

CASE REPORT

Yun-Seng Giang,¹ Ph.D.; Sheng-Meng Wang,¹ Ph.D.; Li-Ling Cho,¹ Ph.D.; Chao-Kai Yang,¹ B.S.; and Chen-Ching Lu,¹ B.S.

Identification of Tiny and Thin Smears of Automotive Paint Following a Traffic Accident

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ABSTRACT: Three complementary methods in the order of stereomicroscopy, micro-FT-IR spectroscopy and solubility tests were used for the purpose of matching known and questioned paint samples in an auto accident case. Grayish green paint smears scattered on a silvery gray coated plastic bar were taken from a blue car and referred to as questioned samples. Green paint chips were collected as known samples from a green car. These were analyzed to determine whether the paint smears found in the blue car could have been the transfers from the green car. Although each of the three methods, when used alone, suffered from unequal bases for making comparison (i.e., layering whole paint vs. smeared paint), insufficient specificity of methodology and the interfering background coating beneath the smeared paint, the limitations were significantly relieved when three methods were used in combination. Based on the results presented in this report, the questioned grayish green paint smears collected from the blue car and the known green paint chips from the green car are of the same class of paint; that is, the possibility of the above stated paint transfers cannot be eliminated.

KEYWORDS: forensic science, forensic paint examination, smeared automotive paint, stereomicroscopy, micro-infrared spectroscopy, solubility test, attenuated total reflectance

The analysis and comparison of automotive paint evidence is undoubtedly an important forensic concern. However, the complexity of modern paint chemistry and automotive finishes, together with the chemical inertness of many paints, tends to frustrate the forensic scientist, resulting in problems in deriving maximum information from paint evidence (1,2). Moreover, forensic paint samples are typically analyzed in limited amounts that preclude the application of standard paint analysis procedures or protocols. Depending on the issues under investigation, sequence of events at the scene, complexity and condition of the samples, environmental effects, and collection methods, a criminalist has often been forced to address such issues as test choice, sample preparation scheme, test sequence, and degree of sample alteration and consumption, which are efficacious to each specific case as well as the interests of all parties, to a litigation (3).

¹ Professor, associate professor, assistant professor, teaching assistant, and research assistant, respectively, Central Police University, Department of Forensic Science, Taoyuan 333, Taiwan, ROC.

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Both known and questioned paint specimens should be properly collected for a forensic paint analysis. Ideally, whole paint flakes provide the most useful questioned samples. Although fragments of films that do not represent the complete layering structure of the original finish offer fewer characteristics for comparison, they can be useful in physical fits and other examination (3). If the topcoat can be defined, then a conclusive comparison to known specimens may be possible. In contrast, smeared or abrasively transferred samples may also provide useful information, but they are generally far more difficult to analyze. Smeared transfers can exhibit pigment and vehicle mingling from paint layers or films that could preclude application of those standard analytical methods described in the forensic science textbook or laboratory manual. This paper deals with the methods used in identifying very thin and tiny suspicious paint smears collected after a traffic accident.

On the midnight of 3 September 1999 in Taoyuan (Taiwan, ROC) an autobike rider was killed when his autobike collided first with an overpassing dark-blue Honda Civic, 1.6 L and then with a light-green Mitsubishi, 1.6 L, which came out from an intersecting road. For some unknown reason, however, a dispute was raised in the later investigation regarding whether a direct crash did occur between the two cars.

A total of eleven items of physical evidence, six from the blue car and five from the green, were submitted for our examination, with Sample I-1 being the known blue paint and II-1 the known green paint, respectively. After a thorough microscopic examination of their surfaces, it was concluded that among the nine questioned samples only Samples I-2 and I-3 (i.e., two silvery-gray coated plastic bars, ca. $60 \times 4.5 \times 0.17 \text{ cm}^3$, taken from the front-right and rear-right doors, respectively, of the blue car) were worth further analysis. These two samples had smeared paint that could have been transferred from the green car. It was also found that, based on the continuous-appearance and the common characteristics of the smears, Samples I-2 and I-3 did share a common origin and were virtually of the same evidential value. Thus, the present report emphasizes the comparative examination of the questioned Sample I-2 and the known Samples I-1 and II-1, with Sample I-2 being associated with the questioned paint smears that were tightly adhered to the underlying and interfering silvery gray coating.

Methods of Identification

The primary objective of this examination is to determine whether Sample II-1 and the paint smears on Sample I-2 (designated

as “Smears I-2”) could have originated from a common source, i.e., the green car. The strategy of analysis was to search for significant differences between Samples I-1 and II-1 (or between I-1 and I-2) and between Smears I-2 and their background coating, while verifying the absence of significant differences between Smears I-2 and Sample II-1. The likelihood of common origin is a function of a number of factors including the type or number, or both, of matching features, the type of components in the paint film, the presence or absence of studies quantifying the uniqueness of these components, and the discriminating power of the methods used (3). Unfortunately, for the following three reasons we had to preclude the use of such methods as microspectrophotometry (or surface colorimetry) (4), pyrolysis GC (5), pyrolysis GC-MS (6), high performance thin-layer chromatography (HPTLC) (7), and scanning electron microscope/energy dispersive X-ray analysis (SEM/EDX) (3,8,9), which had long been established as useful in our laboratory: a) the extremely limited size and thickness along with the uneven thickness and inhomogeneous microstructure of the paint smears; b) the unfeasibility of effectively separating the smears from the interfering background coating; and c) the inherent unequal bases on which the comparative analysis would be made (i.e., Samples I-1 and II-1 were both 5-layered whole paint whereas Smears I-2 showed no layering structure of its original finish). As a matter of fact, we did perform a simple SEM/EDX analysis. However, the above stated limitations made the semi-quantitative composition data far from acceptable with regard to accuracy and precision, which in turn made the comparison between different sample forms in this particular case meaningless. Consequently, our actual analysis was started with the simplest nondestructive microscopic exam-

ination followed by nondestructive infrared spectroscopy [10–13], and ended with destructive solubility tests [7].

The microscopic examination of physical features was carried out using a Zeiss Stemi SV 11 stereomicroscope with a total magnification of 66. The lateral cross sections used for this examination were “borrowed” from those for the following absorption FT-IR tests. The infrared spectroscopy (IR) of the microtomed thin-edge sections (ca. 5- μm thickness) of the three samples was performed using a Janssen Micro-FT-IR Spectrometer operated in the transmission mode with a scanning area of $100 \times 10 \mu\text{m}^2$ at a magnification of 160, while the upper surface of Sample I-2 was also directly profiled using a Nicolet Micro-FT-IR Spectrometer operated in the attenuated total reflectance (ATR) mode with a scanning area of $900 \mu\text{m}^2$ at a magnification of 150. As for the solubility tests, two to four drops, depending on its evaporation rate, of appropriate solvents were added to the upper surface of a $0.3 \sim 0.5 \text{ cm}^2$ sample chip. The changes in appearance and color of the sample were observed under a Zeiss Stemi SV 11 stereomicroscope with a magnification of 66. A total of 13 different solvents were used in the attempt to fulfill the analytical strategy. All of the three types of examination were side-by-side comparisons.

Results and Discussion

Microscopic Examination

The upper surface and lateral cross-section characteristics of Samples I-1, I-2, and II-1 observed with and without magnification are summarized in Table 1. Based on these observations, three conclusions can be drawn: a) The thought-to-be paint smears on Sam-

TABLE 1—Observations of the appearance of samples I-1, I-2, and II-1 with and without magnification.

Sample	Observations	
	Upper Surface	Lateral Cross Section
I-1 (Known blue paint taken from blue car.)	<ol style="list-style-type: none"> 1. Macroscopically: dark blue, glossy 2. Under stereo microscope (66\times): Comprises dark blue, dark green, purple, yellow (fewer), and glittering granules 	<ol style="list-style-type: none"> 1. Under stereo microscope (66\times): Shows 3 layers in noncolor (outermost), blue, and brown, respectively 2. Under micro-FT-IR (160\times): Shows 5 layers with clearcoat being the outermost layer and basecoat the 2nd outermost
II-1 (Known green paint taken from green car.)	<ol style="list-style-type: none"> 1. Macroscopically: light green, glossy 2. Under stereo microscope (66\times): Comprises dark green, light green, purple (fewer), yellow (fewer), and glittering granules 	<ol style="list-style-type: none"> 1. Under stereo microscope (66\times): Shows 3 layers in noncolor (outermost), green, and brown, respectively 2. Under micro-FT-IR (160\times): Shows 5 layers with clearcoat being the outermost layer and basecoat the 2nd outermost
I-2 (Questioned paint smears scattered on a coated plastic bar taken from the blue car.)	<ol style="list-style-type: none"> 1. Macroscopically: Many small scratches come along with gray to grayish green thin paint smears. The only scratch/smear, denoted “Smear I-2”, that is representative enough is 3.5 cm long by 0.3 mm wide, and is in darker green than Sample II-1. 2. Under stereo microscope (66\times): The micro-texture of Smear I-2 is in general the same as that of Sample II-1 except that the former, without an intact clearcoat, has lost its gloss. As a result of a heavy crash, Smear I-2 has a thinner paint film and smaller micro-granules than Sample II-1, a whole paint, does. 3. Under stereo microscope (66\times): The silvery-gray coating of the plastic bar makes an interfering background in that the coating is also composed of micro-granules of the same kinds of color as those for Smear I-2. The only differences are that the green micro-granules of the silvery-gray coating are even finer, fewer, and darker than those of Smear I-2, whereas the purple, yellow, and glittering micro-granules of the silvery gray coating are much greater in number than their counterparts in Smear I-2. 	<ol style="list-style-type: none"> 1. Under stereo microscope (66\times): The plastic bar consists of 3 layers including the outermost silvery-gray coating. 2. Under neither stereo microscope (66\times) nor micro-FT-IR (160\times) can the smeared paint itself be visualized.

ple I-2 are really smeared paint, not any other material. Since the most representative smear (denoted "Smear I-2") appears dark green, it is reasonable to assume that this smear contains paint components mingling at least from the clearcoat and basecoat of another car; b) Smear I-2 is definitely different from Sample I-1 in color and micro-texture and is therefore exogenous, but not endogenous; c) Smear I-2 and Sample II-1 show many matching features in color and micro-texture. However, paint is usually considered as "class evidence" except where there exists a physical match of an irregular contour or any extrinsic surface markings between the evidence and exemplar samples [1]. In the present case, therefore, it is fair to say that the possibility of Smear I-2 being transferred from the green car can not be eliminated.

Infrared Spectroscopy

Although the disagreement between the original absorption data obtained via the transmission mode of Janssen Micro-FT-IR Spectrometer and the reflectance mode of Nicolet Micro-FT-IR Spectrometer has been properly corrected and correlated, the application of IR methodology to the present case inherently suffers from a logical defect; that is, the comparative analysis was based on two unequal bases—Samples I-1 and II-1 were both 5-layered whole paint whereas Smear I-2 showed no layering structure. What is worse is that the spectrum form of Smear I-2 would likely have interferences from the substrate, i.e., a microscopically similar silvery-gray coating. To properly take into account the uneven thick-

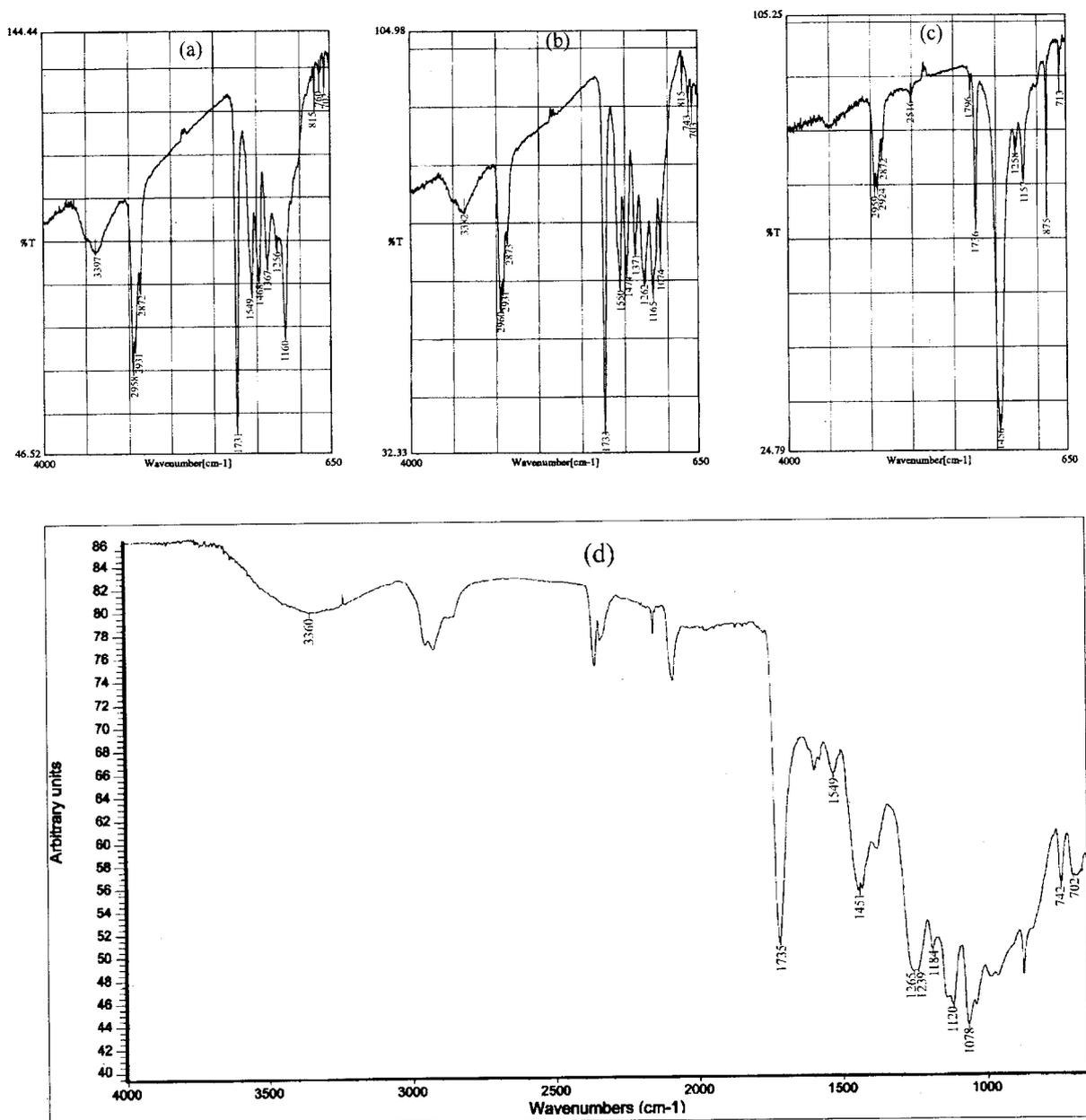


FIG. 1—*a)* The transmission-mode FT-IR spectrum of sample II-1's clearcoat; *b)* the transmission-mode FT-IR spectrum of sample II-1's basecoat; *c)* the transmission-mode FT-IR spectrum of the microtomed thin-edge section of the outermost layer of sample I-2, i.e., the silvery-gray background coating as the blank control of smear I-2; *d)* The ATR-mode FT-IR spectrum of smear I-2 incorporating the paint film itself and part of the silvery-gray background coating.

ness and inhomogeneous microstructure of the paint smear as well as its interfering background coating, the ATR approach scanned six areas (spots) in total on Sample I-2's upper surface, i.e., three were directed toward Smear I-2 itself and three toward the nearby silvery-gray coating (denoted "Blank Control I-2"). Furthermore, to make the comparison between different sample forms simple yet reasonable, we set $\pm 10 \text{ cm}^{-1}$ as the window for establishing a match of two absorption bands under comparison.

The transmission-mode FT-IR spectra of Samples I-1's and II-1's clearcoats (designated as "I-1-cle-TRA" and "II-1-cle-TRA", respectively, with the latter shown in Fig. 1a) are virtually identical. Having gone through the "automotive paint binder infrared classification flow chart" described by Bartick et al. (8), it was found that the specific path "1550 and 815 cm^{-1} (yes) \rightarrow 1510 cm^{-1} (no) \rightarrow $1280\sim 1260 \text{ cm}^{-1}$ (present, but not dominant) \rightarrow $1240\sim 1230 \text{ cm}^{-1}$ (present, but not dominant) \rightarrow $1180\sim 1160$ and $1090\sim 1080 \text{ cm}^{-1}$ (yes) \rightarrow 760 and 700 cm^{-1} (yes) \rightarrow Styrene modified Acrylic Melamine" was well matched by both Samples I-1's and II-1's clearcoats. The correctness of assigning styrene modified acrylic melamine to the binders of Samples I-1's and II-1's clearcoats was further confirmed by the visual pattern recognition between the two evidence spectra and a preexisting standard spectrum. Likewise, the transmission-mode FT-IR spectra of Samples I-1's and II-1's basecoats (denoted "I-1-bas-TRA" and "II-1-bas-TRA", respectively, with the latter shown in Fig. 1b) are virtually identical. They both fully evidence the use of alkyd melamine as the binder.

For a reflection plate made of zinc selenide, the depth that the IR-rays of various wavelengths may penetrate into such sample as paint and its like is estimated to be several submicrons to 4 microns. Since Smear I-2 did show uneven paint film thickness (looked like zero to several submicrons) and inhomogeneous microstructure under the microscope, we were at first concerned about whether the ATR-mode FT-IR scan on the three arbitrarily chosen spots on the smeared paint area would involve unequal IR-ray penetration distances in either the paint film or the silvery-gray background coating, and hence generate too different spectra. At some places of the reflection plate-sample interface where the paint film was thicker, a beam of radiation might penetrate only partial depth of the paint film before reflection occurred. At other places of the interface where the paint film was thinner or even microgranules were absent, however, a beam of radiation might penetrate across the total paint film thickness plus partial depth of the silvery-gray background coating or might penetrate directly into partial depth of the background coating. It turns out no significant differences appear among the three corresponding ATR IR spectra (all denoted "I-2-sme/blk-ATR", where "sme" stands for "smear," and "blk" stands for "blank;" shown in Fig. 1d), probably benefiting from the averaging effect of a great number of scans and total reflection processes within a specific scanned area (spot). As for the silvery-gray background coating (i.e., Blank Control I-2), the spectrum obtained via the transmission mode upon the microtomed thin-edge section of the outermost layer of Sample I-2 (I-2-*blk*-TRA, shown in Fig. 1c) shows no significant differences from those via the ATR mode upon the three arbitrarily chosen spots of the silvery-gray coated area of Sample I-2's upper surface (all denoted "I-2-*blk*-ATR"), except that the latter all have higher background absorptions especially in the fingerprint region. However, both I-2-*blk*-TRA and I-2-*blk*-ATR are significantly different from I-2-sme/blk-ATR, evidencing that Smear I-2 is exogenous, and not endogenous. Although background subtraction may not be totally reliable in the present case (unless the IR-ray penetration depth into the blank background and that into the paint-smears covered back-

ground can be adjusted to be exactly the same), a side-by-side comparison of spectrum I-2-sme/blk-ATR with the foregoing specific paths for spectrum II-1-cle-TRA to get to styrene modified acrylic melamine and spectrum II-1-bas-TRA to alkyd melamine indicated that spectrum I-2-sme/blk-ATR well matched ($\pm 10 \text{ cm}^{-1}$) the coalition of those two paths in such absorptions (cm^{-1}) as 1550 (yes); 1510 (no); $1280\sim 1260$ (dominant); $1240\sim 1230$ (present, but not dominant); $1180\sim 1160$, $1090\sim 1080$ (yes); 1120, 1070, 740, 700 (yes). Those minor unmatched absorptions (cm^{-1}) [815 ("yes" in both paths); 760, 700 ("yes" in the styrene modified acrylic melamine path) were attributed to their weak to moderate intensities in Spectrum I-2-sme/blk-ATR having been interfered with or obstructed by the overlapping absorptions stemming from the silvery-gray background coating, and thus did not alter our main conclusions. In addition to the above key characteristics, there are three absorption bands that should help discriminate between the exogenous paint Smear I-2 and the endogenous silvery-gray background coating (i.e., blank Control I-2), while bring Smear I-2 and Sample II-1 into the same class of paint. Band $3600\sim 3200 \text{ cm}^{-1}$ (weak and broad) is due to diluted hydrogen bonding and occurs consistently in Spectra I-2-sme/blk-ATR, II-1-cle-TRA and II-1-bas-TRA, but is absent from I-2-*blk*-TRA and I-2-*blk*-ATR. Band 1737 cm^{-1} originates from the carbonyl group of ester and is consistently strongest in spectra I-2-sme/blk-ATR, II-1-cle-TRA and II-1-bas-TRA, but is much weaker in I-2-*blk*-TRA and I-2-*blk*-ATR. Band $1430\sim 1460 \text{ cm}^{-1}$ is consistently moderate in spectra I-2-sme/blk-ATR, II-1-cle-TRA and II-1-bas-TRA, but is strongest in I-2-*blk*-TRA and I-2-*blk*-ATR.

Despite the fact that minor differences in the IR spectra could also be caused by varied composition of pigment, extender, and plasticizer, it is safe at this stage to conclude that Sample II-1 and the exogenous paint smears on Sample I-2 are of the same class of paint; that is, their original clearcoats are acrylic melamine while their original basecoats are alkyd melamine.

Solubility Tests

The changes in appearance and color of the samples resulting from the addition of various solvents are summarized in Table 2. Of the 13 solvents tested, methylene chloride, chloroform, and pyridine showed the same solubility behavior, Type B, to both Sample II-1 and Smear I-2, whereas showed another behavior, Type C, to Sample I-1. For the other ten solvents, no discernible differences in solubility behavior among the three paint samples were observed. It may be questioned whether some of the well-correlated results are due to the use of too similar solvents and whether using a smaller number, say six or eight, of solvents will be better in that the same results are obtained with less effort. The fact is that the solubility behavior at room temperature and under atmospheric pressure has to do with many properties, such as the molecular size and shape, polarity (permanent or induced, local or overall), solvent strength, surface tension, mass-transfer, viscosity, diffusibility, solvation mechanism, etc., of the solvent versus their counterparts in or on the solute. Those tested solvents that look similar (e.g., methanol and abs. alcohol; methyl ethyl ketone and acetone; methylene chloride and chloroform) are only similar in part of the above properties. If all related properties are considered, the 13 solvents as a whole still make a significant gradient. Besides, good correlation among similar solvents may also imply good reproducibility, and hence good specificity, of the methodology. Thus, although the specificity gained by single solvent is limited, the combination of 13 different solvents significantly enhances the overall specificity. Conservatively speaking, however, the increase in overall specificity will not

TABLE 2—The changes in appearance and color of samples I-1, II-1 and I-2 upon the solubility tests*†.

	Sample I-2			
	Sample I-1 (Known Blue Paint Taken from Blue Car)	Sample II-1 (Known Green Paint Taken from Green Car)	Smear I-2 (Questioned Paint on a Coated Plastic Bar Taken from the Blue Car)	Blank Control I-2 (Silvery-gray Background Coating)
Acetic acid	A	A	A	A
Acetic anhydride	B	B	B	B
Methanol	B	B	B	B
Methyl ethyl ketone	B	B	B	B
<i>o</i> -Xylene	B	B	B	B
Methylene chloride	C (The size of purple micro-granules enlarged and the number of glittering micro-granules increased. Others remain unchanged.)	B (Part of the green micro-granules separate making the purple and yellow micro-granules more naked.)	B (Some outermost material separate making the surface fresher and clearer, and the purple and yellow micro-granules more naked. Afterwards, the underlying plastics undergo the same changes as those described in the right column.)	B (Some silvery and purple micro-granules separate and re-aggregate on the margin making part of the gray plastics naked. Meanwhile, the whole surface cracks, shrinks, and rolls up.)
Chloroform	C (Same as above)	B (Same as above)	B (Same as above)	B (Same as above)
Pyridine	C (Same as above)	B (Same as above)	B (Same as above)	B (Same as above)
Abs. alcohol	D	D	D	D
Acetone	D	D	D	D
1,4-Dioxane	D	D	D	D
Ethyl acetate	D	D	D	D
Hexanes	D	D	D	D

* Solubility behavior: A, breaks up within 1 min.; B, breaks or separates slowly after 1 min; C, part of the micro-granules shows minor dislocations; D, nothing changed.

† Observed under a Zeiss Stemi SV 11 stereomicroscope with a magnification of 66.

be proportional to the increase in number of tested solvents. Finally, the above stated unequal bases for making comparisons along with the interfering background coating of Smear I-2 have once again reduced the method's specificity.

Conclusions

When used alone, each of the three comparative analytical methods employed in this case suffered from unequal bases for making comparison, insufficient specificity of methodology, and the interfering background coating beneath Smear I-2. However, the limitations were significantly relieved when three methods were used in combination. Based on the above presented results, the following conclusions can be drawn: the thought-to-be paint smears on Sample I-2 are really exogenous smeared paint, but not any other kind of material. Furthermore, Sample II-1 and the exogenous paint smears on Sample I-2 are of the same class of paint; that is, the original clearcoats use acrylic melamine while the original basecoats use alkyd melamine. In other words, the possibility that the paint smears on Sample I-2 have been transferred from the green car cannot be eliminated.

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Additional information and reprint requests:

Yun-Seng F. Giang, Ph.D.
Professor of Forensic Chemistry
Department of Forensic Sciences
Central Police University
Kueishan, Taoyuan
Taiwan 333, ROC
E-mail: ysgiang@sun4.cpu.edu.tw