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Development of dry-origin latent footwear impression on non-porous and semi-porous surfaces using a 5-methylthioninhydrin and L-alanine complex

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Abstract: 5-methylthioninhydrin (5-MTN) is an amino acid sensitive reagent used for the development of latent fingermarks deposited on porous surfaces such as paper and wood. The present study demonstrates that the 5-MTN can be used as a latent footwear impression enhancement reagent, by reacting with trace multivalent metal ions, which are the main components of the latent footwear impression. 5-MTN and L-alanine complex (MTN-ALA) used for the latent footwear impression development was prepared, by mixing 4.5×10^{-3} M 5-MTN (in methanol) and 4.5×10^{-3} M L-alanine (in methanol) in 1:1 ratio, and keeping undisturbed at room temperature for 24 h. The latent footwear impressions were deposited on white and black non-porous surfaces (glass plate, polyethylene panel, polypropylene panel, acryl panel, polyvinyl chloride (PVC) panel, poly(methyl methacrylate) (PMMA) panel, acrylonitrile-butadiene-styrene (ABS) panel, tile), and a semi-porous surfaces (painted wood). The latent footwear impressions on these surfaces were treated with MTN-ALA complex by spraying. The fluorescence of footwear impressions (occurred due to the reaction between MTN-ALA and metal complexes) was observed under a 505 nm forensic light source and an orange barrier filter. The enhancement of latent footwear impression was achieved from black surfaces without any blurring. However, the fluorescence (enhancement) of footwear impression was not observed on the white PVC, PMMA, and ABS surfaces, because the incident light interfered and reflected on the surface. The sensitivity of MTN-ALA was superior to 2,2'-dipyridil, which is a representative non-fluorescing footwear impression enhancement reagent, and similar to 8-hydroxyquinoline, which is a representative fluorescing footwear impression enhancement reagent.

Key words: footwear impression, 5-methylthioninhydrin, enhancement, fluorescence, trace metal

1. Introduction

Footwear impressions found at a crime scene constitute important physical evidence that can link the criminal and the crime. By comparing the footwear impressions found at a crime scene with the impression of a suspect's footwear, law enforcement agencies can link the suspect and the crime scene.[1] However, most impressions found at crime scenes are latent footwear impressions invisible to the naked eye. Therefore, forensic scientists have developed optical, physical, and chemical methods to develop or enhance

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such latent impressions.[2-11] Of such detection methods, the chemical methods became important in criminal investigations because they not only develop but also enhance latent footwear impressions.[1]

Footwear impressions can be left on surfaces with various colors as well as single colors. In this case, some chemical methods cannot provide clear footwear impression images unless a strong color contrast exists between the developed image and background surface. Therefore, forensic scientists have studied techniques to obtain fluorescent images of footwear impression. Representative examples of the procedures established in such studies involve activating an impression with a gelatin lifter and post-treating it with 1,8-diazafluoren-9-one (DFO),[12] or lifting an impression with a white gelatin lifter and treating it with Safranine O[13]. However, such procedures are indirect, cumbersome methods. Additionally, use of a gelatin lifter is too cost-intensive for application to all footwear impressions found at crime scenes. Another method for obtaining fluorescent images is pre-treatment with 8-hydroxyquinoline followed by illumination with ultraviolet (UV).[14] However, since 8-hydroxyquinoline has to be used in the form of an acetone solution, this method cannot be applied to footwear impressions left on synthetic polymer materials or acetone-soluble paints. Moreover, exposure to UV can cause damage to the eyes and skin, and its use at a crime scene should be limited because UV rays can destroy DNA evidence.[15,16] 5-methylthioninhydrin (5-MTN) is a reagent widely used for developing latent fingermarks on a porous surface such as paper[17] because it forms colored complexes with amino acids found in fingermarks.[18] Moreover, addition of trace amounts of multivalent cations to this complex results in the formation of a fluorescent amino acid-5-MTN metal complex responsive to 505 nm light. Thus further enhancement of fingermarks without it is effected by background colors.[19]

It has been reported that if ammunition is fired with fingermarks on it, accelerated corrosion occurs in the part of the cartridge casing where fingermarks are deposited,[20] resulting in increased concentration of free metal ions along the ridge detail. Hong *et al*.[21] demonstrated that color change of ridge detail can be induced by spraying an pre-mixed L-alanine-5-MTN complex (MTN-ALA) solution onto the surface of the fired cartridge casing, because the MTN-ALA reacts with the free metal ions present along the ridge detail. However, they failed to observe the fingermark fluorescence due to the quenching effect of brass, the main component of the cartridge casing.[21]

Soil is the main component of a footwear impression. Soils are made up of various metal oxides or salts containing metal cations.[22,23] Therefore, the authors hypothesized that a fluorescent MTN-ALA-metal complex (excited under 505 nm light source) would be formed on spraying a MTN-ALA solution on a footwear impression.

2. Materials and Methods

2.1. Reagents and materials

The MTN-ALA solution was prepared as follows: 0.10 g of 5-MTN (BVDA, Netherlands) was dissolved in 100 mL methanol; 0.04 g L-alanine (Merck, Germany) was dissolved in the 5-MTN solution, and the resulting mixture was conditioned for 24 h at room temperature. The MTN-ALA solution was directly sprayed onto a footwear impression and observed under a 505 nm forensic light source and a orange filter.[19] The authors used only fresh reagents, not older than one week. A 2,2'-dipyridyl solution was prepared by dissolving 4 g of 2,2'-bipyridine (Junsei, Japan) in 100 mL of ethanol and adding 1 g of ascorbic acid (Sigma-Aldrich, USA) and 3 mL of concentrated HCl to the mixture. The reagent prepared was directly sprayed onto a footwear impression and the development of footwear impression was observed under white forensic light source.[25] A 8-hydroxyquinoline solution was prepared by dissolving 0.5 g of 8-hydroxyquinoline (Junsei, Japan) in 90 mL of acetone and adding 10 mL of deionized water to it. It was directly sprayed onto a footwear impression, which was then observed under 254 nm UV light source.[14]

An object reflecting all light appears white and an object absorbing all light appears black. Therefore, if a footwear impression deposited on a black or white surface becomes fluorescent, it would be possible to obtain fluorescene on any surface irrespective of its color. Therefore, we selected non-porous and semi-porous black and white surfaces as target surfaces. As non-porous surfaces, we used glass; panels of polyethylene, polypropylene, acrylic resin, polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA), and acrylonitrile-butadiene-styrene (ABS); and a commercially available tile. We analyzed the components of each polymer material prior to examination using a FTIR (Fourier transform infrared) spectrometer. Additionally, we prepared semi-porous surfaces by painting a wooden panel with a lacquer paint.

2.2. Equipment

Polilight Flare Plus 2 (Rofin, Australia) was used as the 505 nm light source. Thermo Nicolet iN10 FTIR was used for collecting infrared spectra. Footwear impressions were photographed with a Nikon D80 camera.

2.3. Preparation of footwear impressions

A subject walked freely back and forth along an indoor concrete floor for 10 min with shoes on and then stepped on both feet on specimen surfaces to make footwear impressions. *Fig.* 1 shows images of footwear impressions left on black or white surfaces. The images were taken under white light from various angles to obtain an optimal image. Footwear

Table 1. Evaluation criteria for the grading of footwear impression

Score	Level
-	No development
+	Brief development
++	Visible development
+++	Very clear development

impressions treated with the mentioned reagents were compared with these photographs to determine the enhancement efficiency of the respective substances.

2.4. Assessment of the developed footwear impressions

The enhancement level of footwear impressions was assessed according to the criteria shown in the *Table* 1.[10]

3. Results and Discussion

3.1. Treating footwear impressions on different surfaces with MTN-ALA

Fig. 2 shows footwear impressions on white or black surfaces and enhanced with MTN-ALA, photographed under a 505 nm light source and orange filter. As can be seen in the images, footwear impressions on the black surfaces were all fluorescence-enhanced, although the enhancement efficiency is relatively lower on white PVC, PMMA, and ABS than on other surfaces.

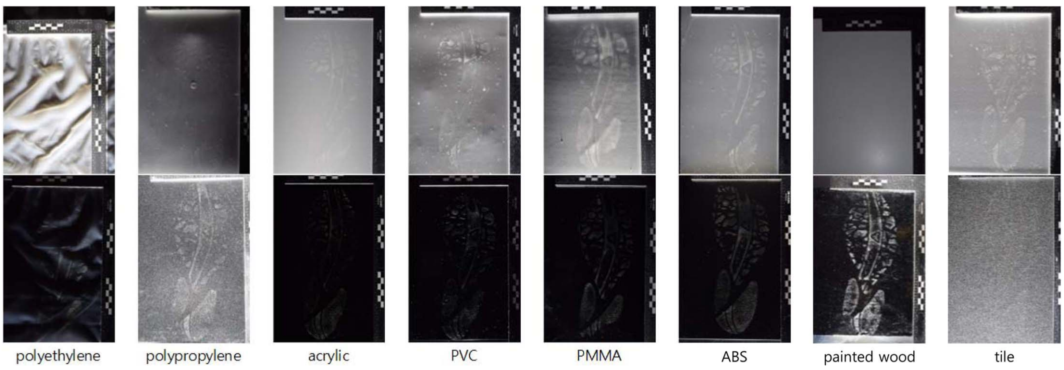

Fig. 1. Images of reference footwear impressions used for comparing the efficiency of footwear impression enhancement reagents. The photographs were taken under the white oblique light source. The top row depicts the enhancement results observed on the white surfaces and the bottom row depicts the enhancement results observed on the black surfaces.

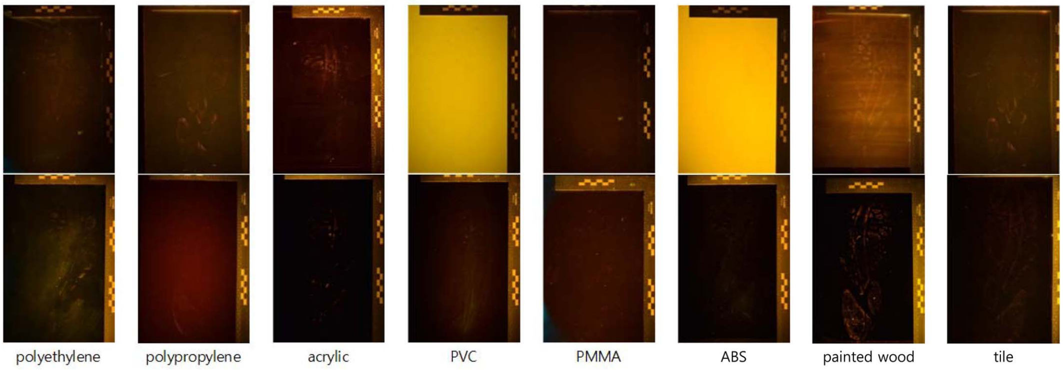

Fig. 2. Images of latent footwear impressions enhanced with MTN-ALA. The surfaces were illuminated with 505 nm forensic light source and photographed using an orange barrier filter. The top row depicts the enhancement results observed on the white surfaces and the bottom row depicts the enhancement results observed on the black surfaces.

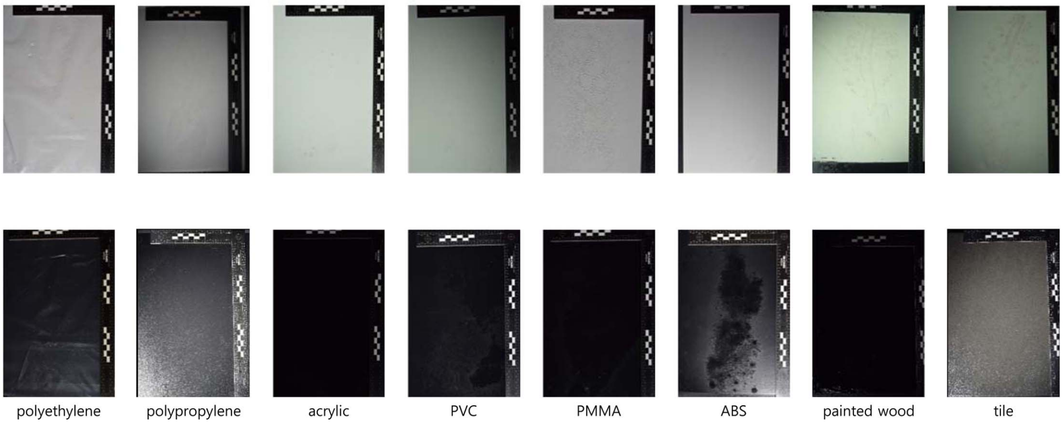

Fig. 3. Images of latent footwear impressions enhanced with 2,2'-dipyridyl. The photographs were taken under the white light. The top row depicts the enhancement results observed on the white surfaces and the bottom row depicts the enhancement results observed on the black surfaces.

Likewise, in case of the white surfaces, it can be seen that the PVC, PMMA and ABS surfaces do not exhibit fluorescence. This phenomenon is attributable to the weak contrast between the surface and footwear impression fluorescence because of the excessive background fluorescence of these surfaces. Enlarged photographs revealed no blurring of footwear impression by the enhancing reagents. Images on the glass panel were excluded because enhancement was not observed in those cases.

3.2. Treating footwear impressions on different surfaces with 2,2'-dipyridyl

2,2'-dipyridyl is not a fluorescent enhancement reagent but widely used for enhancing footwear impressions.[3] Therefore, efficiency of enhancement of footwear impressions treated with MTN-ALA was compared with 2,2'-dipyridyl treatment. *Fig.* 3 shows images of footwear impressions on white surfaces treated with 2,2'-dipyridyl. Impressions on white polypropylene, paint, and tile surfaces appeared red, whereas those on the remaining white surfaces revealed no enhan- cement. Treatment of footwear impressions on black surfaces with 2,2'-dipyridyl resulted in weakening of contrasts comparing to the images enhanced with photographing. Pictures of the images on the glass panel were excluded because enhancement was not observed in such cases.

3.3. Treating footwear impressions on different surfaces with 8-hydroxyquinoline

As mentioned in the introduction section, the 8-hydroxyquinoline is a reagent that reacts with footwear impressions on porous surfaces and produces fluorescenece.[14] On the contrast, the surfaces used in this experiment are non-porous or semi-porous materials. Since no known reagent or technique induces fluorescence of footwear impressions on such surfaces, the fluorescence efficiency of MTN-ALA by reacting with footwear impressions could not be compared with known fluorescence reagent. Therefore, the fluorescence induced by MTN-ALA was compared with the fluorescene induced by 8-hydroxyquinoline.

Fig. 4 presents footwear impressions on black or white surfaces treated with the 8-hydroxyquinoline solution and viewed under a 254 nm UV light source. While fluorescence could be obtained from all footwear impressions on black surfaces, no fluorescence could be obtained from white polypropylene, PVC, and ABS surfaces. This phenomenon is caused by interference of UV light reflected from the background. In the case of the painted surface, fluorescence was observed, but the footwear impression was damaged by the acetone used as solvent. Blurring was observed for the impression on the tile surface. This is due to the fact that 8-hydroxyquinoline is not appropriate for use on non-porous surfaces. No problems other than blurring were encountered when comparing the enhancement efficiency of 8-hydroxyquinoline with that of MTN-ALA. The enhancement results on glass panel were not shown in the *Fig.* 4 because enhancement was not observed.

3.4. Evaluation of enhancement performance

The criteria listed in *Table* 1 were used to evaluate the performance of MTN-ALA, 2,2'-dipyridyl, and 8-hydroxyquinoline in enhancing footwear impressions on white or black surfaces. *Table* 2 outlines the evaluation results; MTN-ALA shows enhancement efficiency superior to that of 2,2'-dipyridyl and similar to that of 8-hydroxyquinoline, which is widely used for enhancing footwear impressions, via fluorescence[14], albeit with some surface-dependent differences. MTN-ALA also successfully enhanced footwear impressions on black as well as white surfaces with the exception of cases where fluorescence could not be observed due to the light reflected from the white background.

Footwear impressions are frequently found on painted or tiled surfaces at crime scenes. Because no direct enhancement reagent is known that can be used on such surfaces, indirect enhancement techniques such as lifting latent footwear impressions with a gelatin lifter or applying enhancement reagent to the gelatin lifted impressions are currently applied.[12,13] However, as mentioned in the introduction section, such techniques are cost-intensive and difficult to

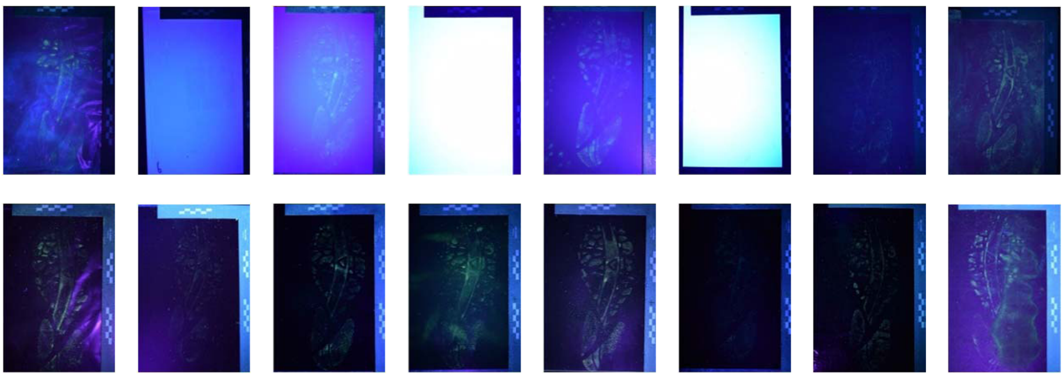

Fig. 4. Images of latent footwear impressions enhanced with 8-hydroxyquinoline. The surfaces were illuminated with 254 nm UV light source and photographed without using a filter. The top row depicts the enhancement results observed on the white surfaces and the bottom row depicts the enhancement results observed on the black surfaces.

Table 2. The enhancement grades of MTN-ALA, 2,2'-dipyridyl and 8-hydroxyquinoline treated footwear impressions

Color	Surfaces	Assessment results			
		Before treatment	MTN-ALA treatment	2,2'-dipyridyl treatment	8-hydroxyquinoline treatment
Transparent	Glass	++	–	–	–
White	Polyethylene	–	+	–	+
	Polypropylene	+	++	+	–
	Acrylic	+	++	–	++
	PVC	++	–	–	–
	PMMA	++	–	–	++
	ABS	+++	–	–	–
	painted wood	–	+++	++	+
	Tile	++	++	+	++
Black	Polyethylene	–	++	–	++
	Polypropylene	++	++	–	++
	Acrylic	++	++	–	+++
	PVC	++	+	–	++
	PMMA	++	+	–	+++
	ABS	+++	++	–	+
	painted wood	+++	+++	–	+++
	Tile	+	+++	–	+++

apply at crime scenes because they are all indirect methods. MTN-ALA is a low-cost and simple alternative for inducing fluorescence of footwear impressions on painted or tile surfaces. In addition, the 505 nm light is safer for crime scene investigators than UV light and does not damage DNA.[15,16]

4. Conclusions

An 5-methylthioninhydrin and L-alanine (MTN-ALA) complex was prepared and used to enhance footwear impressions via fluorescence. After applying this reagent by spraying on latent footwear impressions on non-porous (glass, polyethylene, polypropylene, acrylic resin, PVC, PMMA, ABS, and a tile) and semi-porous (painted wood) surfaces, we observed enhanced images under 505 nm light using an orange filter. Fluorescent images could be obtained for all impressions on black surfaces, and no blurring was observed. However, fluorescence was not observed on white PVC, polypropylene, and ABS surfaces due to intensive background reflection.

Comparison of footwear impression enhancement efficiency revealed that MTN-ALA is superior to 2,2'-dipyridyl and similar to 8-hydroxyquinoline, for such uses.

This paper reports the first demonstration of the applicability of 5-MTN-which is used to detect amino acids present in latent fingermarks on porous surfaces-to footwear impression enhancement via fluorescence by reaction with metal components present in latent footwear impressions.

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