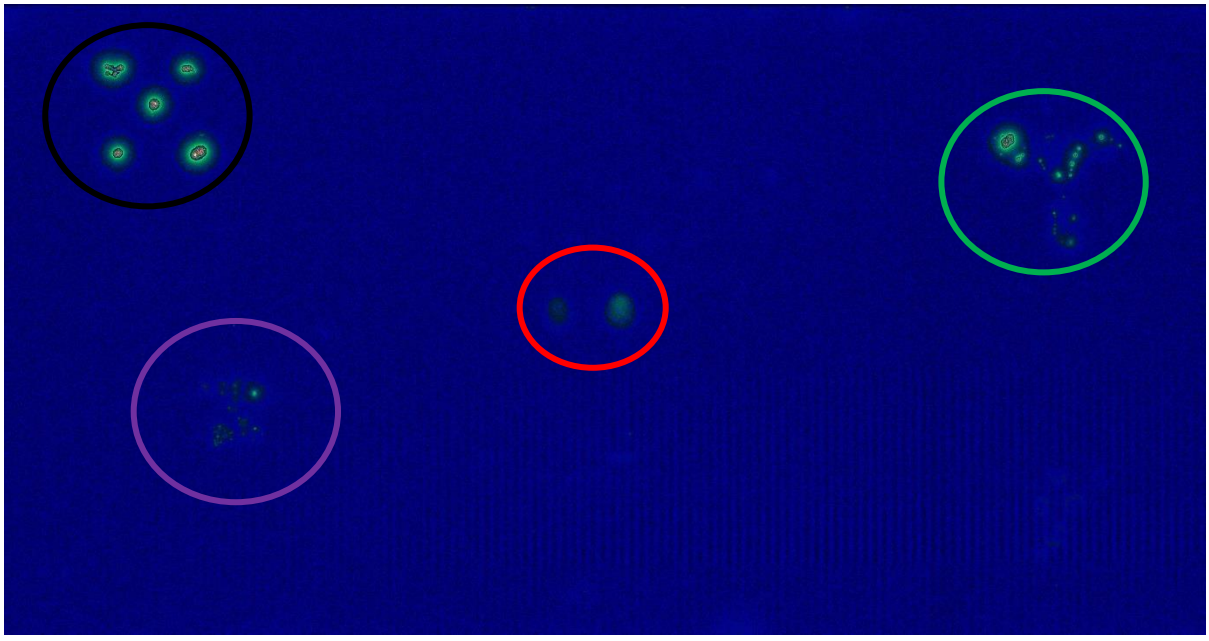


Figure 150: Full Autoradiography Plate Using Fiji and 3-3-2 RGB Filter

The lift from the white tile with the "**X**" pattern transferred strongly to the autoradiography plate. The two plastic samples appeared weaker than the tile. The "**λ**" pattern is only partially visible and the "**/**" pattern is hard to distinguish. The contamination is still present here, despite repeated cleaning (Figure 150).

The "X" pattern from the ceramic tile shows all of the individual droplets which were deposited upon the tile's surface (Figure 151). Unsurprisingly, the heaviest concentrations of radioactivity are at the centres of the droplet circles, since this is where it would concentrate as it dried (Figure 152).

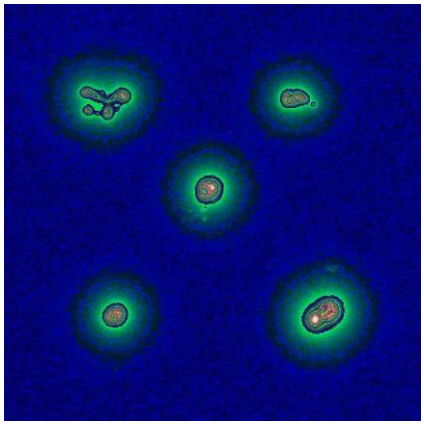


Figure 151: Close-up of "X" Pattern on Autoradiography Plate using Fiji and 3-3-2 RGB Filter

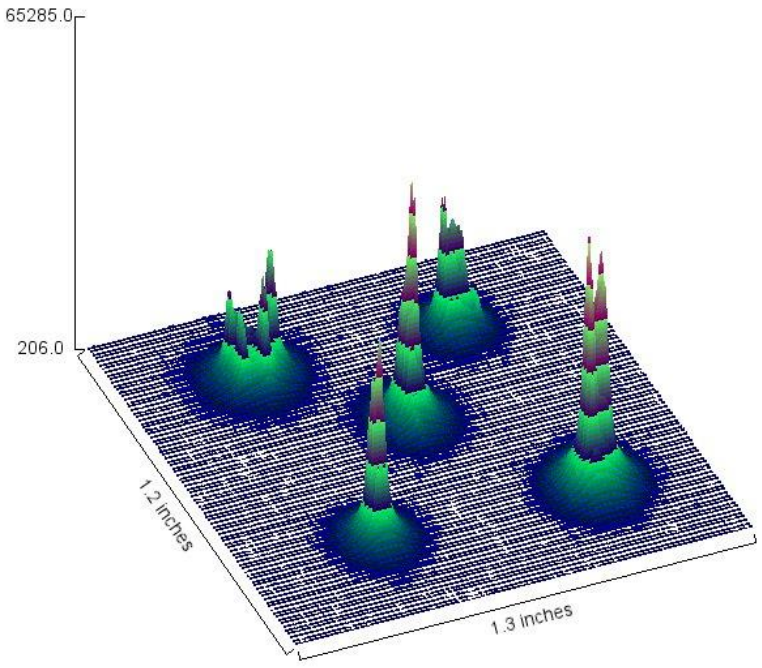


Figure 152: Surface Plot of "X" Pattern using Fiji and 3-3-2 RGB Filter

The P-32 provided some good quality images, so an experiment was set up to test its ability to image fine detail. A synthetic finger with intricate friction ridge patterns (Figure 153), supplied by CAST, was dipped in the aqueous phosphorus solution and allowed to dry. Once dried the pad of the fake finger with the ridge detail was pressed against a ceramic tile surface. A gel lifter was applied to the area of the tile where the finger was pressed, for 30 minutes, to lift any transfer from the finger to the tile.

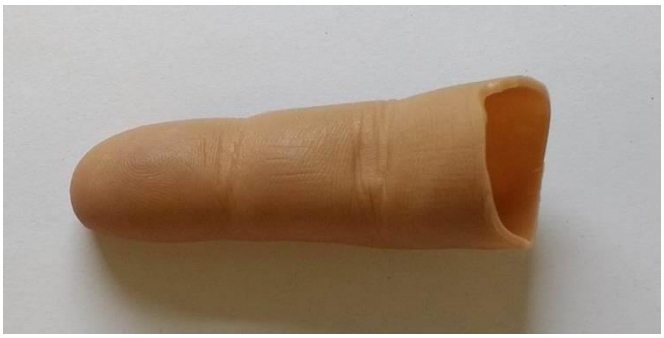


Figure 153: Friction Ridge Detail on Fake Finger

Separately, the fake finger was dipped into the phosphorus solution and the excess shaken off. The finger was then pressed on to another piece of tile. Once dried, a gel lifter was applied to the surface of the tile for 30 minutes.

Both gels, both tiles and the finger were all placed upon an autoradiography plate and left for 24 hours. Once the 24 hours were up, the plate was developed *via* the Cyclone system.

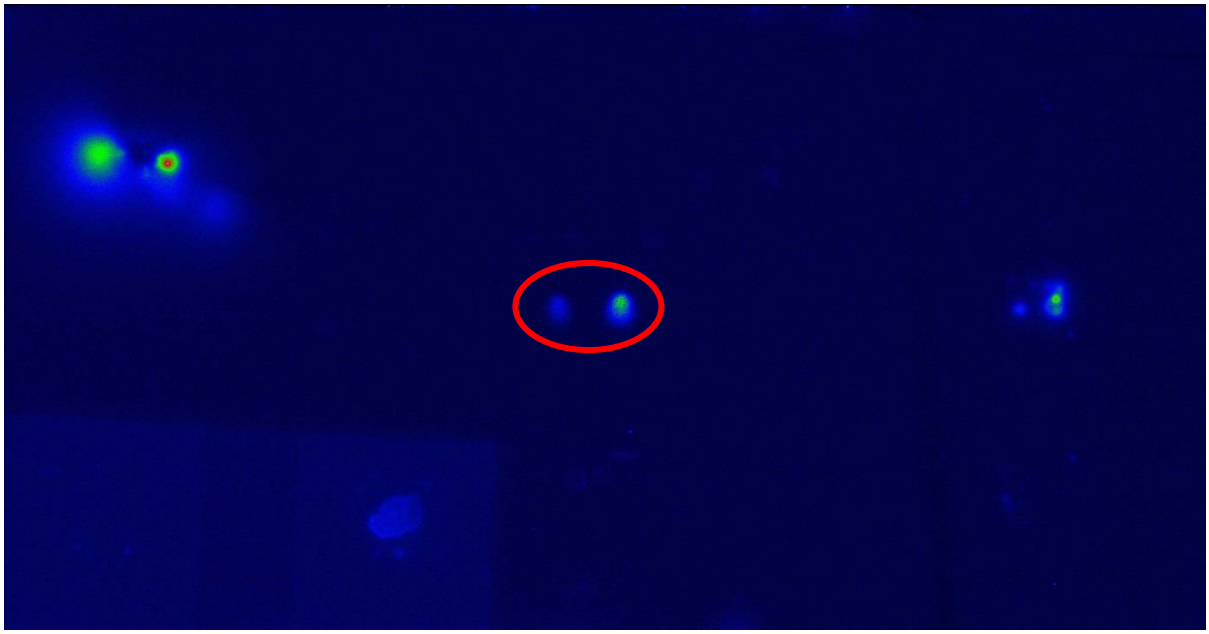


Figure 154: Full Autoradiography Plate of Fake Finger Detail Using Fiji and 3-3-2 RGB Filter

With the exception of the area in **red**, which again is the contamination on the plate, none of the marks imaged on the radiography plate showed any sign of coming from a finger or finger-shaped object. The quality of the marks were not sensitive enough to show any fine detail such as ridge detail. With that in mind, this series of experiments was shelfed as another area of research showed more promise in respect to developing fingermarks with distinguishable minutiae (Figure 154).

6.3.2 Biological Techniques

The first step in this process was to lay fingermarks down on agar gels. Twelve agar plates were premade by a technician, for this purpose. Each plate had its lid carefully removed and a separate finger lightly pressed on to the surface of each gel (Table 20). The lid was removed for as little time as possible to keep external contaminants to a minimum. The plates were placed in an incubation oven at 37°C overnight.

Plate	Finger	Plate	Finger
NA1	Right Thumb	NA6	Left Thumb
NA2	Right Fore	NA7	Left Fore
NA3	Right Middle	NA8	Left Middle
NA4	Right Ring	NA9	Left Ring
NA5	Right Little	NA10	Left Little
NA11	Right Palm	NA12	Left Palm

Table 20: Agar Plate Finger Allocations

Upon inspection each plate exhibited bacterial growth around the entire area touched in each case (Appendix Figure 169 - Figure 180). This was contrary to what was reported by O'Neill (1941), it appeared that the bacterial growth overran the boundaries of the actual fingermark ridges as it grew. Two theories were postulated to overcome this problem; either incubate for a shorter period of time, thus stunting the growth which had been observed and hopefully restricting the bacterial growth to the areas where the friction ridge skin actually touch *or* find a way to impregnate the gels with a bacterial inhibitor with a view to reducing the bacteria's ability to grow without the bounds of the areas contaminated with the friction ridge residues. The former method was deemed to be impractical, since the bacteria may not grow in a uniform manner, meaning that the plates would likely show marks with spotted, broken and incomplete ridge flow. This would prove problematic from the standpoint that it would be unknown where ridges started and stopped, or whether the dots and spots observed were in actual fact dots or short ridges, giving a high level of uncertainty with regards to what was "developed". That left the latter theory to investigate. In order to explore whether or not this could be a viable alternative to what had already been attempted, a number of amino acids, which are present in fingermark residues, were employed to access whether or not they could help inhibit bacterial growth.

From each plate a single bacterial colony was removed using a sterile loop, the colony was then transferred to a fresh agar plate *via* a streaking method (Figure 138 on page 220). Again, each time the lid of a plate had to be removed, it was done carefully and as quickly as possible. The new plates were then incubated at 37°C over the course of a weekend.

The majority of the streak plates showed the typical streak pattern on examination, some had heavier colony lines than others (Appendix Figure 181 - Figure 192). Plate eight had no streak colony, it did however have what looked like a penicillin colony. The most likely scenario for the missing streak colony is that it was missed during the colony transfer and somehow picked up another contaminant.

From each streak plate, a single bacterial colony was isolated and removed using an aseptic transfer method and then transferred to a pre-prepared nutrient broth (Figure 139 on page 221). The broths were then placed in an incubation oven at 37°C for 24 hours. Once removed from the oven, the broths were examined. They had turned a cloudy gold/yellow colour from the translucent golden brown they started as. 200 µl of the inoculated broth was pipetted to a vial of molten agar and mixed thoroughly, the molten agar was then transferred to a Petri dish to set. This was conducted with the twelve broths to prepare twelve inoculated agar plates. To these plates, impregnated paper discs were placed on to the surface of the agar. These discs were impregnated with a variety of amino acids (Table 21), in an effort to examine whether or not they had any inhibitory effects on the bacterial growth of the inoculated agar plates. 50 µl of each amino acid was placed on to each of the discs in question. The agar plates were incubated overnight at 37°C. It was hoped that the inoculated broth would grow throughout the agar plate and the various amino acid disc would inhibit growth around the areas of the discs.

Amino Acid	Concentrations	
Glutamic Acid	10 mg/10 ml	1:1
Lysine	10 mg/10 ml	1:1
Threonine	10 mg/10 ml	1:1
Tryptophan	7 mg/10 ml	7:10
Serine	10 mg/10 ml	1:1
Aspartic Acid	10 mg/10 ml	1:1
Cysteine	10 mg/10 ml	1:1
Tyrosine	5 mg/10 ml	1:2

Table 21: Amino Acids Used for Inhibition

Upon examination, none of the plates showed any bacterial growth. Since there was no growth it could not be determined if any of the amino acids had had any effect. This avenue of research was shelved to be re-examined at a later date, however, that later date never came around due to other, more successful areas of research taking priority.

6.4 Conclusions

6.4.1 Radioactive Techniques

Initial isotope recovery from the metal substrates utilising the forensic gel lifters was below 50%, with the majority coming from the wipe tests rather than the gel lifters. Further investigation determined that the nickel isotope was leaching in to the metal substrates. The radioactive isotope was more readily recovered from substrates such as plastic and ceramic tile; giving recovery rates in excess of 80%.

The autoradiography experiments proved that the nickel isotope was active enough to provide identifiable images, however, this was only possible with samples which had had the aqueous radioactive isotope directly applied. Although a stronger, more active isotope may ultimately be required to image and identify radioactively contaminated fingerprints.

Gel lifting and autoradiography also proved adept at imaging amounts of phosphorus-32, as small as <100 µl, arranged in distinct patterns from tile and plastic surfaces. The resolution of such patterns lead to the hope that finer detail could be imaged. A fake finger, with fine minutiae, was adopted to leave marks contaminated with radioactive material. Although the lifts were able to be imaged *via* autoradiography, it was not sensitive enough to distinguish the fine friction ridge detail of the fake finger.

The forensic gel lifters can lift many types of particulate; including dust and dirt, blood, and reacted reagents from fingermark enhancement processes [141]. However, it is the gel lifter's interactions with radioactive isotopes that adds a slightly different function to them. Since they are a quick, non-invasive method of collecting evidence, they can be used to lift from areas where someone suspected of coming into contact with radioactive material has touched and subsequently imaged using autoradiography.

These initial tests were promising, but further experimentation will be required.

6.4.2 Biological Techniques

The first stage of this experimentation was to leave fingerprints on the surface of agar gels, in order to encourage the growth of the bacteria present on the fingers. The initial plates showed good bacterial growth after incubation, and with a good transference technique streak plates were successfully inoculated. After incubation, the streak plates had single colonies isolated, extracted and transferred to nutrient broths. The broths were incubated for a period of 24 hours and used to seed bacterial agar plates for testing inhibition. Of the eight amino acids tested for their inhibitory effects, none were able to be tested effectively due to the bacterial agar failing to grow any bacteria colonies.

It is not known why the bacterial agar failed to grow. Repetition of the experiment may yield better results if the bacterial agar can be encouraged to grow.

7.0 Overall Conclusions

The primary investigation in this study was the assessment of phosphomolybdic acid as a fingermark development reagent. While investigating solvent carriers for the solution, ethanol was found to be superior to the other solvents tested. In an effort further improve the solution, temperature was assessed. It was during these trials that ultraviolet radiation was found to be able to initiate the development of the phosphomolybdic acid treated fingermarks. The UV treatment method was found to produce fingermarks of better contrast than those produced using an oven.

Once a successful solution had been developed, an attempt was made to combine PMA with other fingermark development reagents used for porous substrates, in an effort to maximise the potential. Through these experiments it was discovered that mixing PMA with like solutions, which target different constituents, caused an adverse reaction. When assessing phosphomolybdic acid in sequence with other reagents, PMA was found to enhance the development potential of Oil Red O when used as a precursor treatment.

Through observations of fingermarks being transferred from one porous surface to another and work being conducted by a colleague. Investigations proceeded to attempting to recover fingermarks from copper which had been brought in contact with substrates with fingermarks deposited upon them. Many substrates of varying porosities were placed against cuprous plates for various durations, after which a forensic gelatin lifter was applied to the surface of the cuprous plate, the gel was then sprayed with rubeanic acid which allowed for fingermarks to become visible.

A variety of environments were examined to ascertain if this had an effect on the quality of the fingermarks recovered. Drying out the marks present on the cuprous surfaces by dehumidification was found to improve the quality of the fingermarks developed on the gel lifters. Since copper is more expensive than its alloyed counterparts, a method to clean and reuse copper plates was investigated. Cleaning with water and detergent was found to be ineffective, as the corrosion signature from initial experiments was still present when subsequent uses were made. The metal cleaner Brasso was found to be effective at removing all traces of previous uses, up to six times before detrimental background staining became an issue.

Work progressed to applying ultra-thin layers of copper to substrates with fingermarks deposited upon them, using vacuum metal deposition. The hope was to be able to gel lift from the VMD exposed substrates, to then be subsequently treated with rubeanic acid. Varying thicknesses of copper were deposited upon polymer banknotes, then gel lifted. The gel lifts were treated with rubeanic acid and fingermarks became visible almost immediately. As a secondary process, the VMD treated banknotes were imaged under reflected UV and reflected IR allowed for background patterns to almost disappear.

Radioactive isotopes were explored to observe whether fingermarks could be enhanced and imaged *via* autoradiography. Various substrates had minute amounts of aqueous radioisotopes placed upon them in varying patterns, once dried these were gel lifted and placed on a autoradiography plate for imaging. Initial tests showed that imaging of these patterns was possible, however, when a fake finger with fine minutiae was attempted no ridge detail was able to be imaged. This area of investigation was abandoned as the technique was deemed not to be sensitive enough.

A biological technique was examined to ascertain if fingermarks could be grown in agar plates. This area of investigation was quickly found to be inefficient as the rate of growth of the bacterial colonies could not be controlled in any way to allow marks to show ridge detail.

Overall this project succeeded in achieving the aims set out at the start. While the radioactive and biological techniques failed to produce favourable results, other areas investigated were more fruitful. The vacuum metal deposition and phosphomolybdic acid techniques showed enough promise that they were subject to articles which were published in leading forensic journals. The final area of study, the cuprous metals and rubeanic acid, is in the process of being submitted for publication.

8.0 Future Work

8.1 Phosphomolybdic Acid

The investigation into phosphomolybdic acid as a feasible development reagent was a successful step toward realising this goal. Moving forward, areas which would benefit from further studies would be:-

- The narrowing of which classes of compounds PMA reacts with within the fingermark residues
- The establishment of where in a sequence of development techniques PMA fits

8.1.1 The narrowing of which classes of compounds PMA reacts with

It is known that phosphomolybdic acid reacts with a number of different types of compound to form the molybdenum blue which allows the visualisation of the treated fingermarks. By narrowing down which compounds PMA reacts with and to what degrees, it would allow for a better understanding of where in a sequence of methods PMA would fit.

8.1.2 Establish where in a sequence of development techniques PMA fits

Within the field of latent fingermark development, many development methods are used in sequence with one another; ninhydrin, DFO, and indandione, to name but a few. As shown with Oil Red O, the use of PMA as a precursor treatment helped the definition of the marks the ORO stained upon treatment. Although this may not always be the case, as with sequential treatment with ninhydrin, knowing what techniques can be used before or after PMA may highlight other instances where marks are developed with clearer ridge detail, or where additional marks are developed.

8.2 Cuprous Surfaces and Rubeanic Acid

This technique demonstrated that it was possible to recover fingermarks from surfaces of varying porosity, non-invasively. Possible further work could include:-

- A study to evaluate the optimum contact time between the cuprous surface and the sample substrate
- Determining which palmer sweat components elicit the best quality marks
- A comprehensive study to determine if the cuprous materials transferred to the fingermark on the substrate surface causes any difference in subsequent development techniques

8.2.1 A study to evaluate the optimum contact time

Establishing how long the cuprous metal needs to be in contact with the fingermarks on the sample substrates would help streamline this technique. This would have many factors including the sample substrate type, and whether adding a weight to the sample helps or hinders a particular substrate type.

8.2.2 Determine which sweat components promote the best quality fingermarks

Within this study subsection sebaceous materials were shown to transfer more readily from porous substrates to the cuprous metals for lifting and subsequent treatment. Eccrine sweat performed almost as well as sebaceous when lifting fingermarks direct from the metals. A study into successfully lifting eccrine marks *via* transfer could show how versatile this technique could be.

8.2.3 Study into the effects of cuprous materials on other techniques

A study into what effects copper and the other metals in copper alloys has on other techniques may show in best case scenario that another technique may develop higher quality fingermarks when exposed to the cuprous materials transferred to a fingermark. At the very least, if the cuprous materials do nothing to affect other techniques, it would make this a great starting point when being non-invasive is the preferred route to go.

8.3 Vacuum Metal Deposition

Despite this technique having limited success within the studies conducted, the failures were fairly minor and could be rectified easily. Whereas the successes could give investigators another weapon in their arsenal when it came to utilising VMD as a fingermark development technique. There are many areas which could benefit from further investigation:-

- A group study to investigate the variation in donor deposition
- A comprehensive comparative study against the gold/zinc and silver techniques already used
- Sequential trials using the traditional metals utilised in VMD treatments, and possibly cyanoacrylate fuming

8.3.1 Group study

Since the initial study which provided extremely good quality fingermarks only utilised a single donor, an in depth group study would allow for the investigation of whether or not different donors had an influence on the quality of the fingermarks developed. In order to test the sensitivity of the technique a variety of good, bad and average donors would have to be included in the trial.

8.3.2 Comparative study with commonly used metals

By comparing the copper VMD technique against those of the commonly used gold/zinc or silver techniques, this would allow for the comparison between how the deposited metals react when imaged *via* reflected IR. It is already known the copper can be less successful when being imaged after a short period of time from treatment. However, it is still superior in the fact that developed marks can be lifted for a secondary treatment by rubeanic acid. A further study could examine how long copper treated marks can be left before imaging using reflected infrared is no longer viable.

8.3.3 Sequential trials

It is well known within the field of fingermark development that many development techniques can be used in sequence with each other. This is true with chemical development as well as physical development. The Au/Zn VMD treatment is a case in point where zinc is used after the gold to further enhance the developed fingermarks, silver can also be used in sequence with gold/zinc. Using copper in sequence, either before or after, Au/Zn or Ag, or both may provide further enhancement. It may be possible to gain superior quality finger marks by utilising copper VMD after CAF.

8.4 Miscellaneous Techniques

Many of the techniques investigated within this section fell prey to time constraints, or to the fact that other techniques were performing better so they were put on hold, in most cases indefinitely. However, the work is still viable and would benefit from further work or fresh approaches. Further experimentation which could be explored could include:

- Re-evaluation which isotopes to utilise for laboratory study into the autoradiography imaging of radiochemical contaminated fingermarks
- Exploring the optimal time for "growing" fingermarks on agar

8.4.1 Re-evaluation of radioisotopes

The studies in to radioisotopes as a fingermark enhancement tool have proven that the forensic gel lifters, although limited by surface type, can lift substantial amounts of the radioactive isotopes. As well as this, autoradiography showed that patterns can be imaged when using a weak beta emitter such as ^{63}Ni. Phosphorus-32 was also able to show certain patterns when applied to a surface and lifted with a forensic gel lifter. Where this technique struggled was in the imaging of the fine minutiae of friction ridges.

There are many routes which could be explored in an effort to improve upon what has already been attempted. Further experimentation could be conducted with; the contact time between the gel and the contaminated surface, the contact time between the gel and the autoradiography plate, or re-examining which radioisotopes to use.

8.4.2 Explore the optimal time for growing marks on agar

The experimentation into this biochemistry aspect of fingermark recovery was still very much in its infancy when progress stalled. So, with that in mind, there are many directions this work could go in in order to achieve the goal of recovering fingermarks by use of bacterial colonies.

One of the most important factors would be the discovery of how long fingermark contaminated agar plates would have to incubate for, for enough bacteria to have grown along the friction ridge marks without growing so far as to completely cover the fingermark area. Research could move to trying to determine whether a fingermark bacteria can be transferred from a substrate surface to the surface of agar for growing. However, this would present its own problems, such as, contamination from “background” bacteria already present on the substrate surface. If they were different, one could possibly be inhibited in order to allow the other to grow, this would allow for either positive or negative fingermarks to be visualised.

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Appendices

Phosphomolybdic Acid Additional Information

Phosphomolybdic Acid Additional Results - Tables

Sample Number	Print Type	Grade
0769	Eccrine Loaded	0
0770		0
0771		0
0772		0
0773		0
0774	Eccrine Depletion	0
0775		0
0776		0
0777		0
0778		0
0779	Natural Loaded	1
0780		1
0781		1
0782		1
0783		1
0784	Natural Depletion	1
0785		1
0786		1
0787		1
0788		1

Table 22: Initial Tests 1

Sample	Print Type	Grade
0789	Eccrine Loaded	0
0790		0
0791	Eccrine Depletion	0
0792		0
0793	Natural Loaded	1-2
0794		1
0795	Natural Depletion	1-2
0796		1

Table 23: Initial Tests 2

Sample	Print Type	Grade
0797	Natural Loaded (RW)	1
0798		1-2
0799	Natural Depletion (RW)	1
0800		1
0801	Natural Loaded (LD)	0
0802		0
0803	Natural Depletion (LD)	0
0804		0

Table 24: Initial Tests 3

Sample	Print Type	Grade
0805	Eccrine Loaded	0
0806	Eccrine Depletion	0
0807	Natural Loaded	1
0808	Natural Depletion	1-2

Table 25: Dilute PMA - Paper - Trial 1

Sample	Print Type	Grade
0809	Eccrine Loaded	0
0810	Eccrine Depletion	0
0811	Natural Loaded	1
0812	Natural Depletion	1

Table 26: Dilute PMA - Photo Paper - Trial 1

Sample	Print Type	Heating Time	Grade
0813	Natural Loaded	10 Min	2
0814			2
0815		15 Min	2-3
0816			2-3
0817		20 Min	3-4
0818			3-4

Table 27: Dilute PMA - Paper - Trial 2

Sample	Print Type	Heating Time	Grade
0819	Natural Loaded	15 Min	2-3
0820	Natural Depletion		2
0821	Natural Loaded	20 Min	2
0822	Natural Depletion		1-2
0823	Natural Loaded	30 Min	2
0824	Natural Depletion		2-3

Table 28: Dilute PMA - Paper - Heating Trial 1

Sample	Print Type	Heating Time	Grade
0825	Natural Loaded	15 Min	2
0826	Natural Depletion		1-2
0827	Natural Loaded	20 Min	1-2
0828	Natural Depletion		1
0829	Natural Loaded	30 Min	2
0830	Natural Depletion		2-3

Table 29: Dilute PMA - Recycled Paper - Heating Trial 1

Sample	Print Type	Heating Time	Grade
0831	Natural Loaded	15 Min	2-3
0832	Natural Depletion		1-2
0833	Natural Loaded	20 Min	1-2
0834	Natural Depletion		1
0835	Natural Loaded	30 Min	1-2
0836	Natural Depletion		1

Table 30: Dilute PMA - Paper - Heating Trial 2

Sample	Print Type	Heating Time	Grade
0837	Natural Loaded	15 Min	1
0838	Natural Depletion		0-1
0839	Natural Loaded	20 Min	0-1
0840	Natural Depletion		1
0841	Natural Loaded	30 Min	1
0842	Natural Depletion		1-2

Table 31: Dilute PMA - Recycled Paper - Heating Trial 2

Sample	Print Type	Heating Time	Grade
0843	Loaded	15 Min	2
0844	Depletion		3
0845	Loaded	20 Min	2-3
0846	Depletion		2
0847	Loaded	30 Min	2-3
0848	Depletion		2

Table 32: Dilute PMA – Paper - Age Trial 1

Sample	Print Type	Heating Time	Grade
0849	Loaded	15 Min	2-3
0850	Depletion		3
0851	Loaded	20 Min	2-3
0852	Depletion		2-3
0853	Loaded	30 Min	3
0854	Depletion		3

Table 33: Dilute PMA – Paper - Age Trial 2

Sample	Print Type	Heating Time	Grade
0855	Loaded	15 Min	3
0856	Depletion		2-3
0857	Loaded	20 Min	3
0858	Depletion		3
0859	Loaded	30 Min	3
0860	Depletion		3

Table 34: Dilute PMA – Paper - Age Trial 3

Sample	Print Type	Heating Time	Grade
0861	Non-Loaded	15 Min	2-3
0862	Depletion		2
0863	Non-Loaded	20 Min	3
0864	Depletion		2
0865	Non-Loaded	30 Min	3
0866	Depletion		2-3

Table 35: Dilute PMA – Paper - Loading Trial 1

Sample	Print Type	Heating Time	Grade
0867	Loaded	5 Min	2
0868	Depletion		2-3
0869	Loaded	15 Min	1-2
0870	Depletion		1
0871	Loaded	20 Min	1
0872	Depletion		2-3
0873	Loaded	30 Min	1
0874	Depletion		3

Table 36: Dilute PMA – Paper - Age Trial 4

Sample	Print Type	Heating Time	Grade
0875	Loaded	5 Min	1-2
0876	Depletion		2
0877	Loaded	15 Min	2
0878	Depletion		2
0879	Loaded	20 Min	2
0880	Depletion		2
0881	Loaded	30 Min	2
0882	Depletion		2-3

Table 37: PMA Hydrate – Paper - Trial 1

Sample	Print Type	Heating Time	Grade	Sunlight Grade
0883	Loaded	15 Min	2-3	3
0884	Depletion		1	1
0885	Loaded	20 Min	2	2-3
0886	Depletion		1	1
0887	Loaded	30 Min	2-3	2-3
0888	Depletion		1-2	1-2

Table 38: PMA Hydrate – Paper - Trial 2

Sample	Print Type	Heating Time	Grade
0889	Loaded	15 Min	1-2
0890	Depletion		1-2
0891	Loaded	20 Min	1-2
0892	Depletion		1-2
0893	Loaded	30 Min	1-2
0894	Depletion		2

Table 39: PMA Hydrate – Paper - Trial 3

Sample	Print Type	Heating Time	Grade
0895	Loaded	15 Min	2
0896	Depletion		2
0897	Loaded	20 Min	2-3
0898	Depletion		3
0899	Loaded	30 Min	3
0900	Depletion		2-3

Table 40: PMA Hydrate – Paper - Concentration Trial 1: 10% v/w Solution

Sample	Print Type	Heating Time	Grade
0901	Loaded	15 Min	2-3
0902	Depletion		3
0903	Loaded	20 Min	2
0904	Depletion		3
0905	Loaded	30 Min	2-3
0906	Depletion		3

Table 41: PMA Hydrate – Paper - Concentration Trial 2: 5% v/w Solution

Sample	Print Type	Heating Time	Grade
0907	Loaded	15 Min	1-2
0908	Depletion		2-3
0909	Loaded	20 Min	1-2
0910	Depletion		1-2
0911	Loaded	30 Min	2
0912	Depletion		3

Table 42: PMA Hydrate – Paper - Concentration Trial 3: 7.5% v/w Solution

Sample	Print Type	Solution	Heating Time	Grade
0913	Non-Loaded	5% v/w	15 Min	1
0914		7.5% v/w		1
0915		10% v/w		1
0916		5% v/w	20 Min	1
0917		7.5% v/w		1
0918		10% v/w		1
0919		5% v/w	30 Min	1
0920		7.5% v/w		1
0921		10% v/w		1

Table 43: PMA Hydrate – Paper - Non-Loaded Concentration Trial 1

Sample	Print Type	Heating Time	Grade
0922	Loaded	15 Min	0
0923	Depletion		0
0924	Loaded	20 Min	0
0925	Depletion		0
0926	Loaded	30 Min	0
0927	Depletion		0

Table 44: Phosphotungstic Acid – Paper - Trial 1

Sample	Print Type	Heating Time	Grade
0928	Loaded	15 Min	2
0929	Depletion		2-3
0930	Loaded	20 Min	2-3
0931	Depletion		2-3
0932	Loaded	30 Min	2
0933	Depletion		2-3

Table 45: Dilute PMA - Paper - Trial 3

Sample	Print Type	Heating Time	Grade
0934	Loaded	15 Min	2
0935	Depletion		2-3
0936	Loaded	20 Min	2
0937	Depletion		2-3
0938	Loaded	30 Min	1-2
0939	Depletion		2

Table 46: PMA - Aluminium Foil - Dull Side - Trial 1

Sample	Print Type	Heating Time	Grade
0940	Loaded	15 Min	2
0941	Depletion		2
0942	Loaded	20 Min	2
0943	Depletion		2
0944	Loaded	30 Min	2
0945	Depletion		2

Table 47: PMA - Aluminium Foil - Shiny Side - Trial 1

Sample	Print Type	Heating Time	Grade
0958	Loaded	15 Min	2
0959	Depletion		2
0960	Loaded	20 Min	2
0961	Depletion		2-3
0962	Loaded	30 Min	2
0963	Depletion		3

Table 48: PMA - Aluminium Foil - Dull Side - Trial 2

Sample	Print Type	Heating Time	Grade
0964	Loaded	15 Min	2-3
0965	Depletion		3
0966	Loaded	20 Min	3
0967	Depletion		3
0968	Loaded	30 Min	2-3
0969	Depletion		2-3

Table 49: PMA - Aluminium Foil - Shiny Side - Trial 2

Sample	Print Type	Heating Time	Grade
0970	Loaded	15 Min	1-2
0971	Depletion		1-2
0972	Loaded	20 Min	1-2
0973	Depletion		1-2
0974	Loaded	30 Min	1-2
0975	Depletion		1-2

Table 50: PMA - Paper - Light Deposits - Trial 1

Sample	Print Type	Heating Time	Grade
0976	Loaded	15 Min	2-3
0977	Depletion		2
0978	Loaded	20 Min	2
0979	Depletion		2-3
0980	Loaded	30 Min	2-3
0981	Depletion		2

Table 51: PMA - Aluminium Foil - Dull Side: Light Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0982	Loaded	15 Min	2-3
0983	Depletion		2-3
0984	Loaded	20 Min	2-3
0985	Depletion		2-3
0986	Loaded	30 Min	2-3
0987	Depletion		2-3

Table 52: PMA - Aluminium Foil - Shiny Side: Light Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0988	Loaded	15 Min	2-3
0989	Depletion		2-3
0990	Loaded	20 Min	2-3
0991	Depletion		2-3
0992	Loaded	30 Min	2-3
0993	Depletion		2-3

Table 53: PMA - Aluminium Foil - Dull Side: Heavy Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0994	Loaded	15 Min	2-3
0995	Depletion		2
0996	Loaded	20 Min	2
0997	Depletion		2-3
0998	Loaded	30 Min	2
0999	Depletion		2

Table 54: PMA - Aluminium Foil - Shiny Side: Heavy Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0001	Loaded	15 Min	2-3
0002	Depletion		2-3
0003	Loaded	20 Min	3
0004	Depletion		3
0005	Loaded	30 Min	2-3
0006	Depletion		2-3

Table 55: PMA - Paper - Light Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0007	Loaded	15 Min	2
0008	Depletion		2-3
0009	Loaded	20 Min	2
0010	Depletion		2
0011	Loaded	30 Min	2
0012	Depletion		2-3

Table 56: PMA - Paper - Heavy Deposit - Trial 1

Sample	Print Type	Heating Time	Grade
0013	Loaded	15 Min	2-3
0014	Depletion		2-3
0015	Loaded	20 Min	2-3
0016	Depletion		2-3
0017	Loaded	30 Min	2-3
0018	Depletion		3

Table 57: PMA - Paper - Light Deposit - Trial 2

Sample	Print Type	Heating Time	Grade
0019	Loaded	15 Min	2
0020	Depletion		2-3
0021	Loaded	20 Min	2
0022	Depletion		2-3
0023	Loaded	30 Min	2
0024	Depletion		2-3

Table 58: PMA - Paper - Heavy Deposit - Trial 2

Sample	Metal	Print Type	Heating Time	Grade
0025	S/less Steel	Loaded	15 Min	3
0026	S/less Steel	Depletion		3
0027	Brass	Loaded		2
0028	Brass	Depletion		2

Table 59: PMA - Metal - Trial 1

Sample	Metal	Print Type	Heating Time	Grade
0029	Brass	Loaded	15 Min	2
0030	Brass	Depletion		2
0031	S/less Steel	Loaded		3
0032	S/less Steel	Depletion		3

Table 60: PMA - Metal - Trial 2

Sample	Print Type	Heating Time	Grade
0033	Loaded	15 Min	2
0034	Depletion		2
0035	Loaded	20 Min	2
0036	Depletion		2-3
0037	Loaded	30 Min	2-3
0038	Depletion		2-3

Table 61: PMA & PTA - Paper - Light Deposit – Trial 1

Sample	Print Type	Heating Time	Grade
0039	Loaded	15 Min	1-2
0040	Depletion		1-2
0041	Loaded	20 Min	2
0042	Depletion		2
0043	Loaded	30 Min	2
0044	Depletion		1-2

Table 62: PMA & PTA - Paper - Heavy Deposit – Trial 1

Sample	Print Type	UV Time	Grade
0045	Loaded	15 Min	3
0046	Depletion		3
0047	Loaded	20 Min	3
0048	Depletion		3
0049	Loaded	30 Min	3
0050	Depletion		3

Table 63: PMA - Paper - Light Deposit - Trial 1

Sample	Print Type	UV Time	Grade
0051	Loaded	15 Min	2-3
0052	Depletion		2-3
0053	Loaded	20 Min	2
0054	Depletion		2-3
0055	Loaded	30 Min	2
0056	Depletion		2

Table 64: PMA - Paper - Heavy Deposit - Trial 1

Sample	Print Type	UV Time	Grade
0057	Loaded	15 Min	2-3
0058	Depletion		2-3
0059	Loaded	20 Min	2-3
0060	Depletion		3
0061	Loaded	30 Min	2-3
0062	Depletion		2-3

Table 65: PMA - Paper - Heavy Deposits – Trial 1

Sample	Print Type	UV Time	Grade
0063	Loaded	15 Min	2-3
0064	Depletion		2-3
0065	Loaded	20 Min	2-3
0066	Depletion		2-3
0067	Loaded	30 Min	2-3
0068	Depletion		2

Table 66: PMA - Paper - Light Deposits - Trial 1

Sample	Print Type	Time	Heat Grade	UV Grade
0069	Loaded	15 Min	1	1
0070	Depletion		1	1-2
0071	Loaded	20 Min	1	2
0072	Depletion		1	1-2
0073	Loaded	30 Min	1	1
0074	Depletion		1	1-2

Table 67: PMA - Paper Splits - Light Deposits - Trial 1

Sample	Print Type	Time	Heat Grade	UV Grade
0075	Loaded	15 Min	1	1
0076	Depletion		1	1
0077	Loaded	20 Min	1	1
0078	Depletion		1	1
0079	Loaded	30 Min	1	1
0080	Depletion		1	1

Table 68: PMA - Paper Splits - Heavy Deposits - Trial 1

Sample	Print Type	Time	Heat Grade	UV Grade
0081	Loaded	15 Min	1	2-3
0082	Depletion		2-3	3
0083	Loaded	20 Min	2	2-3
0084	Depletion		2-3	3
0085	Loaded	30 Min	3	3
0086	Depletion		2-3	2-3

Table 69: PMA - Paper Splits - Light Deposits - Trial 1

Sample	Print Type	Time	Heat Grade	UV Grade
0087	Loaded	15 Min	1	2
0088	Depletion		1	2
0089	Loaded	20 Min	1	2-3
0090	Depletion		1	2-3
0091	Loaded	30 Min	1	1-2
0092	Depletion		2	2-3

Table 70: PMA - Paper Splits - Heavy Deposits - Trial 1

Sample	Print Type	Time	Heat Grade	UV Grade
0093	Loaded	15 Min	2-3	3
0094	Depletion		2-3	3
0095	Loaded	20 Min	2-3	3
0096	Depletion		2-3	3
0097	Loaded	30 Min	3	3
0098	Depletion		2-3	2-3

Table 71: PMA - Paper Splits - Light Deposits - Trial 2

Sample	Print Type	UV Time	Grade
0099	Loaded	15 Min	2
0100	Depletion		2-3
0101	Loaded	20 Min	2-3
0102	Depletion		3
0103	Loaded	30 Min	2-3
0104	Depletion		1-2

Table 72: PMA - Aluminium Foil - Dull Side - Trial 3

Sample	Print Type	UV Time	Grade
0105	Loaded	15 Min	2-3
0106	Depletion		2-3
0107	Loaded	20 Min	2-3
0108	Depletion		3
0109	Loaded	30 Min	2-3
0110	Depletion		2-3

Table 73: PMA - Aluminium Foil - Shiny Side - Trial 3

Sample	Print Type	UV Time	Grade
0111	Loaded	15 Min	1-2
0112	Depletion		1-2
0113	Loaded	20 Min	1-2
0114	Depletion		1-2
0115	Loaded	30 Min	1-2
0116	Depletion		1-2

Table 74: PMA in Petroleum Ether – Paper - Trial 1

Sample	Print Type	UV	Grade
0117	Loaded	5 Min	1
0118	Depletion		1
0119	Loaded	10 Min	0
0120	Depletion		0-1
0121	Loaded	15 Min	1
0122	Depletion		0-1

Table 75: Ninhydrin Solution 1 – Paper - Trial 1

Sample	Print Type	Heat	Grade
0123	Loaded	5 Min	1-2
0124	Depletion		0-1
0125	Loaded	10 Min	0-1
0126	Depletion		0-1
0127	Loaded	15 Min	1
0128	Depletion		0-1

Table 76: Ninhydrin Solution 1 – Paper -Trial 2

Sample	Print Type	Iron	Grade
0129	Loaded	5 Min	1
0130	Depletion		1-2
0131	Loaded	10 Min	2
0132	Depletion		1
0133	Loaded	15 Min	1-2
0134	Depletion		1-2

Table 77: Ninhydrin Solution 1 – Paper -Trial 3

Sample	Print Type	Heat Time	Before Grade	After Grade
0135	Loaded	15 Min	1/2	0
0136	Depletion		0/1	0
0137	Loaded	20 Min	0/1	0
0138	Depletion		0	0
0139	Loaded	30 Min	1	0
0140	Depletion		0/1	0

Table 78: PMA - Paper - Acetone Wash - After Development - Trial 1

Sample	Print Type	Heat Time	Grade
0141	Loaded	15 Min	0
0142	Depletion		0
0143	Loaded	20 Min	0
0144	Depletion		0
0145	Loaded	30 Min	0
0146	Depletion		0

Table 79: PMA - Paper - Acetone Wash - Before Development - Trial 1

Sample	Print Type	UV Time	Before Grade	After Grade
0147	Loaded	15 Min	2/3	0
0148	Depletion		2	0
0149	Loaded	20 Min	3	0
0150	Depletion		2/3	0
0151	Loaded	30 Min	2/3	0
0152	Depletion		2/3	0

Table 80: PMA - Paper - Acetone Wash - After Development - Trial 2

Sample	Print Type	UV Time	Grade
0153	Loaded	15 Min	1
0154	Depletion		0
0155	Loaded	20 Min	0
0156	Depletion		0
0157	Loaded	30 Min	0
0158	Depletion		0

Table 81: PMA - Paper - Acetone Wash - Before Development - Trial 2

Sample	Print Type	UV	Grade
0159	Loaded	5 Min	2-3
0160	Depletion		2-3
0161	Loaded	15 Min	3
0162	Depletion		2-3
0163	Loaded	30 Min	2-3
0164	Depletion		2-3

Table 82: PMA in Propan-1-ol – Paper – Trial 1

Sample	Print Type	UV	Grade
0165	Loaded	5 Min	3
0166	Depletion		3
0167	Loaded	15 Min	2-3
0168	Depletion		3
0169	Loaded	30 Min	3
0170	Depletion		2-3

Table 83: PMA in Methanol – Paper – Trial 1

Sample	Print Type	UV	Grade
0171	Loaded	5 Min	2-3
0172	Depletion		2-3
0173	Loaded	15 Min	3
0174	Depletion		3
0175	Loaded	30 Min	2-3
0176	Depletion		2-3

Table 84: PMA in Methanol – Paper – Trial 2

Sample	Print Type	UV	Grade
0177	Loaded	5 Min	1-2
0178	Depletion		1-2
0179	Loaded	15 Min	1-2
0180	Depletion		1-2
0181	Loaded	30 Min	1
0182	Depletion		1

Table 85: PMA in Methanol - Paper - Age Trial 1

Sample	Print Type	UV	Grade
0183	Loaded	5 Min	2
0184	Depletion		0-1
0185	Loaded	15 Min	1-2
0186	Depletion		1
0187	Loaded	30 Min	1-2
0188	Depletion		1

Table 86: PMA in Methanol - Paper - Age Trial 2

Sample	Print Type	UV	Grade
0189	Loaded	5 Min	2-3
0190	Depletion		2
0191	Loaded	15 Min	2-3
0192	Depletion		2-3
0193	Loaded	30 Min	2-3
0194	Depletion		2-3

Table 87: PMA in Methanol - Paper - Age Trial 3

Sample	Print Type	UV	Grade
0195	Loaded	5 Min	1
0196	Depletion		1
0197	Loaded	15 Min	2
0198	Depletion		2-3
0199	Loaded	30 Min	2-3
0200	Depletion		2-3

Table 88: PMA in Methanol - Paper - Age Trial 4

Sample	Print Type	Oven	Grade
0201	Loaded	15 Min	0-1
0202	Depletion		0
0203	Loaded		0-1
0204	Depletion		0
0205	Depletion		0
0206	Loaded		0

Table 89: PMA in Methanol - Paper - Methanol Wash - Before Development - Trial 1

Sample	Print Type	UV	Grade
0207	Loaded	15 Min	1-2
0208	Depletion		0
0209	Loaded		1-2
0210	Depletion		0
0211	Loaded		0-1
0212	Depletion		0

Table 90: PMA in Methanol - Paper - Methanol Wash - Before Development - Trial 2

Sample	Print Type	Oven	Grade	
0213	Loaded	15 Min	1-2	0
0214	Depletion		0-1	0
0215	Loaded		0-1	0
0216	Depletion		0-1	0
0217	Loaded		0	0
0218	Depletion		0-1	0

Table 91: PMA in Methanol - Paper - Methanol Wash - After Development - Trial 1

Sample	Print Type	UV	Grade	
0219	Loaded	15 Min	2-3	0
0220	Depletion		2-3	0
0221	Loaded		2-3	0
0222	Depletion		2-3	0
0223	Loaded		2-3	0
0224	Depletion		2-3	0

Table 92: PMA in Methanol - Paper - Methanol Wash - After Development - Trial 2

Sample	Print Type	UV	Grade Before NaOH	Grade After NaOH
0225	Loaded	15 Min	2-3	0
0226	Depletion		2-3	0
0227	Loaded		3	0
0228	Depletion		2-3	0

Table 93: PMA in Methanol - Paper – 2M NaOH Wash Trial 1

Sample	Print Type	Oven	Grade Before NaOH	Grade After NaOH
0229	Loaded	15 Min	1	0
0230	Depletion		1	0
0231	Loaded		1	0
0232	Depletion		1	0

Table 94: PMA in Methanol - Paper – 2M NaOH Wash Trial 2

Sample	Print Type	Development	Time	Grade Before NaOH	Grade After NaOH
0233	Loaded	Oven	15 Min	2-3	0
0234	Depletion			2-3	0
0235	Loaded	UV		3	0
0236	Depletion			3	0

Table 95: PMA - Paper – 2M NaOH Wash Trial 1

Sample	Print Type	Development	Time	Grade Before NaOH	Grade After NaOH
0237	Loaded	Oven	15 Min	2-3	2
0238	Depletion			2-3	2
0239	Loaded	UV		2-3	2
0240	Depletion			2-3	2

Table 96: PMA - Paper – 0.2M NaOH Wash Trial 2

Sample	Print Type	Development	Time	EtOH Grade	MeOH Grade
0241	Loaded	Oven	5 Min	1-2	1
0242	Depletion			2	2
0243	Loaded	UV		2-3	2-3
0244	Depletion			3	3
0245	Loaded	Oven	15 Min	1-2	2
0246	Depletion			2	1-2
0247	Loaded	UV		3	3
0248	Depletion			3	3
0249	Loaded	Oven	30 Min	2-3	2
0250	Depletion			2	2
0251	Loaded	UV		3	2-3
0252	Depletion			3	2-3

Table 97: PMA Ethanol & Methanol - Paper - Split Comparison Trial 1

Sample	Print Type	UV	Grade
0253	Loaded	15 Min	3-4
0254	Loaded		3-4
0255	Depletion		3
0256	Depletion		3

Table 98: PMA - Paper - UV Distance Trial 1

Sample	Substrate	Print Type	UV	Grade
0257	Foil (Shiny)	Loaded	5 Min	2
0258	Foil (Shiny)	Depletion		2
0259	Foil (Dull)	Loaded		2
0260	Foil (Dull)	Depletion		2
0261	PE Bag	Loaded		2
0262	PE Bag	Depletion		1-2
0263	PE Bag	Loaded	15 Min	1-2
0264	PE Bag	Depletion		1-2
0265	Foil (Shiny)	Loaded		2
0266	Foil (Shiny)	Depletion		2
0267	Foil (Dull)	Loaded		2
0268	Foil (Dull)	Depletion		2
0269	Cotton	Loaded		0
0270	Cotton	Depletion		0

Table 99: PMA - Various Media - Trial 1

Sample	Substrate	Print Type	UV	Grade
0271	Brass	Loaded	5 Min	0
0272	Brass	Depletion		1
0273	S. Steel	Loaded		1-2
0274	S. Steel	Depletion		1
0275	Cardboard	Loaded		1
0276	Cardboard	Depletion		1-2
0277	Thermal	Loaded		2-3
0278	Thermal	Depletion		2
0279	Brass	Loaded	15 Min	2
0280	Brass	Depletion		0
0281	S. Steel	Loaded		2-3
0282	S. Steel	Depletion		2-3
0283	Cardboard	Loaded		1
0284	Cardboard	Depletion		1
0285	Thermal	Loaded		2-3
0286	Thermal	Depletion		2-3

Table 100: PMA - Various Media - Trial 2

Sample	Print Type	UV	Grade
0287	Loaded	5 Min	1
0288	Depletion		1
0289	Loaded	15 Min	2-3
0290	Depletion		2-3

Table 101: PMA - Silicone Gel - Trial 1

Sample	Print Type	UV	Grade
0291	Loaded	5 Min	0
0292	Depletion		0
0293	Loaded	15 Min	0
0294	Depletion		0

Table 102: PMA - Paper - Eccrine Prints - Trial 1

Sample	Print Type	UV	Grade
0295	Loaded	5 Min	0
0296	Depletion		0
0297	Loaded	15 Min	0
0298	Depletion		0

Table 103: PMA & Ninhydrin Solution 1 - Paper - Trial 1

Sample	Print Type	UV	Grade
0299	Loaded	5 Min	0
0300	Depletion		0
0301	Loaded	15 Min	0
0302	Depletion		0

Table 104: Ninhydrin Solution 2 - Paper - Trial 1

Sample	Print Type	UV	Grade
0303	Loaded	5 Min	1
0304	Depletion		1
0305	Loaded	15 Min	1-2
0306	Depletion		1

Table 105: Ninhydrin Solution 3 - Paper - Trial 1

Sample	Print Type	UV	Grade
0307	Loaded	5 Min	2
0308	Depletion		1-2
0309	Loaded	15 Min	2
0310	Depletion		1-2

Table 106: Ninhydrin Solution 1 - Paper - Trial 4

Sample	Print Type	UV	Grade
0311	Loaded	5 Min	0
0312	Depletion		0
0313	Loaded	15 Min	1
0314	Depletion		1-2

Table 107: PMA & Ninhydrin Solution 2 - Paper - Trial 1

Name	Sex	Age
Lloyd Davis	Male	40
Richard Wilson	Male	23
Emrys Price	Male	23
Jess Shiels	Female	21
Abigail Kwakye	Female	23
Deddy Anak Anjah	Male	23

Table 108: Group Study Participants

Sample	Name	Print Type	Print Age	UV	Grade
0315	Lloyd	Eccrine	Immediate	15 Min	0
0316	Richard				0
0317	Emrys				0
0318	Jess				1-2
0319	Abigail				0
0320	Deddy				0
0321	Lloyd		1 Week		0
0322	Richard				0
0323	Emrys				0
0324	Jess				0
0325	Abigail				0
0326	Deddy				0
0327	Lloyd		2 Weeks		0
0328	Richard				0
0329	Emrys				0
0330	Jess				0
0331	Abigail				0
0332	Deddy				0
0333	Lloyd		4 Weeks		0
0334	Richard				0
0335	Emrys				0
0336	Jess				0
0337	Abigail				0
0338	Deddy				0

Table 109: PMA - Paper - Group Study - Trial 1

Sample	Name	Print Type	Print Age	UV	Grade
0339	Lloyd	Natural	Immediate	15 Min	2
0340	Richard				2
0341	Emrys				2
0342	Jess				1-2
0343	Abigail				2
0344	Deddy				2
0345	Lloyd		1 Week		1
0346	Richard				1-2
0347	Emrys				1
0348	Jess				1
0349	Abigail				1-2
0350	Deddy				1
0351	Lloyd		2 Weeks		2
0352	Richard				1-2
0353	Emrys				1
0354	Jess				1-2
0355	Abigail				1-2
0356	Deddy				1-2
0357	Lloyd		4 Weeks		1-2
0358	Richard				2
0359	Emrys				1
0360	Jess				1
0361	Abigail				1-2
0362	Deddy				1-2

Table 110: PMA - Paper - Group Study - Trial 2

Sample	Print Type	Wetting	Drying	UV	Grade
0363	Loaded	10 Min	Air	15 Min	2
0364	Depletion				2
0365	Loaded	1 Hr			2
0366	Depletion				2
0367	Loaded	10 Min	Oven 100°C 10 Min		2
0368	Depletion				0
0369	Loaded	1 Hr			0
0370	Depletion				1

Table 111: PMA - Wetted Paper - Trial 1

Sample	Print Type	Wetting	Drying	UV	Grade
0371	Loaded	10 Min	Air	15 Min	1-2
0372	Depletion				1
0373	Loaded	1 Hr			1
0374	Depletion				2
0375	Loaded	10 Min	Oven 100°C 20 Min		1-2
0376	Depletion				2
0377	Loaded	1 Hr			2
0378	Depletion				2

Table 112: PMA - Wetted Paper - Trial 2

Sample	Print Type	Wetting	Drying	UV	Grade
0379	Loaded	10 Min	Air	15 Min	0
0380	Depletion				0
0381	Loaded	1 Hr			0
0382	Depletion				0

Table 113: PMA - Wet Paper - Trial 1

Sample	Print Type	Wetting	Drying	UV	Grade
0383	Loaded	10 Min	Air	15 Min	2
0384	Depletion				0-1
0385	Loaded	1 Hr			2-3
0386	Depletion				2
0387	Loaded	10 Min	Oven 100°C 20 Min		1-2
0388	Depletion				1-2
0389	Loaded	1 Hr			1-2
0390	Depletion				1

Table 114: PMA - Wetted Paper - Trial 3

Sample	Print Type	Wetting	Drying	UV	Grade
0391	Loaded	10 Min	Air	15 Min	2-3
0392		1 Hr			2
0393		10 Min	Oven 20 Min		2
0394		1 Hr			2

Table 115: PMA - Wetted Paper - Trial 4

Sample	Print Type	Development	Time	Grade
0423	Loaded	UV	15 Min	0
0424				0
0425		Oven		0
0426				0

Table 116: Cerium Ammonium Molybdate - Paper - Trial 1

Phosphomolybdic Acid Additional Images

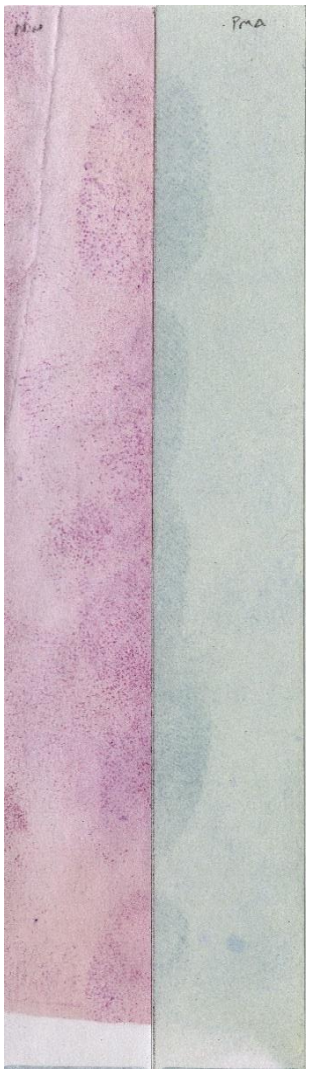


Figure 155: Ninhydrin/PMA Split Results

Figure 156: Ninhydrin/PMA Sequential Trial *via* Humidity Chamber

Figure 157: PMA > Oil Red O Comparison Results

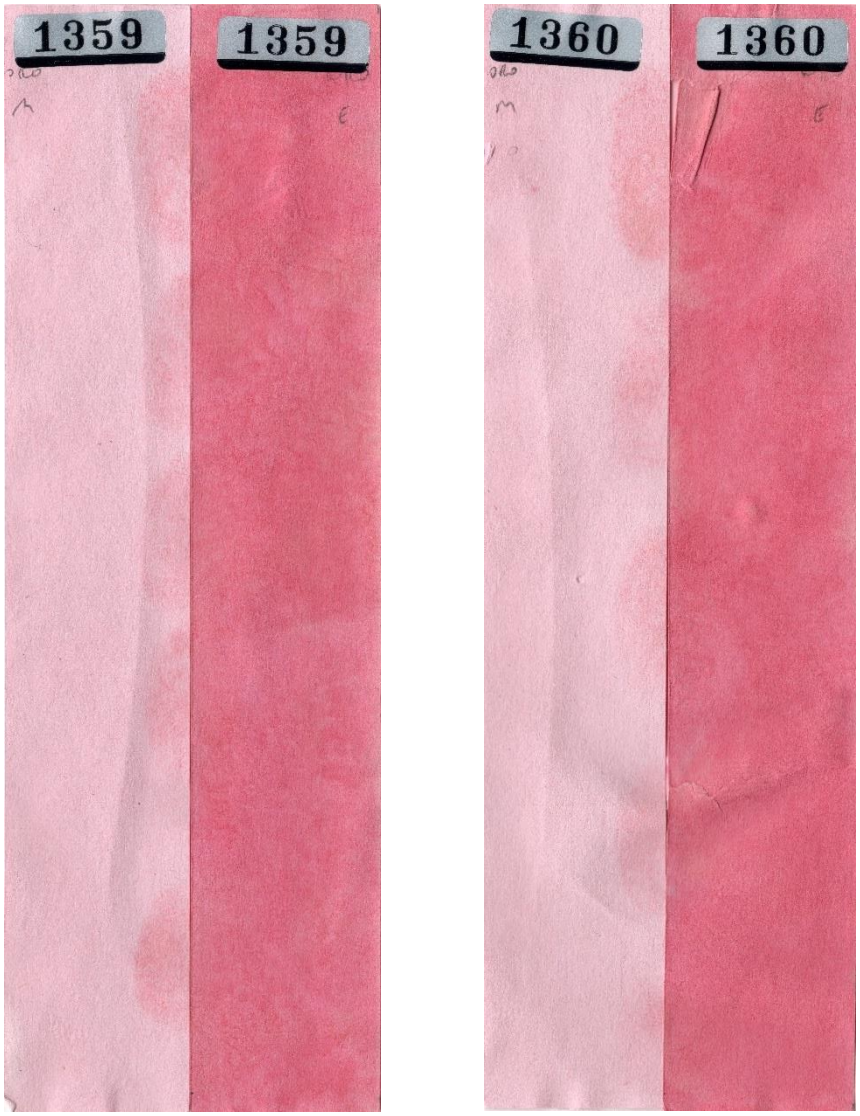


Figure 158: Oil Red O: Ethanol/Methanol Solution Comparison

Ultraviolet Light Box Set Up

Figure 159: Philips UV Facial Lamp

Figure 160: UV Lamp and Box (Pre Operation)

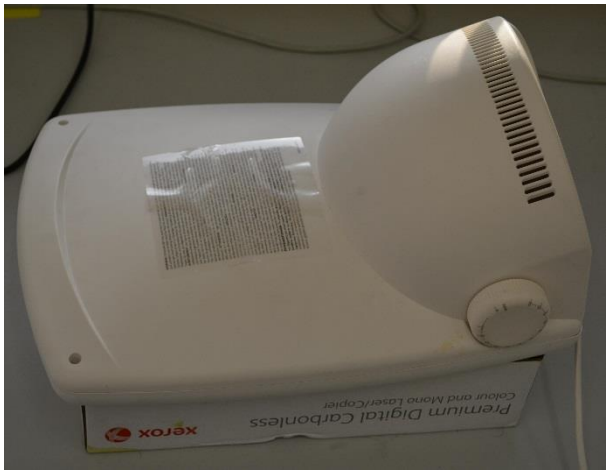


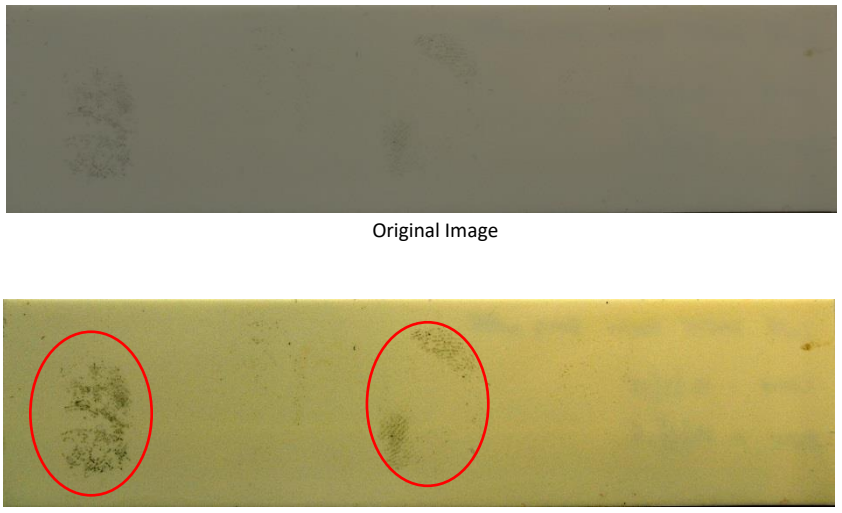
Figure 161: UV Lamp and Box (During Operation)

Cuprous Surfaces and Rubeanic Acid Additional Images

Original Image

Contrast Adjusted (Ridge Detail Circled)

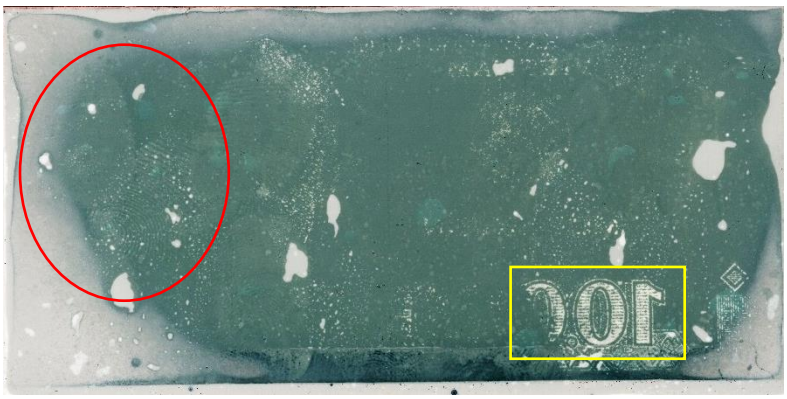
Figure 162: Brass Treated Directly With Rubeanic Acid



Original Image

Contrast Adjusted (Ridge Detail Circled)

Figure 163: Gel Lift Direct From Polymer Note



Ridge Detail
"100" Imprint

Gel Lift from Note

Fingermarks
"100" Imprint

Rubeanic Sprayed Brass Plate

Figure 164: Alternate Gel and Brass Process

Vacuum Metal Deposition Additional Information

Group Study Participants

DONOR #	NAME	AGE
1	Lloyd	42
2	Rich	25
3	Laura	24
4	Matt	33
5	Rae	34
6	Jade	44
7	Boss	49
8	Pauline	53
9	Senyu	23
10	Ruyi	23

Table 117: Group Study Participants

Miscellaneous Techniques Additional Information

Radioactive Techniques Additional Images

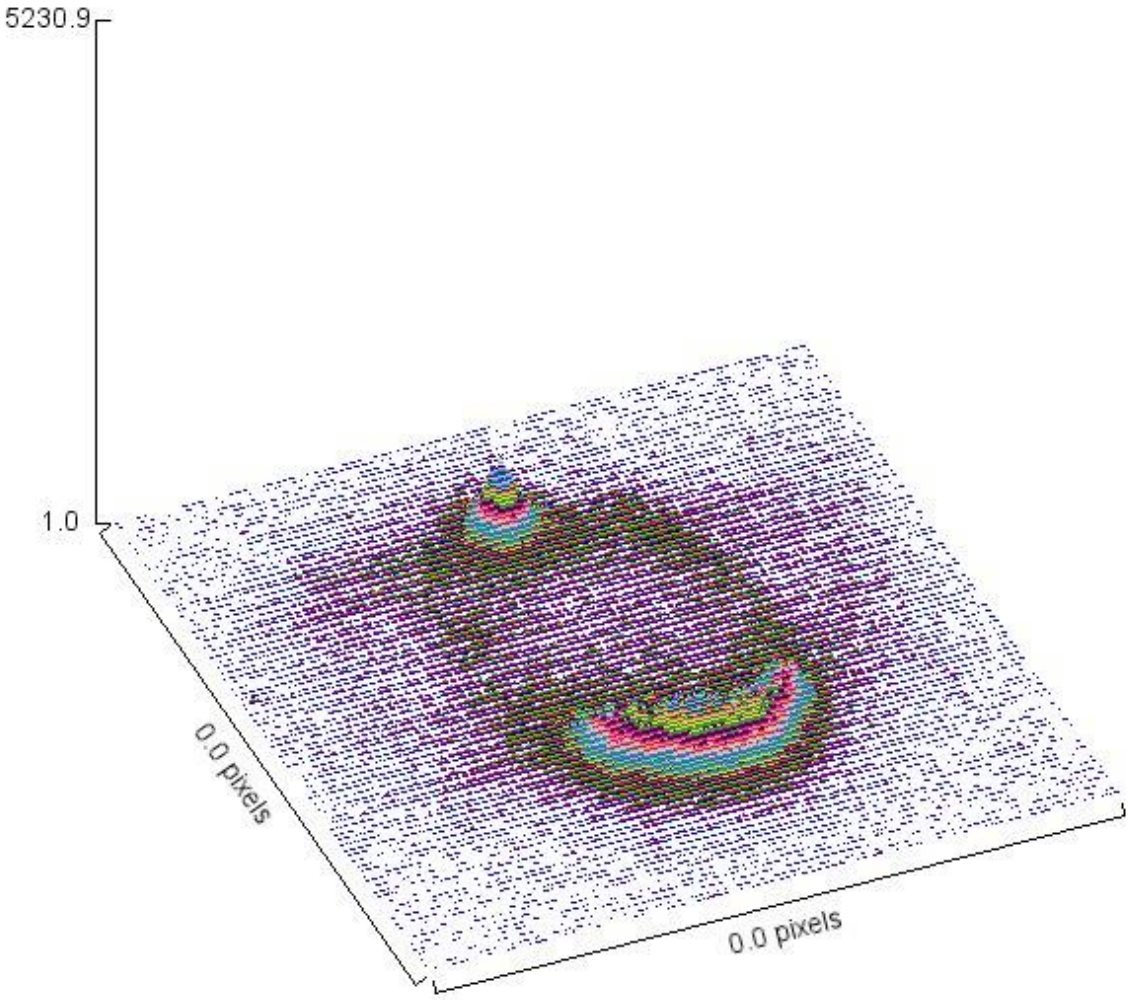


Figure 165: Autoradiography Surface Plot of Metal Sample Using Fiji with Glasbey Filter

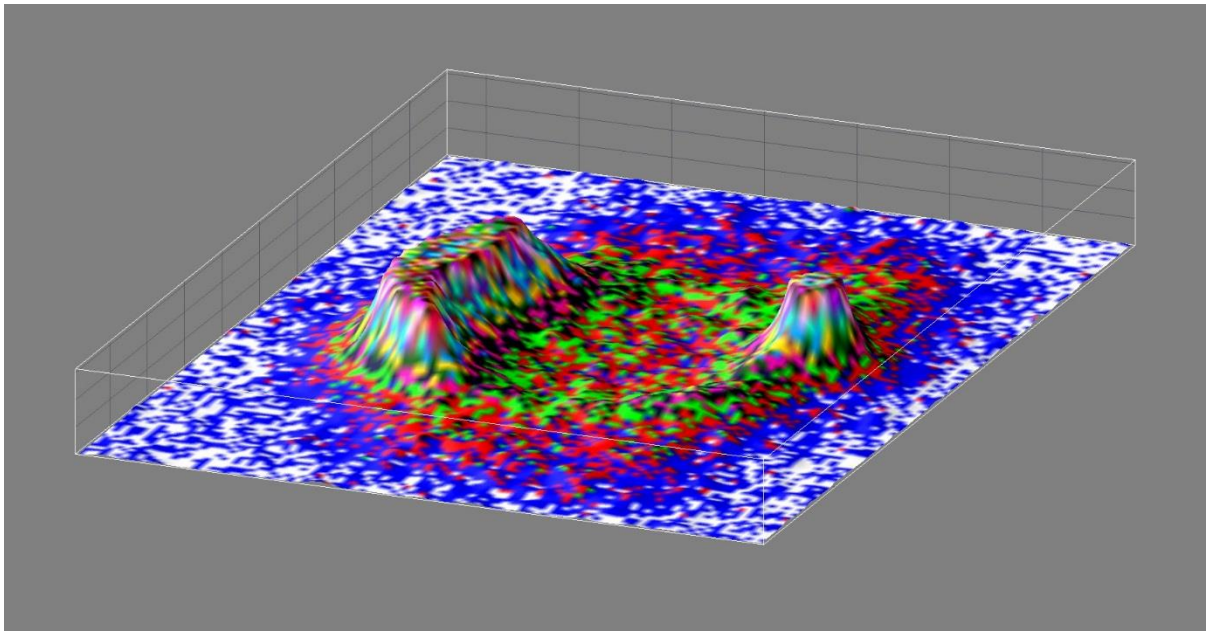


Figure 166: Autoradiography 3D Surface Plot of Metal Sample Using Fiji with Glasbey Filter

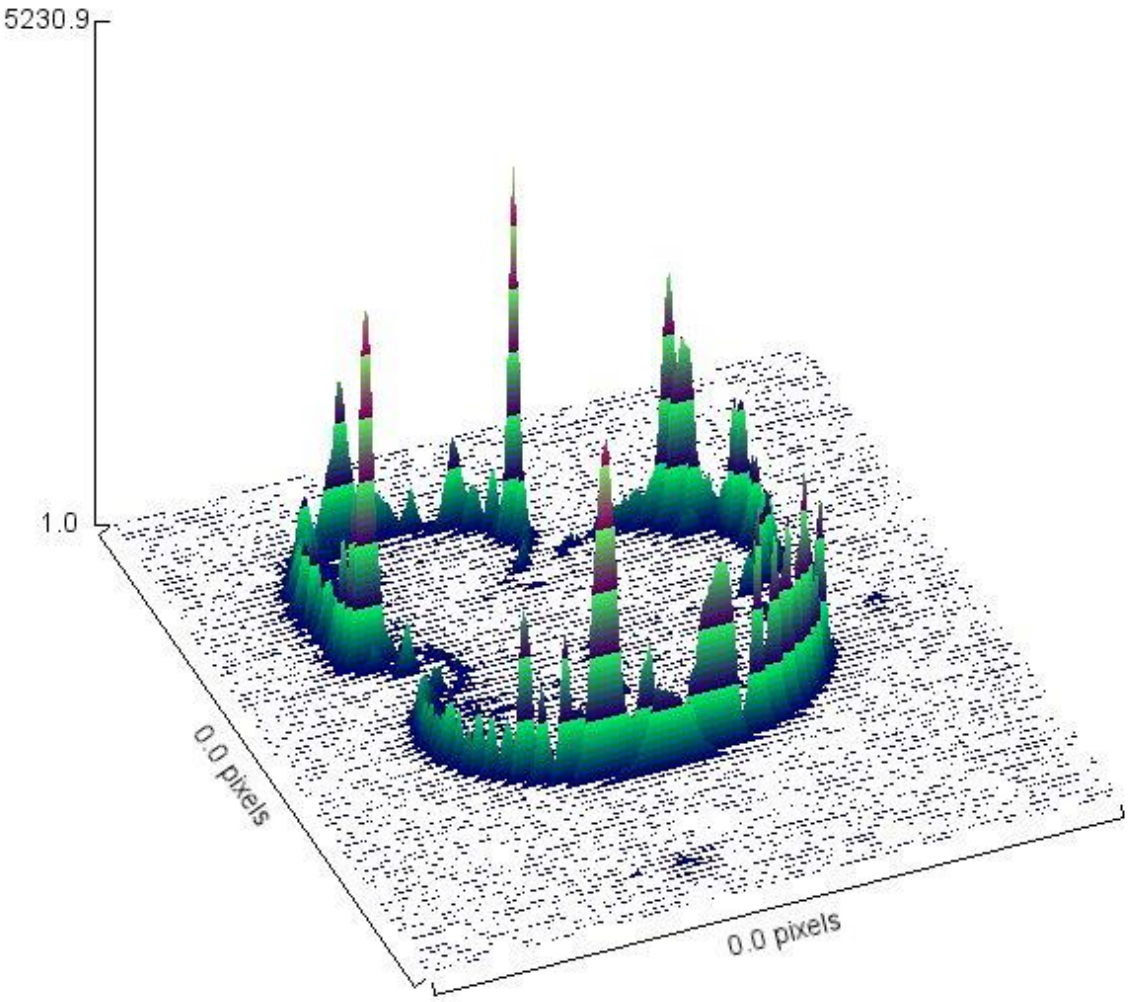


Figure 167: Autoradiography Surface Plot of Gel Sample Using Fiji with BRGBCMYW Filter

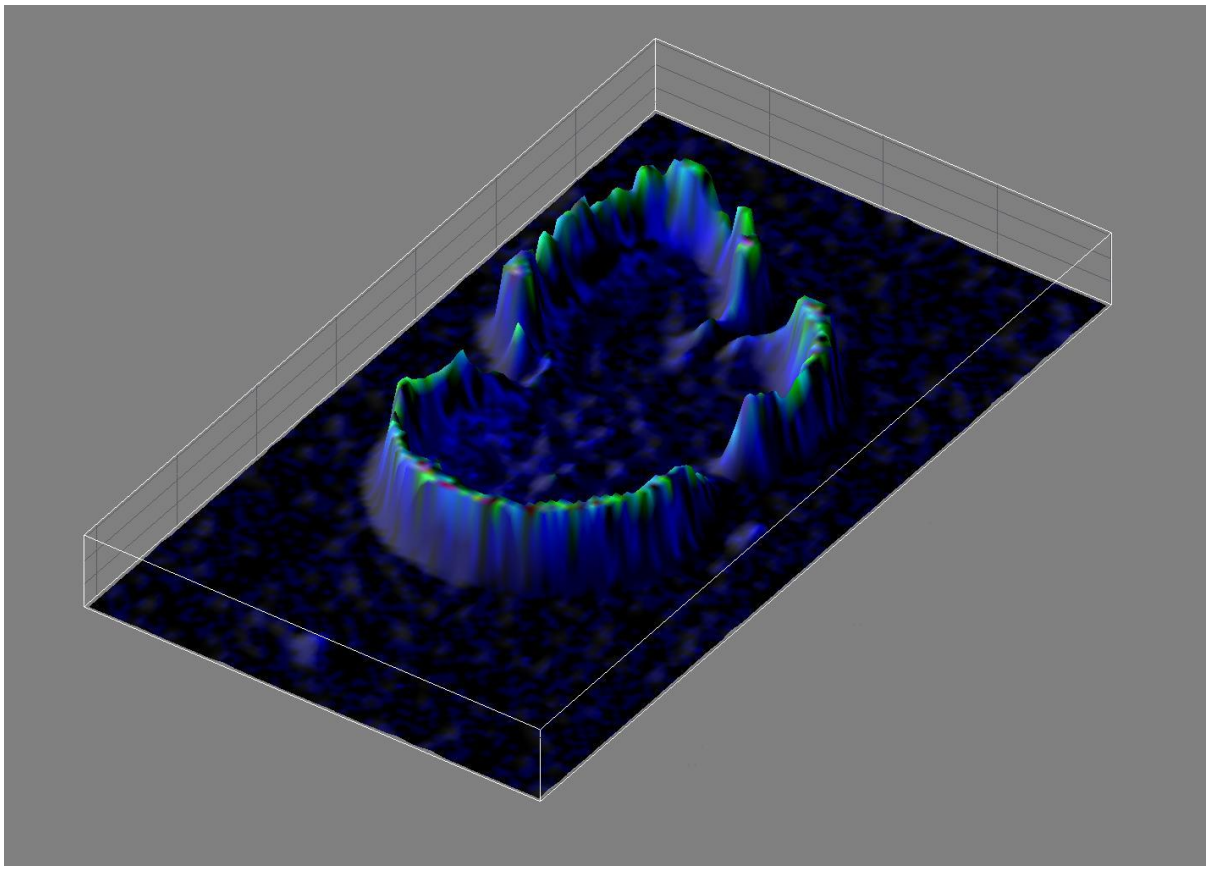


Figure 168: Autoradiography 3D Surface Plot of Gel Sample Using Fiji with BRGBCMYW Filter

Radioactive Techniques Additional Results - Tables

Sample	CPMA
Tile 1.1	17949.8
Tile 1.2	8049.6
Tile 1.3	4174.2
Tile 1.4	8838.6
Total of Tile	**39012.2**

Table 118: Recovery from Tile 1 - Count 1

Sample	CPMA
Tile 1.1	16079.0
Tile 1.2	7098.4
Tile 1.3	3842.6
Tile 1.4	9842.8
Total of Tile	**36862.8**

Table 119: Recovery from Tile 1 - Count 2

Sample	CPMA
Tile 2.1	24264.8
Tile 2.2	4699.2
Tile 2.3	2318.4
Tile 2.4	5644.2
Total of Tile	**36926.6**

Table 120: Recovery from Tile 2 - Count 1

Sample	CPMA
Tile 2.1	25218.6
Tile 2.2	4111.0
Tile 2.3	2097.8
Tile 2.4	6008.4
Total of Tile	**37435.8**

Table 121: Recovery from Tile 2 - Count 2

Sample	CPMA
Brass 1.1	187.0
Brass 1.2	61.0
Brass 1.3	30.4
Brass 1.4	26276.0
Total of Brass	**26554.4**

Table 122: Recovery from Brass 1 - Count 1

Sample	CPMA
Brass 1.1	272.0
Brass 1.2	71.6
Brass 1.3	29.8
Brass 1.4	28652.4
Total of Brass	**29025.8**

Table 123: Recovery from Brass 1 - Count 2

Sample	CPMA
Brass 2.1	1076.6
Brass 2.2	112.2
Brass 2.3	72.6
Brass 2.4	30078.8
Total of Brass	**31340.2**

Table 124: Recovery from Brass 2 - Count 1

Sample	CPMA
Brass 2.1	1365.8
Brass 2.2	105.2
Brass 2.3	68.8
Brass 2.4	31949.4
Total of Brass	**33489.2**

Table 125: Recovery from Brass 2 - Count 2

Sample	CPMA
Plastic 1.1	22397.4
Plastic 1.2	6450.6
Plastic 1.3	3130.6
Plastic 1.4	8473.8
Total of Plastic	**40452.4**

Table 126: Recovery from Plastic 1 - Count 1

Sample	CPMA
Plastic 1.1	20080.2
Plastic 1.2	5711.2
Plastic 1.3	2780.8
Plastic 1.4	9298.0
Total of Plastic	**37871.2**

Table 127: Recovery from Plastic 1 - Count 2

Sample	CPMA
Plastic 2.1	21855.0
Plastic 2.2	7002.6
Plastic 2.3	2784.0
Plastic 2.4	5659.8
Total of Plastic	**37301.4**

Table 128: Recovery from Plastic 2 - Count 1

Sample	CPMA
Plastic 2.1	21394.0
Plastic 2.2	6757.2
Plastic 2.3	2555.0
Plastic 2.4	5853.6
Total of Plastic	**36559.8**

Table 129: Recovery from Plastic 2 - Count 2

Sample	% Recovery
Standard Average	**46597.4**
Tile 1	**83.72%**
Brass 1	**56.99%**
Plastic 1	**86.81%**

Table 130: Percentage Recovery 1 - Count 1

Sample	% Recovery
Standard Average	**46597.4**
Tile 1	**79.11%**
Brass 1	**62.29%**
Plastic 1	**81.27%**

Table 131: Percentage Recovery 1 – Count 2

Sample	% Recovery
Standard Average	**46597.4**
Tile 2	**79.25%**
Brass 2	**67.26%**
Plastic 2	**80.05%**

Table 132: Percentage Recovery 2 - Count 1

Sample	% Recovery
Standard Average	**46597.4**
Tile 2	**80.34%**
Brass 2	**71.87%**
Plastic 2	**78.46%**

Table 133: Percentage Recovery 2 - Count 2

Sample	% Recovery
Standard Average	**46597.4**
Tile 1 Average	**81.42%**
Brass 1 Average	**59.64%**
Plastic 1 Average	**84.04%**

Table 134: Average Percentage Recovery 1

Sample	% Recovery
Standard Average	**46597.4**
Tile 2 Average	**79.80%**
Brass 2 Average	**69.57%**
Plastic 2 Average	**79.26%**

Table 135: Average Percentage Recovery 2

Biological Techniques Additional Images

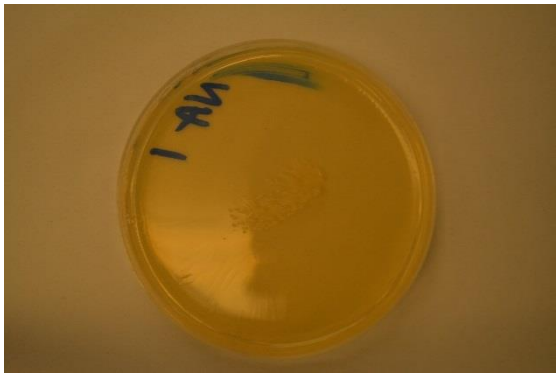


Figure 169: Sample NA1 Initial

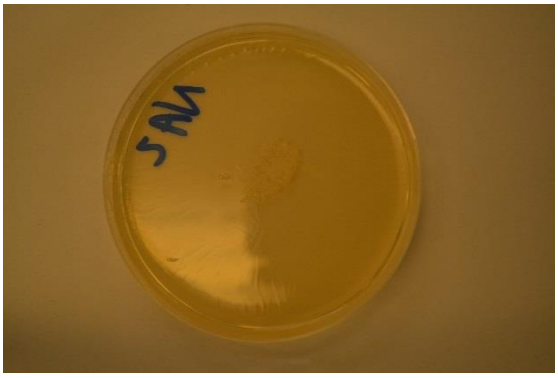


Figure 170: Sample NA2 Initial

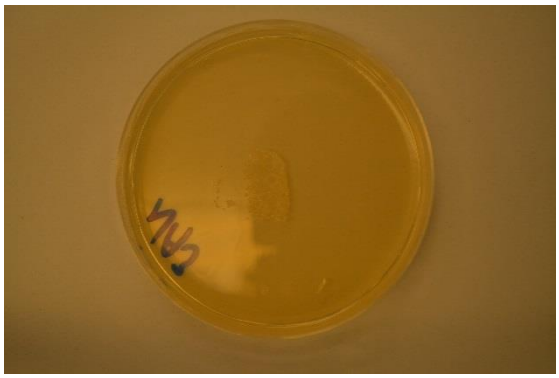


Figure 171: Sample NA3 Initial

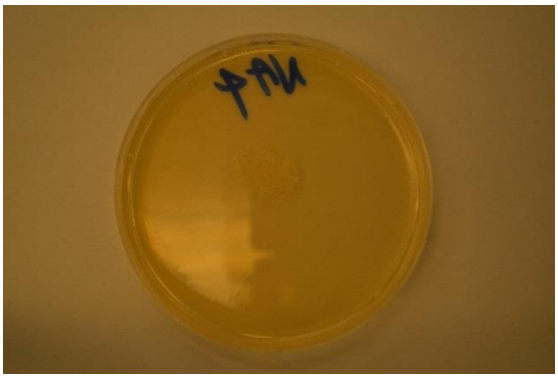


Figure 172: Sample NA4 Initial

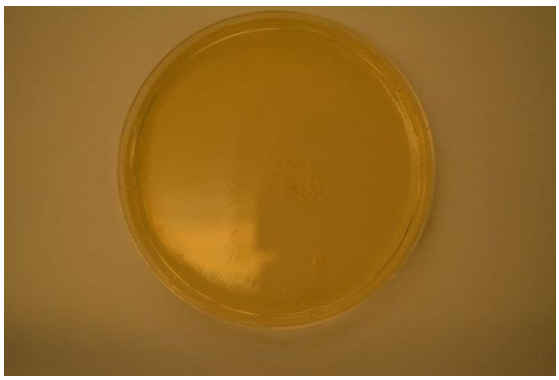


Figure 173: Sample NA5 Initial

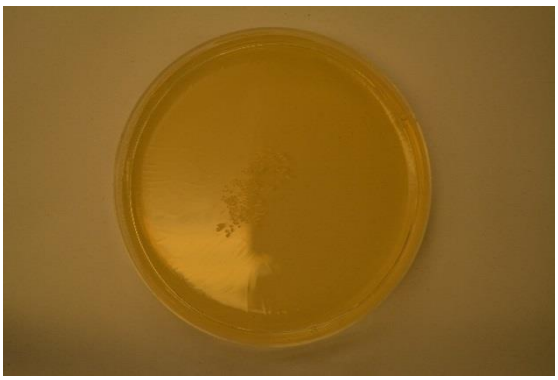


Figure 174: Sample NA6 Initial

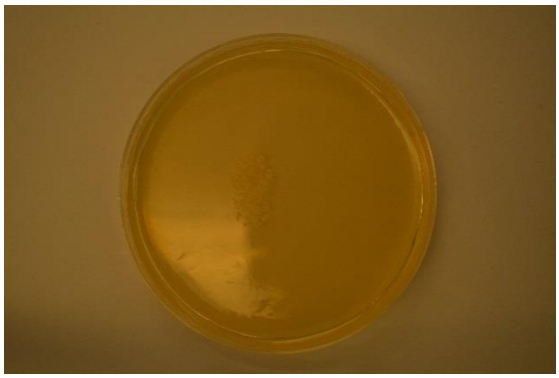
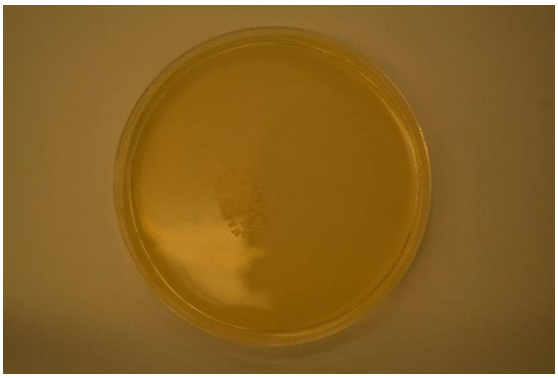


Figure 175: Sample NA7 Initial



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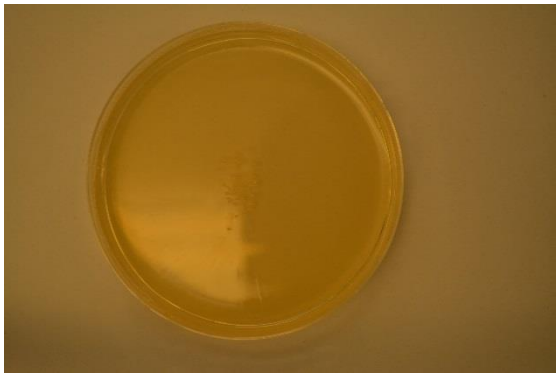
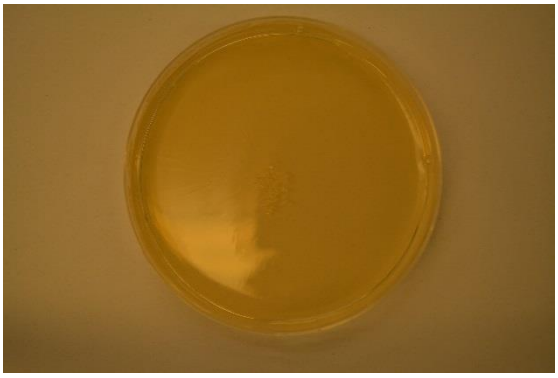


Figure 177: Sample NA9 Initial



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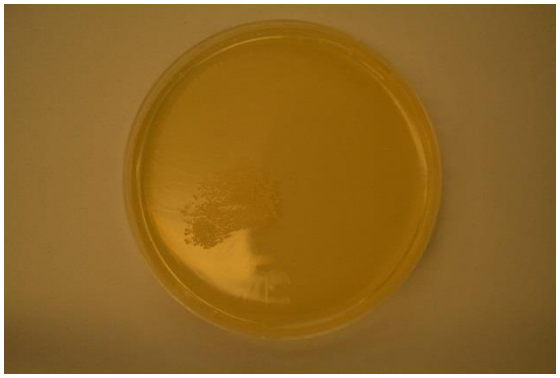

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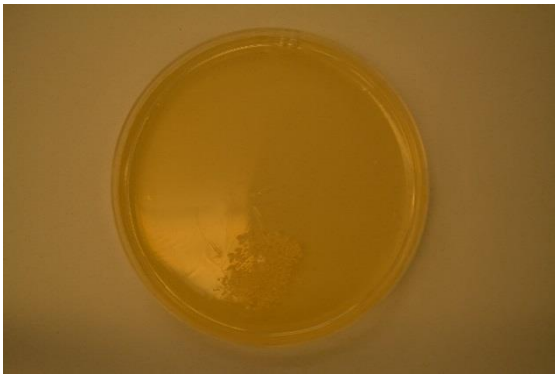

Figure 180: Sample NA12 Initial

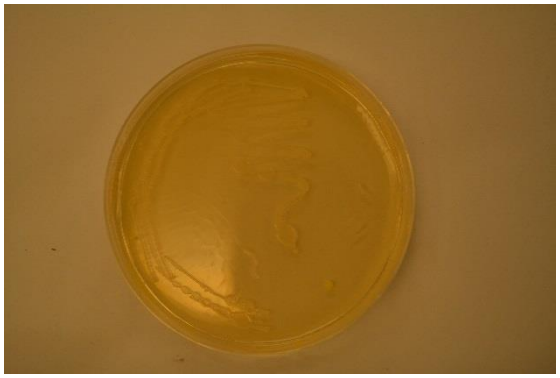

Figure 181: Sample NA1 Streak

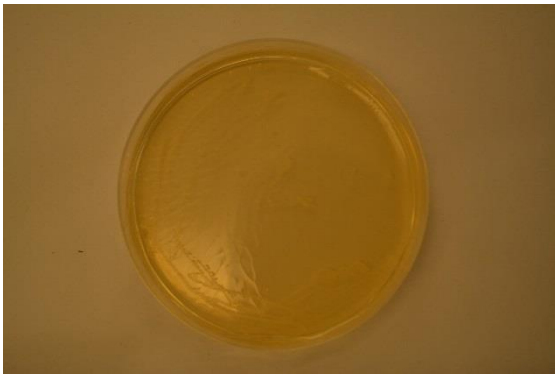

Figure 182: Sample NA2 Streak

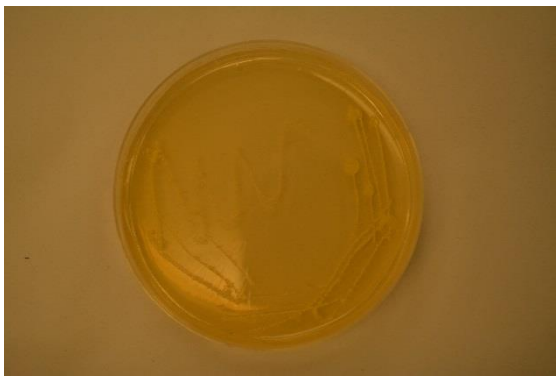

Figure 183: Sample NA3 Streak

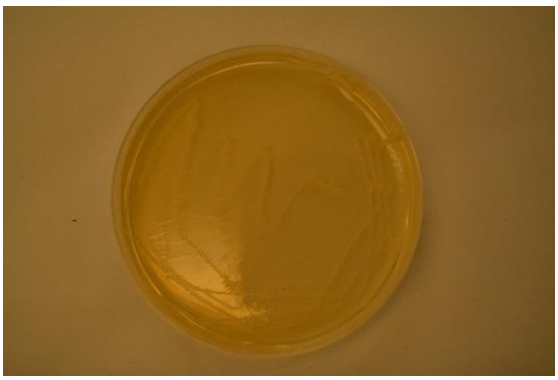

Figure 184: Sample NA4 Streak

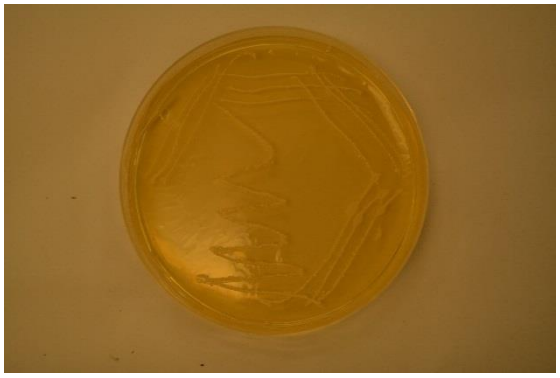

Figure 185: Sample NA5 Streak

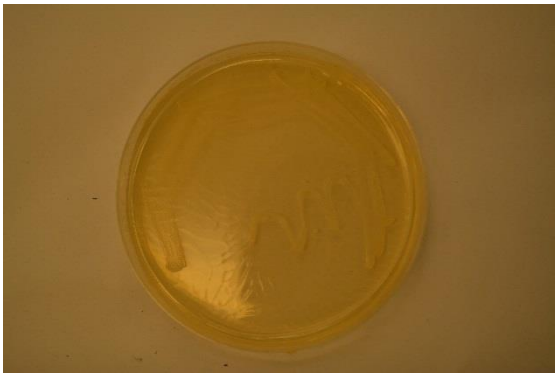

Figure 186: Sample NA6 Streak

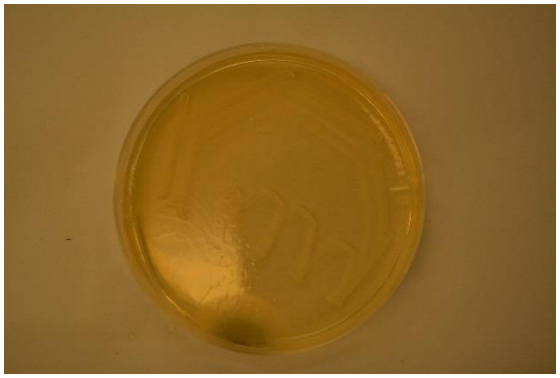

Figure 187: Sample NA7 Streak

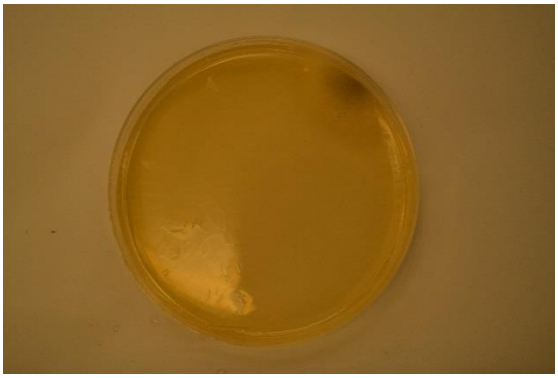

Figure 188: Sample NA8 Streak

Figure 189: Sample NA9 Streak

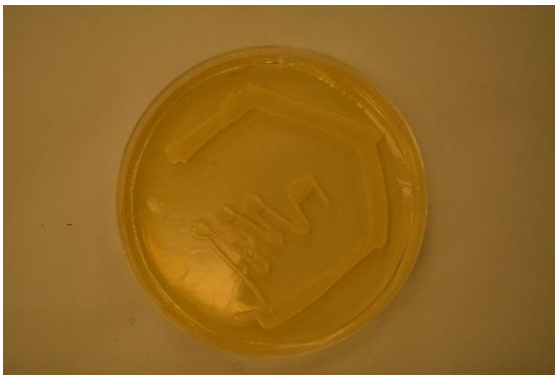

Figure 190: Sample NA10 Streak

Figure 191: Sample NA11 Streak

Figure 192: Sample NA12 Streak

Skills Training Record

Development Courses

Date	Course	Time
22nd January 2014	Postgraduate Induction Day	4 Hours
25th February 2014	Public Engagement and Research	3 Hours
4th March 2014	Finding Information for your Literature Review - Theory	1.5 Hours
11th March 2014	Teaching Skills Part A – 'Preparing to Teach'	2 Hours
12th March 2014	Teaching Skills Part B – 'Promoting Learning'	2 Hours
13th March 2014	Radiation Legislation and Protection Training	1 Hour
19th March 2014	Teaching Skills Part C – 'Supervising Practical Activities'	3 Hours
8th April 2014	Report Writing	3 Hours
30th April 2014	Getting Articles Published for Researchers	3 Hours
7th May 2014	Tools for Creative Thinking	3 Hours
21st May 2014	Working Effectively with Outside Organisations	3 Hours
22nd May 2014	Data Management Planning	1 Hour
25th May 2014	Finding Information for your Literature Review – Practice	1.5 Hours
2nd July 2014	Plagiarism & Citations for PGRs	1.5 Hours
7th July 2014	Keeping Up-to-Date	1.5 Hours
9th July 2014	Managing Your References Effectively	2.5 Hours
22nd January 2015	Demonstrator Skill Workshop	2 Hours
	Total	38.5 Hours

Health & Safety Seminars

Date	Topic	Time
22nd January 2014	Flammable Materials	0.5 Hours
26th February 2014	Liquefied Gases, Cryogenics	0.5 Hours
12th March 2014	Corrosive Materials	0.5 Hours
16th April 2014	Electrical Hazards	0.5 Hours
11th June 2014	High Pressure/High Temperature Operations	0.5 Hours
2nd July 2014	Radioactive Materials and Ionising Radiation	0.5 Hours
21st January 2015	Vacuum Systems	1 Hour
14th April 2015	Workflow	1 Hour
29th April 2015	Project Management	1 Hour
10th June 2015	Record Keeping	1 Hour
19th November 2015	Flammable Materials	0.5 Hours
3rd December 2015	Liquefied Gases, Cryogenics	0.5 Hours
13th January 2016	Corrosive Materials - Presented	0.5 Hours
11th February 2016	Electrical Hazards	0.5 Hours
17th March 2016	Pressurised Gases	0.5 Hours
		9.5 Hours

Conferences & Events

Date	Conference	Time
3rd June 2014	East Midlands Policing Consortium Launch Event	7 Hours
15th April 2015	New Frontiers in Forensics (Leicester University)	7 Hours
29th April 2015	CAST Academia/Industry Meeting 3 (F&F Evesham) – Presented	6 Hours
15th May 2015	Science Matters (Loughborough University)	6.5 Hours
28th October 2015	CAST Academia/Industry Meeting 4 (Staffordshire University)	6 Hours
7th April 2016	CAST Academia/Industry Meeting 5 (Teesside University)	6 Hours
8 – 9th April 2016	The Fingerprint Society Annual Educational Conference 2016 1st Place Poster Prize Winner	14 Hours
20th June 2016	Science Matters (Loughborough University)	6.5 Hours
22nd June 2016	Graduate School Summer Showcase (LU) 2nd Place Poster Prize Winner – Secure and Resilient Societies Category	4 Hours
7th – 13th August 2016	International Association for Identification's 101st Annual International Forensic Education Conference (Cincinnati)	35 Hours
1st November 2016	CAST Academia/Industry Meeting 6 (Loughborough University)	6 Hours
26th April 2017	CAST Academia/Industry Meeting 7 (University of Westminster)	6 Hours
	Total	110 Hours

Publications

Lloyd W.L. Davis, Paul F. Kelly, Roberto S.P. King, Stephen M. Bleay, *Visualisation of latent fingermarks on polymer banknotes using copper vacuum metal deposition: A preliminary study*, Forensic Science International, Volume 266, 2016, Pages e86-e92, ISSN 0379-0738, http://dx.doi.org/10.1016/j.forsciint.2016.05.037.

Lloyd W.L. Davis, Stephen M. Bleay, Paul F. Kelly, 2018, *Assessing Phosphomolybdic Acid as a Fingermark Enhancement Reagent*, Journal of Forensic Identification, Volume 68(2), Pages 257-280

Forensic Science International 266 (2016) e86–e92

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Rapid Communication

Visualisation of latent fingermarks on polymer banknotes using copper vacuum metal deposition: A preliminary study

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Forensic light source

ABSTRACT

The UK's recent move to polymer banknotes has seen some of the currently used fingermark enhancement techniques for currency potentially become redundant, due to the surface characteristics of the polymer substrates. Possessing a non-porous surface with some semi-porous properties, alternate processes are required for polymer banknotes. This preliminary investigation explored the recovery of fingermarks from polymer notes *via* vacuum metal deposition using elemental copper. The study successfully demonstrated that fresh latent fingermarks, from an individual donor, could be clearly developed and imaged in the near infrared. By varying the deposition thickness of the copper, the contrast between the fingermark minutiae and the substrate could be readily optimised. Where the deposition thickness was thin enough to be visually indistinguishable, forensic gelatin lifters could be used to lift the fingermarks. These lifts could then be treated with rubeanic acid to produce a visually distinguishable mark. The technique has shown enough promise that it could be effectively utilised on other semi- and non-porous substrates.

1. Introduction

The United Kingdom's decision to change from traditional cotton paper banknotes to a biaxially orientated polypropylene (BOPP) polymer type note has three principal benefits. Being plastic, they are more resistant to dirt making them a cleaner alternative. They are harder to counterfeit due to the incorporation of advanced security features and they are more durable, meaning that, long-term, they are cheaper and more environmentally friendly. Despite polymer banknotes being non-porous, they also exhibit semi-porous qualities due to the printing materials and surface coatings used. In turn, this has the tendency to result in increased absorption/wicking of a fingermark residue from the surface. This, coupled with the fact that the notes often have complex designs and fluorescent security features, means that most traditional non-porous fingerprint techniques encounter difficulties developing marks on such substrates.

Many countries around the world have already introduced polymer banknotes in to circulation, with Australia being the first to do so in 1988. The main difficulty with polymer banknotes in terms of latent fingermark enhancement is that, although the base polymer is BOPP with an opacifying layer, changes to printing and overcoating layers introduce variables that may alter the effectiveness of the detection sequence. Accordingly, numerous fingermark enhancement investigations have been conducted since their introduction. In 1999, Flynn et al. trialled a number of fingermark enhancement techniques that were, at the time, commonly employed for fingermark enhancement on non-porous substrates and found that the majority were only effective in developing marks for a short time post-deposition. Cyanoacrylate fuming (CAF) and vacuum metal deposition (VMD) were found to be the most successful of the techniques investigated, although results were often limited by the area of the polymer note being treated. Enhancement was found to be improved when a combination of the two was used [1]. When treating polymer banknotes, it was found that fingermarks which were present on the untreated transparent security window area were developed to a greater degree than those on the printed areas [1–4]. In accordance with these findings, and following further evaluation, the processes CAST (Centre for Applied Science and Technology) currently recommend for Biaxially Orientated Polypropylene (BOPP) banknotes are depicted in Fig. 1, although the effectiveness of Powder Suspension followed by Basic Violet 3 is unknown [5].

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0379-0738/

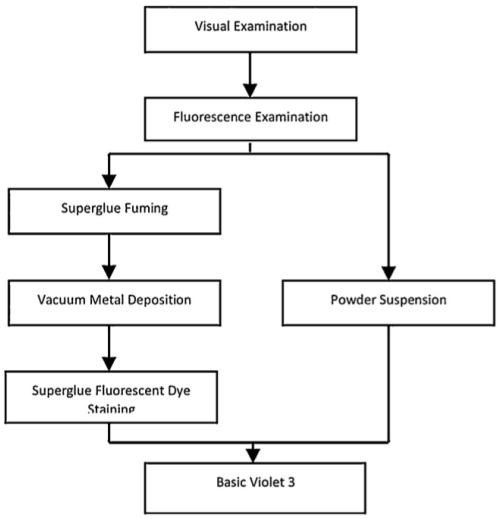


Fig. 1. BOPP recommended process chart [5].

From an operational standpoint, fingermarks which have been developed on multi-coloured or heavily patterned substrates can be difficult to visualise where the ridge flow crosses these areas. Recent pertinent advances in fluorescent fingerprint powders have shown that exploitation of fluorescence in the near infrared (NIR) regions of the spectrum can be extremely beneficial in circumventing such issues. King et al. were able to show that by mixing non-toxic and naturally occurring *spirulina platensis* into a fingerprint powder and utilising its inherent IR fluorescence *via* blue/red excitation, the UV/visible security features of polymer banknotes that often interfere with conventional imaging could be overcome with IR fluorescence examination [6]. In addition, problematic backgrounds which often make it difficult to see developed marks due to their complexity and multi-colour were mitigated *via* imaging at these longer wavelengths. The same authors subsequently developed a tailored cuprorivaite based fingerprint powder which exhibits unique NIR–NIR fluorescence and helps further reduce background artefacts during the IR fluorescent examination given the longer excitation and emission wavelengths being employed [7].

Chadwick et al. have also looked at imaging latent fingermarks in this region of the spectrum *via* modification to commercially available fingerprint powders using styryl dyes [8], although availability and cost of the dye material are a factor to be considered. The use of upconversion powders, such as that by Ma et al., has been suggested as an alternative method to help overcome problematic backgrounds [9]. Tahtouh et al. also utilised IR imaging in the form of Fourier transform infrared (FTIR) to enhance fingermarks on a number of substrates, including polymer banknotes, which contained untreated and cyanoacrylate treated fingermarks [10]. Such a process, however, requires expert operator input and can be largely time consuming.

Vacuum metal deposition is a thin-film deposition technique in which source metal is evaporated in a vacuum, in order to coat a substrate. The technique has been long established in industrial application of metal coatings to the likes of glass for making mirrors. The use of VMD as a tool for the forensic enhancement of latent fingermarks was first proposed in 1964 by Tolansky, however it would be nearly a decade later until the method would gain enough credibility to be seriously considered as a viable development technique [11]. The treatment involves placing the article to be enhanced inside the deposition chamber at high vacuum, typically $<3 \times 10^{-4}$ mbar. The chamber also contains filaments for the containment of the metal to be deposited and a window to allow the operator to view the deposition process. The most commonly used metals in the VMD treatment of latent fingermarks are gold/zinc, whereby gold is applied first, followed by zinc.

Over the last decade and a half VMD has been the focus of many studies involving fingermark deposits on fabrics. These studies applied traditional gold/zinc [12] and silver [13] on dark fabrics to varying degrees of success. Further studies on fabric compared VMD and superglue fuming, which proved VMD to be more effective at developing fingermarks [14]. Despite the recent resurgence in VMD work and the price of VMD chambers dropping substantially over the last decade, very little has emerged recently comparing the efficiency of VMD in developing latent fingermarks on polymer banknotes, and other polymer substrates in general [15–21].

The element chosen for deposition during this study was copper; this was partly due to its ability to react with rubeanic acid and produce a coloured complex as demonstrated during previous work conducted by Kelly et al. [22]. Their work explored novel detection methods for metals that may be conducive to Heritage Crime[1] and exploited a gelatin lifting procedure whereby the presence of metal residues on the hands of an individual could be easily and noninvasively detected and mapped out. Another reason for choosing copper as the source metal for this study was its previously successful VMD trial on a limited number of polymer substrates, none of which were polymer banknotes [23]. Here, it was found to be more successful than the traditional gold/zinc and silver processes on certain polymer types, such as PVC-based cling films.

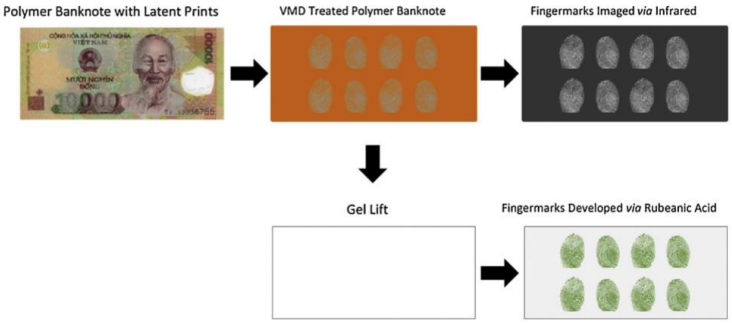
This preliminary study addresses the direct utilisation of a copper source for the enhancement of latent fingermarks on polymer banknotes and explores the benefits of complimentary imaging and post-treatment processing to further enhance the VMD treated samples.

2. Materials and methods

A West Technology Systems Limited VMD560CX VMD system was employed for all VMD treatments. This medium sized unit has a viewing window and a computerised screen with pressure gauge which facilitated process optimisation and efficient reproducibility. An Intellimetrics IL150 film thickness monitor (QCM) was used to accurately monitor and measure the thickness of the metals being deposited. The banknotes, a biaxially orientated polypropylene polymer type, used throughout the study were new and untouched sample test notes provided by the Bank of England. Approximately 24 notes and 240 fingermarks were processed in total during the course of this study.

Fingermarks were deposited upon the surface of each banknote by one male donor. Two rows of five marks were deposited; the latent fingermarks along the upper row were loaded with sebaceous content from brief wiping of the fingertips along the forehead and side of nose. The lower row contained natural latent fingermarks that were deliberately unadulterated in any way. Each fingermark was from a separate finger and the marks were approximately 1 day old.

[1] Heritage crime has been defined as any offence which harms the value of heritage assets and their settings to this and future generations [26]. More information on heritage crime can be found in "Heritage Crime: Progress, Prospects and Prevention" by L. Grove and S. Thomas [27].



Scheme 1. Process of treatments used on polymer banknotes (Vietnamese polymer banknote used for display purposes only).

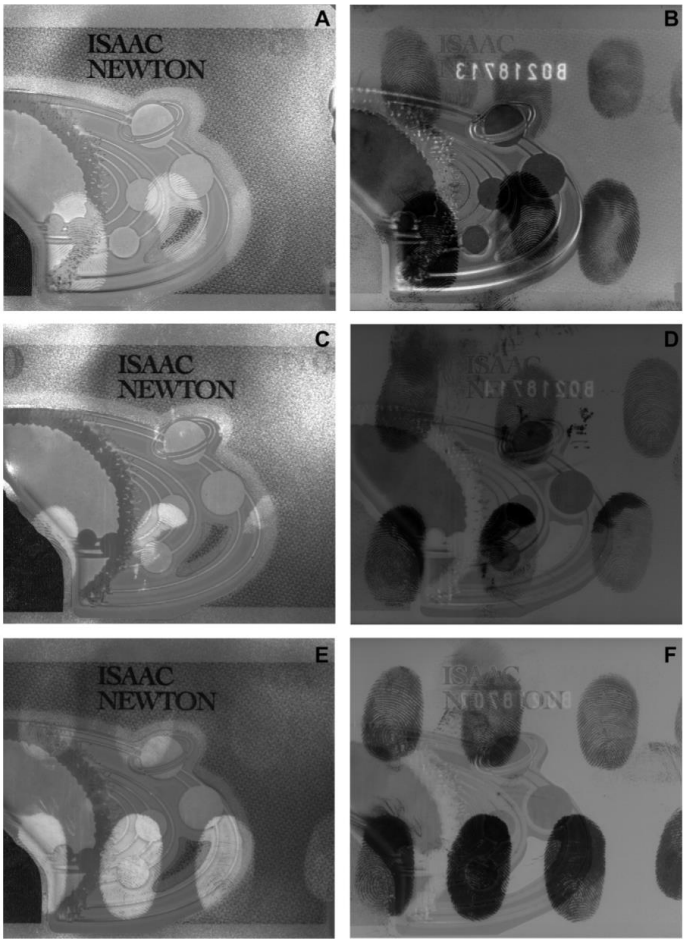


Fig. 2. Copper deposition thickness of: (A) 1.7 nm as viewed under 80 W Halogen light source (B&W), (B) 1.7 nm viewed under 80 W Halogen light source with 780 nm long-pass filter, image inverted, (C) 2.1 nm as viewed under 80 W Halogen light source (B&W), (D) 2.1 nm viewed under 80 W Halogen light source with 780 nm long-pass filter, image inverted, (E) 3.0 nm as viewed under 80 W Halogen light source (B&W) and (F) 3.0 nm viewed under 80 W Halogen light source with 780 nm long-pass filter, image inverted. (A–F) SII imaged using the Crime-lite imager.

The elemental copper used took the form of an insulated copper wire (1.0 mm diameter, Scientific Wire Company). The copper was deposited under the same deposition conditions as routinely utilised for gold; chamber pressure $\leq 3 \times 10^{-4}$ mbar. The source boat temperature was raised until the filament was glowing to allow evaporation of copper. Since very little copper was required during each experiment, one copper sample was used throughout the investigations. The film thickness of the deposited copper varied throughout the investigation from 0.2 nm to 3.0 nm, *vide infra*.

For the purpose of lifting from the VMD treated substrates, white gelatin lifters were employed (BVDA – B155000). These lifts were subsequently treated by spraying with a rubeanic acid solution (0.1, w/v), prepared from dithiooxamide (Sigma Aldrich – 379387) in absolute ethanol. The solution was sprayed using an ECOSPRAY (Labo Chimie, France).

Two imaging systems were used: a desktop Crime-lite Imager (Foster + Freeman Ltd, Evesham, UK) fitted with either 25 mm or 35 mm lens. Vis/IR illumination was provided *via* an integrated 80 W halogen light source and imaging achieved using 780 nm or 850 nm long-pass camera filters directly in front of a 5MP vis/IR monochromatic camera. A DCS-5 (Foster + Freeman Ltd, Evesham, UK) was also employed which comprised a modified Nikon D810 camera fitted with a 105 mm macro lens and similar long-pass filters. Illumination on this system was achieved using either a Polytec 150 W halogen bright field fibre optic ring light or a Crime-lite 82S IR (800–900 nm) (Foster + Freeman Ltd, Evesham, UK).

2.1. Sample treatment

Once treated in the VMD chamber, the notes were visually inspected. Following visual inspection, the notes had a gelatin lifter applied to their surface for 1–2 min. Care should be taken to avoid air bubbles which can interfere with the ridge flow of the lifted fingermark. Once removed, the gel was sprayed with rubeanic acid, and left to dry.

2.2. Sample Imaging

Sample illumination and imaging was initially achieved using an 80 W halogen light source which outputs light over a broad spectral range (400–1000 nm), including the near infrared. Visualisation was achieved using a NIR long-pass 780 nm camera filter which allowed only Infrared radiation to pass to the IR sensitive camera. In the context of this substrate type the background of each banknote almost completely disappears and the fingermark ridge detail becomes more visible.

The process of steps taken is shown in Scheme 1.

3. Results

The ease of visual examination (visual contrast) depended largely on the deposition thickness of the copper. Banknotes deposited with copper to a film thickness below 1.6 nm afforded no visual appearance of fingermarks, due to the copper layer appearing transparent to the naked eye.

However, as the deposition thickness layer increased it became easier to observe the location of marks, as the copper layer became more opaque, even if ridge detail could not be discerned under visual examination (Figs. 2 and 3).

After the visual inspection, the notes had a gelatin lifter applied to their surface, once removed; the gel was sprayed with rubeanic acid, which resulted in the fingermark ridges containing copper deposits becoming visible in the form of polymeric copper rubeanate (Scheme 2).

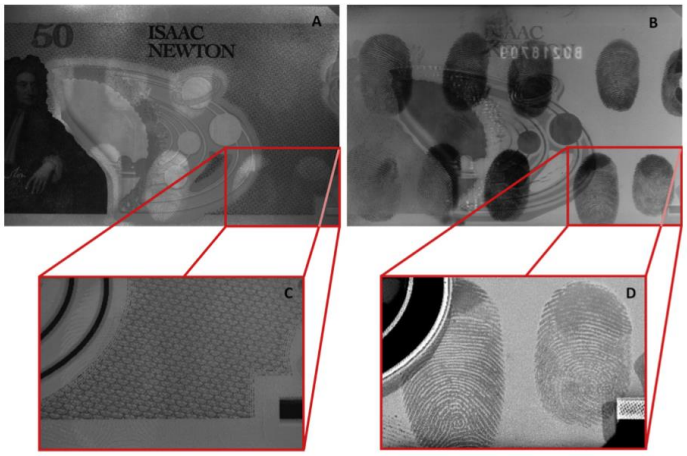
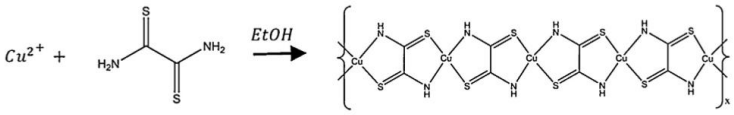


Fig. 3. Copper deposition thickness of: (A) 2.5 nm as viewed under 80 W Halogen light source (B&W), (B) 2.5 nm viewed under 80 W Halogen light source with 780 nm long-pass filter, image inverted, (C) 2.5 nm as viewed under 150 W Halogen light source (B&W), (D) 2.5 nm viewed under 150 W Halogen light source with 780 nm long-pass filter, image inverted. (A and B) imaged using Crime-lite Imager, (C and D) imaged using DCS-5 & Nikon D810 camera.



Scheme 2. The formation of copper rubeanate.

Fig. 4. (A) Gelatin lift from polymer note after application for 1 min, (B) Gelatin lift from polymer note after application for 2 min.

The copper rubeanate presents as dark green, making visualisation on the white gelatin lifter easier with the naked eye (Fig. 4).

4. Discussion and conclusions

The main objective of the study was to evaluate whether copper could be utilised to develop fingermarks on a polymer banknote and employ subsequent imaging processes to improve clarity, with the additional aim of lifting the marks with a forensic gelatin lifter for treatment with rubeanic acid. The decision to utilise gelatin lifts treated with rubeanic acid was twofold; recent work conducted at Loughborough University proved to be very successful in lifting, and non-invasively treating, friction ridge detail that was contaminated with metal residues [22]. In addition, by using the filament temperature dial on the VMD, it was possible to control the amount of copper deposited on the polymer note surface. This not only allowed the visual/IR examination to be optimised based on fingermark enhancement clarity, but also allowed the effects of copper deposition thickness to be explored in terms of its potential for gelatin lifting. The amount deposited was checked using the Intellimetrics IL150 quartz crystal growth rate monitor. The starting thickness was 0.2 nm, increasing in 0.2–0.3 nm increments to 2.1 nm at which point the increments increased to 0.5 nm to a maximum thickness of 3.0 nm per test sample.

The tests undertaken highlighted that while the deposition thickness of the copper impacted visual fingermark observation on the substrate surface, there was marginal difference when viewed under reflected infrared conditions. The thicker the copper deposition layer, the better the contrast between the ridge detail and the substrate to an extent. Samples with 3.0 nm of copper deposited upon their surface began to exhibit overdevelopment which presented as the ridges leaching into each other. This technique is of particular use when developing marks on a substrate with a 'busy' and patterned background.

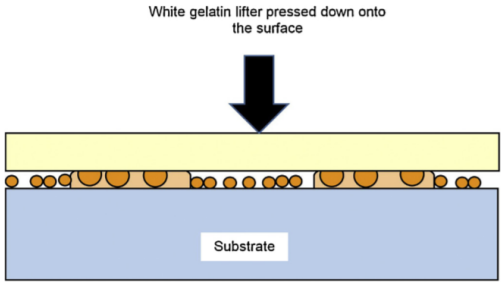


Fig. 6. Schematic diagram of application of gelatin lifter to VMD treated banknote surface.

Fingermarks visualised by infrared imaging presented as negative marks, whereas the gel lifted marks presented as positive. We theorise this is due to the way the elemental copper interacts with the fingermark residues and the underlying substrate, *vide infra*.

When copper is deposited over the surface it begins to form nuclei, the morphology of which is largely dependent on the nature of the surface on which they are being deposited on to. Areas where the substrate is clean and free from contaminants form small tightly packed nuclei. However, areas that have fatty residues from latent fingermarks, act differently. The copper diffuses into the fat and forms larger nuclei that are more disperse (Fig. 5), in a similar way as it does with gold [24,25].

As the thickness of the copper layer increases, the areas where the nuclei are more densely packed reflect the infrared radiation. Conversely, the areas where the copper nuclei have moved into the fingermark residue, and are more disperse, are more transmissive and thus reflect the IR radiation *via* the original substrate beneath. These differences in the infrared radiation absorption and reflection mechanisms provide a clear, enhanced contrast between the fingermark region and the substrate itself.

The application of a white gelatin lifter to the copper VMD treated substrate (Fig. 6) for up to 2 min allows for the selective transfer of copper from the fingermark region. We surmise that this is due to the fact the small tightly packed nuclei are adhering to the substrate surface more strongly and resist removal better than the large nuclei present within the fingermark residues.

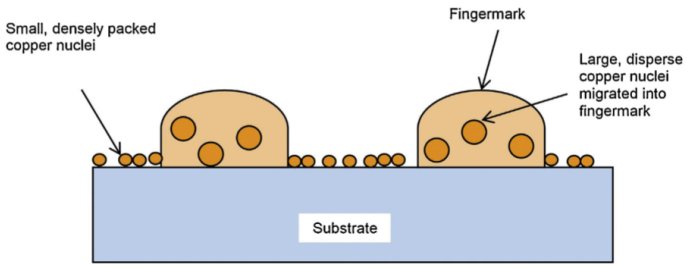


Fig. 5. Schematic diagram of copper deposition on polymer banknote surface.

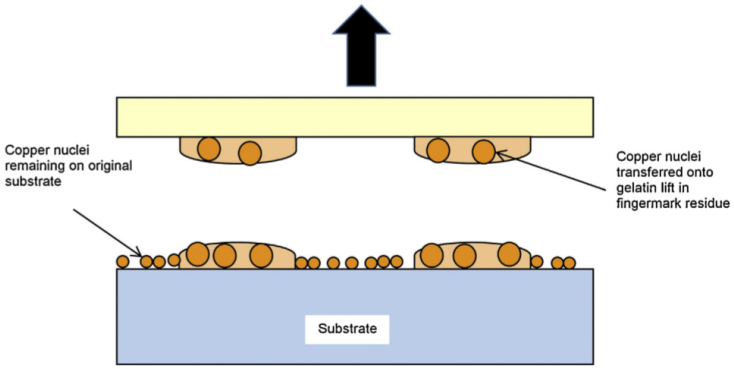


Fig. 7. Schematic diagram of copper infused fingermark residue removal from polymer banknote *via* gelatin lifter.

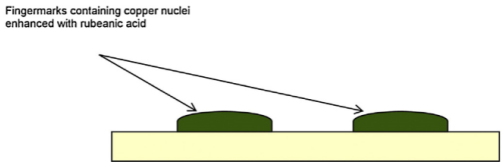


Fig. 8. Schematic diagram of copper containing fingermarks treated with rubeanic acid.

Since the fingermark residue is situated upon the polymer note surface, it is removed easily by the gelatin lifter (Fig. 7).

Once sprayed with the rubeanic acid solution, the copper contained within the fingermark residue becomes visible almost immediately (Fig. 8). The background of the gelatin lifter remains unstained, provided the gel is not in contact with the copper VMD treated sample for too long. If the gel is left in contact with the substrate for an excessive amount of time, background staining can be observed after treatment with rubeanic acid and may interfere with the developed ridge detail, thereby hindering visualisation.

This technique has the potential to be beneficial on many fronts; by depositing very thin films of copper and contrast observing using reflected IR, the risk of overdevelopment when using the VMD is reduced. The use of a thin inconspicuous film coating means that treated notes may potentially re-enter into circulation rather than having to be destroyed, thus contributing to the longevity of the note and reducing overall costs associated with replacing unusable notes. It is a one-step deposition, as opposed to the traditional gold/zinc two-step process, thereby reducing treatment times.

Once lifted and treated, the visible fingermarks on the gelatin lifters show little difference in intensity regardless of the thickness deposition of the copper. This again ties in with reducing risks of overdevelopment and reintroducing notes back in to circulation. This is beneficial to laboratories which may possess VMD capabilities but no IR imaging facility, as they can still utilise the technique and by adding an additional step can visualise the fingermarks *via* rubeanic acid in lieu of IR photography. However, infrared imaging would still be recommended.

It was observed that the substrate surface shows less reflection with thicker layers of copper. As the deposition thickness increases the background substrate absorbs more of the IR illumination giving the background a darker appearance. Conversely, the areas with fingermark residues which have less copper within them allows the underlying substrate to reflect IR back to the camera, thereby increasing the contrast between the two.

This new method of visualising VMD treated polymer banknotes could be easily facilitated in laboratories which already utilise IR imaging equipment and possess a VMD system. These initial trials have shown that this technique can successfully enhance fresh fingermarks on polymer banknotes and has the potential to be as effective on other semi- and non-porous substrates.

Further work would extend to investigations using a larger sample group and would incorporate aging/weathering and handled polymer banknote studies to determine process sensitivity and the effect of typical wear on the development process. In addition, comparison studies between copper and the traditional gold/zinc process would be explored on polymer banknotes as well as other polymer substrates in general.

Acknowledgments

We are grateful to the Bank of England for the provision of polymer test banknotes and to Ian Harris and Eleigh Brewer, West Technology Systems Limited, for the use of their VMD facilities. Many thanks to Richard Wilson for his help and support during this study.

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Article

Assessing Phosphomolybdic Acid as a Fingermark Enhancement Reagent

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Paul F. Kelly [1]

Abstract: The efficacy of an ethanolic solution of phosphomolybdic acid (PMA) was investigated as a latent fingermark visualization reagent, primarily on porous substrates. After treating samples and exposing them to ultraviolet radiation, the PMA solution was shown to develop fingermarks of high quality. Unlike the common amino acid reagents that are used for the development of fingermarks on porous substrates (e.g., ninhydrin and 1,8 diazafluoren-9-one), PMA stains a range of other compounds that are found in fingermark deposits, including lipids. The lysochrome diazo dye Oil Red O (ORO) was used for comparative purposes because of its application in staining some of the same components of fingermark residues for which PMA would be proposed. Initial results indicate that PMA is comparable to ORO at developing fingermarks on porous surfaces and may also have applications on nonporous surfaces.

Introduction

Fingermarks are generally regarded as the most reliable method of personal identification and are therefore viewed as some of the most important contact evidence recoverable from a crime scene [1]. For the successful retrieval of fingermarks from a scene, they first have to be detected. To achieve this, a range of techniques have been developed to visualize such marks. Several chemical and physical methods are currently employed to

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develop latent fingermarks that are invisible to the naked eye [2]; however, these visualization techniques are constantly evolving. Recent years have seen researchers exploring novel approaches to fingermark development, both instrumental and chemical in nature, and in some instances, even repurposing techniques that are not normally utilized for fingerprint work [3–21].

It was with the aforementioned repurposing in mind that phosphomolybdic acid (PMA) was considered as a possible fingermark development reagent. Phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$) [22] is a heteropolyacid that is commonly used in histology as a component of Masson's trichrome stain and as an indicator in thin-layer chromatography, where it is used to visualize a great many compounds including steroids [23], sterols [24], lipids [25], fatty acids [26], and triglycerides [27]. It was PMA's versatility in identifying these compounds that led to its 1973 investigation as a possible fingerprint visualization reagent [28], although this has not been pursued further in the following decades.

PMA has a 1:12 tetrahedral structure [22] (Figure 1), which is structurally identical to its species counterparts with the formula $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (P^V, As^V, Si^V or Ge^{IV}, among others) and M is the addenda atom (usually Mo^{VI} or W^{VI}). Phosphomolybdic acid is reduced to molybdenum blue in the presence of conjugated, unsaturated compounds. Burstein found that the blue color becomes more intense with an increase in the number of double bonds in the molecule being stained [29]. This suggests that the primary use of PMA as a fingermark development reagent would be to detect the water-insoluble, sebaceous constituents of fingermarks, as originally suggested by Vincent [28].

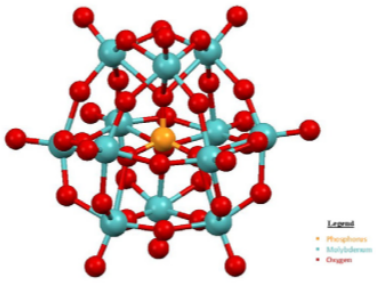


Figure 1

Phosphomolybdate anion.

Vincent [28] originally considered PMA as a spray reagent for use on porous surfaces, including fabrics and paper, and concluded in a report that of 25 reagents tested for the purpose of fingerprint development, PMA outperformed all except ninhydrin. Recent feasibility studies [30, 31] strived to optimize the technique by using different carriers as well as by varying the development process and confirmed this development reagent merited further investigation for the purposes proposed by Vincent. There are several fingermark visualization reagents that have been researched or recommended for staining fatty acids, lipoproteins, and triglycerides on porous surfaces: Nile red, Europium Chelate, and Oil Red O (ORO) [32]. ORO (Figure 2) was chosen as a comparison reagent for this study because it is more widely used operationally, is less expensive than Nile red and Europium Chelate to formulate, and does not require fluorescent illumination conditions to view developed marks. ORO is a lysochrome, or lipid stain, similar to Sudan black (solvent black 3). Initially, ORO was investigated as an azo-dye for the staining of lip prints deposited on tissue paper [33], then as a replacement for physical developer for the development of latent fingermarks on substrates that had been wetted [34]. Beaudoin [35] reported a formulation of ORO that was capable of developing fingermarks, not just on porous surfaces, but also on porous surfaces that had been wetted. It was also found to be effective on semiporous and soiled paper. The process is completed in three stages: (1) an ORO dip bath for up to 90 minutes, (2) immersion in a buffer solution, and (3) submersion in a water bath [35].

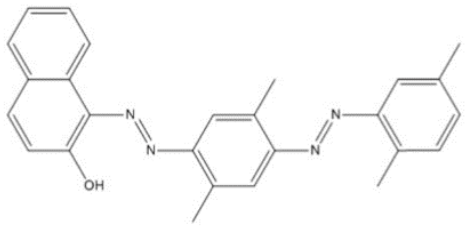


Figure 2
ORO structure.

However, sebaceous fingermarks are not encountered only on porous surfaces, and the application of PMA to nonporous surfaces has not yet been explored. On nonporous surfaces, the development reagent solvent black 3 [36, 37] is most widely recommended for the development of sebaceous and grease-contaminated marks. On dark surfaces, natural yellow 3 has recently been suggested as an alternative [38]. Both reagents are prone to causing excess staining of the background for long exposure times, and alternative reagents are desirable. Although originally proposed for the development of sebaceous-rich marks on porous surfaces, small particle reagent works well on nonporous substrates [39]. On adhesive surfaces, as well as on nonporous, basic violet 3 (gentian violet) is recommended [40]. Iodine solution has been found to be effective on both porous and nonporous substrates [41].

There has also been continued interest in developing fingermarks on metal surfaces (e.g., brass and stainless steel). Recent focus has been on processes that are tailored towards different classes of metal surface, for example electrochromic deposition (stainless steel [14]), and longer established processes may also be used to target different metal types (gun blueing on brass and steel, aluminum black on aluminum).

The purpose of this initial study was to investigate the breadth of applications for PMA on nonporous substrates and to conduct an assessment of its performance in comparison to an existing lipid visualization reagent (ORO) on porous surfaces.

Materials and Method

PMA Study

The substrates that were used in this study were paper, acetate, aluminum, and stainless steel. These are substrates that are found in common, everyday items. The substrates were prepared for fingermark deposition by cutting 12 cm by 3 cm sized samples. These were labelled using photographic twin check labels with the twinned label being logged with details of sample type, fingermark deposition method, donor number, and development day. The 13 donors who were used in this study were a mix of males and females ranging in age from 22 to 40 whose potential to leave fingermark deposits was unknown. Donors had not washed their hands for at least 30 minutes prior to depositing their fingermarks; no extra sebaceous deposits were loaded on the hands, therefore providing more natural deposits

from the donors' hands. Fingermark deposition was carried out by having the donor deposit a mark from each finger of one hand; each donor deposited all of his or her marks at the same time. After the fingermarks had been deposited, the samples were stored in cardboard boxes, in the dark, at room temperature for 1, 2, 4, 8, 14, 21, or 28 days before being processed. In total, 182 samples of each substrate (13 donors, 7 different ages, 2 deposition methods) were used (728 samples in total).

PMA versus ORO Comparison Study

The substrate that was used in this study was paper, which was an 80 gsm copier paper made by Polaroid. The substrates were prepared for fingermark deposition by cutting 12 cm by 5 cm sized samples to allow ample space for the fingermark to be deposited and split down the center. This allowed for the direct comparison between the chosen development reagents. Three donors were used in this study. They were a mix of males and females ranging in age from 22 to 40 whose potential to leave fingermark deposits was unknown. Donors had not washed their hands for at least 30 minutes prior to depositing their fingermarks. Fingermark deposition was carried out by having the donor deposit a single mark from each finger along the center of the substrate (five marks per sample). Each donor deposited all of his or her marks at the same time.

PMA and Wetted Samples

Paper samples had a mixture of natural and sebaceous marks deposited on their surface. These were subsequently placed into a water bath to soak for up to an hour. Samples were allowed to air-dry, or they were placed in an oven at approximately 50 °C to dry out. Once dry, the samples were treated in the same manner as the previous samples.

Reagents

The prepared samples were treated with a 10% w/v PMA solution, prepared from phosphomolybdic acid hydrate (Sigma Aldrich–221856) in absolute ethanol. The samples were sprayed with the PMA solution using an ECOSPRAY (Labo Chimie France) and were developed for 15 minutes under a 15 W longwave UV lamp [42].

Treating fingermarks with ORO is a three-part process: (1) the ORO stain bath, (2) a buffer solution, and (3) a water bath. The ORO stain was prepared by adding 0.77 g ORO (Sigma Aldrich–O0625) to 385 mL methanol, then separately adding

4.6 g sodium hydroxide to 115 mL of deionized water. These two solutions were then mixed together and filtered before being stored in a brown bottle away from light. The buffer solution was prepared by adding 26.5 g of sodium carbonate to 2 liters of deionized water while stirring until dissolve. To this solution, 18.3 mL of concentrated nitric acid was added. Finally, the total volume was made up to 2.5 liters by adding more deionized water.

Samples treated with ORO required up to 90 minutes in the stain bath, after which they were placed in the buffer solution for up to 5 minutes before being rinsed in the water bath and being left to dry.

Treated samples were then photographed using a Nikon D5200 [43] digital camera with an AF-S DX Nikkor 18–55 mm F/3.5–5.6G VR [44] lens. The visualized marks were then graded using one of the CAST grading scales (Table 1) [45, 46].

Grade	Comment
0	No development.
1	Signs of contact, but <1/3 of the mark has continuous ridges.
2	1/3–2/3 of the mark contains continuous ridges. Of sufficient quality to potentially be identified.
3	>2/3 of mark has continuous ridges, but not quite a perfect mark.
4	Full development. Whole mark continuous ridges.

Table 1

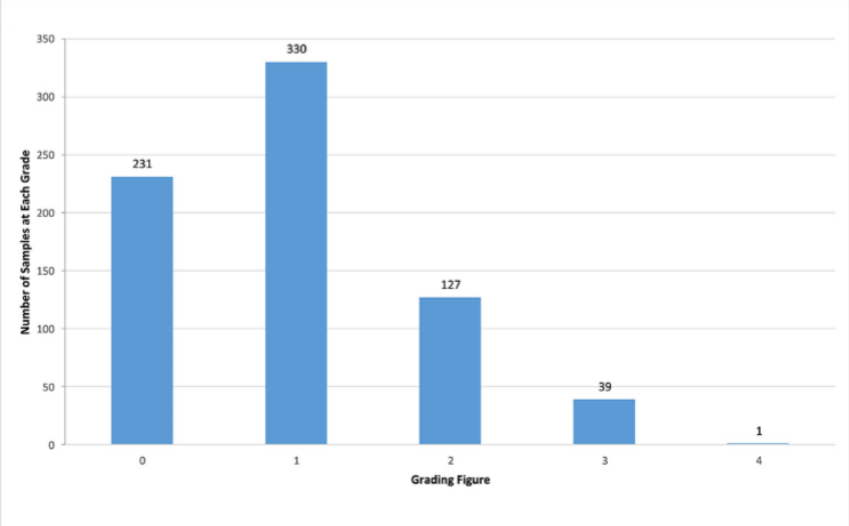
Fingermark grading scale.

Results and Discussion

PMA Study

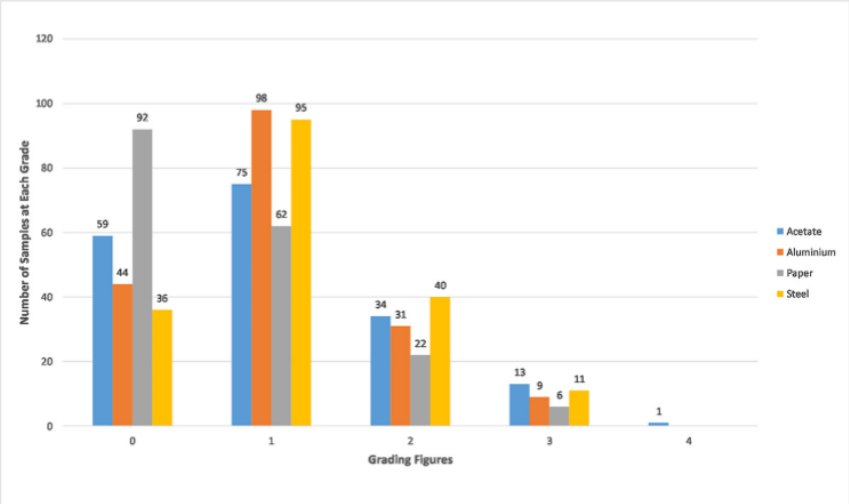
There were 728 sample substrates that were treated, with 4 to 5 fingermarks on each. After treatment, the best developed fingermarks from each sample were graded from 0 to 4 after a visual examination. Of the 728 samples, 45% were graded as 1, 17% were graded 2, and 6% were graded 3 and above (Graph 1).

Paper provided the most 0 graded marks (those containing no development), double the amount of some of the other substrates. Consequently, the number of paper samples within each individual grading value above 0 was markedly less than those of the other substrates (Graph 2). The metal samples (aluminum and stainless steel) both performed very similarly despite having slightly different finishes (i.e., aluminum had a slightly brushed



Graph 1

Distribution of grading values.



Graph 2

Distribution per substrate type.

finish; stainless steel had a clean smooth finish). Performing slightly behind the metals were the acetate samples, which exhibited problems because of high instances of background staining. The paper's poorer performance was expected because of the fingermark residues being absorbed into the paper's porous surface. This is also consistent with the recommended use of amino acid visualization reagents on this type of surface because of the higher proportion of eccrine constituents that are present in natural sweat deposits. Conversely, all constituents of the fingermark residue sit on the surface of the nonporous metal and acetate substrates and are available to interact with the PMA.

The differences in the finishes of the metals made a difference in the visualization of the fingermarks that were present on the surface. The slight brushed finish on the aluminum caused some marks to be visible only at an oblique angle, especially faint marks. There were some instances where the PMA caused high background staining on the substrate, leaving the surface awash with blue staining, although some did show signs of ridge detail, which was broken and spotty in places (Figure 3). Many of the samples that presented usable prints were observed to have little in the way of background staining, and the ridge detail appeared to be lighter than the background (Figure 4). This suggests that for this metal surface, the primary interaction occurred between the PMA and the aluminum metal substrate.

The stainless steel had the greatest number of grade 2 and grade 3 marks; however, it also suffered from the occasional background staining issues that the aluminum had (Figure 5). The fingermarks on the stainless steel substrates developed differently from the aluminum, with ridges presenting as a dark blue or black (Figure 6) and, in some cases, with some yellow staining between the ridges. This suggests that the principal interaction on stainless steel was between the PMA and the fingermarks, which represents a difference in development mode between the two metals that were used.

Figure 3
Aluminum-stained background.

Figure 4
Aluminum with ridge detail.

Figure 5
Stainless steel-stained background.

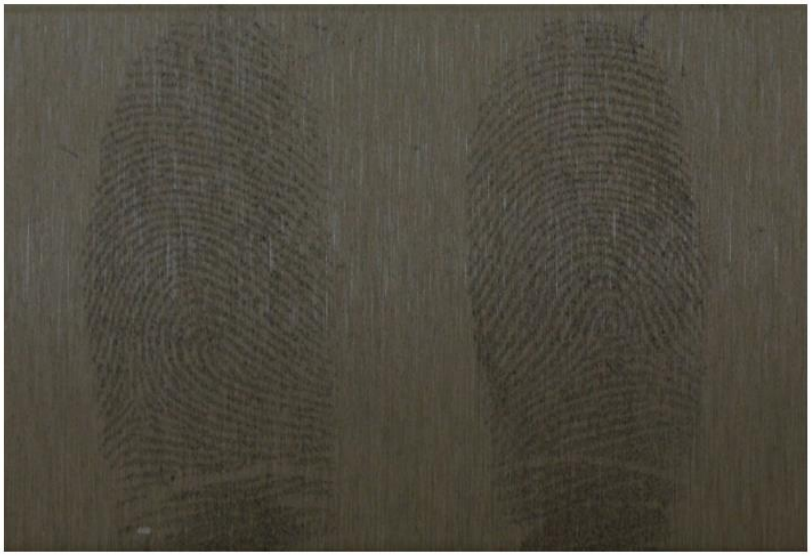


Figure 6
Stainless steel with ridge detail.

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The acetate substrates performed better in terms of fingermark development than the aluminum samples, but to a lesser degree than the stainless steel samples. When applying the PMA to the acetate surface, the PMA would sit in pools around the mark and stain the acetate a color similar to the yellow-green of the original solution. This produced a "halo", probably because the solution was repelled by the oils in the fingerprint residues (Figure 7). The marks or ridges within the voids, however, were visible as the characteristic dark blue or black of the molybdenum blue. The background staining that was observed was similar to that which occurs when using cyanoacrylate fuming and basic yellow 40 dye on certain substrates (e.g., tin foil) [2]. The visualized marks on the acetate surface were very fragile and easily destroyed by light touches (Figure 8). Despite this fragility and the instances of background staining, the acetate did produce instances of grade 2 to 4 prints (Figure 9).

As mentioned previously, the application of PMA to the paper substrates did not produce the same level of fingermark visualization as did the other samples. Over 50% of the paper samples returned no development whatsoever, with only 15% giving marks of grade 2 and above. However, as stated above, this is not inconsistent with operational observations that amino acid development reagents will be more effective on this substrate, and ideally, PMA should be compared to another process targeting noneccrine constituents to get a more representative measure of its effectiveness. Background staining was also noted in the paper samples, albeit to a lesser degree than the other substrates that were tested. The staining was observed to be of a variety of colors ranging from the aforementioned yellow-green to a pale blue. Grade 2 and 3 marks that were present were often faint; however, some very good ridge detail was observed (Figure 10).

No clear pattern was established in the results of the fingermark aging series. This was due to natural fingermarks being used for the study. Because PMA primarily reacts with constituents of sebaceous secretions (which are present in varying and uncontrolled concentrations) and not all experiments commenced on the same day, the intra- and inter-donor variability made clear trends difficult to establish. To confirm the specificity of PMA to sebaceous constituents, two additional, shorter studies were conducted: (1) sebaceous material was artificially added to the finger tips, and (2) eccrine-only fingermark deposits (sweat from the hands only) were used as a control. The number of donors was dropped from 13 to 4, and the age of the fingermark deposits was lowered from 28 days to 8 (1, 2, 4, and 8 days). The number of sample substrates remained the same at four.

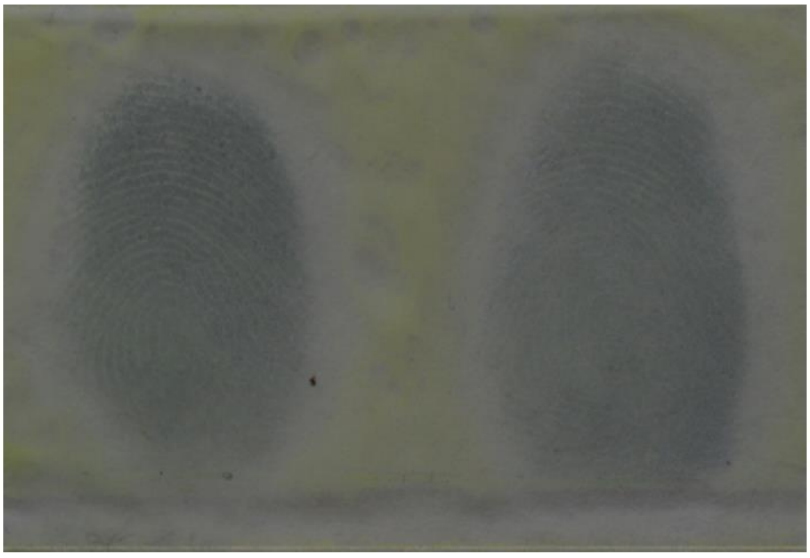

Figure 7
Acetate background staining.

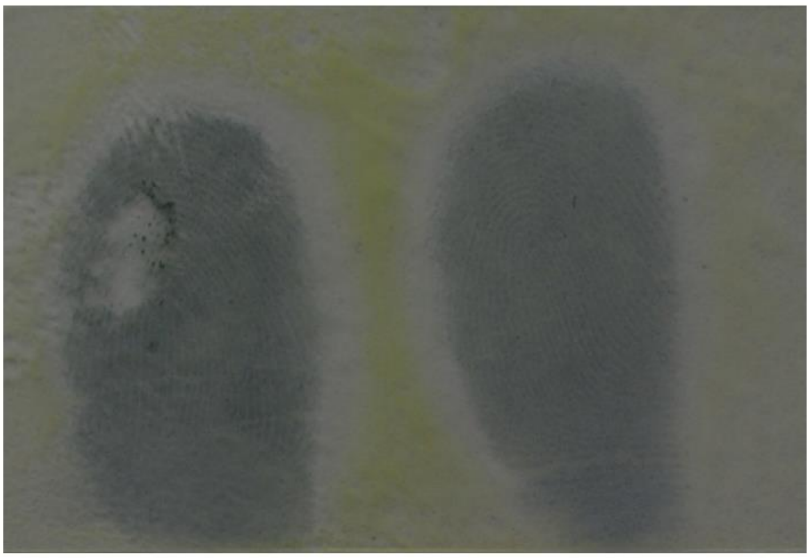

Figure 8
Damaged print on acetate.

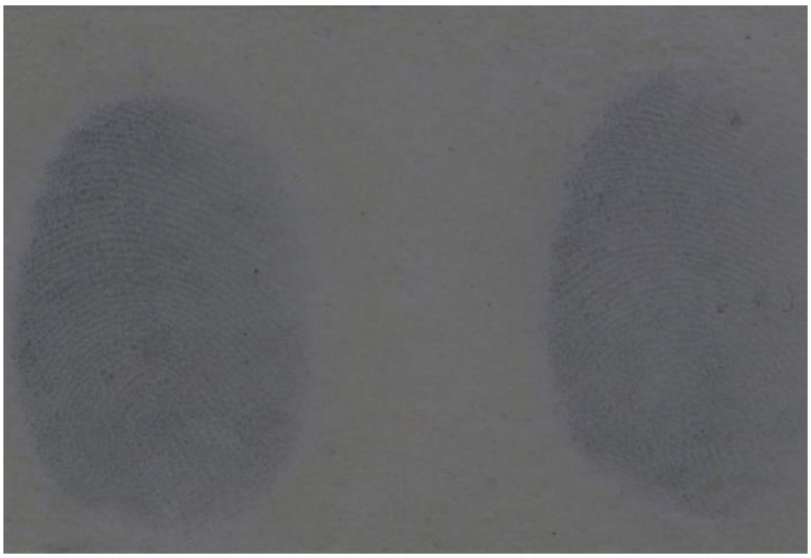

Figure 9
Ridge detail on acetate.

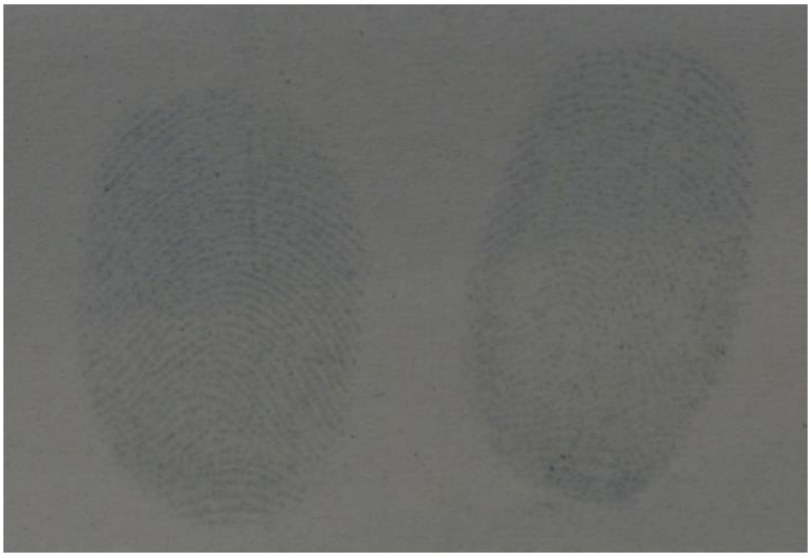

Figure 10
Ridge detail on paper.

For the eccrine study, the donors washed their hands then donned nitrile gloves for up to 30 minutes to allow the hands sufficient time to sweat. Marks were then deposited on the sample substrates. When conducting the sebaceous study, donors were asked to rub their fingertips around their hairline and nose areas where sebaceous sweat glands are abundant. Marks were then deposited upon the sample substrates.

Eccrine Study

The eccrine study failed to yield any positive mark visualization (Table 2), as expected. This occurred across all of the substrate materials. Some showed signs of background staining that was due to the PMA, but no signs of any ridge detail staining.

	Acetate	Aluminum	Paper	Steel
Grade 0	16	16	16	16
Grade 1	0	0	0	0
Grade 2	0	0	0	0
Grade 3	0	0	0	0
Grade 4	0	0	0	0
Total	16	16	16	16
% of Grade 2+ Marks	0	0	0	0

Table 2

Eccrine study results.

Sebaceous Study

The sebaceous study provided many positive marks and instances of fingermark development that could be used in an operational capacity to identify the depositer of the marks (Table 3). The acetate substrate showed the most grade 2 and above marks, although they still suffered from the delicacy mentioned before. The paper samples also showed a noticeable improvement in the amount of grade 2 and above marks that were developed (Figure 11). The age of the fingermark did not appear to influence the results that were gained over the time frame that was studied.

	Acetate	Aluminum	Paper	Steel
Grade 0	2	3	2	3
Grade 1	2	4	3	3
Grade 2	5	3	5	4
Grade 3	5	5	4	4
Grade 4	2	1	2	2
Total	16	16	16	16
% of Grade 2+ Marks	75%	56.25%	68.75%	62.5%

Table 3

Sebaceous study results.

Figure 11

Sebaceous study (paper).

This discovery not only sheds some light on the high number of no-detail results that were gained in the primary trial, because these contained marks that had not been artificially charged with sebaceous deposits, but these success rates are also comparable to other visualization reagents that target sebaceous constituents, such as ORO [47]. Despite this technique's limitation in only developing fingermarks with sebaceous material present, there may well be merit in using PMA in sequence with DFO →indandione → ninhydrin, much in the same way ORO is proposed for use at present [48].

PMA versus ORO Comparison Study

Fresh samples that were treated within a day of the fingermarks being deposited showed developed marks that were comparable between the two processes. Once the individual halves were treated and recombined, it was relatively easy to follow the ridge flow of the fingermark from one half to the other. The only noticeable issue was that the halves of the fingermarks were slightly misaligned; this was due to shrinkage of the paper that was treated with ORO (Figure 12). The ORO-treated halves were also prone to warping.

Samples that had the fingermarks deposited and were then left for over 4 weeks before being developed looked markedly different from those that were developed the day after the fingermarks were deposited. The half treated with ORO barely showed any marks from the fingermark residues, whereas the PMA-treated halves showed development, albeit slightly fainter than previously achieved (Figure 13). This suggests that the constituents of fingermarks targeted by PMA are more persistent within the deposited mark than those targeted by ORO (Table 4).

	1 Day	2 Weeks	4 Weeks
PMA (% of Grade 2+ Marks)	100%	80%	80%
ORO (% of Grade 2+ Marks)	80%	20%	0%

Table 4

Direct comparison percentage grade 2+ marks.

While experimenting with the two reagents sequentially, it was discovered that by using PMA in the first instance, ORO could be used additionally after 4 weeks. The developed fingermarks presented darker with a superior definition than when the ORO was used alone after the same period (Figure 14). On these split comparisons, the ORO developed 20% grade 2 marks and 80% at grade 1, whereas the PMA followed by ORO provided developed marks of 40% at grade 2 and 60% at grade 3.

Using PMA after ORO did nothing to enhance deposited fingermarks beyond what the ORO had already achieved.

Figure 12
ORO vs phosphomolybdic acid.

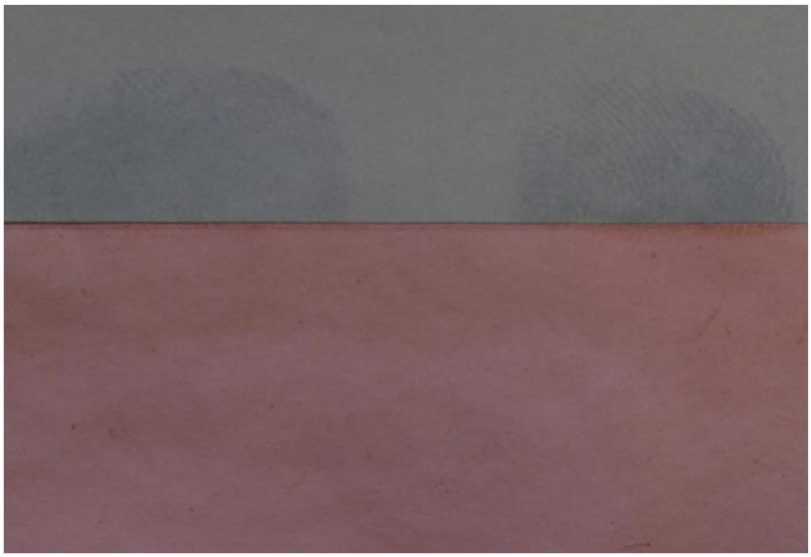

Figure 13
ORO vs PMA (4+ weeks).

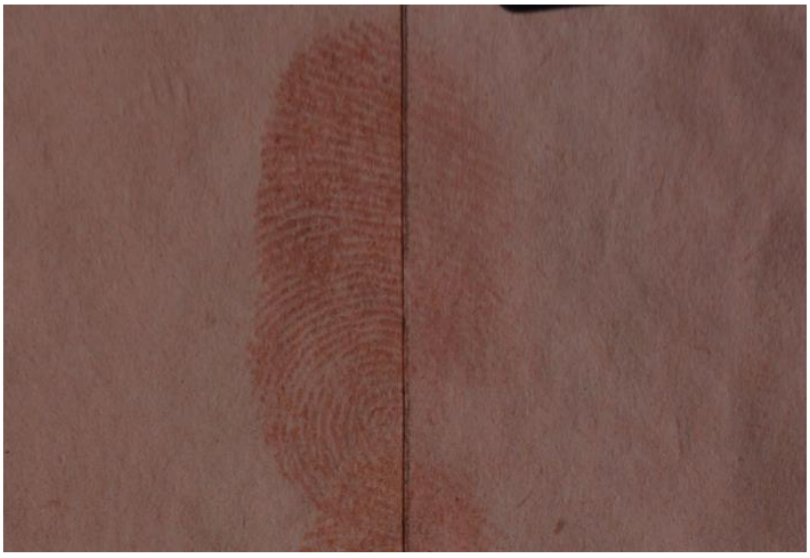

Figure 14
PMA + ORO used in sequence vs ORO.

PMA and Wetted Samples

Once the paper had been placed in the water bath and had completely soaked, fingermarks could be observed on the paper's surface (Figure 15). When they were dry, the samples were sprayed with PMA solution in the same manner as the previously processed dry samples were (i.e., sprayed and a 15 minute UV exposure). After treatment, however, the marks were not developed to the same standard as dry samples. Although faint fingermarks were visible once the development process had been completed, these marks lacked any usable ridge detail (Figure 16).

The fact that PMA is capable of developing fingermarks on both porous and nonporous substrates makes it a potentially more versatile visualization reagent than ORO. Although ORO formulations have been explored for the visualization of fingermarks on nonporous surfaces [2], it was found to be inferior to other dyes, such as basic violet 3 and solvent black 3, which are used for this purpose. Although this pilot study has demonstrated the ability of PMA to develop marks on nonporous substrates, it is recognized that future phases of the work would also need to include comparisons with solvent black 3 and basic violet 3 formulations to establish whether PMA offers any benefit over these existing processes on nonporous surfaces.

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Figure 15
Fingermarks visible on wet paper.

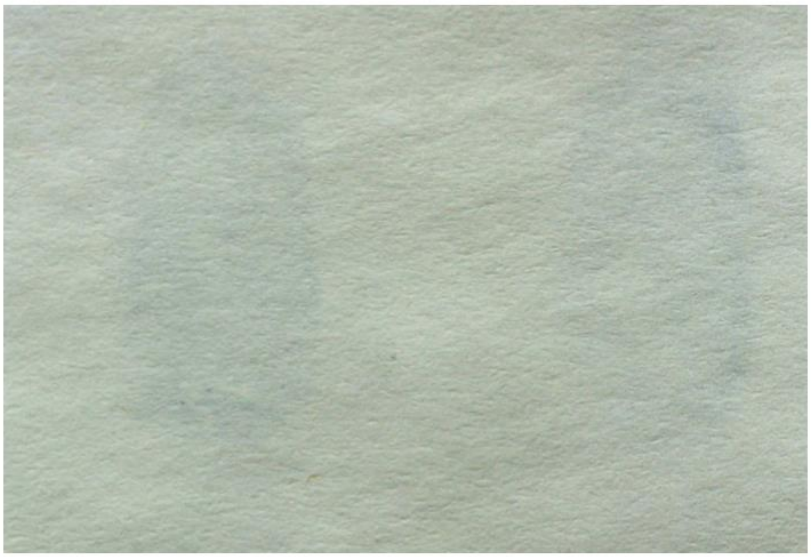

Figure 16
Wetted paper treated with PMA.

Conclusion

Of the substrates tested, it appears that the nonporous substrates provided more positive results than did the porous substrates. On stainless steel, the PMA technique produced positive mark development 80% of the time, 28% of which were grade 2 and above. This was closely followed by the aluminum, with positive mark development 76% of the time, 22% of which were grade 2 and above. The acetate substrate produced positive mark development 68% of the time, 26% of which were grades 2 and above. The smooth, nonporous surface of the acetate meant, however, that the fingermark developed was very fragile and easily wiped away. The paper substrate performed the worst, achieving positive mark development only 50% of the time, only 15% of which were grade 2 and above. Fingermarks aged up to 28 days were still enhanced to grade 2 and greater on all substrate surfaces except the paper.

An addendum trial, using a single donor, found that prints containing only eccrine sweat deposits returned no positive mark development whatsoever, whereas marks with charged sebaceous sweat deposits produced up to 75% positive mark development with greater ridge detail present.

When comparing the efficacy of PMA against ORO on porous substrates, the two seemed to be comparable on newer marks (those less than a week old). However, PMA easily outperformed ORO on older marks (those older than 1 week), possibly because it targets a wider range of constituents, some of which may be more persistent than the constituents targeted by ORO. The degradation observed with PMA after 4 weeks was less than that observed for ORO, so it would be expected that PMA would continue to develop marks for a little longer than the 4-week limit.

PMA struggled to develop marks on paper substrates that had been wetted. Developed marks were visible, however, these lacked any ridge detail. This was an instance where ORO outperformed the PMA. Future studies would further investigate whether this could be resolved or whether it is an instance where ORO would be the preferential treatment.

PMA could be considered as a less expensive (~$175 U.S. per liter vs ~$250 U.S. per liter for ORO), faster alternative to ORO for the same type of development. By using the PMA as a precursor to ORO, fingermarks were able to be developed long past the point where ORO normally fails as a development reagent.

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PMA has a potentially broad application across porous and nonporous surfaces; it is quicker and potentially more effective than ORO, and possibly physical developer, on porous surfaces (particularly for marks older than a month). However, it is unlikely to outperform an amino acid development reagent, and there are some health and safety issues in its flammability and corrosive nature, which would need to be addressed. Overall, PMA has shown significant promising trends in performance that merit further research, particularly with a larger study group to see whether these observed trends are maintained. Other areas that warrant further investigation are the ability of PMA to work in concert with amino acid visualization reagents and its performance comparative to other lipid development reagents on nonporous surfaces.

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