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Metal deposition techniques for the detection and enhancement of latent fingerprints on semi-porous surfaces

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Proverbs 1:7
The fear of the LORD is the beginning of knowledge
(Holy Bible, New International Version)

To the glory of God, the source of all knowledge and truth

With gratitude to those who have encouraged and aided me in searching after the truth

Certificate of Authorship and Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Signature removed prior to publication.

Naomi Jones

5th July 2002

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Abstract

Fingerprints can provide critical evidence in the investigation of crime. Most fingerprints are latent, or invisible, and hence need detection and enhancement before they can be used in the investigation of crime.

While techniques exist for fingerprint development on a range of surfaces, the detection of prints on semi-porous substrates is particularly difficult. Vacuum metal deposition (VMD) and multi-metal deposition (MMD) were investigated for their ability to detect latent prints on such surfaces.

VMD is recognised as a very sensitive method of latent print visualisation but inconsistent results are commonly encountered. This research shows that reproducible VMD development is only obtainable when the amount of gold deposited is carefully controlled. The type and quality of VMD development obtained is influenced by a number of critical factors. These factors include the amount of gold deposited, the polymer type of the surface being treated, the nature of the latent print itself, and the presence of any other contaminants on the surface (whether due to the history of the exhibit or treatment with other fingerprint reagents).

MMD has not found routine application due to its complexity and mediocre results. Recent research that sought to overcome these problems resulted in the development of a new formulation known as MMDII. Several MMD formulations were trialled in this study and MMDII proved to be the superior formulation, giving better overall print detail. On non-porous surfaces, MMDII may offer further print development than that achieved with cyanoacrylate fuming (CAF) and luminescent staining, but VMD always gave superior results to MMD.

Polymer banknotes are a difficult semi-porous surface, causing particular problems for fingerprint laboratories. A procedure utilising CAF followed by VMD and finally luminescent staining enables successful print development on this substrate. Success on new notes was achieved with prints up to 18 months old; unfortunately, the possibility of successful print development decreases on used banknotes. VMD has two important advantages for print visualisation on polymer notes: i) it is sensitive enough to detect the small amounts of residue remaining; and, ii) the zinc layer removes a significant amount of interference caused by the banknote design.

MMD and VMD were compared to standard techniques on other semi-porous surfaces. MMD proved to be the technique of choice on these surfaces. The ability of MMD to react with print residue within and on the surface is believed to be important to its success.

Table of Contents

List of Figures

List of Tables

Abbreviations

AFM = Atomic Force Microscope or Microscopy

AFP = Australian Federal Police

APD = Average Particle Diameter

ASAP = Automatic Standardless Analysis Program

CA = Cyanoacrylate

CAF = Cyanoacrylate fuming (or superglue fuming)

CV = Co-efficient of variation

DFO = 1,8-diaza-9-fluorenone

DNA = Deoxyribose Nucleic Acid

DOVD = Diffractive Optically Variable Device

DMAC = 4-dimethylaminocinnamaldehyde

ESCA = Electron Spectroscopy for Chemical Analysis

FFC = Forensic Fuming Cabinet

FT-IR = Fourier Transform- Infra-Red Spectroscopy

HDPE = High-density polyethylene

Hq = Hydroquinone

ICP-MS = Inductively coupled plasma-mass spectrometry

IR = Infra-red Radiation

LDPE = Low-density polyethylene

MEK = Methyl ethyl ketone

MMD = Multi-metal deposition

MMDI = Original MMD formulation

MMDII = New MMD formulation

MMDIII = MMD formulation used by Forensic Science Service UK

MMDIV = Fourth combination of MMD reagents

NPA = Note Printing Australia

PD = Physical developer

PE = Polyethylene

PET = Polyethylene terephthalate

PP = Polypropylene

PVC = Polyvinyl chloride

RBA = Reserve Bank of Australia

SEM = Scanning Electron Microscopy

UV = Ultra-Violet Light

VCAF = Vacuum cyanoacrylate fuming

VMD = Vacuum metal deposition

XPS = X-ray Photoelectron Spectroscopy

XRF = X-Ray Fluorescence Spectroscopy

1 Introduction

1.1 Fingerprints

1.1.1 Valuable evidence

Fingerprints have long been considered an important form of physical evidence. They are one of the few forms of evidence that allow identification of individuals. Even with the growth in the use of DNA to identify people involved in crime fingerprints still remain essential to the investigation of crime. The ridge patterns found on hands and feet are ideal for identifying individuals. Fingerprint ridges are unique to each person, immutable, as they are formed deep in the skin, universal to all humans and easy to classify using shapes that are formed by the ridgelines. Marks in the shape of these ridgelines are left on any object that is handled with bare hands. These marks can then be used to identify people who have been in contact with the object. (Margot & Lennard, 1994)

The marks left when objects are touched by bare hands are composed of secretions, or sweat, from three glands in the skin: the eccrine, sebaceous and apocrine glands. The palms of the hands are covered exclusively by eccrine glands, so these secretions are always present in fingerprints. Secretions from the sebaceous glands found in areas such as the chest, back and forehead, and apocrine glands, found in the groin, armpits and perianal regions, may be present in differing degrees. Secretions of the eccrine glands are 98% water, with a number of inorganic and organic constituents (Margot & Lennard, 1994). The organic components present include amino acids, urea and sugars, and the inorganic components include chlorides and ammonia (Knowles, 1978).

1.1.2 Fingerprint development

Fingerprints left on objects may be naturally visible due to the surface or due to contamination in the fingerprint residue but are most often latent (invisible). Before latent prints can be useful as evidence, they must be made visible, which is the aim of fingerprint development. A wide variety of methods are used in fingerprint development including optical, physical, physico-chemical and chemical techniques (Margot & Lennard, 1994).

Optical methods, as the name implies, involve the use of light to detect or improve the contrast of a latent print. Luminescence and episcopic co-axial illumination are examples of optical methods used in latent fingerprint visualisation.

Physical methods include the well-known powdering used by police throughout the world. Physico-chemical methods include such techniques as physical developer and cyanoacrylate (or "superglue") fuming.

Chemical methods depend on a chemical reaction between a certain reagent and a component of the fingerprint. The result is generally a coloured or luminescent product.

Fingerprints are encountered on many different surfaces. The type of surface on which a print is located and the environmental conditions it has been exposed to determine the development techniques that will be most effective. Surfaces are classified as porous, semi-porous or non-porous; this is an indication of the extent to which latent print residue will have been absorbed into the surface. Surfaces are also divided into those that are wet, or have been wet, and those that have been kept dry, as this determines which constituents of the print residue will still be present.

Certain surfaces present more difficulty for fingerprint development than others. Polymer banknotes are one type of surface that has caused significant difficulties for fingerprint development. Research into a procedure for latent print development on polymer banknotes is one focus of this thesis.

Multiple development techniques can usually be used on a single surface if they are applied in the correct order. Certain reagents preclude the use or lessen the effectiveness of other reagents making the sequence in which the techniques are used important. Sequences that maximize the overall effectiveness of latent print development are necessary. A sequence that includes complimentary techniques (i.e. techniques that target different components of the latent fingerprint deposit) is generally the most effective.

Techniques used routinely in fingerprint development tend to be those that are simple and yet effective. There are a number of techniques available that require greater technical skill and so are not widely used. Cyanoacrylate fuming (including vacuum cyanoacrylate fuming) and fluorescent staining are relatively simple techniques that are widely used for non-porous surfaces in fingerprint development laboratories. Vacuum metal deposition (VMD) and multi-metal deposition (MMD) are two techniques that offer great potential as very sensitive techniques for fingerprint development but are not widely used because of technical difficulties associated with their application.

A number of techniques were utilised in the research that forms the basis of this thesis. The main techniques used are outlined in the following section. Other techniques that were also employed were:

- Physical developer (PD): an unstable solution of silver ions in a redox solution that is used to treat porous surfaces resulting in silver deposition along the print ridges.

- Ninhydrin: an amino acid sensitive reagent that is used to treat porous surfaces.

- Iodine-Benzoflavone: used to treat porous and semi-porous surfaces, iodine is absorbed by the fingerprint residue and chemically fixed by the benzoflavone.

1.2 Development techniques

1.2.1 Cyanoacrylate (superglue) fuming

Cyanoacrylate fuming (CAF), or 'superglue' fuming, is the standard technique used for the routine detection of latent fingerprints on non-porous surfaces. CAF relies on the selective polymerisation of cyanoacrylate (CA) on the sebaceous and eccrine components of a latent print. CA esters have the general structure shown in figure 1.1. Methyl and/or ethyl esters are the primary compounds in commercially available 'superglue'. The process of CAF requires the evaporation of the CA ester. The vapour formed polymerises to create a solid white polymer. (Fig. 1.1) This polymer forms selectively on the print ridges, distinguishing the print from the surface (Margot & Lennard, 1994; Pounds, 1988).

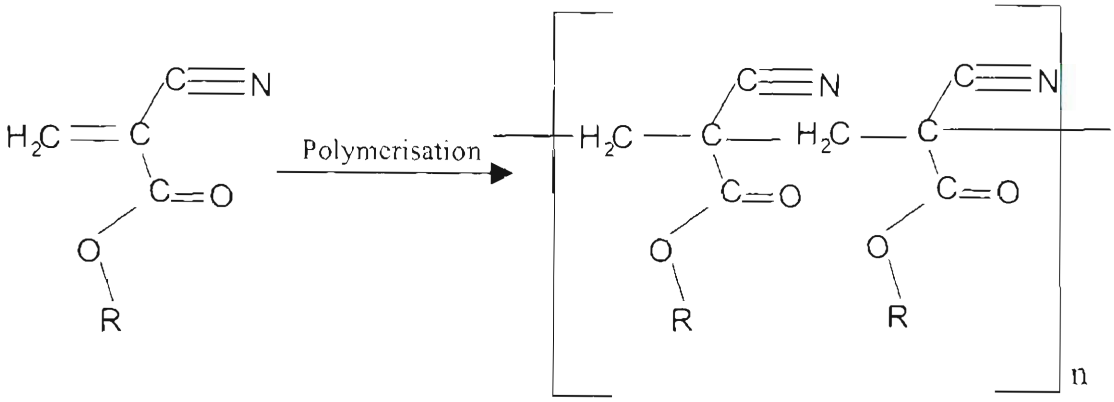


Figure 1.1. Reaction of cyanoacrylate esters to form cyanoacrylate polymer.

Polymerisation of CA esters is an anionic process that is initiated by weakly basic species, such as water, alcohol or trace metals (Burns et al, 1998; Shields, 1984). Water and basic compounds present in the latent print residue are believed to be responsible for initiating the polymerisation of CA vapour.

Scanning electron microscopy (SEM) work has shown that two forms of CA polymer may be produced (Kent & Winfield, 1996; Lewis et al, 2001; Watkin et al, 1994). The polymer may be smooth and rounded, like capsules, or more fibrous, like spaghetti. The differences in polymer formation have been attributed to the development conditions used, in particular pressure and humidity, with capsules being attributed to high humidity and atmospheric pressure and spaghetti to low humidity or vacuum conditions (Kent & Winfield, 1996; Watkin et al, 1994). Recent work (Lewis et al, 2001) suggests that the moisture content of the print residue is the factor controlling the morphology of the polymer formed, with low moisture content resulting in capsules and high moisture content resulting in spaghetti.

CAF is widely used due to its simplicity of use and general effectiveness. CAF is effective on a wide range of non-porous surfaces and has been used to successful develop prints (stored in laboratory conditions) over 3 years old (Taroni et al, 1990). The effectiveness of CAF is decreased when prints have been exposed to environmental factors such as heat and water.

The original CAF process involved placing the exhibit and some superglue (CA) in a closed container. CA vaporises slowly at room temperature and pressure so development times of between several hours and several days were required (Kendall, 1982). The CAF process can be accelerated by increasing vaporisation and prolonging volatilisation. This can be achieved by fume circulation (Pfefferli, 1987), chemical acceleration (Kendall & Rehn, 1982; Martindale, 1983), and heat acceleration. Heat acceleration is most commonly used.

The application of heat accelerates vaporisation and can also create convection currents that help to circulate the CA vapours. Aluminium is often used to prevent the polymerisation of CA that can occur on heating (Olenik, 1983). The optimum heating temperature is reported to be 90-100°C (Pounds, 1988). Care must be taken to avoid excess heat as heating above 120°C increases the toxicity of CA, and heating above 200°C generates hydrogen cyanide (Mock, 1985).

There are alternatives to using liquid CA. CA can be blended with white petroleum jelly into a gel form which is then spread out to increase the surface area for fume generation (Gilman et al, 1985). Polymerised CA can also be used as heating causes decomposition of the polymer to create monomer vapours. Some results achieved using polymerised CA have been inferior to standard CAF (Almog & Gabay, 1986; Howorka & Kretschmer, 1990).

An alternative to vapour fuming is surface contact with CA. Filter paper which has been previously soaked with a CA-ether solution is placed directly on the surface requiring treatment. This technique can be used to target specific areas of an object (such as a section of human skin). However, smudging of prints may occur if the filter paper is moved while in contact with the surface (Jian & Dao-An, 1991).

The particular CA monomer used can affect the amount of CA deposited. Commercially available superglues containing in excess of 95% ethyl CA have been shown to result in greater polymer formation than pure methyl, ethyl, propyl or butyl CA (Burns et al, 1998).

Pre-fuming items with ammonia can increase the amount of polymer formed (Burns et al, 1998; Bush, 1999). Alcohols generally give no significant enhancement except for some slight but inconsistent improvement after pre-treatment by ethylene glycol and diethylene glycol (Bush, 1999). Acetic acid vapours have also shown potential for regenerating old prints before CAF development (Lewis et al, 2001).

Surface contamination, such as drug residues and soot, can interfere with CAF by causing stronger formation of CA polymer on the background (Goetz, 1996).

Over-development of CA prints results in the loss of ridge detail as the formation of polymer on the general surface reduces the contrast between the print and the surface. Excess polymer deposition is a particular problem if luminescence enhancement (using a luminescent stain) is envisaged. Over-development is generally considered irreversible, but the removal of excess CA polymer to reveal the lost detail is possible using heat (Springer, 1995) or solvents (Geng Q, 1998).

1.2.2 Vacuum cyanoacrylate fuming

The most recent modification to CAF is vacuum CAF (VCAF). VCAF is simply CAF performed at low pressure, generally around one thousandth of atmospheric pressure (Campbell, 1991; Watkin et al, 1994).

Fingerprint development using VCAF occurs on the same principle as CAF. The capsule form of CA polymer has been associated with VCAF. This could be due to loss of water from the print residue due to vacuum conditions. It has been suggested that the polymer formed by conventional CAF, due to its greater surface area, is able to scatter light more effectively (Watkin et al, 1994) and absorb more dye (Kent & Winfield, 1996) than the polymer formed by VCAF.

There is some disagreement over the superiority of VCAF over CAF. VCAF has generally been preferred due to its superior detail and uniformity and the lack of background development (Campbell, 1991; Bentsen et al, 1996; Hebrard et al, 1996; Neri, 1992; Watkin et al, 1994). Inferior contrast with VCAF is the main reason given for the preference of CAF over VCAF (Kent & Winfield, 1996).

Another well-recognised advantage of VCAF is its ability to develop prints in situations where CAF would be ineffective, such as inside sealed containers (Campbell, 1991) and under adhesive tapes (Amerkamp, 1997).

1.2.3 Fluorescent staining

Secondary treatment is often required after CAF or VCAF to increase the contrast between the print and the background. In cases where the background is dark, there may be sufficient contrast between the white print and the background, but for prints on light coloured backgrounds, further treatment is generally required. CA developed prints have been found to have a natural luminescence under ultraviolet and blue-green argon laser illumination (Menzel et al, 1983). A variety of secondary treatments, including magnetic, fluorescent and standard fingerprint powders, coloured and fluorescent dyes, can be used to improve the contrast of CA developed prints.

Fluorescent stains are the most common secondary treatment. There are numerous stains available, the most common being Rhodamine 6G, Basic Yellow 40, Ardrox 970-P10, Basic Red 28 and Nile Red. The choice of stain is dependent on the colour and luminescence properties of the background surface (Burt & Menzel, 1985; Kobus et al, 1983; Mazzella & Lennard, 1995; Menzel et al 1983; Morimoto et al, 1998).

Dyes can act by adhering to the polymer or by actually being caught in the mesh of the polymer. Some dyes, such as Rhodamine 6G in water, stain both the latent print residue under the CA polymer as well as the polymer itself. CAF stabilises the latent print preventing the solvents used from damaging ridge detail (Stokes & Brennan, 1995).

The solvent system used to transport the stain is an important factor in the effectiveness of the stain. For the stain to be most effective, it needs to stain the CA polymer and not be retained by the substrate itself. Staining of the CA polymer will be more effective if the stain is actually left within the polymer rather than simply sticking to the outside of the polymer. The transfer of a stain into the CA polymer requires a solvent that will penetrate the polymer but not dissolve it.

A limited amount of research into solvent systems for stains has been conducted. Wilkinson and Watkin (1993) proposed a solvent system based on methyl ethyl ketone (MEK) and water. They found that the percentage of MEK in the formulation had a significant impact on its effectiveness.

Wilkinson and Misner (1994) suggest that MEK penetrates the CA polymer resulting in the transfer of stain into the polymer while methanol does not chemically attack the polymer and stain is absorbed onto the surface rather than penetrating the interior of the polymer.

Gamboe and O'Daniel (1999) found that the solvent system used for Ardrox affected the colour of fluorescence seen and the colour and amount of background fluorescence. They suggest that changes in the solvent system result in changes in the structure of the stain molecules that cause the differences seen in the properties of the stain.

1.2.4 Vacuum metal deposition

Vacuum metal deposition (VMD) is a very sensitive technique of fingerprint development on non-porous and semi-porous surfaces. It is generally recognised as more sensitive than CAF (Kent, 1990; Masters & DeHaan, 1996; Misner, 1992), especially in cases where prints are old or have been exposed to adverse environmental conditions (Batey et al, 1998). VMD also has the advantage of covering the background of a surface hence removing interference caused by printing. VMD is not widely used due to the expense of the equipment and the need for experienced operators.

VMD impacts and is impacted on by other surface treatments. As VMD is a destructive technique, it should only be applied when no further examination of an exhibit is required (Kent, 1988). VMD can be, and generally is, applied after CAF. Luminescent staining may be applied before or after VMD development. Surface contamination such as body fluids and drug residues can interfere with VMD (Batey et al, 1998; Ziv & Springer, 1996).

1.2.4.1 History

Vacuum deposition of metals has been used extensively for the production of evaporated metal films used in the electrical industry. Production of zinc-coated paper for use in the construction of capacitors first commenced in Germany prior to World War II. By the end of the war production plants for the manufacture of zinc-coated paper were in operation in the USA (Holland, 1956). Vacuum deposition of evaporated carbon and metal films has also been long used in sample preparation for scanning electron microscopy (SEM) to overcome problems of sample charging (Wells, 1974).

The first application of VMD for fingerprint detection was by Theys and co-workers (1968) who developed prints on paper by volatising a mixture of zinc, antimony and copper powders. The technique was found to work well for fresh prints on paper but, over time, fingerprint material is absorbed into the surface leading to poorer results. The technique was further developed for use on paper and fabric by Hambley and co-workers [as cited in Thomas (1978)]. VMD was applied to polythene and first used operationally by Kent and co-workers in the mid-1970s (Kent et al, 1976).

Kent and co-workers (1976) experimented with a number of metals and metal combinations. Single metals which will give readable marks in some cases are gold, silver, copper, zinc, cadmium, aluminium, bismuth, chromium, magnesium, platinum, lead, antimony and tin. The combinations of copper, gold or silver with cadmium or zinc also develop readable marks. The best results were seen using lead alone and gold or silver with cadmium or zinc, with the combinations showing advantages over lead alone.

The combination of gold and zinc is generally used for latent print development. Cadmium is not used due to its toxicity (Kent, 1981). Silver attacks fingerprint constituents causing diffusion of the fingerprint over time, hence gold, which is less chemically active than silver, is generally used (Godsell, 1972).

1.2.4.2 Principles of VMD

Development of latent prints by VMD involves the evaporation and deposition, under vacuum, of gold and then zinc. The gold film acts to create nucleation sites to which the zinc can bond, enabling the deposition of a zinc film. The zinc will ideally cover the whole surface except where fingerprint residue is present, resulting in transparent print ridges and a metallic background and print valleys (Fig 1.2).

The deposition of the gold layer is independent of the presence of print residue. The density of gold per unit area is the same for print ridges and clean background (Thomas, 1978). The deposited gold is thought to be buried at some depth in the latent print residue, as has been shown to occur with stearic acid (a component of latent fingerprint residue) (Robinson, 1979). Since the gold is buried within the latent print ridge, zinc cannot deposit onto these areas.

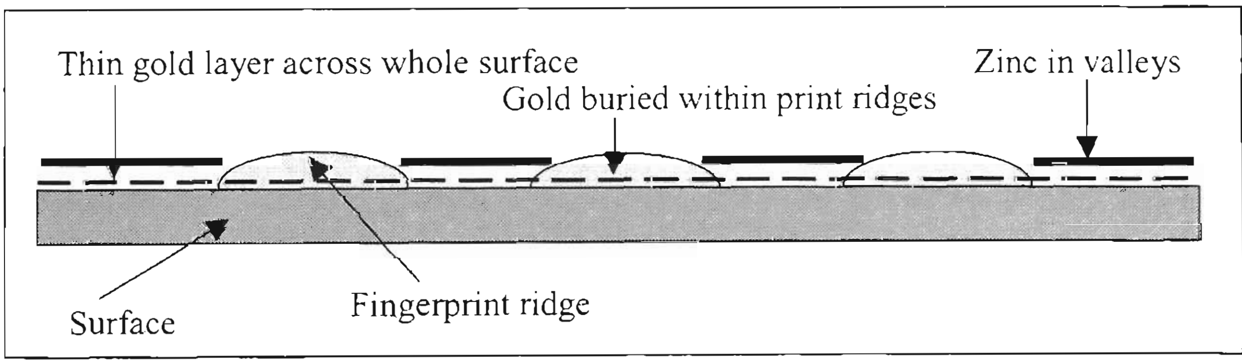


Figure 1.2. Schematic diagram of ideal VMD development

Sebum rich prints have been shown to be more effective than eccrine (sweat) rich prints at inhibiting cadmium (and by inference zinc) deposition (Thomas & Reynoldson, 1975). The difference in chemical composition between the deposits affects the behaviour of gold in the deposit and thus cadmium (and zinc) deposition.

The gold film only needs to have an average thickness of 1 Angstrom and so will be a discontinuous film (Kent et al, 1976). The thickness of the gold layer can be monitored by using a quartz crystal monitor or controlled by evaporating a pre-weighed amount of gold.

Gold film formation

The thin gold film is the critical factor determining the quality of latent prints developed by VMD. The structure of thin films is determined by the bonding between the atoms and the surfaces onto which they are deposited. If the cohesion forces between the atoms are stronger than the adhesion forces between the atoms and the surface, then the atoms will form into clusters, or agglomerates, rather than being evenly spread over the surface (Holland, 1956). This occurs when thin gold films form on plastic surfaces. The presence of discrete clusters has been confirmed by ellipsometry and ion scattering spectrometry (Netterfield et al, 1985).

New atoms that arrive at the surface can join existing clusters, increasing the cluster size, or can form new clusters, increasing cluster density. The size and density of clusters increases until the clusters touch, at which point the film rapidly coalesces to form a continuous film. Small clusters of atoms are thought to be mobile until they reach a certain size (Lewis, 1978), hence these small clusters can be absorbed into larger clusters causing an increase in cluster size rather than an increase in cluster density. The cluster density may reach a point at which freshly nucleated clusters have a high probability of capture before they have grown to immobility. When this occurs, cluster density will remain constant until clusters begin to coalesce.

The gold clusters have been shown with electron micrographs to be far from circular. They are considered, to a good approximation, to be ellipsoids, with their symmetry axes parallel with the substrate plane (Norrman et al, 1978) (Fig 1.3). This ellipsoid shape is generated by cluster surface tension when metal-metal interaction between atoms dominates the metal-substrate interaction (Parmigiani, 1985). As clusters increase in size, the irregularity of shape also increases (Norrman et al, 1978).

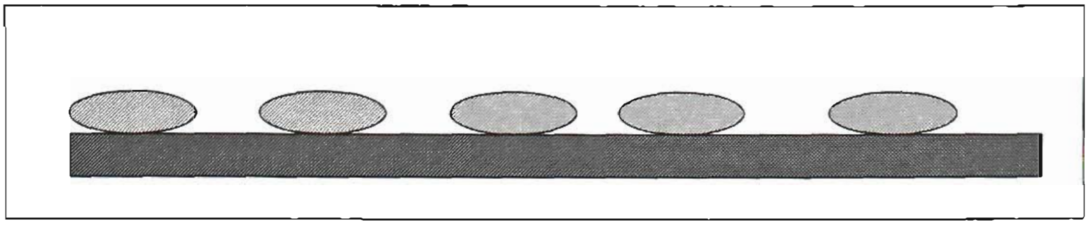


Figure 1.3. Approximate Structure of Thin Gold Films.

The structure of gold films is dependent on the nature of the surface (Kent, 1981). Differences have been found in the density and size of gold clusters formed under the same conditions on different surfaces. Polyethylene was found to have 2.5 times the cluster density of stearic acid. Stearic acid was found to have a much narrower range of cluster size that was within the range of cluster size on polyethylene. These differences were attributed to the molecular structure of the surface (Robinson, 1979).

Zinc (and cadmium) deposition

Zinc and cadmium will not condense on non-metallic surfaces at room temperature due to the small binding energies that exist between zinc and cadmium and these surfaces. Zinc (and cadmium) will nucleate and grow on preferred sites (Lewis, 1978).

Cadmium has been used to visualise gold nuclei that were invisible using electron microscopy (Chapon et al, 1976). Clusters down to 2-3 gold atoms are thought to be present on the surface and susceptible to 'decoration' by cadmium.

1.2.4.3 Difficulties with VMD

While VMD is generally recognized as a very sensitive technique, there are also a number of difficulties associated with the procedure. Inconsistent results are often associated with VMD. Excellent results are obtained on some occasions but poor results on others, with no explanation of the reasons behind this inconsistency. Undesirable forms of development, such as reverse development and empty prints, have also been reported (Masters & DeHaan, 1996). 'Reverse development' is when zinc deposits onto the print ridges and not the background, resulting in dark ridges on a light background. 'Empty prints' are developed when zinc deposits onto the general background but not the print ridges, resulting in a "halo" of zinc formed around the print contact area but poor (if any) development within the print itself.

The high cost of VMD and the expertise required to obtain optimum development has prevented its widespread use in fingerprint laboratories. As a result, VMD is generally reserved for major cases.

A clearer understanding of the technique would enable VMD to be used more effectively and would also widen its application by minimising the experience required for successful operation. An understanding of the 'unexplained phenomena' indicated above would enable operators to avoid or correct for these occurrences, resulting in more consistent and superior results. Optimised training, making VMD more usable and so accessible to a wider range of laboratories and cases, would also be a result of an improved understanding of VMD.

This thesis presents research conducted to promote further understanding of this technique. Explanations for the apparent inconsistency of the technique, the causes of reverse development, and the optimum use of multiple treatments are presented.

Reverse development

"Reverse" or positive development, i.e. the deposition of zinc on to latent print ridges rather than the background around the ridges, has been observed since the initial use of the technique (Grant et al, 1996; Kent et al, 1976; Masters & DeHaan, 1996; Smith, 1989). Possible causes for reverse development, as outlined below, have been suggested, but have not been conclusively identified. The occurrence of reverse development has been unpredictable because its causes are not understood.

Kent and co-workers (1976) suggested that reverse development might be due to the absorption, by the background surface, of the mobile organic constituents from the latent print residue, leaving a more solid inorganic residue on the print ridges. The gold then penetrates more into the background than the inorganic salt, so the zinc deposits on the ridges, producing a 'positive' print.

Smith (1989) reported that reverse development is probably due to 'decoration' or 'epitaxial growth' (the growth on a crystalline substrate of a crystalline substance that mimics the orientation of the substrate) on the sodium chloride crystals contained in the deposit. Neither of these theories explains why zinc does not deposit on the background.

Grant and co-workers (1996) found that the type of development was related to the surface type on which the prints were deposited. On high-density polyethylene (HDPE), development occurred between the ridges (normal development), while on low-density polyethylene (LDPE), development occurred on the ridges (reverse development). The presence and amount of lubricant amide or anti-block were shown not to be determining factors in the occurrence of reverse development. Grant and co-workers also noted that the rate of zinc condensation on the two surfaces differed. Zinc deposition took longer on the LDPE where zinc deposition occurred on the ridges. The authors suggest that, on LDPE, reverse development will always occur and that, on HDPE, normal development will always occur as a result of plastic type.

Normal development is generally preferable to reverse development as it creates greater contrast, especially on patterned surfaces such as banknotes. Hence the unpredictability of reverse development is a problem in the use of VMD. The identification of the cause(s) of reverse development would enable operators to avoid its occurrence. This problem constitutes one of the major focuses of this project.

1.2.5 Multi-metal Deposition

Multi-metal deposition (MMD) is effective for developing prints on a wide range of surfaces: porous and non-porous, wet and dry, adhesive and non-adhesive. Prints in blood can also be developed with MMD. This extent of application is not seen with any other fingerprint development technique.

MMD can be successful on surfaces such as masking tape, beer bottle labels, expanded polystyrene, and plastic gloves, which are difficult to treat with other techniques. Allman and co-workers found MMD to be at least equal, if not superior to CAF and VMD (Allman et al, 1992). In contrast Irrausch reported that MMD is less sensitive than CAF on non-porous surfaces and less sensitive than DFO on porous surfaces. Irrausch did find MMD superior to physical developer (PD) on some paper types (Irrausch, 1991).

The technique was initially developed by Saunders in the late 1980s (Saunders, 1989), but has not been widely used within the forensic community due to its complexity and the mediocre results that are generally obtained in comparison with more conventional methods.

MMD is used at the end of a development sequence and is an alternate technique to PD or VMD. MMD can be used after CAF or amino acid reagents but is incompatible with zinc salt treatment, as multivalent ions will destabilise the gold colloid.

1.2.5.1 Principle of MMD

MMD is a two-step development process. The first step involves immersing the exhibit in a solution of colloidal gold. The colloidal gold binds to the amino acids, peptides and proteins within the latent print residue. The resulting development is generally of very poor contrast hence amplification of the print is required to improve contrast. The second step results in selective silver deposition onto the colloidal gold particles producing a dark grey to black print. A surfactant stabilised redox solution, or physical developer (PD), is used to achieve this.

Colloidal gold

A colloidal gold solution is a homogenous mixture of small gold particles (with at least one dimension in the range 1-1000nm) in water. For a colloid to be stable, the coalescing of the small particles must be prevented. Colloids are generally stabilised by Brownian movement (collisions with constantly moving molecules of the 'solvent'). The negative charge of the gold particles also helps to stabilise the colloid. Detergent can also increase stability.

Colloidal gold solutions, as used in MMD, are formed by the chemical reduction of tetrachloroauric acid. During the reduction reaction, gold atoms are liberated and form into aggregates. These aggregates form into microcrystals to minimise the free surface energy of the particles. They continue to grow until all of the tetrachloroauric acid has been reduced. The reducing agent used, and the concentration of that reducing agent, determine the nucleation and so the speed of crystal growth and ultimately particle size.

The two important characteristics of a colloidal gold solution are the average particle diameter (APD) and the co-efficient of variation (CV). If the CV is less than 15% then the colloid is considered to be homogeneous.

Colloidal gold particles are negatively charged and hydrophobic hence binding of gold particles with organic compounds occurs by both electrostatic and hydrophobic interactions. (Baschong & Stierhof, 1998) At low pH electrostatic interactions dominate while at higher pH hydrophobic interactions dominate. Electrostatic properties of gold particles are believed to be the basis of reaction with latent print residue (Schnetz, 1999). Mildly acidic compounds will carry a positive charge and so will bind with gold particles. Such compounds present in print residue include amino acids, fatty acids and proteins. The pH of the treatment solutions is important as it controls the binding of gold particles with compounds in the print residue.

The size of the gold particles is the critical factor in determining the behaviour of the colloidal gold solution. Smaller gold particles result in better sensitivity and specificity. The sensitivity and specificity required for immunohistochemistry are achieved by using particles of 5-15 nm.

Physical developer

The second step of the technique is the amplification of the colloidal gold using physical developer (PD). The PD solution contains silver ions in the presence of a reducing system. The solution is inherently unstable but is stabilised by the presence of a surfactant. The silver ions are reduced to form silver metal. The gold, which has bound to the print residue, acts as a nucleation site for the precipitation of the silver from the PD solution. The gold particles allow the transfer of electrons from the reducing agent in the solution to the silver ions i.e. they catalyse the reduction of the silver. As the gold particles have adhered to the latent print residue, silver is deposited along the print ridges.

The treatment of alkaline paper by conventional PD is preceded by acid treatment to minimise background development. This cannot be used before MMD treatment as the release of calcium ions that occurs will destabilise the gold colloid (Cantu, 2001).

1.2.5.2 Multi-metal deposition II

Recent work by Schnetz (1999) has resulted in a new MMD formulation (MMDII). The original MMD formulation was modified to produce a more sensitive and reliable method.

Colloidal gold

Saunder's procedure utilised the Frens' method of colloidal gold formation. This results in a heterogeneous colloid with relatively large particles (approx. 30 nm). The gold particles produced vary in size and are not spherical. In contrast, Schnetz recommends the Slot and Geuze method of colloidal gold formation. This offers much greater control of the colloid formed. The gold particles formed are spherical and the colloid is homogeneous. The size of the gold particles can be controlled by varying the concentration of tannic acid used.

The size of the gold particles is important to print development. Smaller gold particles are more sensitive and selective but result in less colour after the initial colloidal gold step. This weaker colour may be corrected by PD treatment. The optimum diameter of gold particles for print development was determined to be 14 nm. The gold particles are small enough to gain some of the advantages of small particle size in terms of sensitivity, specificity and low background, but they are large enough to give sufficient colour, allowing better control of the reaction. This means that over- and under-development can be more easily prevented.

The shape of the colloidal gold particles is also important. The Slot and Gueze method results in more uniformly spherical particles, which results in greater colloid stability. There is also more uniform charge distribution over the particles.

The pH of the colloidal gold solution is also critical as this determines the binding between the gold particles and latent print compounds. Schnetz determined the optimum pH to be 2.5-2.8 depending on the surface type, as the addition of the surface to the solution can increase the pH of the solution by 0.1-0.2. Saunders suggested that the pH should be approximately 3. If the pH is too high, above 3.5, then the electrostatic interactions between the gold particles and the latent print compounds will not occur and so no print development will be achieved. The pH of the solution needs to be accurately controlled and so use of a pH meter rather than pH paper is required. (Gold particles can tend to block the electrode but this can be minimised by the addition of Tween.)

The optimum concentration of the colloidal gold solution was found to be 0.01%w/v. Lower concentrations result in slow reaction rates and higher concentrations do not result in effective reaction as the gold particles repel each other.

The addition of Tween (a detergent) stabilises the colloidal gold solution and so reduces the background development. Since the Slot and Geuze colloidal gold is more stable than the Saunders solution, it was predicted that the required concentration of Tween could be reduced. A detergent concentration of 0.1% w/v was determined to be optimum; this is a compromise between the increased reaction that occurs with less Tween and the increase in background that also results.

The temperature at which the reaction between the latent print and the colloidal gold is carried out was found to be insignificant.

Physical developer

Saunders' MMD method utilised a silver nitrate/iron(II) iron(III) redox system in the physical developer system. Schnetz found an alternate redox system (silver acetate/hydroquinone) that was superior to that used by Saunders.

Silver acetate and hydroquinone are considered the reagents of choice for PD in the biochemistry field. The low co-efficient of dissociation of the silver salt allows control of the reduction reaction. The silver acetate/hydroquinone system is more sensitive and practical than the silver nitrate/iron(II) iron(III) system.

The Ag^+ ions and the reducing agent (hydroquinone: Hq) adhere simultaneously to the surface of the gold particle. Hq detaches from the gold surface donating an electron. This electron then joins with the Ag^+ ion also on the surface, resulting in the production of Ag^0 (silver metal). The silver metal formed stays attached to the gold particle, increasing the size of the particle. The reaction continues for as long as Ag^+ and the reducing agent exist in the solution.

The silver acetate/hydroquinone system reacts much more slowly then the silver nitrate/iron(II) iron(III) system. A similar amount of silver deposition occurs within 10-15 minutes in the first system or a few seconds in the second system (Schnetz, 1999) The greater control of silver deposition enable better control of latent fingerprint development.

The silver acetate/hydroquinone system is much more specific to gold particles reducing the amount of random silver deposition and so background development.

UK modification

Another MMD formulation is in use at the Forensic Science Service, UK. The 30 nm colloidal gold solution is used in combination with the silver acetate/hydroquinone physical developer. This formulation was adopted because the difference between the 14 nm and 30 nm colloidal gold solutions was not found to be significant, especially in comparison to the time needed to prepare the 14 nm colloidal gold solution. The 14 nm colloidal gold solution was produced using an interim procedure, which required 2 boiling/cooling steps and a 2 hour incubation with hydrogen peroxide and hence took significantly longer to prepare than the 30 nm colloidal gold solution or the 14 nm colloidal gold solution using Schnetz's final procedure. (Brennan, 2001) Schnetz's final procedure only requires 1 boiling/cooling step and doesn't require incubation with hydrogen peroxide hence the production time has bee significantly reduces and so similar to that required for the 30nm colloidal gold solution.

Reagent preparation

Care and precision are required to prepare reagents properly and obtain good results with this technique. Good quality reagents are required and must be stored appropriately to prevent contamination or degradation. Without great care reproducible results will not be achieved.

Scrupulously clean glassware and ultra-pure distilled water are both essential to the success of MMD. Lack of appropriate glassware or distilled water results in a large variation in gold particles size and indiscriminate silver precipitation during the PD step. Siliconised glassware is recommended to obtain the required cleanliness of glassware.

Washing times in distilled water, prior to MMD development, of 20-30 mins for non-porous surfaces and 5-10 mins for porous surfaces were previously recommended. As a proportion of compounds that will bind to colloidal gold are water-soluble this would be detrimental to print development. Schntez found that sufficient washing could be achieved much more quickly minimising the loss of useful compounds from the print residue. He suggests non-porous exhibits only require to be passed through distilled water and that porous exhibits only require around 2 minutes of soaking in distilled water. (Schnetz, 1999; Schnetz & Margot, 2001)

Evaluation

MMDII is reported to have increased reactivity, improved resolution and greater selectivity than MMDI. This results in sharper images and less background development making MMDII a superior technique compared to MMDI.

(Schnetz, 1999; Schnetz & Margot, 2001) Schnetz also reported that MMDII was superior to PD on porous surfaces in 80% of cases, with PD only being superior on newspaper.

MMDII was utilised in an evaluation of techniques used for the development of latent prints on cartridge cases (Schutz et al, 2000). MMDII was found to be inferior to *blueing* techniques although there is less danger of over development in using MMDII. It is suggested that the physical developer component of the MMDII is solely responsible for the development seen.

MMDII appears to provide superior and more consistent results than the original MMD formulation. However, the effectiveness of the new formulation under a range of conditions and in comparison to standard techniques has yet to be reported. An evaluation of this formulation is presented within this thesis.

1.3 Difficult surfaces

Despite advances in fingerprint development techniques certain surfaces still present significant difficulties for fingerprint development. These surfaces include skin, leather, cloth and semi-porous surfaces.

Semi-porous surfaces present problems for latent fingerprint development. Semi-porous surfaces are those that do not fit well into the groups of porous and non-porous surfaces. The water-soluble components of the residue are slowly absorbed into the surface but diffuse across the surface rather than maintaining the pattern of the fingerprint hence techniques designed for porous surfaces are only useful for fresh prints. The fatty-waxy components of the residue remain on the top of the surface but not as long as would occur on non-porous surfaces; hence techniques designed for non-porous surfaces are not fully effective either. Generally only fresh prints can be developed on semi-porous surfaces. Typical examples of semi-porous surfaces are rubber gloves, waxed surfaces, varnished wood and certain glossy papers. (Stoilovic & Lennard, 2000)

The increased awareness of fingerprint evidence in the general population has resulted in increased use of gloves by criminals. The semi-porous nature of latex and nitrile gloves makes them a difficult surface for latent print development. Although very little has been published on this matter, success has been reported with ninhydrin (Pressly, 1999; Rinehart, 2000) and MMD (Allman et al. 1992; Brennan, 2001).

Polymer banknotes, such as those used in Australia, are another example of a semi-porous surface. They have proven to be a difficult surface for the development of latent prints due to their semi-porous nature and complex design and printing. Polymer banknotes may be encountered in a range of criminal activity, including drug cases and armed hold-ups. Hence the ability to develop latent prints on polymer banknotes would provide valuable information in the investigation of crime. The development of a procedure capable of effectively visualising latent prints on polymer banknotes is one of the major issues addressed within this thesis.

1.3.1 Polymer banknotes

Polymer banknotes were developed as a means of preventing counterfeiting and were first introduced into circulation in Australia in 1988, with the commemorative Bicentennial $10 note. Circulating notes were introduced between 1992 and 1996 and have almost replaced paper notes. The notes are manufactured by Note Printing Australia (NPA), a subsidiary of the Reserve Bank of Australia (RBA).

Polymer notes are being used in a growing number of countries. New Zealand and Romania have converted their entire banknote series to polymer. Other countries which have issued polymer notes include Bangladesh, Brazil, Brunei, China, Indonesia, Kuwait, Malaysia, Mexico (issue forecast for 2002), Northern Ireland, Papua New Guinea, Romania, Singapore, Solomon Islands, Sri Lanka, Taiwan, Thailand, Vietnam and Western Samoa (Kerrison, 2002).

The base of the notes is a biaxially orientated polypropylene. The clear polypropylene base (except for window areas) is coated on both sides with opacifier to enable printing to occur. This opacified film is known as Guardian® Substrate. A variety of printing techniques are used on the notes. A dry offset

Simultan press is used for the background colours, intaglio printing is used for the raised illustration and numerals, and a letterpress process for the serial number. The printed notes are then coated with a primer and then a mattcoat, which are cured with UV light (Colditz, 1995). (Fig. 1.4)

Unless a Diffractive Optically Variable Device (DOVD) is placed in the window, such as in the Australian commemorative $10 banknote. the clear windows are free from the printing, primer and matt coats and only some areas of the window are opacified. This results in a very different surface to the rest of the note.

Side 1	Matt Coat
	Primer
	Print (Background, Intaglio And Letterpress)
	Opacifier
	Polypropylene Base
Side 2	Opacifier
	Print (Background, Intaglio And Letterpress)
	Primer
	Matt Coat

Figure 1.4. Structure of Polymer Banknotes.

Polymer notes are more durable than paper, with the average life of polymer notes approximately four times that of paper notes. The notes are reportedly impervious to moisture and resistant to water, sweat, oils and other contaminants. (Note Printing Australia, 2001) The increased life of polymer notes over traditional paper notes is due to the polymer substrate and the protective overcoat. The notes are significantly more resistant to high humidity and temperatures that adversely affected traditional paper notes (Note Printing Australia, 2001). This makes polymer more cost effective than their paper counterparts because their extended lifetime out weighs their greater cost. Polymer notes are less polluting, more energy efficient in production and recyclable after use (Coventry, 1999).

Enhanced security and so decreased counterfeiting are one of the main advantages of polymer banknotes. Polymer notes make counterfeiting more difficult, time consuming and costly and they also make it easier to recognise counterfeits. The superior security of polymer notes is achieved by printing on polymer rather than paper and is enhanced by a range of security features that are unique to polymer. The Reserve Bank of Australia believes that polymer notes have virtually stopped "casual" counterfeiters completely (Coventry, 1998).

Unfortunately, polymer bank notes have proven to be a difficult surface to develop latent prints on. Many of the standard development techniques for non-porous surfaces are only effective for a limited length of time (Flynn et al, 1999; McLeod & Siebert, 2000) (Table 1.1 & 1.2). The difficulties of latent print detection and enhancement on polymer banknotes are caused by two factors. The first is the semi-porous nature of the surface that results in less fingerprint residue remaining on the top of the surface meaning that the techniques used have to be especially sensitive to develop the latent prints. The second factor is the complex design and printing of the banknote. This means that even if the development technique is successful it is difficult to differentiate the developed fingerprint from the banknote design.

Flynn and co-workers found that the standard non-porous development techniques were only successful on prints less than a week old, unless prints were located on the clear window.

Table 1.1 Effectiveness of some fingerprint development techniques on polymer banknotes (Flynn et al, 1999).

Technique	**Effectiveness on polymer banknotes**
Physical Developer	Not effective
DMAC (4-Dimethylaminocinnamaldehyde)	Not effective

Cyanoacrylate Fuming + Black magnetic powdering	Developed prints up to 4 hours old
Cyanoacrylate Fuming + Fluorescent stains	Developed prints up to 3 days old on "cleaner" areas and up to 6 months old on clear window
Iodine-Benzoflavone	Developed prints up to 7 days old on "cleaner" areas- only successful in light areas
Fluorescent Powdering	Developed prints up to 7 days old on "cleaner" parts of note
Cyanoacrylate Fuming + fluorescent powdering	Developed prints up to 7 days old on "cleaner" areas and up to 6 months old on clear window
Cyanoacrylate fuming + Vacuum Metal Deposition	Developed excellent prints up to 6 months old

Table 1.2 Development of latent prints on polymer banknotes by various fingerprint development techniques (McLeod & Siebert, 2000).

Treatment	**Background Response**	**Results with 3 day old prints**	**Results with 30 minute old prints**
Ninhydrin	Nil	Not tried	No prints developed
Gential Violet	Dark	Not tried	Identifiable prints developed
Fingerprint Powder	Dark	Not Tried	Identifiable prints developed
Superglue + Gentian Violet	-	Identifiable prints developed	Identifiable prints developed
Superglue + Panacryl	High	No prints developed	Identifiable prints developed
Superglue + Lamp Black	Dark	Identifiable prints developed	Identifiable prints developed
Superglue + Magna Black	Dark	Identifiable prints developed	Identifiable prints developed

The published research has highlighted the difficulties associated with the development of latent prints on polymer banknotes. The standard techniques used on non-porous surfaces are not effective on polymer notes. Flynn and co-workers suggest the possible solution to this difficulty to be cyanoacrylate fuming followed by VMD.

The ability to develop latent prints on polymer banknotes could provide information in the investigation of a variety of crimes. The development and evaluation of a procedure that could achieve this is presented within this thesis.

2 Optimisation of Vacuum Metal Deposition

2.1 General materials and methods

2.1.1 VMD unit

The Vacuum Metal Deposition (VMD) unit employed in this research was designed and manufactured specifically for latent fingerprint development, according to Australian Federal Police requirements, by Dynavac (Melbourne, Australia) (Fig 2.1). The horizontal chamber of the VMD is 60 cm in diameter by 1 m in length. The chamber was evacuated to less than 5 x 10^{-4} mbar before the commencement of metal (gold and zinc) evaporation.

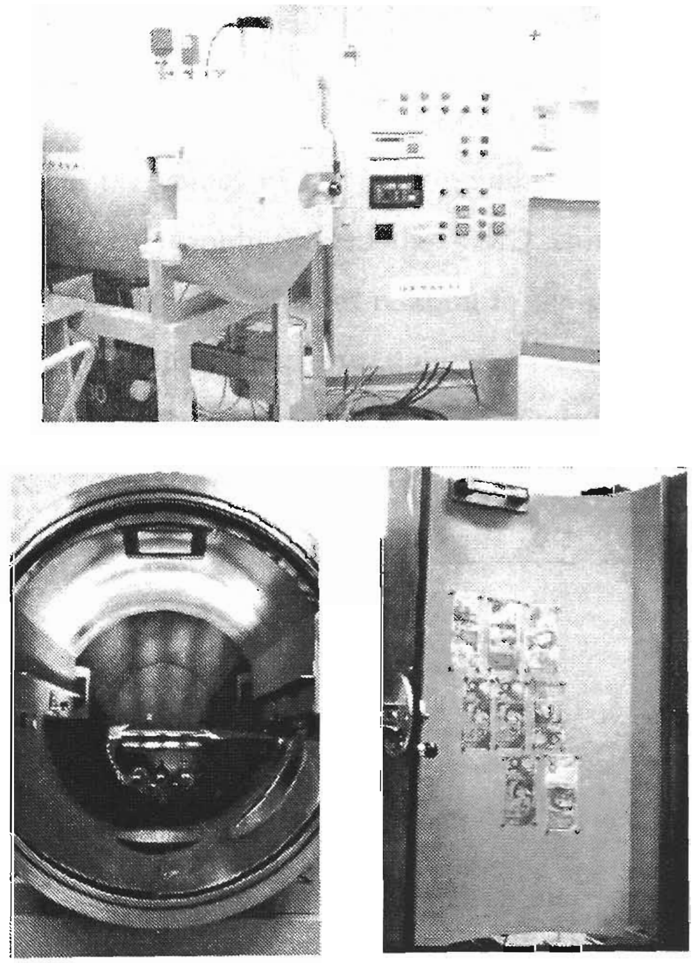


Figure 2.1. VMD unit: general view, interior of chamber and exhibit tray

Tungsten boats were employed for the evaporation of gold (width 7 mm; Balzers BD482000-T) and zinc (width 13 mm; Balzers BD482001-T). Three boats were used for each metal and were positioned alternately down the centre of the chamber. The boats are covered by a movable shutter to allow more accurate control of metal evaporation.

Thin gold wire (thickness 0.5 mm, purity > 99%) was used in the experiments. Unless otherwise noted, the evaporation of gold was conducted at a constant rate using a current of approximately 110 A. Gold boats were allowed to preheat for 30s before the shutter was opened, except in instances when new gold was added to the boats when 45s were allowed for preheating. The amount of gold evaporated was monitored using an Edwards FMT7 quartz crystal monitor ('thickness monitor'), which gives readings in arbitrary units termed 'gold monitor counts'. The thickness monitor was used to control gold evaporation; a predetermined value is set on the monitor and once this value is reached the shutter closes and the current is turned off.

It should be noted that the values of the gold monitor counts listed throughout this thesis are only directly applicable to the VMD unit employed and to a specific position of the crystal monitor in relation to the gold boats. Figure 2.2 shows the approximate position of the crystal monitor, relative to the gold boats, in the VMD unit employed. Relative values of gold counts should be transferable to other VMD units.

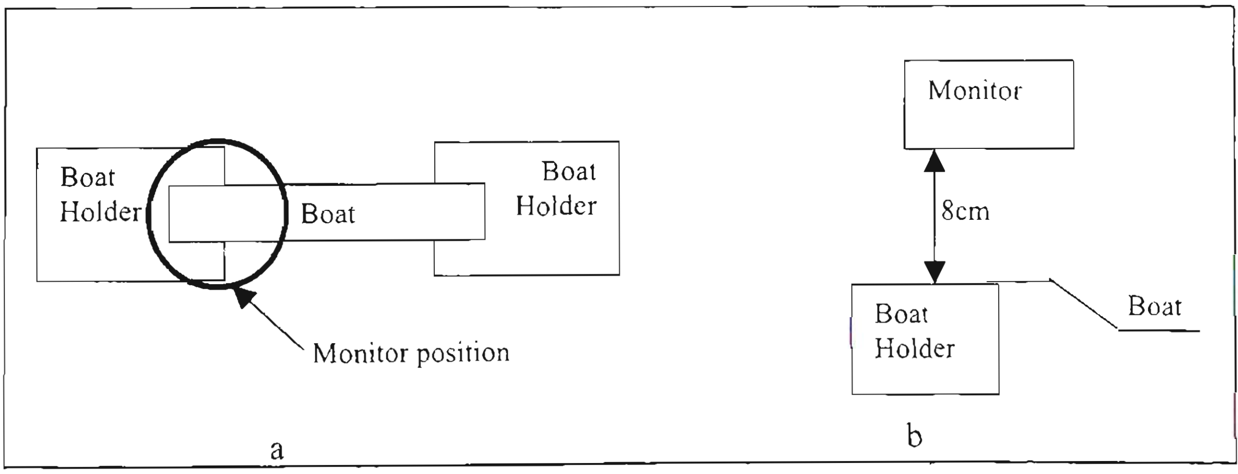


Figure 2.2. Monitor position: **a**. Top view; **b**. Side view

Zinc wire (thickness 2 mm, purity > 99%) was used for the majority of experiments but other forms of zinc (pellets, wire, ribbon and mossy zinc), all with purity greater than 99%, were used for early experiments. The form of zinc used did not have a significant impact on the results obtained although different evaporation times were used to allow for the different lengths of times required for the zinc to melt. Zinc evaporation was conducted using a current of approximately 135 A. The shutter was not used for zinc evaporation. Maximum zinc exposure was controlled by a timer. Zinc exposure was either manually stopped when appropriate development had been achieved or was stopped by the timer when the set time had elapsed.

2.1.2 Comparison of print development conditions, techniques or sequences

Standard methods of comparing different fingerprint development techniques, conditions or sequences were employed throughout this research. Latent prints were generally deposited after wiping fingers over the forehead. Successive impressions of prints were obtained by depositing multiple prints, without recharging the fingers with sebum between impressions. Figure 2.3 shows the arrangement of deposited prints for comparison of development techniques. The numerals I-IV indicate successive impressions. A majority of the latent prints were from one donor who gave good quality prints.

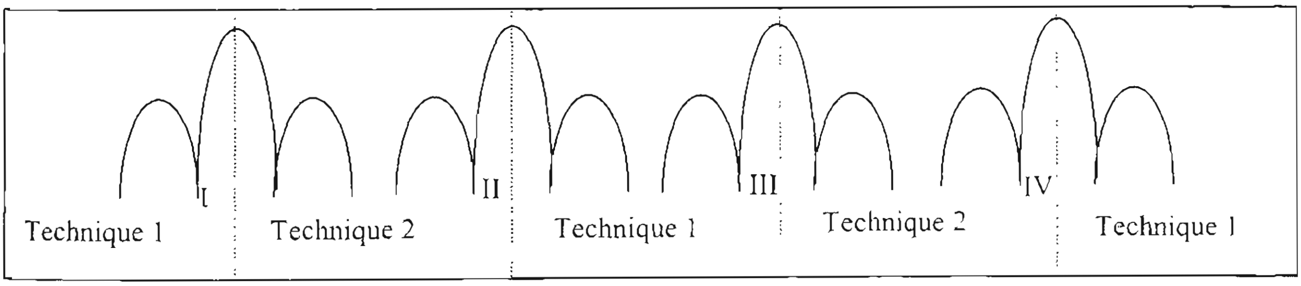


Figure 2.3. Arrangement of deposited prints for comparison of development techniques

Prints were stored in paper envelopes at ambient temperature and humidity while they were aged. When prints had reached the necessary age, they were used to compare either different development conditions for a technique, different development techniques, or different sequences of development techniques. Prints were cut in half and the two halves were developed with different conditions/techniques/sequences to be compared. After development, the two halves were re-combined so that the development achieved by the different conditions/techniques/sequences could be easily evaluated. This method is used to minimise the differences that occur from print to print, even when prints are from the same donor and are deposited under similar conditions. It must be remembered that there may still be differences within a print that could account for some of the observed differences in development.

2.2 Factors affecting normal and reverse development on polyethylene substrates

2.2.1 Introduction

The occurrence of reverse development has created difficulties and confusion for VMD operators. While reverse developed prints can contain adequate detail for identification, normal development is preferable. Normal development results in greater contrast, especially when luminescent stains are used, and removes the effect of background printing, which can be extreme is instances such as banknotes. The occurrence of reverse development has been unpredictable and so confusing for operators because its causes had not previously been identified. An investigation of the factors critical to the occurrence of reverse development was conducted to minimise, or even remove, the difficulties and uncertainty caused by reverse development.

2.2.2 Materials and methods

Four different plastic substrates, purchased from supermarkets as plastic bags, were used in this stage of experimentation. The four plastics were clear, yellow, green and white polyethylene film. The development achieved with a range of gold counts was measured by a few methods. Visual examination determined the type and quality of development. Relative zinc deposition was determined using densitometry and inductively coupled plasma-mass spectrometry (ICP-MS) enabled the determination of the quantities of deposited gold and zinc. Micro-X-ray fluorescence spectrometry (µ-XRF) was used to compare relative gold deposition in areas with and without fingerprint residue. The polyethylene (PE) subtype was identified using Fourier Transform Infrared (FTIR) Spectroscopy.

2.2.2.1 Visual examination and densitometry

Strips of each plastic substrate were prepared with four successive three-finger impressions (index, middle and ring fingers) from the same donor. Strips were treated with varying amounts of gold in order to evaluate the effect on zinc deposition. Zinc deposition was conducted at a constant rate for a set time (1 minute). The rate of gold evaporation and the amount of gold deposited were varied.

For each plastic substrate, two sets of strips were developed. Slow gold deposition was conducted on one set of strips and fast evaporation on the second set. The rate of gold evaporation was altered by changing the current used to heat the gold boats and hence changing the temperature of the gold boats. According to the crystal monitor, the fast rate used was approximately 3 times the slow evaporation rate. Gold monitor counts used ranged from 2 to 4000, and were doubled for consecutive samples.

The fingerprints developed under each set of conditions were visually examined to determine the type and quality of developed prints.

The relative quantity of zinc deposited on each sample was measured using a Compumaster TR 90 densitometer (Esco, USA). Measurements were conducted in the transmission mode for the clear, white and yellow plastic samples, while the green plastic samples were measured in the reflectance mode.

2.2.2.2 Inductively coupled plasma-mass spectrometry (ICP-MS)

A Sciex Elan 5100 ICP-MS (Perkin Elmer, USA) was used to determine the quantity of gold and zinc deposited onto 10 x 10 cm squares of each plastic type. Gold was deposited onto clean squares of plastic using two evaporation rates, fast and slow, and varying monitor counts. Zinc deposition was then conducted for a set time using a constant evaporation rate. Samples of the same plastic type were treated at different positions (designated as A, B, C and D) within the VMD chamber to assess any positional effects.

After VMD treatment, the gold and zinc on each sample were dissolved off the plastic using a solution of dilute *aqua regia* (50% water, 40% HCl and 10% HNO_3). The squares were cut into strips and placed into a plastic tube containing 10 ml of the acid solution. The tubes were placed in an ultra-sonic bath for 5 minutes and then, after an additional 10 minutes, the plastic was removed from the solution.

A solution containing 10% HCl and 2.5% HNO_3 was used as a rinse in the ICP-MS and also to dilute the sample solutions and make up standard solutions. The sample solutions were diluted either 1 in 100 or 1 in 1000 before ICP-MS analysis depending on the expected metal concentration. Samples were run using the auto-sampler on the ICP-MS with a 60-second wash between each sample and a 50-second delay before each reading.

Blank solutions and ICP-MS calibration standards, containing known quantities of gold and zinc, were measured before each set of 12 samples.

2.2.2.3 X-Ray fluorescence (XRF) spectrometry

XRF measurements were conducted on an Omicron X-ray microfluorescence spectrometer (Kevex, USA) to assess the relative amount of gold deposited on to an area of clean background compared to an area containing a fingerprint. XRF measurements were also conducted to compare the amount of gold deposited using different evaporation rates. The instrument was fitted with a 500 μm beam collimator and the X-ray tube operated at 20 kV. A semi-quantitative 'Automatic Standardless Analysis Program' (ASAP) procedure was employed. After the elements of interest have been identified by the operator, the background (including spectrum artefacts) is removed. Peaks are then deconvoluted (using a Gaussian model), integrated and transferred into normalised percentage concentrations for the identified elements. Given that ASAP is a standardless protocol, the calculated values are not true elemental concentrations but may be used for comparison purposes.

2.2.2.4 Fourier transform infrared (FTIR) spectroscopy

Polymer identification was conducted using a MB-Series FTIR spectrometer (Bomem, Canada) fitted with an Analytical IR microscope (Spectra-Tech, USA). Each plastic sample was scanned in the transmission mode from 4000 cm^{-1} to 700 cm^{-1} at a resolution of 4 cm^{-1} to identify the polymer class and sub-class. Spectra were compared to library spectra or those of known samples. Differentiation between high-density polyethylene (HDPE) and low-density polyethylene (LDPE) was possible using the 1400–1340cm^{-1} region of the spectra as reported by Koenig (1992).

2.2.3 Results

Based on the VMD results obtained, the four plastic samples could be readily classed into two groups: Group I – clear and yellow plastics: and Group II - white and green plastics.

2.2.3.1 Fourier transform infrared spectroscopy

FTIR analysis enabled the determination of the polymer type for the plastic samples employed. All four substrates were identified as PE. Group I plastics (yellow and clear) were identified as LDPE and group II plastics (green and white) were identified as HDPE.

2.2.3.2 Densitometry

The samples prepared for densitometry measurements allowed the identification of the range of gold monitor counts over which different types of development occurred. On LDPE, three types of development were observed: normal development (Fig. 2.4), reverse development (Fig. 2.5) and no development (Fig. 2.6). Figures 2.4, 2.5 & 2.6 show prints developed on clear plastic and so the zinc covered areas are dark compared to the background. Figure 2.7a shows how zinc deposition, as measured by densitometry. varied with gold monitor counts on LDPE (clear plastic used as an example). The regions over which normal development, reverse development and no development occurred are indicated. Figure 2.7b shows in more detail the regions over which normal and reverse development occurred. Reverse development was found to occur immediately after the drop-off in zinc deposition.

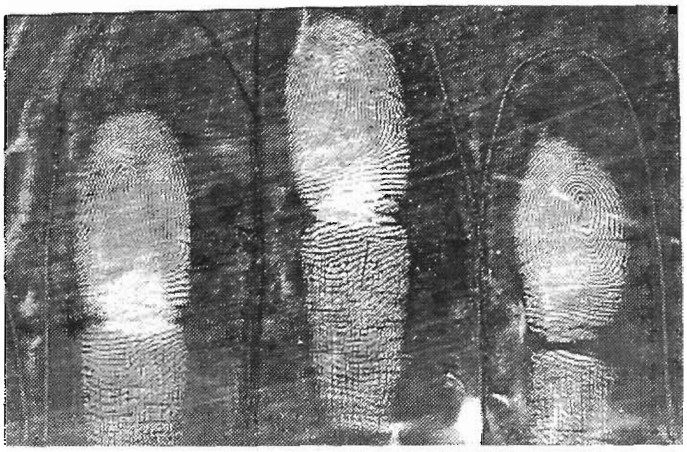


Figure 2.4. Normal development on LDPE

Figure 2.5. Reverse development on LDPE

Figure 2.6. No development on LDPE,

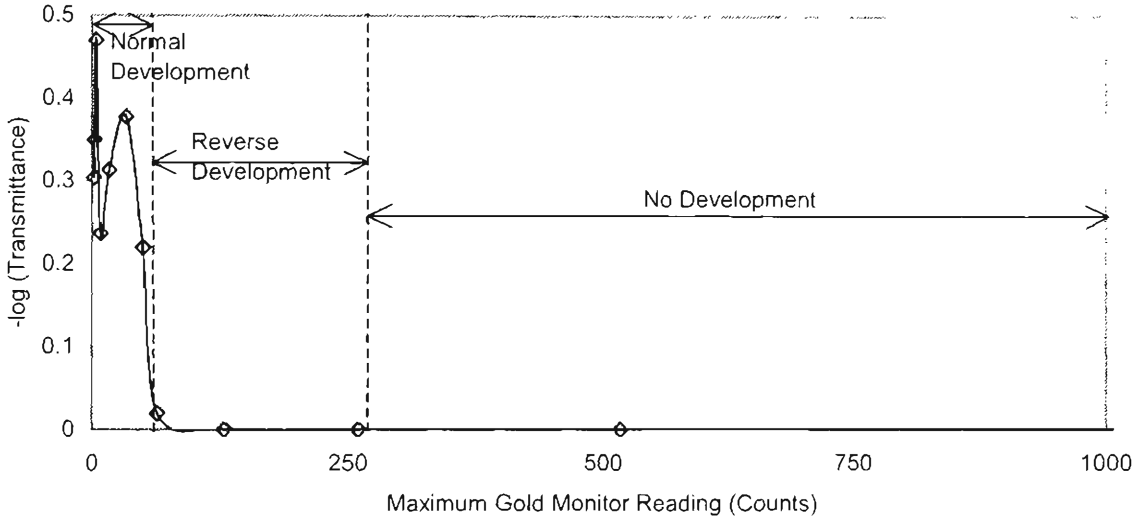
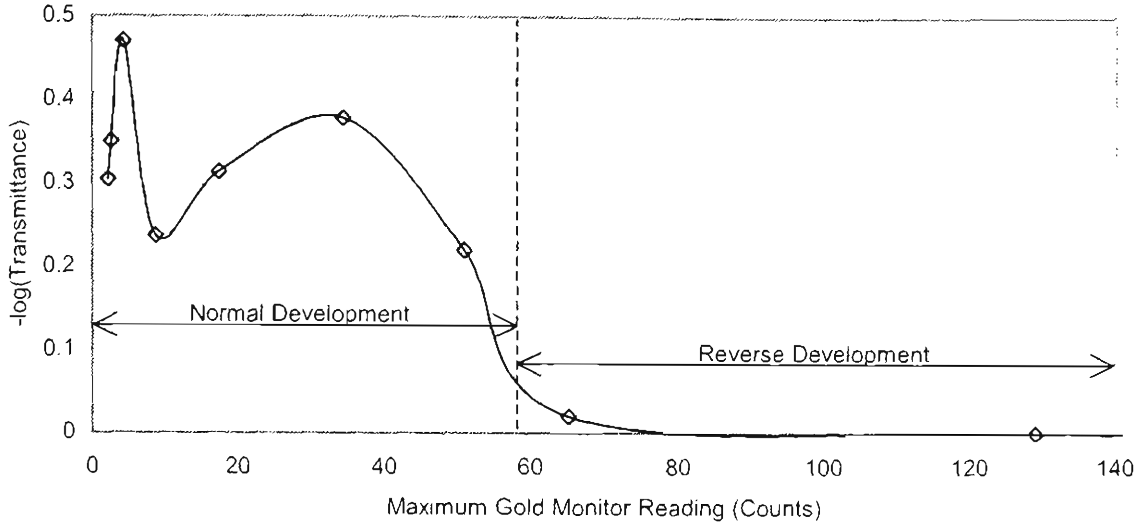


Figure 2.7. (a) Relationship between gold monitor reading and zinc deposition on clear plastic (LDPE) as measured by densitometry (absorbed light).



(b) Relationship between gold monitor reading and zinc deposition on clear plastic (LDPE) as measured by densitometry (absorbed light) — expanded X-axis

Reverse development was not observed on HDPE within the range of gold monitor counts used. Rather, prints became over-developed as more gold was applied (Fig. 2.8 & 2.9). Further deposition of gold resulted in normal development again being observed, however this was of lower quality than that achieved under optimum conditions (Fig. 2.10). Figures 2.8, 2.9 & 2.10 show prints developed on dark green plastic and so the zinc covered areas are light compared to the background. A decrease in zinc deposition did occur with increasing gold, but not to the point where zinc no longer deposited on the background (Fig. 2.11a & 2.11b).

Figure 2.8. Normal development on HDPE (Dark Green PE)

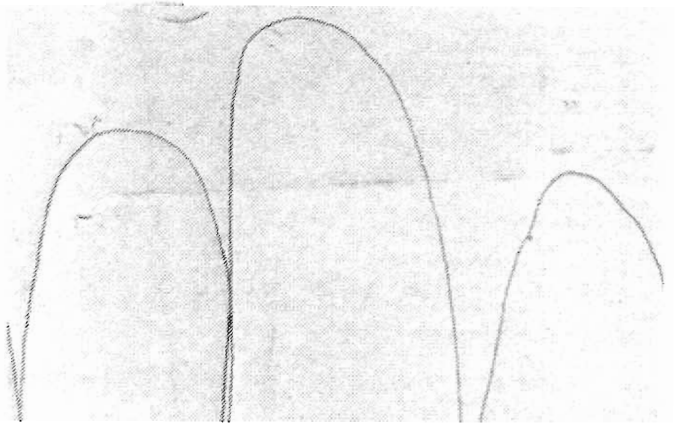


Figure 2.9. Over-development on HDPE (Dark Green PE)

Figure 2.10. Poor-quality development on HDPE (Dark Green PE)

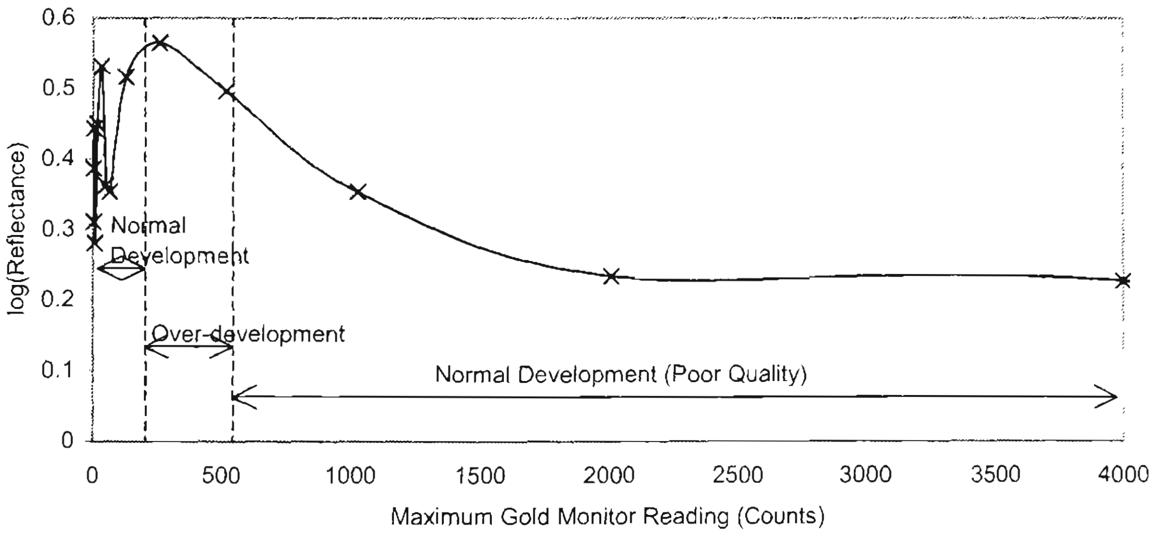
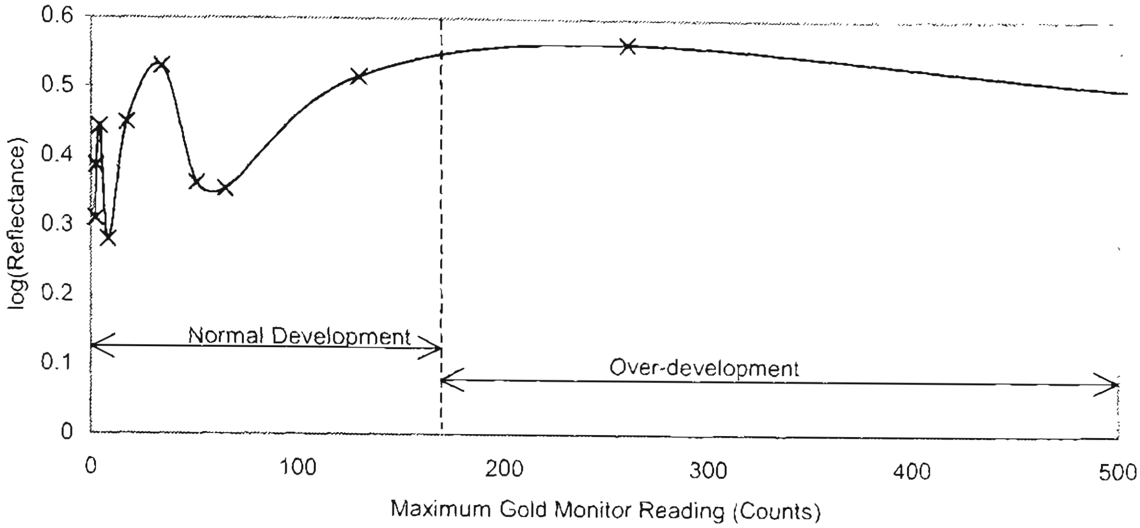


Figure 2.11. (a) Relationship between gold monitor reading and zinc deposition on green plastic (HDPE) as measured by densitometry (reflected light).



(b) Relationship between gold monitor reading and zinc deposition on green plastic (HDPE) as measured by densitometry (reflected light) — expanded X-axis

Empty prints were developed on the white plastic used. The factors causing the development of empty prints were not investigated within the bounds of this thesis but were investigated in associated research (Jones et al, 2001) (See section 2.3.3).

Figures 2.7 and 2.11 indicate the difference in the optimum amount of gold required on the different plastic substrates. For LDPE plastics, the optimum gold monitor reading is around 35 counts, while for HDPE plastics, the optimum gold monitor reading is approximately 150 counts.

The rate of gold deposition was found to affect zinc deposition. As can be seen in figures 2.12 and 2.13, the faster rate of gold evaporation resulted in an increase in deposited zinc at higher thickness monitor readings (observed as a right-shift in the densitometric curves). This suggested that a slower gold evaporation rate resulted in more deposited gold for a given thickness monitor reading.

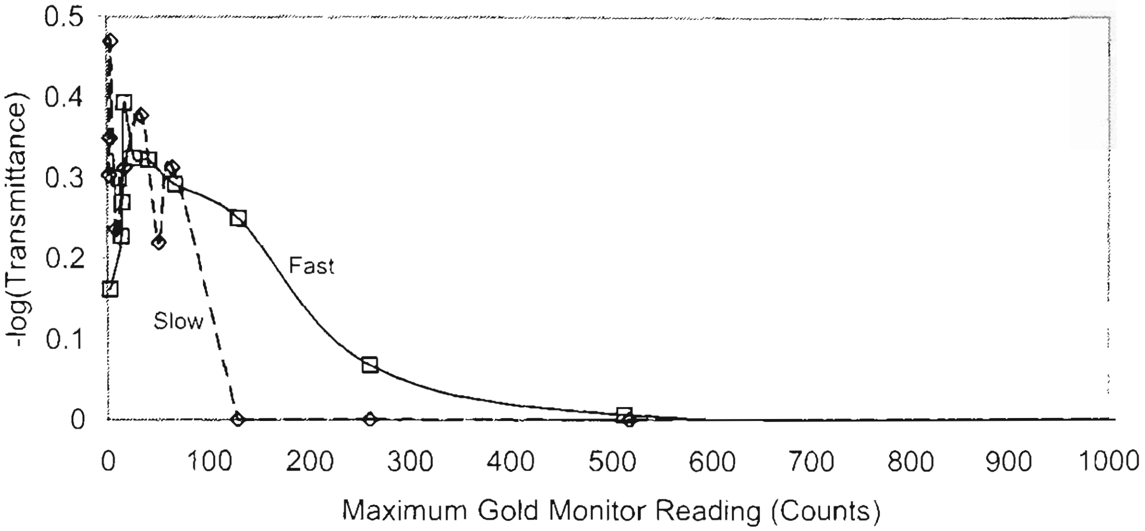


Figure 2.12. Relationship between gold monitor reading and zinc deposition on clear plastic (LDPE) as measured by densitometry (absorbed light) — effect of fast and slow gold evaporation rates

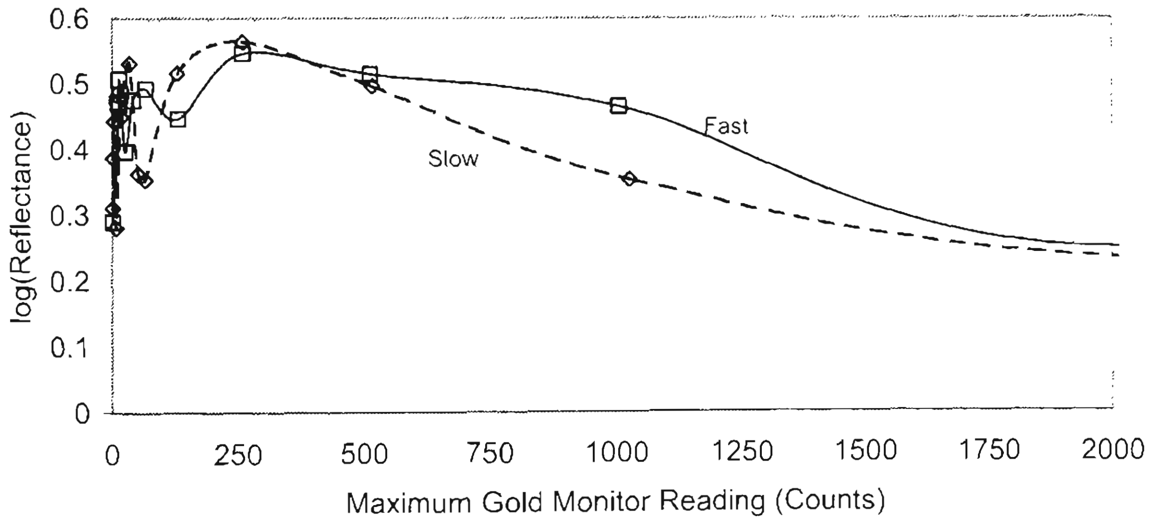


Figure 2.13. Relationship between gold monitor reading and zinc deposition on green plastic (HDPE) as measured by densitometry (reflected light) — effect of fast and slow gold evaporation rates

2.2.3.3 XRF spectrometry

XRF spectrometry failed to detect deposited gold for monitor readings below 1000 counts. As can be seen from the results discussed above, optimum fingerprint development occurred at gold monitor readings well below this figure (35 counts for LDPE plastics; 150 counts for HDPE plastics). Therefore, XRF analyses were only effective for samples with excessively more gold than that needed for good fingerprint development.

The comparative XRF analysis of areas that did and did not contain fingerprints showed that there was no significant difference in the amount of gold deposition on either area. This indicated that the amount of gold deposited is not affected by the presence of fingerprint residue.

Analysis by XRF spectrometry also indicated differences in the amount of gold actually deposited onto a surface as the rate of gold evaporation was varied. The analysis showed that, for the same thickness monitor reading, a slower evaporation rate resulted in more gold being deposited onto the surface compared to a faster rate. This confirmed the observations made during the densitometric analyses.

2.2.3.4 Inductively coupled plasma–mass spectrometry

ICP-MS was used to measure the weight of deposited zinc and gold per unit area on an uncontaminated square of plastic. The measurement of gold density (recorded as $\mu g/cm^2$) permitted the calibration of the crystal thickness monitor.

Gold deposition — Crystal monitor calibration

The ICP-MS results for deposited gold could be related to monitor counts but it was found that the evaporation rate (gold current) was a determining factor. The relationship between monitor counts and the density of deposited gold is essentially linear for a restricted range of monitor readings, but the relationship becomes polynomial over a larger range. Figures 2.14 and 2.15 show the relationship between monitor counts and gold density for LDPE and HDPE respectively [for all graphs the y-intercept was set to zero and the correlation factor (r^2) calculated]. The slower gold evaporation rate (lower gold current) clearly results in greater gold deposition on the substrate, for a given monitor reading, than the faster evaporation rate.

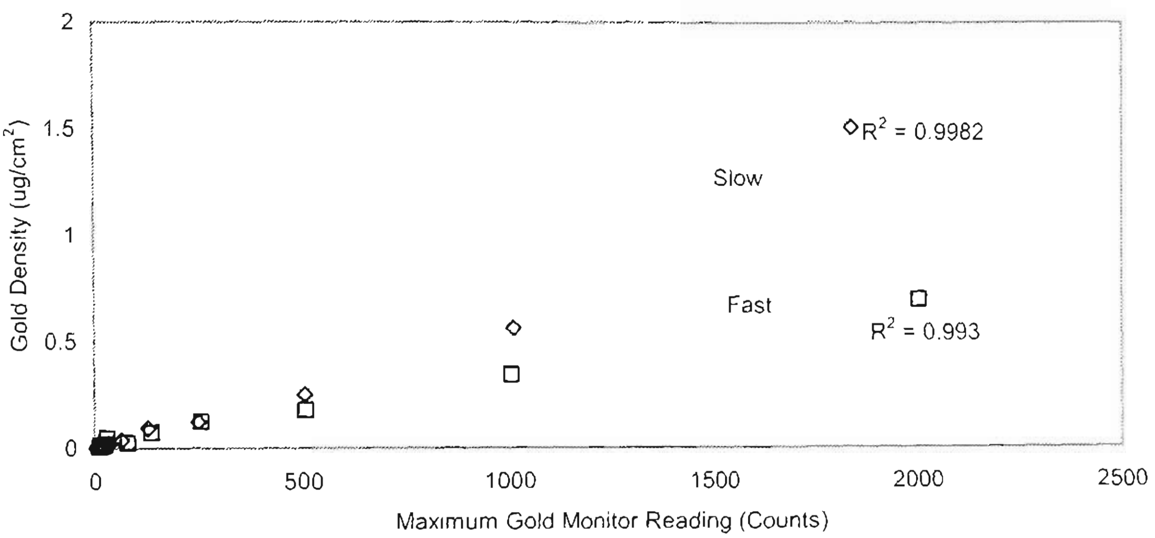


Figure 2.14. Relationship between gold monitor reading and gold density on clear plastic (LDPE) as measured by ICP-MS — effect of fast and slow gold evaporation rates.

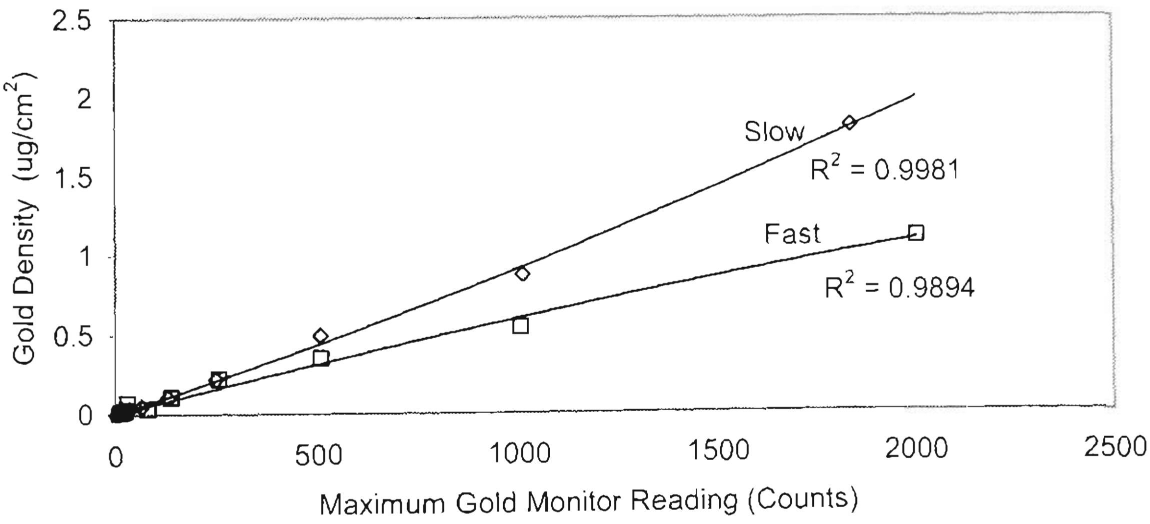


Figure 2.15. Relationship between gold monitor reading and gold density on green plastic (HDPE) as measured by ICP-MS — effect of fast and slow gold evaporation rates

Zinc deposition

The quantification of zinc by ICP-MS confirmed the general relationship between gold and zinc deposition that was established by densitometry. The relationship between gold monitor counts and the density of deposited zinc is given in figure 2.16, for LDPE, and figure 2.17, for HDPE.

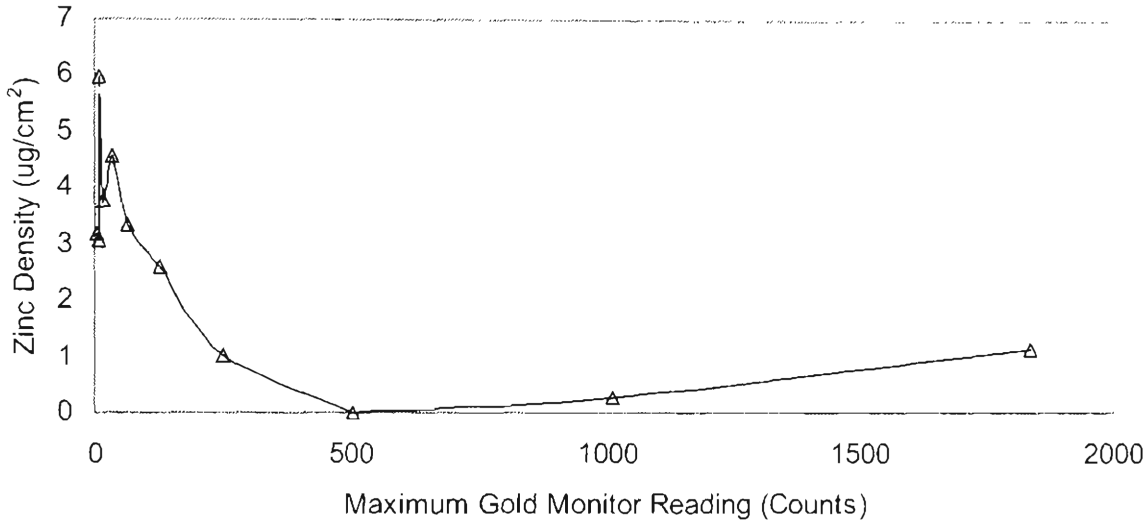


Figure 2.16. Relationship between gold monitor reading and zinc density on clear plastic (LDPE) as measured by ICP-MS

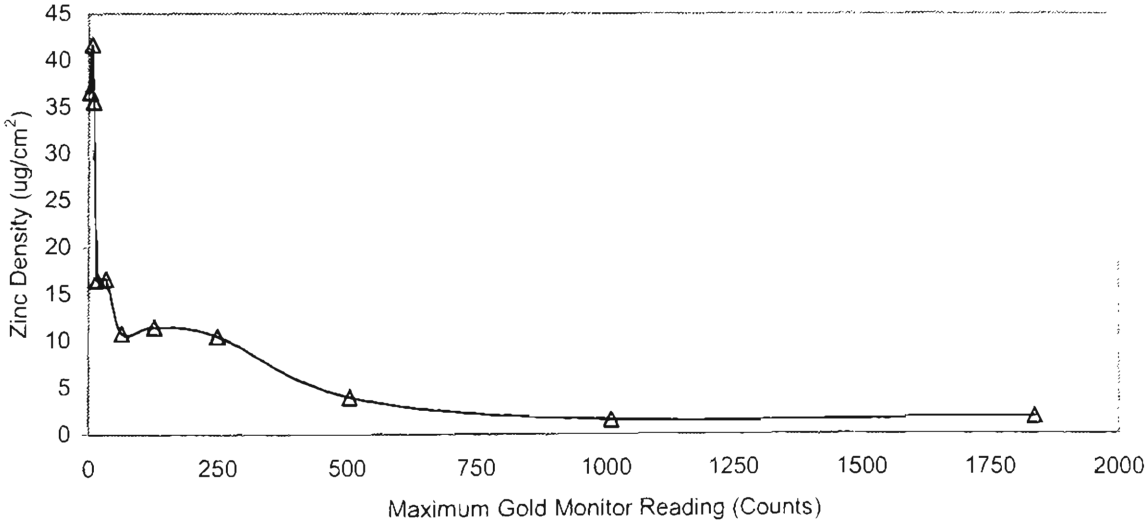


Figure 2.17. Relationship between gold monitor reading and zinc density on green plastic (HDPE) as measured by ICP-MS.

The ICP-MS determination of gold and zinc concentrations permitted the direct comparison of gold and zinc density on the samples, rather than only considering monitor readings as was the case using densitometry. This indicated that the differences seen with fast and slow evaporation of gold were only due to the difference in the amount of gold deposited for the same monitor reading. As can be seen in figure 2.18, the gold evaporation rate had no significant effect on zinc deposition when gold density is considered rather than monitor counts.

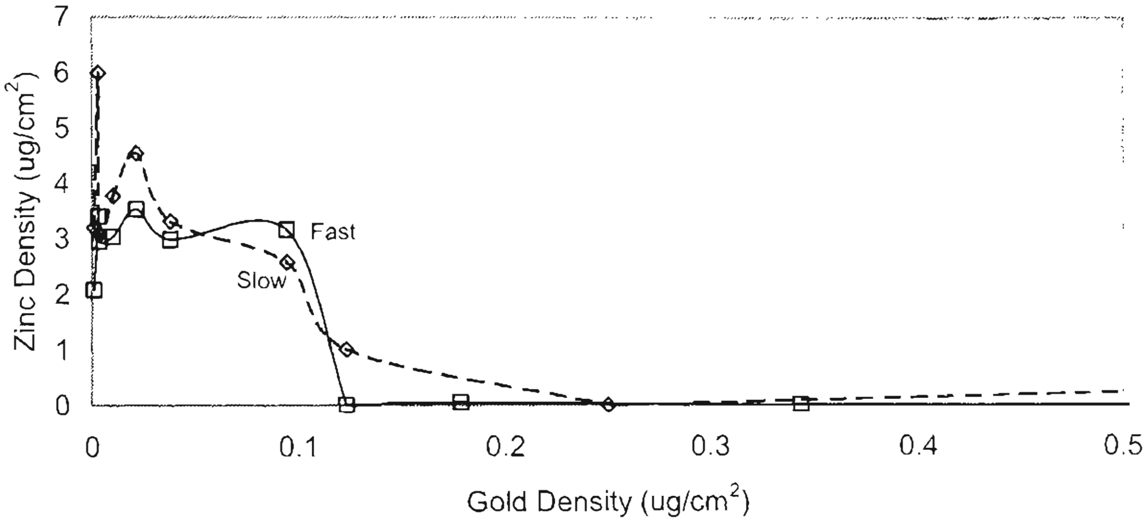


Figure 2.18. Relationship between gold density and zinc density on clear plastic (LDPE) as measured by ICP-MS — effect of fast and slow gold evaporation rates.

Differences between group I and group II plastics

Significant differences in fingerprint development were noted between LDPE and HDPE. Figure 2.19 gives the density of deposited gold for a constant monitor count of 64. Samples A to D represent the four different positions in the VMD chamber where the test squares were placed. The results indicate that there is no significant difference in the density of deposited gold between the two groups of plastics. Hence gold density is not the cause of the differences observed between LDPE and HDPE. Figure 2.20 illustrates a clear difference in zinc deposition observed on the same test squares. For the same density of gold, there is an obvious difference in zinc deposition between LDPE and HDPE.

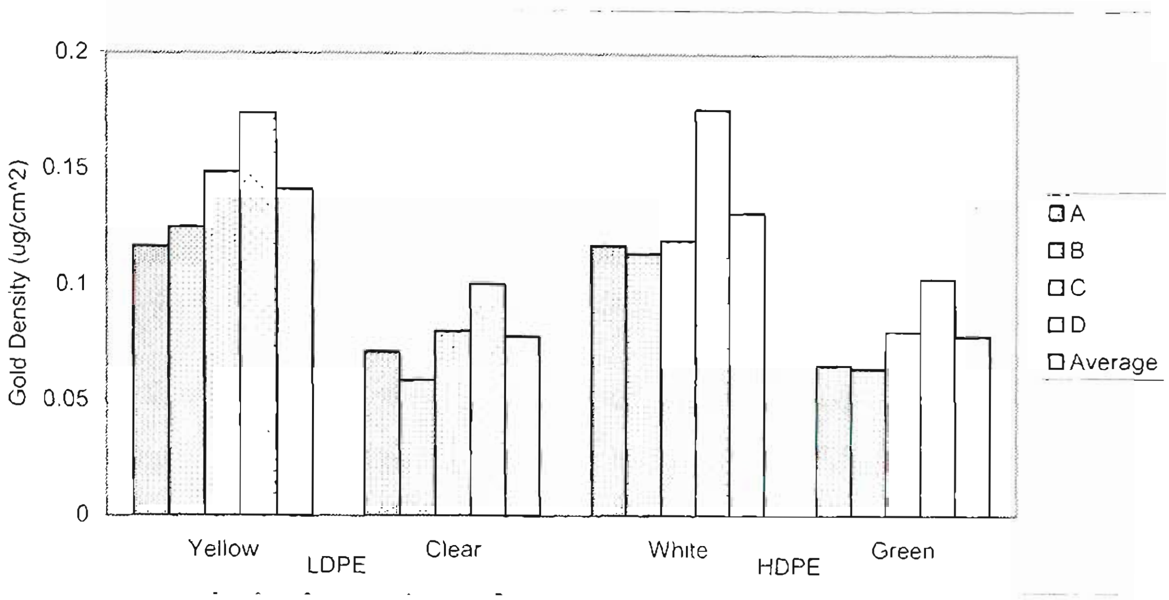


Figure 2.19. Gold density as measured by ICP-MS for plastic samples treated at a constant gold monitor reading of 64 counts. (A, B, C and D represent samples placed at four different positions within the VMD chamber.)

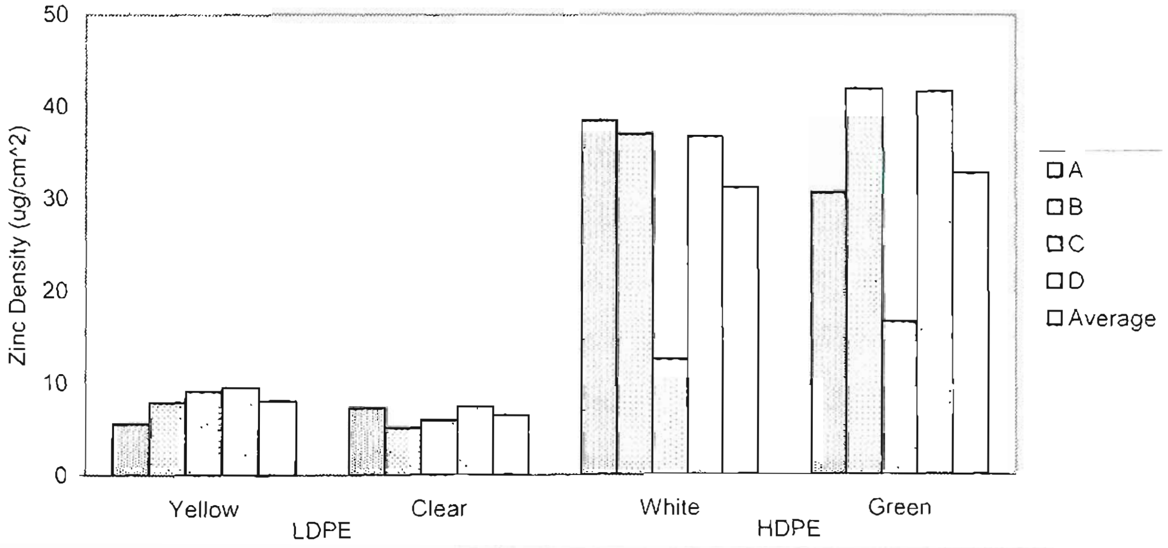


Figure 2.20. Zinc density as measured by ICP-MS for plastic samples treated at a constant gold monitor reading of 64 counts. (A, B, C and D represent samples placed at four different positions within the VMD chamber.)

2.2.4 Discussion

2.2.4.1 Differences in development between polymers

Significant differences were observed between print development on LDPE and HDPE. The types of development obtained and the gold counts necessary for optimum development were found to be dependent on polymer type.

The results from this study demonstrate that, under the same conditions, the amount of deposited zinc varies depending on the nature of the plastic substrate. The quantification of gold on different plastics has shown that plastics developed under the same conditions have a similar gold density on their surface, hence the differences in zinc deposition are not due to differences in the amount of gold. The difference in zinc deposition is most likely due to a difference in structure of the gold film.

The first step of the VMD process is the formation of a thin gold film. Initially small discrete clusters of gold, perhaps down to 2-3 atoms in size, are formed. As more gold is deposited, the number and/or size of these clusters increases. The bonding between gold atoms and the surface determines the structure of the gold film. Cohesion forces between gold atoms are generally stronger than the adhesion forces between gold atoms and the surface. As a result, clusters (or agglomerates) of gold atoms will form (Holland, 1956). Differences in the surface structure of plastics cause variations in the adhesion force between gold atoms and the substrate, and so differences in the gold film structure. These differences will be in terms of the density and size of the gold clusters. It appears that the morphology of the gold clusters is critical to the deposition of zinc.

The significant chemical difference between LDPE and HDPE is in the structure of the polymer molecules. HDPE contains only linear molecules while LDPE is composed of branched molecules. This difference affects the packing of the molecules (Fig. 2.21). HDPE is more closely packed than LDPE, as the side chains prevent LDPE from close packing. This creates differences in surface characteristics between the polymers, which result in differences in the structure of the gold film that is formed.

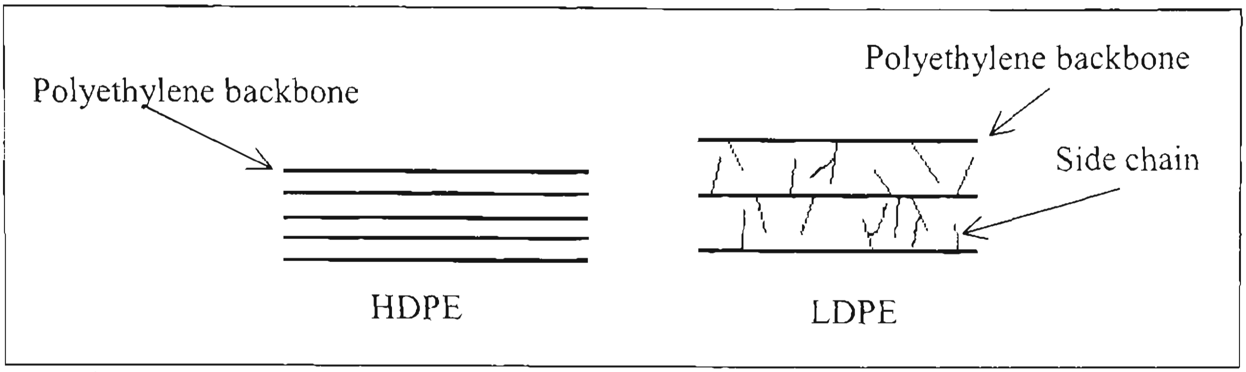


Figure 2.21. Comparison of structures of HDPE and LDPE

For LDPE (clear and yellow plastic), the best zinc deposition occurs at a gold monitor reading of approximately 35 counts, and excess gold will cause reverse development and then no development. The stages of fingerprint development on LDPE are summarised in figure 2.22.

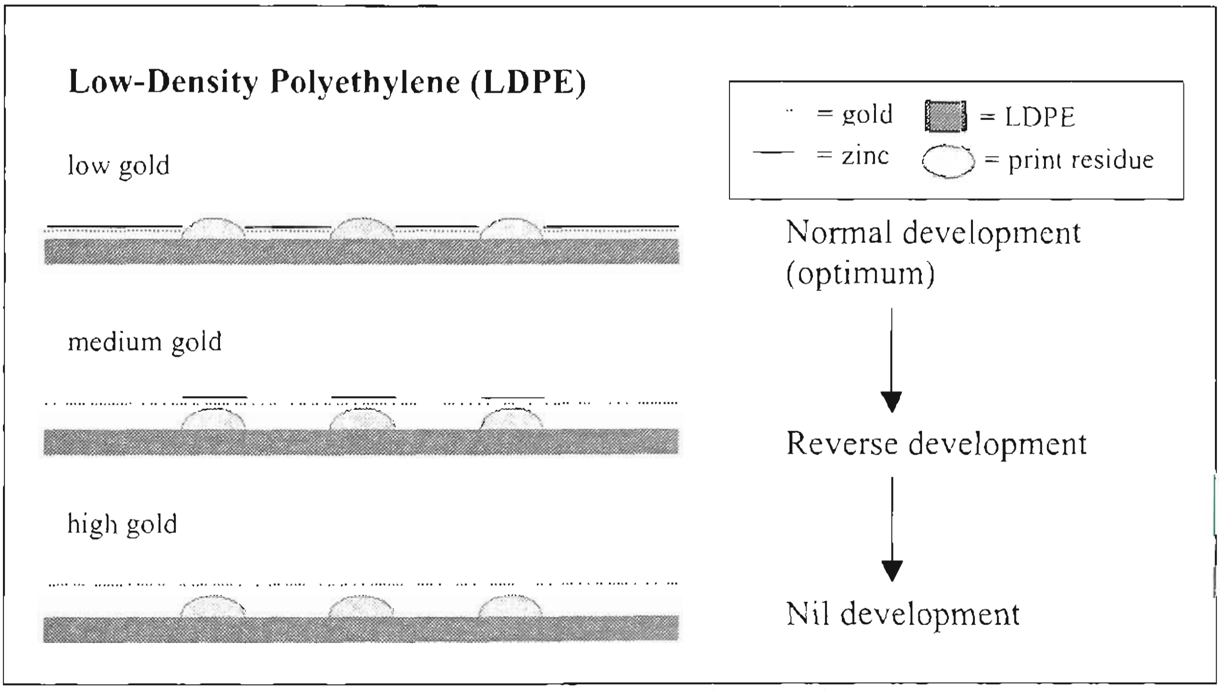


Figure 2.22. Schematic representation of the different stages of VMD development on LDPE substrates as the amount of deposited gold is increased

On LDPE, zinc will no longer deposit after a certain amount of gold has been deposited. As more gold is deposited onto these plastics, the size of the gold clusters will increase. The results suggest that when the gold clusters are relatively small zinc will deposit effectively. However, as the clusters grow in size, there is a point above which zinc will no longer deposit on the gold film. This suggests that once the gold clusters reach a certain morphology they no longer act as nucleation sites for zinc.

For HDPE (white and green plastic), the best zinc deposition occurs at a gold monitor reading of approximately 150 counts, and excess gold will result in overdevelopment. The stages of fingerprint development on HDPE are summarised on figure 2.23.

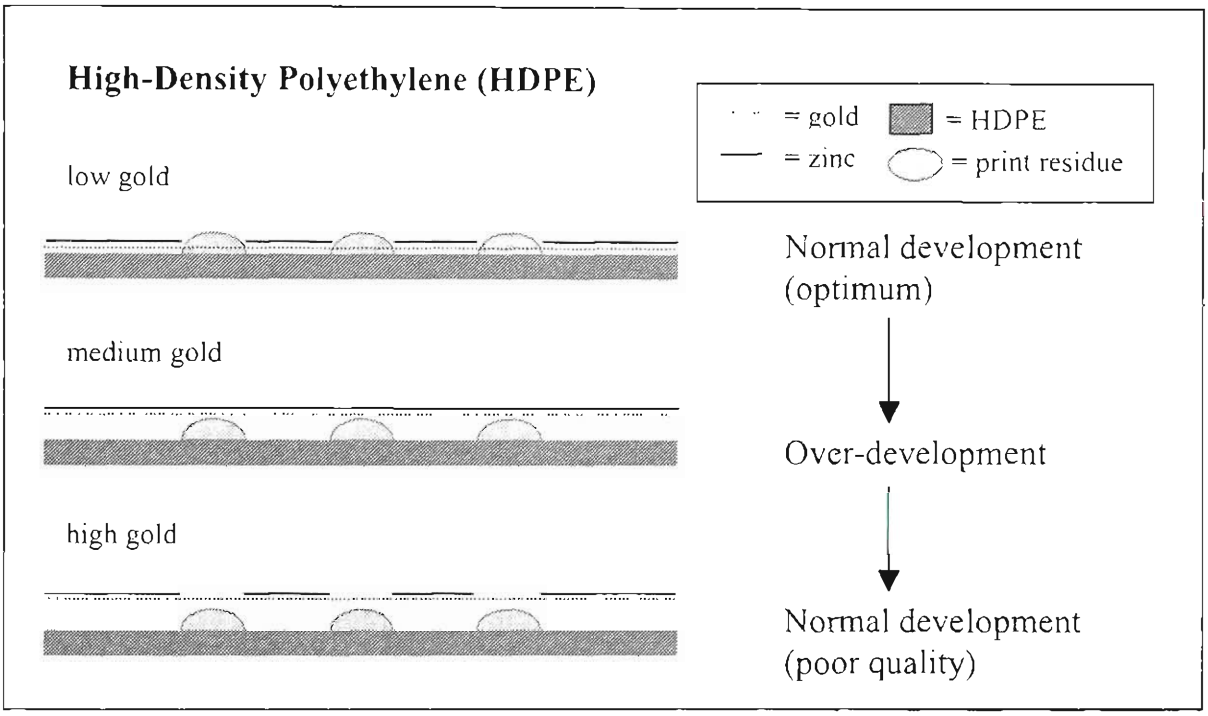


Figure 2.23. Schematic representation of the different stages of VMD development on HDPE as the amount of deposited gold is increased

On HDPE, zinc continues to deposit over a wide range of gold densities, although there is some drop in the amount of deposited zinc with excess gold. This suggests that the gold clusters on HDPE are smaller and more densely packed than those on LDPE (Fig. 2.24). As more gold is deposited, the number of small clusters is increased rather than the size of the clusters. Since the gold clusters remain small, they do not reach the critical morphology that prevents zinc deposition and so they continue to act as nucleation sites for zinc deposition. Gold clusters on HDPE may never reach the critical morphology as coalescence may occur before the clusters reach this state.

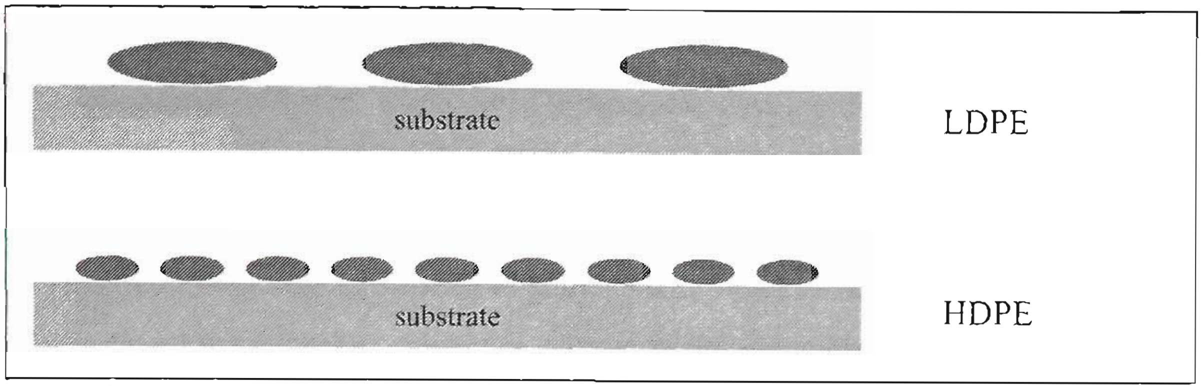


Figure 2.24. Suggested difference between gold clusters on different plastic substrates

2.2.4.2 Reverse development

Possible causes of reverse development have previously been suggested. These results highlight deficiencies in these explanations of reverse development and lead to a new explanation.

Kent and co-workers (1976) suggested that reverse development occurred when mobile organic components from the print residue were absorbed by polythene leaving behind a solid residue of inorganic constituents. As a result, gold penetrates more easily into the polythene than the print residue resulting in preferential deposition onto the print ridges. Results in this study show that, for prints of the same age, from the same donor and on the same surface (LDPE), both normal and reverse development can be achieved depending on the amount of gold deposited on the surface. This indicates that the essential factor determining whether normal or reverse development occurs is the amount of gold rather than the absorption of organic mobile components by the plastic.

Smith (1989) suggested that reverse development is due to sodium chloride crystals in the fingerprint residue. These results show that, for prints of the same age and from the same donor, for which the presence of sodium chloride crystals would be similar, it is possible to develop both normal and reverse prints. The determining factor is not the presence of sodium chloride crystals but rather the nature of the surface and the level of gold deposition employed.

Grant, Springer and Ziv (1996) found that the type of development was related to the surface type on which the prints were deposited. On HDPE, normal development occurred, while on LDPE reverse development occurred. Grant and co-workers suggested that on LDPE reverse development will always occur and on HDPE normal development will always occur as a result of the substrate type. This hypothesis was confirmed to some extent by these findings. The plastic type was found to affect the occurrence of reverse development. Reverse development was found to occur within an identified range of gold deposition levels on LDPE while reverse development was not found to occur on HDPE. However, on LDPE both reverse and normal development are possible depending on the level of gold deposition.

New explanation

As outlined above, the differences in development on LDPE and HDPE are attributed to differences in the morphology of the gold clusters formed on the two surfaces. Once the gold clusters reach a critical morphology they no longer act as effective nucleating sites for zinc.

For low gold monitor counts, zinc will not deposit onto the print ridges resulting in normal development. This is thought to be because the gold is buried in the print residue (Thomas, 1978). As more gold is deposited, gold emerges from the print residue resulting in zinc being deposited onto the print ridges. Zinc deposition onto the print ridges occurs in both over-development and reverse development. The critical difference over-development and reverse development is the zinc deposition onto the background rather than the ridges.

As a result of the structure of the gold film formed on LDPE, when enough gold has been deposited to enable zinc to deposit onto the print ridges, the gold clusters on the background have reached the critical morphology that prevents zinc deposition. The combination of zinc deposition onto the print ridges and not the background is reverse development.

When excessive gold is deposited, no development occurs on LDPE. This stage is reached when the gold clusters on both the print ridges and the background are too large to act as nucleation sites for zinc deposition. For some prints on LDPE there could also be a range of gold deposition levels between normal and reverse development where no fingerprint development occurs. This would occur when the gold clusters on the background are too large to act as nucleation sites but there is insufficient gold on the surface of the print residue to allow zinc deposition.

Grant, Springer and Ziv (1996) reported that they often observed, on LDPE, no zinc deposition for fresh prints (1 day old) but reverse development for older prints (4 weeks). This can be understood with the above explanation of reverse development. Constant development conditions were used that resulted in gold clusters on the substrate that were too large to act as nucleation sites. For the fresh prints (thicker residue along the ridges), there was not enough gold on the surface of the print residue for zinc deposition to occur along the ridges. For older prints that had dried out (thinner residue along the ridges), the same quantity of deposited gold produced gold nucleation sites on the print ridges leading to reverse development.

This understanding of the manner in which gold clusters affect the type of development obtained also explains the development obtained on HDPE. Overdevelopment occurs because, when enough gold has been deposited to allow zinc deposition on the print ridges, zinc will still deposit onto the background as the gold clusters have not reached a critical morphology (size and/or shape). When further gold was deposited onto HDPE (far in excess of that required for optimum development), zinc deposition ceased on the ridges (as was observed with LDPE) as gold clusters on the ridges had grown beyond the morphology critical to zinc deposition.

2.3 Factors affecting VMD development

2.3.1 *Rate of gold evaporation*

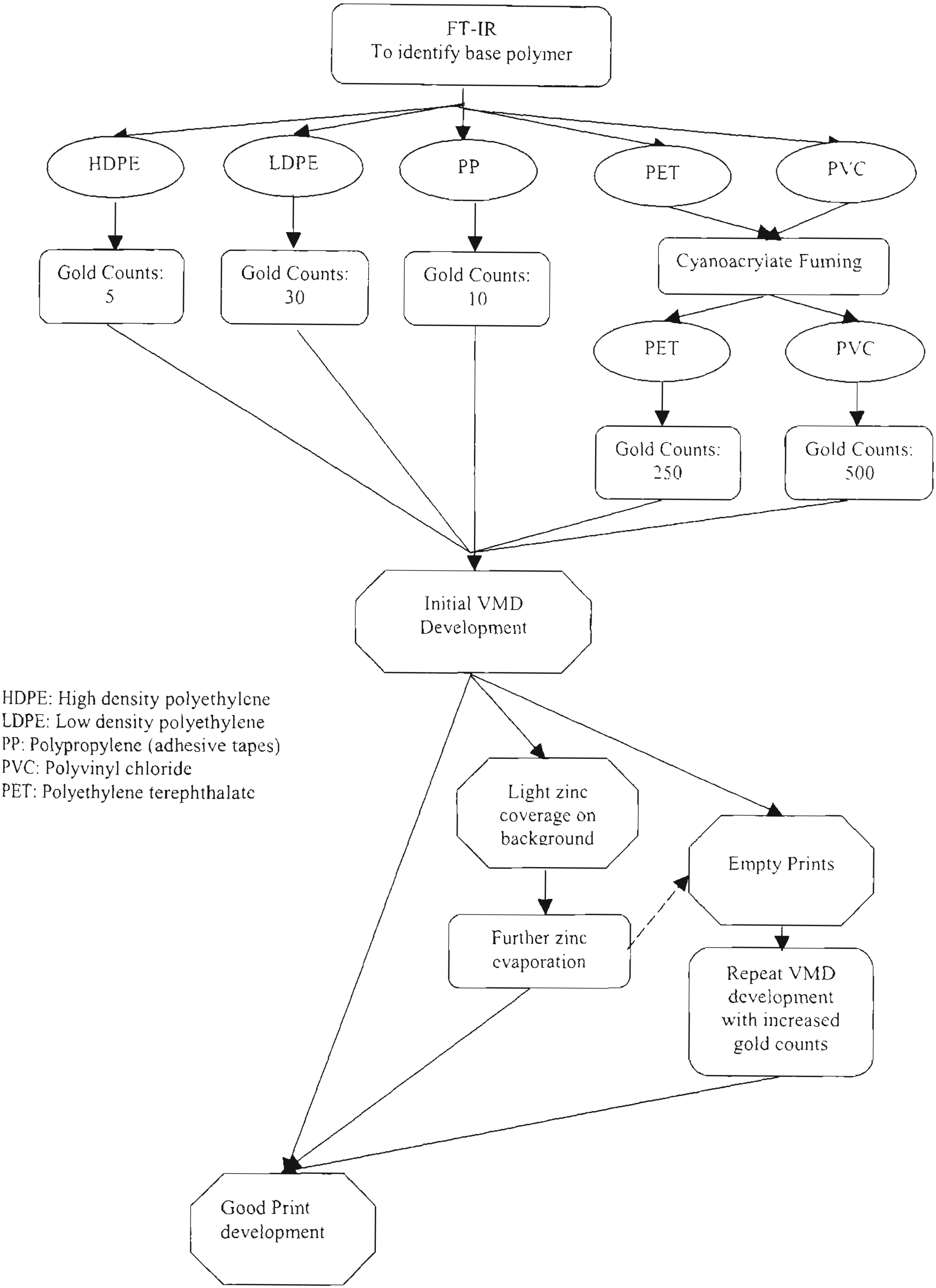
The results obtained show that the rate of gold evaporation affects the amount of gold deposited but not the structure of the gold film. Figure 2.18 (gold density vs. zinc density) illustrates that the rate of gold evaporation does not affect the deposition of zinc. For a given gold density, there is no significant difference in zinc deposition despite a significant difference in gold evaporation rate. This suggests that the rate of gold evaporation does not have a significant effect on the structure of the gold film as a change in the gold film structure would be reflected in a difference in zinc deposition. The quality of fingerprint development was not influenced by the rate of gold evaporation (determined by the gold current) as long as the same quantity of gold is deposited.

The rate of gold evaporation does affect the amount of gold deposited for a given monitor reading. The graphs of monitor reading versus gold density indicate that a slow evaporation rate (i.e. lower gold current) is a more effective way to deposit gold on to the sample. For the same monitor reading, more gold is deposited on the sample using slow evaporation than with the fast evaporation rate (higher gold current). The VMD system employed in this study has a crystal monitor positioned significantly closer to the tungsten boats than the samples to be treated. As a result, the monitor counts recorded can be taken to represent the amount of gold evaporated as opposed to the amount of gold actually deposited on the sample (which was measured by ICP-MS). The higher evaporation rate would be expected to produce gold atoms with a higher kinetic energy. These higher energy atoms appear to be less prone to deposition on the plastic substrates compared to the lower energy atoms produced using the slower evaporation rate (lower current).

2.3.2 *Polymer type*

The important distinction between group I and group II plastics was found to be the base polymer type. The variation of base polymer appears to cause a difference in gold film structure. This creates significant differences in VMD development in terms of the types of development obtained and the gold counts required for optimum development. The results obtained suggest that polymer type is a critical factor in determining optimum conditions for VMD development.

Research conducted by Jones and co-workers (2001) further investigated the suggestion that polymer type is critical to VMD development. VMD development with a range of gold counts was conducted on LDPE, HDPE, polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). The types of development obtained, and the gold counts at which they were obtained, were shown to be dependent on polymer type, confirming that polymer type is critical to VMD development. Figure 2.25 shows the development recommendations developed by this research.



HDPE: High density polyethylene
LDPE: Low density polyethylene
PP: Polypropylene (adhesive tapes)
PVC: Polyvinyl chloride
PET: Polyethylene terephthalate

Figure 2.25. Recommended development conditions for a range of polymers (Jones et al, 2001)

Differences were also seen in VMD development on different plastics with the same base polymer. Generally the same pattern of development was seen within each polymer type but the gold counts at which optimum development occurred varied. The differences observed between polymers in the types of development obtained are more significant than the differences in gold counts seen within a polymer type. This confirms that polymer type has a significant effect on VMD development. The differences between plastics of the same base polymer may be due to the presence of additives, such as plasticisers, dyes and even some metals.

ICP-MS analysis determined the relationship between gold and zinc deposition on each polymer type. The differences in zinc deposition between the different polymer types could not be correlated to differences in gold deposition. No direct relationship is evident between gold and zinc deposition on any of the plastics; an increase in gold does not consistently cause an increase or decrease in zinc deposition. This suggests that the structure of the gold film that forms (i.e. the size, shape and density of gold clusters), and not only the amount of gold deposited, is critical to VMD development. No consistent correlation between gold and zinc deposition was present across the different polymer types. The structure of the gold film, and hence resulting VMD development, is affected by polymer type.

2.3.3 Empty prints

Empty prints, i.e. zinc deposition around the print area but not in the print valleys (Fig. 2.26), were observed during the investigation of reverse development but the factors important to their occurrence were not investigated. Jones and co-workers (2001) investigated the contributing factors in associated research. The strength of a print (i.e. the amount of residue composing the print), the substrate polymer type, and the amount of gold deposited, were found to be contributing factors in the occurrence of empty prints.

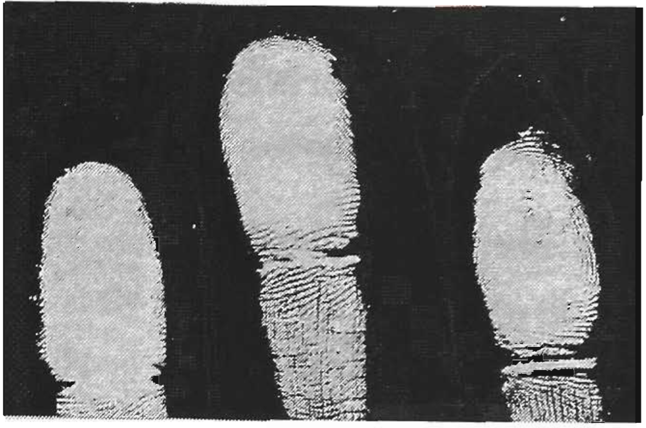


Figure 2.26. Empty Print

Empty prints were found to be more likely to develop with fresh, strong, sebaceous (sebum-rich) prints. Jones and co-workers (2001) suggest that empty prints form when the print residue is so thick that it is no longer perfectly retained in the ridges but seeps into the valleys of the print. Gold could then become buried within the valleys, as it is in the ridges, resulting in no zinc deposition in the print area. (Fig. 2.27)

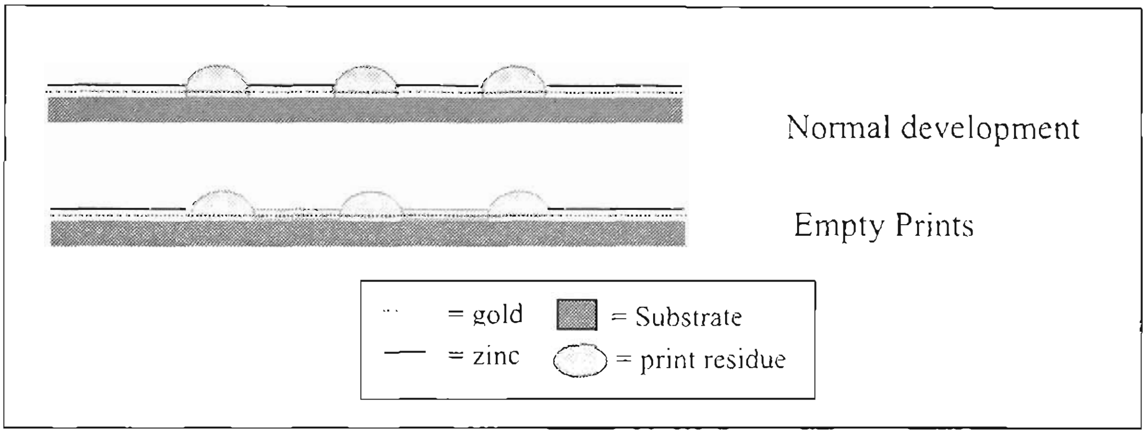


Figure 2.27. The possible differences in fingerprint regions leading to the development of normal prints and to the development of empty prints

Observations supporting the fact that a layer of contamination is produced over the whole area of fingerprint contact have been previously reported (Thomas & Reynoldson, 1975). The superior ability of sebum-rich prints (in comparison to eccrine-rich prints) to inhibit cadmium (and zinc) deposition is also known (Thomas & Reynoldson, 1975). These two observations support the explanation of empty prints presented by Jones and co-workers. In all prints, a contamination layer is present in the valleys. In the case of fresh, strong sebaceous prints, this layer will be thicker and better able to inhibit zinc deposition. The inhibition of zinc deposition in the print valleys causes the phenomenon of 'empty prints'.

Empty prints were also more likely to occur on certain polymer types. Of the polymers used in the study by Jones and co-workers, the occurrence of empty prints was most significant on PET and PVC. The impact of polymer type is explained by the effect of polymer type on the adhesion of a print to the surface. On certain polymers where that adhesion is lower, the print residue more easily diffuses into the print valleys resulting in the development of empty prints.

The amount of gold deposited also has an impact on the development of empty prints. It may be possible to develop print detail within empty prints by retreating the exhibit with VMD using more gold than previously. Instances were also observed where even the deposition of large amounts of gold did not result in the development of print detail. Print residue may be present within the print valley to differing degrees. If there is only a small amount of residue within the valley, then more gold will be needed than on the uncontaminated background but zinc will still deposit in the valley with slightly more gold. If a more significant amount of residue is present within the valley, then even with large amounts of gold, zinc deposition in the valleys will not be possible.

2.3.4 Print characteristics

Jones and co-workers (2001) also investigated the impact of print characteristics on VMD development. The print donor, manner in which the print was deposited, and the age of the print all affect the strength of the print. Jones and co-workers found that the stronger a print is, i.e. the heavier the print deposit, the greater the number of gold counts required to develop print detail. Conversely, the thinner the print residue (whether due to less residue being deposited, the print being aged or subjected to adverse environmental conditions), the less gold will be required for development and the more easily the print will be overdeveloped.

Variability between print donors also impacted on the quality of VMD development. Jones and co-workers developed prints from six donors, which had been collected both with and without extra residue from the donor's forehead. Certain donors consistently gave prints with superior, or inferior, detail in comparison to other donors. (Jones et al, 2001) This is most likely caused by differences in the chemical composition of latent print residue and possible differences in skin morphology between donors.

2.3.5 Impact of CAF

Casework experience demonstrated that treatment of a surface by CAF and staining may have a significant impact on the necessary VMD conditions and the quality of prints developed. The effect of CAF and staining on subsequent VMD on common plastics, LDPE, HDPE, PP, PVC and PET, was investigated by Kiprovich (2001). The presence of CA polymer on the surface of an exhibit was found to affect VMD treatment. Given the influence of polymer type on VMD (section 2.3.2), this is expected.

Strong CA polymer formation on print ridges (i.e. well-developed prints) resulted in zinc deposition onto print ridges at much lower gold counts. Weak CA development has little or no impact on VMD. It is suggested that the mesh of CA polymer formed on well-developed prints prevents the gold atoms from being buried within the print residue, resulting in zinc deposition onto the print ridges.

CA polymer formation on the general surface (i.e. background development) resulted in decreased zinc deposition onto the surface. On some plastics a fuming time existed below which background development was too weak to impact VMD and above which background development had a significant impact on VMD. The presence of background CA polymer was confirmed using FT-IR and was found to be influenced by the individual plastic and the CAF procedure/equipment used.

Applied to print development, this means that strongly CA developed prints will not be further enhanced by VMD treatment although it is possible that weaker prints not developed by CAF may develop with VMD. Background CA development that can occur, particularly with long fuming times, is detrimental to VMD and should be avoided if possible.

2.3.6 Impact of staining

Fluorescent staining was generally detrimental to VMD development. Both of the stain formulations used (Rhodamine 6G in methyl ethyl ketone, isopropanol & water and Basic Yellow 40 in methanol) inhibited zinc deposition. The methanol-based formulation had a more significant effect. Best development will be obtained by treating exhibits with VMD before staining. Development after staining is possible and so VMD treatment of exhibits that have been stained is worthwhile although not ideal. (Kiprovich, 2001)

2.4 Effect of zinc and air on thin gold films

2.4.1 Introduction

Research into the causes of reverse development identified a range of gold counts where very light zinc deposition, and so no print development, occurred on LDPE, due to excess gold deposition. This means that, even though a latent print may be present, the application of excess gold has inhibited effective zinc deposition and no significant print development can occur. In this way, valuable fingerprint evidence can be lost. A method has been developed by which prints can be re-developed in situations like this. The type of development achieved is believed to be controlled by the morphology of the gold clusters formed.

Chapon, Henry and Mutaftschiev (1976), in their work on the 'decoration' of gold nuclei by cadmium, reported that if a system is in contact with air between the evaporation of gold and cadmium, then cadmium will no longer condense on the gold (i.e. the gold clusters become deactivated as nucleation sites). Cadmium and zinc have similar properties and bind to surfaces in a similar manner (Lewis, 1978). Therefore, it is possible that exposure of the gold layer to air will also have an effect on zinc deposition. This consideration lead to the possibility that excess gold deposition could be corrected by exposure to air and then re-treatment by VMD.

2.4.2 Methods

The same two low-density polyethylene (LDPE) samples as used in previous experiments were used as substrates for each experiment. Four consecutive impressions of the index, middle and ring finger of a single donor were placed on each plastic sample. Each middle finger impression was cut in two to enable direct comparison between two sets of development conditions.

Optimum development on LDPE, which occurs at 30 gold monitor counts in the VMD unit employed, was used as the control to which all other development was compared. Excess gold deposition on LDPE occurs at over 500 gold monitor counts in the VMD unit used so gold monitor counts of 800 were used to ensure excess gold deposition. The possibility that exposure to air could deactivate gold nucleation sites was investigated via a number of experiments.

2.4.2.1 Experiment A

Excess gold (800 counts) was deposited on the surface and then the surface was exposed to zinc. Air was then admitted into the chamber. After re-evacuation, optimum gold (30 counts) was deposited and again the surface was exposed to zinc.

2.4.2.2 Experiment B

Excess gold was deposited on the surface and then the surface was exposed to zinc. The chamber remained under vacuum and optimum gold was deposited and again the surface was exposed to zinc.

2.4.2.3 Experiment C

Excess gold was deposited on the surface, the gold boats were allowed to cool, and then optimum gold was deposited. The surface was then exposed to zinc.

2.4.2.4 Experiment D

The combined total of excess and optimum gold (800 + 30 = 830 counts) was deposited in one exposure and then the surface was exposed to zinc.

2.4.2.5 Experiment E

Excess gold was deposited on the surface and then the surface was exposed to zinc before air was readmitted to the chamber. The chamber was re-evacuated and the sample left under vacuum for 4 hours with the vacuum pumps continuously operating. Optimum gold was then deposited on the surface and then the surface exposed to zinc.

2.4.2.6 Experiment F

Excess gold was deposited on the surface then air was readmitted to the chamber. After re-evacuation, optimum gold was deposited and the surface was exposed to zinc.

2.4.2.7 Experiment G

The amount of gold deposited after the deposition of excess gold, exposure to zinc and readmission of air was varied to determine if this would improve the observed development. Quantities representing half (15 counts), one and a half times (45 counts), and double (60 counts) the optimum amount of gold were tested.

2.4.2.8 X-ray photoelectron spectroscopy (XPS)

XPS (or Electron Spectroscopy for Chemical Analysis (ESCA)) analysis was utilised to determine what, if any, chemical interaction occurred between the initial metal layers (gold and zinc) and the air introduced when the chamber vacuum is broken. During XPS analysis, samples are irradiated with x-rays that cause the emission of inner shell electrons (photoelectrons). The energy contained by these electrons is characteristic of the elements present in the surface and the chemical state of these elements. Auger electrons are also emitted; these electrons possess the excess energy released when an outer shell electron drops down to fill the position left vacant by the emission of the photoelectron.

A Vacuum Generators Ltd ESCA 3 was used for the analysis. An aluminium x-ray source set at 50eV was used. For each sample, a general scan over binding energies from 1210 to 80eV was conducted followed by a more detailed scan over the peaks of interest. Peaks were identified by comparison with standard values (Moulder et al, 1995). Charging of the surface being analysed can occur, causing a shift in the binding energies recorded for the peaks. As is standard procedure for interpreting XPS spectra, the known value of the gold $4f_{7/2}$ line (84eV) was used to determine the size of this shift and then all other peaks adjusted accordingly. The charging shift was confirmed using the carbon 1s peak. In one instance (sample vi), the gold peak was obscured by zinc peaks and so the carbon 1s line alone was used to determine the shift due to charging.

All samples were prepared on one of the LDPE substrates used for the above experiments. The samples analysed were:

i) Excess gold

ii) Excess gold, exposed to zinc

iii) Excess gold, exposed to zinc, optimum gold (vacuum maintained)

iv) Excess gold, exposed to zinc, optimum gold, exposed to zinc (vacuum maintained)

v) Excess gold, exposed to zinc, vacuum broken, optimum gold

vi) Excess gold, exposed to zinc, vacuum broken, optimum gold, exposed to zinc

For sample vi, a spot of conducting silver paint was applied to the sample in an attempt to minimise charge build-up. Samples iv and vi were etched using ion bombardment and then reanalysed.

2.4.3 Results

2.4.3.1 Experiment A

Deposition of excess gold on the LDPE samples resulted, as expected, in very minimal, usually invisible, zinc deposition (Fig. 2.28). The deposition of the optimum gold amount on the same samples, after admission of air into the chamber and re-evacuation of the chamber, resulted in normal fingerprint development (Fig. 2.29). The quality of development obtained by this re-treatment process was, however, inferior to that obtained by optimum gold deposition on the same surface.

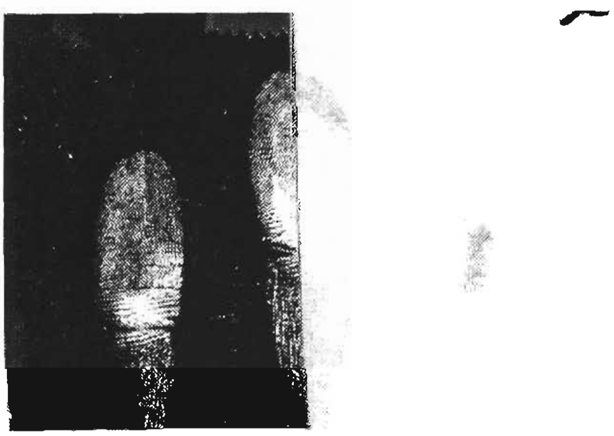


Figure 2.28. Fingerprints on LDPE after VMD treatment: Excess gold deposition (right) compared to optimum gold deposition (left).

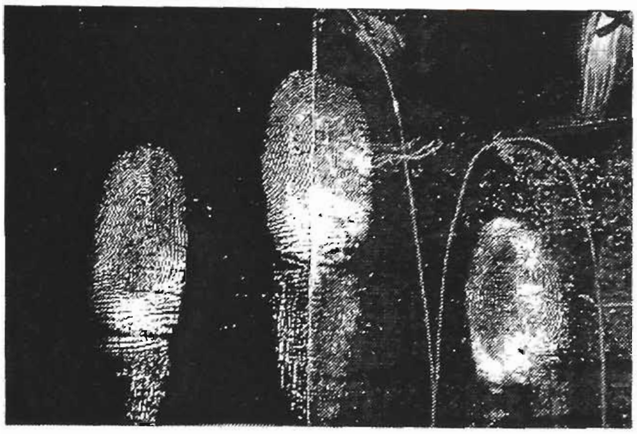


Figure 2.29. Fingerprints on LDPE after VMD treatment: Optimum gold deposition after excess gold deposition and readmission of air (right), compared to optimum gold deposition (left).

2.4.3.2 Experiment B

Inconsistent results were obtained when air was not readmitted to the chamber between the two VMD treatments. On some occasions, the second treatment resulted in normal fingerprint development similar to that observed in experiment A (Fig. 2.30). On other occasions, reverse development resulted with no zinc deposition on the background (Fig. 2.31). These two results were obtained on both LDPE samples employed. Both result types were even observed within the same batch of samples, with differences possibly being due to the position of each sample in the chamber relative to the gold and zinc boats.

Figure 2.30. Fingerprints on LDPE after VMD treatment: Optimum Normal development from optimum gold deposition after excess gold deposition without the readmission of air (right), compared to optimum gold deposition (left).

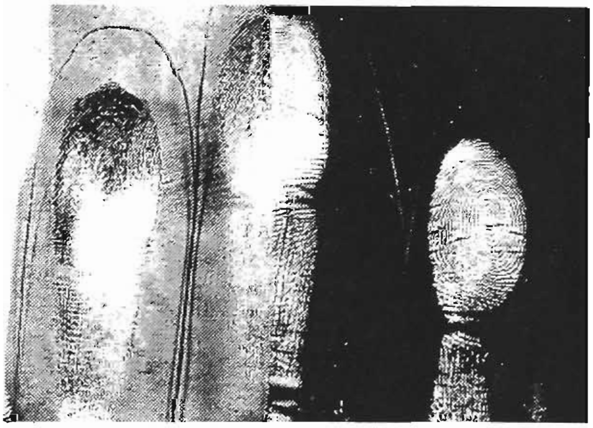


Figure 2.31. Fingerprints on LDPE after VMD treatment: Reverse development from optimum gold deposition after excess gold deposition without the readmission of air (left), compared to optimum gold deposition (right).

2.4.3.3 Experiment C

When the two gold deposition steps were performed without any exposure to zinc, or the readmission of air between them, subsequent zinc exposure resulted in very light, or negligible zinc deposition. The observed development was typical of that resulting from excess gold deposition (Fig. 2.32).

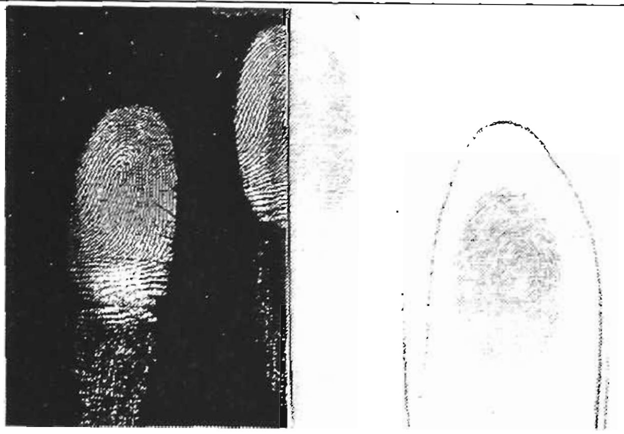


Figure 2.32. Fingerprints on LDPE after VMD treatment: Optimum gold deposition after excess gold deposition without the readmission of air or exposure to zinc (right), compared to optimum gold deposition (left).

2.4.3.4 Experiment D

The deposition, in one step, of the combined total of the excess and optimum gold counts resulted in very minimal zinc deposition as is expected when excess gold is present on a LDPE surface (Fig. 2.33).

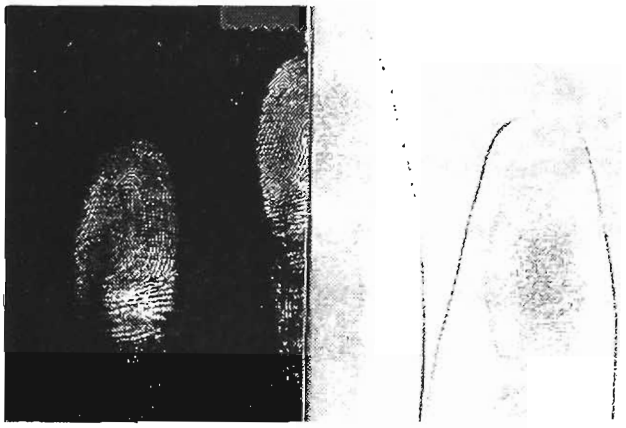


Figure 2.33. Fingerprints on LDPE after VMD treatment: Combined Deposition of combined gold counts amounts (excess + optimum) (right), compared to optimum gold deposition (left).

2.4.3.5 Experiment E

Leaving the samples under vacuum for 4 hours followed by the deposition of optimum gold significantly reduced the positive effects of air exposure observed in experiment A. Reverse development occurred as well as light zinc deposition on the background (Fig. 2.34).

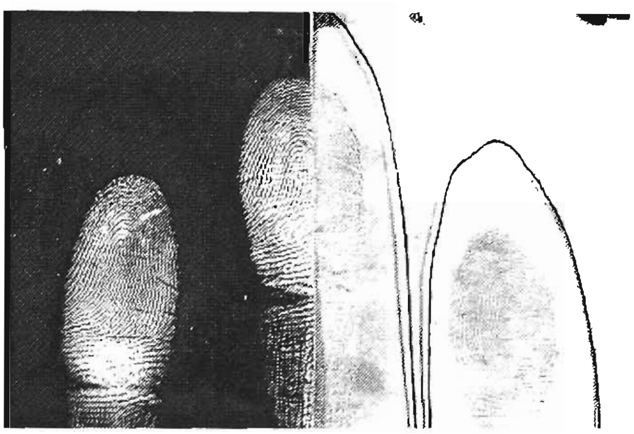


Figure 2.34. Fingerprints on LDPE after VMD treatment: Optimum gold deposition after excess gold deposition and readmission of air and long exposure to vacuum (right), compared to optimum gold deposition (left).

2.4.3.6 Experiment F

The deposition of optimum gold, after the deposition of excess gold and the readmission of air, without exposure to zinc, resulted in light zinc deposition (Fig. 2.35). The zinc deposition was heavier than that normally seen after excess gold deposition but lighter than that seen after optimum gold deposition.

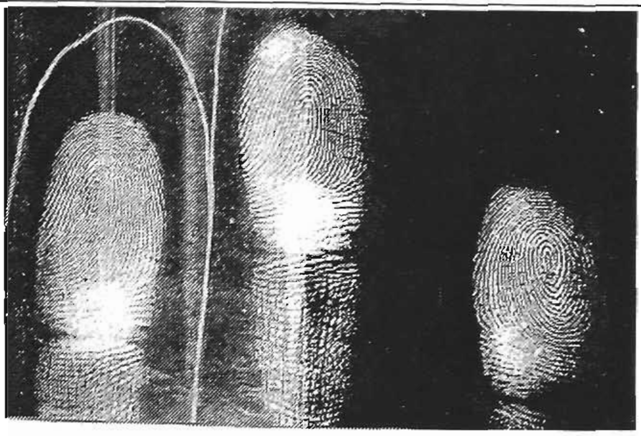


Figure 2.35. Fingerprints on LDPE after VMD treatment: Optimum gold deposition after excess gold deposition, without zinc exposure, and readmission of air (left), compared to optimum gold deposition (right).

2.4.3.7 Experiment G

Use of one-and-a-half-times the optimum gold amount resulted in the best development following excess gold deposition. Optimum gold deposition (30 gold counts) resulted in reasonable fingerprint development (Fig. 2.29), but an increase in the second deposition of gold (to 45 counts) resulted in greater zinc deposition and so superior print detail (Fig. 2.36). Using half the optimum gold (15 counts) resulted in poor development (Fig. 2.37). Similarly, doubling the amount of gold (60 counts) lead to inferior results more typical of excess gold deposition (Fig. 2.38).

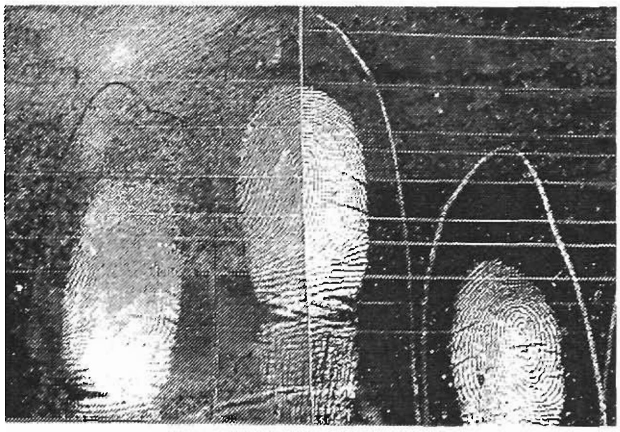


Figure 2.36. Fingerprints on LDPE after VMD treatment: Slightly increased optimum gold deposition (45 counts) after excess gold deposition and readmission of air (left), compared to optimum gold deposition (30 counts) (right).

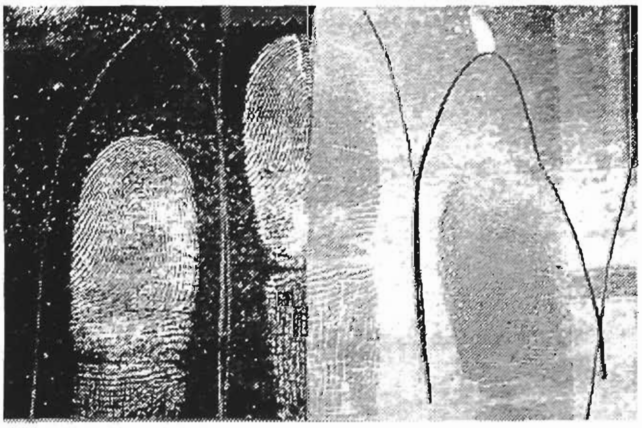


Figure 2.37. Fingerprints on LDPE after VMD treatment: Half of optimum gold deposition (15 counts) after excess gold deposition and readmission of air (right), compared to optimum gold deposition (30 counts) (left)

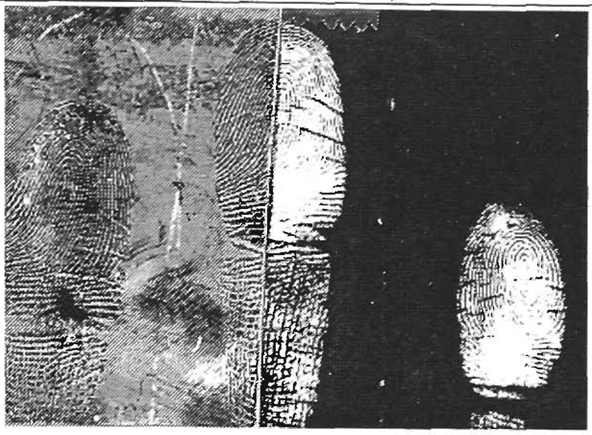


Figure 2.38. Fingerprints on LDPE after VMD treatment: Double optimum gold deposition (60 counts) after excess gold deposition and readmission of air (left), compared to optimum gold deposition (30 counts) (right).

2.4.3.8 XPS

XPS data from the experiments is contained in Table 2.1. Expected peak positions for zinc and oxygen are contained in Table 2.2 (Moulder et al, 1995).

Table 2.1 XPS results

Sample	**Shift due to charging (eV)**	**Position of peak after adjusting for shift due to charging (eV)**	
		Oxygen 1s	**Zinc $2p_{3/2}$**
i	6.0	(532.2)	-
ii	6.0	532.6	1022.7
iii	5.6	532.2	1022.7
iv	9.0	532.0	1022.0
iv (etched)	3.0	(532.0)	1022.0
v	6.0	532.4	1022.7
vi (with spot of silver conducting paint)	1.6	531.3	1021.6
vi (etched) (without silver paint)	6	(530.4)	1021.7

Table 2.2 Published XPS data (Moulder et al, 1995)

Compound	**Published Value (eV)**	
	Oxygen 1s	**Zinc $2p_{3/2}$**
Zinc Metal (Zn)	-	1021.8
Zinc Oxide (ZnO)	530.4	1022.5
Water (H_2O)	533.2	-

By considering the ratio of carbon 1s and oxygen 1s in a sample of 'clean' plastic, the oxygen peaks from samples i, iv (etched) and vi (etched) were determined to be only slightly larger than the oxygen peak that would be expected from the plastic base. Hence these oxygen peaks were considered to be predominately due to oxygen on the polymer substrate.

Surface charging was decreased by the application of conducting silver paint but the values determined were not significantly different from those obtained when the silver paint was not used.

The positioning of the zinc peaks indicate the presence of zinc oxide in samples ii, iii and v, zinc metal in sample vi, and possibly a combination of both zinc metal and zinc oxide in sample iv. Sample vi had a much thicker layer of zinc than the other samples so it is possible that zinc oxide is present but zinc metal dominates.

The position of the oxygen peak does not correlate with zinc oxide. This could be due to contributions to the oxygen peak from other sources. The XPS spectrum of the plastic base contains an oxygen peak, hence there is a contribution from oxygen present in the plastic base. There could also be a contribution from moisture on the surface. The presence of water on the substrate would result in a shift of the oxygen peak to a higher binding energy. The etching of samples d and f resulted in a significant decrease in the height of the oxygen peak showing that oxygen has been removed by etching the surface.

Hence, the XPS results indicate that, when air is readmitted into the vacuum chamber, a thin layer of zinc oxide forms on top of the zinc layer. Water or air molecules may also be adsorbed by the sample

2.4.3.9 Summary

Table 2.3 summarises the results and implications of the experiments conducted.

Table 2.3 Summary of results from experiments investigating the effect of zinc and air on thin gold films

Experiment	**Treatment of sample**	**Result**	**Indications from results**
A	Excess gold Zinc Vacuum Broken (exposure to air) Optimum gold Zinc	Normal development	Exposure to zinc and air have a significant effect on the gold film
B	Excess gold Zinc Optimum gold Zinc	Normal or reverse development	Exposure to zinc alone does not have the complete effect
C	Excess gold Optimum gold Zinc	Very light zinc deposition	Effect not due to deposition of gold in 2 steps
D	Excess + optimum gold Zinc	Very light zinc deposition	Effect not due to total amount of gold

E	Excess gold Zinc Vacuum Broken (exposure to air) Under vacuum for 4 hours Optimum gold Zinc	Very light zinc deposition and reverse development	Vacuum decreases the effect. Effect due to physical adsorption
F	Excess gold Vacuum Broken (exposure to air) Optimum gold Zinc	Very light zinc deposition	Exposure to air alone does not have the complete effect
G	Excess gold Zinc Vacuum Broken (exposure to air) 0.5, 1.5 or 2 x Optimum gold Zinc	Best development obtained with 1.5 x optimum gold	Optimum amount of gold to use after excess gold is 1.5 x optimum amount

2.4.4 Discussion

Excess gold deposition on low-density polyethylene (LDPE) can inhibit subsequent zinc deposition. It is believed that this is due to the morphology of the clusters (or 'agglomerates') of gold atoms. Once the gold clusters grow beyond a certain size and/or shape, they no longer act as effective nucleation sites for zinc deposition.

These results indicate that exposure to zinc followed by the readmission of air to the VMD chamber has a significant effect on the thin layer of deposited gold. Gold that is deposited after exposure to zinc and the readmission of air (and subsequent re-evacuation of the chamber) appears to behave more like gold deposited onto a 'gold-free' surface than gold deposited onto a surface with excess gold. This can be seen by comparison of the development observed in experiments A and C. The poor zinc development observed in experiment C is as would be expected from excess gold deposition. However, in experiment A, normal zinc development is observed, as would be the case after optimum gold deposition. These results suggest that the majority of the second quantity of gold deposited onto the surface forms new gold clusters (some of the gold deposited during the second treatment is believed to combine with the gold clusters formed by the initial gold deposition). The new gold clusters have the correct morphology to enable good zinc deposition, therefore producing normal fingerprint development.

The second deposition of gold forms new gold clusters as the primary gold clusters have been deactivated by zinc and air. Both zinc and air are necessary to deactivate the gold clusters; neither is effective on its own. Zinc and air form a 'contamination layer' on the primary gold film that prevents, to a certain extent, the new gold from adding to the already present gold clusters. XPS analysis confirmed that a small amount of zinc deposits onto the layer of 'excess' gold. It is still uncertain why a small amount of zinc will deposit yet zinc does not continue to build up a significant layer.

When air is readmitted to the chamber, a thin layer of zinc oxide forms and water and air molecules adhere to the surface. The formation of zinc oxide explains the necessity of both zinc and air for effective deactivation. Lengthy exposure to vacuum is believed to remove the adsorbed air and water molecules thus reducing the deactivation effect.

The second VMD treatment can produce good quality prints although the development achieved after excess gold deposition is of lesser quality than that obtained by depositing the optimum quantity of gold at the outset. Depositing the optimum amount of gold the first time is hence preferable but it is nevertheless possible to develop prints after excess gold deposition. Correction for excess gold deposition is best achieved via exposure to zinc and readmission of air followed by reapplication of gold. As some of the newly deposited gold will join the already present gold clusters, approximately 1.5 times the optimum gold count for the surface will result in the best development.

The indication that a subsequently deposited gold film partially combines with the already present gold film, after zinc deposition and exposure to air, has further implications for VMD development. During VMD development, more than one treatment may be required to achieve good development — an exhibit will be treated with VMD, removed from the chamber for examination, and then returned to the chamber in the hope that further treatment will develop greater print detail or improve contrast. The results from this study indicate that the second VMD process will be almost independent from the first treatment. This must be taken into account when determining the amount of gold required for the second development. If the second gold layer is less than 1½ times the initial gold layer, then no further development will be achieved. Gold counts in excess of twice those initially employed may be required if under-development is to be corrected by a second VMD treatment. The application of these findings is pertinent for all polymer substrates, not just LDPE.

2.5 Contributions to greater understanding of VMD

A greater understanding of VMD and the factors that control development has been obtained through the research conducted.

2.5.1 Gold deposition

The amount of gold deposited is a critical factor for VMD development and so controlling gold thickness is essential for consistently good development. The more accurately gold deposition can be controlled the more consistent development will be. In the case of LDPE, an excess of 30 gold counts could be the difference between good quality normal development and the region where reverse development might occur.

Many users of VMD control development by controlling zinc rather than gold deposition. Standard VMD procedures (Kent, 1986; Trozzi et al, 2000) use an approximate weight of gold and heat the gold boats until all the gold has evaporated. The fingerprint development achieved is then determined by controlling zinc deposition. Controlling developing using zinc evaporation may be successful in some circumstances while controlling development using gold evaporation will be successful in all circumstances. For example, over-development can be prevented by controlling zinc evaporation but reverse development and empty prints can only be avoided by controlling gold evaporation. As the amount of gold deposited is a critical factor in VMD development, proper control of this will result in consistently superior development.

For all the VMD results reported in this thesis, a quartz crystal monitor positioned within the chamber was used to monitor and control gold evaporation. This proved to be an accurate and consistent way of controlling gold evaporation. Attempts were made to control gold deposition using current and time but this did not prove to be an accurate way of controlling gold evaporation. This is most likely due to the impact the amount of gold present on the boat has on the current running through the boat.

The relationship between gold counts recorded on the crystal monitor and the amount of gold deposited on a sample is dependent on a few factors. These factors include the position of the monitor relative to the gold boats and the surface being treated, the rate of gold evaporation and the settings on the monitor. As these factors will vary between VMD units the gold counts recorded in this thesis will not be directly transferable to other VMD units. Relative values will be applicable to all VMD units.

2.5.2 Polymer type

Another critical factor in VMD development is the polymer type being treated. This research and that by Jones and co-workers (2001) has shown that VMD conditions, especially the amount of gold evaporated, must be tailored to the polymer type being treated. There is no one set of conditions that will result in good development on all polymers. The types of development obtained and the gold counts required for optimum development are dependent on polymer type. The results suggest that the surface characteristics of the different polymers affect the binding of the gold atoms to the surface, thus affecting the structure of the gold film formed. The morphology of the resulting gold clusters is believed to be a critical factor in the zinc deposition.

Differences were also found between plastics of the same polymer type, but these differences were less significant than the differences between different polymer types.

General development guidelines based on polymer type can be established with an indication of the types of development that will generally be obtained. Suggested conditions for good development can be given, but an allowance must be made for variations within the same polymer category. It is beneficial to determine the polymer type being treated before commencing VMD treatment. Polymer type can be quickly and easily determined using Fourier Transform Infrared spectroscopy (FT-IR) (Suzuki, in: R. Saferstein, 1993). While actual gold counts will vary between VMD units, relative values (such as those indicated by Jones et al (2001)) will be useful to all operators.

2.5.3 Reverse development

Both polymer type and the amount of gold deposited are contributing factors in the occurrence of reverse development. The morphology of the gold clusters appears to be critical to zinc deposition; once the clusters reach a certain size and/or shape, they are no longer effective nucleation sites for zinc deposition. A small amount of zinc still deposits onto these clusters but the reasons why zinc does not build up to a visible layer are still unclear.

When normal development occurs, zinc does not deposit on the print ridges as the gold is buried within the print residue and so cannot act as a nucleation site for zinc. If enough gold is deposited then the gold clusters can grow such that they emerge from the print residue and so zinc can deposit onto the print ridges. This occurs in over-development as well as reverse development.

Reverse development results when the gold clusters on the background are too large to act as effective nucleation site for zinc and when the gold clusters on the print ridges are the appropriate size for zinc deposition. Reverse development was only seen to occur on LDPE within a certain range of gold counts.

Reverse development can be prevented by the deposition of the appropriate amount of gold.

2.5.4 Empty prints

Polymer type and amount of gold deposited were also contributing factors in the development of empty prints. The strength of a print (i.e. the amount of residue composing the print) was also found to be significant. Fresh, strong, sebaceous prints on certain polymers are most likely to develop into empty prints. Jones et al (2001) suggest that on certain polymers with strong prints the print residue is not perfectly retained within the print ridges but diffuses into the print valleys resulting in empty prints. In some instances it is possible to develop print detail in empty prints by retreating the exhibit with VMD using more gold but in others even the use of large amounts of gold will not result in the development of print detail.

2.5.5 Effect of air and zinc

Air and zinc have been shown to have a significant effect on thin gold films. This has significant implications for VMD development.

A small amount of zinc was shown to deposit even in situations when the zinc layer is invisible. When air is readmitted into the vacuum chamber, oxidation of the outermost zinc layer results in the formation of zinc oxide. Air, and particularly water, molecules are also believed to be adsorbed onto the surface. The presence of the zinc oxide film, and adsorbed air and water molecules, deactivates the gold clusters. When new gold is deposited onto the surface, a majority of the gold creates new gold clusters rather than adding to those already present.

This has two major implications for VMD development. If excess gold has been deposited on LDPE such that no fingerprint development has occurred, then normal development can be obtained by readmitting air into the chamber and retreating the exhibit with an appropriate amount of gold. Not all of the new gold will form new clusters, so more gold will be required than would be the case for an untreated surface. It was found that one-and-a-half times the optimum gold required for an untreated surface will be required to achieve the best development on a surface previously exposed to excess gold.

The second implication is applicable to all polymer types. Exhibits will often be treated more than once with VMD to obtain the best development. A natural assumption might be that the second treatment would have a combined effect with the first, i.e. that if the first treatment used 100 gold counts then treating a second time with 100 gold counts would double the development. The effect of air and zinc means that this is not the case. Due to the deactivation of the gold clusters by zinc oxide and air and water molecules, the newly deposited gold does not combine with the already present gold clusters but rather a majority of the gold forms new gold clusters. Hence, when retreating an exhibit after air has been readmitted in the chamber, using less than 1½ times the previously used gold counts will result in no improvement in development, at least double the previously used gold is required if a significant improvement in development is to be obtained.

2.5.6 Effect of CA and staining

Treatment by CAF and luminescent staining can have a significant impact on subsequent VMD development. The presence of CA polymer on a surface will effect VMD development. If a significant amount of CA polymer has formed on either the print ridges or the background then VMD will not further enhance the prints present but if no significant CA polymer formation has occurred then VMD can be successfully used after CAF. As luminescent stains are detrimental to VMD, VMD is best applied before staining although VMD can be successful after staining. (Kiprovich, 2001)

2.6 Conclusion

The major factors that must be appreciated by VMD users to permit consistently superior VMD development are as follows:

- Gold deposition is the most critical factor in VMD development and must be accurately controlled (the use of a thickness monitor is critical);
- VMD conditions must be tailored to the polymer type being treated (and hence the polymer type must be determined before proceeding);
- Reverse development and empty prints are a function of polymer type but may be prevented by using correct gold deposition; and,
- Previous treatment of a surface, with CAF, staining or VMD, will affect the gold counts necessary for optimum development.

Current standard operating procedures generally do not take these factors into account and so must be changed to incorporate these considerations.

The implementation of these recommendations will lead to more accurate and efficient use of VMD. It is hoped that this will result in more wide spread use of this very sensitive technique.

3 Evaluation of Multi-Metal Deposition II

3.1 Introduction

The original MMD formulation (Saunders, 1989) has not received widespread use due to its complexity and mediocre results. Recent optimisation of MMD (Schnetz, 1999; Schnetz & Margot, 2001) has resulted in a new formulation, termed Multi-Metal Deposition II (MMDII), which reportedly gives improved sensitivity and specificity. The initial section of this chapter is an evaluation of this new MMD formulation in comparison to the old formulation to verify the results reported by Schnetz and to further investigate the application of this new formulation. A determination of correct sequencing with other fingerprint detection techniques was also made. The optimised sequence was then compared to those involving CAF, luminescent staining, and VMD for the detection and enhancement of latent prints on non-porous surfaces.

3.2 Materials and methods

3.2.1 MMD formulations

All four combinations of colloidal gold and physical developer formulations from the original MMD and the new MMDII were used within this study. Table 3.1 shows the details of each formulation. Procedures for the preparation of the colloidal gold and physical developer solutions used and the treatment of exhibits are outlined in appendix 3.

Table 3.1 MMD reagent combinations evaluated.

MMD Formulation	**Source**	**Colloidal Gold Solution**	**Physical Developer Solution**
MMDI	Saunders (1989)	30 nm colloidal gold	Iron(II)/Iron (III) & silver nitrate
MMDII	Schnetz (1999) Schnetz & Margot (2001)	14 nm colloidal gold	Hydroquinone & silver acetate
MMDIII	UK Forensic Science Service (Brennan, 2001)	30 nm colloidal gold	Hydroquinone & silver acetate
MMDIV	Fourth possible combination of reagents	14 nm colloidal gold	Iron(II)/Iron (III) & silver nitrate

3.2.2 Comparison of MMD Formulations

3.2.2.1 Non-porous surfaces

The non-porous surfaces used in the comparisons are listed in table 3.2.

Table 3.2 Surfaces used for the comparison of MMD formulations.

Clear Plastic Clip Lock Bag	White Textured Shopping Bag
Orange Garbage Bag	Clear Shopping Bag
Green Garbage Bag	White Bin Liner

Initially, comparisons were conducted between the first three formulations on the whole range of plastics using 4 successive fingerprint impressions. Latent prints that were less than 2 weeks old and others that were more than 2 months old were used.

Using only clear plastic samples, comparisons between all 4 formulations were conducted on prints that had been weathered for 3 days and 1 week.

Using prints on clear plastic that had been weathered for 3 days and 1 week, comparisons were also conducted between MMDII, MMDII plus repeated treatment with the silver acetate/hydroquinone physical developer, and MMDII plus treatment with the silver nitrate/iron(II)/iron(III) physical developer.

3.2.2.2 Polymer banknotes

The development achieved by MMDI, MMDII and MMDIII was also compared on polymer banknotes, using 2-day, 2-week and 1-month-old latent prints.

3.2.2.3 Porous surfaces

Initial results on paper were not promising, indicating that conventional physical developer (PD) might still be the technique of choice on porous surfaces. Hence, instead of comparison between the different MMD formulations, comparisons were conducted between PD, MMDI and MMDII. The paper samples used are listed in table 3.3, with latent prints being aged 5 days and 3 months before treatment.

Table 3.3 Porous surfaces used for the comparison of PD, MMDI and MMDII.

White Photocopy Paper	Brown Paper
White Lined Writing Pad Paper	Yellow Envelope
Recycled Lined Paper	Yellow Thin Paper
Printed Note Pad Paper	Newspaper
Magazine	Advertising Brochure

3.2.3 *Enhancement of colloidal gold by zinc deposited under vacuum*

The possibility of enhancing colloidal gold development by zinc deposited under vacuum was investigated. Samples of fresh prints on clear plastic samples were treated with either 14 nm or 30 nm colloidal gold solution for 15 minutes. The samples were washed in ultra-pure water and then dried before being placed in the VMD unit. After vacuum was achieved, the samples were exposed to evaporated zinc. Zinc was evaporated for 3 minutes using a current of approximately 135 A.

3.2.4 *Sequencing of MMDII*

3.2.4.1 Non-porous surfaces

For the purposes of these experiments, clear plastic clip lock bags were taken to be typical of non-porous surfaces and were used for all experiments.

Cyanoacrylate fuming

As previous research (Irrausch, 1991; Allman et al. 1992) disagreed about the usefulness of MMD after CAF, an investigation of the impact of CAF on MMD was conducted. The MMDII development obtained following increasing fuming times was compared to the development obtained on control sections that had not been treated with CAF. CAF times of 10, 20, 40 and 80 minutes were used.

As CAF was found to have an impact on MMD development, comparisons were conducted to determine the effect of increased fuming times. Control sections were fumed for 10 minutes while corresponding sections were fumed for 20, 40 or 80 minutes. All sections were treated with MMDII and the development obtained compared.

Luminescent staining

Comparisons were also conducted to determine if MMD could be successfully used after CAF and luminescent staining. Control sections that had been treated with CA fuming for 10 minutes and then developed using MMDII were compared to sections that had been treated with CA fuming for 10 minutes, stained with either Rhodamine 6G or Basic Yellow 40, and then developed using MMDII.

As staining was found to have an impact on MMD development, an attempt was made to determine if this was due to an influence of the binding of the colloidal gold solution or the deposition of silver from the physical developer. Samples the same as those above were used, but these were treated with only the colloidal gold solution or the physical developer solution.

3.2.4.2 Polymer banknotes

Two-day-old prints on new notes were used for this set of experiments.

Cyanoacrylate fuming

The effect of CAF on MMDII development on polymer banknotes was investigated by comparing the MMDII development obtained after various fuming times to the development obtained with MMDII alone. Fuming times of 10, 30 and 90 minutes were evaluated.

Luminescent staining

The effect of staining was investigated via comparison between CAF/MMD and CAF/stain/MMD, and also between MMD and CAF/Stain/MMD. Basic Yellow 40 was used as this is the standard stain used on banknotes.

3.2.5 Comparison of MMD and VMD sequences on non-porous surfaces

Preliminary results indicated the MMD should be used following CAF treatment and staining. Hence CAF/stain/MMD was compared to 3 other sequences: CAF/stain, CAF/stain/VMD and CAF/VMD/stain. While CAF/VMD/stain is considered the optimum sequence (Kiprovich, 2001), in operational situations CAF/stain is commonly applied hence comparison between VMD and MMD after this combination was important.

The prints used for these comparisons had been exposed to varying forms of artificial and genuine weathering. Prints that were artificially weathered were soaked in deionised water for increasing times (1 hour, 4 hours, 8-10 hours, 24 hours) and were then heated in an oven at 60^{0} for the same length of time. Genuinely weathered prints were left outdoors, in a location that would be exposed to rain and sun, for increasing times (overnight, 1 day, 2 days, 3 days, 1 week, 2 weeks).

All prints were fumed with CA for 2 hours and stained with the standard Rhodamine 6G formulation. VMD treatment started with 30 gold counts followed by zinc deposition. The treatment was repeated, doubling the gold counts each time, until good zinc deposition was obtained.

As determined by the results to section 3.3.1.1, development by MMDII was followed by re-treatment with the silver acetate/hydroquinone physical developer if development was not strong.

3.3 Results

3.3.1 *Comparison of MMD formulations*

3.3.1.1 Non-porous surface

MMDII consistently developed superior detail to MMDI (Fig. 3.1). Ridges developed by MMDII were generally finer, with better definition of pores and edges. MMDI resulted in stronger silver deposition than MMDII in many instances especially with older prints. This was generally accompanied by stronger background development.

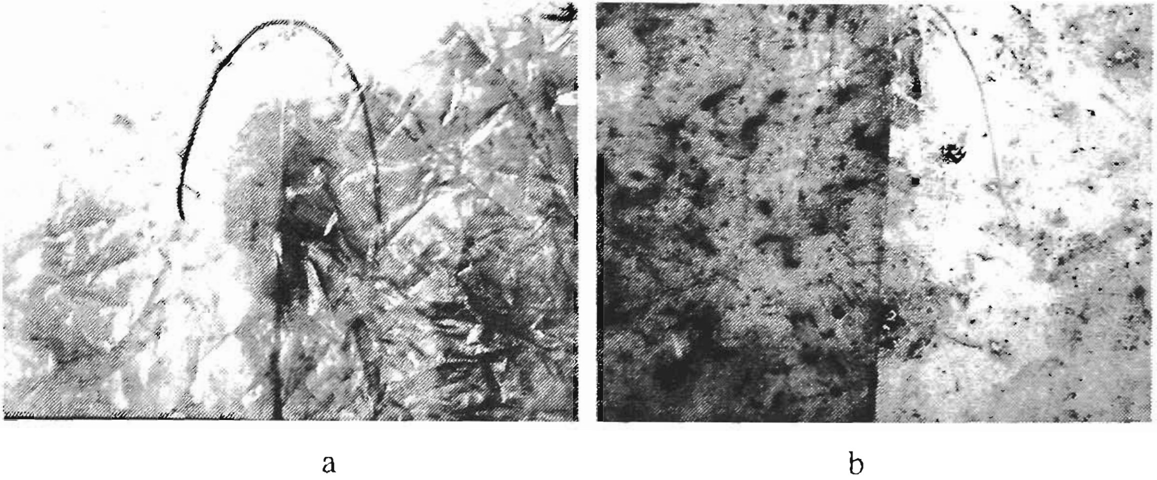


Figure 3.1. Comparison of MMDI and MMDII a) Left: MMDII Right: MMDI b) Left: MMDI Right: MMDII

Comparisons between the 4 MMD formulations allowed individual comparison of the colloidal gold and physical developer solutions. Comparison between MMDI & MMDIV and MMDII & MMDIII showed that the 14 nm colloidal gold solution gave greater detail and stronger development than the 30 nm colloidal gold solution (Fig 3.2). Comparison between MMDI & MMDIII and MMDII & MMDIV showed that the silver acetate/hydroquinone physical developer gave superior detail while the silver nitrate/iron(II)/iron(III) physical developer gave stronger development (Fig 3.3). In some instances, prints were developed with the silver nitrate/iron(II)/iron(III) physical developer that were not developed with the silver acetate/hydroquinone physical developer.

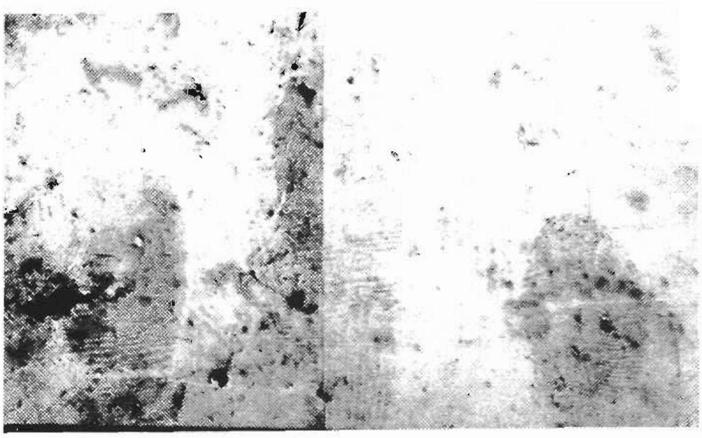


Figure 3.2. Comparison of 14 nm and 30 nm colloidal gold particles Left: 14 nm Right: 30 nm

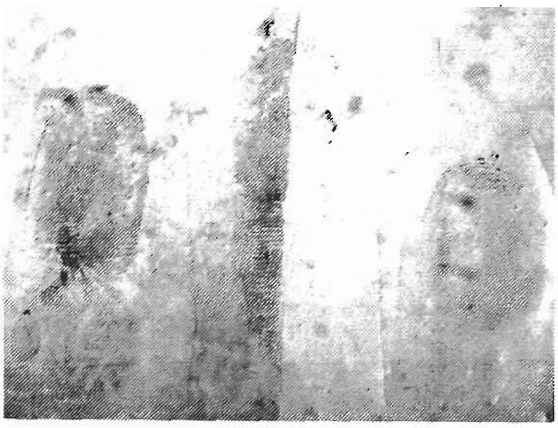


Figure 3.3. Comparison of Physical developer solutions: Silver Nitrate/Iron(II)/Iron(III) (left) and Silver Acetate/ Hydroquinone (right)

Samples that had been developed with MMDII generally obtained further silver deposition when they were retreated with physical developer (Fig 3.4). Those retreated with the silver nitrate/iron(II)/iron(III) physical developer had stronger development but the detail achieved with the silver acetate/hydroquinone physical developer was superior.

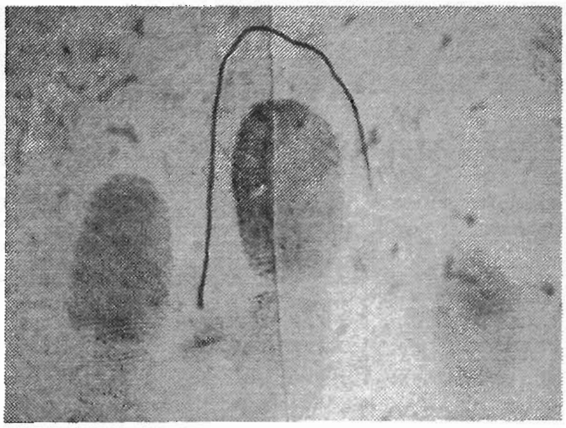


Figure 3.4. Retreatment with physical developer Left: Retreated with PD Right: MMD only

3.3.1.2 Polymer banknotes

The results obtained on polymer banknotes reflected those from non-porous surfaces. MMDII gave superior detail while MMDI gave stronger detail and more background development.

3.3.1.3 Porous surfaces

In a majority of instances, conventional physical developer gave superior detail and contrast to MMD II. In many cases, PD developed prints while MMDII failed to develop any ridge detail (Fig 3.5).

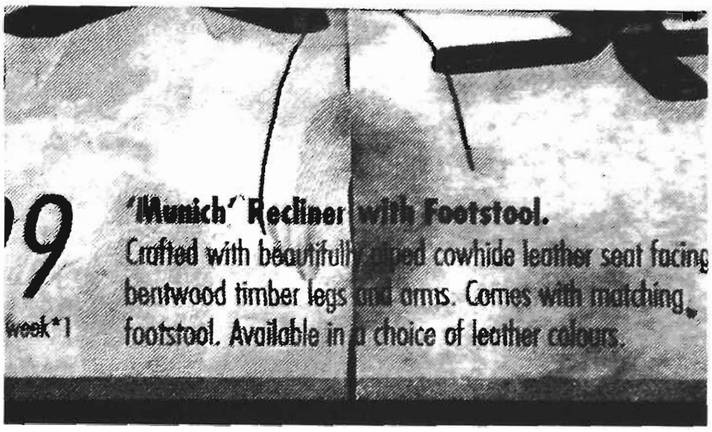


Figure 3.5. Comparison of MMDII and PD on porous samples Left: PD Right: MMDII

3.3.2 Enhancement of colloidal gold by zinc deposited under vacuum

Light zinc deposition occurred on all of the samples but the development obtained was weak. As a result, this treatment does not offer a viable alternative to enhancement by silver physical developers.

3.3.3 Sequencing of MMDII

3.3.3.1 Non-porous surfaces

Cyanoacylate fuming

CAF was found to have an impact on MMD development. Although it is still possible to obtained MMD development after CAF, CA development decreased the effectiveness of MMD treatment. Less silver deposition occurred on latent prints that had been treated with CAF than on untreated prints (Fig 3.6).

Figure 3.6. Effect of CAF on MMD Left: MMDII alone Right: CAF/MMDII

Increasing the fuming times did not have an increased impact on the MMD development obtained, but this could be because all prints used were already well developed at the end of the minimum fuming time.

Luminescent staining

Treatment of the surface with either Rhodamine 6G or Basic Yellow 40 after CAF increased the MMD development obtained compared to what would have been developed after CAF alone (Fig 3.7). MMD alone still resulted in greater silver deposition than MMD following CAF/luminescent stain.

Figure 3.7. Effect of staining on MMD: Left: CAF/Rhodamine 6G/MMDII Right: CAF/MMDII

A difference in the colloidal gold binding between sections that had and had not been stained with Basic Yellow 40 was visible. The sections that had been stained with Basic Yellow 40 obtained a stronger pinkish colour, due to colloidal gold, than the sections that had not been stained. No difference was visible between sections that had and hadn't been stained with Rhodamine 6G but the pink colour of Rhodamine 6G made any visual determination of colloidal gold binding difficult.

With the absence of colloidal gold, no silver deposition occurred on any of the sections, independent on whether or not the sections had been stained.

Silver deposition effectively quenched any luminescence caused by staining.

3.3.3.2 Polymer banknotes

The results on polymer banknotes reflected those obtained on non-porous surfaces. CA development decreased the effectiveness of MMD, while staining increased the silver deposition obtained. MMD alone was more effective than CAF/stain/MMD.

3.3.4 Comparison of MMD and VMD sequences on non-porous surfaces

As the examples (Fig 3.8-3.10) show, a range of results was obtained in the comparison of CAF/luminescent stain and CAF/luminescent stain/MMD. There were instances in which MMD failed to develop prints that were well developed by CAF/luminescent stain (Fig 3.8), instances in which MMD developed with similar detail prints as for CAF/luminescent stain (Fig 3.9), and also instances in which MMD developed prints that were not developed by CAF/luminescent stain (Fig 3.10).

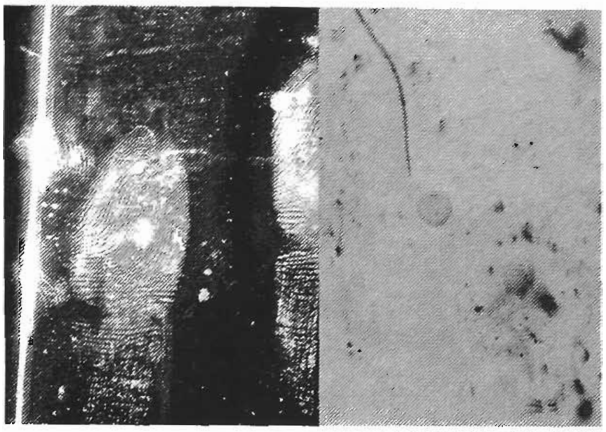


Figure 3.8. Example of superior development by CAF/stain (left: photographed under luminescence conditions) over CAF/stain/MMDII (right: photographed under white light)

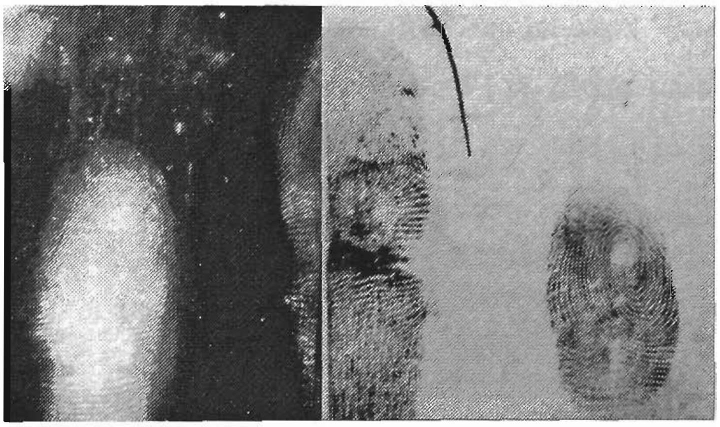


Figure 3.9. Example of similar development by CAF/stain (left: photographed under luminescence conditions) and CAF/stain/MMDII (right: photographed under white light)

Figure 3.10. Example of superior development by CAF/stain/MMDII (left: photographed under white light) over CAF/stain (right: photographed under luminescence conditions)

VMD, whether performed before or after luminescent staining, generally developed superior print detail to MMD (Fig 3.11). There were some instances in which the development obtained by MMD was similar to that obtained by VMD after luminescent staining. Greater degradation of the print residue made the superiority of VMD more apparent.

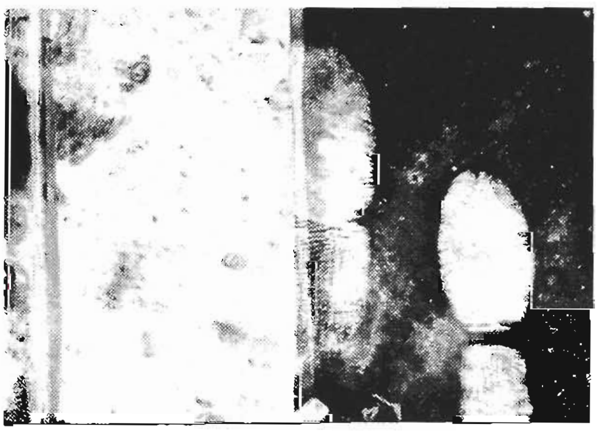


Figure 3.11. Example of superior development by CAF/VMD (right) than by CAF/stain/MMDII (left)

3.4 Discussion

3.4.1 Comparison of MMD formulations

MMDII proved to be a superior development technique to MMDI on non-porous surfaces and polymer banknotes. The superiority of MMDII over MMDI was in terms of quality of detail developed rather than strength of development. MMDII results in superior pore and edge detail to MMDI but, in some instances, MMDI resulted in stronger development compared to MMDII.

Recent changes in print identification methodology have resulted in increased use of pore and edge detail by fingerprint identification experts. This increases the importance of optimising pore and edge details when developing latent prints.

The results obtained are in agreement with Schnetz (Schnetz, 1999; Schnetz & Margot, 2001) who reports that MMDII is superior to MMDI because of sharper detail and less background development.

Independent comparisons of the colloidal gold and physical developer solutions were conducted. The 14 nm colloidal gold resulted in superior detail and stronger development than the 30nm colloidal gold. The new physical developer gave superior detail and less background development but weaker print development than the old physical developer. Hence the superior detail of MMDII is a result of both the colloidal gold and physical developer solutions, but the weaker development of MMDII is attributed to the new physical developer.

The 14 nm colloidal gold demonstrated greater specificity, which results in superior detail, and greater sensitivity, which results in stronger development, than the 30 nm colloidal gold. This is in agreement with Schentz (Schnetz, 1999; Schnetz & Margot, 2001) who found that the optimal size for colloidal gold particles is 14 nm, which give good resolution and sensitivity. In contrast to these findings, work by the UK FSS found that there was no great advantage to 14 nm colloidal gold particles over 30 nm colloidal gold particles (Brennan, 2001). The added disadvantage to longer preparation times for the 14 nm colloidal gold solution lead to the continuation of use of 30 nm colloidal gold solutions by the

UK FSS (Brennan, 2001). Using the procedures outlined in appendix 3. there is no significant difference in the difficulty or time required for the production of the two colloidal gold solutions. The 14 nm colloidal gold production may require slightly more precision while the 30 nm colloidal gold production requires slightly more time. The only factor making the 14 nm colloidal gold production more time consuming is that only 500 ml of solution can be produced in one batch to ensure that a homogeneous solution is obtained, while any volume of the 30 nm colloidal gold can be produced in one process. The advantages of the 14 nm colloidal gold in terms of detail and strength of development definitely outweigh the slight increase in production time.

The new physical developer formulation demonstrated greater specificity but less sensitivity than the old physical developer formulation. That is, the new physical developer results in finer print detail and less background development but at the expense of weaker print development. The old physical developer is much stronger and so reacts at a much faster rate. The slower reaction rate of the new physical developer allows more accurate control of the development obtained. In some instances, re-treatment with fresh physical developer solutions resulted in further silver deposition showing that the initial physical developer treatment had not developed all the detail detected by the colloidal gold solution. Hence, in instances where little silver deposition occurred during the first physical developer treatment, it may be useful to re-treat the exhibit with fresh physical developer solutions. Treatment with a modified PD, of similar strength to the original MMDI PD, is used by the UK FSS following MMDIII treatment (Brennan, 2001) Modifications to the physical developer solutions were not investigated but a physical developer of moderate strength, between the old and new formulations, may offer stronger development than the new formulation without sacrificing ridge detail.

Overall, MMDII is a superior technique to MMDI due to the superior quality of detail obtained. In some instances, weaker development may result due to the new physical developer formulation. Re-treatment with fresh physical developer solution can assist in overcoming this weaker development.

3.4.2 *Porous surfaces*

In contrast to Schnetz's findings (Schnetz, 1999), MMDII was found to be inferior to PD on porous surfaces. On all of the paper surfaces tested, including advertising brochures and magazine paper, conventional PD was superior, giving better detail and less background. PD was also more consistent in its development. The MMDII development obtained showed more variation, with print quality being dependant on paper type.

The non-specific attachment of colloidal gold to paper fibres is suggested as the cause of the strong background observed. Possible modifications for the MMDII procedure that could improve the effectiveness of MMDII on porous surfaces were not investigated, as conventional physical developer is already an effective means of detecting non-water-soluble fingerprint components on porous surfaces. As the binding of colloidal gold particles to the print residue should be stronger than the attachment of colloidal gold particles to the paper fibres, shorter times in the colloidal gold bath and longer rinsing before physical developer may decrease the background development obtained.

3.4.3 *Practicality of MMDII*

One of the factors impacting on the use of the initial MMD formulation was the apparent complexity of the procedure. The production of the MMDII reagents requires accurate measurement of volumes, clean, siliconised glassware, and ultra-pure water. However, no specialised chemical skills are required for the production or use of MMD. The procedures appear to be fairly robust, giving consistently good results.

3.4.4 *Sequencing*

3.4.4.1 Cyanoacrylate fuming

Previous recommendations concerning the use of MMD in development sequences have been contradictory. Irrausch (1991) concluded that MMD following CAF/stain is useful and even necessary while Allman and co-workers

(1992) concluded that, because of the negative impact of CAF on MMD. MMD cannot be used in the usual development sequence.

The results from this study confirm that CAF can have a negative impact on MMD, but it is important to recognise that it is the extent of CA development rather than CAF treatment that is the cause of this. Strong CA development will inhibit, or even prevent, MMD development, while weaker CA development will have little, or no impact on MMD development. It has been suggested that the formation of CA polymer binds the proteins in the print residue preventing them from binding with the colloidal gold, hence preventing MMD development (Allman et al , 1992). This fits with the results obtained. In instances where strong CA polymer formation occurs, MMD development is inhibited. But, in instances where CA polymer does not form on the print ridges, MMD development is not inhibited.

The value of MMD in the development sequence is not in further enhancing prints that are well developed, but rather in developing prints which were too weak, or of the wrong composition, to be developed by CAF. In light of this, the impact of CAF on MMD is not detrimental. The weaker prints that it is hoped MMD will develop are not adversely affected by CAF treatment. MMD is a complimentary technique to CAF and so the two techniques can be used in sequence.

3.4.4.2 Luminescent staining

Both of the luminescent stains used (Rhodamine 6G and Basic Yellow 40) increased the extent of MMD development. Hence MMD can be used successfully on surfaces that have been treated with CAF/stain.

The brief experiments conducted suggest that the stains influenced the binding of colloidal gold to the print residue rather than the deposition of silver from the physical developer. The binding of colloidal gold particles can occur via electrostatic or hydrophobic interactions. At the low pH used in the MMD treatment, the electrostatic interactions are believed to dominate (Schnetz, 1999). Colloidal gold particles are negatively charged and so bind to positively charged molecules. Rhodamine 6G (structure shown in fig 3.12) has a positive charge (i) and also a further site which could be protonated (ii) and so will be positively charged at low pH. Basic Yellow 40 (structure shown in fig 3.13) contains 3 nitrogen sites (i, ii & iii) that could be protonated and so positively charged at low pH. This positive charge on the Rhodamine 6G and Basic Yellow 40 molecules could result in binding of colloidal gold particles, and so stronger MMD development, in areas where the dye has adhered.

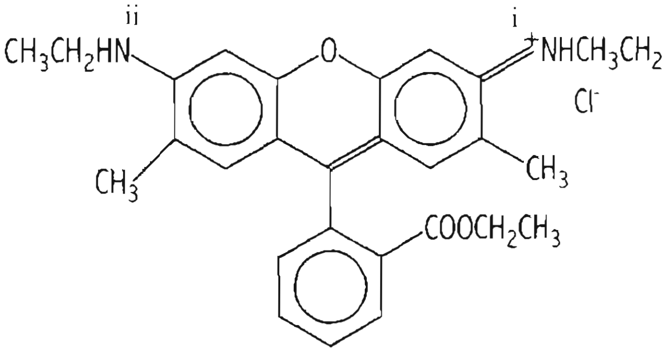


Figure 3.12. Structure of Rhodamine 6G: i-positively charged site, ii-site of possible protonation (Brackmann, 1994).

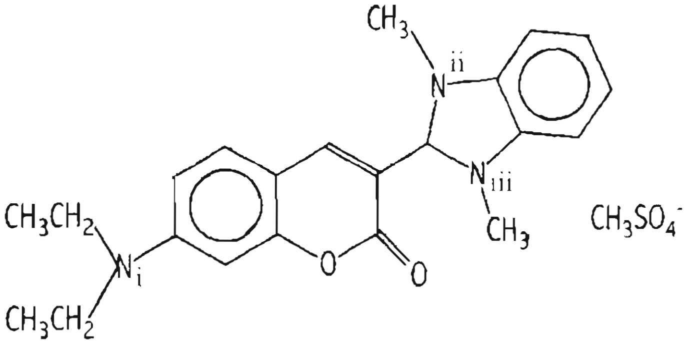


Figure 3.13. Structure of Basic Yellow 40: i, ii, iii-sites of possible protonation (Registry Handbook, 1977)

3.4.4.3 Optimum sequence

As an individual technique, MMD is more effective alone than following CAF/stain, but the optimum use of MMD on non-porous surfaces is in sequence with CAF and luminescent staining. The simplicity and efficiency of CAF/stain for developing latent prints on non-porous surfaces means there is great value in maintaining their presence in the development sequence.

On banknotes, MMD alone is preferred to CAF/stain/MMD. Since CAF/stain has very limited effectiveness on banknotes, the loss of MMD development it causes is not worth the slim chance of detecting latent prints. CAF is still recommended for use before VMD on banknotes as in contrast to its impact on MMD CAF is advantageous to VMD treatment of banknotes.

3.4.5 Comparison of VMD and MMD

On non-porous surfaces, fingerprint residue is not absorbed by the surface as occurs on semi-porous and porous surfaces, rather the residue remains on the surface until it is removed. Over time, environmental conditions cause the evaporation, degradation and/or physical removal of print residue constituents leaving a small amount of residue on the surface. This residue that remains on the surface must be detected by development techniques if prints are to be successfully visualised.

These results show that VMD is more successful at detecting this small amount of surface residue than MMD. At least some of the components that MMD reacts with are water-soluble, while all of the components detected by VMD are oily and so not water-soluble. Hence it is feasible that the weathering of print residue, in particular contact with water, on non-porous surfaces will have more of an impact on the print residue components that react with MMD rather than VMD.

Very little has been published on the comparison between VMD and MMD. One study by Allman and co-workers (1992) reported that MMDI developed 2.3 times more prints than VMD but there are difficulties in accepting this as evidence of MMD having greater sensitivity than VMD.

The same study also reported that CAF/stain developed 1.8 times more prints than VMD. This finding is in contrast with other comparisons between CAF and VMD. Other studies have found VMD to be 1.12-1.2 times more sensitive than CAF/stain (Kent, 1990; Misner, 1992) and 1.4-2 times more sensitive than CAF (Kent, 1990; Masters & DeHaan, 1996), although one study reported equal sensitivity for VMD and CAF/stain (Taroni, 1990). This difference in results between the work of Allman and co-workers and other researchers leads to the suggestion that VMD unit and/or procedure used were not properly optimised and so reduced the sensitivity of VMD reported to well below that which is possible.

This has consequences for the reported superiority of MMD over VMD by Allman and co-workers, as if VMD was not used at its optimum then this result is not valid.

3.5 Conclusion

MMDII was found to be superior technique to MMDI because of the better detail developed even though, in some instances, MMDII development was weaker in colour. The superior detail of MMDII is due to the smaller colloidal gold size and the slower physical developer. However, the slower physical developer is also the cause of the weaker development.

Strong CA development was found to inhibit MMD development but MMD development is still successful after weak CA development. Luminescent staining increases silver deposition. Hence MMD can be successfully used in sequence after CAF and luminescent staining. In some instances, MMD successfully developed prints that were not detected by CAF and luminescent staining.

Sequences including VMD — either CAF/VMD/stain or CAF/stain/VMD — proved to be more sensitive at visualising weathered prints on non-porous surfaces.

4 Detection and Enhancement of Latent Fingerprints on Polymer Banknotes

This work extends the preliminary research conducted by Flynn, Stoilovic and Lennard (1999). Their research identified CAF, luminescent staining and VMD as the most promising combination of techniques for the detection and enhancement of aged prints on polymer banknotes.

Research was conducted in three stages. With the aim of identifying the causes of the difficulties in detecting and enhancing prints on polymer banknotes, the first stage investigated the factors that affect print detection and enhancement on polymer notes. In the second stage, an optimised fingerprint detection procedure was developed using uncirculated notes. Uncirculated notes present the 'ideal' banknote surface, because the surface has not been affected by use. The third stage was the modification of the fingerprint detection protocol to improve its effectiveness on circulated notes. Use of notes results in damage to the outer coating and, as such, changes the surface being treated; hence alterations to the print detection procedure may be required.

4.1 Factors affecting latent print detection and enhancement

4.1.1 Introduction

The first stage was designed to evaluate the factors that affect latent print detection and enhancement on polymer banknotes. A better understanding of these factors would enable a more informed and focused development of a detection procedure.

An understanding of the influence of certain layers of the banknote was achieved by comparison of standard notes to notes that were specifically produced for this research by Note Printing Australia (NPA). The non-standard notes were:

- Uncoated: without primer or matt coats;

- Double cured: UV cured twice after the application of the matt coat; and,
- Double coated: coated twice each with alternating primer and matt coats.

The interaction of the development techniques used was also investigated.

4.1.2 Method

4.1.2.1 Comparison of different notes

Strips of banknote without prints on them were used to establish the gold counts that would be required for good zinc deposition. The four types of banknote available (standard notes plus the three non-standard notes) were used. The gold counts were varied from 5 to 3200. Zinc exposure was maintained relatively constant by using a set current (135 A) and exposure time (1 minute).

4.1.2.2 Effect of CAF on standard notes

Strips of standard banknotes with no prints were fumed with cyanoacrylate for varying times and then treated with the same VMD conditions (~100 gold counts). Fuming times used were 5, 10, 20, 40 and 80 minutes, 2 hours and 10 hours.

4.1.2.3 Effect of CAF on other types of notes

Strips of all four banknote types without prints were fumed for 80 minutes. They were then treated with VMD using a range of gold counts to determine how the gold count required for good zinc deposition was affected by CAF. Gold counts were started at 25 and doubled up to 3200.

4.1.2.4 ICP-MS

ICP-MS was used to quantify the deposition of gold and zinc onto standard, double cured and uncoated notes. (Double coated notes were not included as results had shown that double coating created an even more difficult surface to detect and enhance prints on and so would not be of any practical use.) Notes that were treated and untreated with CAF were analysed.

Whole clean notes were used. Each note type was consistently placed at the same position within the VMD chamber. The gold range used on the different notes was tailored to cover the range from minimal to good zinc development. On unfumed standard notes, gold counts from 50 to 2000 were used, on unfumed double cured notes gold counts from 10 to 500 were used, and on the other types of note (unfumed uncoated, and fumed standard, double cured and uncoated) gold counts from 5 to 250 were used.

An area of 25 cm^2 from the same location of each note was removed for ICP-MS analysis. The zinc and gold layers were dissolved off this section of the note using 5 mL dilute *aqua regia*. The banknote sections were left in solution for 15 minutes, which included 5 minutes in an ultra sonic bath. Prior to ICP-MS analysis, samples were diluted either 1:100 or 1:1000, depending on the expected metal concentration, using a solution containing 2% HCl and 1% HNO_3. Samples were analysed on a Sciex Elan 5100 ICP-MS (Perkin Elmer, USA) using the auto-sampler with a 50 s read delay and 30 s wash time employed to remove carry over from any previous samples. Blank solutions and calibration standards were run between each set of 12 samples.

4.1.3 Results

4.1.3.1 Comparison of different notes

The gold counts required for good zinc deposition on the different banknote types were significantly different. Uncoated notes required the least gold (~10 gold counts) for good zinc deposition, followed by double cured notes (which required ~50 gold counts), then standard notes (which required ~500 gold counts), and finally double-coated notes (which only had light zinc deposition after 2000 gold counts).

4.1.3.2 Effect of CAF on standard notes

After treatment with 100 gold counts, significant differences in zinc deposition were found depending on the CAF treatment of the notes. After 5 minutes of fuming only a thin coverage of zinc was achieved. The level of zinc deposition increased with increased fuming time until the fuming time reached 80 minutes. Further increases in fuming time did not have a significant effect on the zinc development achieved.

4.1.3.3 Effect of CAF on other types of notes

For double cured and double-coated notes, treatment by CAF reduced the gold counts required for good zinc deposition. On uncoated notes no significant effect of CAF treatment was seen but, as the gold counts required for zinc deposition were already low, any effect would be difficult to detect. Treatment by CAF reduced the difference in gold counts required for standard and double cured notes.

4.1.3.4 ICP-MS

Gold levels were successfully measured but zinc levels often saturated the instrument preventing quantification of zinc. Notes that had been treated with CAF generally had greater gold deposited onto them than those that hadn't been treated. (Fig. 4.1)

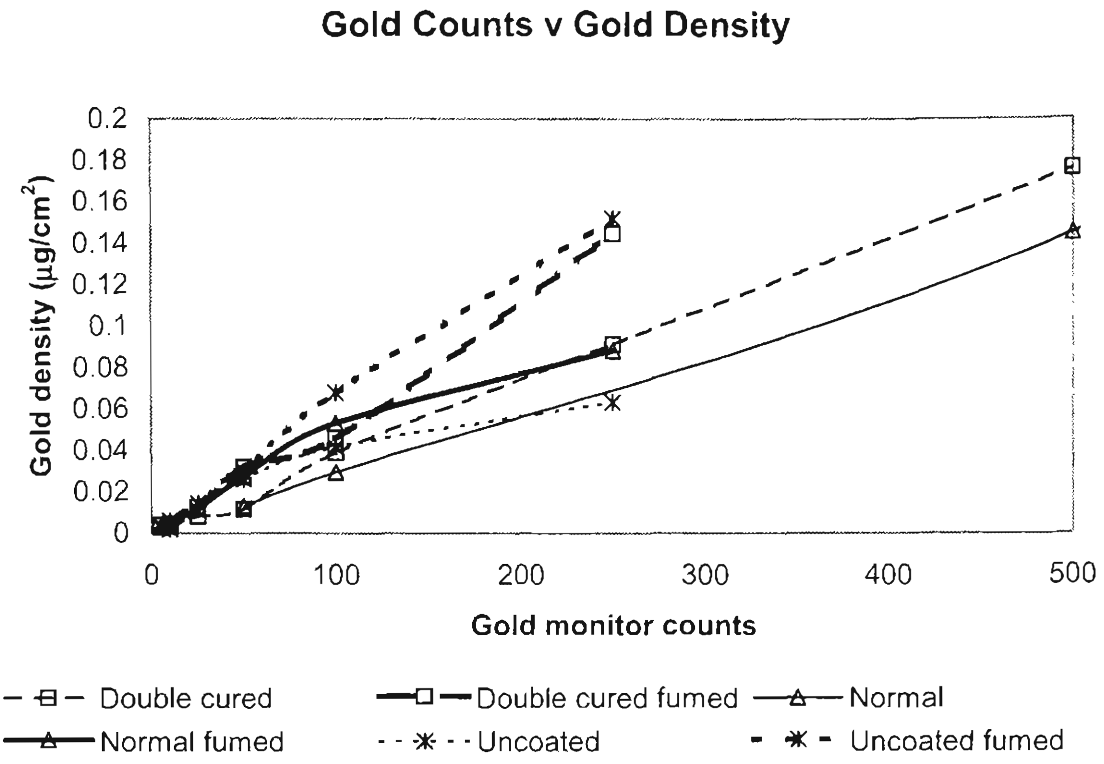


Figure 4.1 Gold counts vs. gold density for fumed and unfumed standard, uncoated and double cured notes.

4.1.4 Discussion

Comparison of the results from the different types of notes allows the identification of the factors within the banknotes that impact on latent print detection and enhancement. The significant differences noted between uncoated and standard notes shows that the protective overcoat has a significant impact on latent print detection and enhancement. The uncoated banknote surface appears to be much more similar to a standard plastic surface than the coated banknote surface. The protective overcoat contributed to making the banknote surface difficult for latent print detection. While the overcoat is a disadvantage for print detection, it is a necessary layer of the notes as it prevents the ink layers from being quickly worn away and ensures that the notes remain relatively clean. Hence the overcoat significantly increases the durability and life span of the notes.

The degree of cure of the protective overcoat impacts on the banknote surface and so on latent print detection. Increased curing decreased the gold counts necessary for zinc deposition and resulted in a surface more favourable to latent print detection. Increased curing also affects other properties of the notes such as the brittleness of the surface. Double coating of the notes increases gold counts required for reasonable VMD development and so further increases the detrimental effect of the overcoat.

Any modification of the banknotes is an extensive process requiring exhaustive testing and consultation of all the stakeholders, including ATM and vending machine manufacturers, bank tellers and large cash handlers, as well as the general public. Hence changes to the banknotes to favour latent print detection are unlikely but an understanding of the impact of the different factors within the notes is still helpful.

The significant impact of CAF on the standard banknote surface is noticeable in terms of the change in the necessary gold counts for optimum zinc deposition. The ICP-MS results suggest that CAF treatment affects the binding of gold onto the surface. Generally, for the same gold counts (which equates to gold evaporation) greater gold deposited on the notes that had been treated with CAF.

The impact of CAF treatment on the banknote surface, and so its effect on VMD, was further investigated by Kelly (2000). A range of surface analysis techniques was applied to standard banknote samples, standard banknotes that had been treated with CAF, and standard banknotes that had been treated with CAF and solvents (equivalent to those used in the standard Rhodamine 6G staining formulation). Table 4.1 summarises the techniques employed, the results obtained, and the implications of these results.

Table 4.1 Summary of results from Kelly (2000)

Technique employed	Results obtained	Relationship to results observed with VMD development
Fourier Transform-Infra-Red Spectroscopy	Differences could be detected between standard and fumed notes. Problems arise due to the inks also being detected but spectra suggest that unreacted urethane groups on the surface may be reacting with the CA vapour.	Indicator of a different polymer being present on the surface. This would contribute to a different gold count (i.e. conditions need to be varied to obtain optimum results).
X-Ray Photoelectron Spectroscopy	Nitrogen is detected on the surface of the fumed note. No other changes observed between standard and fumed note.	Further indicator of above (i.e. further evidence that a different polymer is present on the surface).
Micro-spectrophotometry	No information – layers too thin to be observed	-
Environmental Scanning Electron Microscopy	General information about surface. No differences observed.	-
Scanning Electron Microscopy	General information about surface. No differences observed.	-

Atomic Force Microscopy	Standard, fumed, stained, and VMD treated notes can all be visualised and differences between them observed. CAF treatment results in a rougher surface than the standard banknote. CAF and solvent treatment results in a smoother surface than the standard banknote.	The different surfaces indicate that: Standard note is a rough surface. The fuming results in a different surface, most likely a coating of the surface. Different polymer leads to a different gold count. The staining results in a smoothing of the surface that lowers the gold count.

Kelly (2000) showed that, during CAF treatment, a chemical reaction between the banknote surface and the cyanoacrylate vapours occurs causing the formation of an uneven polymer layer over the original banknote surface. As was shown earlier (section 2.3.2), the polymer type of a surface has a significant impact on VMD development. Similarly, a change in the polymer on the banknote surface results in a change of the binding of gold onto the surface that is reflected in a change in VMD development.

A chemical reaction between the banknote surface and CA vapours explains the observation that increasing fuming times over 80 minutes has no greater impact on the banknote surface. Chemical reactions have an effective end-point after which no further reaction appears to occur. An 80-minute fuming time reflects the point where the majority of unreacted groups on the banknote surface have reacted with CA vapour and so longer fuming times result in very little further reaction and so no greater impact on the banknote surface.

The effect of CAF on double cured notes was much less significant than the effect on standard notes. The further curing of these notes would result in less unreacted groups being present on the surface. As the CA vapours have been shown to react with these unreacted groups on the surface it is logical that the effect on double cured notes would be less than on the standard notes.

4.2 Uncirculated banknotes

4.2.1 Method

4.2.1.1 General

Standard Australian legal tender notes that had never been released into circulation were obtained from the Reverse Bank of Australia for use in this stage of experimentation. These notes present the ideal banknote surface as they are undamaged by use. The use of uncirculated notes simplified the initial procedural development by removing variables relating to the wear of the notes and surface contamination, although it was recognised that the final procedure would have to be optimised for circulated notes.

The standard procedure employed was to leave prints overnight between CAF treatment and staining and also between staining and VMD treatment.

Unless otherwise specified, the Basic Yellow 40 formulation used was 1.5 g/L Basic Yellow 40 in methanol and the Rhodamine 6G formulation was 100 mg/L Rhodamine 6G in 10% isopropanol, 15% methyl ethyl ketone (MEK) and 75% distilled water. These are the standard AFP formulations for both these stains.

4.2.1.2 The Impact of CAF on VMD

The development achieved by VMD alone was compared to that obtained with CAF and VMD for prints aged from 3 days to 2 weeks.

The development achieved by staining followed by VMD was compared to that obtained by CAF/Stain/VMD. These comparisons were conducted with both Basic Yellow 40 and Rhodamine 6G luminescence staining.

4.2.1.3 CAF times

Comparisons were performed to determine the optimum duration of cyanoacrylate fuming. Initially the comparisons were performed using first impressions of 2-day-old prints. A fuming time of 12 hours was used as the control as a long fuming time, such as 10 hours, had been recommended in the preliminary study (Flynn, Stoilovic and Lennard, 1999). This was compared to fuming times of 1.5, 3, 6 and 24 hours. All prints were stained with Basic Yellow 40, treated with VMD, and viewed under luminescence conditions. The same comparisons were also performed using 7-day-old prints with a fuming time of 1.5 hours as the control.

Further comparisons were performed using 3 successive impressions of 4-week-old prints. A control of 1.5 hours fuming was compared to 30 mins, 1, 3 and 6 hours. All samples were stained with Rhodamine 6G, treated with VMD, and viewed under luminescence conditions.

4.2.1.4 Staining

To evaluate the effect of staining on VMD, 2- to 3-day-old prints that had been fumed for 1.5 hours were stained with Basic Yellow 40 or Rhodamine 6G (stained, rinsed in water, and stained a second time before a final rinse in water) and then developed using VMD. A range of gold counts was used on different samples to determine the gold counts necessary for good development.

Using 2-day-old prints that had been fumed with cyanoacrylate for 1.5 hours, the various combinations of staining (stained twice, with a water rinse after each staining step) and VMD were compared. The comparisons were:

- Basic Yellow 40 before VMD vs. Basic Yellow 40 after VMD
- Rhodamine 6G before VMD vs. Rhodamine 6G after VMD
- Rhodamine 6G after VMD vs. Basic Yellow 40 after VMD
- Rhodamine 6G before VMD vs. Basic Yellow 40 after VMD

As initial results showed that Basic Yellow 40 was detrimental when applied before VMD, further comparisons with this combination were not performed.

In the initial experiments, notes were stained twice, with a water rinse after each staining step. Using 2-day-old prints that had been fumed for 1.5 hours, comparisons were performed between single and double dipping in both Rhodamine 6G and Basic Yellow 40. Prints were then treated with VMD.

Initial results showed a significant difference between the effects of Basic Yellow 40 and Rhodamine 6G before VMD treatment. Comparisons were made between the effect of the complete stain solution and the solvent system without the actual stain. Hence the standard Basic Yellow 40 stain solution was compared to methanol and the standard Rhodamine 6G stain solution was compared to a solution of 10% isopropanol, 15% methyl ethyl ketone and 75% distilled water. Prints were treated with CAF, dipped in either the complete stain solution or solvents only, rinsed in water and then treated with VMD. Differences in VMD development were taken as an indication of the effect of the solution on the banknote surface.

Comparisons were also conducted between the same stain concentrations in different solvent solution. Standard Rhodamine 6G solution was compared to Rhodamine 6G of the same concentration but in methanol. Prints were treated with CAF, dipped in either stain solution, rinsed in water and then treated with VMD.

The results obtained indicated that the solvents in the stain solutions were responsible for the effect observed on the banknote surface. Pure methanol had a more significant effect than the isopropanol/methyl ethyl ketone/water system suggesting that, by minimising the organic component of the stain solution, the effect of the stain on the banknote surface (and so subsequent effect on VMD development) could be minimised. To further investigate this possibility, solutions of Rhodamine 6G with the same stain concentration but varied percentages of organic solvents were compared (Table 4.2). The ratio of isopropanol to methyl ethyl ketone was maintained.

Table 4.2 Modifications to the Rhodamine 6G solvent system that were tested

Percentage of organic solvent	**Individual Components (Percentage)**		
	Isopropanol	**Methyl Ethyl Ketone**	**Distilled Water**
15	6	9	85
20	8	12	80
25 (Standard)	10	15	75
30	12	18	70

Using strong CA developed prints on LDPE, comparisons were made between the luminescence produced by the different solutions. Further comparisons between the solutions were made using 2-day and 2-month-old prints on banknotes. Prints were treated with CAF before staining, followed by VMD treatment. The luminescence obtained and the effect on subsequent VMD development was observed.

4.2.1.5 VMD conditions

The VMD conditions required for the above experiments were monitored and utilised to determine the optimum VMD conditions for various situations. Prints were aged for 1 week, 2 weeks, 1 month, 3 months and 6 months to determine if the developed procedure was effective on aged prints and also to determine how the required VMD conditions changed with increased age of the prints.

Reverse development was noted in a number of situations so a more focused study of the VMD conditions that produce reverse development was conducted. Two-day-old prints that had been fumed with cyanoacrylate for 1.5 hours and stained with Rhodamine 6G were treated with VMD using a range of low gold counts.

4.2.1.6 Print degradation over time

Experiments were conducted to determine the extent of print degradation on uncirculated banknotes over time and what measures can be used to minimise this degradation.

The first experiment was to determine whether cyanoacrylate fuming was effective in preventing print degradation. Using 3 successive impressions, comparisons were performed on prints of increasing ages. Two-day-old prints were used as the control and were compared to prints aged 1 week, 2 weeks and 1 month. Prints were fumed for 1.5 hours and stained with Rhodamine 6G when they had reached the appropriate age and then the aged and control prints were treated with VMD at the same time.

In the next experiment all prints were fumed for 1.5 hours and stained with Rhodamine 6G when they had aged for 2 days. Control prints were treated with VMD on the following day. Comparison prints were left for 3 days, 1 week, 2 weeks and 1 month before VMD treatment.

A third experiment was conducted in which all prints were fumed for 1.5 hours when they had aged for 2 days. Control prints were stained with Rhodamine 6G at that time and treated with VMD the following day. Comparison prints were aged for 3 days, 1 week, 2 weeks and 1 month before being stained with Rhodamine 6G and treated with VMD the day following staining.

4.2.1.7 Comparison of CAF vs. VCAF

The VCAF chamber employed (manufactured by Dynavac, Australia) consists of a chamber (150 cm by 34 cm internal diameter) with heated boats for glue (and a pre-fuming agent) external to the chamber. A pressure of 6×10^{-1} mbar is attained, using a rotary pump, before glue is released into the chamber from the external boat. At this point the chamber is isolated from the vacuum pump and so the chamber pressure gradually rises as fuming occurs. The glue is heated to approximately 100 °C before being released into the chamber.

Using 2-day-old prints on new notes, comparisons were made between total fuming times from 10 to 160 minutes. Fuming times greater than 40 minutes were attained by fuming notes multiple times.

The development obtained by using VCAF, with 40 minute fuming time, or conventional CAF, with 90 minute fuming time, were compared on new notes using prints aged from 3 days to 1 month. Notes were treated with the same procedure except for the use of VCAF or CAF.

4.2.2 Results

4.2.2.1 The Impact of CAF on VMD

When VMD alone was used to detect prints, very high gold counts were required and the development achieved was of relatively poor quality. VMD development after CAF was much easier to obtain (lower gold counts required) and of superior quality. Treatment with CAF prior to VMD decreased the gold counts required by approximately a factor of 10. Figure 4.2 shows the increase in detail that can be obtained after CAF.

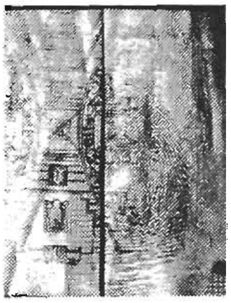


Figure 4.2 Comparison of detail achieved on banknote by VMD (left) and CAF/VMD (right)

The print detail of the sections that had been fumed before staining was greater than that of the sections that had not been fumed. The application of stain solutions before any other treatment such as CAF or VMD is detrimental to any prints as the solvents can effectively wash away the latent fingerprint residue.

4.2.2.2 CAF times

Fuming times longer than 1.5 hours did not result in any greater luminescence of prints or in any significant impact on VMD. With the 4-week-old prints, fuming times shorter than 1.5 hours resulted in slightly less zinc deposition.

4.2.2.3 Staining

Basic Yellow 40 and Rhodamine 6G were both found to have a significant effect on subsequent treatment with VMD. The number of gold counts required for zinc deposition was significantly reduced by the application of either stain solution. Generally, neither stain caused significant unevenness in the VMD development on the notes.

Treatment with Basic Yellow 40 was detrimental to print development. The application of even minimal gold counts resulted in zinc deposition across the whole surface, both the ridges and background were covered with zinc although zinc deposition was lighter on the ridges. Prints were difficult to visualise in the luminescence mode due to the zinc over the print ridges. Hence Basic Yellow 40 treatment *before* VMD was not considered an acceptable option.

Staining with Rhodamine 6G also significantly decreased the gold counts required for good VMD development. The decrease in the gold counts required to obtain good print detail rather than empty prints was the most significant impact of the stain. For strong, fresh sebaceous prints staining before VMD can decrease by a factor of 10 the gold required to obtain print detail rather than empty prints.

Table 4.3 shows the comparisons between the different combinations of staining and VMD.

Table 4.3 Comparison between stains before and after VMD treatment

Comparison between	Rhodamine 6G after VMD	Basic Yellow 40 after VMD
Rhodamine 6G before VMD	Rhodamine 6G before VMD gave superior results (lower gold counts required, brighter luminescence) (Fig. 4.3)	Rhodamine 6G before VMD gave superior results (lower gold counts required, better print quality) (Fig. 4.4)
Rhodamine 6G after VMD	–	No significant difference

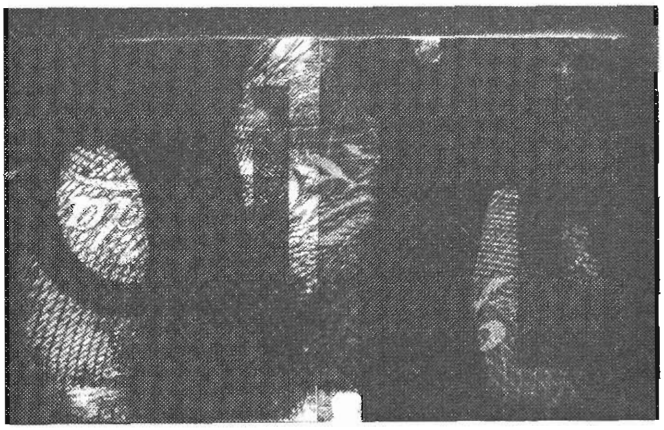


Figure 4.3 Detail obtained by CAF/Rhodamine 6G/VMD (left) compared to CAF/VMD/Rhodamine 6G (right)

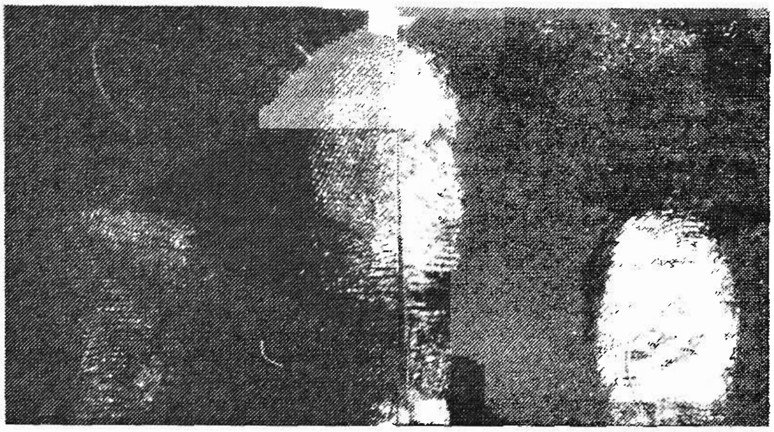


Figure 4.4 Detail obtained by CAF/Rhodamine 6G/VMD (left) compared to CAF/VMD/Basic Yellow 40

Repeated staining of a sample in Rhodamine 6G did not significantly increase the contrast obtained nor did it significantly impact on subsequent VMD development. Repeated staining of a sample with Basic Yellow 40 did not significantly increase the contrast obtained but it did significantly increase the impact on subsequent VMD development. The gold counts required and the quality of print detail were both decreased by repeated staining with Basic Yellow 40.

Treatment with the complete stain solution or solvent system only resulted in the same impact on VMD. Solution of the same stain and concentration but different solvent systems had different impacts on VMD. These results show that the impact of the stain solutions on VMD is caused by the solvents used and not the luminescent stain itself (Basic Yellow 40 or Rhodamine 6G).

In the comparisons on LDPE, the 15% and 20% organic solutions produced less luminescence than the 25% (standard) and 30% organic solutions, which produced equivalent luminescence. Comparisons on banknotes showed only minimal differences with changes in organic strength of solutions. The general trend was that the greater the organic component the less gold counts were needed for good zinc deposition. The difference between the solutions was not significant enough to warrant changing the standard AFP Rhodamine 6G formulation.

4.2.2.4 VMD conditions

The optimum VMD conditions were found to vary significantly with the age of the prints being developed. The fresher the print the higher the gold counts required to obtain good print detail.

'Empty prints' were commonly developed with fresh prints (up to 2 days old). High gold counts (~120) were required to obtain good print detail. With older prints (3 months), print detail was developed at much lower gold counts (~20) and, at the high gold counts required for fresh prints, over-development would occur.

Reverse development was observed on a variety of prints aged from 2 days to 3 months. In all situations, reverse development occurred with low gold counts. The systematic development of equivalent prints with increasing gold counts showed that light reverse development occurred when only minimal gold had been deposited onto the surface. A slight increase in the gold counts used resulted in low contrast as zinc deposited lightly on to the ridges and the background. Further increasing the gold counts (~10) resulted in normal development. Using gold counts below 10 should therefore be avoided, as there is a risk of reverse development occurring.

4.2.2.5 Print degradation over time

The print quality achieved with 2 day old prints was significantly superior to that achieved with the aged prints, even though all prints were treated with VMD at the same time. The difference in print quality increased with the age of the comparison prints. The difference that just a few days make is demonstrated in figure 4.5.

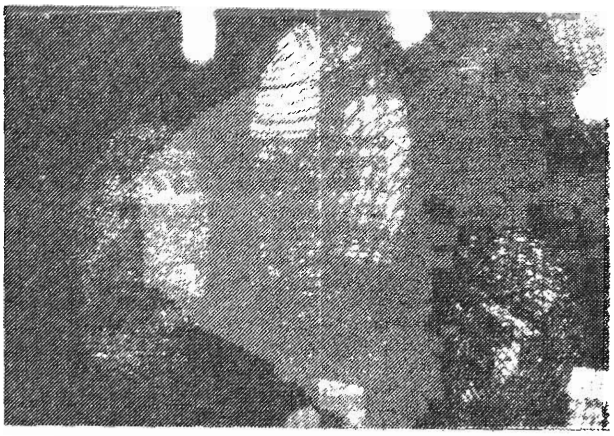


Figure 4.5 Effect of time before CAF: CAF after 2 days (left) compared to CAF after 7 days (right), VMD treatment at the same time.

For the shorter time periods (up to 1 week) between staining and VMD, the difference in print quality was minimal but, for the longer time periods (over 2 weeks), the difference in print quality became significant. (Fig. 4.6)

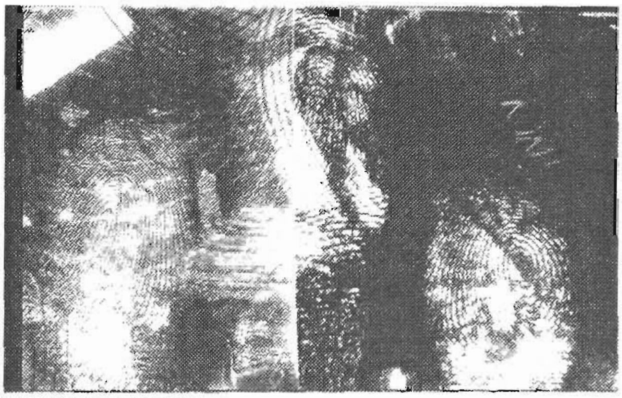


Figure 4.6 Effect of time between CAF and VMD: CAF together, VMD at 2 days (right) compared to VMD at 2 weeks (left)

As with the time between staining and VMD, the time between fuming and staining/VMD only resulted in a significant difference in print quality when the time period was 2 weeks or longer. For the shorter time periods (up to 1 week), the difference in print quality was minimal.

4.2.2.6 VCAF

As with CAF treatment, an optimum fuming time was identified and increasing fuming times beyond this did not increase the impact of CAF. For VCAF, a fuming time of 40 minutes was found to be optimal.

No significant differences in print quality were observed when VCAF was used in place of CAF. (Fig. 4.7) The only significant difference is in the fuming times required to obtain the same impact. With the fuming chambers employed in this study, 40 minutes VCAF had the equivalent impact as 90 minutes conventional CAF.

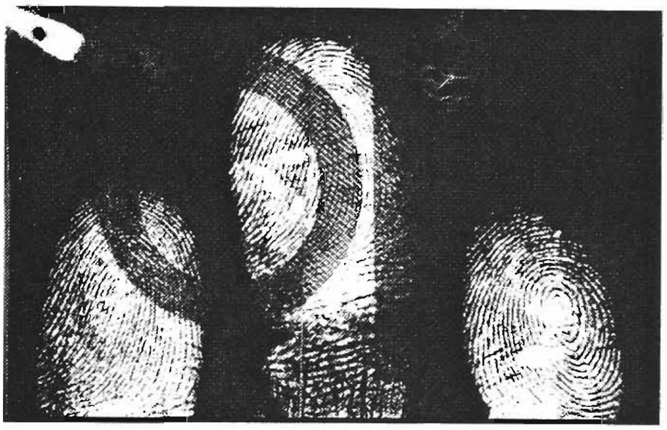


Figure 4.7 VCAF (left) compared to CAF (right)

4.2.3 Discussion

4.2.3.1 CAF

Despite the ineffectiveness of CAF at detecting prints on the general banknote surface (Flynn et al., 1999), CAF is an important step in the development procedure. These results highlight three reasons for the inclusion of CAF in the procedure.

CAF is important for the detection and enhancement of any prints present on the clear window area. The clear window is similar to a standard plastic surface and so CAF is an effective technique for the detection and enhancement of prints in this area of the banknote. As VMD conditions must be tailored to the surface being treated, and there are significant differences between the clear window and the general banknote surface, the VMD conditions used do not suit the clear window. Hence prints on the clear window will not be successfully detected by VMD making CAF treatment critical for the detection and enhancement of prints on the part of the banknote.

The impact of CAF on VMD, as seen in section 4.1, is confirmed by these results. CAF treatment results in a banknote surface that is more easily treated with VMD. The use of high gold counts can result in the formation of a visible gold layer. The resulting grey layer quenches luminescence and so significantly decreases the contrast seen. Hence the decrease in gold counts caused by treatment with CAF is advantageous. The gold counts necessary for general zinc deposition, and also for the enhancement of good print detail, are decreased by CAF treatment.

CAF also has a significant impact on the degradation of the print residue. Print residue on any surface is degraded over time as moisture evaporates and other components diffuse into the surface. This degradation occurs very quickly on banknotes due to the semi-porous nature of the surface. CAF can play a significant role in minimising the print degradation that occurs, as the CA polymer formed over the print residue appears to protect it from further degradation. Early CAF treatment will greatly improve the quality of print detected even when further treatment is delayed. To obtain the best print quality possible, banknotes should be treated with CAF as soon as they are received by the forensic laboratory. The results show that a delay of even a few days will have a detrimental effect on the quality of prints detected.

The results show that VCAF can be substituted for CAF with no significant impact on the quality of prints detected. The only significant difference is in the length of the required fuming time, which is more than halved by the use of VCAF.

4.2.3.2 Staining

Luminescent stain solutions were also found to have a significant effect on subsequent VMD treatment. The application of either stain (Basic Yellow 40 or

Rhodamine 6G) resulted in a decrease in the gold counts necessary for zinc deposition. The results show that the solvents used in the stain solution are responsible for the impact on the banknote surface.

Surface analysis showed that the effect of solvents is physical rather than chemical (Kelly, 2000). The solvents appear to even out the polymer layer formed during CAF, perhaps via partial dissolution and redistribution of the additional polymer formed by CAF. As with other changes in surface polymer, VMD conditions are affected.

Methanol-based stains had a more significant impact on print quality than the water based system (containing 10% isopropanol and 15% methyl ethyl ketone) used for Rhodamine 6G. This could be an indication that methanol is a strong enough solvent to affect the CA polymer formed on the print ridges as well as that formed on the general banknote surface.

Due to the semi-porous nature of the banknote surface, staining results in general luminescence of the whole surface, not just luminescence of the print ridges as would be ideal. Basic Yellow 40 gives greater contrast with the banknote surface than Rhodamine 6G.

Despite the greater contrast of Basic Yellow 40, staining with Rhodamine 6G before VMD was found to be the best combination of luminescence staining and VMD for uncirculated notes. Staining before VMD is advantageous in terms of decreasing the necessary gold counts, without being detrimental to the quality of print detected, and also in ensuring that excess zinc deposition (over-development) doesn't prevent effective staining.

4.2.3.3 VMD

VMD has a number of significant advantages for latent print detection and enhancement on polymer banknotes. The primary advantage of VMD is its sensitivity, which means that VMD is able to detect prints on banknotes when the small amount of residue remaining is too small to be detected by other development techniques.

Another key advantage of VMD is that the zinc layer removes interference from the printing on the banknote. The intricate printing on the banknotes can present difficulties for fingerprint identification experts so the removal of this interference can be a significant advantage.

The necessary VMD conditions have been shown to vary with the properties of the individual print being treated (Section 2.3.4; Jones et al, 2001). As print degradation occurs quickly on banknotes, the effect of print age on VMD conditions is even more significant. Although it is not possible to select one set of conditions that will result in good development in all situations, it was possible to determine a sequence of treatments that would result in good development in the majority of situations. The exact gold counts used had to be later modified to suit circulated banknotes.

At low gold counts, weak reverse development was observed for both fresh and aged prints on new notes. Zinc deposition onto the background does not occur at these low gold counts because insufficient gold has been deposited onto the surface. The gold clusters are not yet large enough to act as effective nucleating sites for zinc deposition.

At such low gold counts, the gold clusters formed are expected to be buried within the print residue preventing zinc deposition onto the ridges. The presence of CA polymer on the ridges could contribute to the deposition of zinc at low gold counts (Kiprovich, 2001). Instead of being buried within the fingerprint residue, the gold clusters may remain on the top of the CA polymer, hence zinc deposition can occur on the ridges.

Weak reverse development is not an ideal form of fingerprint development on this surface. Given the very patterned nature of the banknote, weak zinc deposition onto the print ridges is difficult to clearly differentiate from the background pattern. Hence, such reverse development creates difficulties for fingerprint identification experts. An added difficulty is that reverse development cannot be corrected once it has occurred. Increased gold counts would result in 'normal deposition', i.e. zinc deposition onto the background and print ridges. As zinc has already deposited onto the print ridges, this can, at best, result in weak contrast if the zinc deposition onto the background is strong. Reverse development was only obtained when gold counts below 10 were used; hence, by not using a gold count below 20, reverse development can be avoided.

4.2.3.4 Treatment time

The results demonstrate the importance of treating notes as soon as possible. A delay of a few days before CAF treatment resulted in a noticeable decrease in the quality of detected prints; hence it is critical that notes be treated with CAF immediately after being received.

The degradation of print residue occurs on all surfaces via the evaporation of water and the diffusion of both eccrine and sebaceous components into the surface, provided that the surface has some porosity. This degradation is thought to occur more quickly on the banknote surface due to its semi-porous nature.

Although the length of time between CAF and VMD is not as critical as the time before VMD, the results highlight that earlier VMD treatment will result in a superior quality of prints.

4.3 Circulated notes

4.3.1 Introduction

Banknotes that are encountered in criminal cases will, apart from the rare exception, be notes that have been in circulation. As the notes are used, gradual wear of the protective overcoat, and even eventually the print layers, occurs. This changes the surface of the banknote that is to be treated for latent prints. Hence the procedure developed on uncirculated notes required optimisation for circulated notes.

Initial experiments were used to test the effectiveness of the initial procedure on circulated notes and so to evaluate how significant the effect of wear on the notes is on print detection and enhancement. Individual factors were then tested to determine if and how each factor could be modified to improve print detection on the circulated notes.

The circulated notes obtained from RBA had been classified into 5 categories of wear, with category 1 being those notes with the least wear and category 5 being those notes with the most wear. Visual examination of the degree of wear of the printed inks was used to classify the banknotes (Kerrison, 2002). In general terms the categories of wear used were:

1. Close to new- Little evidence of ink wear
2. Light ink wear- Abrasion of intaglio inks first appears down the centre crease line
3. Increased ink wear- Abrasion of intaglio inks in additional areas. Abrasion of simultan inks may have begun at edges of notes.
4. General ink wear- Thin lines of intaglio areas are wider and deeper
5. Heavy ink wear-Abrasion of intaglio inks across the note. More widespread abrasion of simultan inks.

4.3.2 *Method*

4.3.2.1 Testing of initial procedure

The procedure that had been developed on the uncirculated notes was CAF treatment with a fuming time of 1.5 hours, staining with Rhodamine 6G and then VMD treatment, starting with a gold count of 20. Two-day-old prints on notes from each wear category were treated with this procedure to evaluate the effect of banknote wear on print detection and enhancement.

4.3.2.2 Modification of procedure

Initial results showed that modification of the fingerprint detection procedure was required to increase its effectiveness on circulated notes. The first difficulty was that staining of prints was not effective on the circulated notes. The background of the banknote was effectively stained but not the print ridges, resulting in the appearance of dark ridges. Two factors were considered to improve this; fuming time and staining. The stain formulation required and the position of staining within the sequence were investigated. Modification of the VMD conditions used was required as a result of the other changes made to the procedure.

Cyanoacrylate fuming

Fuming time

An initial suggestion that the ridges were not stained because of a lack of CA polymer on the ridges was investigated by comparison of different CA fuming times. Using 2-day-old prints on notes from each wear category, CA fuming times of 3 and 6 hours were compared to a fuming time of 1.5 hours. All sections were stained with Rhodamine 6G.

Further comparison was made, on category 1 notes, between 1.5 and 12 hours fuming times. Both Basic Yellow 40 and Rhodamine 6G were used.

It was later determined that VMD treatment before staining may be preferable, so comparisons were preformed to determine the effect of increased fuming times on VMD. Two-day-old prints on category 3 notes were used and comparisons were performed of 1.5 hours fuming against 2 x 1.5 and 4 x 1.5 hours. Sections were treated with VMD together and then stained afterwards.

Impact of CAF

Using category 1 to 3 notes, the impact of fuming was further investigated. Prints aged 3 days, 1 week, 2 weeks and 1 month were used to compare CAF/VMD/Stain and VMD/Stain.

The impact of CAF on print degradation was also confirmed for circulated notes. Control halves were treated with CAF when 2 days old. Corresponding halves were treated with CAF when 1 week, 2 weeks or 1 month old. Both halves were treated with VMD and stained together.

Staining

Different Rhodamine 6G stain formulations

Due to the ineffectiveness of the standard Rhodamine 6G formulation, a variety of Rhodamine 6G stain formulations were compared. Stain formulations used were:

- Current Australian Federal Police (AFP) formulation: 10% Isopropyl alcohol, 15% Methyl ethyl ketone, 75% distilled water
- Methanol: 100% methanol
- Current AFP formulation with Acetonitrile: 10% Isopropyl alcohol, 15% Methyl ethyl ketone, 2% Acetonitrile, 73% distilled water
- HFE7100 with ethanol: 17% Ethanol, 83% HFE7100 (Rhodamine 6G in HFE7100 then ethanol added until dissolved)
- HFE7100 formulation: 6% Ethanol, 94% HFE7100 (Rhodamine 6G dissolved in ethanol then HFE7100 added)

Stain formulation compared to solvents and no treatment before VMD

The impact of staining and solvents on VMD was determined by comparison of the VMD development obtained after CA fuming (1.5 hours) followed by treatment with stain solution, solvent system alone and nothing. All categories of note were used in the comparisons.

Effect of cyanoacrylate fuming on staining

Using 1-day-old prints on category 1 notes, comparisons were made between the staining that was achieved with and without CAF treatment. Comparisons were made using standard Rhodamine 6G and Basic Yellow 40 formulations.

Rhodamine 6G vs. Basic Yellow 40

Staining with Rhodamine 6G or Basic Yellow 40 after VMD were compared. Notes were treated with CAF, then VMD and finally stained. The standard Basic Yellow 40 formulation and Rhodamine 6G in pure methanol (of the same stain concentration as the standard formulation) were used. Prints aged 3 days, 1 week, 2 weeks and 1 month old on category 1 to 3 notes were used in the comparisons.

VMD conditions

As VMD is sensitive to all changes on a surface, the optimum VMD conditions had to be re-evaluated in light of the modifications made to the procedure. The effectiveness of the range of VMD conditions used in all of the experiments was evaluated to determine the best procedure for VMD treatment within the modified procedure.

4.3.2.3 Testing of modified procedure

The effectiveness of the modified procedure was examined.

Application of procedure to new notes

The effectiveness of the modified procedure was evaluated on new notes. Prints aged 2 days, 1 week, 2 weeks, 1 month, 6 months, 1 year, 1½ years and 3 years were treated.

Limits of the procedure on circulated notes

The limits of the effectiveness of the procedure in terms of the age of print that can be detected and the extent of damage a note can endure and still be successfully treated were evaluated by the application of the procedure to prints in increasing age on notes of increasing wear. Prints aged 3 days, 1 week, 2 weeks, 1 month, 3 months, 6 months and 10 months on notes from all 5 wear categories were treated.

Differences between denominations

Apparent differences between denominations were highlighted during casework treatment of large numbers of notes. Higher denomination notes tended to develop with lower gold counts while lower denomination tended to require higher gold counts for development. The quality of development achieved on higher denomination notes also appeared to be generally superior. The differences seen could be due to actual differences between notes of different denominations or could be due to differences in average wear between the different denominations, with higher denomination notes expected to have the least wear.

To investigate the possibility that the differences were due to actual differences between notes of different denominations, notes from every denomination with similar degrees of wear were obtained from RBA. Prints deposited under similar conditions and aged 3 days, 1 week, 2 weeks and 1 month on notes of each denomination were treated.

4.3.2.4 Changes to banknotes with use

The thickness of intaglio areas for notes were measured with a micrometer to quantify any changes in the notes with use. Repeat measurements at three different locations were made on three notes from each category.

4.3.2.5 Visualisation of VMD developed prints

Diffuse reflection

Diffuse reflected light was obtained by reflecting the white light from a Polilight (Rofin, Australia) off the ceiling of the room. The exact positioning of the light was altered until a good position was located. The samples imaged were 18-month-old prints on new, used banknote that had been treated with CAF and VMD but not stained.

Episcopic coaxial illumination

As episcopic coaxial illumination of VMD developed prints has been recommended (Ziv & Springer, 1993; Bullock et el, 1994; Batey et al, 1996). it was trialled on banknote samples. An episcopic coaxial illumination attachment (Rofin, Australia) was used in conjunction with a Polilight (Rofin, Australia) to image samples. The samples imaged were 18-month-old prints on new, used banknote that had been treated with CAF and VMD but not stained.

Environmental scanning electron microscopy

A XL30 ESEM (Philips, USA) was used in wet mode to image samples with moisture pressure at 0.2-0.3 torr. The x-ray beam was used at 10kV with a beam strength of 5. Images were obtained using a backscatter electron detection. The minimum possible magnification of 50x was used. The samples imaged were 18-month-old prints on new, used banknote that had been treated with CAF and VMD but not stained.

Staining and luminescent visualisation

The same samples were finally stained with Basic Yellow 40, carefully rinsed and viewed under luminescence conditions.

4.3.3 Results

4.3.3.1 Testing of initial procedure

The initial procedure was not effective on circulated notes. Even fresh (2-day-old) prints on category 1 notes (those with the least wear) did not result in identifiable detail.

When viewed under luminescence before VMD, dark ridges contrasting a bright background were visible. As a result of the ineffective staining of the ridges, very little contrast was visible after VMD.

The degree of wear of the notes had a significant impact on VMD conditions and the quality of prints obtained. Increased wear of the notes caused an increase in the gold counts required and also in the unevenness of the zinc layer formed.

4.3.3.2 Modification of procedure

Cyanoacrylate fuming

Fuming time

Increased fuming times did not result in increased luminescence on the print ridges nor was there a significant impact on VMD, when conducted before staining.

Necessity of fuming in sequence

Overall, CAF/VMD/stain resulted in superior developed to VMD/stain. As occurred with new notes, CAF developed prints on the clear windows, reduced the gold counts required for zinc deposition and minimised print degradation. CAF also had one disadvantage that was not seen on new notes; CAF increased the likelihood of zinc deposition occurring on the print ridges. This only occurred occasionally and so was not significant enough to outweigh the advantages of CAF.

Staining

Different Rhodamine 6G stain formulations

Table 4.4 Staining achieved with different Rhodamine 6G stain formulations

Stain Formulation	**Luminescence obtained**
Current AFP Formulation	Dark ridges on a bright background
Methanol	No ridges visible - ridges and background bright
Current AFP formulation with Acetonitrile	Dark ridges on a bright background

HFE7100 with ethanol	Uneven staining, patches
HFE7100 formulation	Dark ridges on a bright background

As the results contained in table 4.4 and figure 4.8 show, only the methanol formulation of Rhodamine 6G was successful in staining print ridges. The other formulations resulted in either dark ridges on a brighter background or uneven staining across with surface. Comparison with unstained notes showed that some staining of the ridges occurred but the luminescence of the background was stronger than that of the ridges. Staining with Basic Yellow 40 had similar results to staining with Rhodamine 6G in methanol; the ridges and background were equally stained.

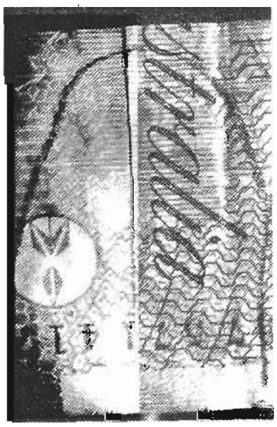


Figure 4.8 Effect of solvent systems: Rhodamine 6G in methanol (left) compared to current AFP Rhodamine 6G formulation (right)

The comparison of the Rhodamine 6G formulations showed the effect that the solvent system has on the efficiency of the stain. The solvents used determine the 'penetrating power' of the stain.

Staining of print ridges was achieved with the standard Rhodamine 6G formulation if staining was for a prolonged period of time (approx. 70s).

Effect of cyanoacrylate fuming on staining

Treatment with CAF was found to decrease the luminescence achieved, i.e. unfumed notes were more strongly stained than fumed notes.

Stain formulation compared to solvents and no treatment before VMD

The VMD development obtained was consistently superior in the absence of treatment by the stain formulation or solvent system. (Fig. 4.9) Print detail was successfully detected on category 1 to 3 notes when VMD was applied after CAF without staining. There was no significant difference between the VMD development obtained after treatment by a stain formulation or its corresponding solvent system alone.

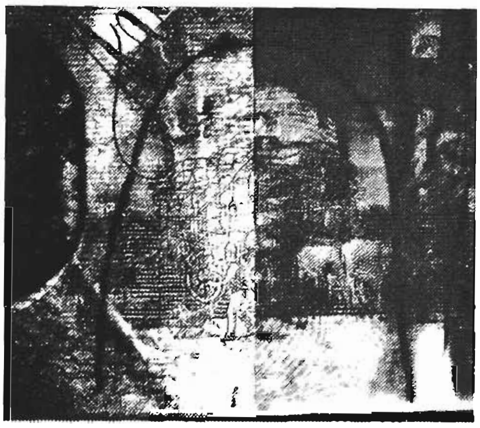


Figure 4.9 VMD before staining (right) compared to VMD after staining (left)

Rhodamine 6G vs. Basic Yellow 40

When good VMD development was achieved there was not a significant difference between the two stains. Both were generally effective, as figure 4.10 shows. There were instances when Basic Yellow 40 was a more effective stain than Rhodamine 6G. These were instances where the Rhodamine 6G formulation did not effectively stain the print ridges (even though a methanol formulation was used) and instances where the zinc layer did not completely remove the background interference and Basic Yellow 40 gave better contrast with the banknote.

Figure 4.10 Rhodamine 6G (outside sections) compared to Basic Yellow 40 (inner sections)

VMD conditions

No one set of VMD conditions will result in good development on all banknotes due to the impact of the age of the prints being treated and the wear of the banknotes, but a procedure that results in good detection and enhancement over a wide range of circumstances was developed. The initial treatment utilises 100 gold counts and gold counts for each subsequent treatment are determined by doubling those previously used.

4.3.3.3 Procedure

The optimised procedure is outlined in figure 4.11. The detailed procedure is contained in appendix 2.

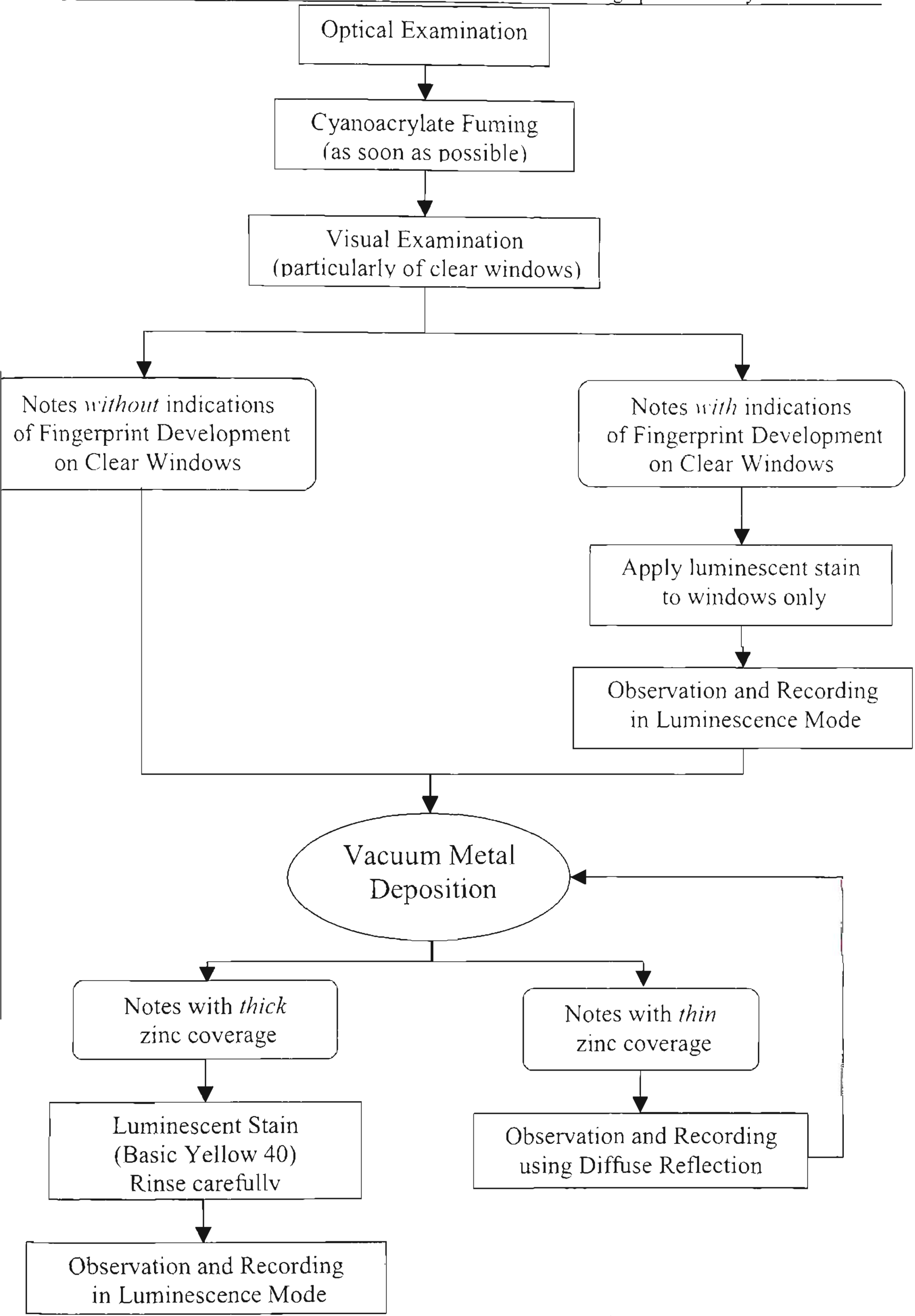


Figure 4.11 Flowchart outlining the procedure for the detection and enhancement of latent prints on polymer banknotes

4.3.3.4 Testing of modified procedure

Application of procedure to new notes

The procedure was successful in detecting and enhancing prints on new notes. Prints aged up to 18 months old were detected. (Fig. 4.12) An attempt to detect 3-year-old prints was only successful at detecting prints on the clear window.

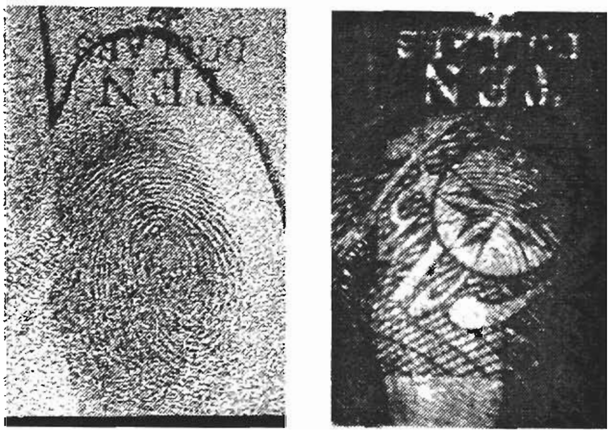


Figure 4.12 18 month old print on new banknote imaged with diffuse reflection and luminescence

Limits of the procedure on circulated notes

Overall, as the wear of notes increased the success of the procedure decreased significantly. Each wear category resulted in a decrease in the effectiveness of print detection and enhancement. Yet with 10-month-old prints some success was achieved on category 1-4 notes (Fig. 4.13).

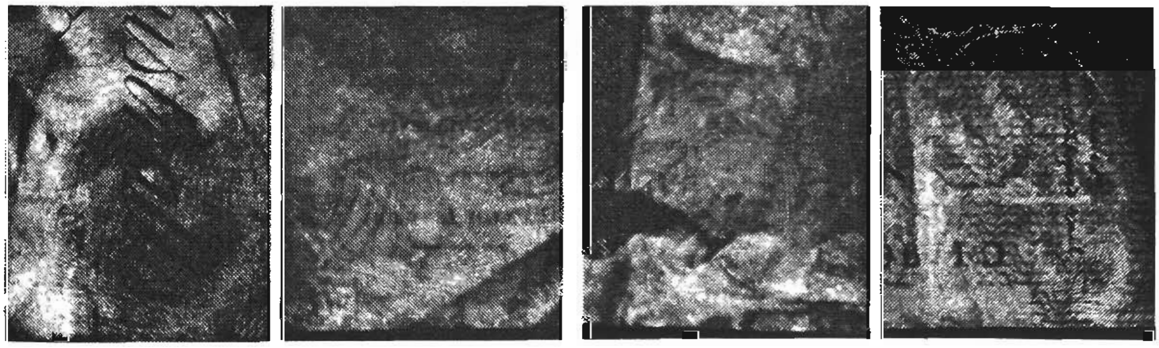


Figure 4.13 Development of 10-month-old prints on category 1-4 notes

On more worn notes greater gold counts are required to obtain zinc deposition and the zinc layer formed is more uneven and fragile.

Unsuccessful development occurred in 3 forms i) little zinc deposition- particularly on very worn notes even at high gold counts very little zinc deposition occurred ii) reverse development or iii) over-development.

On worn notes, particularly with weak prints, diffuse reflection was found to be an effective means of visualising VMD development. This was most effective at revealing development in a thin zinc layer hence the VMD procedure adopted was to firstly deposit a thin zinc layer and examine the notes using diffusely reflected light and then to deposit a thicker zinc layer before staining and examining the notes in luminescence mode.

Differences between denominations

Initially, with fresher prints, there did not appear to be significant differences between the detail obtained on the different denominations. However, as prints of increasing age were treated, the differences between the denominations became more apparent. The detail obtained on the higher denominations was generally superior to that obtained on lower denominations.

The differences in detail across wear categories were more significant than the differences across denominations. The differences between denominations could be related to the different patterns of use of the denominations.

4.3.3.5 Changes to banknotes with use

The graph (Fig. 4.14) shows the average thickness of the notes in each category with the standard deviation represented by the error bar. There is a gradual but noticeable decrease in the thickness of the notes with increased use.

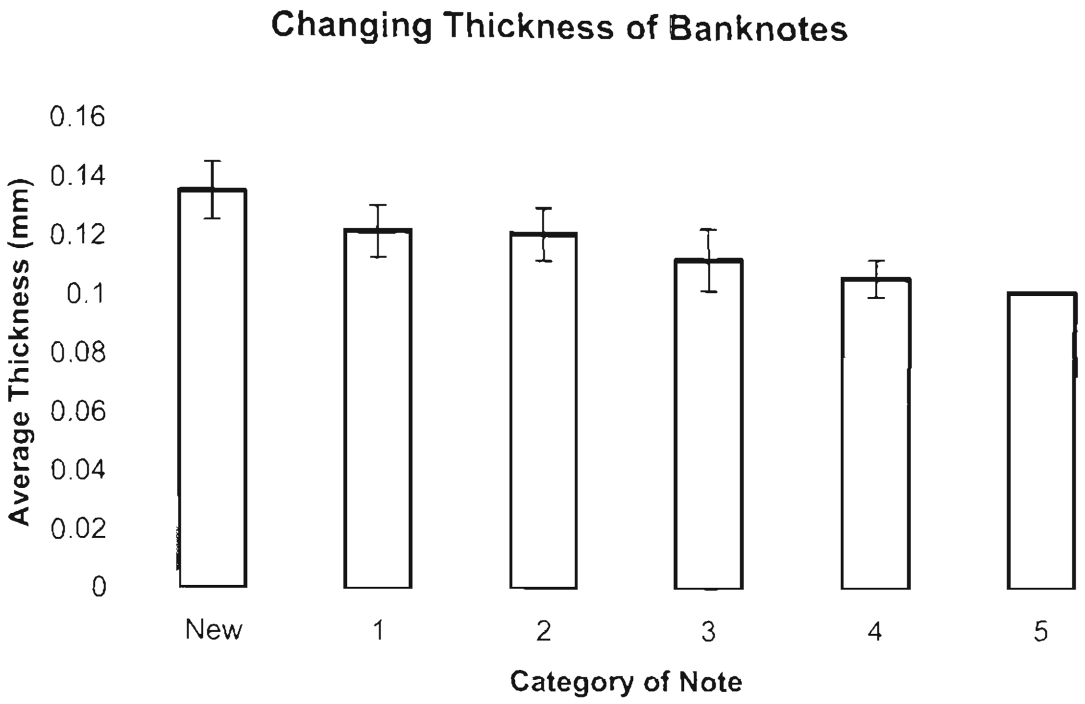


Figure 4.14 Changes to banknote thickness occurring with use

4.3.3.6 Visualisation of VMD developed prints

Diffuse reflection

The 1st impression was successfully detected using diffuse reflection (Fig. 4.15a). Some detail was revealed in the 3rd impression but it was not of good quality (Fig. 4.15b).

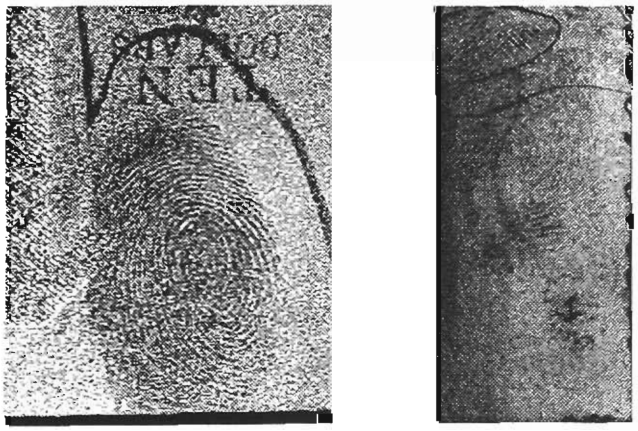


Figure 4.15 1st and 3rd impressions of 18 month old prints visualised using diffuse reflection

Episcopic coaxial illumination

Detail could be seen in the 1st impression (Fig. 4.16a) although the contrast achieved was less than that obtained by using diffuse reflection. Detail was very difficult to see in the 3rd impression (Fig. 4.16b).

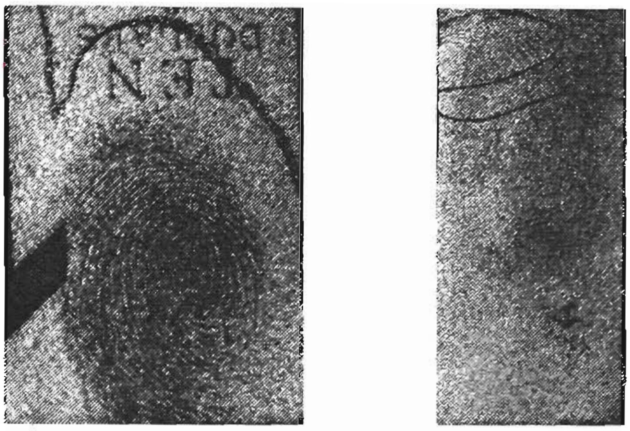


Figure 4.16 1st and 3rd impressions of 18 month old prints visualised using episcopic coaxial illumination

Environmental scanning electron microscopy

Both 1st and 3rd impressions on non-intaglio areas of the note were successfully imaged using ESEM (Fig. 4.17). The area that could be imaged was restricted to an area 3.5 mm in diameter and so imaging a significant area of latent print would require the combining of multiple ESEM images.

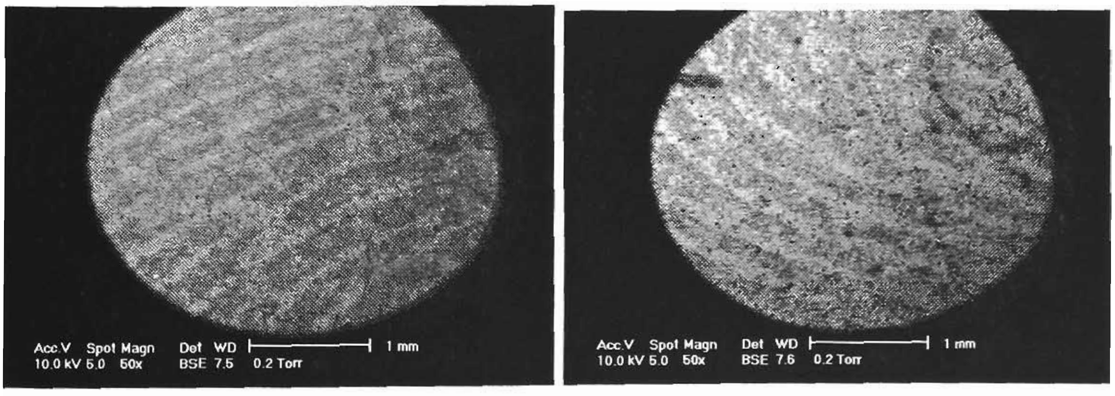


Figure 4.17 1st and 3rd impressions of 18 month old prints visualised using ESEM

Staining and luminescent visualisation

The 1st impression was successfully imaged but detail was not visible in the 3rd impression. (Fig. 4.18)

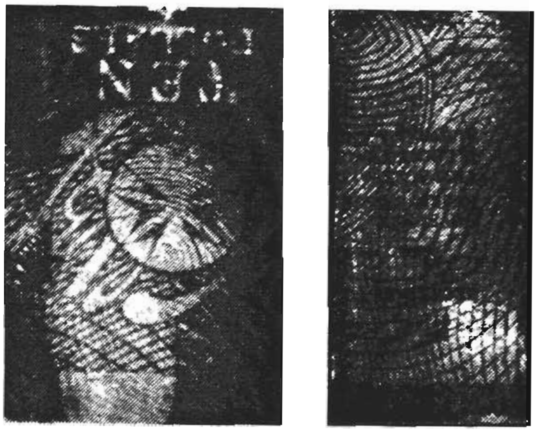


Figure 4.18 1st and 3rd impressions of 18 month old prints visualised using Staining and Luminescence

4.3.4 Discussion

4.3.4.1 Staining

The major difficulty encountered with print detection and enhancement on circulated banknotes was the ineffective staining of the print ridges. Nearly all of the Rhodamine 6G formulations trialled resulted in the appearance of dark print ridges on a bright background. This occurs because the stain was more effective at staining the general banknote than the CA polymer formed on the print ridges. The very weak luminescence of the print ridges that resulted meant that prints were difficult to visualise after VMD. A number of factors were investigated in an attempt to overcome this problem.

CAF

Initially it was thought that the print ridges were not staining properly because there was not sufficient CA polymer formed on the ridges. Longer fuming times should result in greater CA polymer formation on the print ridges. Hence if the weak staining was due to lack of CA polymer then increased fuming times should remove, or at least reduce, the problem. As longer fuming times did not improve the staining of the print ridges, this explanation was discounted.

Comparison between the staining achieved on fumed and unfumed notes showed that CAF treatment actually inhibited staining. This could be a result of a decrease in the porosity of the banknote surface caused by CAF treatment, or the formation of a CA copolymer (with the banknote surface) that is not conducive to luminescence staining.

Solvent

The results show that the solvent system used is a significant factor in determining the efficiency of the stain formulation. Pure methanol was the only solvent system capable of staining the print ridges after treatment with CAF on circulated banknotes. The other solvent systems trialled did not effectively transfer the stain from the formulation into the CA polymer.

Previous research into stain formulations has shown that the solvent system used has a significant impact on the effectiveness of a stain solution (Gamboe & O'Daniel, 1999; Wilkinson & Misner, 1994; Wilkinson & Watkin, 1993). Wilkinson & Misner (1994) suggest that methyl ethyl ketone (MEK), a component of the standard Rhodamine 6G formulation, is a more effective solvent as it allows the transfer of the stain into the CA polymer while methanol results in the absorption of the stain onto the surface of the polymer.

The results in this study show that in some circumstances methanol is a more effective solvent for the transfer of stain than the standard Rhodamine 6G solvent system (containing MEK, isopropanol and water). It is possible that the CA polymer formed on circulated banknotes is impervious to MEK, hence the standard formulations is ineffective in staining. Methanol still results in the absorption of the stain onto the surface, hence the methanol solution is still effective.

An attempt was made to use SEM to determine the morphology of the CA polymer formed on the print ridges as it was thought possible that a difference in polymer morphology could be the cause of the difference in staining.

Unfortunately, ridges could not be identified on the new banknote samples imaged, and so comparison of the CA polymer morphology formed on new and used banknotes was not possible.

Staining times

Longer staining times were found to be more successful. If the notes are left in the standard Rhodamine 6G formulation for long enough then the ridges will be stained. This shows that there is some penetration by the standard solution but that it is not very effective. If the polymer is left in the stain solution for long enough then, eventually, sufficient stain will be transferred into the polymer. The negative effect of the solvent on the surface (with respect to subsequent VMD development) is also increased by the longer staining times hence this is not a practical option.

4.3.4.2 Procedure

There are a few points about the finalised procedure worth particular mention.

Treat immediately

It is essential that banknotes be treated with CAF as soon as possible. Untreated prints will degrade quickly as the residue diffuses into the semi-porous banknote surface. Treatment with CAF will minimise the print degradation that occurs and so early treatment will greatly increase the quality of prints detected.

The print degradation occurring between treatment with CAF and VMD is not as dramatic as that which occurs before CAF, but VMD treatment should also be applied as soon as practical to obtain the best detection and enhancement possible.

Print detail can also be damaged via handling of the notes hence this must also be minimised.

Money in police possession will obviously need to be carefully documented but the process of repeated counting, and so handling, of the notes may damage print detail that is present. Notes will most likely be rubbed against other notes and surfaces during the counting process. As the print residue sits on the surface of the notes, this contact with other surfaces can damage the detail in the print. Hence care must be taken to avoid any unnecessary handling.

Banknotes may often be associated with drug offences. In these instances there is a need to detect drug residues on the notes as well as detecting latent prints. Unfortunately, procedures for the detection of drug residues may involve rinsing the notes in water and drying them in an oven, as is currently employed by the Australian Capital Territory Government Analytical Laboratories (ACTGAL) (Imhoff, 2000). Both of these actions can cause significant degradation of the latent print residue. Degradation of the print residue has obvious consequences for latent print detection. In cases where print detection will be of more evidential value than the detection of drug residues, consideration should be given to sending notes directly for latent print detection and enhancement and by-passing drug residue detection.

Windows

The clear window areas of the note are composed of the PP base with only some areas opacified but all without printing and overcoating. This results in a totally different surface to the rest of the banknote. Prints on the clear window will usually be well developed by CAF therefore all clear windows should be carefully examined before VMD for any prints. In instances where prints are detected, the window area may be stained to improve the contrast. Photos must be taken at this point. When staining the window area, care must be taken to avoid staining any other parts of the note, as this will be detrimental to print detail on those areas. Due to the necessity of tailoring VMD conditions to the surface being treated (section 2.3.2), it is not possible to use the optimum VMD conditions for both the general banknote surface and the clear window. Hence prints on the clear window may be destroyed by the VMD treatment used for the rest of the banknote surface.

Other treatment

No other treatment, apart from those outlined in the procedure, should be applied to banknotes before VMD treatment. The sensitivity of VMD means that any unnecessary treatment of the notes should be avoided, as this will be detrimental to VMD development. Previous work (Flynn et al, 1999; McLeod & Siebert, 2000) has shown that other techniques of fingerprint detection and enhancement will be unsuccessful on polymer banknotes. Hence there are only disadvantages to the application of other techniques and they should be avoided.

VMD treatment and imaging

Two stages of VMD treatment and optical examination are included in the procedure. Firstly, treatment is stopped when a thin layer of zinc has deposited on the notes. The notes as then examined, and photographed where necessary, using diffuse reflected light. This was found to be very effective at revealing weak prints. Episcopic coaxial illumination was also effective in some situations but diffuse reflection was found to be superior.

Notes are then retreated with VMD until a thick zinc layer has formed. At this point the notes are stained. Due to the impact that staining can have on the zinc layer (see below), a thick zinc layer is required for luminescence enhancement to be effective.

ESEM was successful at imaging detail that was not imaged by other techniques. The major difficulty is the restriction on the area that can be imaged. This means that multiple images would have to be combined to image sufficient print area but it may be worth investigating in serious cases.

Care when staining

Casework experience has showed that staining and rinsing of notes may remove some of the zinc layer. As a result of this, slightly more zinc than initially appears necessary should be deposited onto the notes. If this is not done, then the zinc layer will be thinner than required and the contrast of the print will be decreased due to the ineffective removal of the background luminescence.

Care must be taken when staining and rinsing the notes to avoid unnecessary damage of the zinc layer. Gentle rinsing in a water bath rather than under running water will limit damage to the zinc layer.

4.3.4.3 Effect of wear of banknotes

Significant differences were found between the print detail obtained on notes from the different wear categories. As notes are more used, print detection and enhancement becomes more difficult and the quality of detail obtained decreases. The impact of the notes on the quality of latent prints is due to two main factors: (i) damage to the surface of the note; and, (ii) the accumulation of contamination on the surface.

There were occasions when notes from a particular category were significantly less successful then expected. The classification of the banknotes used was based on the wear of the inks and so there could have been significant contamination on these notes, which was not detected in the notes classification, that caused the results seen.

The protective overcoat of the notes is gradually damaged and eventually worn away through normal use. The wearing away of the protective overcoat is reflected in the decreasing thickness of the notes with increased use. These changes to the banknote surface contribute to the increase in the gold counts required to achieve good zinc deposition. Damage to the overcoat will cause inconsistencies across the banknote resulting in uneven zinc deposition. Uneven zinc deposition decreases the quality of prints detected. Unevenness of the surface could also decrease the initial quality of prints deposited.

As notes remain in general circulation for an increased time, the amount of contaminants accumulated on the surface is likely to increase. Since VMD is sensitive to all surface contamination, not just fingerprint residue, VMD development becomes more difficult as more contaminants are present on the surface. Contamination on the surface also makes it more difficult to detect and enhance print detail. The differentiation is no longer between a clean surface and contaminants (fingerprint residue) but between different levels of contamination. The represents a 'signal-to-noise' problem that limits the contrast that can be obtained in any prints.

A further consequence of wear of the banknotes was the occurrence of reverse development in some instances. As increased wear increases the gold counts needed to achieve zinc deposition, a point is reached at which the gold counts required for deposition onto the print ridges (CA polymer) are lower than those required for the background and so reverse development occurs.

The impact of wear on the notes on the quality of print detail means that this should be an important consideration when sampling notes to be treated. Notes with the least surface damage will have a great possibility of successful print detection and enhancement.

The differences between wear of notes that are to be treated together increases the times required for VMD treatment. All of the notes are initially treated together and treatment is stopped when the first note has an adequate zinc covering. The chamber must then be opened to allow proper examination of the notes and removal of all notes with adequate zinc deposition. The remaining notes are retreated with increased gold counts. This process is repeated until all notes have an adequate covering of zinc. Repeating VMD treatment in this manner is necessary to obtain the best development on each note but results in a very time-consuming process.

4.4 Conclusion

A sequence of techniques has been optimised for the detection and enhancement of latent prints on polymer banknotes. The sequence utilises optical examination, CAF, VMD and luminescent staining. It is outlined in figure 4.11 and detailed fully in appendix 2. The implementation of this procedure will enable fingerprint laboratories to successfully process polymer banknotes for latent prints, which could provide important evidence in the investigation of crime.

The procedure has been very successful on new notes, detecting and enhancing prints up to 18 months old. Unfortunately, success on used notes has been more limited although some successful development of 10-month-old prints was achieved on category 1-4 notes. Normal usage of the notes, causing surface damage and the accumulation of contaminants, reduces the likelihood of fingerprint detection and decreases the quality of prints enhanced.

Notes must be treated as soon as possible to increase the possibility of good quality print detection. Any delay before treatment will decrease this possibility.

5 Detection and Enhancement of Latent Fingerprints on Semi-porous Surfaces

5.1 Introduction

MMDII and VMD were applied to a number of semi-porous surfaces; latex and nitrile gloves, expanded polystyrene, waxed paper, and polymer banknotes. The effectiveness of MMDII and VMD on each surface was evaluated in comparison with standard techniques, including CAF/stain, PD, ninhydrin and iodine-benzoflavone.

5.2 Method

5.2.1 Techniques evaluated

5.2.1.1 MMDII

Procedures for the production of the MMDII reagents and application of the technique are contained in appendix 3. Following the results of chapter 3 (section 3.3.1.1), items were retreated with the physical developer solution if good silver deposition was not achieved with the first treatment.

5.2.1.2 VMD

VMD was conducted using the procedure contained in appendix 2. The number of gold counts to be used for each surface had to be determined. This was achieved by starting with a gold count of 5, and then retreating with increased gold counts until good zinc deposition was achieved. The gold counts at which good zinc deposition occurred were then used to treat a new item to ensure that the appropriate gold counts had been identified.

5.2.1.3 CAF/luminescent staining

A Forensic Fuming Cabinet (FFC) (Carter-Scott Design, Australia) and 'Loctite 406' glue was used for all CAF treatments. Treatments were conducted at ambient humidity (i.e. no additional moisture was added to the chamber).

The current Australian Federal Police (AFP) Rhodamine 6G formulation was used. This consists of 100mg/L rhodamine 6G in 10% isopropanol, 15% methyl ethyl ketone, and 75% distilled water.

5.2.1.4 Ninhydrin

The current AFP ninhydrin formulation was used and this was applied by spraying. The formulation consists of 5 g/L ninhydrin in 3.5 % absolute ethanol, 0.5 % ethyl acetate, 1 % acetic acid, and 95 % HFC4310mee (Vertrel XF; Dupont).

5.2.1.5 Iodine-benzoflavone

The current AFP iodine-benzoflavone spray formulation was used. The benzoflavone solution is 120 g/L 7,8-benzoflavone in dichloromethane, and the iodine solution is 1 g/L in Arklone P (CFC113). The working solution is 2 mL of benzoflavone solution in 100 mL of iodine solution; this must be allowed to stand for 5 minutes and then filtered before use.

5.2.1.6 Physical developer

The current AFP physical developer (PD) formulation was used. The redox solution is 30 g ferric nitrate, 80 g ammonium ferrous sulphate and 20 g citric acid in 900 mL distilled water, to which is added 40 mL detergent solution (4 g/L N-dodecylamine acetate and 4 g/L Synperonic N in distilled water). The silver solution is 200 g/L silver nitrate in distilled water. The working physical developer is composed of 5 % silver solution and 95 % redox solution.

5.2.2 Latex and nitrile gloves

Two types of laboratory plastic gloves were used in this evaluation. The first were yellow latex gloves (Promed) that were textured and powder free. The second were blue nitrile gloves (Supergloves) that were textured and lightly powdered. In the palm area of the gloves, 4 successive latent fingerprint impressions were deposited.

MMDII, VMD, ninhydrin, iodine-benzoflavone, and CAF/luminescent staining were tested on each type of glove with prints that were 1 day old and 7 days old.

As initial trials indicated that MMDII would be the most effective technique on both glove types, MMDII was compared to the other techniques. The development achieved on 7-day-old and 1-month-old prints was compared.

5.2.3 Expanded polystyrene

Expanded polystyrene foam in the form of cups was used. Sets of 3 successive impressions were deposited onto the outside of the cups. For some treatments, in particular the VMD treatment, an attempt was made to flatten pieces of the cup to enable more even development.

MMDII, VMD and CAF/luminescent staining were evaluated on the expanded polystyrene samples. The techniques were trialled on latent prints that were 1 day

Each of the 3 techniques was compared to the other two using prints that were 7 days and 1 month old.

5.2.4 Waxed paper

Waxed paper in the form of cups was used. Sets of 3 impressions were deposited onto the inside of the cups as this surface had no printing and was more heavily waxed. For some treatments, in particular the VMD treatment, an attempt was made to flatten pieces of the cup to enable more even development.

MMDII, VMD, CAF/luminescent stain, ninhydrin and PD were trialled on latent prints that were 2 days and 6 days old.

As the initial trials suggested that MMDII was the most effective technique, MMDII was compared to the other techniques for the development of 7-day-old and 1-month-old prints.

5.2.5 *Polymer banknotes*

The optimised procedure for banknotes, developed in the course of this research (chapter 4), was compared to CAF/stain/MMDII and to MMDII alone. Comparisons were conducted with 1-, 2- and 4-week-old prints on new banknotes, and 1-month-old prints on all categories of banknote.

5.2.6 *Summary*

Table 5.1 lists the techniques evaluated on each semi-porous surface.

Table 5.1 Techniques evaluated on each semi-porous surface

Surface	**Techniques Evaluated**
Latex & Nitrile Gloves	MMDII VMD Ninhydrin Iodine-Benzoflavone CAF + luminescent stain
Expanded Polystyrene	MMDII VMD CAF + luminescent stain

Waxed Paper	MMDII VMD CAF + luminescent stain Ninhydrin Physical developer
Polymer Banknotes	MMDII CAF/stain/MMDII CAF/VMD/stain

5.3 Results

A summary of the effectiveness of the techniques evaluated, for all surfaces except banknotes, is contained in table 5.2. Techniques were deemed effective if print detail was successfully developed and ineffective if ridge detail could not be detected.

Table 5.2 Summary of technique effectiveness on semi-porous surfaces

Technique	**Latex Gloves**	**Nitrile Gloves**	**Expanded Polystyrene**	**Waxed Paper**
MMDII	Effective on 1-month-old prints	Effective on 1-month-old prints	Effective on 1-month-old prints	Effective on 1-month-old prints

VMD	Print detail developed although uneven zinc deposition	Print detail only developed on non-textured areas	Fresh prints developed well but older prints empty	Difficult to obtain good detail due to empty prints
CAF/Stain	Ineffective due to background staining	Ineffective due to background staining	Ineffective; print area defined but no print detail	Effective on 1-month-old prints
Ninhydrin	Ineffective	Ineffective	-	Ineffective
Iodine-Benzoflavone	Ineffective	Ineffective	-	-
Physical Developer	Ineffective	Ineffective	-	Ineffective

5.3.1 Latex and nitrile gloves

MMDII was very effective on both types of gloves, although latex gloves gave significant background development on occasions. Background development was minimised by ensuring that the samples floated on the top of the treatment solutions rather than being immersed in the solutions.

Treatment of the nitrile gloves caused the colloidal gold solution to coagulate (i.e. the gold particles join together to form larger particles). This was evidenced by a change in colour of the colloidal gold solution. The nitrile gloves used were 'lightly powdered' and it seems most likely that this powder was not completely removed by the brief washing step employed, and so caused the coagulation of the colloidal gold solution. Despite this, MMDII was still effective at developing prints on the nitrile gloves.

As was expected from previous research, the required VMD conditions were dependent on the surface being treated. It was determined that VMD treatment of the nitrile gloves should commence at 5 gold counts, while treatment of the latex gloves should begin with 60 gold counts.

The nature of the surface decreased the quality of the VMD development obtained. VMD is most successful on smooth surfaces that can be easily made to fit the curved shape of the exhibit tray. The moulded shape and textured surface of the gloves results in uneven zinc deposition that decreases the quality of VMD development obtained.

Figure 5.1 shows examples of 1-month-old prints on nitrile gloves developed by MMDII and VMD. Due to the nature of the surface, cutting the prints in half was found to be detrimental to the development obtained, hence examples of whole prints are shown.

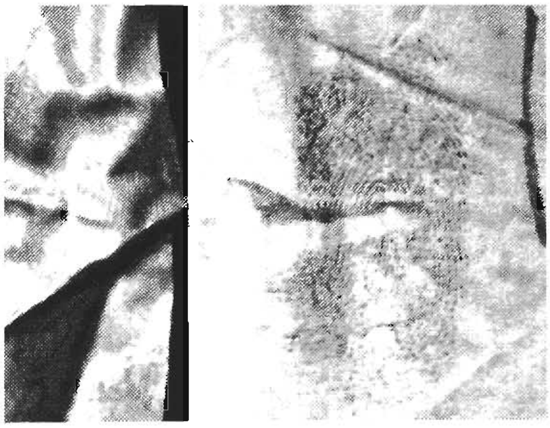


Figure 5.1. VMD and MMDII development for 1-month-old prints on nitrile gloves

5.3.2 Expanded polystyrene

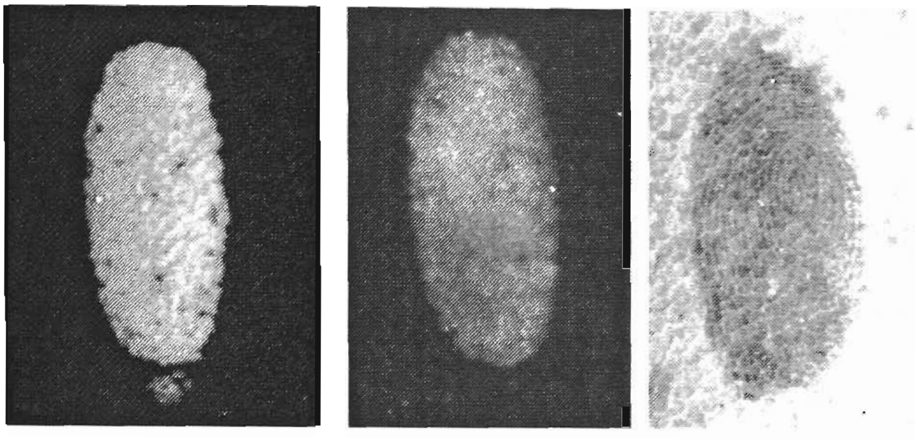


Figure 5.2. VMD, CAF/stain and MMDII development for 1-month-old prints on expanded polystyrene

Figure 5.2 shows examples of 1-month-old prints developed by MMDII, VMD and CAF/stain. As with the gloves, cutting the prints in half was found to be detrimental to the development obtained, hence examples of whole prints are shown.

It was determined that VMD treatment of expanded polystyrene should commence with 10 gold counts. Very fresh prints (a few hours old) were well developed by VMD with clear ridge detail, but older prints consistently developed as empty prints.

The use of expanded polystyrene cups also creates other difficulties for VMD treatment. VMD development is more even when surfaces can be shaped to fit the exhibit tray. The cups used had to be cut in an attempt to match the shape of the exhibit tray. Such destruction of exhibits should normally be avoided; hence this is a significant disadvantage to VMD in this instance.

Treatment by CAF/luminescent stain gave similar results to VMD, with fresh prints developing good print detail. With older prints, the general print area was well defined but no ridge detail was distinguishable.

5.3.3 Waxed paper

Unusual results were obtained from the application of VMD to waxed paper. The optimum starting point for VMD treatment was identified as 20 gold counts. Fresh prints (2 days old) were generally empty but some print detail was developed with increased gold counts. However, with prints over 1 week old, zinc deposition still occurred on the background outside the print area but, within the print area, zinc deposited onto the print ridges and not the valleys.

The necessity of cutting the waxed cups to allow even VMD development was once again a significant disadvantage with VMD.

CAF and luminescent staining also gave very good results on waxed paper. For the 1-month-old prints, the development obtained by CAF/luminescent staining and MMDII was comparable.

Figure 5.3 shows examples of 1-month-old prints developed by MMDII, VMD and CAF/stain. As with the other surfaces, cutting the prints in half was found to be detrimental to the development obtained hence examples of whole prints are shown.

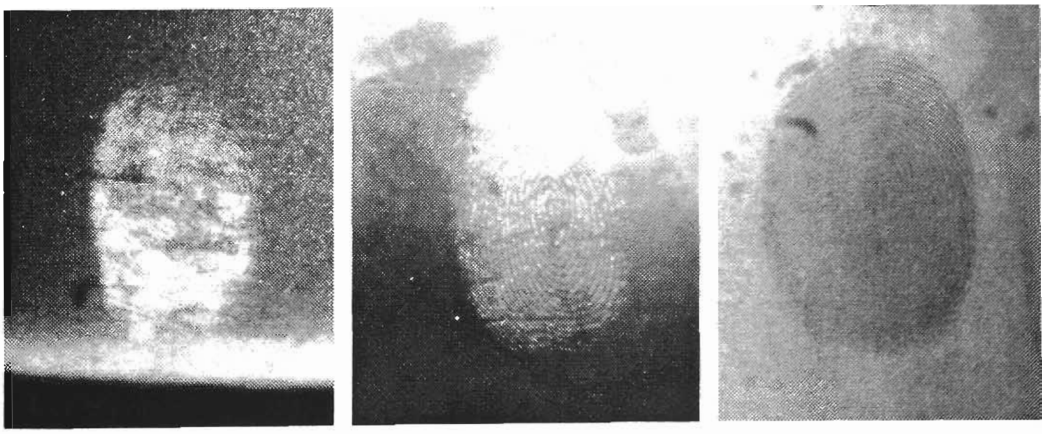


Figure 5.3. VMD, CAF/stain and MMDII development for 1-month-old prints on waxed paper

5.3.4 Polymer banknotes

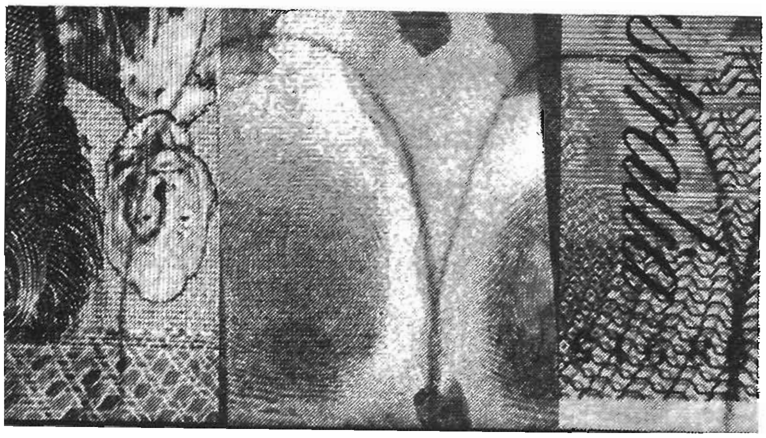


Figure 5.4. Comparison of MMDII (outside sections) and CAF/VMD/stain (inside section) development for 1-month-old prints on a polymer banknote

The CAF/VMD/luminescent stain sequence developed in this thesis proved to be more effective than MMDII, or CAF/stain/MMDII (Fig. 5.4). In many instances, MMDII development was visible on the white or lightly-coloured areas of the note, but was not visible on the more heavily printed areas of the note. In contrast, the VMD sequence was effective on all areas of the note, even the areas of heavy intaglio printing.

The effectiveness of MMDII appeared to be less affected by the wear of the banknotes than the VMD sequence but, even on the used notes, the VMD sequence gave better overall results than MMDII.

5.4 Discussion

5.4.1 Success of MMD on semi-porous surfaces

The ability of MMD to develop prints on both non-porous and porous surfaces suggests that MMD would be an ideal technique for print development on semi-porous surfaces. Semi-porous surfaces have characteristics intermediate between porous and non-porous surfaces. With porous surfaces, the water-soluble components of the print residue are rapidly absorbed into the surface and as they are bound to the fibrous structure of the surface remain in the pattern of the print ridges. On semi-porous surfaces, the absorption of the water-soluble components occurs at a slower rate and as the surfaces are generally non-fibrous the absorbed components are not retained in the print ridges but diffuse through out the surface. Non-water soluble components remain on the surface of non-porous and semi-porous surfaces but there will generally be less residue remaining on the surface of a semi-porous surface than a non-porous surface. The characteristics of print residue on semi-porous surfaces presents difficulties in latent print development that are highlighted by the ineffectiveness of the standard porous and non-porous techniques on the semi-porous surfaces tested.

Standard porous surface techniques tend to be ineffective on semi-porous surfaces due to the diffusion of print components that occurs. Standard non-porous surface techniques tend to have limited effectiveness due to the limited lifespan of print residue components on the top of semi-porous surfaces.

Even VMD, which is very sensitive to surface residue, has a more limited effectiveness on semi-porous surfaces. On some of the surfaces investigated in this study, the diffusion of non water-soluble components appeared to inhibit the development of print detail by VMD. On expanded polystyrene, very fresh prints were successfully developed by VMD while slightly older marks resulted in empty prints. Hence it appears that the non water-soluble components are not well retained in their original ridge patterns but rather diffuse across the surface. This diffusion of residue from the ridges into the valleys causes the development of empty prints. This hypothesis is supported by the fingerprint development observed with CAF/stain.

The textured and moulded nature of some surfaces makes VMD development more difficult. Due to the directional manner in which gold arrives at surfaces being treated by VMD, surfaces that are smooth and able to be fitted to the curve of the exhibit tray are best suited to VMD. Uneven development, which may obscure print visualisation, is likely to occur on surfaces that don't fit these specifications. Each of the semi-porous surfaces tested had surface attributes which decreased the effectiveness of VMD. The cups had to be cut into pieces to minimise the curve of the surface being treated, allowing them to at least partially follow the curve of the exhibit tray. The textured nature of the gloves and the expanded polystyrene caused uneven zinc deposition. These factors contributed to the ineffectiveness and inappropriateness of VMD on these surfaces.

MMD proved to be effective at developing prints on the semi-porous surfaces tested. At least in part, the effectiveness of MMD can be attributed to the nature of the MMD reagents. Most reagents are effective on either porous or non-porous surface, i.e. they react with either the absorbed components or the surface components of the print residue. The success of MMD on porous and non-porous surfaces demonstrates the ability of MMD to react with both components of the print residue. This is a key advantage of MMD on semi-porous surfaces as it means that MMD is able to react with a greater proportion of the print residue than other reagents that only react with either the absorbed or the surface components.

The liquid nature of the MMD reagents also makes MMD more flexible in treating surfaces with moulded and textured characteristics, such as those used in this evaluation. All parts of the surface can be exposed to the reagent at the same time, without any need for reshaping the surface. This is an added advantage of MMD over VMD.

5.4.2 *Comparison of VMD and MMDII on banknotes*

Three major difficulties have to be overcome in the visualisation of latent prints on polymer banknotes. They are i) the semi-porous nature of the surface, ii) the heavy and complex printing present and iii) the dynamic nature of the surface that is changing due to wear and tear caused by use of the notes. Development that would have been strong enough to visualise a print on a white surface may not be strong enough to visualise a print on a banknote, as the development is easily lost within the printing present on the banknote.

VMD is different to other development techniques in that the development (zinc deposition) occurs on the background and in the print valleys rather than on the print ridges as occurs with other techniques. This is a major advantage on banknotes. VMD significantly removes interference from the printing as the zinc film covers a majority of the background. In contrast, MMDII results in thin black ridges that are difficult to differentiate from the general printing. The gap in the zinc layer that occurs on ridges developed by VMD is much easier to visualise than the thin silver deposit formed by MMDII.

In many cases, MMDII development was easily seen on the white areas of the note but was difficult to see on the printed areas and was not visible on the intaglio printed regions. This shows that MMDII is able to overcome the difficulties caused by the semi-porous nature of the banknotes surface but is not able to overcome the difficulties caused by the banknote design. Hence, even though MMDII is able to overcome the difficulties due to the semi-porous nature of the banknote surface, VMD will always be preferred on banknotes due to the added difficulties of the banknote design.

The degree of wear of the banknotes appeared to have less impact on MMDII than it has on the VMD sequence. The surface that is being treated has a much more significant impact on VMD treatment than with other techniques. With VMD, the development occurs on the surface whereas with most other techniques the development occurs on the latent print residue. Hence it is understandable that the wear of the banknotes will have a greater impact on VMD treatment than with MMDII.

5.4.3 *VMD on waxed paper*

The cause of the VMD development observed with older prints on waxed paper is still not understood. Due to the semi-porous nature of the surface, it is expected that residue will be more quickly absorbed than would occur on non-porous surfaces. Hence, over-development might be expected to occur quickly on such a surface as the quick thinning of the print residue means that gold is no longer buried within the print residue allowing zinc deposition to occur on the print ridges. The strange phenomenon observed on waxed paper is that, under these conditions, zinc deposits onto the general background outside the print area but zinc does not deposit in the print valleys. The influence of the print residue prevents zinc deposition into the print valleys but the mechanism by which this occurs is not understood.

5.4.4 Recommended procedures

For all of the semi-porous surfaces tested, MMDII was an effective means of latent print visualisation. MMDII only 'failed' on polymer banknotes due to the heavy and complex printing which makes it difficult to differentiate the silver deposition from the background printing. Hence, in the case of polymer banknotes, VMD is preferred as it removes a significant amount of the interference caused by the banknote design.

The effectiveness of MMDII for latent print visualisation has been demonstrated on a range of semi-porous surfaces. Although other semi-porous surfaces must still be subjected to testing before exhibits are treated, these results suggest that MMDII will be an effective technique.

5.5 Conclusion

MMDII was effective on all of the semi-porous surfaces tested. MMDII is recommended for use on latex and nitrile gloves, expanded polystyrene and waxed paper. The optimised VMD sequence is recommended for use on polymer banknotes as it is best able to overcome the interference caused by the banknote printing and design.

6 Conclusions & Recommendations

6.1 Understanding of VMD

Despite being used for latent fingerprint detection and enhancement for approximately 30 years, understanding of the factors that control VMD development has been limited. This has resulted in inconsistent and unpredictable VMD results, such as reverse development and empty prints, which have troubled VMD operators.

This research has greatly increased the understanding of the factors that control the quality of VMD development obtained. The accurate control of the amount of gold deposited has been demonstrated to be crucial. It controls the quality and also type of development obtained. This is the most important factor in obtaining consistently good VMD development; without accurate control of gold evaporation, VMD will only ever be a 'hit and miss' technique.

The amount of gold deposited must be tailored to the specific exhibit being treated. There is no one amount of gold that will result in good development in all situations. Factors that influence the amount of gold required are the type of surface (i.e. the base polymer of the surface), any previous treatment of the surface (in particular CAF + luminescent staining) and the properties of the individual print. While the combination of these factors do not make it easy to identify the optimum conditions for a particular exhibit, an understanding and consideration of these factors is essential in obtaining optimum results with VMD. Consideration of these factors also allows the prediction of when reverse development and empty prints will occur, enabling these phenomena to be avoided.

A further consequence of this research into VMD is an understanding of the impact that air and zinc have on the gold clusters. The formation of a thin layer of zinc oxide and the adherence of air, and in particular water, molecules 'deactivate' the gold clusters present on the surface hence when new gold is deposited onto the surface new gold clusters form rather than the old gold clusters growing in size. This has two important implications for VMD treatment. If too much gold has been deposited onto a surface, exposure to zinc and air will deactivate this gold, making it possible to retreat the exhibit with the correct amount of gold. When VMD is conducted in multiple treatments, these treatments do not have a combined effect; rather, each acts almost independent of previous treatment. Hence re-treatment with the same amount of gold will not result in further development. An increase of the amount of gold deposited will be required to obtain further development. Doubling the amount of previously deposited gold is recommended.

The increased understanding of VMD contributed by this research will enable VMD operators to more accurately control and predict the development obtained. Current operating procedures generally do not take into account these considerations. The incorporation of these findings into operating procedures will lead to more consistently superior VMD development and so it is hoped will result in more wide spread use of this very sensitive technique.

6.2 Usefulness of MMD

MMDII has proven to be a very effective technique for the development of latent prints on non-porous and semi-porous surfaces. The combination of 14 nm colloidal gold and a silver acetate/ hydroquinone physical developer resulted in the best detail. In some situations, the development was slightly lighter in contrast but this can be overcome by re-treatment with fresh physical developer. MMDII was found to be ineffective at print development on porous surfaces, with conventional physical developer consistently producing superior development. On polymer banknotes, MMDII is of limited value due to the interference between developed prints and the heavy background printing on the notes.

6.3 Recommended procedures

6.3.1 Non-porous surfaces

VMD is a more sensitive technique than MMDII for the development of heavily weathered prints on non-porous surfaces. CAF/VMD/luminescent staining is the optimal sequence of techniques, although CAF/luminescent staining/VMD was also successful in a wide range of situations.

6.3.2 Banknotes

A procedure combining CAF, VMD and luminescent staining has been successful at developing prints on this difficult surface. Prints up to 18 months old were development in ideal circumstances, i.e. on new notes, aged in a paper envelope with no further handling. This is a significant increase from the 1-week-old prints able to be developed by other techniques. Unfortunately, less success has been achieved in real case situations due to the condition of the notes being treated and the handling of the notes between print deposition and treatment. In particular, the damage caused to the banknote surface and accumulation of contaminants that occur through normal use was found to be detrimental to the quality of prints developed.

6.3.3 Other semi-porous surfaces

MMDII was found to be effective on 1-month-old prints on all of the semi-porous surfaces tested, which were expanded polystyrene, waxed paper, latex and nitrile gloves. On expanded polystyrene, latex and nitrile gloves MMDII was the only effective technique evaluated while on waxed paper MMDII and CAF/stain were both effective.

6.4 Further research

As Securency and Note Printing Australia continue research into the polymer banknote substrate and manufacture there will be further research required. In particular changes to the overcoating are likely to have an impact on fingerprint detection and enhancement. Evaluation of potential changes and input into such decisions will hopefully result in changes to the notes that are favourable to fingerprint detection and enhancement.

Possibilities also remain for further improvement to VMD procedures for the treatment of banknotes and other difficult surfaces. The impact of changes to the rate of gold evaporation and the use of chromium before or instead of gold are being investigated.

The application of MMDII to other semi-porous surfaces is also warranted by these results.

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Ziv, Z & Springer, E (1993) More applications of coaxial illumination in fingerprint detecting and photography *Journal of Forensic Identification* 43: 362-367

Ziv, Z & Springer, E (1996) Additional methods for pre-treatment of drug contaminated polyethylene bags prior to vacuum metal deposition of latent fingerprints. *Proceedings of the International Symposium on Fingerprint Detection and Identification, Ne'urim, Israel*. 179-196

A1 Appendix 1: List of Related Publications

Jones, N, Stoilovic, M, Lennard C & Roux, C (2001) Vacuum metal deposition: factors affecting normal and reverse development of latent fingerprints on polyethylene substrates *Forensic Science International* 115: 73-88

Jones, N, Stoilovic, N, Lennard, C & Roux, C (2001) Vacuum metal deposition: developing latent fingerprints on polyethylene substrates after the deposition of excess gold *Forensic Science International* 123: 5-12

Jones, N, Mansour, D, Stoilovic, M, Lennard, C & Roux, C (2001) The influence of polymer type, print donor and age on the quality of fingerprints developed on plastic substrates using vacuum metal deposition *Forensic Science International* 124: 167-177

Jones, N, Kelly, M, Stoilovic, M, Lennard, C & Roux, C (2002) The development of latent fingerprints on polymer banknotes *Journal of Forensic Identification* (submitted)

Jones, N, Lennard, C, Stoilovic, M & Roux, C (2002) An evaluation of multi-metal deposition II *Journal of Forensic Identification* (submitted)

A2 Appendix 2: Development of Latent Fingerprints by Vacuum Metal Deposition

A2.1 Scope

This procedure outlines the following:

- operating the Vacuum Metal Deposition Unit;
- development of latent fingerprints on polymer banknotes; and,
- development of latent fingerprints on other polymeric substrates.

A2.2 Definitions & abbreviations

The following definitions and abbreviations will be used in this procedure manual:

Latent fingerprint(s): Invisible impressions of ridged skin (friction ridges) of the palmar surfaces of the hands or plantar surfaces of the feet.

HDPE:	High density polyethylene
LDPE:	Low density polyethylene
PET:	Polyethylene tetraphthalate
PP:	Polypropylene
PVC:	Polyvinyl chloride
VMD:	Vacuum metal deposition
VMDU:	Vacuum metal deposition unit

A2.3 Principles

Vacuum Metal Deposition (VMD) is a very sensitive technique for latent print development on non-porous and semi-porous surfaces. VMD is generally considered to be more sensitive than cyanoacrylate fuming especially in cases where prints are old or have been exposed to adverse environmental conditions (Kent, 1990; Misner, 1992; Masters & DeHaan, 1996).

The VMD development of latent prints is based on the properties of two metals, zinc and cadmium. Zinc and cadmium will not deposit on non-metallic surfaces under vacuum, unless nucleating sites of an other metal are previously formed on that surface. Zinc was selected as it is non-toxic. The VMD technique involves evaporation and deposition, under high vacuum, of a small amount of gold and then a large amount of zinc. The thin gold layer acts as a catalyst, ie. forms 'nucleating' sites upon which zinc atoms start to build up a much thicker layer. The deposited gold layer is very thin, such that it is invisible. The zinc layer is much thicker and ideally should not deposit on the fingerprint ridges, leaving them transparent.

The thin gold layer is discontinuous, ie. the surface is not completely covered with gold. The gold atoms form clusters (agglomerates) on the surface, due to a stronger attractive force between gold atoms than between gold atoms and the surface, Fig. A2.1.

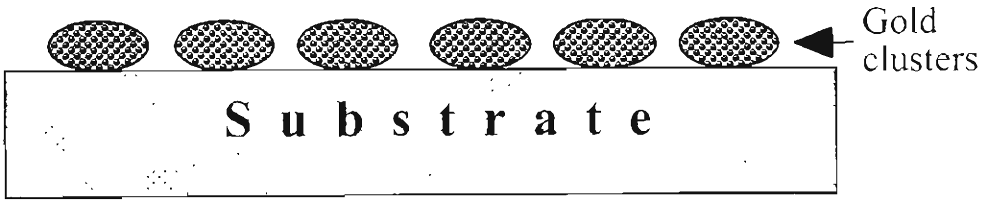

Fig.A2.1. Gold atoms congregate into clusters on top of the surface.

The size, shape and density of gold clusters are believed to be crucial for the deposition of zinc onto the surface (Jones et al, 2001a). Since the thickness of the gold layer is very critical, it has to be monitored carefully. Monitoring is done indirectly with an inbuilt 'Crystal monitor' where the active crystal (the probe) is positioned closely above the last gold boat in the VMD chamber.

Gold deposits everywhere on the surface, regardless of any contamination on top of the surface (Thomas, 1978). In the case of a latent print residue, gold in the form of clusters is buried in the residue itself, ie. within the print ridges (Robinson, 1979) (provided that clusters are small enough). Zinc will only deposit onto the surface where it can find exposed gold clusters. Therefore zinc will deposit on the exposed surface and in the print valleys, but not on the print ridges, producing 'normal' development, Fig. A2.2.

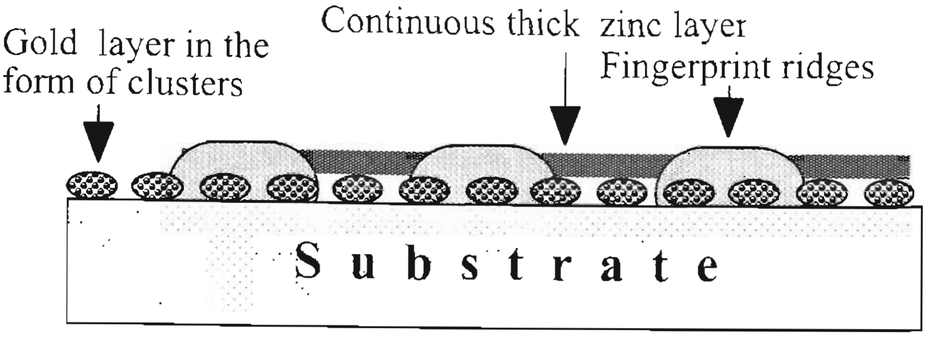

Fig. A2.2. Basic principle of 'normal' VMD development.

In the case of a large amount of deposited gold, the clusters may grow to the extent that they protrude above the print residue, Fig. A2.3. Incoming zinc may deposit on the print ridges as well as on clusters formed on the rest of the surface. In this way, differentiation between the print and the rest of the surface is not obtained and over-development occurs.

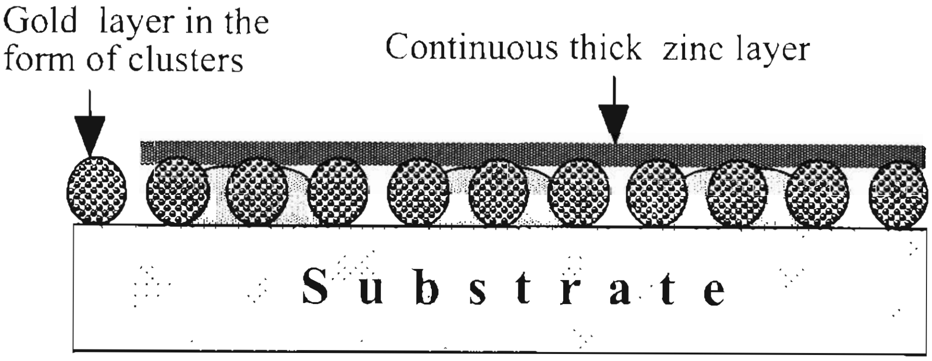

Fig. A2.3. In the case of a large amount of gold, the gold clusters 'protrude' through the print residue, producing overdevelopment.

It is obvious that formation of the correct size, shape and density of gold clusters is the most important factor for successful VMD development. This will depend on two variables: the amount of evaporated gold and the type of surface. Depending on these two variables, different types of development are possible with VMD:

> 'Normal' development occurs when zinc deposits strongly onto the background and in the valleys of the latent print but not on the print ridges.

'Empty prints' occur when zinc deposits onto the background but not in the valleys nor on the ridges of the latent print. This happens when insufficient gold has been deposited and is more likely to occur on certain types of surfaces with strong, fresh prints.

'Over-development' occurs when zinc deposits onto the background, print ridges and valleys, ie. the whole surface is covered with zinc. This happens when too much gold has been deposited.

'Reverse development' has been observed since the initial use of the technique (Kent et al, 1976) and occurs when zinc deposits onto the print ridges and not in the print valleys or on the background. This may happen on certain types of surfaces when too much gold has been deposited (Jones et al, 2001a).

No development occurs when zinc fails to deposit onto any part of the surface. This may be a sign of too little or too much gold depending on the surface type.

Over-development should be avoided at all cost. To achieve good normal development, an optimum amount of gold has to be deposited. Firstly, this depends on the type of surface and secondly on the type of latent prints (eg. heavy or light, fresh or old). With respect to surface type, different polymers require a different optimum amount of gold for good development to be obtained (Jones et al, 2001c).

Due to many unknowns, it is normal practice to treat an exhibit several times, starting with a very small amount of gold. The amount of gold is successively increased until a good result is obtained. The amount of gold, monitored by a 'Crystal monitor', is given in arbitrary units known as gold counts.

There are two effects, exposure to zinc and exposure to air, that influence the choice of gold counts for subsequent VMD treatments:

It was found that, in cases when gold clusters do not have the right size/shape, a small amount (perhaps a monolayer) of zinc atoms covers a good proportion of the gold clusters. Because the size/shape of gold clusters is not correct, further deposition of zinc atoms is prevented. In this way the zinc deactivates the gold clusters so that they no longer act as nucleating sites. With subsequent VMD treatment, the majority of new gold arriving at the surface forms new gold clusters, while a smaller amount joins to the old (mostly deactivated) gold clusters (Jones et al, 2001b).

> The second effect occurs when the exhibit is exposed to air following the first VMD treatment. The zinc attached to the gold clusters in previous VMD treatment, in the presence of oxygen from air, forms zinc oxide. In addition, air and water molecules attach to the surface of previously formed gold clusters. The layer of zinc oxide and air/water molecules further deactivates the existing gold clusters. With subsequent VMD treatment, the majority of the new gold arriving at the surface forms new gold clusters, while a smaller amount joins to the old (mostly deactivated) gold clusters (Jones et al, 2001b).

When the zinc and air effects are taken into account, the following recommendations can be made:

1. If the exhibit is still under vacuum in the chamber following the first VMD treatment, then at least 1.5 times the previously used gold counts is required for improved latent print development.
2. If the exhibit has been exposed to air following the first VMD treatment, then at least double the previously used gold counts is required for improved latent print development.

A2.4 Procedure for operating Vacuum Metal Deposition Unit

A2.4.1 Starting the unit

The following steps are necessary when starting the unit:

1. Turn on the main power switch on the wall, if not already on.
2. Turn on the power switch on the side of the unit ('Power On' indicator lit).
3. While holding the 'alarm reset' switch to 'reset', turn the 'rotary pump' switch to 'start' ('Rotary Pump On' indicator lit).
4. Turn on 'diffusion pump' by switching to 'start' ('Diffusion Pump On' indicator lit).

Note: *1. Check the water flow to reduce water wastage. It should be at the minimum needed for the VMD to operate. If the water flow is large reduce the flow. If the water flow is too low (alarm will sound), increase the water flow slightly.*

2. The diffusion pump will take 45 minutes to warm up before an evacuation cycle can be started.

A2.4.2 Loading exhibits

1. Release the chamber door. Turn the 'Air admit' switch to 'open', to open the air admit valve ('Air Admit On' indicator lit). Once the chamber is at atmospheric pressure the door is released so it can be opened.

Note: *It is only possible to open the chamber when it is at atmospheric pressure.*

2. Open wide the chamber door then carefully pull the exhibit holder out of the chamber using the handle on top of the holder.

Rotate the holder to a vertical position while pulling the pin located on the left side of the holder.

3. While wearing cotton gloves, place exhibits on the holder using small magnets.

Note: *Wet, oily or heavily soiled exhibits must not be placed in the VMD chamber. Wet exhibits should be dried and heavily soiled exhibits should be washed gently in cold water and then air-dried.*

4. Return the holder to the horizontal position then slide the holder back into the chamber.

Note: *Magnets should be placed in such a way as to cover the smallest possible exhibit surface, as any area covered will not be developed. Exhibits should be flat on the exhibit holder. Only the side of the exhibit facing the bottom of the chamber will be developed.*

A2.4.3 Loading the boats

1. Put the 'mode selector' switch to 'manual' and the 'shutter' switch to 'open' to open the shutter.
2. Check that there is gold in the three boats on the left-hand side of the chamber. If there is not sufficient gold, place two pieces of gold wire about 5mm long in each gold boat.
3. Ensure that each zinc boat on the right hand side of the chamber has 3 pieces of zinc wire about 1cm long.

A2.4.4 Commencing the evacuation cycle

1. Close the chamber door and tighten the screw.
2. Turn the 'air admit' switch to 'close' to close the air admit valve.
3. Turn the 'cycle' switch to the right to start the evacuation cycle.

***Note**: Evaporation of gold and zinc cannot be conducted unless the chamber is below the fire ready pressure. It may take around 10 minutes for the 'fire ready' pressure to be reached.*

A2.4.5 Thickness monitor controlled gold evaporation

The thickness monitor provides the most accurate way of controlling the amount of gold that is deposited onto a surface and so should normally be used. If the thickness monitor is faulty, alternate methods of gold evaporation are available and are outlined at the end of the procedure.

1. On the thickness monitor, check the following settings relevant to gold evaporation by pressing the 'Data' button once to advance for each setting. The small lights on the monitor indicate which property is selected. Check that the value for each property is that listed below.

Table A2.1. Standard parameter values for gold.

Property	**Standard Value (for gold only)**
Layer	1
Density	19.30
z-value	23.2
Terminate	Set to required counts for surface
Tooling	60.00
Xtal	1
Usage	This value is determined by how much the crystal has been used and is not set by the operator

2. Set the 'Terminate' to the number of gold counts at which the shutter will close and gold evaporation will stop. This should be set to the optimum gold counts, which depends on the surface type. Use the up and down buttons to change the data values if needed.
3. When all values are correctly set, hold the 'data' button until the 'rate' is selected ('rate' light will illuminate).

Note: *The amount of gold deposited is critical; too much gold will inhibit zinc deposition on certain surfaces so it's better to put less gold initially than too much. See procedures for individual surfaces.*

1. Select 'Auto' on the 'fire mode' switch.
2. Turn the 'Thickness monitor' switch located on the front panel to 'on'.
3. Select Gold on the 'material selector' switch.
4. Set 30s on the gold preheat timer (the top right of the four timers).

Note: *A gold preheat time of 45 second sis required if new gold has been placed on the boats.*

1. Press the 'run' button on the thickness monitor.

Note: *Gold boats will be preheated for 30 seconds, and then the shutter will open.*

2. Check that the rate of gold evaporation on the thickness monitor is between 0.4 and 1.2. If the rate of gold evaporation is outside this range then change the current to adjust this rate. The current is changed by rotating the 'gold current' control; to the right will increase the current (increase the rate of evaporation) and to the left will decrease the current (decrease the rate of evaporation).

Note: *Once the number of gold counts set for 'termination' is reached, the shutter will close and the gold current will turn off.*

A2.4.6 Zinc evaporation

1. Turn the 'thickness monitor' switch located on the front panel to 'off'.
2. Turn the 'material selector' switch to 'zinc'.
3. Set the 'zinc timer' to 3 minutes.
4. Turn the chamber light on
5. Put on the special safety goggles or face shield.
6. Turn the 'fire' switch to 'start' to start the zinc evaporation. Monitor zinc deposition onto the surface by watching the exhibits through the small window in the chamber door. Be careful not to deposit too much zinc as this may destroy the prints.
7. Once fingerprints have developed, or there is a uniform zinc layer over the surface, turn the 'fire' switch to 'stop' to stop zinc evaporation, otherwise zinc evaporation will stop after 3 minutes

If after 3 minutes of zinc evaporation a zinc layer has not formed on the surface, more gold must be deposited. Select 'manual' on the 'mode selector' switch and 'open' on the 'shutter' switch and check if there is any zinc left on the boats.

a) If there is no zinc left on the boats

- Proceed to Removing Exhibits but do not remove the exhibits from the tray
- Repeat the procedure commencing with Loading the Boats
- During Gold Evaporation set the 'terminate' value to double the value previously set.

- Turn off the chamber light after finishing the zinc evaporation.

b) If there is still zinc on the boats

- Repeat the procedure commencing with Gold Evaporation. If this is the first repeat set the 'Terminate' value to 1.5 times the value previously set. If this is the second, or greater, repeat set the 'terminate' value to double the value previously set.
- Turn off the chamber light after finishing the zinc evaporation.

Table A2.2: Examples of increasing gold counts for successive VMD treatments.

Development	Example 1	Example 2
1st	**Initial gold counts** = 30	**Initial gold counts** = 100
2nd	**Zinc remains** (vacuum chamber door not opened) Select 1.5 times value previously set Gold count = 45	**No zinc remains** (vacuum chamber door opened) Select double value previously set Gold count = **200**
3rd	**Zinc remains** (vacuum chamber door not opened) Select double value previously set Gold counts = **90**	**No zinc remains** (vacuum chamber door opened) Select double value previously set Gold counts = **400**
4th	**No zinc remains** (vacuum chamber door opened) Select double value previously set Gold counts = **180**	**No zinc remains** (vacuum chamber door opened) Select double value previously set Gold counts = **800**

A2.4.7 Removing exhibits

1. Once development is complete or new zinc is required, turn the 'cycle' switch to 'stop' to stop the evacuation cycle.
2. When the vacuum is released, release the chamber door. Turn the 'air admit' switch to 'open'.
3. Open wide the chamber door then pull the exhibit holder out of the chamber using the handle on the holder.

4. Rotate the holder to a vertical position while pulling the pin located on the left side of the holder.
5. While wearing cotton gloves, remove exhibits from the holder.
6. Return the holder to the horizontal position then slide the holder back into the chamber.
7. Wipe down the window in the door and the window in the bottom of the chamber with a cloth to remove zinc that has deposited.
8. If the zinc is not easily removed with a cloth, then dip the cloth in a 10% acetic acid solution and use this to clean the windows. Clean both windows with ethanol to remove any acetic acid residue.

Note: *Once development can be seen, exhibits should be removed from the chamber to allow proper inspection of development. Exhibits can be returned to the chamber and the procedure repeated for further development if required.*

9. If an exhibit has well-developed prints on some areas but other areas require further development then the well-developed areas should be covered (aluminium foil is suggested). The cover should be held in place with magnets.

10. If the second side of the exhibit also requires development, the procedure must be repeated with the alternate side of the exhibit facing out of the exhibit tray.

A2.4.8 Shutting down VMDU

Note: *The VMDU should be kept under vacuum when it is not in use. The chamber must be empty (exhibits must not be left in the chamber).*

1. Close the chamber. Tighten the screw on the door.
2. Turn the 'cycle' switch to 'start' to commence the evacuation cycle.
3. When the chamber is at or below the 'fire ready' pressure ($5x10^{-4}$mbar) turn the 'cycle' switch to 'stop' to stop the evacuation cycle.
4. Turn the diffusion pump off

5. Turn the rotary pump off.

Note: *The rotary pump will continue to operate for 30 minutes to allow the diffusion pump to cool down and will automatically turn off after this time. Water will be automatically turned off.*

A2.4.9 Timer controlled gold evaporation

1. Select 'auto' on the 'fire mode' switch
2. Turn the 'thickness monitor' switch to 'off'.
3. Set the required time on the 'gold timer'.
4. Set the gold preheat timer (the top right of the four timers) to 30s or 45s if fresh gold has been placed on the boats.
5. Turn the 'fire' switch to 'start' to commence the evaporation of gold.

Note: *Gold boats will be preheated, then the shutter will open for the pre-set time (3) allowing gold to deposit on the exhibit. Once the set time has elapsed, the shutter will close and the gold current will turn off.*

A2.4.10 Manual gold evaporation

1. Select 'manual' on the 'fire mode' switch
2. Turn the 'shutter' switch to 'close'
3. Turn the 'fire' switch to 'start' to commence heating the gold boats.
4. Use a stop watch to time the gold preheat time. After the required preheating time has elapsed, turn the 'shutter' switch to 'open'.
5. Use a stopwatch to time the gold evaporation time. Once the required gold evaporation has been completed, turn the 'shutter' switch to 'close'. This will close the shutter and turn off the current to the boats.

A2.5 Development of latent prints on polymer banknotes

A2.5.1 Construction of polymer banknotes

Polymer banknotes have replaced paper notes in circulation in Australia. The notes are composed of a number of different layers, Fig. A2.4. The base of the notes is a biaxially orientated polypropylene, known as Guardian® Substrate. The clear polypropylene base (except for window areas) is coated on both sides with opacifier to enable printing to occur. A variety of printing techniques are used on the notes. A dry offset 'Simultan' press is used for the background colours, intaglio printing is used for the raised illustration, and a letterpress process for the serial number. The printed notes are then coated with a primer and then a matt coat which are cured with UV light (Colditz, 1995).

SIDE 1	**Clear matt coat**
	Clear primer
	Print (background, intaglio and letterpress)
	Opacifier
Polypropylene Base	
SIDE 2	**Opacifier**
	Print (background, intaglio and letterpress)
	Clear primer
	Clear matt coat

Fig. A2.4: Structure of polymer banknotes.

Unless a Diffractive Optically Variable Device (DOVD) is placed in the window, such as with the Australian commemorative $10 banknote, the clear windows are free from the opacifier, primer and matt coats and have minimal printing on them. This results in a very different surface to the rest of the notes. The window surface has to be treated as a non-porous surface.

The primer and matt coats combine to form a protective overcoat for the notes. This overcoat minimises wear on the printing of the notes. The protective overcoat gives the notes overall a semi-porous surface. This means that latent prints are more quickly absorbed into banknotes than other plastic surfaces. Notes must be treated with superglue fuming and vacuum metal deposition as soon as possible as latent prints degrade quickly.

As notes in circulation are used, the over-coating is gradually damaged and worn away. The damage of the overcoat makes the notes more difficult to develop prints on. Useful print detail is more likely to be developed on newer, less worn and less damaged notes.

A2.5.2 Procedure for latent print development

Note: *Banknotes should be treated by cyanoacrylate fuming as soon as possible as this will protect, to a certain extent, prints from further degradation. VMD treatment should be conducted as soon as possible after cyanoacrylate treatment.*

A2.5.2.1 Visual examination

All notes should be examined in both absorption and photoluminescence modes prior to any physical or chemical technique for latent print development. If any print is observed it should be recorded immediately before any further treatment.

A2.5.2.2 Cyanoacrylate fuming at atmospheric pressure

Note: *Cyanoacrylate fuming at atmospheric pressure can be used as an alternative method to vacuum cyanoacrylate fuming.*

1. Hang each note separately in a superglue cabinet such as the Forensic Fuming Cabinet (FFC).
2. Follow the FFC procedure for cleaning the spoons (Stoilovic & Lennard, 2001).
3. Place 6-10 drops of superglue onto both side sections of the evaporation spoon
4. Set fuming time to 1.5 hours, then press 'evaporate' button to begin the evaporative and fuming cycles.
5. When the fuming and exhaust cycles have finished, remove the notes from the cabinet

A2.5.2.3 Vacuum cyanoacrylate fuming

Note: *Vacuum cyanoacrylate fuming can be used as an alternative method to atmospheric pressure fuming.*

1. Turn on the boat heater controller at the power point on the wall and then switch on the selected boat on the front panel. Check that the transformer is set to 80 V. Leave for 30 minutes to allow the boat to heat up
2. Turn on the vacuum superglue unit at the power point. Turn on the power switch on the side of the unit.
3. Place all the banknotes within the chamber. Close the doors on both ends of the chamber.
4. Turn the vacuum pump on at the power point.
5. Check that the vacuum gauge (on the front of the unit) 'head select' is set to 1. While holding down the 'set point' button, check that the vacuum set point is set to 6 x 10^{-1} mbar. The set point can be adjusted by turning the screw marked 'set point 1' with a small screwdriver.
6. Press the 'start' button to begin the evacuation of the chamber.
7. Set a fuming time of 40 minutes on the 'cycle time', check that the timer is in mode A and that the range is appropriate. Ensure that the 'ammonia valve delay' is set to zero.
8. Turn the 'CA valve' on the right side of the control unit to 'Off'.
9. Manufacture aluminium boat using aluminium foil and the boat stamp. Check that the aluminium has not ripped.
10. Place 8 drops of glue in the aluminium boat.
11. When the set pressure has been reached the light in the top left hand corner of the vacuum gauge will turn orange. Place the aluminium boat into the left evaporation chamber and replace the lid.
12. Place a small amount of pressure on the lid of the boat and turn the 'CA valve' to 'On'. After 3 minutes turn the 'CA valve' to 'Off'. Take the lid off the boat and remove the aluminium boat.
13. When the fuming time has elapsed, the valve on the top of the chamber will open allowing air back into the chamber. With the fume cupboard on, open the right door of the chamber (within the

fume cupboard), pull down the sliding door on the fume cupboard, and then open the left door to the chamber.

14. After allowing 10 minutes or more to remove the superglue fumes from the chamber. remove the exhibits from the chamber.

A2.5.2.4 Examination on clear windows

1. All clear windows should be examined for any signs of superglue development
2. Any window with evidence of development should be stained with Basic Yellow 40. Stain should be applied with a pipette, taking care to apply the stain only to the window. The stain should be rinsed off with water.
3. Examine the stained area in the photoluminescence mode (the 450nm Polilight band, through Yellow goggles).
4. Record any useable prints (the 450 nm Polilight band, using 505 or 530 nm barrier filter). Prints on windows may be destroyed by VMD as conditions are optimised for the general note surface rather than the window area.
5. Process banknotes with VMD.

A2.5.2.5 Vacuum metal deposition

1. Place up to 30 notes on the exhibit tray using the small magnets. Magnets should cover the least area of the notes possible.

***Note**: it will be easier to keep track of development if the same side of each denomination is treated together*

2. Using the VMD operating procedure, conduct the VMD development. Set 'Terminate' (the gold counts that will be deposited) to **100** for the first development.
3. Stop zinc development when the first note has a solid zinc layer.
4. Open the chamber and remove any notes on which zinc deposition is visible. View these notes using oblique white light and photoluminescence conditions for the inherent luminescence of the notes (the 450 nm Poililight band and orange goggles).

5. Notes on which adequate print detail is visible should be placed aside for staining. Notes that were completely covered with zinc should be set aside, as no further development is possible. Return all other notes to the VMD for further development.

VMD development is then repeated until all the notes have a good zinc coverage.

6. Repeat VMD development on banknotes that have little or no zinc.
    (a) Increase the 'terminate' gold counts to double those previously used.
    (b) Stop zinc deposition each time when one of the notes has a solid zinc layer.
    (c) Open the chamber, remove all notes with visible zinc deposition and view notes using oblique white light and photoluminescence conditions. Set aside any notes with adequate print detail or a complete layer of zinc.
7. Return all other notes to the chamber for further development and repeat VMD development (follow sub-steps a-c).
8. When all of the notes have either been set aside due to the presence of print detail or a complete coverage of zinc on the first side, place all the notes back in the chamber with the second side facing out. Repeat the whole VMD procedure on the second side.
9. Photograph all areas with sufficient detail using coaxial illumination or photoluminescence conditions.

A2.5.2.6 Staining

Any note on which print detail was developed using VMD should be stained, as this will increase the contrast of the print. All graph labels must be removed before staining.

1. Basic Yellow 40 staining solution (2 g/L Basic Yellow 40 in methanol) is recommended for use on polymer banknotes.
2. Notes should be left in the stain solution for approximately 10 seconds to allow adequate staining. As the zinc deposition can be

disturbed, notes should be left to sit in the stain solution and not moved around unnecessarily.

3. Excess stain must be rinsed off the surface but this must be done gently so that the VMD development is not disturbed. Hence rinsing should be done by placing notes in a water bath, rather than under a stream of running water. Notes should be rinsed at least twice. The water must be changed between rinses.
4. After notes have dried, examine in the photoluminescence mode for Basic Yellow 40 (450 nm; with yellow/orange goggles).
5. Record all prints in the photoluminescence mode (450nm excitation, 505 or 530nm barrier filter)
6. If print contrast is not very good, due to limited zinc deposition, repeat the VMD development. Any visible print should be recorded before further VMD treatment. Set the 'Terminate' gold counts to 1.5 times the value of the last VMD treatment on that note. Zinc deposition should be watched closely and stopped once the zinc layer has been made stronger. It is quite easy to lose the detail previously developed if zinc deposition is not closely monitored.

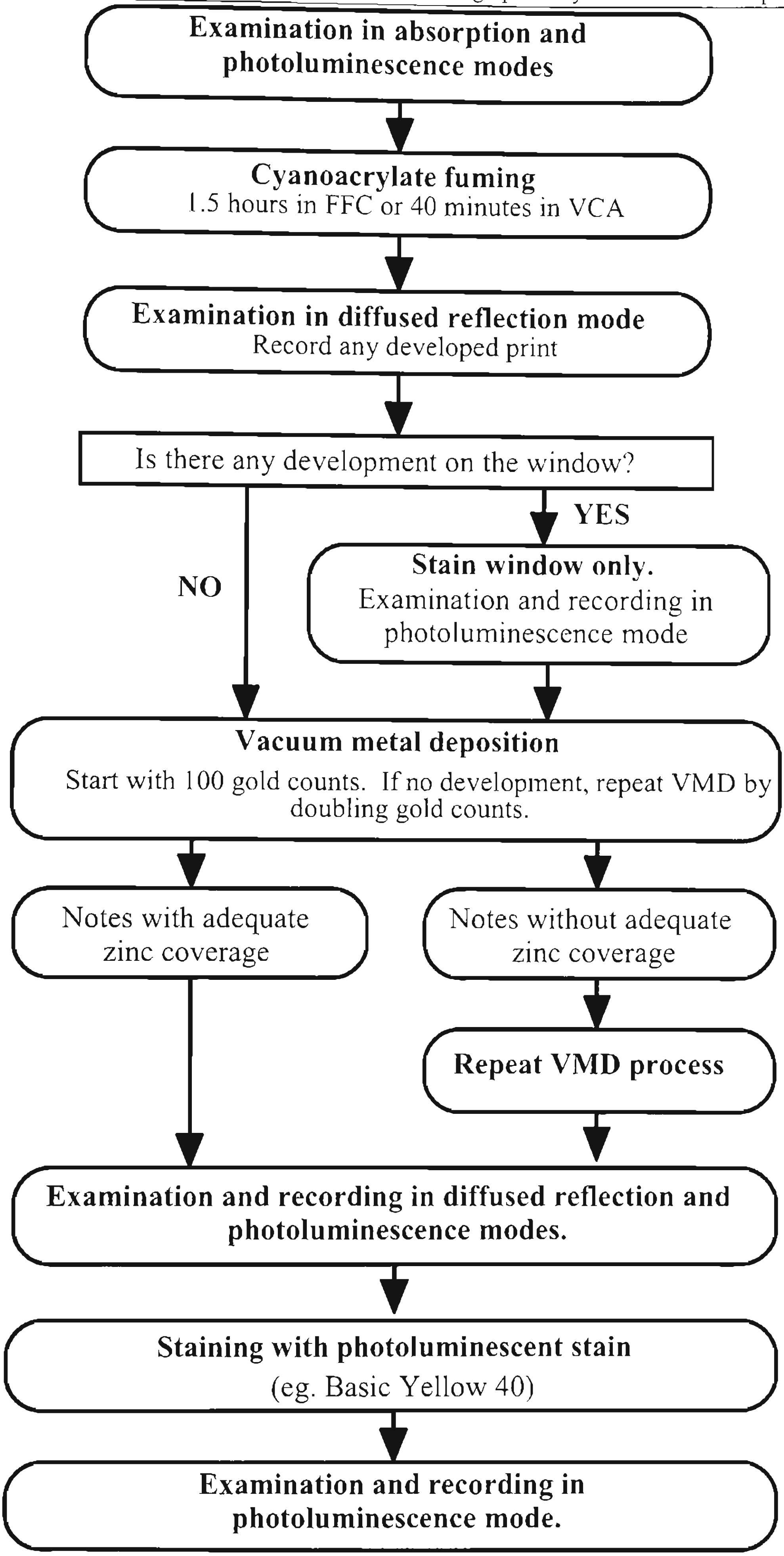

Figure A2.5 Procedure for development of latent prints on polymer banknotes.

A2.6 VMD application on various substrates

VMD conditions used must be those for the specific substrate being treated. Plastic exhibits should be analysed by FT-IR to determine their base polymer. Once the polymer type has been determined then the VMD conditions specific to that polymer can be selected resulting in the best VMD development.

The gold count listed below for each plastic should be set as the 'terminate' value for the first development. Gold counts for subsequent treatments should then be increased as described in the VMD procedure. If a zinc layer does not form and the second treatment can be conducted without opening the chamber, then the gold counts should be increased to 1.5 times the initial gold counts. In all other circumstances, when further VMD treatment is required the gold count should be doubled.

Table.A2.3. Recommended initial gold counts on various substrates.

Substrate	Recommended initial gold counts
Low-density polyethylene (LDPE)	30
High-density polyethylene (HDPE)	5
Polypropylene (PP)	10
Polyvinyl chloride (PVC)	500 (after superglue fuming)
Polyethylene terephthalate (PET)	250 (after superglue fuming)
Banknotes	100 (after superglue fuming)

The polymer type and the amount of gold that has been deposited determine the types of development that occur. The types of development expected on each polymer type are listed below.

The gold counts listed here are only valid when the gold monitor is in a particular position relative to the last gold boat. For the gold counts listed here the front of the monitor should be directly in line with the front of the left boat holder and the centre of the monitor over the right edge of the left boat holder. The gold monitor should be 8cm above the boat over the left boat holder and facing directly down, Fig. A2.6.

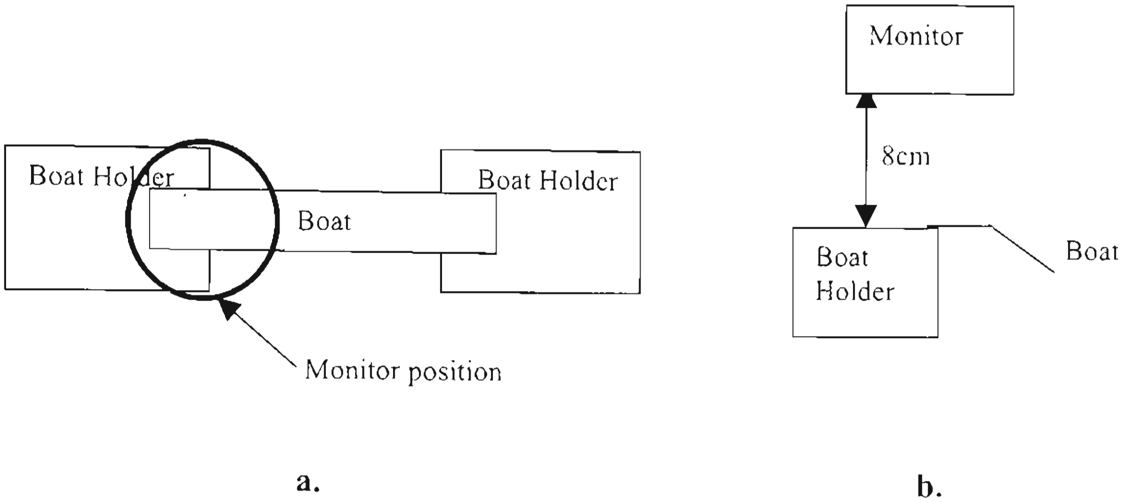

Fig. A2.6. Monitor position: **a**. Top view; **b**. Side view.

A2.6.1 Low-density polyethylene (LDPE)

- Initial gold count to be used: 30
- Expected types of development (with increasing gold counts): Normal development, reverse development, no development
- Special note: If no development occurs with high gold counts (>500) this can be corrected. Open the chamber to allow air in. Retreat with VMD using a gold count of 45.

A2.6.2 High density polyethylene (HDPE)

- Initial gold count to be used: 5
- Expected types of development (with increasing gold counts): Normal development (may be weak at low gold counts), over-development
- Special Note: Different forms of HDPE have been found to develop with different gold counts. Some forms (generally thin, clear samples) develop well with low gold counts while others (generally thick, coloured samples) require higher gold counts. Initial gold

count must be set to 5 but if no zinc deposits with 5 or 10 gold counts then gold counts may be increased to 100 without the intermediate treatments.

A2.6.3 Polypropylene (PP)

- Initial gold count to be used: 10
- Expected types of development (with increasing gold counts): Empty prints, normal development, over-development

A2.6.4 Polyvinyl Chloride (PVC)

- Initial gold count to be used: 500
- Expected types of development (with increasing gold counts): Empty prints, normal development
- Special note: The occurrence of empty prints may be minimised by the use of superglue fuming before VMD, hence superglue fuming should be conducted before VMD on PVC

A2.6.5 Polyethylene terephthalate (PET)

- Initial gold count to be used: 250
- Expected types of development (with increasing gold counts): Empty prints, normal development
- Special note: The occurrence of empty prints may be minimised by the use of superglue fuming before VMD, hence superglue fuming should be conducted before VMD on PET

A2.7 References

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A3 Appendix 3: MMD Procedures

A3.1 Preparation of 30 nm Colloidal Gold Solution

A3.1.1 Reagent solutions:

10% w/v gold chloride solution

1% w/v sodium citrate solution

0.5M citric acid solution or 0.1M citric acid solution

Tween 20 or Tween 80

A3.1.2 Preparation

1. Add 1ml 10% w/v gold chloride solution to 1 litre of ultra-pure water
2. Bring solution to the boil
3. Add 15ml 1% w/v sodium citrate
4. Boil gentle for 10 minutes, the solution should be a deep red-ruby colour
5. While still hot, stir in 5ml Tween 20 (MMDI) or 1ml Tween 80 (MMDUK), let the solution cool
6. Adjust pH to approximately 3 with 0.5M citric acid (MMDI) or pH 2.8 with 0.1M citric acid (MMDUK). *All colloidal gold solutions were adjusted to pH 2.65 in accordance with Schnetz's recommendation.*
7. Restore volume to 1 litre with ultra-pure water

A3.2 14 nm Colloidal gold solution

A3.2.1 Reagent solutions

0.1g/ml tetrachloroauric acid (use fresh reagent, store in fridge)

1% sodium citrate (store at room temperature)

0.1M (96g/L) citric acid (store at room temperature)

1% tannic acid (store in fridge)

A3.2.2 Preparation

1. Mix 400ml double distilled water and 500 µl 0.1g/ml tetrachloroauric acid
2. Separately mix 75 ml double distilled water, 20ml 1% sodium citrate and 100 µl 1% tannic acid
3. Heat the two mixtures separately to 60°C
4. At 60°C quickly add the second solution (sodium citrate and tannic acid) to the first (tetrachloroauric acid) while mixing vigorously
5. Bring the mixture to boiling point- the solution turns orange
6. Allow to cool to room temperature
7. Adjust the volume back to 500ml with double distilled water
8. Allow to cool to room temperature-Store in plastic in fridge at 4°C
9. Immediately before use: restore to room temperature
10. Add 500 µl of Tween 20 (or 80) to the solution with stirring
11. Adjust the pH to 2.5-2.8 with 0.1M citric acid. *Solutions were adjusted to pH 2.65 in accordance with Schnetz's recommendation.*

Note: Don't make more than 500 ml of colloidal gold solution at once as this will result in a heterogenous solution

A3.3 Iron (II)/Iron(III) physical developer

A3.3.1 Redox solution

Into 1 litre of ultra-pure water dissolve the following *in order*

16g ferric nitrate

44g ferrous ammonium sulfate

11g citric acid

0.25ml 1% Tween 20

A3.3.2 Silver nitrate solution

Dissolve 10g silver nitrate in 100ml ultra-pure water

A3.3.3 Working solution

Add 2ml silver nitrate solution slowly with stirring to 100ml redox solution.

A3.4 Silver acetate/hydroquinone physical developer

A3.4.1 Silver acetate solution

Dissolve 200mg of silver acetate in 100ml double distilled water. Stir with magnetic stirrer in beaker covered with aluminium foil, will dissolve slowly so prepare 30 minutes before use

A3.4.2 Hydroquinone solution

A3.4.2.1 Solutions

Citric acid solution: 255g in 1L double distilled water

Sodium citrate solution: 235g in 1L double distilled water

A3.4.2.2 Preparation

Mix together 24 units citric acid solution, 22 units sodium citrate solution, 50 units double distilled water to from the citrate buffer. Buffer should have a pH of 3.8, add citric acid or sodium citrate solutions to adjust the pH of the buffer as required.

Dissolve 1g hydroquinone in 200ml citrate buffer

A3.4.3 Working solution

A3.4.3.1 Hydroquinone rinse

Add 100ml double distilled water to 100 ml of Hydroquinone solution

A3.4.3.2 Physical developer

Mix 100ml silver acetate solution and 100ml hydroquinone solution. Prepare seconds before use

A3.5 Application-Saunder's procedure

Scrupulously clean glassware is required.

1. Soak the item in distilled water- 5-10 minutes for non-porous substrates and 20-30 minutes for porous substrates

2. Immerse the exhibit into the 30nm colloidal gold solutions. Agitate gently for 30-120 minutes. Some fingerprints may already develop at this stage.
3. Rinse the exhibit in distilled water- briefly for non-porous surface. about 15 minutes for porous surfaces.
4. Immerse in freshly prepared iron(II)/iron(III) physical developer solution. Remove when good silver deposition has occurred, usually 1-5 minutes.
5. Rinse the exhibit thoroughly in distilled or tap water
6. Air dry the exhibit

A3.6 Application-Schnetz's procedure

Silionised glassware should be used. (see section A2.8)

1. Wash surface before treatment:
    - Non-porous surfaces: pass quickly through distilled water
    - Porous surfaces: soak for approx. 2 minutes in distilled water
2. Immerse exhibit in 15nm colloidal gold solution for 5-15 minutes, gently move with solution
3. Rinse in double distilled water
4. Soak for 2- 5 minutes in hydroquinone working solution
5. Transfer to freshly prepared silver acetate/hydroquinone physical developer solution, soak for approx. 18 minutes at room temperature (solution will become dark grey after 10-20 minutes but this will not affect results)
6. Rinse in double distilled water
7. Fix with photographic fixer (dilution 1:9) for 2-5 minutes
8. Rinse with tap water

A3.7 Application-FSS method

1. Place the item in distilled water for 2-5 minutes.
2. Transfer to 30nm gold colloidal solution for at least 10 minutes, ensuring all surfaces of the item remain in contact with the gold.
3. Place the item in the hydroquinone working solution containing a sufficient volume to fully immerse the item.
4. Place the item in the silver acetate/hydroquinone physical developer solution and allow any marks to develop over a period of 5-40 minutes. Observe the item for development of marks. If any are developed remove the item when it is judged that the optimum contrast has been reached.

5. Drain off the excess silver acetate solution and place the item in the distilled water wash tray (number 5) and agitate the tray. This will remove the bulk of any silver acetate carried over
6. The item should be dried and examined for marks again.

A3.8 Siliconisation of glassware

(This will produce siliconised glassware that will be resistant to numerous washings)

1. Soak glassware overnight in bath of 10% Extran (Niaprooof Type 8) (Sodium 2-ethylhexyl sulphate)
2. Rinse well in hot water and then cold water
3. Dry in an oven at 100°C
4. Remove from oven and cool to room temperature
5. Soak for 5 secs in treatment solution – 4ml of 3-amino propyltriethoxysilane in 200ml acetone
6. Rinse twice in acetone
7. Rinse twice in distilled water
8. Dry in an oven at 42°C for 1 night