

Micro-Spectroscopic Interrogation of Automobile Paints

Introduction

In 2009, 246 million motor vehicles were registered in the US with 10.8 million of them being involved in an accident¹. Many of those accidents involved fatalities, hit-and-runs, and in general, uncertainty in accident cause and responsibility. Identifying potential subjects in an accident routinely involves the collection of paint chips or smears. This is especially the case in hit and run accident investigations where the strong need to link paint samples to the vehicles involved is apparent. Fortunately, vehicle manufacturers constantly change the chemical makeup of their paints. Automobile paints are comprised of binders (resins), dispersants, additives, and dyes. All of the components of paint exhibit unique spectral features when analyzed with Fourier Transform Infrared Spectroscopy (FT-IR).

FT-IR utilizes infrared light to cause molecular vibrations which vary in position and intensity for different compounds. These vibrations create a “molecular fingerprint” which can be used to identify covalently bound compounds like those found in automobile paint. The inherent nondestructive nature of FT-IR’s sampling allows for other identification techniques to be used in conjunction. The SurveyIR microspectroscopy accessory can collect spectral information in transmission, reflection, and attenuated total reflection (ATR), allowing the analysis of a wide range of potential samples. The investigation of an automobile paint chip is presented in this note.

Results and Discussion

One of the most challenging parts of automobile paint identification is the sample itself. Ideally, large amounts of paint would allow for a range of tests to be concluded. However, this is not always the case and in some instances just a small paint chip or smear may be all that is available for analysis. A paint sample that exhibits multiple paint layers was collected from a vehicle and is shown in Fig. 1.

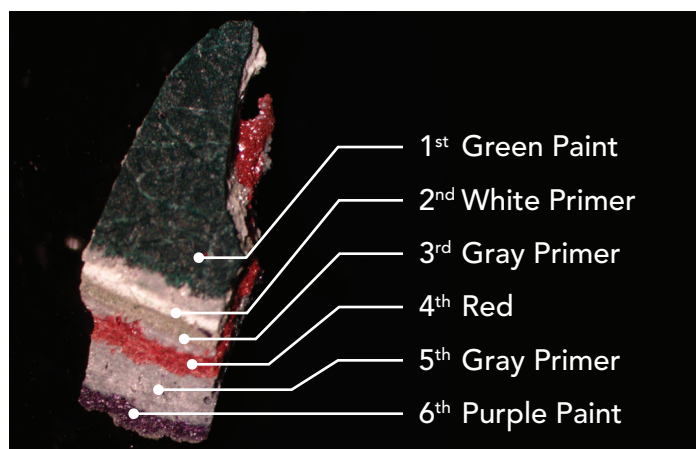


Figure 1: Multilayered paint chip from a '79 Pontiac Firebird.

In order to sample layers 1-5, a tungsten needle was used to extract small chips from each layer. The small chips were then rolled flat on plain glass microscope slides, and transferred to KBr 13X2 mm windows.

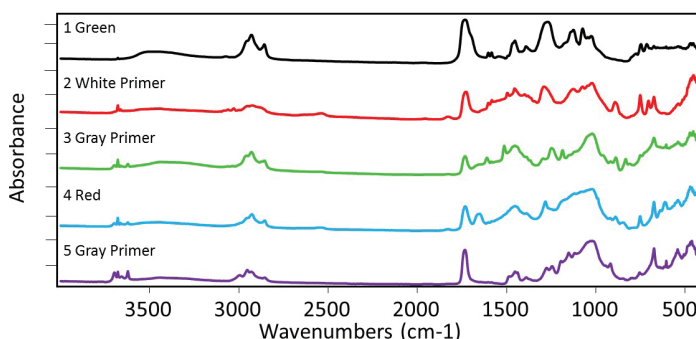


Figure 2: IR spectra from layers 1-5 in the paint chip in figure 1.

Corresponding spectra of each layer (Fig. 2) were recorded at 8 cm⁻¹ resolution with 32 co-added scans. The ability to differentiate paint layers can be readily seen in the IR spectra

in Fig. 2. An additional advantage of SurveyIR, through use of the instrument mounted DTGS detector, is the observation of bands in the lower frequency range, 700-400 cm^{-1} . Most microspectroscopy systems are limited in spectral range and require liquid nitrogen cooling. The observation of bands in this range is especially important with regard to paints, as the spectra of many inorganic additives in paint give rise to distinctive spectra in this region, as demonstrated in Fig. 4. Some common features exist throughout all the samples such as the strong intense band seen around 1730 cm^{-1} . This band is due to C=O stretching, most likely from common alkyd resins used in more modern paints. In addition, the spectrum of talc is observed, exhibiting varying intensities throughout the different layers. Talc is a very common additive in paint.

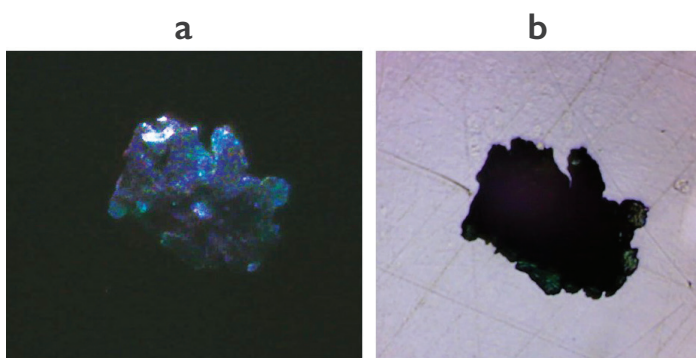


Figure 3: Top paint layer (Fig 1, Green Paint) shown in oblique illumination (left, a) and transmitted light illumination (right, b)

A novelty of the SurveyIR is the ability to quickly switch between viewing illuminations while simultaneously viewing the sample. For this sample, transmitted light allows the user to visualize the sample edges and some color of the sample can be seen in Fig. 3, b. The oblique illumination (dark field illumination) provides much more detail with regard to the surface of the paint, accentuating the color. This can be extremely useful in the case of small paint smears. Compared to a chip, a paint smear may be too small to remove from the surface and the clip-on ATR gives the investigator the ability to analyze the sample on the surface while the oblique illumination provides the best contrast to locate the sample.

The top green paint layer shows a strong correlation with an alkyd resin-based paint as displayed in Fig. 4. A particular resin which is very close to an exact match (Fig. 3, red), contained 38% vegetable oils and 32% phthalic anhydride amongst other additives. Due to the vast number of different compositions of alkyd resins, an exact library match of the particular resin used can be difficult to make.

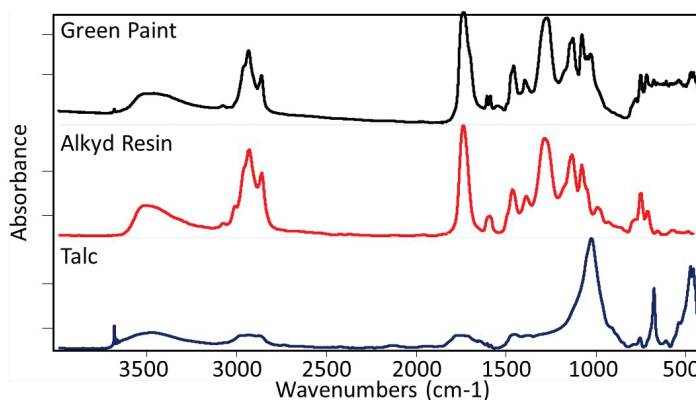


Figure 4: Spectra of Green Paint (Black) with 2 identified components: Alkyd Resin (Red) and Talc (Blue)

The other component in the green paint that can be identified is Talc (Fig. 3, blue). Talc absorption bands overlap at 3676, 465, and 451 cm^{-1} . Talc, a very common paint extender due to its chemical inertness, helps pigments adhere to vehicle surfaces, resulting in increased durability. The pigment in the green paint layer was not identified. The pigment could be present at a relatively low concentration and its spectrum masked by the spectra of the other constituents.

Conclusion

The spectra shown in Fig. 2 are unique from one layer to the next and can be analyzed individually as shown with the first green paint layer (Fig. 4). The wealth of information gathered from all the different paint layers creates indisputable evidence in the case that this car was involved in an accident. The general ability of FT-IR's to assist in the identification of paint samples to be later used in a criminal case is well known and described in ASTM method E2937 - 13.² The SurveyIR microspectroscopy accessory enhances the investigation of paint chips or smears by providing both illumination and sampling options covering a wide range of samples. The SurveyIR can be used to analyze coatings and is applicable to forensic investigations and industrial coatings analysis.

References:

1. "Motor Vehicle Accidents--Number and Deaths." The United States Census Bureau, 30 Sept. 2011. Web.<http://www.census.gov/library/publications/2011/compendia/statab/131ed/transportation.html>
2. ASTM E2937 - 13, "Standard Guide for Using Infrared Spectroscopy in Forensic Paint Examinations," ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA