Review Article

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Application of Metals and Metal Salts in Latent Fingerprint Detection: A Review

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Abstract

There are a host of chemical methods for detection and enhancement of latent fingerprints. Those which involve the use of metals or metal derivatives are reviewed in this communication.

Keywords: Fingerprints; Fluorescence; Metals; Photoluinescence

Introduction

It may be claimed that there is no more effective deterrent to crime than the certainty of detection. Equally true is that there is no surer way of establishing identity than by fingerprints. The detection of latent fingerprints at the scene of crime and their subsequent development is therefore one of the most powerful tools available in casework investigations. The fingerprints found at the scene of crime or an article removed from it are formed when the papillary ridges leave a deposit of perspiration on a surface with which the finger has been brought into contact.

The palms of hand are endowed with frictional ridges, also referred to as papillary ridges, which assist in holding or grasping an object.[1] The ridges are studded all along with minute openings, called sweat pores. As the name implies, sweat continuously oozes out of these pores. When the finger touches a surface, it leaves behind a deposition of sweat exactly in the same pattern as the ridge design. However, this deposition is not visible since sweat is colorless. Hence it is called a latent fingerprint.[2]

The latent fingerprints found at crime scenes are rendered visible by an array of chemical methods. In many of these methods, metals or their salts/complexes play a significant role. These procedures are the focus of the present review.

Powder Method

The simplest and most commonly used method for detecting latent fingerprints is the powder dusting. This technique relies on the mechanical adherence of the detecting composition to the oily components of sweat.[3,4] While selecting the powder it must be ascertained that its ingredients do not interact chemically with the surface bearing the latent impression.[2] Nor should it be strongly physically attracted to the surface.

Powder formulations containing meshed metals have been used for a considerable time. These have relatively long shelf lives. Silver powder

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containing aluminium flake and pulverized quartz; gold powder containing bronze flake and pulverized quartz; and gray powder containing meshed aluminium and kaolin are some examples of metallic dusting compositions.[2] Fig. 1 shows a fingerprint developed by a metal-based composition on glossy magazine cover.

Fig. 1: Fingerprint developed on a glossy magazine cover

A good number of powder formulations contain metals or metal salts in concert with organic derivatives that fluoresce or phosphoresce upon exposure to ultraviolet or laser light.[5,6] The advantage of such compositions is that these are useful for visualization of latent prints impinged on multicolored surfaces that would present a problem of contrast if developed with conventional powders. Moreover, these may be used for detecting weak, chance and fragmented fingerprints that are often encountered at crime scenes. Their disadvantage is that these can rarely be used in field work. Some common organic compounds that have been used for preparing luminescent powders are rhodamine B, acridine orange and crystal violet. A latent fingerprint developed on paper under fluorescent conditions is depicted in Fig. 2.

Fig. 2: Fingerprint developed on paper under fluorescent conditions

Nanotechnology-based Methods

Conventional fingerprint dusting powders pick up prints since the oil secreted by fingertips has a natural tackiness. In the course of time the oil tends to evaporate and, therefore, old fingerprints are difficult to detect by powder method. This problem is specifically relevant to a tropical country like India where hot climate prevails eight out of twelve months in a year. Nanotechnology provides a solution to this problem. Nanoparticles have the ability to actively seek out oil from the fingerprint residue, however small the amount may be. This paves the way for development of even extremely faint fingerprints.

The adhesion of a powder formulation to fingerprint residue is governed by the pressure deficit mechanism. If a powder particle is wetted only on its lower side by the sweat deposition then owing to the curvature of the meniscus there will be a pressure deficit inside the droplet, causing the particle to adhere. The electrostatic attraction between the sweat residue and the powder particles too play a role in adhesion, albeit a minor one.[7]

The effectiveness with which the powder adheres to the ridges depends on the size and shape of the particles that compose the formulation.[8] Small, fine particles adhere more easily than large, coarse ones. Particles with size in nanometer range have excellent adhesion ability. Hence, as shown in Fig. 3, the nanotechnology-based compositions develop clearer and more detailed fingerprints as compared to conventional powder formulations.[9]

(A) (B)

Fig. 3: Fingerprint developed with a nanotechnology-based composition (A) is sharper as compared to the one developed by conventional composition (B)

Fluorescent fingerprint dusting compositions based on nanoparticles of metal salts, in concert with eosin Y dye, have shown promising results. These develop fingermarks on a broad spectrum of items.[10,11] It has been observed that better quality fingerprints are obtained when nanoparticles of an ionic metal salt, rather than of a pure metal or an alloy is used as the base material for preparing the composition.[12] The reason being that the quality of developed fingerprints was profoundly affected by the degree of attraction between the adhesive material (alumina or copper) and the colorant (eosin Y). Stronger the interaction better is the quality of the developed fingerprints. The attraction between the adhesive and the colorant, in turn, is dictated by dipole-dipole forces between the two chemical entities. Eosin Y is a polar species, with small positive and negative charges residing on carbon and oxygen atoms, respectively in its molecular structure (Fig. 4). In alumina too a partial positive charge resides on aluminium, while a partial negative charge resides on oxygen. The dipole-dipole attraction between alumina and eosin Y is substantially large. On the other hand, there is no charge separation on the nanoparticles of copper. The dipole-dipole attraction with eosin Y is concomitantly small or altogether absent. For this reason, the fingerprints developed by alumina-based composition are clearer and sharper as compared to those detected by copper-based composition.

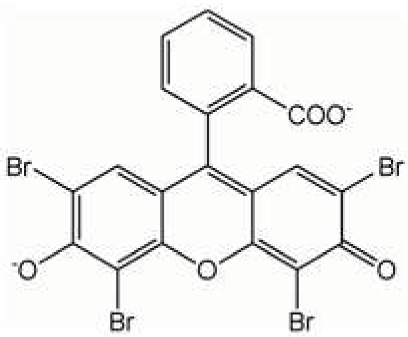

Fig. 4: Structure of eosin Y

A comparison of fingerprints developed on glass by alumina-containing formulation and copper-containing formulation supports this assertion (Fig. 5).

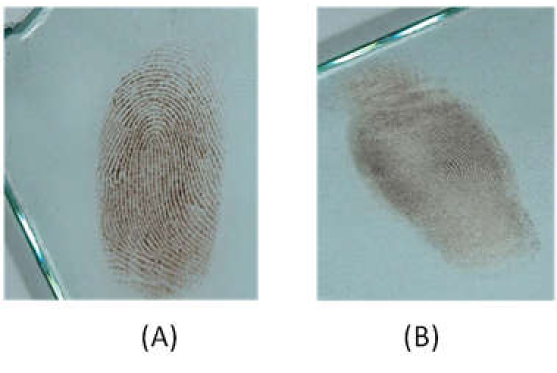

Fig. 5: Fingerprint developed on glass by (A) alumina-based composition; and (B) copper-based composition

Ninhydrin Method

Ninhydrin treatment is one of the premier techniques for development of the latent prints on porous surfaces, such as paper. Ninhydrin (Fig. 6A) reacts with amino acid content of sweat, forming a purple complex called Ruhemann purple (Fig. 6B).[13,14]

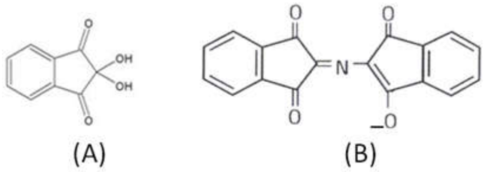

Fig. 6: Structure of (A) ninhydrin; and (B) Ruhemann purple

However, the concentration of amino acids in sweat is quite low, as a result of which the developed prints do not show sharp contrast. To improve their clarity, prints are post-treated with salts of Group 12 elements of the periodic table. This results in conversion of non-fluorescent Ruhemann purple into a photoluminescent complex. The color of ninhydrin-developed fingerprints changes to red or orange on post-treatment with zinc chloride or cadmium nitrate. Subsequent observation under an argon ion laser produces appreciable luminescence.[15] The intensity of photoluminescence increases at low temperatures (77 K).[16–18]

Ruhemann purple is an active chelating agent and forms colored coordination complexes with variety of metals.[19] Spectroscopic studies, coupled with X-ray diffraction analysis, have revealed that such complexes contain metal ion and Ruhemann purple in the stoichiometric ratio of 1:1.[20] Further, models for structural and photophysical features have been developed to establish guidelines for the formation of fluorescent metal-Ruhemann purple complexes.[21] Treatment with methylthioninhydrin, followed by reaction with zinc (II) ions, produces more intense fluorescence than that obtained by using ninhydrin alone. Likewise, several ninhydrin analogs, including 5-methoxyninhydrin, 5-ethoxyninhydrin, 5-(4-nitrophenyl)ninhydrin and benzo (f) furoninhydrin give optimum results after the latent prints have been post-treated with zinc (II) salts.[22–26]

Vacuum Metal Deposition Method

Vacuum metal deposition, a technique largely used for development of latent fingerprints on non-porous surfaces like plastics and polythene, involves successive deposition of gold and zinc under low pressure.[27] Normally, zinc deposits uniformly throughout the surface, except where fingerprints are impinged. This results in development of 'negative prints' in which ridges remain transparent while the background is plated with the metallic zinc.[28]

Vacuum metal deposition is an extremely sensitive technique for old prints, as well as for prints exposed to adverse environmental conditions.[29] Beside the gold-zinc mixture, a number of other metals may also be used in this technique. For example, a mixture of zinc (73%), antimony (21.5%) and copper (5.5%) gives optimum results even up to a temperature of 1540 degree Celsius. On polythene items, a slower rate of evaporation of metal(s) favors effective deposition and development.[30,31] In case excess gold gets deposited, the coating of zinc is hindered. The quality of developed prints is influenced by the type of polymer surface, as well as by the age of the donor.[32] Vacuum metal deposition detects 11% more fingerprints than DFO on paper samples less than 21 days old.[33]

Small Particle Reagent Method

An aqueous suspension of an insoluble, powdered metal salt in a surfactant may be used to develop latent fingerprints on wet surfaces. It fixes the lipid content of the fingerprint residue. Conventional small particle reagent formulation is a suspension of dark grey molybdenum disulfide in Molibond detergent.[2] Small particle suspension of black iron oxide (Fe_3O_4) powder gives prints with good contrast on smooth surfaces.[34] Zinc carbonate-based formulation is used for developing prints on dark and wet surfaces.[35]

A fluorescent small particle reagent may be prepared by adding Basic Yellow 40 dye to the stock solution of conventional small particle reagent. The developed prints may then be visualized at 450 nm.[36] Another novel formulation containing a natural surface active reagent instead of a conventional detergent has been found to be effective.[37] A combination of basic zinc carbonate with eosin B dye gives a small particle reagent[38] that can detect fingerprints on aluminium foils that have remained suspended in water for up to 7 hours (Fig. 7).

Fig. 7: Fingerprint developed by small particle reagent method on aluminium foil after it had remain suspended in water for 7 hours

Cyanoacrylate fuming is a good alternative to small particle reagent, but it works well only on dry surfaces.[39] On the other hand, a titanium dioxide-based formulation of small particles is known to develop white imprints on moist plastic, glass and metals.[40] The technique is also effective in detecting fingermarks on soaked firearms.[41]

Physical Developer Method

A physical developer composition normally contains a mixture of a reducible metal salt, a reducing agent and a buffer. Most formulations incorporate silver nitrate as the metal salt. It is reduced *in situ* to metallic silver which becomes adhered to the fingerprint residue.[42] When latent prints are required to be developed on paper, the alkali content of the latter must be neutralized by pre-treatment with maleic acid.[43] Prints may be intensified by hypochlorite treatment. The performance of the technique is dependent on the quality of water used for preparing the formulation.[44] A variant of physical developer, involves a modified, two-step procedure. First, the sample is treated colloidal gold and next, it is sprayed with the physical developer solution. Another variation of physical developer, the multimetal deposition, has immense potential in detecting fingermarks on surfaces like beer labels and gloves. The effectiveness of the multimetal deposition method depends on the particulate size of the solute and the pH of the stock solution.[45] A modified version of multimetal deposition has been found to be effective on number of semi-porous surfaces, such as latex gloves and wax paper.[46] A dilute physical developer solution may also be used to enhance silver nitrate developed fingerprints.[47]

Silver Nitrate Method

Silver nitrate is one of the vintage methods used for the development of latent fingerprints, and is most suited for porous surfaces like paper and wood. The reagent fixes the sodium chloride content of sweat, leading to the formation of silver chloride. The latter decomposes into finely divide silver by the action of sunlight or ultraviolet radiation. The metallic silver gets deposited on the ridges, rendering these visible.[2] A solution of silver nitrate in ethyl alcohol has been used for enhancement of faint marks developed with ninhydrin.[48] When used in conjunction with iodine-silver plate transfer technique, the reagent develops latent fingerprints on human skin.[49–52] While using the silver nitrate method, care has to be taken to avoid overdevelopment of prints. This invariably leads to background coloration.[53]

Lanthanides and Actinides

Complexes of lanthanides and actinides find applications in the detection of latent fingerprints. The rare earth metal ions form colored, fluorescent chelates with Ruhemann purple, the reaction product of ninhydrin and amino acids.[54] For example, europium chelates, produced by the reaction of the europium (III) ions with aryl-beta-diketones, are fluorescent in nature, and are of help in detection of latent fingerprints on the human cadaver skin.[55] Europium complexes also impart luminescence to prints pre-treated with cyanoacrylate.[56] Both europium (III) and terbium (III) ions, on complexation with Ruhemann purple produce luminescent derivatives.[57] Lanthanide complexes tie-up the lipid constituent of sweat. These are useful for lifting fingerprints on currency notes, as well as on conventional porous and non-porous surfaces.[58] A few europium chelates serve as fluorescent, lipid-specific, follow-up reagents after the fingerprints have been developed by ninhydrin or DFO methods.[59] Europium (III) complexes have also been used as one-step reagents for luminescent investigation of latent prints.[60] Other lanthanide derivatives too have proved useful in this context.[61]

Miscellaneous Methods

Metals also find use in some of the unconventional methods of latent print development. For example, a DC initiated metal sputtering process, involving copper, zinc, platinum and gold gives satisfactory results.[62] Metal flake powders of aluminium, zinc, copper and iron too have been used for detection of latent fingerprints.[63] Similarly, using milling procedures, aluminium, brass, copper, zinc and iron flake powders were manufactured for detecting fingermarks on light backgrounds.[64] Cadmium sulfide, commonly used as a photoluminescent semiconductor, may also be employed as a fingerprint reagent.[65,66]

Conclusion

Metals and metal salts are important ingredients of several fingerprint compositions. Such compositions have the utility of lifting latent impressions from a host of crime scene evidence, including, white, colored and multi-colored; smooth and rough; absorbent and non-absorbent; dry and wet. The metals and metal salts may serve as direct formulations or may be used in post-treatment procedures. Such formulations have been used in solid, solution or vapor phase reagent. These have improved the chances of fingerprint detection in casework investigations.

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