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Vapor Phase Methods for Detection of Latent Fingerprints: A Review

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Abstract

This communication critically examines the utility of three reagents, viz. cyanoacrylate, iodine and ruthenium tetroxide, which, in vapor state, develop latent fingerprints on a host of crime scene evidence.

Keywords: Criminalistics; Fingerprints; Latent impressions; Post-treatment; Vapors.

Introduction

A good number of techniques for detecting latent fingerprints on crime scene evidence have been standardized. Some of these use solid reagents, such as powders,[1] for developing prints while others resort to dissolved reagents, such as ninhydrin[2] for this purpose. The problem with such conventional techniques is that the latent impressions on the relevant evidence must first be located either visually or with the aid of a light source and thereafter the concerned reagent applied over it. With vapor phase methods there is no need to first scan the surface. The object bearing the fingermarks is suspended in a fuming cabinet and the vapors of the developing reagents get preferentially adsorbed on the sweat residue, revealing the ridges. Moreover, the chances of the ridge details getting smudged are almost negligible with fuming developers. However, vapor phase developing methods do pose occupational hazard, unless a proper protective gear is used.

Three vapor phase fingerprint detecting techniques – cyanoacrylate, iodine and ruthenium tetroxide methods – are reviewed herein.

Cyanoacrylate Method

Cyanoacrylate method, also called the super glue technique, is based on the premise that when alkyl 2-cyanoacrylate reagent is allowed to vaporize it undergoes polymerization. The polymerized ester gets adsorbed on the sweat residue, imparting a white colour to the ridge pattern.[3] The color contrast may be improved by various post-treatment methods.

Methodology: A china dish, containing a few drops of cyanoacrylate ester, is placed in a fuming cabinet. The object bearing the latent prints in suspended from the roof of the cabinet. The item is exposed to the cyanoacrylate vapors for about 2 hours until whitish colored fingerprint pattern develops.[4]

For successful processing of prints, the design

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of the fuming cabinet has been modified from time to time. Care is taken that the cupboard has a proper ventilation system. One such variety is shown in Fig. 1.

Fig. 1: A cyanoacrylate fuming chamber

Nakada and Nagasawa[5] used a transparent acrylic resin cabinet for pursuing cyanoacrylate method. These authors meshed a mixture of cyanoacrylate reagent, sulfurous acid and hydroquinone with soybean and placed the mass in a china dish. The dish, covered with the surface bearing latent fingermarks was placed inside the cabinet. The ester monomer volatilized and room temperature and fingerprints developed within 30 seconds. This method was particularly useful for developing prints on polythene surfaces. Stokes and Bernnan[6] devised a sophisticated cabinet for conducting cyanoacrylate fuming. Using robust technology, these investigators achieved reliability and ease of evaporation for automatic development of latent fingerprints. The cabinet had self-scrubbing and free-suspension facilities.

Fingerprint kits based on cyanoacrylate fuming procedure have also been designed. Such kits normally contain a vapor activator pad impregnated with cyanoacrylate monomer and a fluorescent dye. The pad is place in an enclosed area to fume the object suspected of containing latent fingerprints.[7] Eisele et al.[8] devised a cartridge which may be carried in a conventional fingerprint kit. The cartridge comprised of a cylindrical vessel containing a thermally stable and thermally conducive porous support material. The support material was saturated with cyanoacrylate cured to a solid form. It also contained a fluorescent dye for enhancement of developed prints.

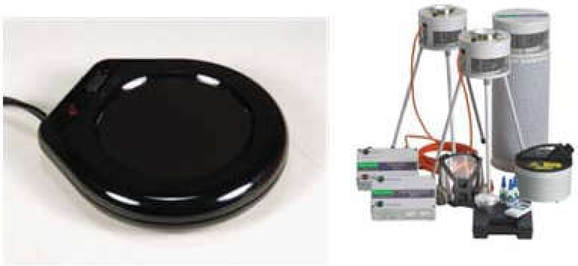
Cyanoacrylate ester, being a liquid, is difficult to handle. Hence it is often incorporated into different matrices so that it can be used with ease. Most commonly, cyanoacrylate ester is impregnated into a gel matrix which is then placed in a reusable foil pouch.[9] Gilman et al.[10] sandwiched a mixture of cyanoacrylate and petroleum jelly between acetate sheets. Alternately, a thin film of the ester may be pressed between aluminium foils by using a fingerprint roller.[11]

There are two broad techniques by which the developing time of cyanoacrylate fuming may be reduced: Fume circulation and heat acceleration. These techniques serve to convert the ester into vapors at an accelerated pace and thereby increase the rate of its polymerization. The two techniques may be used in concert with each other.

The fume circulation technique requires a small battery-operated fan (Fig. 2) or an air circulation pump in the fuming cabinet. When the fan or the pump is turned on, the motion of the fumes increases. By this method the latent prints may be developed in 1 hour as against 2 hours required for natural fuming.[12]

Fig. 2: A battery-operated fan for fume circulation

The heat acceleration technique requires a heating device, such as a light bulb, a portable heater, a hot plate or a hair dryer in the fuming cabinet (Fig. 3).



(A) (B)

Fig. 3: Devices for heat acceleration: (A) hot plate; and (B) heating blocks

Under the influence of heat, the monomer volatilizes and polymerizes faster, thus reducing the development time to about 30 minutes.[13,14]

Mechanism: The mechanism leading to the polymerization of cyanoacrylate ester is depicted in the Fig. 4.

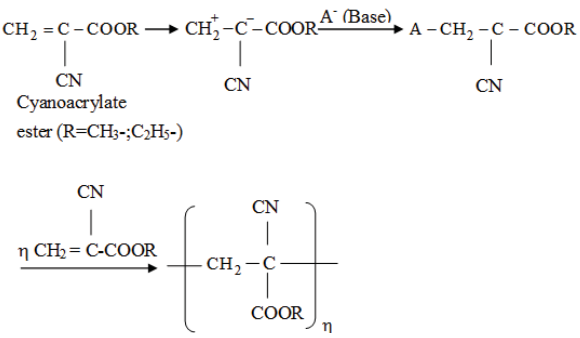


Fig. 4: Mechanism of cyanoacrylate ester fuming

The reaction initiates with the abstraction of a proton from the alkene carbon by a base (A). Even if no alkali is added, the reaction still proceeds since the water molecules, present as moisture in air, act as Lewis base. Therefore, at times two heating systems are simultaneously used in the fuming chamber, one to transform cyanoacrylate ester into vapors at a fast pace and the other to generate water vapors. One such set up is depicted in Fig. 5.

Fig. 5: A fuming chamber equipped with two heating systems

Alternately, the polymerization is accelerated if a base is added to the reaction mixture. Thus, when a cotton pad, soaked in cyanoacrylate and a 0.5 N solution of sodium hydroxide, is placed in the evaporation dish, the fingerprints developed within 30 minutes to 1 hour.[12]

Burns et al.[15] used Fourier Transform infrared spectroscopy to demonstrate that a better deposition of the polymerized cyanoacrylate on the fingerprint residue occurs in the presence of a base. Therefore, these authors recommended that prior to cyanoacrylate fuming, the surface in question be exposed to ammonia vapors.

Post-treatment: Even though cyanoacrylate fuming is a convenient and reliable method of detecting latent fingerprints, the developed imprints are white in color and, therefore, lack contrast. In order to improve their clarity, the developed prints are often further treated with a chemical reagent. The post-treatment procedures not only increase the contrast, but also enable detection of impressions on elusive surfaces.

The most common post-treatment method is dust the cyanoacrylate-developed prints with a regular fingerprint powder. Such formulations contain a resinous polymer for adhesion and a colorant for contrast. The adhesive gets adsorbed on the moisture and oily components of the sweat residue, while the colorant gets adsorbed on the adhesive. In this manner the ridge pattern is visualized. Since moisture and oily contents of sweat tend to evaporate with the passage of time, conventional powder dusting technique in incapable of developing old prints. However, old prints may be developed by cyanoacrylate method, followed by treatment with a powder composition. The polycyanoacrylate deposition has a tendency to absorb the powder. For example, using a Sudan black based formulation for post-treatment of cyanoacrylate-developed prints, it is possible to develop fingerprints on several items, including cement matrix.[16]

The fingerprints developed by cyanoacrylate fuming may also be enhanced by post-treating these with a luminescent dye. Such stains fluoresce or phosphoresce upon exposure to ultraviolet or laser light. This post-treatment procedure is useful for visualization of latent prints deposited on multi-colored surfaces. Moreover, it can be used for developing weak prints. When luminescent stains alone are used for print processing, the results are not satisfactory. The reason being that the dye solution tends to wash off the sweat residue, However, when stains are used in conjunction with cyanoacrylate fuming, this problem is avoided. The cyanoacrylate polymer stabilizes the latent prints, so that solution dye staining does not wash it away.[17]

Luminescent dyes such as gentian violet and coumarin 540, are generally used for improving the contrast of weak prints developed by cyanoacrylate method.[18] These stains get selectively adsorbed on the polymerized Super Glue and thus revealed the ridges. While gentian violet is suitable for developing imprints on transparent polythene surfaces, coumarin 540 works on reflective surfaces like aluminum foil and chrome. In the latter case, further enhancement is achieved by observing the post-treated fingermarks under a laser. Rhodamine 6G treated prints are also suitable for laser examination. The stain gets preferentially adhered to the polycyanoacrylate deposition. Moreover, the absorption spectrum of the stain matches with the blue-green illumination of the argon laser.[19]

Staining the cyanoacrylate-developed prints can be carried out with Ardrox dye dissolved in freon-113 solvent.[20] Observing the post-treated imprints under ultraviolet light remarkably improves the contrast. Cyanoacrylate-staining dye procedure is one of the few techniques which can develop blood prints. Bloody fingerprints are often found on weapons, victims' bodies and other articles removed from the scene of crime. For detecting such prints, the blood protein must first be denatured and fixed on the surface. This is done by baking the sample in an oven for about 5 minutes. Cyanoacrylate fuming, in combination with Coomassie blue stain, is effective in developing bloody fingerprints on plastic items.[21] However, the method does not work on metallic or glass surfaces.[22]

Complexes of lanthanides, especially those of europium (III) or terbium (III) may be used instead of staining dyes for post-treatment operations. These complexes show luminescence via intramolecular energy transfer. Moreover, the lifetime of the luminescence is much larger than that of the surface fluorescence. The complexes are, therefore, suitable for time-resolved luminescence image.[23] Post-treatment of cyanoacrylate-developed prints give excellent luminescence intensity, a stokes shift of 262 nm and suppressed surface fluorescence.[24]

Iodine Method

The iodine fuming techniques for visualizing latent fingermarks on porous surfaces has been used for almost a century. Iodine is a crystalline solid, which upon heating sublimes into violet vapors. The vapors are absorbed by the sweat deposition of the latent imprint thereby revealing the ridge pattern.[25] Initially, it was believed that iodine added chemically and reversibly, to double bonds of the unsaturated fatty acids present in the fingerprint residue. However, it was later suggested that the mechanism of the reaction involved physical absorption of iodine on the fatty acid content. The iodine-fatty acid interaction imparts a yellowish brown color to the ridge pattern.[26]

Methodology: Latent fingerprints may be developed by iodine fuming technique by one of the following experimental procedures.[27]

Fuming gun method: An iodine fuming gum is made of either glass or plastic. The butt-end of the gum contains a dehydrating agent, usually calcium chloride. There is also a mouthpiece for blowing air at this end. An iodine fuming gun is displayed in Fig. 6.

Fig. 6: An iodine fuming gun

Near the nozzle-end of the gun about 0.5 g iodine crystals are placed. Air is blown though the mouthpiece and the gun nozzle is moved above the surface impinged with the latent prints. The optimum distance between the gun and the surface is 2 cm. As soon as the latent fingerprints begin to appear, the iodine fumes are concentrated over the imprinted area. The prints so developed are photographed immediately.

Fuming cabinet method: A china dish containing about 1g iodine crystals is placed in a fuming cabinet (Fig. 7).

Fig. 7: An iodine fuming cabinet

The object bearing the latent prints is suspended from the roof the cabinet. Iodine crystals are gently heated to about 50 degrees C using a heating block. After a few minutes latent fingerprints begin to appear. The object is exposed to the fumes till maximum contrast has been achieved between the prints and the background. The developed fingerprints are immediately photographed.

Powder dusting method: Iodine crystals are pulverized into a fine powder and spread out over the surface bearing the latent fingerprints by a camel hair brush. The excess powder is blown off. This method does not require any equipment and is, therefore, both simple and cost-effective. However, it exposes the user to the toxic fumes of iodine. As a result, this method is now obsolete.

Post-treatment: Fingerprints developed by iodine are not permanent in nature. These tend to fade out on standing. In presence of air the fading of prints is accelerated. For this reason the iodine developed prints have to be photographed immediately. Nevertheless, it is possible to fix the prints by using iodine in conjunction with other chemical reagents.

Iodine is known to react with starch giving a stable, deep blue complex. Thus, post-treatment of iodine-developed fingerprints with starch solution gives long-lasting blue impressions.[28] The fading problem may also be avoided by pressing a silver foil onto the iodine developed fingermarks. The interaction of iodine, absorbed on the fingerprint residue, with silver produces yellow colored silver iodide. The latter, on exposure to light decomposes into finely divided silver, revealing the ridge pattern as a stable, black deposition.[29]

Trowell[30] devised a method for fixing iodine exposed fingerprints by post-treatment with a solution of tetramethyl diaminodiphenylmethane reagent. Although the color of the prints changed from brown to green-blue, their quality and clarity were not affected. Moreover, these did not deteriorate with lapse of time. The most common reagent for fixing iodine-developed fingerprints is 7, 8-benzoflavone.[31] Haque et al.[32] used iodine in combination with 7, 8-benzoflavone reagent for developing old latent fingerprints on porous surfaces, such as bond paper, news prints and facial tissue paper. The composition proved to be non-destructive.

Ruthenium teroxide Method

Ruthenium tetroxide, also referred to as ruthenium (VIII) oxide, RuO_4 is a volatile and unstable liquid at normal temperatures and atmospheric pressure. It is a versatile reagent for detecting latent fingerprints on a host of crime scene evidence. Its use as a fingerprint reagent emanates from its tendency to oxidize the oily components of fingertip sweat. In this reaction, ruthenium tetroxide itself is reduced to relatively stable ruthenium dioxide (or ruthenium (IV) oxide), RuO_2 which settles on the ridges as black or black-gray deposition. The dark colored prints persist over prolonged periods of time.[33,34]

Methodology: For the purpose of detecting fingerprints, ruthenium tetroxide may be applied to the crime scene evidence in several ways. One method is to prepare a solution of the reagent in water and treat the sample by dipping, spraying or swabbing. However, the solubility of ruthenium tetroxide in water is quite low, as a result of which the aqueous solution of the reagent takes a considerably long time to develop the fingermarks.

In order to speed-up the development process, an alternate route may be adopted. Rather than applying the reagent in solution state, the crystals of ruthenium tetroxide may be sublimed by heating in a water bath and the vapors, so generated, be impinged on the evidence.[34] However, this technique too has a shortcoming. If the heating is too rapid or if the temperature goes beyond 50 degrees C, ruthenium tetroxide is likely to decompose explosively into ruthenium dioxide and oxygen. This problem may be overcome by modifying the fuming procedure.[33] A solution of 0.1g ruthenium tetroxide in 100 ml water is mixed with another solution containing 11.3g of ammonium cerium (IV) nitrate dissolved in 100 ml of water. Fumes of ruthenium tetroxide, as set out in the following reaction are generated.

$$RuCl_3 + (NH_4)_2[Ce(NO_3)_6] \rightarrow RuO_4 + 2\ NH_4NO_3 + CeCl_3 + 4\ NO_2$$

The reaction is carried out in a closed chamber in which the evidence to be processed is suspended. The surface is exposed to the vapors for 20-60 minutes, whereby black colored fingerprints develop.

Yet another method is to dissolve ruthenium tetroxide in a halogenated organic solvent and vaporize the yellow colored solution at low pressures.[34] The fumes are directed on the crime scene evidence. An assembly for generating the vapors of ruthenium tetroxide, dissolved in a halogenated solvent, is shown in Fig. 8.

Fig. 8: An assembly for generating ruthenium tetroxide fumes

By this method optimum quality fingerprints may be developed on thermal paper, leather, vinyl and wood. It also helps in detecting prints on human skin; better results are obtained on dead skin, rather than on live skin.[35] Fingerprints may also be detected on metallic surfaces, including the greasy ones.[36] The developed prints are stable over long periods. The ridges, which are visualized in black or black-gray hue, produce a sharp contrast against a light colored background. If the background itself happens to be dark, the developed prints may be lifted and transferred on to a white substrate. If the method fails to give positive results, the ninhydrin or 1, 8-diazafluoren-9-one (DFO) method may still be tried out on the same article.

However, the health effects of ruthenium tetroxide severely restricts its applications.[37] The reagent elicits toxic effects both on inhalation and on coming in contact with skin. Moreover, it is explosive in nature.

Mechanism: Ruthenium tetroxide is an aggressive oxidant. It oxidizes virtually every hydrocarbon. It also oxidizes compounds of carbonyl classification. It cleaves the double bonds of unsaturated organic derivatives. It is this latter reaction which paves the way for detection of latent fingerprints by ruthenium tetroxide. The reagent attacks the double bonds of unsaturated fatty acids present in fingerprint residue and yields an intermediate ruthenate ester. This intermediate is unstable and spontaneously decomposes into hydrated ruthenium (IV) oxide, $RuO_2.nH_2O$. The latter oxide of ruthenium is quite stable and imparts black color to the finger ridges.[38]

Taking oleic acid as a representative unsaturated fatty acid in fingerprint residue, the mechanism of oxidation by ruthenium tetroxide is set out in Fig. 9.

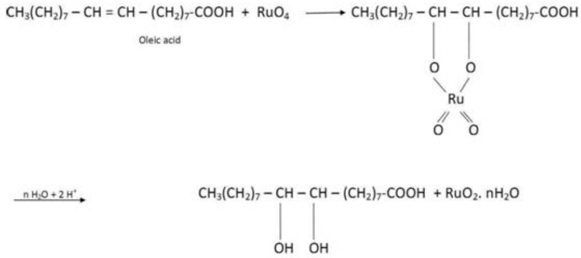


Fig. 9: Mechanism of oxidation of unsaturated fatty acids by ruthenium tetroxide

It is the hydrated ruthenium (IV) oxide which imparts black color to the developed prints.

Conclusion

Fuming reagents of fingerprint detection offer several advantages vis-a-vis solution formulations or compositions in solid, powdered state. Most conventional fingerprint development techniques are surface-specific, For example, powder method is largely used on non-absorbent surfaces, while the ninhydrin reagent is normally used on absorbent surfaces. Vapor phase methods have been used for the development of latent prints on diverse surfaces like plastics, electrical tape, polythene bags, carbon paper, aluminium foil, polished and raw wood, rubber, cellophane and metals.

Before the conventional chemical developing reagents are applied to a surface, the latent fingerprints are visually searched. The relevant spray or powder formulation is then applied. With vapor phase techniques, there is no need to first scan the surface. The object bearing the fingermarks is suspended in a fuming cabinet and the reagent on its own gets preferentially adsorbed on the sweat deposit, revealing the ridges. Moreover, even if the target sweat component is present in the fingerprint residue in trace amounts, the chances of development are substantially higher with fuming reagents as compared with their solid or solution counterparts. Above all, the chances of ridge details getting smudged are almost ineligible with fuming reagents than with conventional formulations.

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