The effect of environmental degradation on the characterisation of automotive clear coats by infrared spectroscopy

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ABSTRACT

This paper presents a study into the chemical changes occurring within automotive clear coats as a result of environmental weathering, and their potential effect upon the characterisation of samples using infrared spectroscopy combined with chemometric modelling. Testing of three samples, collected from separate vehicles, exposed to the outside environment revealed no changes in model predictions over a 175 day period; however, incorrect predictions were observed following 435 days of exposure. Inspection of the corresponding infrared spectra revealed that these changes were likely due to the hydrolysis and photodegradation of polymer chains present in the clear coat, which were not observed in samples stored away from the outside environment over a one-year period. Analysis of previously weathered samples using synchrotron infrared microscopy found these changes occurred in a top-down fashion rather than within the bulk of the clear coat. This indicates that although weathering may affect the surface characterisation of clear coats over time, the targeting of deeper portions of the clear coat layer may still provide useful information as to the identity of the vehicle.

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1. Introduction

In vehicle collisions, automotive paint is likely to be transferred or chipped off through physical contact, and may therefore be used to link vehicles, people or objects to the scene of the incident [1]. Paint chips are of particular interest in crimes involving vehicles as they represent the full layer sequence of the paint, and so their analysis may provide leads pertaining to the identification of the vehicle and/or perpetrator. This is especially valuable when there is little or no existing knowledge of any persons involved, and may be vital in the process of reconstructing past events [2–4].

Modern automotive paint formulations are typically made up of four main layers; an electrocoat primer, primer surfacer, base coat and a clear coat [5,6]. Each layer has a distinct chemical composition which may contain polymeric binders, such as alkyds, acrylics, epoxies, and polyurethanes, as well as inorganic and organic pigments and fillers [2,5,7]. It is the potential variation in each layer's individual composition that allows the discrimination between samples from different sources. However, variations between samples may be subtle, requiring multivariate statistical techniques (chemometrics) to clearly visualise any differences and provide a more objective means of comparison [8,9].

The clear coat layer of automotive coatings is applied on top of the coloured base coat layer (which may also contain metallic or pearlescent flakes) to reduce scratching, prevent UV degradation and to keep the paint in good condition [5,10,11]. Analysis of forensic paint evidence usually focuses on the pigmented base coat; however, the clear coat has recently become of great interest, as it is the most likely to be transferred through contact and hence recovered at a crime scene.

Recent studies by Liszewski [12] and Mendlein [13] found that clear coats could be differentiated into broad classes based on their UV microspectrophotometry or micro Raman spectra with chemometric analysis, although they were unable to correlate the separation of samples with the make, model or year of vehicle manufacture. Several publications by Lavine et al. took an alternative approach by investigating the use of search prefilters and genetic algorithms to search the IR spectral library of the Paint Data Query (PDQ) database. These studies found that it was possible to distinguish automotive clear coats from Chrysler and General Motor vehicles manufactured between 2000 and 2006 according to their assembly plant, allowing identification of the

model, line and in some cases manufacturing year of the source vehicles [14–20]. However, as the samples utilised in this study originated solely from North American manufacturing plants, the methodology developed currently has limited applicability within an international context, and additionally relies upon a matching IR spectrum being present within the PDQ database.

Earlier research by the authors Maric et al. [21] employed attenuated total reflection infrared (ATR-IR) spectroscopy with chemometric analysis for the discrimination of automotive clear coats from a range of Australian and international vehicles, establishing a predictive model that could assign unknown clear coat samples into one of nine distinct classes [21]. These classes were found to be related to the country of vehicle manufacturer, and in some instances to specific year ranges or manufacturing plants [21]. This is significant as it allows the possible identification of vehicle class characteristics for a questioned paint sample recovered from a crime scene.

As the model built by Maric was constructed using near-factory finish vehicles, Sauzier et al. [22] expanded upon this work by examining the effect that environmental exposure may have upon the classification of clear coat samples. Samples that were deliberately aged over an 8 month period showed no apparent changes in their chemometric classifications. However, 12 samples originating from pre-2000 vehicles with an unknown prior history were incorrectly classified. 11 of these samples were later found to possess a post-manufacturer coating, resulting in misclassification due to their substantially different chemical composition in comparison to the original finish samples used to build the predictive model. The incorrect classification of the remaining sample was considered to potentially be due to the UV degradation of polyurethane. It should be noted, however, that this study focussed solely on the chemometric classification of samples, and did not examine visual changes occurring in the spectra or how any changes in clear coat composition progressed though the layer.

The rationale behind this current study was to evaluate in more detail the effect of weathering over an extended period on the analysis of automotive coatings within a forensic context. This more detailed study investigated the degradation of automotive clear coats with regular monitoring, as well as examining any chemical changes in the clear coat which could result in the misclassification of unknown samples. This study also examined how the degradation progressed through the clear coat layer using synchrotron IR microscopy, and whether changes occurred to samples not exposed to outside environmental conditions.

2. Materials and method

2.1. Sample collection and preparation

Automotive paint samples in the form of roof and body panels were donated by a car sunroof fitting company (Prestige Sunroofs WA) and an automotive mechanic (De Jonge's Auto Haus WA). Where possible, the vehicle identification number (VIN) of each source vehicle was recorded in order to provide an expected class for each sample.

Three samples from three different vehicles selected for environmental exposure studies were attached to steel roof struts of a building at Curtin University. The three samples were selected on the basis of providing sufficient subsamples for subsequent analysis over an extended period of environmental exposure. Due to practicality and potential safety issues with securing these samples to the building roof for an extended period, only a limited number could be investigated. It should also be noted that as the samples were obtained from real vehicles rather being specifically prepared for this research, the exact composition of each clear coat

was not known. However, previous work has established that clear coat formulations generally consist of acrylic, melamine, styrene and polyurethane polymers in varying proportions [21]. Analysis was conducted twice a week for 25 weeks, and again after 435 days of exposure. At each analysis interval, 5 cm^2 sections were cut from the samples and stored in individual yellow A5 envelopes. A scalpel blade was then used to remove paint chips from each sample for infrared analysis [21,22].

An additional five samples selected at random from those collected for the previous studies [21,22] were stored under controlled office conditions for a period of one year, to determine whether any degradation would be observed in samples stored away from weather exposure. These samples were stored in the dark, with temperature remaining between approximately 21–23 °C.

Samples analysed via synchrotron IR microscopy were cross-sectioned to 8 μm thicknesses using a microtome with a stainless steel blade. Paint chips were removed with a scalpel and placed between two pieces of polyethylene plastic before microtoming to prevent the paint layers splitting. The sample was removed from the plastic and laid flat between microdiamond cell windows (Thermo Scientific).

2.2. Analysis

2.2.1. Infrared spectroscopy

Automotive paint samples were analysed by ATR-IR spectroscopy in the same manner as previous studies [21,22]. To determine the compatibility of the existing chemometric model with different instruments, multiple IR spectrometers were used to analyse five different samples (Table 1). All other analyses utilised the FTIR 1 instrument only. The resolution of each instrument was 4 cm^{-1} and the scan range 4000–650 cm^{-1}.

2.2.2. IR microspectroscopy

Segments from three samples used in the previous degradation studies [22] were analysed at the IR microspectroscopy (IRM) beamline at the Australian Synchrotron, Melbourne, Australia to map the progression of ageing in the clear coats over time. These samples had been exposed to environmental conditions as previously described, with segments removed at 2-month intervals for an 8-month period [22]. As these samples had remained on the roof, additional segments were also taken at the commencement of this study, at which point the samples had experienced 25 months of exposure.

Sample preparation and analysis were carried out as described in Maric et al. [2]. The beamline is comprised of a Bruker Vertex V80v FTIR spectrometer equipped with a liquid nitrogen cooled narrow band mercury cadmium telluride (MCT) detector in conjunction with a Bruker Hyperion 2000 microscope (Bruker Optik GmbH, Ettlingen, Germany). Paint sections were mapped in transmission mode using a step size of 2.5 μm in the XY direction, with a 5 μm × 5 μm sampling aperture. Spectra were acquired over the range of 3900–730 cm^{-1} at a spectral resolution of 4 cm^{-1},

Table 1
List of ATR-IR spectrometers used for automotive clear coat analysis.

Manufacturer	Model	ATR crystal	Scans (n)	Software
Perkin Elmer	Spectrum 100 (FTIR 1)	Diamond-ZnSe	8	Perkin Elmer Spectrum 6.3.2
Perkin Elmer	Spectrum 100 (FTIR 2)	Diamond-ZnSe	8	Perkin Elmer Spectrum 10.03
Thermo-Fisher	Nicolet iS50	Diamond	64	Nicolet Omnic 9
Perkin Elmer	Spectrum 1	Diamond	8	Perkin Elmer Spectrum 5.01