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Comparison of embedding methods used in examining cross-sections of automotive paints with micro-Fourier transform infrared spectroscopy

Wei-Tun Chang,[1,*] Ph.D.; Tai-Hung Chen,[2] M.S.; Chi-Chung Yu,[3] M.S.; Jenn-Yu Kau,[4] Ph.D.

[1] *Department of Forensic Science, Central Police University, 56 Shu Jen Road, Taoyuan, 333, Taiwan, ROC.*
[2] *Chemistry Unit, Department of Forensic Science, Criminal Investigation Bureau, Taipei, Taiwan*
[3] *Forensic Science Center, Taipei Municipal Police Department, Taipei, Taiwan*
[4] *Lee-Ming Technology College, Taipei, Taiwan*

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ABSTRACT

Micro-fourier transform infrared spectroscopy (Micro/FTIR) combined with embedding and microtoming procedures has been commonly adopted to determine binder and pigment in the cross-sections of automotive paints. Over the past decade, various embedding media were individually used to handle small paint chips and determine multiple layers. In this current study, seven media were investigated for their potential interference with the analyses of samples by Micro/FTIR to evaluate the effectiveness of various embedding methods. Spurr's kit, methacrylate, polyester, water-emiscible, cyanoacrylate adhesive, fast epoxy adhesive, and wax media were used to embed intact paint chips that consisted of multiple layers and non-compact samples. As a result, appropriate embedding methods for paint analysis without contamination were suggested for forensic purposes. Microtomed cross-sections of 5 or 15 µm thickness were determined layerwise with Micro/FTIR in the transmission mode assisted by a stereomicroscope.

Resulting data indicate that methacrylate, polyester, and water-emiscible types of embedding systems were ineffective for most samples. Spurr's kit and cyanoacrylate embedding media interfere with parts of the samples. Both media are inadmissible on account of the "chain-of-custody" consideration in the experimental procedures. Fast epoxy adhesive and wax types are the most effective embedding media for intact samples without interference as established observed from IR spectra. While some intact samples were not interfered by Spurr's kit, cyanoacrylate and wax media, non-compact samples revealed a slight interference. All embedding methods were critically evaluated here.

Keywords: Forensic Science, Automotive Paint Analysis, Embedding Medium, Micro/FTIR

Introduction

Trace automotive paints are frequently encountered in forensic laboratories for the investigations of hit-and-run cases. The microscope in conjunction with a fourier transform infrared spectrophotometer (Micro/FTIR) has been employed for nearly two decades to detect, compare and even identify binder and pigment compositions in the trace paint samples. Most Micro/FTIR systems enable the determination of the spectra of paint samples in either the reflectance or the transmittance mode. The reflectance mode, however, is not frequently used to determine automotive paints for a number of reasons, such as poor signal-to-noise ratio, spectrum distortion, and problems of reproducibility [1]. The transmittance mode, avoiding these problems, is commonly adopted to produce high-quality spectra derived from the cross-sections of multiple automotive paints [2]. To prepare a cross-section slice (about 5 to 15 µm), the embedding method with the microtoming procedure is commonly used for a small and fragile paint. An ideal embedding medium should be free of interference when used for mounting. For forensic purposes, the appropriate embedding medium should meet the following requirements: (a) curable at room temperature without exothermic reaction and shrinking; (b) unreactive with (and not soaking into) the sample; (c) easily microtomed [3]. In the past decade, various embedding media including wax [4], acrylic type [5], epoxy type [6], polyester type [7], water-soluble type [2] and cyanoacrylate [8] were individually used to handle small paint chips for the determination of multiple layers.

* Corresponding author, e-mail:una030@sun4.cpu.edu.tw

This work compared seven embedding media for their potential interference with samples during analyses by Micro/FTIR to evaluate the effectiveness of embedding methods. Intact and non-compact original and refinish automotive paints containing multiple layers were considered in this study based on the practical consideration for questioned samples. The appropriate embedding protocols used for paint analysis without contamination are discussed.

Experimental

Embedding media and paints

Five embedding media, including the low viscosity embedding kit (spurr's kit, Cat. No:14300), methacrylate embedding medium (Cat. No: 14520), the polyester embedding kit (Cat. No: 14650), the GMA/PEG embedding kit (water-emiscible type, Cat. No: 14250), and wax embedding medium (Cat. No: 19312) were purchased from Electron Microscope Science company (Ft. Washington, Pennsylvania). The cyanoacrylate adhesive was obtained from Yi Shin Lung LTD (Keelong, Taiwan) and the fast (5 min) hardening epoxy adhesive was purchased from Nan Pao Resins Chemical Co., LTD (Tainan, Taiwan). Six intact paints (three original and three refinish paint chips) currently used on modern automotives were provided by automotive repair shops. Non-compact samples were scraped from the outer surface of each intact paint chip with the # 11 surgical blade. Carbon was coated with the SPI-Module (Carbon Coater (Division of STRUCTURE PROBE inc. USA) on the surface of the clearcoat prior to the embedding procedure to determine easily the colorless clearcoat. Intact and smear samples were mounted with seven embedding media according to the instructions in the manuals in silicone rubber molds or polyethylene tubes consisting of caps.

Microtoming procedures

A MEDIM DDM-P500-OM microtome equipped with a freezing system was employed to microtome the sample. Samples embedded with wax must be microtomed in a freezing environment (-10˚C to enhance the hardness. The embedded mold was microtomed with a tungsten carbide blade in slices of 5 or 15 μm.

Infrared analysis

The microtomed slices and not embedded slices, which were sampled with the # 11 surgical blade, were pelleted using two KBr crystals just as in the sandwich-mode structure. A Jasco Micro/FTIR system equipped with a mercury cadmium telluride (MCT) detector was operated in the transmission mode to investigate the cross-sections layerwise and thereby evaluate the distribution of interference. The analysis area of the IR aperture shown in Fig. 1 was approximately 30 × 30 or 15 × 60 μm depending on the thickness of the layer. The spectra were collected by the sum of 200 scans from 650 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

Results and Discussion

Comparison of embedding effectiveness

This work primarily seeks to observe interference deriving from the embedding procedure for trace automotive paints. Paints dissolved by solvent in the embedding medium or the infiltration due to shrinkage stress were the underlying causes of interference. Resulting data shown in Tables 1 and Table 2 via comparing the IR spectra of embedding media and layers in intact paints reveal the following characteristics:

1. Methacrylate type embedding medium is found to interfere seriously with all layers in multiple intact samples of original and refinish paints. This medium consists of a mixture of n-butyl and methyl methacrylate with benzol peroxide as the catalyst. The paint chip was placed into a cover-tube and filled with embedding mixture to prevent the reactant from evaporating. After the cap of the tube was closed, polymerization occurred over night at 65˚C. The extended period of immersion in the embedding mixture and the large shrinkage during polymerization cause the binder and pigment to significantly dissolve. The example spectra shown in Fig. 2 indicate that absorption bands of topcoat, surfacer and primer layers in # White refinish paint completely change to the patterns similar to that of the methacrylate embedding medium.

2. The interference phenomenon described as Fig. 2 is also observed with the polyester embedding medium when it is used to mount intact paints. This medium consists of monomeric styrene, n-butyl methacrylate and benzoyl peroxide. Polymerization is achieved in an oven

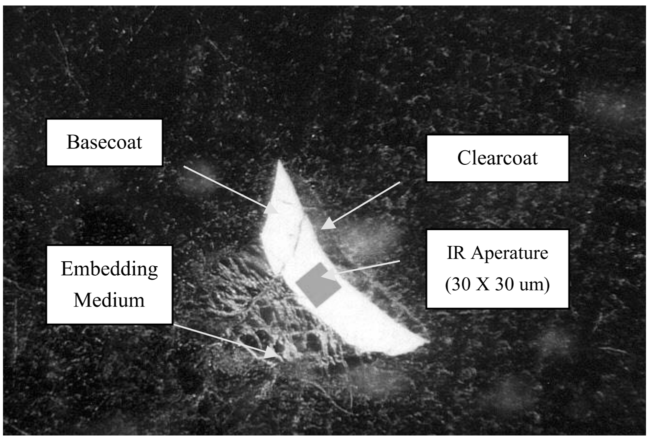

Fig. 1 The cross-section structure of the paint slice under the Micro/FTIR observation.

at 60˚C for 24 hours in a sealed tube. Two factors including the immersion time and the approximate 17% shrinkage by polymerization promote serious contamination. The spectra of the clearcoat, basecoat and surfacer in #Black original paint displayed in Fig. 3 indicate that the infiltration of the styrene monomer and the shrinkage are the fundamental causes of interference.

3. The water-emiscible embedding medium is the modified glycol methacrylate (GMA) mixture consisting of GMA, n-butyl methamacrylate, ethylene dimethacrylate, polyethlene glycol (PEG) and benzoyl peroxide. Polymerization occurs in an oven at 60˚C for 24 hours in a sealed tube. Although the water-emiscible embedding media are ideal for the preparation of tissues for cytochemical studies [9], the serious interference appears in the same way as with methacrylate and polyester media in paint embedding. Clearly, these three media can not be used as embedding media.

4. Spurr's kit and cyanoacrylate embedding media can interfere with only some of the intact samples. This Spurr's kit is a low viscosity embedding medium, which including vinyl cyclohexene, diglycidyl ether polypropylene glycol, nonenyl succinic anhydride and dimethylamino ethanol. Curing takes 24 hours at 60˚C. Fig. 4

Table 1 Comparisons of results in embedding intact original paints [a].

Layers	Clearcoat of # Black	Basecoat of # Black	Surfacer of # Black	Clearcoat of # Silver	Basecoat of # Silver	Surfacer of # Silver	Topcoat of # Blue[b]	Surfacer of # Blue[b]
Binder Composition	Acrylic-melamine	Acrylic-alkyd-melamine	Epoxy	Acrylic-melamine	Acrylic-alkyd-melamine	Epoxy	Acrylic-melamine	Alkyd-melamine
Embedding Media								
Methacrylate	++	++	++	++	++	++	++	++
Water-soluble	++	++	++	++	++	++	++	++
Polyester	++	++	++	++	++	++	++	++
Spurr's Kit	-	-	-	+	-	+	+	-
Cyanoacrylate	-	-	-	-	-	-	+	+
Fast Adhesive	-	-	-	-	-	-	-	-
Wax	-	-	-	-	-	-	-	-

[a] The "++" mark indicates serious interference, the "+" mark indicates slight interference and the "-" mark indicates no interference with embedding media.
[b] # Blue is the solid paint having no clearcoat layer.

Table 2 Comparisons of results in embedding intact refinish paints [a].

Layers	Clearcoat of # Brown	Basecoat of # Brown	Clearcoat of # Purple	Basecoat of # Purple	Topcoat of # Whiteb	Surfacer of # White[b]	Primer of # White[b]
Binder Composition	Acrylic-urethane	Acrylic-urethane	Acrylic-urethane	Acrylic-alkyd-melamine	Acrylic-urethane	Alkyd-melamine	Epoxy
Embedding Media							
Methacrylate	++	++	++	++	++	++	++
Water-soluble	++	++	++	++	++	++	++
Polyester	++	++	++	++	++	++	++
Spurr's Kit	+	-	-	-	+	-	-
Cyanoacrylate	+	-	-	-	+	-	-
Fast Adhesive	-	-	-	-	-	-	-
Wax	-	-	-	-	-	-	-

[a] The "++" mark indicates serious interference, the "+" mark indicates slight interference and the "-" mark indicates no interference with embedding media.
[b] # white is the solid paint having no clearcoat.

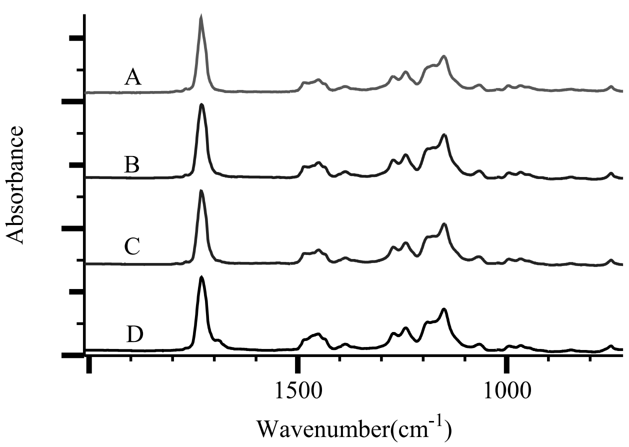

Fig. 2 Absorption bands of layers in # White refinish paint when they were embedded with methacrylate media appear the similar patterns as that of the methacrylate embedding medium. (A) methacrylate embedding medium, (B) topcoat with serious interference, (C) surfacer with serious interference and (D) primer with serious interference.

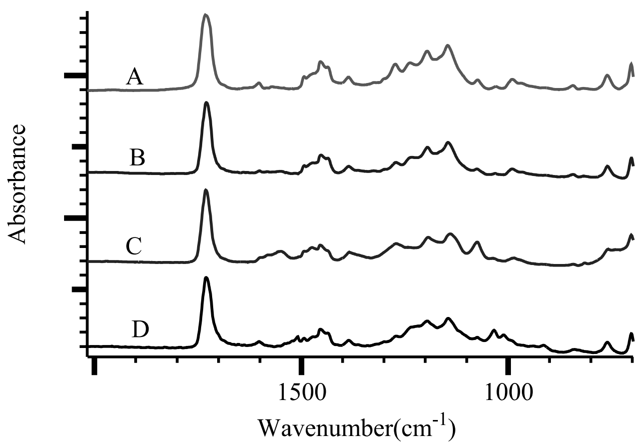

Fig. 3 Absorption bands of layers in #Black original paint when they were embedded with polyester medium appear the similar patterns as that of the polyester embedding medium. (A) polyester embedding medium, (B) clearcoat with serious interference, (C) basecoat with serious interference, and (D) surfacer with serious interference.

reveals that the interference on the outer part of the clearcoat of # silver is greater than that in the interior part. Similarly, polymerization of the cyanoacrylate embedding medium is achieved at room temperature over 72 hours. Compared to spectra in Fig.6 and Fig. 7, the spectra shown in Fig. 5 indicate that cyanoacrylate medium interferes with the topcoat of # White but not with the surfacer and primer layers. These two embedding methods result in partial interference due to either the high curing temperature or a long curing time. According to the critical requirement for "chain-of-custody", these two methods can not be used in forensic paint analysis.

5. Fast epoxy adhesive and wax appear to be the most effective media for mounting all intact samples without causing interference. The fast epoxy adhesive is composed of two parts, binder and hardener pastes. The curing time of this fast epoxy adhesive is only 5 minutes following premixing of the binder and hardener at room temperature. This embedding medium does not interfere with the paints because of its short curing time. Compared to those in Fig. 2 and Fig. 7, the spectra shown in Fig. 6 indicate that the absorption bands of layers of # White refinish paint do not correspond to that of the fast adhesive embedding medium and are consistent with those of layers of # White in Fig. 7. This result indicates that fast adhesive medium is free of interference on the paint sample. Wax medium without solvent component was melted at 70˚C for 5 minutes prior to the embedding procedure. The paint chip was consequently immersed into the melted wax in the oven. By the way of the fast cooling and hardening after moving out the oven under room temperature, the intact paint sample may not be interfered by the embedding medium. Compared to Fig. 2 and Fig. 6, the IR spectra of layers of #White refinish paint in Fig. 7 are consistent with those in Fig. 6. It indicates that without spectrum interference wax assisted with the freezing system is an appropriate embedding medium for intact paints.

Infiltration problem on non-compact samples

A non-compact paint sample is one in which the

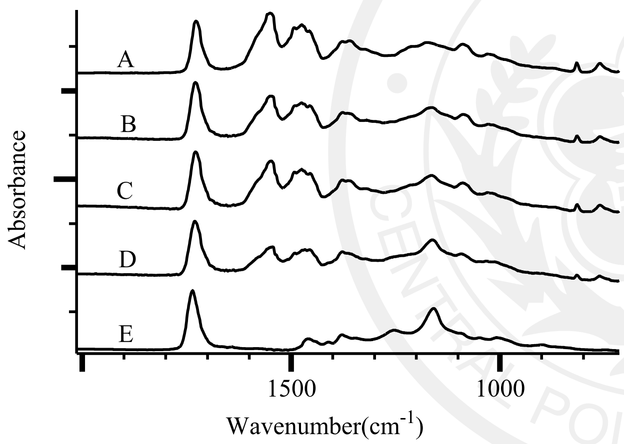

Fig. 4 Interfered absorption bands along with the cross-section from interior to outer in clearcoat of # silver. (A) clearcoat without embedding, (B) 50 (m, (C) 30 (m, (D) 10 (m, and (E) Spurr's kit embedding medium.

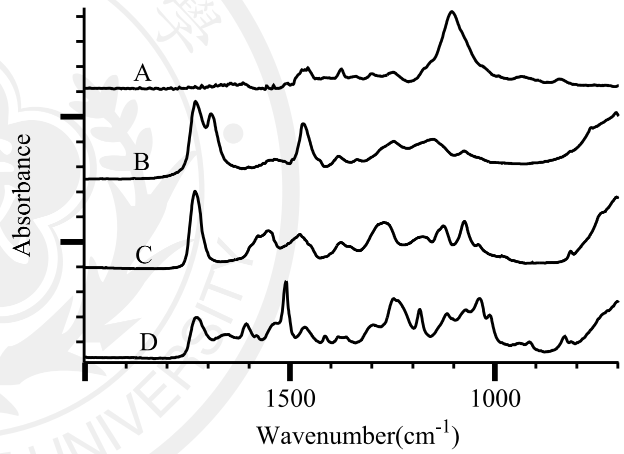

Fig. 6 Absorption bands of layers along with the cross-section of # White refinish paint when they were embedded with fast epoxy adhesive medium. (A) fast epoxy adhesive embedding medium, (B) clearcoat without interference, (C) surfacer without interference, (D) primer without interference.

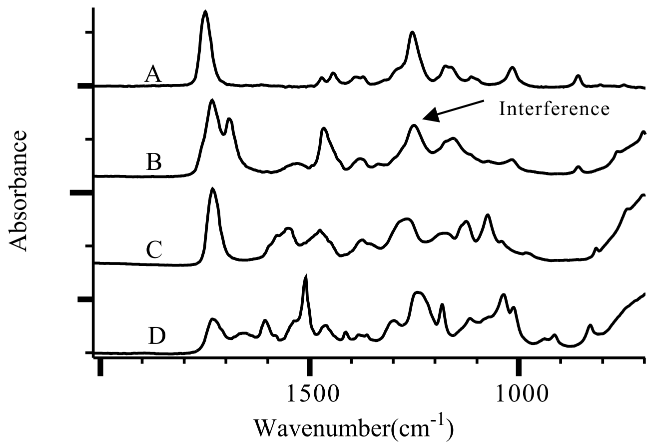

Fig. 5 Absorption bands of layers along with the cross-section of # White refinish paint when they were embedded with cyanoacrylate medium. (A) cyanoacrylate embedding medium, (B) clearcoat with slight interference, (C) surfacer without interference, (D) primer without interference.

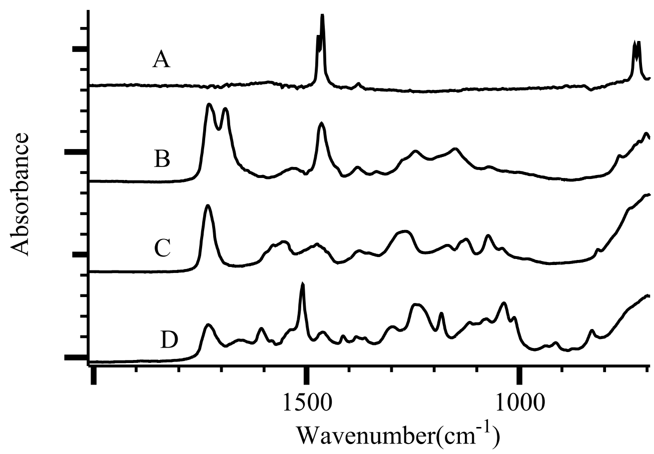

Fig. 7 Absorption bands of layers along with the cross-section of # White refinish paint when they were embedded with wax media. (A) wax embedding media, (B) clearcoat without interference, (C) surfacer without interference, (D) primer without interference.

impact of an intact paint film by an external force results in damage of the network structure. This kind of sample is frequently encountered in the forensic laboratory. The embedding results derived from various embedding media for intact and non-compact samples were further evaluated to investigate whether they exhibit same interference phenomenon. Spurr's kit, cyanoacrylate, and wax were found the slight interference derived from embedding the non-compact sample in clearcoat of # Purple refinish paint. These media, however, did not generate interference when the intact samples were embedded as shown in Table 1 and Table 2. The infiltration problem may be the underlying cause of this interference phenomenon. Fig. 8 shows that absorption bands of clearcoat were slightly interfered by the embedding medium spectrum when cyanoacrylate medium was used as the embedding material for the non-compact clearcoat of # Purple refinish paint. However, fast epoxy adhesive still performs excellently without interference when embedding the non-compact clearcoat of # Purple paint.

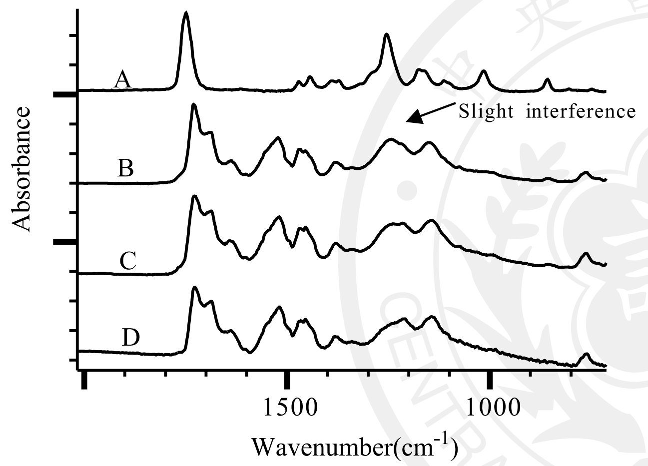

Fig. 8 Absorption bands of non-compact and intact clearcoats of # Purple refinish paint when they were embedded with cyanoacrylate medium. (A) cyanoacrylate embedding medium, (B) non-compact sample with slight interference, (C) intact sample without interference, (D) clearcoat without embedding.

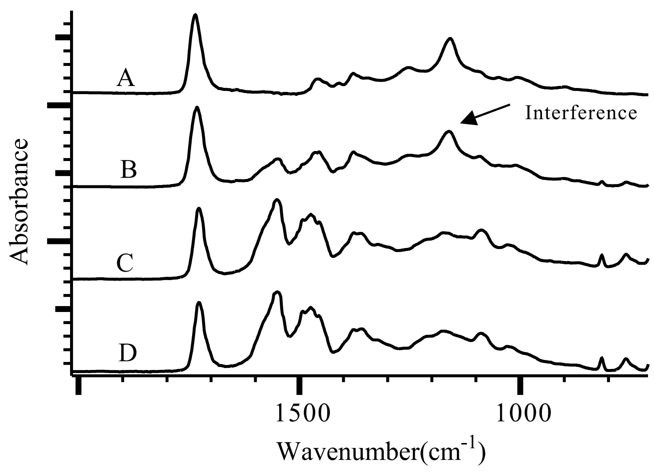

Fig. 9 Absorption bands of clearcoat of # silver original paint when using different embedding procedure. (A) Spurr's kit embedding medium, (B) when embedding with Spurr's kit- with interference, (C) when coating with fast epoxy adhesive prior to the embedding with Spurr's kit-without interference, (D) clearcoat without embedding.

Prevention of interference

The handling and identifying of the trace paint chip required by the experimental procedure often challenges the examiner of the paint analysis. Polyethylene film, silicone sealant and fast epoxy adhesive were used to evaluate the protection effectiveness prior to the embedding step to protect the trace sample from interference as critically required in forensic paint analysis. The protection films were coated on the surface of the paint sample, and then the coated sample was mounted with embedding media. Compared to the spectra in Fig. 4, Fig. 9 shows that the clearcoat of # Silver original paint was not interfered by Spurr's kit when fast epoxy adhesive was used as the protection film. This finding not only verifies that fast epoxy adhesive medium is excellent for embedding but also indicates that Spurr's kit interferes with automotive paints. Polyethylene film and silicone sealant, however, can not reduce interference problem.

Conclusions

The interference problem should be considered when embedding media are used to embed automotive paint. Methacrylate, polyester and water-emiscible type media exhibit very serious interference in both original and refinish automotive paints due to the long curing period at high temperatures. Spurr's kit and cyanoacrylate embedding media interfere with some samples regardless of whether the paints are intact or non-compact. Neither medium is admissible based on the "chain-of-custody" requirement in the experimental procedures. Fast epoxy adhesive is the most appropriate medium for intact and non-compact paints due to its shorter curing time at room temperature. This medium not only can be solely used for embedding but also can be used as the protection film in conjunction with other embedding media. While wax may be an excellent medium for intact samples when used with freezing condition, the non-compact samples may be interfered in the embedding procedure. The embedding media may more easily interfere with non-compact samples than intact samples resulting from infiltration in the damaged part of the network structure. To select the most appropriate embedding medium, the various paints, which contain different binders used in automobiles and buildings, should be extensively evaluated for the forensic purpose.

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