

REVIEW

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Development of fingerprints on thermal papers—a review



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Abstract

Background: In recent times, the use of thermal papers has increased exponentially and the fingerprints on thermal papers are frequently encountered. Although fingerprint development on paper has been standardized, that on thermal paper is complicated. Thermal papers turn black on the application of heat which poses a problem in the visualization of fingerprints which makes it difficult to visualize.

Main body: One solution to this problem is to use heat or steam for the development of white fingerprints on darker backgrounds. Second solution might be to dissolve the chemicals present on the surface of the thermal papers using acetone. Many studies to develop fingerprints on thermal papers using iodine fuming, ninhydrin, 1,8-diazofluorene-9-one, and p-dimethylaminocinnamaldehyde have been performed. In the present review, an attempt has been made to summarize the problem posed to fingerprint development on thermal papers and the probable solutions attempted by different authors.

Conclusion: Although the development of fingerprints is difficult on thermal papers, it can be achieved either by subjecting the thermal paper to controlled heat or by removing the temperature-sensitive layer before treating it with other fingerprint development methods.

Keywords: Fingerprints, Thermal papers, Iodine fuming, Ninhydrin, 1,8-Diazafluorene-9-one, p-Dimethylaminocinnamaldehyde

Background

Fingerprints are an important piece of evidence in crime investigation. They play a key role in crime investigation due to their permanency, universality, uniqueness, and availability. Fingerprints are composed of eccrine components whose main constituent is amino acid and sebaceous components whose main constituents are oil and fats (Almog 2001). Fingerprints have been a subject of investigation for a long time, but with the advent of facsimile documents in the 1980s, fingerprint research has gained a new speed. New methods are being developed for the visualization of fingerprints on different types of substrates (Bissonnette et al. 2010). Substrates can be broadly classified into three types based on their ability to absorb water-soluble deposits: (1) porous surfaces, (2) non-porous surfaces, and (3) semi-porous surfaces (Champod et al. 2016). Fingerprints on porous surfaces can be developed using ninhydrin and its analogs

(Lennard et al. 1986; Jasuja et al. 2009; Yang and Lian 2014; Chen et al. 2015), diazafluorenone (DFO) (Stoilovic 1993; D'Elia et al. 2015), physical developers (PD) (de la Hunty et al. 2015; Sodhi and Kaur 2016), and multimetal deposition (MMD) (Stauffer et al. 2007; Becue et al. 2012; Newland et al. 2016). Fingerprints on non-porous surfaces can be developed using fingerprint powders (Garg et al. 2011; King et al. 2015; Barros and Stefani 2019), small particle reagent (Cucè et al. 2004; Jasuja et al. 2008; Sodhi and Kaur 2012; Rohatgi et al. 2015), cyanoacrylate fuming, and vacuum metal deposition (VMD) (Jones et al. 2001; Yu et al. 2011; Davis et al. 2016). Often at the crime scene, surfaces which pose a difficulty in the development of fingerprints are encountered. One such surface is that of thermal papers, which often requires special treatment before the development of fingerprints. In the present review, we take a closer look at the composition of thermal papers and various available methods for the development of fingerprints on thermal papers.

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Historical development of thermal papers

Thermal papers are used everywhere in every form of receipts because of its low cost, low noise, and rapid printing nature (Bond 2013). This type of printing is being used in our daily routines like fax machines, ATM, shopping bills, grocery store bills, and bus tickets. Thermal papers are also being used in some spectroscopy and medical instruments like ECG. The thermal paper consists of a base layer, an undercoat, and a thermal coat. The base coat is a wood-free paper, and only the highest quality raw materials and additives are used. Above base paper or layer, there is an optimizing layer known as an undercoat, which provides an even and smooth surface. The thermal coat is applied on the top of undercoat and enables high-resolution printing, supports a high image quality, prevents heat conduction into paper, and thus helps in optimizing the sensitivity of thermal coat. The thermal coat consists of leuco dyes such as triaryl methane phthalides, developers such as bisphenol A (BPA), stabilizers, and sensitizers. Sensitizers are added to optimize the color development of leuco dyes, whereas stabilizers are added to increase the shelf life of thermal papers (Thermalrollshop 2014). An additional topcoat may be present on the top of the thermal layer. This coating protects the thermal paper from external influences like mechanical abrasions, chemical influences, and environmental influences.

Thermal paper or thermosensitive paper was firstly introduced in the market in 1968 by the National Cash Register Company and contained a top coating of leuco dyes with some other co-reactants. Leuco dyes contain a lactone ring structure which forms color compounds in the presence of acidic components. The process of ring opening results in color formation, but this process is reversible that is why thermal paper fades with the passage of time (1969; Yoshida and Kitao 1989; Muthyala 1997). Thermal papers were improved by using iron soap and phenolic components which help in paint formation. Moreover, a binder such as cellulose acetate was added to enhance the thermal paper (Truitt 1974). Recently, BPA (bisphenol A) is being used as a color developer in thermal paper.

Problems of developing fingerprints on thermal papers

When thermal papers are being subjected to heat, they produce a black surface which indicates the presence of unsubstituted leuco dyes. Therefore, any heat treatment while developing fingerprints results in a decrease of color contrast because of the black background produced by thermal paper. For this reason, conventional methods do not yield good results while developing fingerprints on thermal papers. The problem may be overcome by three strategies: (a) to remove the thermosensitive layer by washing with solvents before the development of

fingerprints, (b) to use chemicals which can react with the thermosensitive layer to make it inactive, and (3) to decolorize the thermosensitive layer after the development of fingerprints.

Five different types of methods have emerged for the development of fingerprints on thermal paper. The first method recommends fewer polar solvents as the carrier solvent for ninhydrin development. The second method involves the use of ninhydrin in polar solvents and then destaining technique to reverse the reaction causing the emulsion side to overlap. The third method replaces the use of ninhydrin with other reacting compounds. The fourth method includes various chemicals for fuming, whereas the fifth method involves a solvent-free method for the development of fingerprints (Bissonnette et al. 2010).

Main text

Development and visualization of fingerprints on thermal papers

Development of fingerprints on thermal paper has gained a growing interest from the research community in recent years. Thermal papers are used in the form of bills and receipt at every counter because of the low cost. Therefore, they are often encountered at crime scenes bearing the fingerprints. In such cases, it is important to develop and identify the fingerprints. Following are the methods which have been used for the development of fingerprints on thermal papers. Figure 1 summarizes methods used for the development of fingerprints on thermal paper.

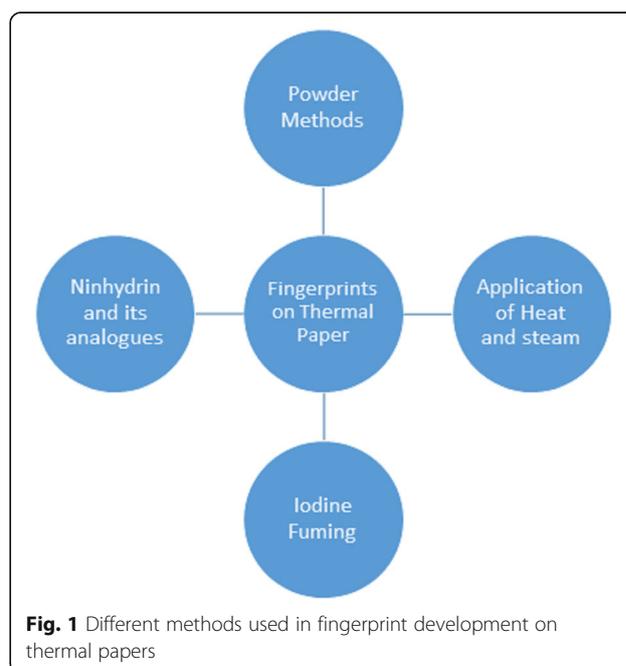


Fig. 1 Different methods used in fingerprint development on thermal papers

Visualization of fingerprints on thermal papers using a UV light source

Various optical brighteners are added to papers to enhance the brightness and appearance of the final product. These optical brighteners absorb UV radiations and produce blue fluorescence at 365 nm. Area of paper having fingerprints has fewer radiations emitted when illuminated by UV radiations in comparison to areas where no fingerprint is present (Bond 2015a). This decrease in the emission of radiations might be due to absorption by the components of sweat or dye pigments of paper. UV fingerprint imaging is non-contact in nature, therefore allowing other methods to be used after visualization. Secondly, because of its blue fluorescence, it produces high contrast between the fingerprint and the background (Akiba et al. 2017).

Bond has described the visualization of fingerprints on thermal paper using various kinds of light sources including white and blue Crime-lites and a LED torch. It was observed that the LED torch produced the best results for both male and female donors (Fig. 2) (Bond 2015a). Near-infrared radiations have also been used to

visualize latent fingerprints on thermal papers. Modica et al. successfully used NIR to visualize latent fingerprints on highway tickets, receipts, and ATM paper receipts (Modica et al. 2014).

Development of fingerprints on thermal paper using physical methods

Physical methods include different types of fingerprint powders which are a fast, effective, and low-cost method for the development of fingerprints. The powder particles adhere mechanically to the lipid and water particles present in the latent print residues. This method is best recommended for the development of fingerprints on non-porous surfaces; however, as the fingerprint grows old, the efficiency of this method continuously decreases (Ramotowski 2013; Daluz 2015). Garg et al. used turmeric powder to develop fingerprints on thermal paper (Garg et al. 2011). Because the fingerprints developed were of yellow color, they provided good contrast on the white background of thermal papers. Figure 3 illustrates



Fig. 2 Example of fingerprints on thermal paper developed with LED torch (adapted from Bond (2015b))

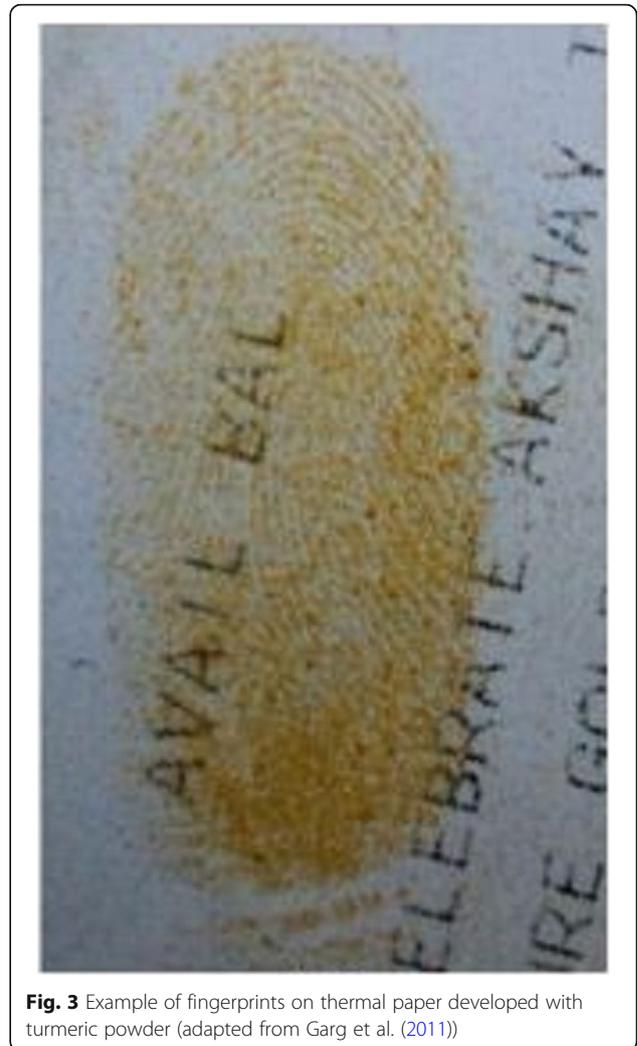


Fig. 3 Example of fingerprints on thermal paper developed with turmeric powder (adapted from Garg et al. (2011))

an example of fingerprints on thermal paper developed using turmeric powder.

Development of fingerprints on thermal paper by application of steam

One of the first uses of steam for developing latent prints comes from a serendipity. A member of the Toronto Police Service Forensic Identification Services (FIS) observed that the fingerprints on the emulsion side of the thermal paper had been developed from the steam emanating from lunch boxes.

Bissonnette et al. used a fabric steamer to develop latent fingerprints on various thermal receipts. Standard fingerprints made up of three saturated fatty acids (myristic acids, palmitic acid, and stearic acid), two unsaturated fatty acids (oleic acid and palmitoleic acid), and squalene was also used as a control. Fingerprints were kept for 1 h, 1 day, 1 week, and 6 weeks for age-related studies. Although fingerprints of available ages could be developed using steam, it was observed that the percentage of identifiable prints dropped from 100% for 1-h samples to 35% for 6-week samples. Maximum fingerprints developed using steam treatment were of good contrast and could be successfully used for identification purposes (Fig. 4). Most of the fingerprints started to fade after half an hour, but some persisted for 4 months after development also (Bissonnette et al. 2010).



Fig. 4 Example of fingerprints on thermal paper developed using controlled heat (adapted from Bond (2015a))

Development of fingerprints on thermal paper by application of heat

Bond used the controlled application of heat to develop fingerprints on thermal papers. The surface having the fingerprint was uniformly heated using an instrument at 45 °C to 50 °C. Developed prints were evaluated using the grading system suggested by Bandey and Gibson (Bandey and Gibson 2006). A brass plate and a glass plate were used to lower the temperature. These developed fingerprints were further visualized using 465 nm wavelength LED lamps. Age-related studies were done for 1-h-, 1-day-, 2-day-, 1-week-, 2-week-, 3-week-, and 4-week-old fingerprints. It was observed that 95%, i.e., 38 out of 40 prints, scored a grading of 4 for 1-h-old fingerprints. However, as the age of fingerprints was increased to 4 weeks, the number of developed prints scoring dropped to 19 (Bond 2013).

A similar study was conducted by Bond on thermal paper receipts from four different countries, i.e., USA, China, UK, and Australia, using heat treatment. Developed fingerprints were evaluated using the quality of fingerprint ridges through the grading system. Furthermore, the developed fingerprints were classified into two types on the basis of the color of fingerprints and the background. Black fingerprints on a white background were classified as type 1 fingerprints, whereas black fingerprints on a white background were classified as type 2 fingerprints. Type 1 fingerprints comprised of 71.5% of all developed fingerprints with 30.5% type 1 from USA, 91.6% type 1 from China, and 100% type 1 from UK and Australia. Type 2 fingerprints comprised of only 28.5% of total developed fingerprints. It is interesting to note that no type 2 fingerprints were observed in thermal papers from UK and Australia. Type 1 fingerprints show diminished fingerprint ridges as the fingerprint age was increased from 24 h to 7 days. However, diminishing of type 2 fingerprints was found to be temperature-dependent. It was observed that the developed fingerprint faded within 24 h of development. However, the fading was slow for type 2 fingerprints in comparison to type 1 fingerprint (Bond 2015b).

Bond used Hot Print System and Thermanin to develop latent fingerprints on thermal papers and then compared the results. It was observed that Thermanin-developed fingerprints were graded as 4 for only two of five donors over all time periods. One donor produced one grade 4 Thermanin print (developed after 1 hr), and other donors produced three grade 4 Thermanin prints developed after 2 days, 1 week, and 2 weeks. Two donors each produced one grade 3 Thermanin-developed print, both after a time period of 1 day. Grade 4 prints were produced for four out of five donors using HPS development. However, only 2 donors produced grade 4 fingerprints for all time intervals. Another important finding

was that the prints produced using HPS did not all occur in early time periods or consecutively in time. It is evident that Thermanin produced grade 3 or grade 4 prints for all ages, but HPS did not produce grade 3 or grade 4 fingerprints for fingerprints of age 2 days and 1 week. However, a number of grade 3 or grade 4 fingerprints for fingerprints of age 1 h, 1 day, 2 weeks, 3 weeks, and 4 weeks was significantly larger for HPS as compared to the Thermanin. Depletion series studies showed that no Thermanin-developed fingerprint showed grade 4 fingerprint for all donors and all nine sequences, whereas for HPS 4 donors produced grade 4 fingerprints. It was noted that for two donors, fingerprints developed by HPS produced grade 4 fingerprints even for the last sequence. The big difference between the results of Thermanin and HPS might be the result of limited heating used as a measure to counter the darkening of the active side of thermal papers (Bond 2014).

Development of fingerprints on thermal paper using iodine fuming

Fingerprints have been developed by iodine fuming which has been used for over a century. In this method, the iodine crystals sublimate in the closed chamber where the fingerprints are held for development. These iodine molecules react with the fatty and oil components of fingerprints and produce yellowish-brown color where the fingerprints are present. However, this color is not permanent and different fixation methods are to be used to make it permanent (Yamashita et al. 2010; Daluz 2015; Champod et al. 2016). Jasuja and Singh have investigated the possible use of iodine fuming in developing the fingerprints on thermal paper (Fig. 5). Fresh and aged fingerprints (aged up to 1 year) on different types of thermal papers such as fax paper, DP print paper, and ATM print paper were used for the study. The developed prints were observed simultaneously and after 1 year of development. It was observed that developed fingerprints were permanent on the thermosensitive side, whereas on the non-glossy side, the developed prints were non-permanent. However, the permanency of the fingerprints was dependent on the type of paper. Moreover, fingerprints on different types of thermal papers resulted in differently colored fingerprints ranging from green/greenish-black to black/brown/yellowish. No background coloration was observed in this study (Jasuja and Singh 2009).

Development of fingerprints on thermal paper using ninhydrin and its analogs

Ninhydrin (2,2-dihydroxy-1,3-indanedione) is colorless to pale yellow crystalline solid which is highly soluble in water and other polar solvents (Yamashita et al. 2010). Primary and secondary amines present in the eccrine

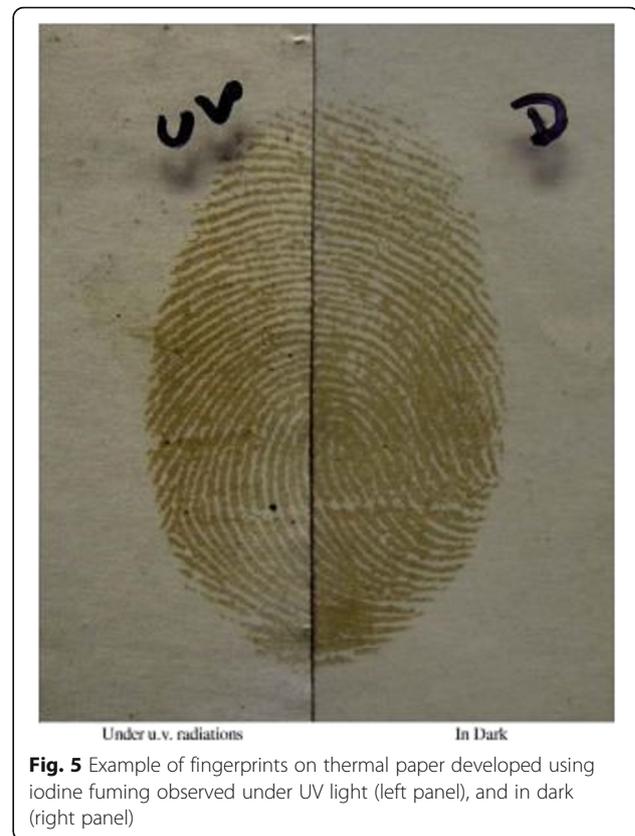


Fig. 5 Example of fingerprints on thermal paper developed using iodine fuming observed under UV light (left panel), and in dark (right panel)

secretions of fingers react with ninhydrin to produce a dark purple product known as Ruhemann's purple. Development using ninhydrin has been an efficient technique to develop fingerprints since its inception in 1954 by Oden and von Hofsten (Champod et al. 2016). However, the heat treatment required to develop the prints causes the background to blacken, which further reduces the visibility of fingerprints.

Schwarz and Klenke (2007) used a different whitening agent for the enhancement of ninhydrin-treated fingerprints on thermal papers. Different whitening agents such as (1) acetone washing, (2) testing compounds (oenanthoactam, 1-octyl-2-pyrrolidone, 1-cyclohexylpyrrolidone, and 4-pyrrolidino-pyridine each used individually), (3) solution of mixture 3 "G3" (12.5 nm each of 4-pyrrolidino-pyridine, oenotholactam, 1-cyclohexylpyrrolidone, and 1-cyclohexyl-pyrrolidone), and (4) solutions of mixture 3 "G3N" containing ninhydrin were used to increase the contrast of fingerprints developed on fingerprints. It was observed that the best whitening was observed with the application of 100 mM 4-pyrrolidino-pyridine (91% positive results) followed by a mixture of "G3" (87.5% positive results). One hundred millimolar of 4-pyrrolidino-pyridine showed good results for fingerprints of all ages, however, it failed to develop a fingerprint for two brands of thermal papers for 7-day-

old fingerprints. On the other hand, G3 developed fingerprints for all types of thermal papers and for all ages except one 0-day fingerprint and two 7-day fingerprints. However, in the case of G3-developed fingerprints, whitening was observed during the dipping itself and it persisted for a week, often for a month depending upon the brand of thermal paper. It was observed that the solution can be used for several times before losing its ability to produce whitening. In comparison to whitening using acetone, the fingerprints developed had a sharper and higher contrast as the color of ninhydrin-developed fingerprints changed to blue (Fig. 6). It is also important to note 10 times more acetone is required to produce similar results as that of G3 mixture.

Schwarz and Klenke (2010) stated that the abovementioned method has two-pronged limitations: (1) it is a very time-consuming process and (2) it is not a permanent process, and the contrast between print and background decreases with time. Therefore, they recommended the use of ninhydrin and polyvinylpyrrolidone (PVP) to develop fingerprints on thermal paper. For comparative purposes, 1-day-old, 1-week-old, and 1-month-old fingerprints were also analyzed. Prints developed by the ninhydrin solution containing PVP are a bluish-violet color, whereas the prints developed by ninhydrin + acetone washing are a reddish color. Also, these results did not change during the 6-month observation period. PVP is a non-toxic and comparatively cheap chemical which is easily available. Furthermore, its mixture of ninhydrin produces a single-step development process to develop fingerprints on thermal papers.

DFO (1,8-diazafluorene-9-one) which is a ninhydrin analog reacts with amino acids to produce red pigment which closely resembled that of Ruhemann's purple. DFO-treated fingerprints produce faint red color, however produce

fluorescence under green light with an absorption maximum at about 470 nm and emission maximum at about 570 nm. DFO is often considered one of the best fluorogenic fingerprint reagent for paper and porous surfaces.

Luo et al. (2013) improved the results of fingerprint development on thermal papers using the mixture of 1, 8-diazafluorene-9-one (DFO) and polyvinylpyrrolidone (PVP). It was observed that PVD reduced black background staining without diluting the thermosensitive layer. The results of prints developed using DFO/PVP were compared with the prints developed with only DFO. After the treatment of latent fingerprints with DFO/PVP, fluorescent prints were obtained, which provided a better contrast with the background in comparison to the ones developed using only DFO (Fig. 7). The comparison between DFO/PVP and ninhydrin for a 3-day-old fingerprint was also done. It was evident that the results obtained using DFO/PVP were better than that of ninhydrin. Therefore, it can be concluded that a mixture of DFO and PVP produced better results in comparison to both DFO only and ninhydrin development.

p-Dimethylaminocinnamaldehyde (DMAC) is a photoluminescent analog of p-dimethylaminobenzaldehyde (DMAB) which is often used to visualize amino acids during histochemical studies (Fritz et al. 2015). The DMAB reacts with the amino acid and urea, which is present in the human sweat to produce color complex through an imine or Schiff base formation. A solution of pH 4–5 is considered to give the best results (Lee and Gaensslen 2001). DMAC as an agent of fingerprint development was first studied in 1973. Initially, it was considered to be a good substitute of ninhydrin; however, with in-depth research, it was found that DMAC was inferior to ninhydrin development (Fritz et al. 2015).

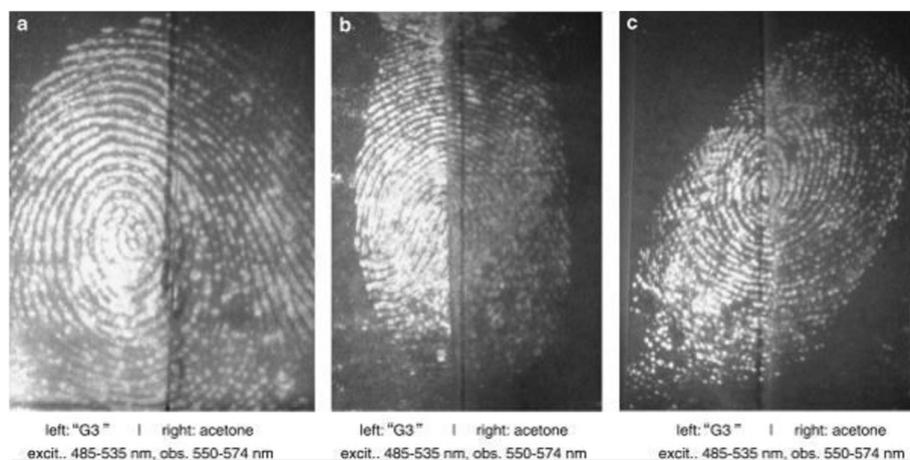


Fig. 6 Example of fingerprints on thermal paper developed using 1,8-diazafluorene-9-one (DFO) when compared with fingerprints developed with acetone (a and b) and ninhydrin treated prints (c) (adapted from Schwarz (2007))

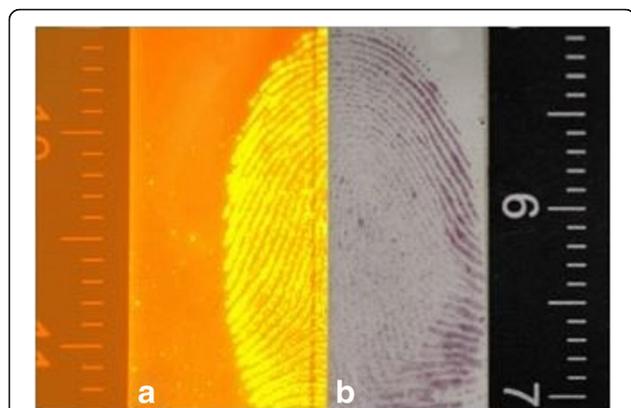


Fig. 7 Example of fingerprints on thermal paper developed using **a**) PVP/DFO with polilight lamp at 515nm excitation and **b**) One step PVP/ninhydrin observed using white light

Lee et al. used DMAC for the development of latent fingerprints of three types (split depletion series, different depletion series, and pseudo-operational trial) through the contact transfer process. In this process, the exhibit possessing latent fingerprint is pressed in between two sheets of paper soaked with the chemical solution (Flynn et al., Detection and enhancement of latent fingerprints on polymer banknotes: a preliminary study). Results from development using DFO and ninhydrin were also compared to the results from development using dimethylaminocinnamaldehyde. DFO and ninhydrin solution was prepared in accordance with the procedure outlined by HOSDB manual of fingerprint development techniques. However, the concentration of ethanol is higher as compared to that of regular DFO and ninhydrin solution. DMAC solution was prepared by adding 0.25 g DMAC in 100 ml ethanol and mix for 2 min. Dip sheets of photocopier paper into the solution for a few minutes and allow them to dry in nylon bags. Once dry sandwich the thermal paper with latent fingerprints between the sheets and cover with the help of aluminum foil. Place the sandwich in the press for 24 h. DMAC produces a yellow fluorescence after reacting with the urea component of a latent fingerprint. However, the emission and excitation spectra suggest that DMAC reacts with amino acid component rather than urea. It was observed that the number and quality of marks developed from all the three methods were very low. However, the results obtained for prints developed by DFO were significantly better than that by ninhydrin and DMAC. DMAC gave better results for 1-day-old fingerprints compared to ninhydrin. However, as the age of fingerprints increased, the performance of DMAC decreased considerably (Lee et al. 2009).

Conclusion

Fingerprint development on thermal papers is challenging because of the darkening of the surface of thermal papers. This darkening obscures the visualization of developed fingerprints. To tackle this problem, many attempts have been made using various methods including application of heat and steam and dissolving the surface layer of thermal papers. In the present study, an attempt has been made to summarize the various studies available till date for the development of fingerprints on thermal papers. It is apparent that more studies are required to propose a suitable standard method for the development of fingerprints on thermal papers.

Abbreviations

BPA: Bisphenol A; DFO: 1,8-Diazofluorene-9-one; DMAB: p-Dimethylaminobenzaldehyde; DMAC: p-Dimethylaminocinnamaldehyde; FIS: Fingerprint identification services; LED: Light-emitting devices; MMD: Multimetal deposition; PD: Physical developer; PVP: Polyvinylpyrrolidone

Acknowledgements

None to declare.

Authors' contributions

PKY contributed to the literature collection and manuscript preparation. All author read and approved the final manuscript.

Funding

No funding organization is involved in this study.

Availability of data and materials

Not applicable.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The author declares that there are no competing interests.

Received: 12 June 2019 Accepted: 22 July 2019

Published online: 07 August 2019

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