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Review

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Fingerprint Development Techniques: A Review

Técnicas de Revelação de Impressões Digitais: Uma Revisão

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Fingerprints have been used as a method of human identification for more than a century and are still considered fundamental evidence in the resolution of crimes due to their uniqueness. In most cases, the fingerprints found are latent, and therefore it is necessary to use some kind of developer to enable their visualization. Thus, this review aims to present the various types of physical and chemical developers currently used and their interactions or reactions with fingerprint compounds. In addition, low-toxicity and nanomaterial-based developers currently under study will also be presented.

Keywords: Fingerprints; physical developers; chemical developers; green methods; nanomaterials

1. Introduction

One of the most commonly used methods of human identification is the one based on friction ridges, which can be found on the palms of the hands and soles of the feet. In criminal investigations, for the identification of the culprit or the elimination of a suspect, fingerprints are mostly used, due to the existence of a larger database.[1,2]

Fingerprints can be found at crime scenes in their visible, plastic or latent form. Visible fingerprints are those that can be easily seen with the naked eye because of the presence of a colored substance, such as ink, blood, or dust, among others. In this case, it is only necessary to photograph the fingerprint. Plastic fingerprints are formed when the finger is pressed against a malleable substance, creating a mold. In this case, the print can also be directly photographed or a mold can be made with a casting material.[2,3]

However, latent fingerprints are the most commonly found at crime scenes, and, being invisible to the naked eye, adequate dactyloscopic methods are needed for their visualization. Ideally, optical techniques would always be used, because they are non-destructive and easy to use. Nevertheless, most of the time these techniques are not enough, and a physical or chemical process is required in order to provide color or luminescence. The selection of the most suitable developer for each situation depends mainly on two factors: the composition of the particular fingerprint, and the surface on which the fingerprint is located.[3,4]

Therefore, this review aims to present and discuss the different types of developers, physical and chemical, currently used. In addition, developers that are still being researched will also be presented, such as those with low or no toxicity and those containing nanomaterials.

2. Fingerprints Composition

The composition of the fingerprints interferes directly in their development because it is the interaction between the components of the latent fingerprint and the developers that allow their visualization. However, the composition of the fingerprints is complex, as it depends on intrinsic and extrinsic factors.[1,2,5]

The intrinsic components of fingerprints are mainly the natural secretions of the eccrine and sebaceous glands, in addition to metabolites and traces of drugs. Moreover, variables such as age, gender, race, health, diet, metabolism, and others, influence the composition.[2,6]

The eccrine glands are present throughout the body and their secretion is mostly composed of water, along with amino acids, proteins, urea, uric acid, lactic acid, carbohydrates, creatinine, choline, chlorides, metal ions, sulfates, phosphates, carbonates and ammonia. The sebaceous glands are present in the regions of the body where there are hair follicles and their secretion (sebum) is composed of triglycerides, wax monoesters, free fatty acids, squalene, cholesterol and other lipidic esters. Although these glands are not present in the palms of the hands and soles of the

feet, due to the inexistence of hair follicles, their secretion is very much found in the fingerprints due to the contact of the hands with other regions of the body, more commonly with the face, where there is an abundance of them.[5,6,7]

The extrinsic components of fingerprints are substances that a person may have contact with during the day, such as dust, cosmetics, blood, grease, food, among others. In addition, environmental factors such as climate and weather can influence, because degradation, evaporation of volatiles, action of microorganisms and oxidation can occur, affecting the composition.[1,5]

3. Surfaces

During an investigation, determining the type of surface on which a fingerprint was left is very important. As each surface has its own characteristics, the technique that should be used to develop the fingerprint will vary according to them.

Surfaces can be classified as porous or non-porous. On porous surfaces, when a fingerprint is deposited, its compounds migrate beneath it, because these surfaces are mostly absorbent. For this type of surface, it is recommended the use of reagents that interact with amino acids, because when they are absorbed, they remain stationary.[4]

Non-porous surfaces, smooth or rough, are often found at crime scenes. Since they have no pores, the fingerprint becomes a deposit on the surface and are therefore fragile and easily destroyed.[8]

4. Physical Methods

Physical fingerprint developers are those whose performance is based on the adherence or solubility of their compounds to the components present in latent. The physical developers currently in use will be presented below.

4.1. Powder technique

The application of powder is one of the oldest fingerprint development methods and is still one of the most used in the world. In the past, highly toxic powders containing mercury and cadmium were used, but studies proving their harmful effects on health have led to new powders being manufactured. Their use is recommended for non-porous smooth surfaces.[9]

This technique is based on the adsorption of powder particles onto moisture and oily fingerprint components, which is controlled by a pressure deficit mechanism. The wetting of only the bottom part of a particle of powder by substances present in the fingerprint causes a pressure deficit within the droplet due to the curvature of the meniscus. This causes the dust particles to stick to the fingerprint. In addition, factors such as the electrostatic attraction between the dust residue and the particles, the size and shape of the particles (fine, round powders have better results) and their composition also affect the adhesion.[10]

Today, there are different types of powders, which can be classified as regular (e.g., the Black Powder and the White Powder), metallic (e.g., Aluminum Powder and Magnetic Black Powder), or fluorescent (e.g., the GREENescent and the PINKescent Fluorescent Fingerprint Powder, sold by Sirchie®).[4]

The composition of the regular powders varies, but generally a binder and a pigment substance are present. The pigment is the substance that creates a contrast with the surface and allows visualization, while the binder is what promotes a maximum and selective adhesion to the components of the fingerprint. Some examples of dyes are: carbon black, talc, kaolin, aluminum, metal flakes, among others, whereas examples of good binders are: iron powder, corn starch and gum arabic.[4]

Metallic powders are those that have metal in their composition, such as iron, aluminum, copper, bronze and many others. Most of these powders are also magnetic, so their application is done with a magnetic brush. The advantage of this technique is that there is no brushing, so there are much lower chances of fingerprint destruction.[9,10]

Fluorescent powders are those which contain in their composition organic substances that exhibit fluorescent or phosphorescent properties when exposed to ultraviolet or laser light, such as acridine, violet crystal, and coumarin 6. These powders are used when the surface is reflective or multicolored, which may cause contrast problems if common powders are used.[9,10]

4.2. Small particles reagent

The small particle reagent (SPR) is also used for non-porous surfaces, but is indicated when the surface is wet. This reagent is conventionally composed of molybdenum disulfide in a surfactant solution, although studies have proved the possibility of replacing molybdenum disulfide with titanium dioxide, zinc oxide, magnetite, graphite or zinc carbonate. Additionally, fluorescent compounds such as violet crystal, rhodamine and basic yellow may be added for the preparation of fluorescent SPR.[9,11,12,13]

A wet surface makes it impossible to use fingerprint developers which interact with water-soluble compounds or that need to be applied dry, such as powders. For this reason, SPR is used, since it adheres onto oily fingerprint compounds (sebum).[9,11,14]

There is also another type of powder suspension, used for developing the adhesive side of tapes called sticky-side powder. Its composition is basically a powder, usually black, added to a detergent. This suspension is applied with a brush over the tape containing the fingerprint and removed with water after 10 - 30 seconds.[9]

4.3. Iodine

The iodine fumigation method has been used for more than a century. In the past it was believed that a chemical reaction occurred between iodine and fingerprint compounds, but more recent studies suggest that in reality a physical adsorption occurs.[11,15]

When heated, the iodine crystals sublimate, producing a purple vapor. This vapor then adheres to the lipidic compounds of the fingerprint, which is believed to occur through non-covalent intermolecular bonds such as van der Waals interactions. As a result, yellow-brownish fingerprints are developed. However, the color is not stable and disappears after some time.[11,15]

Iodine can be used for both non-porous and porous surfaces and there are four ways of using this technique. It is possible to use an iodine fuming gun, which consists of a thin tube containing the iodine crystals, heated by blowing. Another way is to use an iodine fumigation cabinet, which consists of a sealed compartment in which the crystals are placed on a heating plate and the material containing the latents is hung on the lid, in this way, as the iodine sublimates the fingerprints are developed. The third way is by scanning the iodine, which occurs in the same way as when a common powder is applied.[15,16]

The fourth and last way is to use the iodine in a 7,8-benzoflavone solution (Figure 1) or to apply the 7,8-benzoflavone solution immediately after iodine fumigation. The aim of this technique is to increase stability by preventing color from disappearing easily, and to improve contrast as this method develops dark blue fingerprints.[9,15]

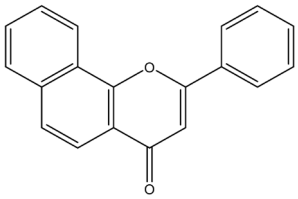


Figure 1. Chemical structure of the 7,8-benzoflavone

Although it is a simple technique, iodine vapors are toxic and corrosive. Moreover, as already mentioned, its complex is not a stable substance, so the color tends to disappear.[9,15]

4.4. Vacuum metal deposition

The deposition of metal using vacuum was already known, but it was only applied to fingerprints around 1970. This technique is based on the deposition of gold and zinc metals on the surface containing the latent, and has been used for non-porous surfaces. For this, thin gold and zinc wires are used, both with purity >99%. Additionally, a chamber previously evacuated to less than 5×10^{-4} mbar is needed.[17]

The first step is the deposition of gold particles on the surface through their evaporation under vacuum, forming a thin film, invisible to the naked eye. The gold film covers the entire surface, and the particles that are on top of the fingerprint compounds are absorbed by them.[11,17]

After that, the zinc is evaporated under the same conditions. However, the zinc is deposited preferentially on the gold and is not absorbed by the fingerprint residues (Figure 2). Therefore, fingerprints remain transparent, but the background is covered with zinc, allowing them to be visualized.[9,11,17]

Studies have shown that this technique can also be efficient on surfaces of white cotton, nylon, polyester and polycotton fabrics. In addition, other studies have investigated the phenomenon of reverse development, i.e., when the deposition of zinc is on the fingerprint and not on the background.[9,11]

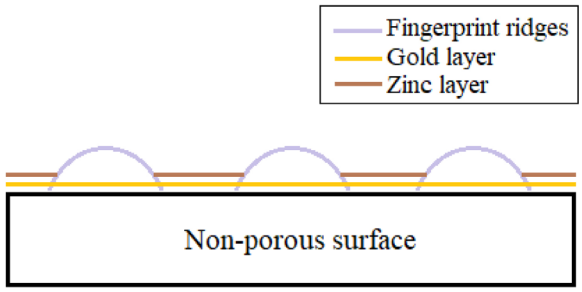


Figure 2. Representation of the development of fingerprints by vacuum metal deposition. Adapted from Champod *et al.* (2016) [9]

4.5. ESDA

The electrostatic detection device (ESDA) was introduced as a fingerprint developer in the 1970s. This technique is considered non-destructive and therefore used mainly in documents, as they must not be damaged. However, studies have shown that documents with pencil writings may exhibit small damage. ESDA is not only used for fingerprint enhancement but also for detecting indented writing.[18,19]

The exact mechanism of this technique has not yet been elucidated; however, its operation is simple. First, the paper containing the fingerprints is placed on the ESDA equipment. Then, a Mylar film (polymer film) is gently placed on the sample. Only then the vacuum is turned on and consequently, the Mylar film adheres to the paper. After that, a device known as a corotron is turned on and passed a few times over the surface, without touching it. This device contains a high voltage wire and, therefore, is used to apply an electrostatic charge. When the Mylar film is charged, the corotron is turned off and the cascade developer (fine glass spheres mixed with toner particles, i.e. carbon black) is poured. Consequently, the toner particles adhere preferably to the charged pattern developed on the surface (Figure 3).[21,19,20]

There are two theories for the working mechanism of this technique. Briefly, the first one, called the Thickness Variation Theory (TVT), says that, in the place where the

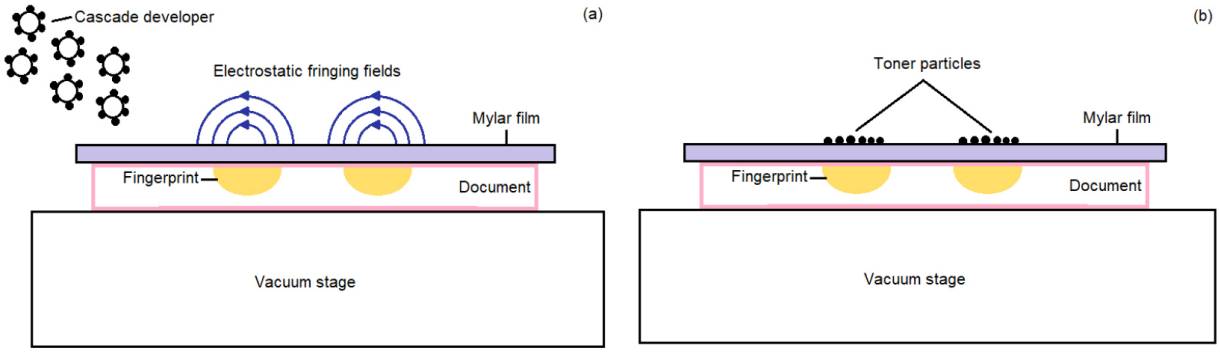


Figure 3. Representation of the fingerprint development mechanism using ESDA, a) Cascade developer poured after electrostatic charge; b) Fingerprints developed with toner. Adapted from Bleay, Croxton and Puit (2018).[21]

paper fibers were disturbed because of the writing process, indentations are caused and, because of this, there will be a difference in potential across the paper, which causes the toner particles to adhere preferentially to those regions with indentations. However, this theory does not explain the development of fingerprints.[21,19]

The second one, called Surface Variation Theory, explains that when the humidity is below 40%, the development of images probably occurs according to the TVT. Nevertheless, when the humidity is above 60%, impressions are developed for another reason. When the humidity is low, the paper acts as a dielectric surface, but when the humidity is high, the paper becomes a conductor. Therefore, the increase in softness of the paper makes it closer to the film, decreasing the electrostatic potential of this particular place, allowing the development of indented writing or fingerprints. This theory also explains why ESDA works best on recent latents. [21,19]

4.6. Lipid stains

Lipid stains are fat-soluble dyes. The most common lipid dyes used for fingerprint development are shown below.

4.6.1. Sudan black

Sudan black (Figure 4) is a reagent recommended for developing latents on non-porous surfaces that contains grease or sticky substances. [9,22]

When the Sudan black solution comes in contact with the fingerprint residues, the lipophilic dye molecules are preferably transferred from the solution to the oily compounds of the fingerprint, developing a black fingerprint.[9,22]

4.6.2. Oil red O

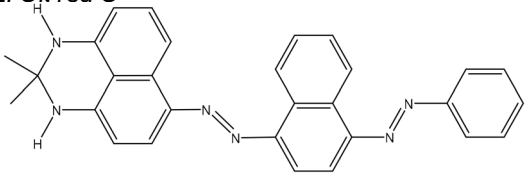


Figure 4. Chemical structure of the Sudan Black

Oil red O (ORO) (Figure 5) is a lipophilic dye used since the 1920s to stain biological materials. However, it was only in 2004 that this dye was used as a fingerprint developer. [23,24]

ORO is an azo dye, which makes its ionization difficult, contributing to the solubility in lipids. This lysochrome (lipid-soluble dye) is used on porous surfaces and stains the lipoproteins separated by electrophoresis. As a result, visible red marks will be developed. [23,24]

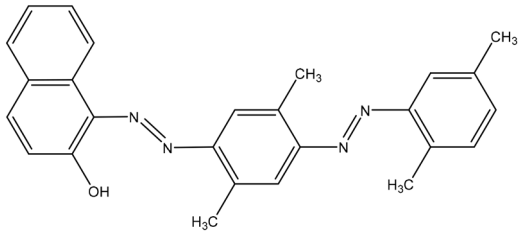


Figure 5. Chemical structure of the Oil red O

Its solution is made from a mixture of two solutions. One of them contains only ORO (dyeing agent) and methanol (solvent), the other contains only sodium hydroxide (this creates a basic environment to facilitate the dyeing) and water (to increase ORO's preference for the lipidic environment). The mechanism is the same as for Sudan Black.[21,23,25]

In addition, a buffer solution is also required, which contains sodium carbonate, nitric acid and water. Its function is to neutralize and stabilize the medium, allowing the development of fingerprints, being used about one hour after the immersion in ORO. To finish the fingerprint development, the surface is then washed with distilled water and left to dry naturally.[21,23,25]

However, this method is not widely used because it is a time demanding technique, the solvent methanol is toxic and it does not work for fingerprints older than four weeks. Furthermore, another reagent, the physical developer (presented in the 5.11 section) has the same applicability as ORO and can be more efficient.[25]

4.6.3. Nile red and Nile blue A

Nile Red was first proposed in 1993 by Saunders, aiming to replace the physical developer (presented in section 5.11 of this article) for use as a latent developer

in porous surfaces. The advantage of this reagent is its luminescent property, which eliminates interferences from the background.[26]

The solution used for Nile Red is a mixture of two solutions. One is the solution of Nile Red in the solvent methanol and the other is sodium hydroxide in the solvent deionized water. Immediately before and after the immersion of the surface in this solution, which lasts until fingerprints are visible, the surface must be immersed in deionized water for 5 minutes.[26]

However, Nile red is an expensive reagent and is used in a methanol solution, which is a toxic solvent. As a result, the reagent Nile Blue A was proposed, with the intention of replacing it.[27]

The solution for Nile Blue A contains only this dye and deionized water as a solvent. This developer stains the acid constituents of the fingerprint, such as phospholipids and fatty acids, with a dark blue color. In addition, it can undergo spontaneous hydrolysis, resulting in Nile Red, and thus also stains neutral lipids with the color red and develops luminescent marks. The mechanism is shown in Scheme 1.[27]

Nile Red interacts with the fingerprint in the same way as Sudan Black and Oil red O, since it also has a preference for the lipid environment and is therefore transferred from the solution to the oily compounds in the latent, developing red fingerprints with fluorescent properties. The interaction of the Nile Blue A with the acid molecules occurs by salt linkage, and when it suffers hydrolysis, forming the Nile Red, the interaction is the one explained above. When observed under a forensic light source, fluorescent fingerprints are seen, with maximum absorption around 490 nm and emission around 560 nm.[26,27]

5. Chemical Methods

Chemical methods are those in which some chemical reaction occurs between the residue of the fingerprint and the developer. The chemical developers currently in use will be presented below.

5.1. Gentian Violet

Gentian violet (Figure 6), also known as violet crystal and Basic Violet 3, is an organic dye used primarily for developing fingerprints on adhesive tapes, on the adhesive side.[11]

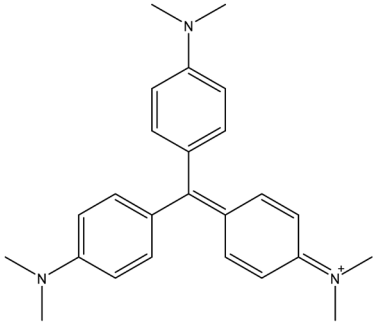
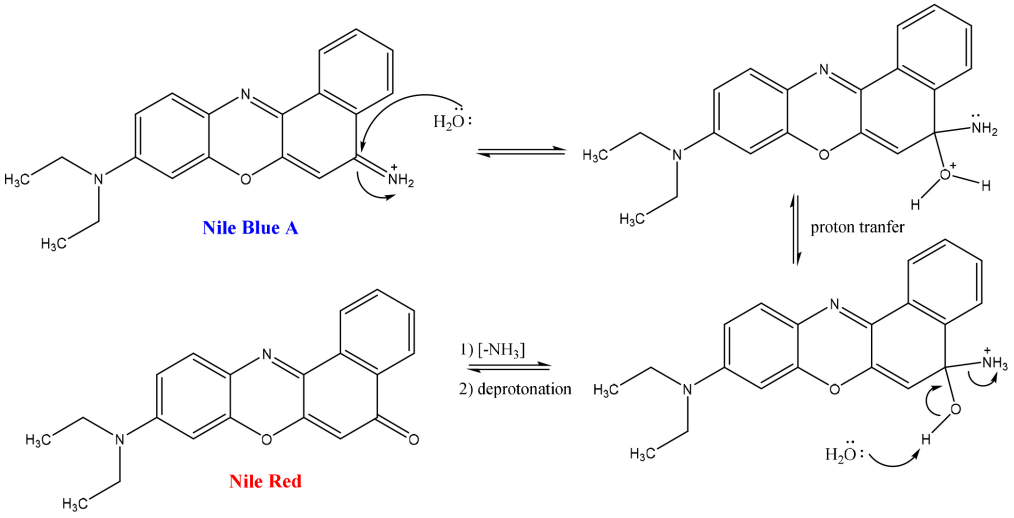


Figure 6. Chemical structure of the Gentian Violet

Gentian violet is also known to be used as a nuclear or chromatin dye. This is because it binds externally to DNA. In forensic science, the application of the violet crystal solution triggers a reaction believed to be between epithelial cells (likely to be present on the adhesive side of tapes) and the reagent, developing purple fingerprints. However, this has not been proved and the exact mechanism is still unknown.[11,28,29]

One problem with this technique is that it is considered toxic and requires adequate Personal Protective Equipment (PPE), since the reaction between the reagent and the skin is fast and the staining cannot be easily removed.[16]

There is also the basic violet 2 compound, which, although not used as a fingerprint developer, has been the subject of some studies in this area. Garret and Bleay (2013) emphasize that this compound should be better studied, as



Scheme 1. Spontaneous hydrolysis of Nile Blue A, resulting in Nile Red, adapted from Frick *et al.* (2014)[27]

it interacts with more fingerprint constituents than the basic violet 3. In addition, the basic violet 2 exhibits an easier to visualize fluorescence, with an emission in the orange-red region, while the emission of the violet crystal is in the infrared region.[30]

5.2. Cyanoacrylate

Cyanoacrylate, also called superglue, is a chemical reagent that develops white fingerprints on non-porous surfaces. This process involves the vaporization of cyanoacrylate, which reacts with the residue of the latent.[4,31]

The cyanoacrylate fuming method is based on a three-step anionic polymerization reaction. The initialization consists of the nucleophilic attack on the electron-deficient carbon of the cyanoacrylate monomer. The nucleophile can be an amino acid, water, ammonia, alcohol, a carboxylic group, and others.[4,31]

The second step consists of the successive reaction between monomers, forming the polymer. The third step is the termination, and occurs when there are no more monomers for the reaction and the polymer chain is finalized. The polymerization reaction is shown in Scheme 2.[4,31]

The sensitivity of cyanoacrylate to the nucleophile is explained by the fact that its monomer has electron withdrawing group with strong inductive effects, such as nitrile (C≡N) and carbonyl (C=O).[4,31]

One disadvantage of this technique is that the polymer formed has a white color, so a contrast problem may occur, depending on the surface. However, there are some solutions for this, such as the use of powders or fluorescent compounds such as Ardrox reagents, Basic Yellow 40, Rhodamine 6G and 4-(4-methoxybenzylamino)-7-nitrobenzofurazan (MBD) (Figure 7).[31]

All these dyes are lysochrome and adhere to lysophilic surfaces by non-covalent forces. They are visualized using a UV light, with Ardrox absorbing between 435-480 nm, Basic Yellow 40 between 415-485 nm, MBD between 415-505 nm and Rodamine 6G between 495-540 nm.[11,32]

5.3. Silver nitrate

The use of silver nitrate for fingerprint development is one of the oldest techniques, used since 1891, although today it is less used.[15]

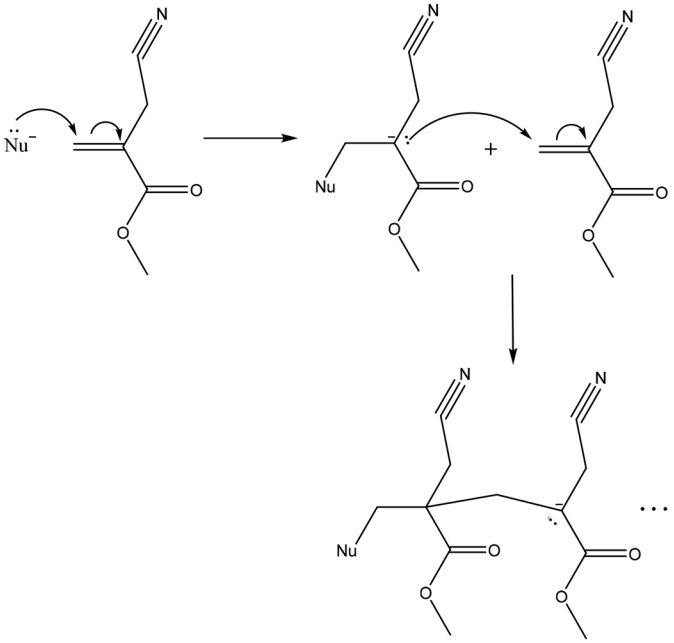
The principle of this technique is the reaction of silver nitrate with the chloride anion present in fingerprint residues. The development occurs in two stages. First, the precipitation reaction of silver chloride (AgCl) occurs, according to the reaction (1).[4,11]

$$AgNO_{3(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} + NO_{3(aq)} \quad (1)$$

Then, the silver chloride formed, when exposed to ambient light (UV light), undergoes a process of oxidation-reduction forming solid silver (2). Elemental silver has a dark grey color, which makes the visualization of the fingerprint possible.[4,11]

$$2AgCl_{(s)} + h\nu \rightarrow 2Ag^{0}_{(s)} + Cl_{2(g)} \quad (2)$$

This reagent works well on porous surfaces for two main reasons. The first is that the precipitation reaction is much faster than dissolution. The second is that AgCl, due to its insolubility, is retained at the interstices of the surface where the fingerprint residues were previously absorbed.[4]



Scheme 2. Polymerization reaction of cyanoacrylate. Adapted from Bumbrah (2017)[31]

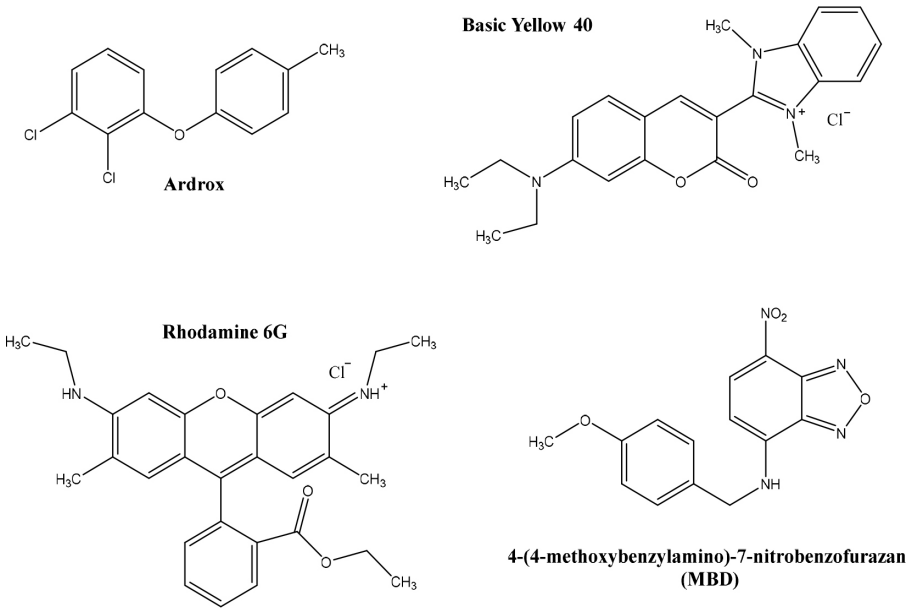


Figure 7. Chemical structures of the Ardrox, Basic Yellow 40, Rhodamine 6G and MBD

5.4. 1,8-Dazafluoren-9-one (DFO)

The 1,8-diazafluoren-9-one (DFO) is a substance used on porous surfaces and reacts with the amino acids present in the fingerprint. The result is a pale red product, which, besides being visible, has strong luminescence under green light, with absorbance at 470 nm and emission at 570 nm.[33] The proposed mechanism for the DFO reaction is shown in Scheme 3.

The first step occurs by nucleophilic attack of the electron-deficient carbon of the DFO carbonyl by the amino group of the amino acid, forming the intermediate I. Then, two successive proton transfers occurs, forming the intermediate II and the intermediate III, which suffers dehydration, producing a Schiff base (intermediate IV), characterized by the formation of a CN bond.[24,25]

After that, a deprotonation occurs, resulting in the intermediate V, followed by a decarboxylation, producing the corresponding imine (intermediate VI), which undergoes a nucleophilic attack and a protonation, resulting in the intermediate VII.[34,35]

Subsequently, another proton transfer occurs to form the intermediate VIII, followed by the elimination of the aldehyde, resulting in the intermediate IX.

Next, another DFO molecule reacts with the aromatic amine, leading to the formation of the intermediate X, in which a proton transfer occurs to form the intermediate XI. Finally, a dehydration reaction forms an azomethine ylide with a greater extension of conjugation (molecule XII), which explains the fluorescence.[34,35]

5.5. 1,2-Indanedione (1,2-IND)

The 1,2-indanedione is a substance first synthesized in 1997 used for the development of fingerprints on porous surfaces. The 1,2-IND reacts with amino acids resulting in a pale pink product, but with strong luminescence under a light with a wavelength between 480-560 nm. [36]

The mechanism for the reaction of the 1,2-IND is very similar to the DFO mechanism, therefore only its reaction scheme is presented in Scheme 4. The 1,2-IND reaction also starts with a nucleophilic attack from an amino acid, followed by the same stages explained for the DFO. At the end, there is a reaction with another 1,2-IND molecule that will result in a molecule called Joullié's Pink (JP), an azomethine ylide with greater conjugation extension, pale pink color and fluorescence. [35,36]

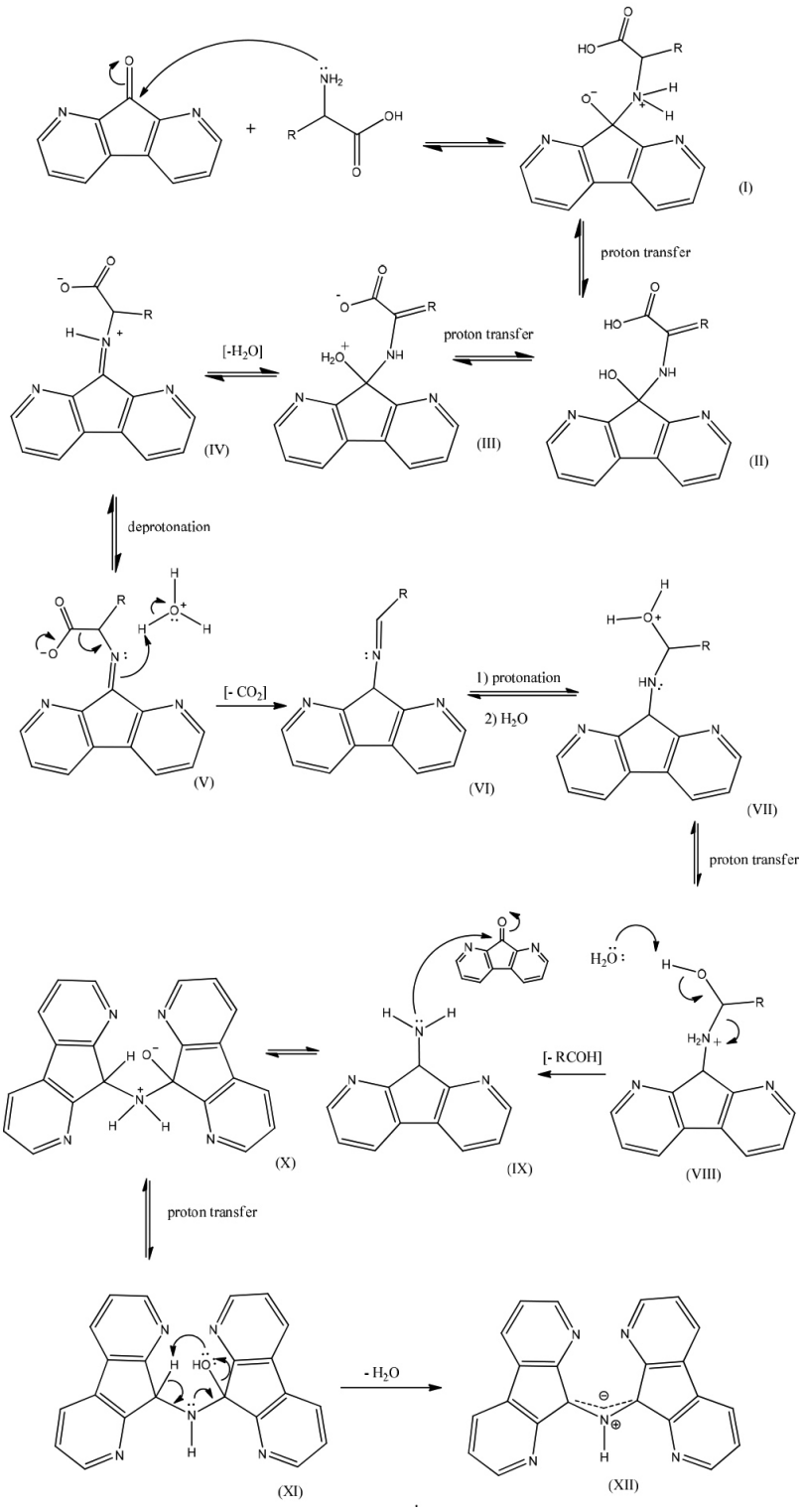
The problem with this technique is that loss of color and luminescence can occur after a few days. However, studies have shown that the addition of zinc or cadmium salts is able to improve color and luminescence as well as prolong the duration of these effects from a complexation reaction between the metal and JP.[6,9,36]

5.6. Ninhydrin

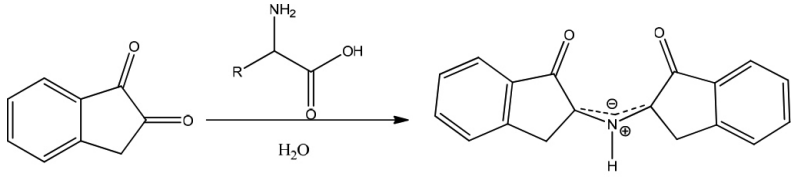
The application of ninhydrin for latent development is an old technique, with references dating back to 1959, and is to this day one of the most popular methods used on porous surfaces, especially on paper.[4,37]

Ninhydrin is a pale-yellow substance and reacts in contact with amino acids, generating a non-fluorescent purple product known as Ruhemann's Purple. The mechanism for this reaction is very similar to the DFO mechanism, therefore only the reaction scheme was presented in Scheme 5. [6,9,37]

First, a ninhydrin molecule is dehydrated, forming indan-1,2,3-trione, which reacts with amino acids, just like in the DFO mechanism. After that, the reaction continues as shown for the DFO. Finally, there is a reaction with another



Scheme 3. Mechanism for the reaction between DFO and amino acids. Adapted from Wilkinson (2000) and Ramachandran (2007)[34,35]



Scheme 4. Proposed mechanism for the reaction of 1,2-IND with amino acids. Adapted from Ramachandran (2007)[35]

dehydrated ninhydrin molecule to form an azomethine ylide, a product with a large conjugation extension, called Ruhemann's Purple. [6,9,37]

A problem with this method is that, even though it is very efficient, it can present contrast problems, making it difficult to visualize. Therefore, a second treatment with metal salts can be carried out, using zinc or cadmium. However, as cadmium is very toxic, the use of zinc is recommended. [6,9]

When this second treatment is carried out, a coordination complex is formed (Scheme 6), changing the color of the developed fingerprint, besides granting luminescence properties. The use of zinc changes the color of the fingerprint from purple to orange, showing maximum absorption around 490 nm. The use of cadmium changes the color to red and exhibits maximum absorption around 505 nm. The luminescence is best visualized when the fingerprints developed are cooled down with liquid nitrogen.[6,9]

5.7. Dimethylaminocinnamaldehyde

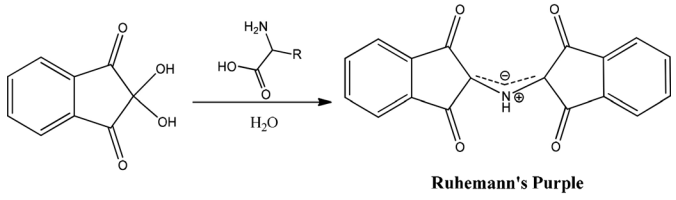
The dimethylaminocinnamaldehyde (DMAC) was proposed as a fingerprint developer in 1973. The interest in this reagent occurred because, in addition to reacting with amino acids, it reacts mainly with urea, which is highly present in the eccrine secretion.[9,21,38]

DMAC has an analogous compound, dimethylaminobenzaldehyde (DMAB), which can also be used in fingerprint development. However, DMAC has better performance, exhibiting more intense color and luminance. The molecules are shown in Figure 8.[38]

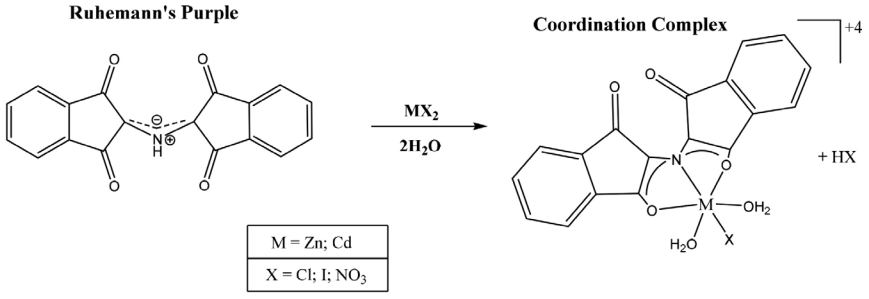
DMAC and DMAB are both used on porous surfaces. Fritz, Van Bronswijk e Lewis (2015) found that DMAC reacts with primary and secondary amines to produce blue and purple compounds, respectively, while a yellow and an orange product are formed when DMAB reacts with monoamines and di- and polyamines, respectively. However, Bleay, Croxton e Puit (2018) found that a magenta-colored product is obtained in the reaction between DMAC and urea. All reactions result in products with luminescent properties.[21,38]

The proposed mechanism for this developer's reaction with a molecule of urea is presented in Scheme 7. The reaction requires an acid medium to take place, and occurs between the DMAC and a primary amine, present in the residues of the fingerprint, producing an imine, or Schiff base, with maximum absorbance around 480 nm and emission at 525 nm. The reaction mechanism for DMAB is essentially the same. When reacting with a secondary amine, both developers produce enamines and the difference in the mechanism is that instead of the nitrogen, it is the adjacent carbon that loses a proton.[21,38]

The problem with DMAC is that urea migrates easily through porous surfaces, so fingerprint development after a few days is difficult. Because of this, research has been



Scheme 5. Proposed reaction scheme for the reaction of ninhydrin with amino acids. Adapted from Alves (2014)[37]



Scheme 6. Second treatment reaction for fingerprints developed with ninhydrin. Adapted from Aumeer-Donavan, Lennard and Roux (2009) [44]

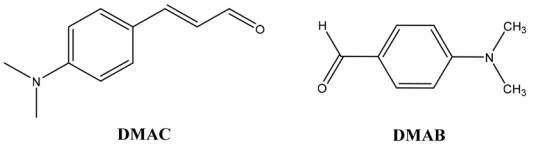
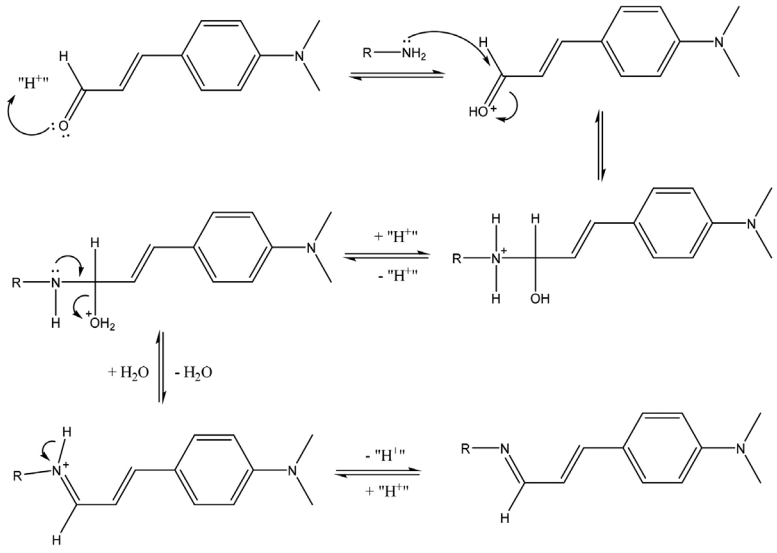


Figure 8. Chemical structures of the DMAC and DMAB



Scheme 7. Proposed mechanism for the reaction of DMAC with a primary amine

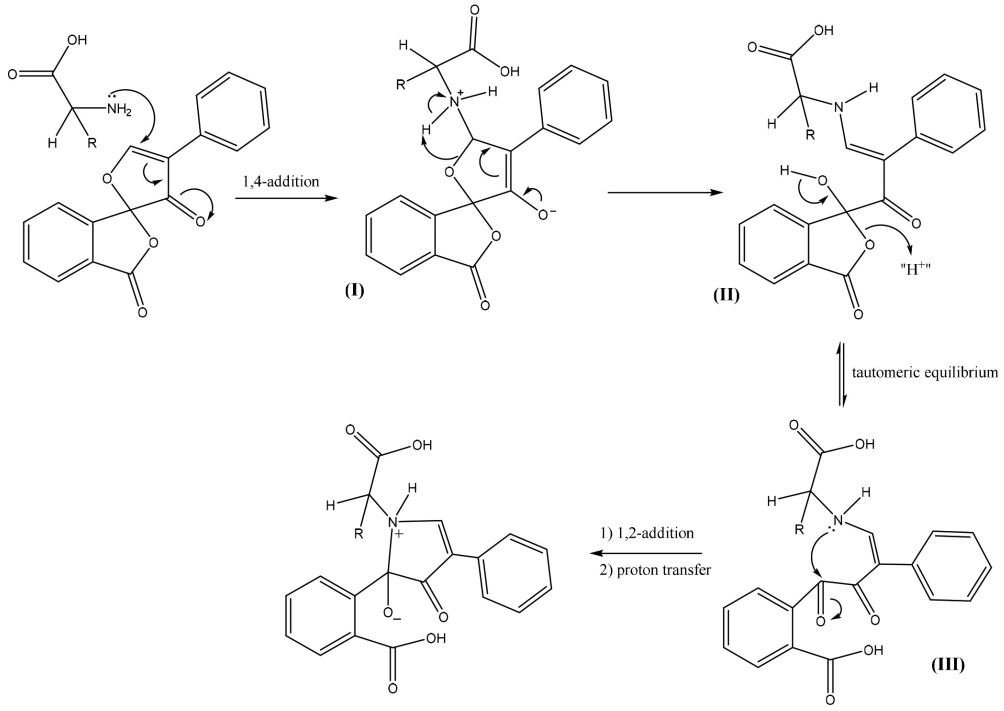
carried out to improve its performance, such as the creation of new formulations, using different solvents, and new application methods, such as fumigation. Although the surveys have had positive results, in most cases reagents such as DFO and ninhydrin were considered superior and therefore DMAC is not so commonly used.[9,21,38]

5.8. Fluorescamine

Fluorescamine is a fluorescent reagent developed in the 1970s and pointed out as a possible fingerprint developer by Ohki in 1976.[21,25,39]

This substance is used in porous surfaces and it reacts with primary amines of amino acids, peptides and proteins, forming fluorophores, which present a light blue fluorescence with absorption at wavelength around 390 nm and an emission around 475 nm. The proposed mechanism for the reaction is presented in Scheme 8.[21,25,39]

The first stage involves a 1,4-addition to fluorescamine by an amino acid, forming the intermediate I. Then a proton transfer occurs, opening the ring and forming the intermediary II, which is in tautomeric equilibrium with the intermediate III. Finally, the intermediate III undergoes a 1,2-addition and a proton transfer, forming the final product, which has nitrogen as a heteroatom and exhibits fluorescent characteristics.[35]



Scheme 8. Proposed mechanism for the reaction of fluorescamine with amino acids. Adapted from Ramachandran (2007)[35]

However, fluorescamine is not so much used nowadays, as it does not exhibit long-term stability, its reaction with water results in a nonfluorescent product and its solvent is acetone, which is quite flammable. In addition, the wavelength required to excite the molecule is the same as for some compounds used in modern papers, making visualization of the fingerprints difficult.[25,35]

5.9. *O*-Phthalaldehyde

O-Phthalaldehyde was proposed as a fingerprint developer in 1975. This reagent is similar to fluorescamine, as it also reacts with primary amines, present in amino acids, peptides and proteins, and is used on porous surfaces.[25]

The reaction of *o*-phthalaldehyde with primary amines present in the fingerprint residues, in the presence of a primary thiol, 2-mercaptoethanol, forms a product derived from isoindol, which is highly fluorescent, showing absorption at 340 nm and emission at 455 nm. The proposed mechanism for the reaction is presented in Scheme 9.[21,25]

The first stage involves the nucleophilic attack of the amine on the carbonyl carbon of the *o*-phthalaldehyde, forming the intermediate I. The intermediate II results from a proton transfer.[35]

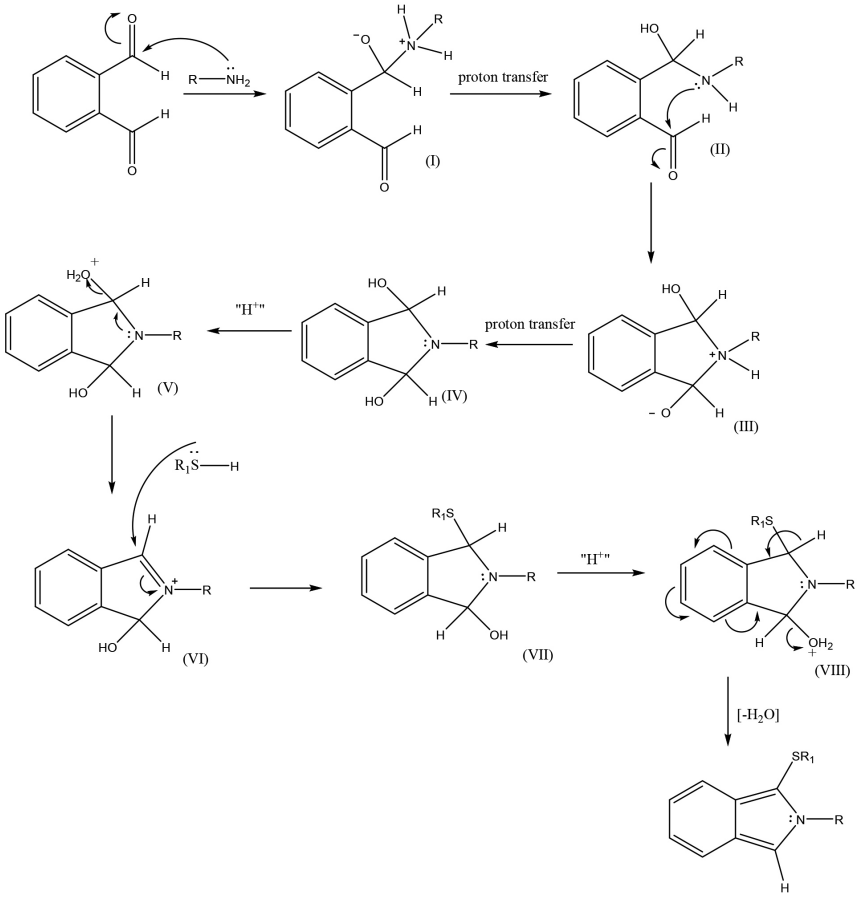
Next, the intermediate III is formed by a cyclization. Then a proton transfer occurs, forming the intermediates IV and V. After that, a dehydration occurs, resulting in the intermediate VI. Then, the nucleophilic attack by the thiol results in the intermediate VII, which undergoes a protonation to form the intermediate VIII. Finally, there is an elimination of water, forming the derivative of isoindol.[35]

O-Ptalaldehyde is also no longer recommended for the development of fingerprints, since its formulation, containing 2-mercaptoethanol, is toxic, corrosive and dangerous to the environment. Furthermore, similarly to fluorescamine, there are problems due to the wavelength at which it absorbs.[21,25]

5.10. NBD and Dansyl Chloride

There are two types of NBD investigated for use as a fingerprint developer, NBD-chloride and NBD-fluoride. The 4-chloro-7-nitrobenzofuran (NBD) chloride was suggested as a fingerprint developer in the 1970s by Salares, Eves and Carey. The Dansyl chloride (5-Dimethylamino naphthalene-1-sulfonyl chloride) was suggested in the '80s by Burt and Menzel.[21]

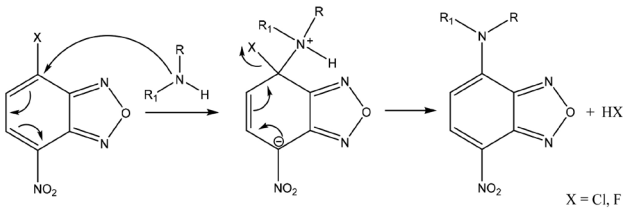
These reagents are also used on porous surfaces. The two NBDs are nonfluorescent compounds that react with amino acids forming fluorescent products that absorb around 475 nm and emit around 550 nm. Dansyl chloride also reacts



Scheme 9. Proposed mechanism for the reaction of o-phthalaldehyde with primary amines. Adapted from Ramachandran (2007)[35]

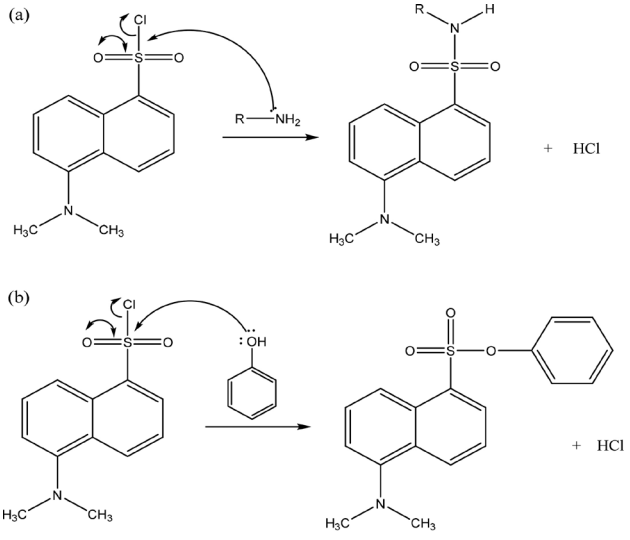
with amino acids, producing a fluorescent compound that absorbs around 360 nm and emits around 475 nm.[21,40]

The reaction mechanism is the nucleophilic attack by primary or secondary aliphatic amines on the NBD (chloride or fluoride) reagents, via S_NAr. The reaction is simple and is represented in Scheme 10. The product is a fluorescent substance.[21,35]



Scheme 10. Proposed mechanism for the reaction of NBD with amines

Dansyl chloride reacts with amines, but also with phenols. Its mechanism is similar to the NBD and is also based on the nucleophilic attack in this case of the sulfonyl chloride group by the amine or phenol. The product exhibits fluorescence. Both mechanisms are shown in Scheme 11.[21,35]



Scheme 11. Mechanism for the reactions of Dansyl chloride with (a) amines and (b) phenols. Adapted from Ramachandran (2007)[35]

However, the use of these reagents is no longer recommended. First, techniques such as ninhydrin, 1,2-indandione and DFO have been shown to be superior. Furthermore, a mutagenic effect of NBD is suspected and its compounds pose problems with background fluorescence, while dansyl chloride is corrosive and potentially explosive. Finally, it is known that both NBD compounds and dansyl chloride are not as selective to fingerprint compounds, as they can also react with thiols, alcohols and anilines.[21,25,35]

5.11. Physical developer

The physical developer is a reagent that was initially used as a film developer. It was then used to develop fingerprints on porous surfaces, working even when the surface is wet, since it reacts with insoluble substances present in the residue of the fingerprint.[4,11]

This reagent consists of a complex mixture, containing silver nitrate, iron (II) and iron (III), citric acid and a cationic detergent, usually odecylamine acetate. The reactions are shown below (3)(4). [11,41]

$$Ag^{+} + Fe^{2+} \rightarrow Ag^{0} + Fe^{3+} \quad (3)$$

$$Fe^{3+} + C_6H_8O_7 \rightarrow FeC_6H_5O_7 + 3H^{+} \quad (4)$$

The physical developer's reaction mechanism begins with the reduction of silver by iron (II), which oxidizes to iron (III). Theoretically, since it is a reversible reaction, Fe(III) would be expected to oxidize silver, but the addition of citric acid prevents this from happening, since it is complexed with Fe(III) as shown in the second equation. This allows the formed silver particles, which have a colloidal nature, to interact with the fatty acids and lipids present in the latent, developing a dark grey or black fingerprint.[4,41]

One problem that could occur is an excess of metallic silver, which would cause its agglutination and subsequent precipitation, preventing the development of fingerprints. However, the addition of cationic detergent prevents this from happening as it retains some silver particles within spheres of positively charged surfactant molecules known as micelles. In this way, silver ions and micelles repel each other, avoiding their agglomeration.[9,41]

5.12. Gun blue

Gun blue reagent is used to develop fingerprints on metal surfaces, especially on bullet cartridges. This reagent is often used in combination with another technique, such as fumigation with cyanoacrylate and fluorescent dyes, but there is also work proving the efficiency of using only gun blue.[42,43]

This technique is based on the deposition of two metals in combination with an etching process. Its formulation contains three main ingredients: an acid, a copper salt and selenous acid. The general equations of the gun blue reaction are shown below (5)(6).[4,42]

$$H_2SeO_3 + 4H^{+} + 4e^{-} \rightarrow Se^{0} + 3H_2O \quad (5)$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu^{0} \quad (6)$$

In an acid environment, both selenous acid and a copper solution are strong oxidizing and etching agents, being capable of oxidizing elements such as lead, nickel, zinc and aluminum. In the reactions (5) and (6), the electrons coming from any of these metals, depends on the surface.[4,42]

These reactions occur with the surface metal, but if there is any oily contaminant on it such as a latent, the reaction

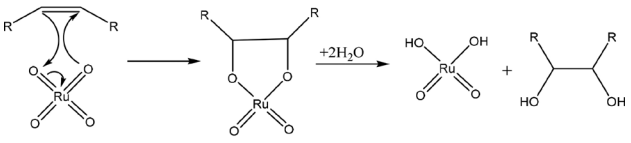
will not occur there. Therefore, this reagent forms a blue-black metallic coating on the surface (Cu-Se), except where the fingerprint is.[4,42]

5.13. Ruthenium and osmium tetroxides

Ruthenium tetroxides (RTX) and osmium tetroxide are two compounds that were used in forensic science in the 1920's. Both are fumigation techniques, however, RTX is not as volatile as osmium tetroxide, requiring heating.[21,25,44]

The problem is that RTX decomposes explosively at 108 °C. To avoid this, the safest thing is to mix equal volumes of a solution containing 0.1% hydrated ruthenium (III) chloride and 11.3% of a solution of ceric ammonium nitrate. There is also a newer formulation using these same reagents but with an addition of Methyl Nonafluorobutyl Ether (HFE7100).[21,25,44]

Both developers react with the unsaturated organic compounds of fingerprints, resulting in dark gray products. This technique can be used on porous and non-porous surfaces. The proposed mechanism is shown in Scheme 12. [21,25] The reaction with osmium tetroxide happens in a similar way.[45]



Scheme 12. Proposed mechanism for the reaction of RTX with unsaturated organic compounds. Adapted from Bleay *et al.* (2013)[25]

However, both reagents are highly toxic and therefore no longer recommended for fingerprint development. In addition, their efficiency is no higher than that of other fingerprint developers already in use.[21,25,44]

5.14. Europium chelate

Europium chelate was introduced as a fingerprint developer in 1990, but only as a post-treatment. After that, in 1997 and 1999, new formulations appeared, aiming to use this chelate directly on the fingerprint.[21,25,46,47]

Europium chelate is a reagent that can be used on porous and non-porous surfaces. It reacts with the lipids present in the fingerprint residue, forming a colorless compound that has a red fluorescence, absorbing at 335 nm and emitting at 615 nm.[21,46]

In its formulation, proposed by Wilkinson (1999), are present europium chloride hexahydrate, distilled water, Tergitol 7, thenoyltrifluoroacetone, trioctylphosphine oxide and methanol. The europium chloride hexahydrate is the source of europium, thenoyltrifluoroacetone and the trioctylphosphine oxide contributes to the formation of the complex, Tergitol 7 is a detergent that helps in the stability of the complex, isolating it from water molecules, and methanol helps with the transfer of the complex to the organic phase, since it is partially soluble in it. The complex in the aqueous phase is shown in Figure 9.[21,25,46]

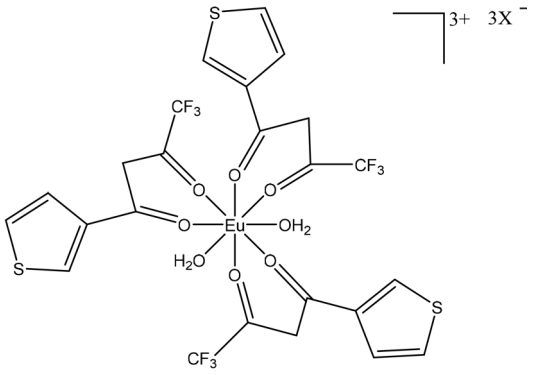


Figure 9. Chemical structure of the europium chelate in aqueous phase. Based on Wilkison (1999)[46]

When transferred to the fingerprint residue, the water molecules are replaced by lipid ligands, forming the fluorescent compound (Figure 10).[21,25,46]

However, there is not extensive work on europium chelate and its use is not common. This is because the efficiency of this reagent falls with the aging of the fingerprint. Moreover, the chelate does not present advantages compared to other more used developers.[21,25]

5.15. Rubeanic acid–copper acetate

Rubeanic acid-copper acetate was proposed as a fingerprint developer in 1973, but new studies were not conducted after that, and therefore this reagent was not used for that purpose. However, in 2014, a study using rubeanic acid to develop handprints of an individual who had touched copper was published. After that, Davis *et al.* (2016) published an article on the development of fingerprints using this same method, in this case, in polymer banknotes.[21,48,49]

The development of latents by this method basically requires two steps. The first is the addition of copper to the non-porous surfaces containing the fingerprint, which can be done by vacuum metal deposition (VMD) or immersion in copper(II) acetate. Copper reacts with the fatty residues of the latent, forming insoluble copper salts (Scheme 13), when using copper acetate.[21,48,49]

When using VMD technique, dispersed copper nuclei are formed (Figure 11).[21,48,49]

The second is the addition of rubeanic acid, which reacts with copper, developing dark green fingerprints. The reaction forming copper rubeanate is presented in Scheme 14.[48,49]

However, this method still needs to be studied in more detail in order to define whether it is worth using it instead of the other reagents already widely used.

5.16. Phosphomolybdic acid

Phosphomolybdic acid (PMA) (Figure 12) was

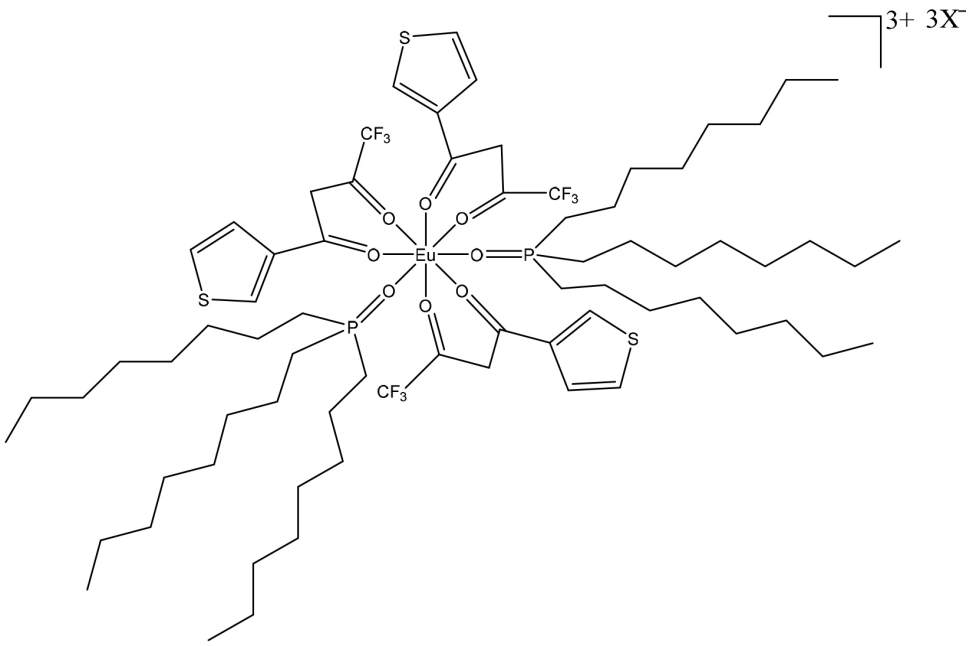
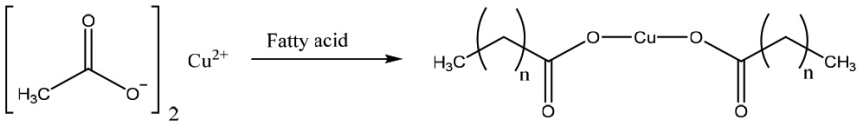


Figure 10. Chemical structure of the europium chelate in oil phase. Based on Bleay (2018)[21]



Scheme 13. Reaction between copper acetate and fatty acids, resulting in insoluble copper salts. Based Bleay, Croxton and Puit (2018)[21]

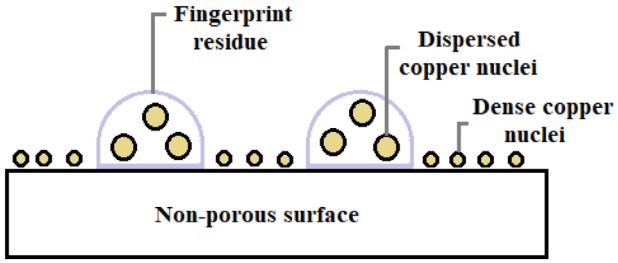
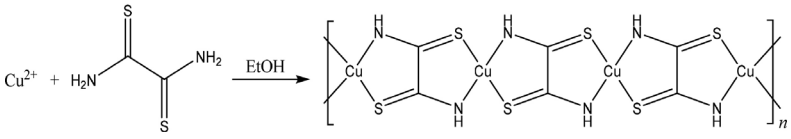


Figure 11. Interaction of copper and fatty acids using VMD technique. Adapted from Davis *et al.* (2016) [48]



Scheme 14. Chemical reaction of copper rubeanate formation [48,49]

proposed in 1973 as a fabric fingerprint developer, and has not been studied much since then either. Only in 2013 was another research using this reagent in this context carried out by Shah, and after that, Davis, Bleay and Kelly (2018) published an article about its use as a fingerprint developer.[21,50,51]

PMA is a yellow-green reagent which reacts with the sebaceous components found in fingerprint residues, such as lipids and steroids, and is reduced to a heteropolymolybdate complex, called molybdenum blue (Fig. 13). It is known

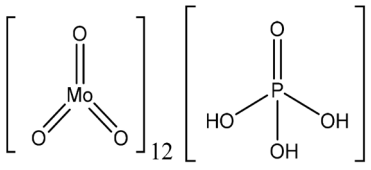


Figure 12. Chemical structure of the phosphomolybdic acid molecule[50]

that the greater the number of double bonds present in the sebaceous components, the more intense the blue color is.[21,50,51,52]

This reagent is known to work best on non-porous surfaces and over recent fingerprints. Furthermore, studies have shown that its efficiency can be compared to that of Oil red O and that better results are obtained with PMA in a 10% (w/v) solution in ethanol.[50,51]

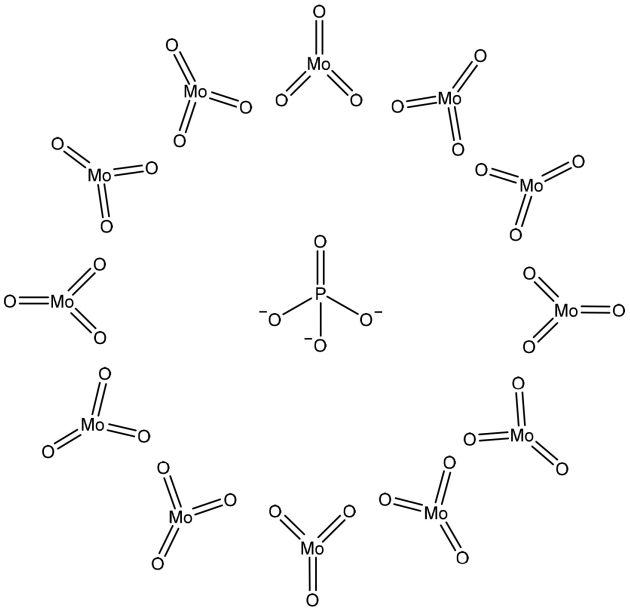


Figure 13. Chemical structure of the molybdenum blue molecule[51]

The mechanism of this reaction has not yet been elucidated. However, it is known that on metallic surfaces, PMA reacts with the metal, forming colored salts, while the residue of the fingerprint inhibits the PMA from coming into contact with the surface, therefore, the latent is developed due to the contrast created with the background color.[21]

Nevertheless, this method also needs to be further investigated in order to define whether it is worth using it instead of the other reagents already widely used.[21]

5.17. Radioactive sulfur dioxide

Radioactive sulfur dioxide (SO_2) was a fingerprint developer used on porous surfaces, mainly fabrics. It was proposed as a developer in 1963, but there are not many studies about it and, nowadays, it is no longer used.[21,25]

The apparatus used for this technique is relatively complex and the process must always be monitored. The surfaces containing the fingerprints are hung in the camera, then the SO_2, initially contained in filter paper discs, is released in the form of vapor inside the sealed chamber, which should have a relative humidity of 55%. At the end of this process, the remaining steam is removed with activated charcoal.[21,25]

For fingerprint visualization, the surface is placed between two sheets of X-ray film (Figure 14), which is developed due to the β-particles emitted by the SO_2 present in the fingerprint residue, resulting in autoradiographs.[21,25]

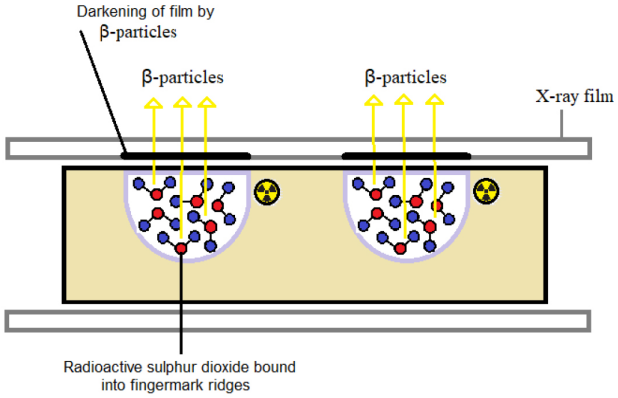


Figure 14. Radioactive sulfur dioxide technique. Adapted from Bleay, Croxton and Puit (2018) and Bleay *et al.* (2013)[21,25]

The theory about the interaction of SO_2 with fingerprint residues consists of the combination of three different mechanisms. The first of them proposes that the SO_2 is converted to SO_4^{-2} and fixed in the aqueous phase of the fingerprint. The second is the adsorption of water layers causing sensitization of the wet surface due to contact with the latent. Finally, a reaction is believed to occur between the SO_2 and the lipid components of the fingerprint.[21,25]

However, due to the introduction of new techniques, the complexity of the equipment needed for this technique and its health and safety hazards, it has not been used since 2005.[21,25]

5.18. Blood enhancement techniques

It is common to find at violent crime scenes fingerprints contaminated with blood, which is a body fluid of complex composition. For these cases, reagents that interact with the blood proteins, amino acids or heme group are used.[44]

Two or three stages are required to develop blood fingerprints. The first is the fixation step, which is necessary for the proteins to be denatured, becoming insoluble and adhering to the surface, otherwise, when applying the dye solution, the blood can be washed off or diffused, making it impossible to develop the latent. For this step methanol or 5-sulfosalicylic acid (Figure 15) solution can be used and the process takes 5 to 15 minutes.[9,25,44,53]

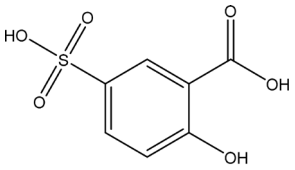


Figure 15. Chemical structure of the 5-sulfosalicylic acid

The second step is when the fingerprint is developed. Commonly used reagents include acid dyes (Amido black, Coomassie blue, Acid violet 17, Acid yellow 7, Hungarian red and Crowle's double stain are the ones recommended), amino acid developers (ninhydrin, DFO and indanedione, which have already been explained

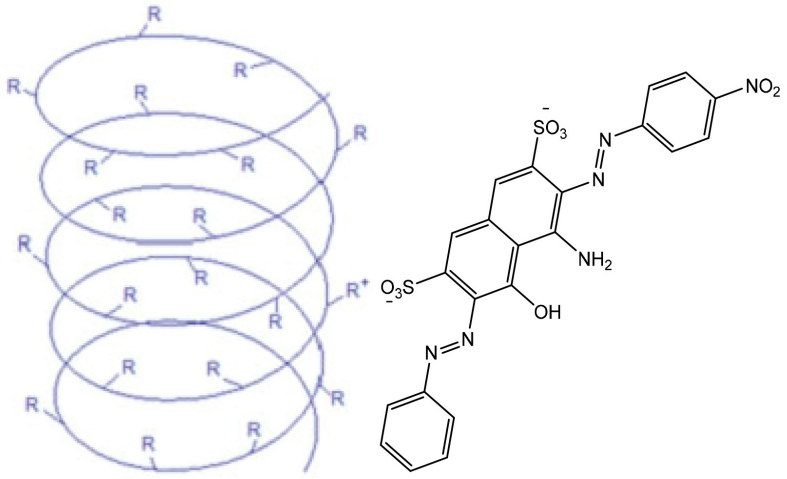


Figure 16. Interaction between acid dyes and a protein from the blood. Adapted from Bossers *et al.* (2011)[53]

in this article), or heme-reacting chemicals (leuco malachite green, leuco crystal violet, leuco rhodamine 6G, diaminobenzidine, fluorescein, phenolphthalein, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, Blue Star and luminol).[9,25,44,53,54]

The final step, needed after using one of the acid dyes, is the de-staining. For this part, a solution containing the same substances present in the staining solution is used (usually, ethanol, distilled water and acetic acid), except the dye. This step aims to remove the dye molecules that did not bind to the proteins.[9,53]

Besides that, some methods like vacuum metal deposition (VMD) and powder suspensions can be used. However, since they are not blood specific methods, they would normally require a second confirmatory test. [21,44]

The choice of the appropriate developer will depend on the type of surface, its color, in order to achieve a good contrast, as well as the amount of blood and the condition of the fingerprint.[54]

5.18.1. Acid dyes

The interaction between acid dyes and blood occurs through the anionic sulfonate groups present in the dyes, which bind to the cationic groups of blood proteins in a moderately acidic environment. An example of this is illustrated in Figure 16, which shows the interaction between a protein and a molecule of amido black.[53]

Amido black (Figure 17) is the most common reagent used to reveal fingerprints in blood and it works on both porous and non-porous surfaces, but preferably on non-porous ones, because if the Amido black is absorbed it will leave a stain [1,9]

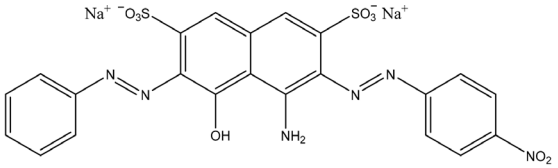


Figure 17. Chemical structure of the Amido black molecule

Amido black is a diazo dye that reacts by binding to proteins in the blood or other body fluids, as shown in Figure 17, but does not interact with common fingerprint components, so it should only be used for fingerprints that consist of all or part of blood. This reaction develops dark blue fingerprints.[1,9,55]

Coomassie Brilliant Blue (CBB) (Figure 18), just like Amido black, can also be used for porous and non-porous surfaces, but it gives the best results when used on smooth non-porous surfaces. It reacts similarly to amido black, but the fingerprints developed are of a lighter blue. Studies have shown that CBB is more efficient than amido black for faint bloody fingerprints and that the fingerprints developed can be lifted with a white gelatin lifter.[9,56,57]

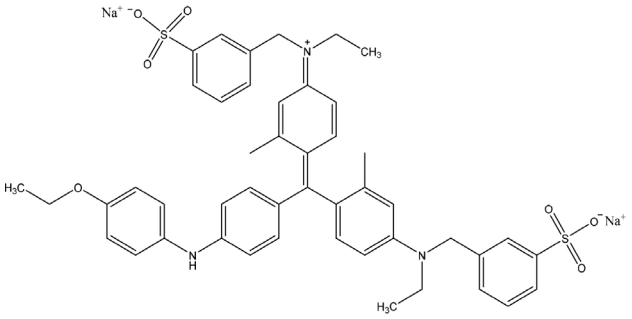


Figure 18. Chemical structure of the CBB

Acid Violet 17 (AV17) (Figure 19) is a dye with a molecular structure quite similar to CBB and reacts with proteins in the same way shown for Amido black, and it also develops a visible fingerprint, although it gives a bright violet color. This dye is also used for non-porous surfaces due to the possibility of staining. [21]

Acid Yellow 7 (AY7) is a dye also used on non-porous surfaces, as it can stain porous ones, and it is recommended mainly for dark surfaces, since it has a luminescent property. AY7 (Figure 20) can bind to the proteins found in the blood in the same way as the other dyes already mentioned and it develops yellow fingerprints

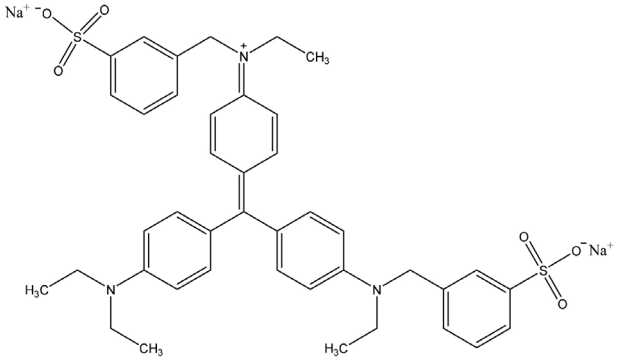


Figure 19. Chemical structure of the AV17

which fluoresce when subjected to a light of 400-490 nm (blue-green light). [58] However, if the fingerprint contains a large amount of blood, the heme groups in the blood can reabsorb the luminesce and hence AY7 may lose its effectiveness.[53]

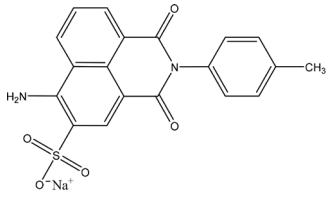


Figure 20. Chemical structure of the AY7

Hungarian Red (Figure 21), also called Acid Fuchsin or Acid Violet 19, just like CBB, works well on smooth non-porous surfaces and, therefore, is recommended for faint bloody fingerprints.[53,59]

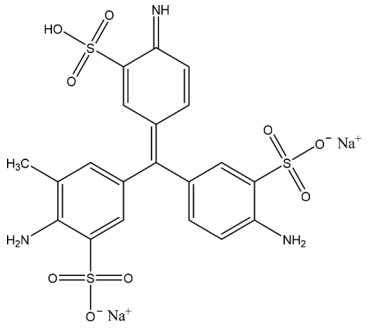


Figure 21. Chemical structure of the Hungarian Red.

This dye has two advantages: the first is that, in the same way as Acid Yellow 7, it is fluorescent under a green light (473-548 nm); the second is that, after the development, the fingerprint can be lifted with a white gelatin lifter.[53,59]

Crowle's double stain is a solution containing a mixture of two dyes, Coomassie Brilliant Blue and Crocein Scarlet 7B. This dye develops red fingerprints on non-porous surfaces, similarly to Hungarian Red. However, marks enhanced with Hungarian Red can fluoresce and be lifted, and therefore Crowle's double stain has not been used so often.[57]

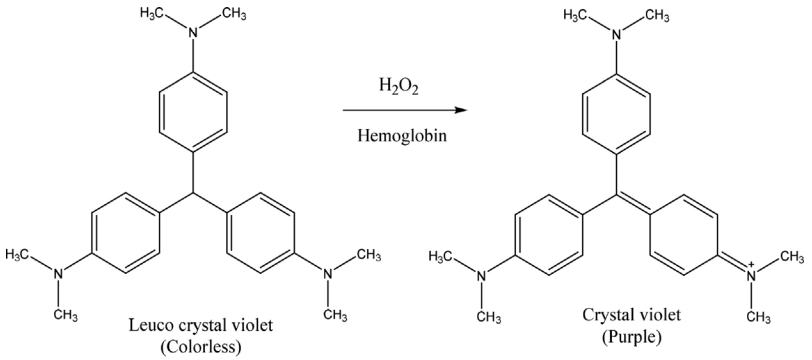
Some other protein dyes are Benzoxanthene Yellow (BY), Lucifer Yellow (LY) and SYPRO Ruby protein bloodstain. BY is a luminescent dye. However, it is no longer available and producing it especially for fingerprint development would not be reasonable. There are not many articles about the use of LY and SYPRO Ruby for fingerprint enhancement, but it is known that LY works similarly to Acid Yellow 7 and that SYPRO Ruby works similarly to Coomassie Brilliant Blue.[9,53,60]

5.18.2. Heme-reacting chemicals

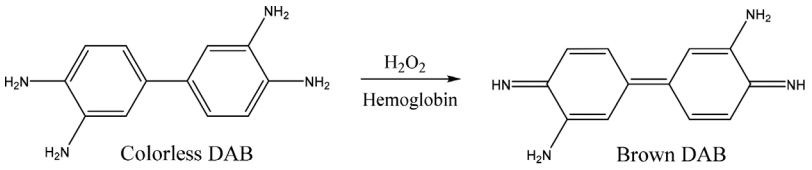
Heme-reacting chemicals are the most specific developers for fingerprints in blood, as they do not react with any other body fluid. These substances, also known as peroxidase reagents, react with the heme group of hemoglobin and are oxidized, resulting in colored products. Heme-reacting chemicals will be presented below.[61]

The function of the heme group is to catalyze the oxidation reaction of colorless compounds in order to obtain a colorful or luminescent product and, therefore, develop bloody fingerprints. The first example of colorless compounds used is the leuco form of the dyes Crystal Violet, Rhodamine 6G (both previously mentioned in this article) and Malachite Green.[53,61]

These three dyes work on both porous and non-porous surfaces. Leuco malachite green reacts with the heme group of hemoglobin resulting in green colored fingerprints, while the leuco crystal violet reaction results in a vivid purple color, which also fluoresces under a light with a wavelength of 400-600 nm. Leuco rhodamine 6G reaction results in a red color. An example of this is shown in Scheme 15.[53,61]



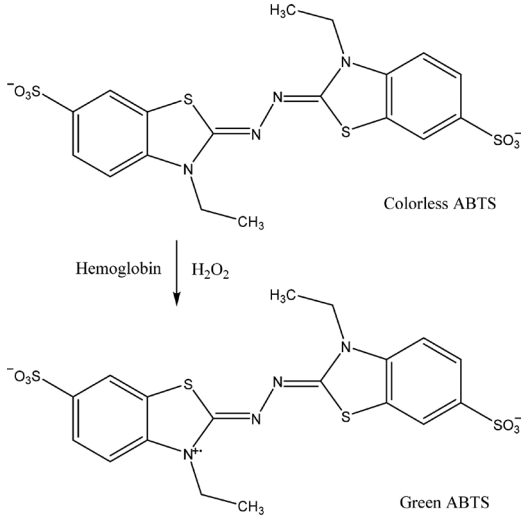
Scheme 15. Leuco crystal violet reaction with hemoglobin results in purple crystal violet[53]



Scheme 16. Hemoglobin reaction with diaminobenzidine[9]

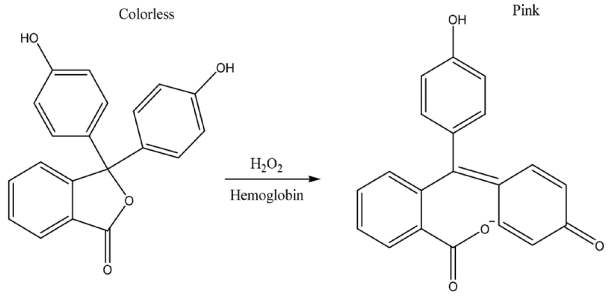
Diaminobenzidine is another substance whose reaction is catalyzed by the peroxidase-like activity of the heme group (Scheme 16). This reagent is used preferentially in porous surfaces and it develops dark brown fingerprints.[9]

The 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) was proposed to be an alternative to DAB because it is non-toxic and safe to use. The reaction with ABTS is the same as DAB, however, it develops fingerprints of a bright green color (Scheme 17).[9,53]



Scheme 17. Hemoglobin reaction with ABTS[53]

Phenolphthalein is a quite common pH indicator used in chemistry; however, it can also work as a developer for bloody fingerprints. The reaction is the same as the others above, and it happens in the presence of hemoglobin and hydrogen peroxide, producing a purple/pink color (Scheme 18). Studies have shown that a phenolphthalein solution containing ethanol and peroxide has good stability, sensitivity, and specificity to blood.[62]



Scheme 18. Hemoglobin reaction with phenolphthalein[62]

Fluorescein, Luminol (Figure 22), Hemascein™ and Blue Star are common reagents used to detect latent blood. However, they are not recommended for fingerprint development. They are most often used for detecting the presence of blood in crime scenes and this process may enhance fingerprints too, but usually without fine details.

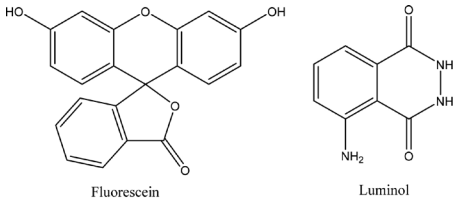


Figure 22. Chemical structures of the fluorescein and luminol

These four products are fluorescent. Fluorescein absorbs blue light (425-485 nm) and emits a green-yellow fluorescence at 521 nm; Hemascein is a commercial formulation of fluorescein, which is more stable; luminol absorbs at 420 nm and emits a blue chemiluminescence around 455 nm; and Blue Star is a commercially optimized formulation of luminol, created in order to obtain a brighter luminescence. Their oxidizing reactions occur with hydrogen peroxide in the presence of the heme group from hemoglobin.[53,61,63,64]

Tetrametylbenzidine, merbromin, *ortho*-tolidine and benzidine are other examples of heme-reacting chemicals. However, they are carcinogenic and not safe to use, therefore, they are no longer recommended for fingerprint development.[53]

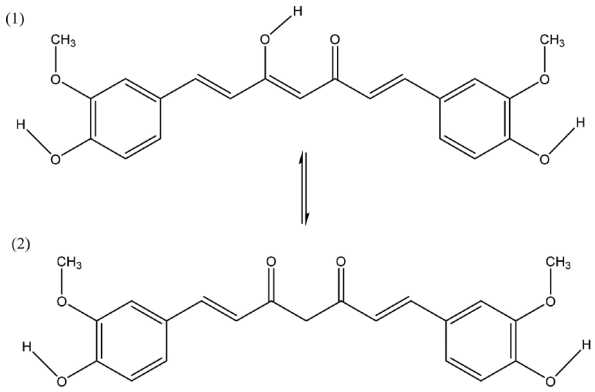
6. Green Methods

Over the years it has become more evident how important it is to replace toxic products with greener ones, which, in other words, do not cause any hazard to people's health or to the environment. As already mentioned in this article, most fingerprint developers are toxic and, therefore, some non-toxic alternatives that have already been researched and tested will be presented below.

6.1. Curcumin

Curcumin, also called Natural Yellow 3 (Scheme 19), is a yellow pigment found in the turmeric plant. It was considered as a fingerprint developer because it is a natural product, less expensive, simple to use, easily available and fluorescent.[65,66]

This compound can be used in two ways for fingerprint



Scheme 19. Chemical structures of the enolic (1) and ketonic (2) forms of curcumin

development. The first method is to use it as a powder. For this, the curcumin must undergo a reduction in size, as finer powders adhere better to the residue of the latent. The application can be done with a brush or by deposition of the powder on the surface followed by removal of the excess, to avoid possible damage to the fingerprint.[65]

The second method is to use curcumin in solution in the same way as Sudan Black and other lipid dyes. The solution is composed of ethanol, distilled water, and the dye. Its use is indicated for dark-colored non-porous surfaces and works on latents contaminated with oils and fats. Curcumin absorbs light at around 490 nm and emits a yellow fluorescence at around 540 nm.[66]

Further studies are still needed, but curcumin has shown good results, therefore, it is a good alternative for toxic reagents.[65]

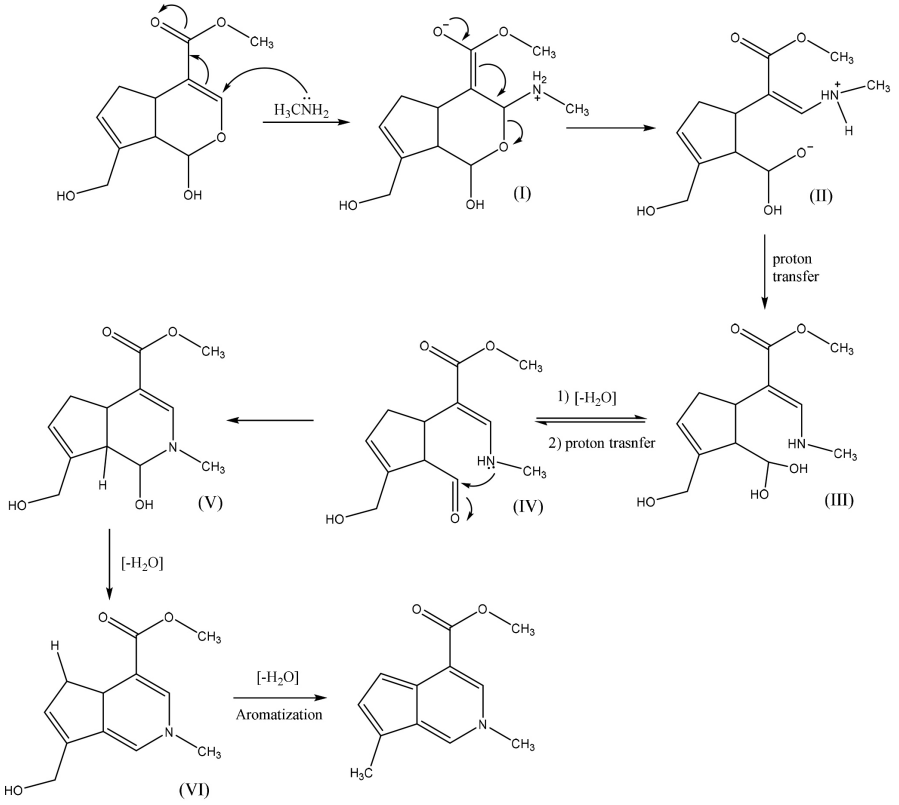
6.2. Genipin

Genipin is a dye extracted from the fruit of the genipap (*Genipa Americana*). This substance reacts with amino acids from the skin, forming a blue compound, which has red fluorescence. Due to this characteristic, in 2004 it was proposed as a fingerprint developer for porous surfaces.[29,31]

The first stage involves the nucleophilic attack of methylamine to the genipin, forming the intermediate I. The intermediate I, bearing the dihydropyran moiety, has its ring opened to form the intermediate II. Then, a proton transfer occurs to form the intermediate III, followed by a dehydration and another proton transfer, forming the intermediate IV. Next, it undergoes a cyclization, forming a ring with nitrogen as the heteroatom (intermediate V). After that, a dehydration occurs to form the intermediate VI and, finally, another dehydration and the aromatization process yields the final blue-colored product, which absorbs light around 575 nm and emits around 610 nm.[21,25,35,67]

The Scheme 20 shows the proposed mechanism for the reaction between genipin and primary amines.

However, genipin is not so used in the development of fingerprints because, although it has the advantage of being natural, its efficiency is lower than that of ninhydrin and DFO.[21,25]



Scheme 20. Proposed mechanism for the reaction of genipin with amines. Adapted from Ramachandran (2007)[35]

6.3. Lawsone

Lawsone is a compound that has been used as a skin and hair dye for millennia and is extracted from the leaves of the plant *Lawsonia inermis* (Henna). It was introduced as a possible fingerprint developer in 2008 and reacts with amino acids, producing a dark purple/brown product, which is also fluorescent.[6,9,68]

The Scheme 21 shows the proposed mechanism for the reaction between lawsone and amino acid, which is very similar to the DFO mechanism. The first stage involves the nucleophilic attack of an amino acid primary amine to the lawsone, forming the intermediate I. Then, the intermediate I, undergoes a proton transfer and a dehydration, forming the intermediate II, followed by a proton transfer, resulting in the intermediate III (imine). Then, a decarboxylation occurs to form the intermediate IV. Next, a nucleophilic attack and a proton transfer occurs, forming the intermediate V, which, in the presence of water, has its aldehyde eliminated in order to form the amine derivative (intermediate VI). After that, the intermediate VI makes a nucleophilic attack on another molecule of lawsone, forming the intermediate VII, which suffers dehydration and a proton transfer, forming the fluorescent-colored compound, which absorbs light around 590 nm and emits around 640 nm.[6,68]

However, like genipin, lawsone is also less efficient than other fingerprint developers that react with amino acids on porous surfaces. Therefore, it is not widely used.[9]

6.4. Other natural developers

Isatin and its derivatives can be found in several plants, such as *Isatis genus* and *Couroupita guianensis* and, since isatin synthesis in 1840, they have been widely studied, as they present several applications, mainly pharmacological [69]

In 2010, its potential as a fingerprint developer was studied. Its molecular structure (Figure 23) is similar to ninhydrin and IND; however, the reaction with the fingerprint results in a colorless but fluorescent product (under light with a wavelength of 505 nm).[9]

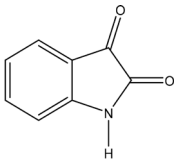
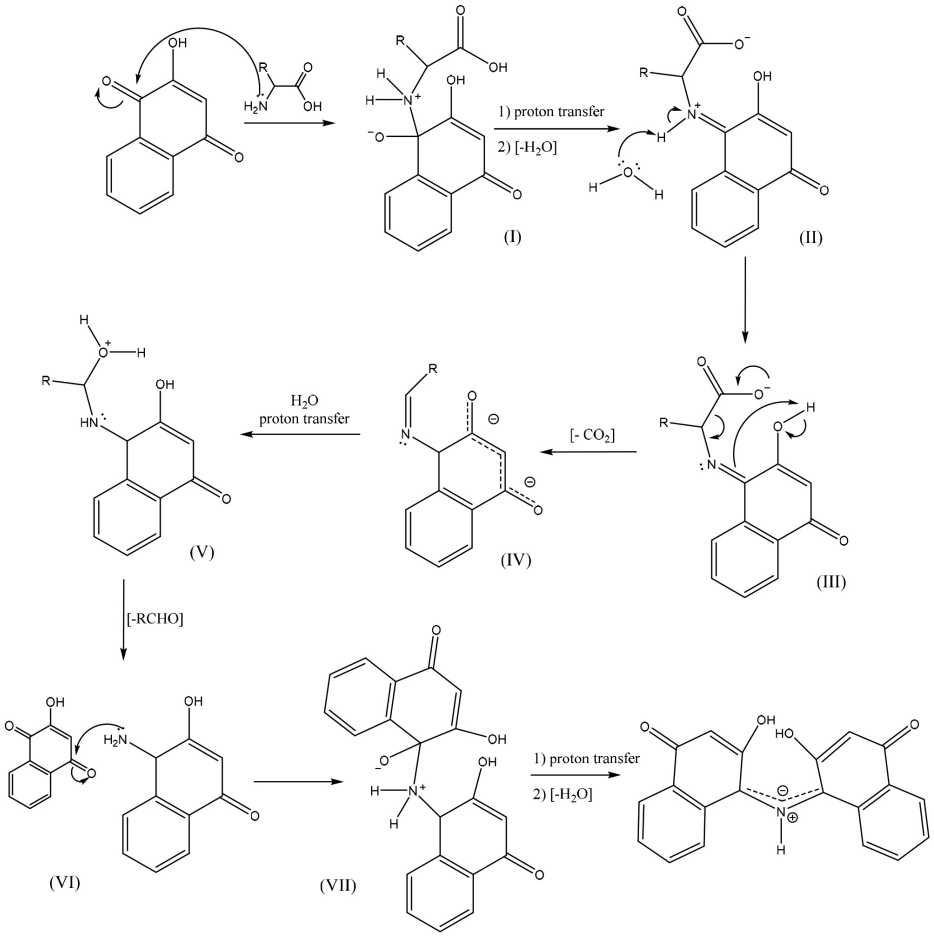


Figure 23. Chemical structure of the isatin

Unfortunately, like genipin and lawsone, isatin also has a lower efficiency than other developers and requires another



Scheme 21. Proposed mechanism for the reaction of lawsone with amines. Adapted from JELLY *et al.* (2009) and JELLY *et al.* (2008)[6,68]

step, a post-treatment with zinc chloride.[9]

Several natural powders have been studied as potential alternatives for the powders used for fingerprint development today. Some of the natural products tested are gambir powder, that can be extracted from the leaves of *Uncaria gambir* and has successfully developed latents with a white colour. Black charcoal, marigold powder, mustard oil soot, and red chili powder (*Capsicum spp*.) were also used to develop fingerprints. With the exception of red chili, all developed prints clearly.[70,71]

Moreover, synthetic food and festival colors (Orange Red, Lemon Yellow and Bright Green) powders were also tested and successfully developed latent fingerprints. Futhermore, other interesting studies have been carried out on the use of different colors of soil powder (white, red, brown and black) and the development of a powder made from steel industry waste as fingerprint developers, achieving satisfying results.[72,73,82]

These are just a few natural, easily available, non-toxic and simple methods already tested and they demonstrate the potential of natural products to be applied in fingerprint development.

7. Nanomaterials

In the past few years, the amount of research in nanotechnology has increased greatly in the most different areas of science. The reasons for that are the new physical, chemical and electronic properties that materials acquire when used in nanoscale. Therefore, nanomaterials are also being researched to be used as fingerprint developers, showing great results. Some of the techniques are presented below.

7.1. Nanopowders

The different types of powders already used in brushing technique for fingerprint development have been previously explained in this article, so in this section will be presented a new type of powder, which is still being researched.

Nanopowders usually have dimensions between 1-100 nm and, because of that, they have better adhesion to the residues of the latent and can reveal more details. One way to use nanoparticles in this method is to functionalize them using antibodies in order to enable them to bind specifically to a compound present in the latent residue, such as amino acids, different proteins, drugs etc.[9,21]

The most common nanoparticles used in this way are gold ones, but silver, iron, silica and titanium have also been studied. However, for these nanoparticles to bind to antibodies, first, it is necessary to treat them with linking molecules, as shown in Figure 24.[21]

After the treatment, they can be used for the development of fingerprints, as illustrated in Figure 25.

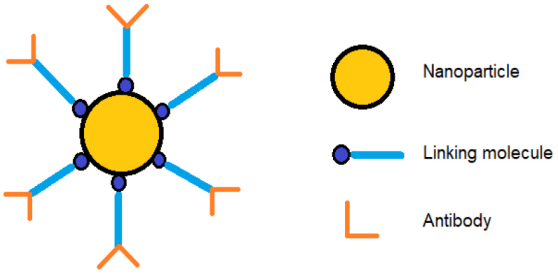


Figure 24. Nanoparticle first treated with linking molecules and then linked to antibodies. Adapted from Bleay, Croxton and Puit (2018) and Leggett (2007)[21,75]

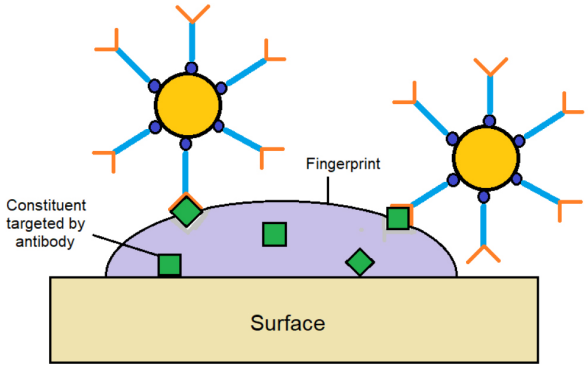


Figure 25. Nanopowder interaction with a fingerprint through the antibodies linked to it. Adapted from Bleay, Croxton and Puit (2018) and Leggett (2007)[21,75]

7.2. Multimetal deposition

The multimetal deposition (MMD-I) is a technique proposed in 1989 that uses nanoparticles of metals (gold and silver) for the development of fingerprints. This method consists of two main steps and, in the end, develops brown fingerprints.[9,21,76]

The procedure for this technique consists of a series of immersions of the surface containing the latent in the following order: in distilled water, in a solution with colloidal gold, in distilled water, in a modified physical developer (PD) and in distilled water. Figure 26 illustrates this procedure.[21,76]

The great advantage of the multimetal deposition technique is that it works on all kinds of surfaces, porous, non-porous and semi-porous and it can be used in wet or dry conditions. However, it has some disadvantages, such as the fact that it is very time-consuming, expensive and labor-intensive, the pH for the gold solution is very specific, there may be darkening of the background in the step with the silver solution and it may be difficult to visualize the prints developed on dark surfaces.[76]

Over the years, researchers have tried to improve this technique in order to eliminate the disadvantages mentioned above. One study showed good results, decreasing the time needed by approximately 40 minutes and the darkening of the background, but the other problems remain. The only modification made was in the solution containing silver, which now uses silver acetate instead of silver nitrate and

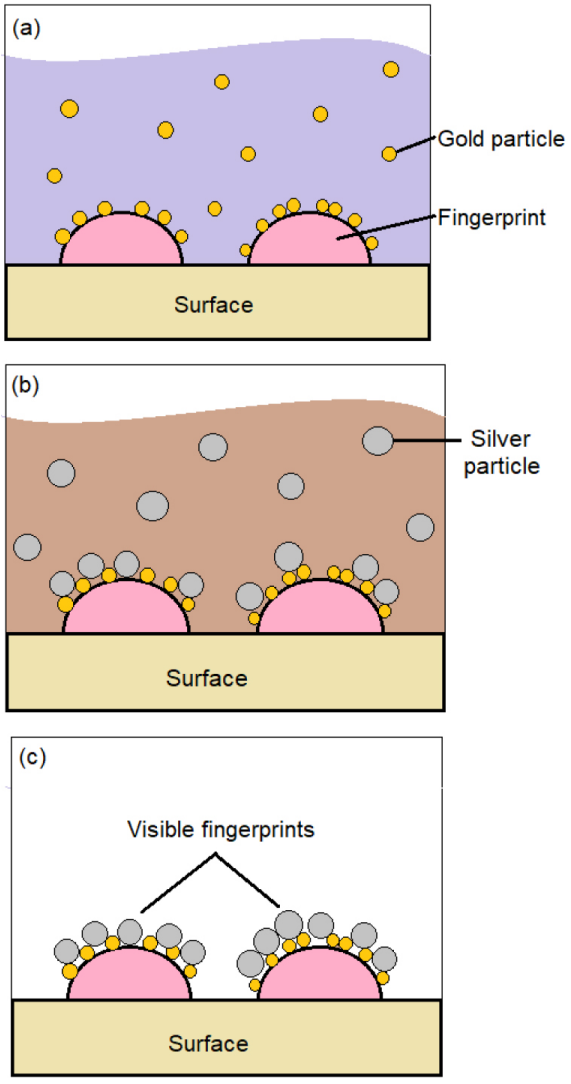


Figure 26. Multimetal deposition technique. Immersion in solution with colloidal gold (a), in modified physical developer (b) and visible fingerprints (c). Adapted from Bleay, Croxton and Puit (2018) [21]

hydroquinone instead of Fe(II)/Fe(III). This new technique is called MMD-II.[9,76]

7.3. Single-metal deposition

Single-metal deposition (SMD) was developed in 2007 as an alternative to MMD-II. The major difference is that, instead of using two metals, gold and silver, it only uses gold, but the procedures remain the same.[21,76]

The first step uses the same Au-citrate solution (particle diameter around 14 nm) used in MMD. However, in SMD the solution containing silver is replaced for a chloroauric acid ($HAuCl_4$) solution with hydroxylamine [21,76]

Tests carried out with the SMD have shown that its efficiency is equal or superior to the MMD-II. Moreover, it is cheaper, does not cause background darkening, uses less reagents and is less labor-intensive. The only remaining problem is the small pH range. Therefore, research is still underway in order to improve SMD and MMD.[21,76]

7.4. Quantum dots

Quantum dots (QD) are a type of nanoparticles that have attracted the interest of researchers mainly for their outstanding luminescence. These particles are semiconductor nanocrystals with a diameter ranging from 1 to 10 nm that present many advantages besides their fluorescence. They can be functionalized with chemical groups, for example, to be able to target specific molecules, and they can be soluble in both water and organic solvents. Moreover, their excitation and emission characteristics can be modified by adjusting the particle size.[9,77]

Menzel and co-workers (2000) were the first to suggest the use of quantum dots as fingerprint developers. In their study, cadmium sulfide (CdS) QDs capped with dioctyl sulfosuccinate were used, but the development was not successful. After that, dioctyl sulfosuccinate was replaced by polyamidoamine (PAMAM) and the latents were successfully developed. Other researchers also used these same QDs, sometimes varying the solvent, despite always using harsh organic solvents. Due to this fact, CdTe QDs were developed and capped with thioglycolic acid (TGA) which allowed the use of water as a solvent. The fingerprint development with these QDs was successful, showing good luminesce and, therefore, other studies have been made with this combination, including one to detect blood fingermarks.[77,78]

Due to satisfactory results developing fingerprints with QD, other works have been done exploring different solutions and combinations with Cd. However, studies are still needed to evaluate the toxicity of these developers, since cadmium is known to be carcinogenic.[78]

7.5. Silica-based nanocomposites

The use of silica-based nanoparticles for fingerprint development is a relatively new method. The first study was conducted by Liu and collaborators (2008), who succeeded in trapping a complex of europium (Eu) ions and the sensitizer 1,10-phenanthroline (OP) in silicon dioxide-based nanocomposites (tetraethoxysilane, TEOS), developing fluorescent fingerprints.[79]

After that, some other works were also published. Moret *et al.* (2014) developed fingerprints with silicon dioxide-based nanocomposites, but replaced the europium with Rhodamine 6G and some other reagents/solvents, also achieving success. In another study, Divya and collaborators (2018) modified the surface of the silica nanocomposites with different alkyl chains and, to obtain fluorescence, added a platinum luminophore with a long aliphatic chain and, with this, also obtained success developing fingerprints.[80,81]

This is a promising field, as these silica nanocomposites are simple and low-cost to produce and relatively easy to modify/optimize. Therefore, it is worth investigating further this method of fingerprint development.[81]

8. Conclusion

In this review work, several substances and techniques that are used in the development of latent fingerprints were presented. The procedures and compounds presented act in a physical or chemical way on fingerprint residues, making them visible in order to provide evidence and assist the criminal justice system.

In addition to all that has been presented, it is important to note that there are other methods of fingerprint development, especially the optical methods, which are always the first option because they are non-destructive. However, this article focuses on the chemistry associated with forensic science.

Furthermore, it should be pointed out that several substances and methods were used in the past, but due to research related to safety and efficiency, they are being left aside, while other methods remain very popular and are used all over the world, and there are still those that are new and still being researched, such as different green developers and nanomaterials. More than that, it is now possible to find studies that involve not only the development of fingerprints, but also their chemical analysis, obtaining new information.

Therefore, we must recognize the importance of research to make forensic chemistry more efficient and safer for professionals in the field.

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