FORENSIC EXAMINATION OF CAR PAINTS

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Introduction

Car paint as physical evidence is probably one of the samples most commonly received by forensic laboratories. Paint chips or paint smears are very often transferred on to the clothing of a car accident victim on impact with an automobile. Micro traces of the paint are also transferred during a robbery from the opened door on to the tool which was used while breaking-in.

Two kinds of forensic investigations are usually performed: identifications/classifications of the paint sample and comparison of samples taken from the crime scene and the suspected object. The first one is performed when only a small sample was found on the crime scene and the questions given to the forensic examiner are: what kind of paint is it? what was the model of the car taking part in the accident? etc. The answers might be given on the basis of a detailed analysis and search in data bases of car paints. In the other case the comparison of two samples is performed in order to answer the question given whether the two samples could have come from the same object or not.

In order to solve the problems mentioned above it is necessary to obtain information on both the morphology and the chemical composition of the analysed samples.

Typical new automotive refinishment consists of at least four layers: primer, primer surfacer, basecoat and clear coat. Each layer of the coating is a mixture of different components:

- polymers (e.g. alkyd, melamine, acrylic, epoxy, polyurethane),
- inorganic and organic pigments,
- fillers and other substances.

Each layer is investigated by means of a different analytical method and therefore it is possible to acquire a lot of information important for the investigation from one, even very small, sample (Figure 1). First of all, different techniques of optical microscopy are used to define the colour, surface texture and layer sequence. Unfortunately, most paint specimens do not have a full layer structure and other methods have to be used to characterise the samples. Infrared spectrometry is another analytical technique routinely applied to determine the type of paint, i.e. to identify binder and the main inorganic pigments and fillers. Organic groups absorb radiation selectively, so the obtained IR spectrum is characteristic for the examined sample. All inorganic pigments can be identified on the base of elemental contents of the sample obtained by the use of X-ray methods: SEM/EDX or XRF. Clear coat layer is often analysed by pyrolysis gas chromatography-mass spectrometry. All these methods are briefly described in this paper.

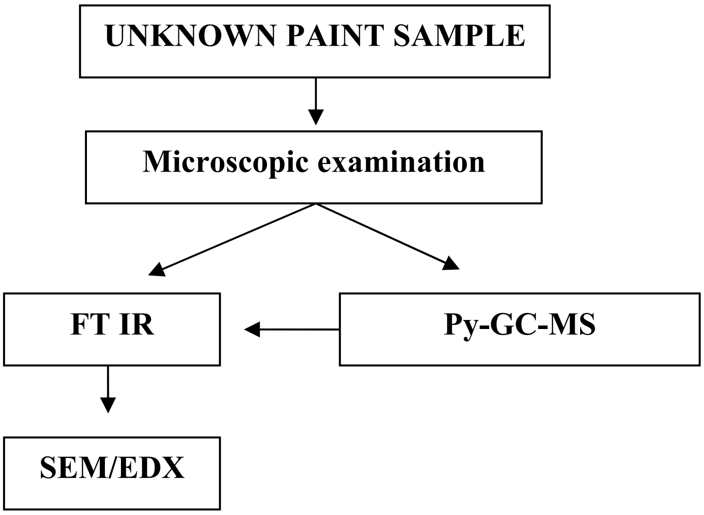

Figure 1. Standard procedure in forensic examination of car paints

Microscopic examination

In most cases an initial microscopic examination is conducted using a stereo microscope to determine the number, sequence, colour, thickness and texture of each layer in a car paint system (Figure 2). The layers of a paint chip are revealed on cross-section of the sample prepared by cutting it perpendicular to the surface by scalpel or microtome. They may also be observed under a polarised microscope. Unique or

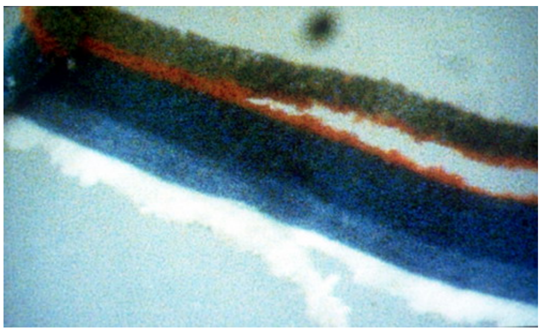

Figure 2. Layer structure of a paint chip

accidental features such as overspray, irregularities or peculiar characteristics in, on or between each layer are also noted very often. As layers are sampled from the horizontal chip, they are cut or scraped away to reveal the layers below.

Fourier transform infrared spectroscopy (FTIR)

The most popular and powerful technique for paint characterisation is infrared spectroscopy. Almost all substances absorb selectively infrared radiation and create characteristic infrared spectra. The measurement with the IR instrument consists in comparing the IR radiation energy transferred through the sample with the energy transferred through the reference. IR method makes it possible to examine even small samples with a little or without any loss, which is important in forensic investigations.

Samples for infrared analysis are obtained mid-layer to avoid any chances of surface contamination and weathering effects or to limit the possible contributions of component migration from substrate materials and adjoining layers, especially in wet-on-wet applications.

This method makes it possible to identify polymer binder, main pigments and fillers in each layer of the paint coat sample. Binder is typically built of different types of resins modified and none- modified (alkyd, acryl, melamine, epoxy etc.). The small peaks visible in the spectra are signals from pigments and fillers. These signals are most intensive in the region of 400 – 1000 cm^{-1}. Signals from TiO_2 and ZnO are intensive even in a low concentration of these compounds. Signals from $BaSO_4$, $CaCO_3$, talc and kaolin are also clear visible. Organic pigments are hard to identify due to their low concentration in the analysed samples. Signals from many pigments are overlapped by signals characteristic for resins.

In most cases, identification of polymer type is based on the comparison of the obtained spectra with the spectra from library. As an example, Figure 3 presents a comparison of FTIR spectra of four different red car paints.

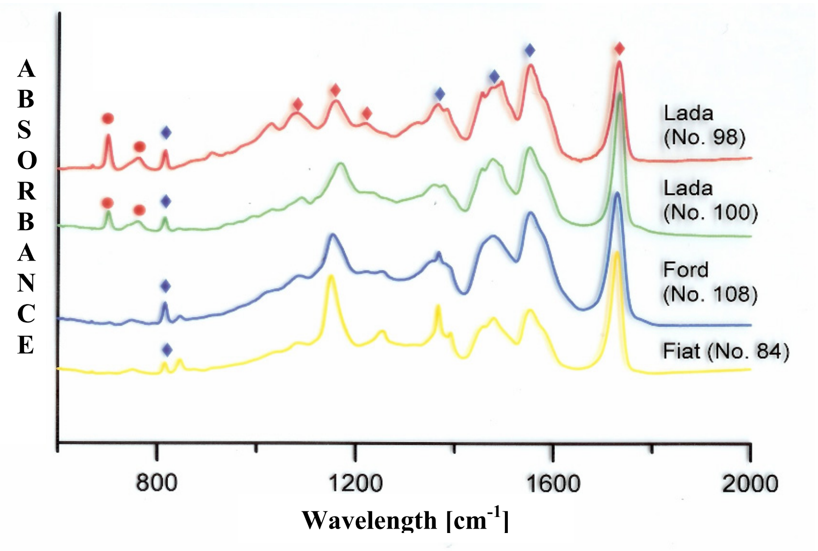

Figure 3. FTIR spectra of external layers of paints taken from 4 different cars

Pyrolysis gas chromatography (Py-GC-MS)

Py-GC-MS is an analytical method where small samples of organic complex molecules are decomposed by heat to gaseous products, later separated on a chromatographic column and detected in a mass spectrometer. As a result, chromatograms called "pyrograms" are obtained, which may help to distinguish one polymer from another (Figure 4).

Gas chromatography provides very good separation of the compounds obtained during pyrolysis and high sensitivity, whereas pyrolysis is a perfect method for breaking apart large molecules into smaller through a short application of heat. Mass spectra allow us to identify compounds correlated to particular peaks. Therefore, combining all those three methods creates a high sensitive tool for the analysis of various polymer samples

Frequently, the major peaks (often monomer) in the obtained chromatogram (pyrogram) are easily identifiable and give direct structural information about the material being pyrolyzed; in other cases pyrograms are more complex and contain "fingerprints" which may be used to distinguish between very similar materials. Only a few micrograms of the sample is needed to acquire good results. This is the real advantage of the pyrolytic method. There are only trace amounts of paint samples found on the crime scene, so it is important to treat them with special care.

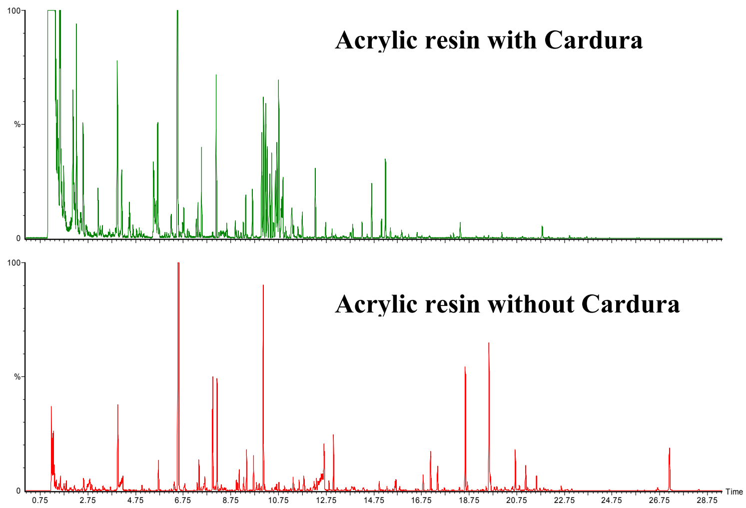

Figure 4. Pyrograms of two different clearcoats

Derivatization is applied in pyrolytic gas chromatography (as in other chromatographic methods) with the aim of improving selectivity. Methylation of alcohols and of carboxylic acids is most often performed using trimethyl sulfate or tetramethylammonium hydroxide (TMAH). This modification of analyte allows for the improvement of selectivity of the applied system and, consequently, the improvement of differentiation and identification of the analysed samples.

Scanning electron microscopy / energy dispersive X-ray spectrometry (SEM/EDX)

In order to use a magnitude higher then the one in optical microscope, scanning electron microscopy (SEM) is used. SEM is a high magnification microscope which uses a focused electron beam to produce images of the sample. The surface of the analysed object can be observed at magnification ranging from x 15 to x 300 000, with the resolution of 2 nm, where accelerating voltage is between 1 and 30 keV. However, the magnification up to 20 000 is normally used. Secondary and backscatter electron imaging also allows for surface observing, stereo imaging and stereo height measurement.

The energy dispersive X-ray spectrometer (EDX) connected to SEM uses X-ray radiation, which is produced whenever the electron beam interacts with the analysed sample. This technique enables qualitative and quantitative analysis for all elements from boron upwards. In the case of car paints, only qualitative analyses are performed. Detection limit is typically 10^{-19} g for most elements. The area of the operational field of the electron beam is typically from 0.01 to 0.05 μm^2. The other possibilities of EDX are multi-element X-ray mapping and line scans.

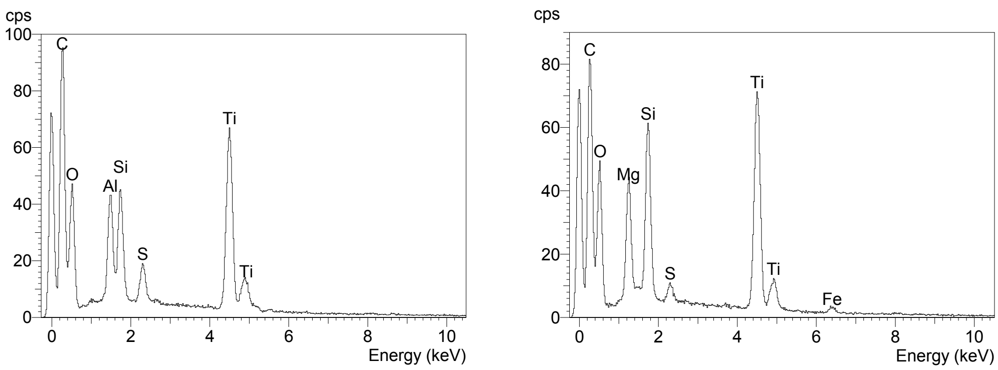

Figure 5. Elemental composition of two different paint layers

SEM/EDX can be very useful when the compared paint samples are similar in the microscopic properties relating to their morphology (the number and sequence of layers, theirs thickness, colour) and the results of infra-red spectroscopy and Py-GC-MS analysis. Thus, the identification of a particular paint layer can be carried out by comparing the contents of elements as they are characteristic for a given layer and do not repeat (Figure 5). The advantage of SEM/EDX method is that it is non-destructive, which is very important in forensic analysis because the sample can be kept for further examinations. Results obtained by the SEM/EDX can be evaluated using suitable methods of chemometric analysis.

Summary

All the above-mentioned analytical methods facilitate the process of solving any case of a road accident involving car crashes where the identification of car paint may be crucial for further judicial procedures. In some cases, microscopic examination might be sufficient, but in others the forensic scientists have to go through the whole procedure using all available methods. In typical cases, there is a necessity of a simultaneous application of at least two of them, so that they verify and complement each other.

Nowadays, there is a big need for building databases of automotive paint which could be used when it is important to find the culprit's car basing on a single small paint flake left on the crime scene without any further knowledge of the suspect. At the moment, such libraries are ready for the FTIR method and it is also suggested that work on creating a database of car paint pyrograms should be started (in both analogue and digital form). Yet, forensic laboratories still need more samples for this purpose. Currently, the major problem is to encourage cooperation between car paint producers and forensic laboratories.

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