

A Study of the Discrimination of Some Automotive Paint Films Having Identical Color Codes

Michael Eyring, BS^{1*} and
Mathew Lovelace, BS², Dawn Sy, BS²

ABSTRACT

This study was conducted into the discrimination of OEM automotive paint films, under the worst-case condition of distinguishing “plain”, or “non-effect”, paint systems with identical color codes. Each color code is associated with only one automobile manufacturer and is used to control the color of normally visually indistinguishable, sometimes metameric, paint systems. The study might be considered an extension of work done by Edmondstone³ in Canada. That work evaluated the infrared (IR) spectroscopic discrimination of randomly selected automotive clearcoats. Ryland⁴⁻⁶ also studied the application of multiple analytical techniques in the evaluation of automotive paint films. It should be made clear that no claim is made that the results of this study are necessarily applicable to non-automotive paint systems. Other paint systems though, are generally more diverse and less tightly controlled than automotive paint systems, and may well prove to be as easily discriminated as these automotive system were.

INTRODUCTION

The forensic analysis of cured paint films is generally guided by a standard guideline, ASTM E1610-02⁷, that was developed in the early 1990’s and jointly revised and approved by the American Society of Testing and Materials (ASTM) Committee E-30.01 and the Scientific Working Group on Materials Analysis (SWGMA) Paint Analysis Subcommittee. Numerous other forensic paint analysis schemes have preceded this document, and most of them are included in E1610 and referenced by it. ASTM E1610 is designed to assist forensic scientists in the analysis of a wide variety of paint systems including: automotive original equipment (OEM), automotive repaint, coil, architectural, maintenance, and wood, but not artistic, paint films. The actual forensic testing used in the analysis of a paint film is mediated by a number of factors, including: forensic issues or questions, film chemistry, sample size, sample damage or condition, sample origin, and

the effects caused by delay of sample discovery/recovery. These and other factors lead to ASTM E1610's use as a guideline and not as a protocol.

The training of criminalists in trace paint analysis and comparison can involve the use of almost every instrument in the trace analysis laboratory. A few of the many issues that are addressed in training include: practicing and perfecting sampling techniques, learning to identify significant differences in each analytical technique, validating laboratory analytical guidelines, and developing an appreciation for what constitutes a meaningful or sufficient analysis in a particular case. All of those considerations were part of the impetus for this study.

MATERIALS AND METHODS

The current study draws on about one thousand OEM automotive paint film samples that were collected as part of the Paint Database Query (PDQ)⁸ program, by the Arizona Department of Public Safety (DPS) Crime Laboratory. The study variously covered model years 1998 through 2005. Thirty-four (34) red samples, including Ford's color code E-4 and Chrysler's code PR-4, and seventy (70) white samples, including Ford's color codes WT and YZ, Hyundai's code NW, and Chrysler's code PW -7 were subjected to analysis. These samples were collected from undamaged, new vehicles that were being modified to meet custom feature requirements of new car buyers. The samples are cataloged by unique sample number, vehicle identification number (VIN), make, model, year of manufacture, color code, and vehicle manufacturing plant.

The analysis of each film progressed to the point of discrimination within its color group (red or white), beginning with micro-diamond attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy, then reflectance or transmittance microspectrophotometry (MSP), and finally, scanning electron microscopy (SEM) energy dispersive spectrometry (EDS) if needed. The order of examination was selected on the basis of analytical discriminating power, ease of sampling, and sample preservation (non-destructiveness).

Each FTIR-ATR spectrum was entered into a dedicated search library as it was produced, and compared to all other paint surface IR spectra in the study. Spectra, that were found

to be most closely related by the Nicolet search algorithm, were then visually compared by computer overlay and hard-copy printout. Areas of similarity and difference were evaluated to determine if significant differences existed in computer-associated spectra. When areas of spectral difference were small or questionable, spectra were run in replicate to determine if the difference(s) was reproducible. Very few spectra were closely similar, but an example of two is shown in Figure 1.

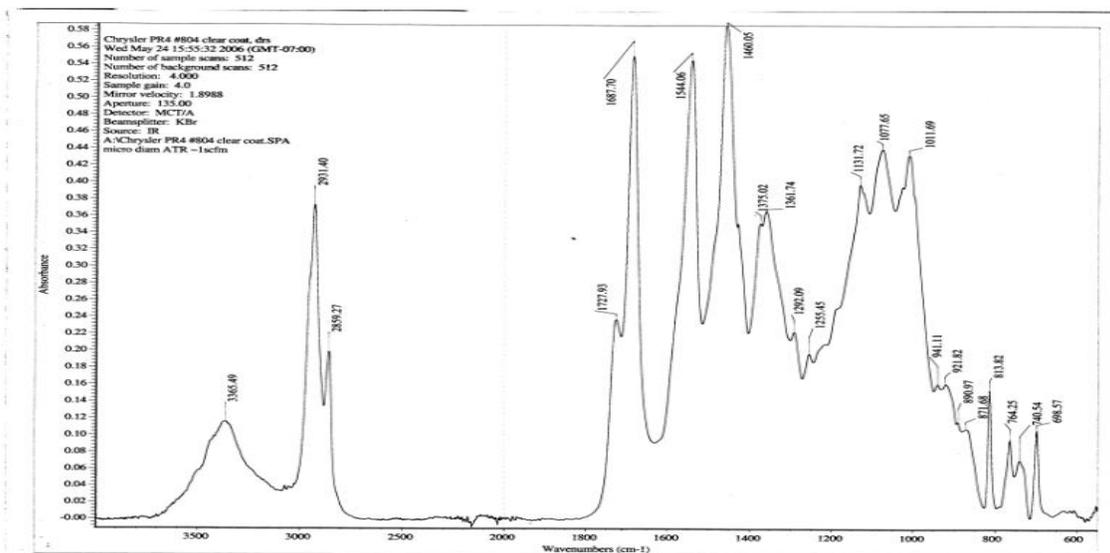


Figure 1a: Chrysler PR-4 Sample #804 clear-coat, micro ATR-FTIR.

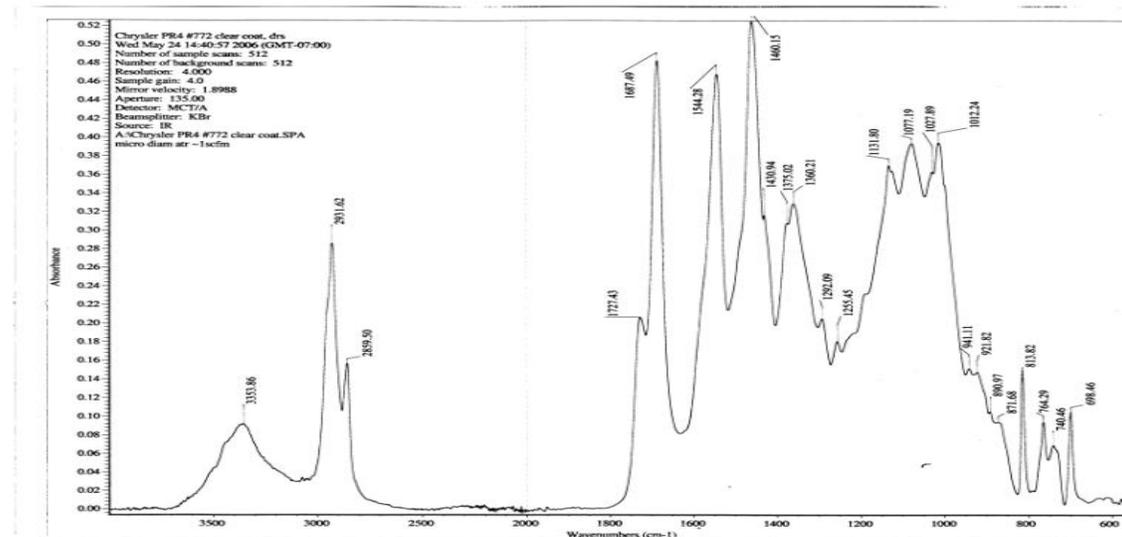


Figure 1b: Chrysler PR-4 Sample #772 clear-coat, micro ATR-FTIR.

The only real difference in these two spectra is a slightly lower abundance of C-H stretching absorbance relative to the carbonyl and C-H bending absorbances, but there are no peak inversions that typically indicate different polymer systems. The majority of the films were distinguished by the ATR-FTIR examination of their clear coats, and most of

those remaining, by the ATR-FTIR examination of a combination of their clear coat and primer surfaces, without further sample preparation.

The few samples that exhibited similar clear coat and primer ATR-FTIR's were further examined by MSP. MSP spectra were first run in diffuse reflectance mode with a 45 degree illuminated, 20X, dark-field objective. These spectra were run in replicates of ten (10) due to the small sampling area of the MSP detector and its resultant high noise levels at shorter spectral wavelengths. Spectral sets were then averaged for comparison. An example of a pair spectral sets, associated with the FTIR's in Figure 1, is shown in Figure 2. The averaged spectral sets were then visually compared after hard copy overlay plotting as shown in Figure 3. The spectra were plotted above 430nm to avoid noise.

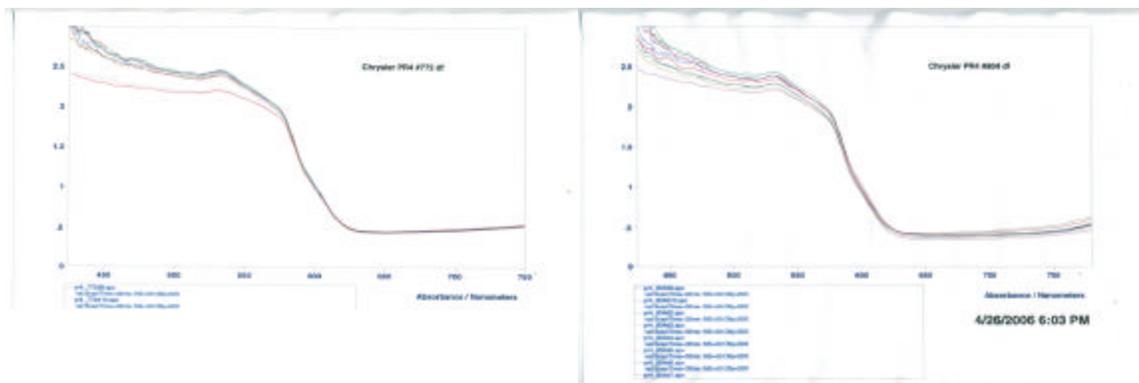


Figure 2a: Reflectance MSP of PR-4 #772 Figure 2b: Reflectance MSP of PR-4 #804

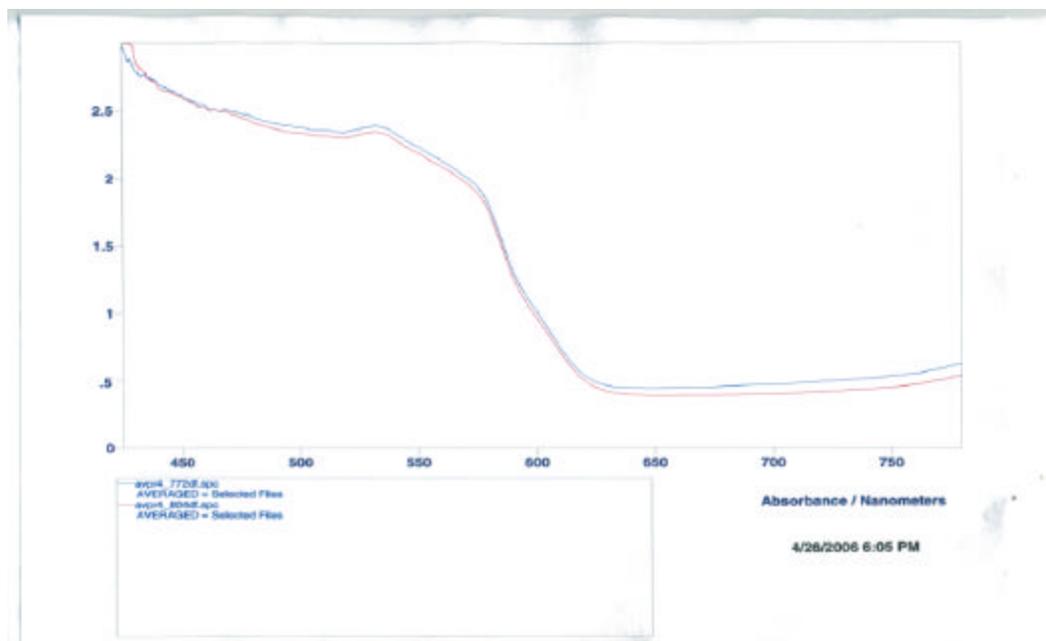


Figure 3: Comparison of averaged reflectance MSP spectra of PR-4's #772 and #804.

These diffuse reflectance spectra in Figure 3 seem to exhibit a slight difference in spectral cut-off between 575nm and 625nm, but it is not obvious and might be due to sampling or surface artifacts. In this situation, an additional sub-sample of the films were potted and thin cross-sectioned for transmission MSP. Once again, ten (10) spectra were collected from each film's color/base coat layer, and the resulting sample sets were averaged and compared as shown in Figure 4.

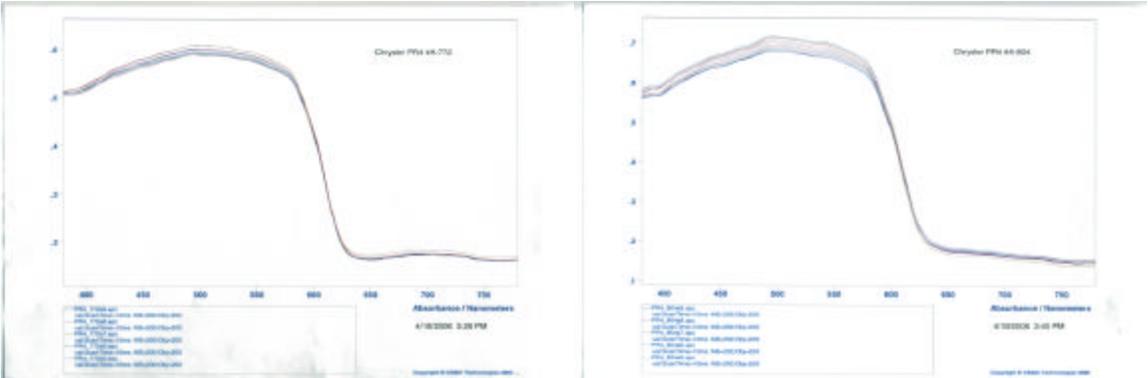


Figure 4a: Transmission MSP of PR-4 #772 Figure 4b: Transmission MSP of PR-4 #804



Figure 4c: Comparison of averaged transmission MSP spectra of PR-4's #772 and #804.

Compared to the diffuse reflectance MSP data for these samples, the transmission spectra show greater reproducibility and lower noise. The resulting comparison of spectral averages of samples #772 and #804 show a clear difference in cutoff slope and a metameric inversion at ~675nm. This is sufficient to distinguish the samples.

A second pair of red (PR-4) samples, #60 and #407, with similar FTIR's, also showed a similar metameric inversion in this region that can be seen in their absorbance plotted transmission spectra, but is more obvious in their percent transmittance (%T) plots as shown in Figure 5. The FTIR spectra of this pair of samples are distinctly different than those of samples #772 and #804.

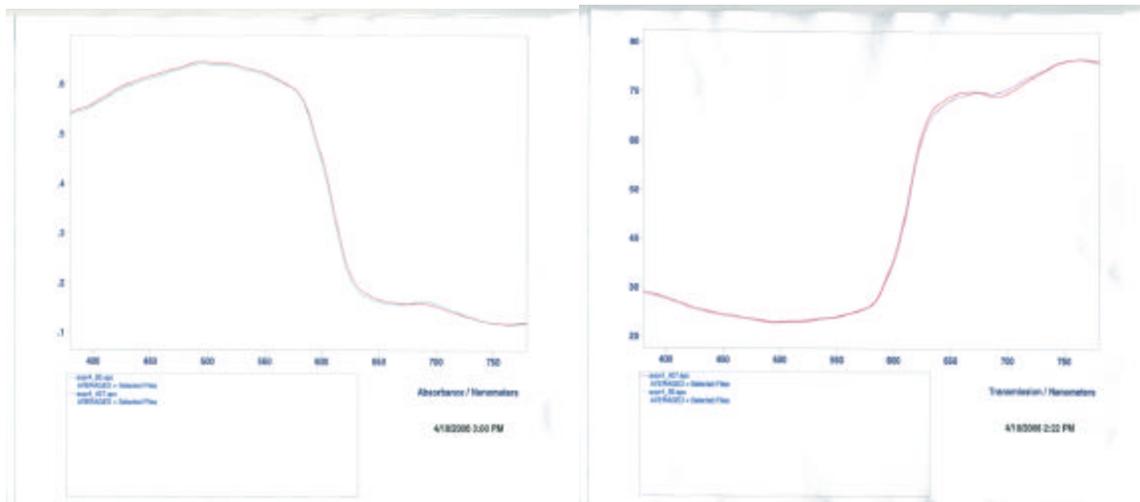


Figure 5: Comparison of averaged transmission MSP spectra of PR-4's #60 and 407, plotted left in Absorbance and right in % Transmittance.

When FTIR and MSP comparisons were found to be inadequate to distinguish a pair of samples, the final differentiating analysis was the comparison of primer EDS spectra. Such a continuation of analysis was necessary only for three (3) samples of Ford's white color code "WT". An example of two samples' EDS primer spectra comparison is shown in Figure 6. Four (4) EDS spectra were collected and averaged from each sub-sample.

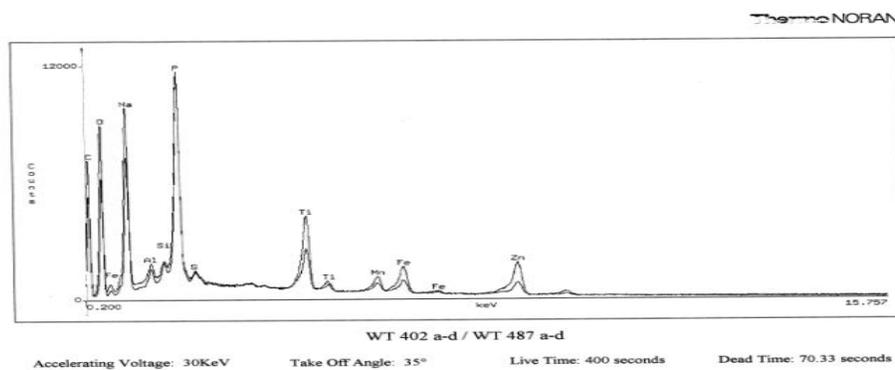


Figure 6: Primers' EDS comparison of white Ford WT s samples #402 and #487.

EQUIPMENT

ATR-FTIR spectra were collected on a Thermo Electron (Nicolet) Magna IR 550 through a Nic Plan IR microscope using a Spectra-Tech micro-diamond ATR crystal. The sampling area of the hexagonal crystal face is approximately 250 μm to 300 μm in diameter. The face of the objective is shown in Figure 7.



Figure 7: Micro-Diamond ATR Objective

The FTIR system was purged with dried, CO₂ stripped air provided by a Balston Purge Gas Generator at 1cfm. Residual H₂O vapor and CO₂ present in spectra was directly subtracted out using stored vapor spectra collected with the FTIR system in ATR mode. The main bench of the FTIR was operated at 100% aperture opening and a mirror velocity of ~1.9cm/sec. A total of 512 scans were collected and co-added at a resolution of 4cm⁻¹ to yield each sample spectrum. The resulting spectra exhibit low noise and good reproducibility.

Diffuse reflectance MSP spectra were collected with a Craic QDi Spectrophotometer using 100watt xenon arc illumination and a 20X, 0.40NA dark field objective. Transmission MSP spectra were produced through a 15x, 0.28NA cassagrainian objective with 100watt tungsten halogen illumination. The MSP's darkened rectangular sampling areas for the two objectives are shown in Figure 8, below. Both areas are approximately 10 μm square. A general discussion of MSP, including sampling area affects, is given by Eyring⁹.

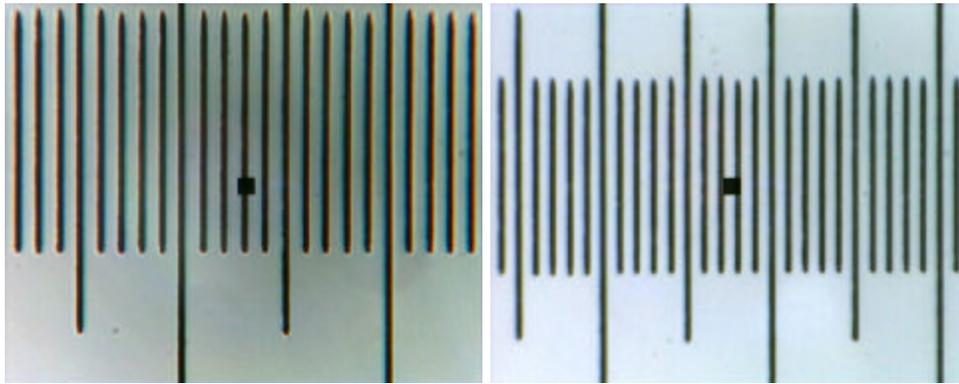


Figure 8a: 20X MSP sample area. Figure 8b: 15X MSP sample area.
(10 μ m per scale division)

Microtomed samples were prepared using a Microm HM360 microtome and DDK Tungsten knives with an inclination of 10 degrees.

The SEM-EDS system, used to evaluate a few samples, is a Zeiss (Leo) 1430, constant vacuum SEM, operated at 30keV. It is fitted with a Thermo Electron (Noran) 2232A NanoTrace EDS made up of a thin polymer (Norvar) window, liquid N₂ cooled, 30mm² Li drifted Si detector [Si(Li)], with a resolution (Mn @ 5.89keV) of about 135ev.

EDS samples were carbon coated in a Polaron E5200 sputter coater with a carbon yarn evaporation power supply accessory. Conductivity from the upper surface of the paint film sub-samples to the base ground was provided by a thin line of colloidal carbon paint at one edge of each sample.

SAMPLE PREPARATION

Each paint film was sampled by flexing the underlying sheet metal paint substrate to remove flakes of the intact paint film. Each paint film was typically three (3) to four (4) layers thick. When a layer of zinc galvanizing was present on the primer sub-surface, it was either peeled away, or ignored when it only covered a portion of the sample. The presence or absence of galvanizing is certainly a significant point of comparison between paint films, but it was not considered in this study.

Two small sub-samples of each film were mounted on colloidal carbon/graphite filled adhesive tape applied to aluminum SEM stubs, one sub-sample with its clear-coat uppermost, and the second with its primer, or lowest layer, uppermost. The exposed surfaces were wiped with a cotton swab or dental micro-swab to remove any loosely held surface particles. The goal was to conduct meaningful sample discrimination with minimum sample preparation and consumption. A typical prepared sample is shown in Figure 9. Sub-millimeter samples can easily be prepared by this method.

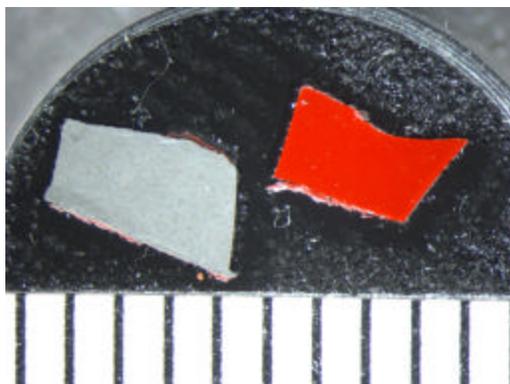


Figure 9: Typical Paint Film Sample. Scale: 1mm per division

The prepared SEM stubs were left uncoated, and used for ATR-FTIR and diffuse reflectance MSP analysis without further preparation. If a stub subsequently needed to be used for EDS analysis, it was coated with evaporated carbon.

A few paint films, that were the most difficult to discriminate, were also prepared for transmission MSP. These sub-samples were imbedded in Technovit 2000 LC, blue light curing epoxy, and microtomed at $0.5\mu\text{m}$ thickness for pigment color comparison. A view of red and white typical samples is shown in Figure 10.

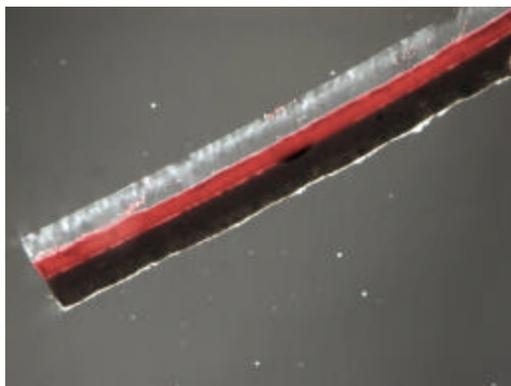


Figure 10a: Cross-section @ ~100X

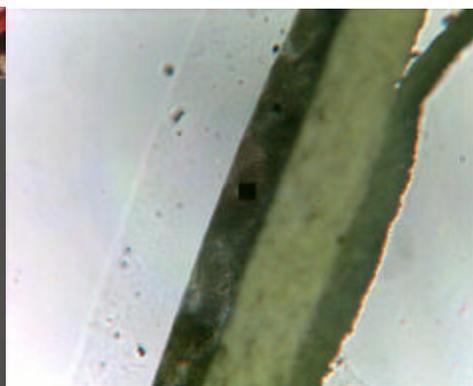


Figure 10b: Cross-section @ ~200X

RESULTS

All one hundred-four (104) red and white automotive paint samples in this study were differentiated by the foregoing analytical scheme. The majority of samples were found to have unique clear-coat ATR-FTIR spectra, but the additional comparison of primer IR's was needed to distinguish some samples. It was decided that both clear-coat and primer IR's were generally need to distinguish such closely related samples as were used in this study.

Three (3) pairs of red Chrysler color code PR-4, and one pair of Ford color code E-4 samples required the addition of MSP spectral analysis to distinguish each pair.

Three (3) samples of Ford WT white paint films were found to have similar clear-coat and primer IR's that were not distinguishable by MSP spectral analysis, and additional SEM-EDS spectral comparisons were needed to separate these samples.

In all, ninety-three (93), or ninety percent (90%) of the original samples were distinguishable by ATR-FTIR alone. Ninety seven percent (97%) were distinguished by a combination of ATR-FTIR and MSP spectral comparisons. All 104 samples were distinguishable with the addition of SEM-EDS analysis.

CONCLUSIONS/DISCUSSION

The results of this "worst case" sample automotive paint study indicate that the recommendations of SWGMAT/ASTM guideline E-1610-02 are well suited for automotive paint film discrimination and comparison. The study served to validate the methods used in the study laboratory, and to assist in the training of the study scientists through repetitive sample preparation and analysis.

It is also clear that elaborate sample preparation and significant sample consumption are not generally necessary for discriminating analysis. This is in line with forensic scientists' need to preserve evidence and to allow for reanalysis of case items. The samples prepared in this study are completely suitable for long-term preservation and reanalysis, and can be recovered, if necessary, for additional preparation and testing.

The study showed the need for larger MSP sampling areas for diffuse reflectance analysis of paint surfaces. This is even more of an issue for the analysis of effect pigmented paint systems in general.

It is clear from the work done in this study and others, that an essential criteria for the successful use of E-1610 is the production of high quality spectral or chromatographic data from properly maintained, calibrated and well operated equipment.

The continuing value of this work lays in the fact that additional samples of the paint panels that were tested are still available from the Arizona DPS Crime Lab, and the Micro Forensics Institute. These same samples, and additional ones, of the same color codes, donated by other forensic laboratories, might also be available through the FBI crime laboratory and the RCMP PDQ System sample archives. More comprehensive, and also blind studies, can easily be prepared and conducted.

LITERATURE CITATIONS

¹ Micro Forensics Institute, Ltd, P. O. Box 40048, Phoenix, AZ 85067 USA. E-mail: microfor@fastq.com

*(Contact)

² Arizona Department of Public Safety, Central Regional Crime Laboratory, Trace Analysis Unit, MD 1150,
P. O. Box 6638, Phoenix, AZ 85005 USA.

³ Edmondstone, G., Hellman, J., Legate, K., Vardy, G.L., and Lindsay, E.,
"An Assessment of the Evidential Value of Automotive Paint Comparisons,"
Can. Soc. Forensic Sci. J., 37, No.3, 2004, pp. 147-153.

⁴ Ryland, S. G., "Advances and Changes in Forensic Paint Examinations," (a one day workshop presented to the Fall Seminar of the California Association of Criminalists, Temecula, California, October 9-13, 2006.)

⁵ Ryland, S.G., et. al., "Discrimination of 1990s Original Automotive Paint Systems: A Collaborative Study Of Black Nonmetallic Base Coat/Clear Coat Finishes Using Infrared Spectroscopy," *Journal of Forensic Sciences*, Vol. 46, No. 1, 2001, pp. 31-45.

⁶ Ryland, S., Jergovich, T. and Kirkbride, P., "Current Trends in Forensic Paint Examination," *Forensic Science Review*, Vol. 18, No. 2, July 2006, pp. 97-117.

⁷ "Standard Guide for Forensic Paint Analysis and Comparison", ASTM Book of Standards Volume: 14.02, 2007.

⁸ PDQ Maintenance Team, 15707 118th Ave., Edmonton Alberta T5V 1B7, Canada.

⁹ Eyring M. B., "Visible Microscopical Spectrophotometry in the Forensic Sciences", *Forensic Science Handbook, Vol. I (2nd Ed.)*, R. Saferstein, Ed. Prentice-Hall, New Jersey, pp. 321-388. 2001