IMPROVING THE INTERPRETATION OF THE EVIDENTIAL VALUE OF VEHICLE AND ARCHITECTURAL PAINT

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the degree of

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under the supervision of Distinguished Professor Claude Roux and Dr Philip Maynard

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

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Covid-19 Statement

The planning and writing of my thesis was disrupted by the Covid-19 global pandemic in a number of different ways. Firstly, my access to the laboratory and instruments was restricted due to the closuer of the university campus for a period of time. This meant I was unable to check the data that was collected during my research project or to run any additional statistical analysis that was needed.

As a result of the campus closure, I was forced to work entirely from home, which meant that I had to rely on the resources that were already set up at home. I did have to purchase a few additional software and computer accessories to help with the data viewing and writing of the thesis at home. All communication with my PhD supervisors was now via online Zoom meetings or emails only, this made it very difficult to get quick responses at times and to express or share any visual ideas. During the time that the campus and library was closed down, my access to resources and literature was very limited as any books and resources that I had access to previously at the university was not able to be accessed.

The impact of the Covid-19 global pandemic effected on my overall thesis with both my access to resources being restricted and my ability to focus on the writing of the thesis with such major global disaster stories and concern for the safety of family and friends both in Australia and overseas.

List of Publications and Presentations

Publications

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Abbreviations

MSP……Micro Spectrophotometry

FTIR……Fourier Transform Infrared Spectroscopy

µm……Micrometres

%……Percentage

UV……Ultraviolet

GC/MS……Gas Chromatography Mass Spectrometry

Py GC/MS……Pyrolysis Gas Chromatography Mass Spectrometry

CIE……Commission Internationale de l'Eclairage

PDQ……Paint Data Query

RMS……Roads and Maritime Services

NSW……New South Wales

TiO_2……Titanium Dioxide

nm……Nanometres

mm……Millimetres

cm……Centreimeters

s……Seconds

cm^{-1}……Number of Wavelength Per Unit Distance

C-H……Carbon Hydrogen Bond

CH_2 Scissor bond……..Carbon Hydrogen Bond Movement

SE……Secondary Electrons

BSE……Backscatter Electrons

ANOVA……Analysis of Variance

UVA……Ultraviolet Light Absorbers

HALS……Hindered Amine Light Stabiliser

UTS……University of Technology Sydney

Abstract

This research explores three separate routes to assist with the interpretation of the evidential value of vehicle and architectural paint.

The main questions that were answered with this research were:

- *Can the evaluation of the evidential value of paint evidence be improved with the addition of up-to-date surveys that can provide the forensic examiners and the investigators with more accurate data and add to the strength of the evaluation of the paint samples? Can the environmental weathering effects on the paint samples, generate additional acquired characteristics that can be used when comparing paint traces?*

1. Weathering can add acquired features that may increase the comparative value and discriminate paints that would not be otherwise (e.g. two paint samples of the same paint manufacture, colour and layer structure, but with slightly different chemical composition of the paint due to the changes that occur eith the different UV exosures).

2. Weathering can also add features that may differentiate paints that shiouldn't be differentitated (eg. If the trace specimen was collected a long time before the known source).

This would therefore improve the evidential value of the paint evidence, but it could potentially highlight the risk that false positives could be made in some cases as well. A potential risk that is possible in some paint cases, could be that paint samples have been found to be from the same manufacture and paint type, yet they are from different vehicles. The use of the added comparative feature that the weathering effects on the paint samples brings, will reduce and/or eliminate the false inclusion of a vehicle.

- *Can paint samples originating from the same vehicle, architectural structure or object be chemically differentiated as a result of the different impacts that weathering can have on the paint that is exposed to the sun and subjected to the damaging high UV concentrations, compared to the paint that is covered and will have little to no exposure to the same harmful weathering conditions?*

The answer to this last question will not only provide the forensic scientist with crucial source level evidence, but it may also offer more information as to what actually happened.

To help with the first question that was asked above, a survey was conducted on the most common colour of vehicles that were seen on the roads and a motorway within Western Sydney and another survey was carried out in five different carparks, also around Western Sydney, this second survey looked at the most common colours that were found on the stationary objects, such as on the pillars and wall. This data not only provided much needed up to date information but also more relevant data that to the Australian environment.

The next part of the research focused on the effects of weathering on the clear coat and other paint layers to not only identify but also help differentiate it from other paint sources. This was carried out with already weathered paint samples and also by preparing and weathering both vehicle an architectural paint samples in the Sydney, Australian climate. This study demonstrated that it is possible to not only differentiate between two paint sources that have be exposed to the natural climate, but even between different panels on the same vehicle. This could then provide the forensic scientist with enough information to allow them to report the paint evidence with an activity level weighting.

The next part of the research was then focused onto the weathering of architectural paint which was conducted on eight different paint samples from either oil or water-based formulations. These samples were exposed to the natural weathering climate in Sydney, Australia for up to 3 years. A number of the physical and chemical profiles were found to be altered by the effects of weathering.. There was unexpected and significant changes that were seen across all of the paint samples after a period of 12-months of weathering, more notable within the water-based samples. These unique weathering results are of great benefit to the forensic science community in that they add more characteristics that can be examined when assessing painted objects. None-the-less, it is also important to note that the changes in the paint that can occur due to weathering, may mislead the forensic scienist, particularly when evaluating a weathered questioned paint trace to a known paint trace that has not been weathered, even if they are the same type of paint but just have not been exposed to the same conditions.

Overall, the findings from this research study have provided supporting information that will assist in improving the evaluation of the evidential value of paint. Still future work will be needed to keep providing up to date information which should include additional and broader types of vehicle and architectural paint samples and should be exposed for longer or over different weathering periods and different climates.

Chapter 1: Introduction

1.1 Microtraces

Microtraces[1] are pivotal to the practice of forensic science because they are transferred as a result of interaction between objects and individuals. As a result, they often play a vital role in numerous cases, from the early investigative phases to the later corroborative stages and in the presentation of evidence at trial [1]. In practical terms, they are often found in the form of small amounts of chemicals, such as gunshot residue or explosives, that can remain on a suspect's hands or clothing. Or they can be in the form of other types of materials, such as fabric and glass [1]. They may be broken, torn, cut or it can even be separated during forcible interactions [2]. Similarly, vehicle parts can be bent during a crash, separating fragments of paint from the original substrate. As a result of these forcible interactions, it is possible that the materials that are transferred during such activities may be physically re-aligned with the original source [2]. These types of materials are often relatively small, microscopic in size but can offer information as to what may have occurred, where the sample may have come from, and how the materials may have transferred [2].

Margot describes the main object of forensic science as the "trace," which is "a pattern, a signal, or material transferred during an event. It is the remnant (the memory) of the source (identity—who, with what?) and of the activity (what, how, when, why) that produced it" [3]. Microtraces are *traces* in the forensic sense of this term. They may be transferred and may persist as explained by Locard: "*The truth is that none can act with the intensity induced by criminal activities without leaving multiple traces of his path. […] The clues I want to speak of here are of two kinds: Sometimes the perpetrator leaves traces at a scene by their actions; sometimes, alternatively, he/she picked up on their clothes or their body traces of their location or presence" [4].*

[1] The term 'trace evidence' is often widely used instead of 'microtraces' in literature, but I shall refrain from using 'trace evidence' because it wrongly uses the term trace to infer a size which is small, and it does not align with the forensic definition of trace [1].

There are three main aspects in Locard's definition: (i) the nature of the criminal activity influences the types of material that are exchanged, and how they are dispersed in the environment or taken by the offender; (ii) these materials, remnants of the activity, are the traces that become signs when detected, recognized, collected and measured; and (iii) an interpretation process, with the help of forensic science, aims at transforming them into clues in order to reconstruct what occurred [4].

Paint materials can be found as microtraces and are the topic of this doctoral research.

1.2 Paint microtraces

Forensic Scientists widely encounter paint, particularly working in the field of microtrace and its presence has considerable potential as a source of information for investigation and court [5]. Forensic Science examiners frequently encounter paint specimens in the laboratory, this type of microtrace can play an important role in many investigations and prosecutions [6]. Paint on its own has considerable potential as a source of forensic information, it has the means of establishing an association between people, places, or things [7]. Paint samples are often not pristine as they can be subjected to effects from the uncontrolled environment and the different collection methods [6]. The typical size of paint traces that have been left and often collected are small to minute in size or it may be only smears left by a car or painted object such as a toolbar/crowbar. Paint as microtraces can arises in a variety of different ways [8]. Paint can be recovered in many cases such as road accidents, burglaries, acts of vandalism and, in a more general way, in every situation where a painted object is involved in a criminal act [9]. In such situations where original paint from a vehicle is recovered, the make and model of the suspect car may be determined [10]. This has been made possible because the chemistry of the original factory undercoats is well established [10]. When a suspect vehicle/article has been found and the paint from the vehicle/article sampled, then a paint comparison can be undertaken with the paint collected from the scene [10]. Original undercoats can easily be discriminated by comparing the colour, layer sequence, and chemistry of the layers present [10]. However, it may be more difficult to distinguish the presence of original automotive topcoats as they often consist of a single layer and the chemicals that are used are often very similar [10].

The main aim of a paint examination for forensic scientists, is to evaluate the significance of the trace that is left behind and often to establish the degree of dissimilarity and similarity between a paint trace and a sample originating from a suspect (from a vehicle, the tools that

were used in the criminal act, etc.) [11]. The importance of vehicle, architectural surveys and other background information relating to the paint trace, comes into play when evaluating the importance of the paint trace and determining the right likelihood ratio and strength that can be applied. If only a questioned paint specimen is received, then the use of the databases such as the Paint Data Query (PDQ) and other databases can be used to help investigators learn about the type of vehicle or object the paint might have originated from [12]. The PDQ gathers information on the chemical and colour information on vehicle paints that can be used to search against questioned paint samples to assist in identification. If both questioned and known paints are submitted, then a comparison is the desired process [13].

1.3 Forensic examination of paint

There are several different analytical techniques that are used to characterise paint traces [14, 15], a few of these techniques are listed and explained below. The size of the paint sample, condition of the sample, and the particular information that is required from the evidence will guide the forensic examiner in choosing the correct scientific methods and techniques to employ for the physical and chemical analysis of the paint evidence [16]. The continuous advancements in the technology and the likely need to preserve the evidence will also play a role in determining the techniques that are utilised.

Generally, the sequence for the analytical examination of paint starts with general stereomicroscopy (to see if there is a physical fit between the questioned and known paint sample, recording the colour, the number of layers that are present and to undertake a simple visual comparison). Then light microscopy can be used (bright field, dark field, fluorescence), before moving onto the more technical and sometimes, destructive techniques such as Microspectrophotometry (MSP) followed by Fourier Transform Infrared spectroscopy (FTIR) and Raman spectroscopy. If available and required, pyrolysis gas chromatography with/without mass spectroscopy (Py-GC-MS) can be performed as well as elemental analysis using scanning electron microscopy coupled with energy dispersive x-ray spectrometry (SEM/EDS). X-ray fluorescence spectrometry (XRF) or other elemental techniques can also be utilised. A more general and indepth overview of some of these techniques is described below. Forensic laboratories will differ slightly in the techniques that are performed based on the type and amount of equipment available to them and the specific procedures that are implemented for that laboratory.

More information about paint chemistry and analytical tools is provided in the next section.

1.4 Paint

Paints (surface coatings) are materials that are applied to a variety of substrates like wood, paper, metals, and plastics. They are used in a variety of different ways and can be seen wherever you look on items all around. Paint can be defined as a fluid material which, when spread over a surface in a thin layer, will form a solid, cohesive, and adherent film [17]. The term paint describes a variety of materials including enamels, undercoats, varnishes and lacquers [18]. They generally have a dual role:

- to protect and,
- to decorate, the latter role includes the ability to disguise [19].

Paint systems are invariably multilayered, as adhesion to a substrate, anticorrosion properties, barrier effects, attainment of the required appearance and resistance to atmospheric degradation are difficult to attain from a single layer [19].Paint systems consist of several different components, although the general paint formulas usually consist of:

- Resin (binder)
- Pigments
- Solvents
- Additives

Resin (binder)

Resins are the film-forming components that characterises paint [20], it is the key element of any paint [21]. The resin provides adhesion and cohesion, keeping the pigment within the coating and ensuring that the paint remains attached to the substrate [19]. There are a variety of different resins and polymers that are used in paint, a few are listed and described below.

Oils and Oleoresinous Varnishes

The use of drying oils in paint formulations have declined over the years as the improvement of polymers that could be used for a broader variety of coatings have arisen. Oils are often used as modifying components in the preparation of oleoresinous varnishes and especially in the oil-modified alkyd resins [20].

Alkyd Resins

These resins are organic polyesters that are derived from a polybasic acid, a molecule with two or more acid groups and a polyhydric alcohol, a molecule with two or more hydroxyl groups [22]. Phthalic anhydride and glycerol are examples [22]. They are modified with several oils, including soya, linseed, dehydrated castor, and coconut. They are inexpensive and have a variety of properties [20].

Polyester Resins

These resins are typically used in heat-cured coatings that need to be high in paint solids and low in solvent content. These resins have extremely good colour retention that provides good over-bake protection and has very good UV resistance [20].

Acrylic Resins

Acrylic resins are available in solvent-based systems and as aqueous emulsions, are very versatile and popular for industrial and automotive liquid coatings. They provide toughness, good weathering ability, resistance to abrasion and chemical attack and are commonly used in acrylic emulsions. Also, they are considered to be better for their gloss retention than alkyd resins [20]. Plastic substrates are a growing market for acrylic coatings, especially since there are now more grades of acrylic polymers that are soluble in solvents that do not attack the plastic. The type of solvents includes ethanol, isopropanol, naphtha, and straight-chain hydrocarbons [20]. The resin systems are usually low to medium molecular weight homopolymers and copolymers of ethyl and n-butyl methacrylate [20].

Amino Resins

These resins are typically used in heat-cured coatings that need to be high in paint solids and low in solvent content. These resins have extremely good colour retention that provides good over-bake protection and has very good UV resistance [20].

Epoxy Resins

These resins are known for their excellent corrosion and chemical resistance. Due to their tendency to fade and chalk when exposed to sunlight, they are primarily used for interior topcoat applications or as a primer for exteriors applications [20].

Urethane Resins

Urethane resins are very popular as they provide a combination of chemical resistance, toughness, abrasion resistance, and exterior durability. Their effective application on plastics has led to a substantial growth in urethane technology [20].

Pigments

The pigment is intended to control only two major properties of paint: colour and opacity [21]. It does however provide a number of ancillary influences, such as anti-corrosive properties and it can also influence the weatherability of a paint, as well as its more general durability such as alkali resistance [21]. They may be made from inorganic or organic materials; organic pigments are mainly used for decoration purposes, while the inorganic material have traditionally been added for their protective properties [20]. The size and shape of the pigment particles are important factors as they can affect the agglomeration or packing within the paint binder or matrix [20]. The size of the particles also affects the finished gloss, settling of the pigment during storage, and wetting by the binder [20]. A wide variety of colouring agents can be added to provide a considerable wide range of colours and shades. The most common pigments are:

- White
- Yellow
- Red
- Green
- Blue
- Black, and
- Metallic powder

Solvents

A solvent is a pure or mixed liquid that is utilised to make the paint flowable prior to its application, they make it possible to process, apply, clean or separate materials [20]. The solvent system is required to perform only one basic function; to enable the paint to be satisfactorily applied [21]. They are present to aid manufacture and application, but are lost from the paint coating during application and the subsequent period of curing [19]. Nonetheless, The selection of a solvent type can effect a number of other properties of the paint [21].

Additives

The term ‘additives’ covers a wide range of ancillary raw materials used in the formulation of a paint. They are added to paint, usually in small quantities, to achieve the special and desired effects [20]. Additives can affect the material characteristics and the finished film properties of the paint [20]. They can vary from extender pigments to anti-skinning agents, fungicides and other materials which are used in minor quantities [21]. The properties that can be adjusted with paint additives include viscosity, foaming, skinning, pigment dispersion, stability, flexibility/hardness, gloss, UV resistance, fire resistance, bacteria resistance, and many more [20]. Over the recent years the increased use of UV blockers and other additives that can prevent or slow down the harmful effects of weathering on the paint systems, have be developed and used within the paint industry. The type of UV blockers that are used can be separated into two groups based on their chemistry: UV absorbers (UVAs) and Hindered Amine Light Stabilisers (HALS). With more research and study into the area of weathering and degradation of paint, more advancements and changes are occurring

1.5 Vehicle paint

The typical layer system of vehicle paint is applied using several layers to a total thickness of around 100 µm(0.1mm). The application of these paint layers requires proper preparation to ensure adequate application. Normally a basecoat layer, then the coloured layer is applied after the primer paint is put down. To help ensure the basecoat layer and overall desired appearance of the paint is met and maintained, a clearcoat layer is applied that forms a glossy and transparent coating. The clear coat layer of a paint system is typically around 40 µm thick and frequently contains UV absorbers such as ultraviolet light absorbers (UVAs) and hindered amine light stabilisers (HALS) that are designed to protect the colour coat and underlying layers from degradation. Two classes of UV absorbers that are generally added to the clear coats are: 2-hydroxyphenyl-s-triazines, and 2-hydroxyphenylbenzotriazoles [23]. Aside from giving the important benefit of the increased resistance to weathering, the clear coat layer also provides the underlying paint with the added benefit of gloss appearance, hardness, the physical protection from road debris and also resistance to attack from solvents and chemicals [19].

1.6 Architectural Paint

The term architectural paint involves any paint that imparts colour and/or protection to a surface on and inside a building [13]. This type of paint comprises of a resin, colour, extender

pigments and solvent, and can be applied by either a brush, roller, or spray device. The type of solvent used is important as they have a key function that involves keeping the film-forming resins, pigments, and other additives in liquid form so as the paint can be easily applied [13]. The choice of solvent depends on the resin and the type of application that is used to apply the paint [19]. The role of the colour and extender pigments are to add colour and bulk to the paint, they also provide the overall desired quality of the paint [13]. However, not all paints contain pigments, such is the case with colourless paint. The type of coloured pigments can be divided into; organic and inorganic pigments, they both can add different properties to the paint system and therefore the choice between the two is dependent on the application and desired effect that is required. Extender pigments are not only added to bulk up the volume of the paint, but they can change the properties of the paint [13]. The common types of extenders that are used include calcium, magnesium, calcium carbonate, magnesium silicate, aluminium silicate, potassium aluminium silicate, amorphous silicas, and calcium silicate.

The resin component of architectural paints provide the overall resistance and the physical properties [13]. The ratio of resin to pigment affects the gloss of the coating: the higher the proportion the higher the gloss of the paint [13]. The types of resins that are used in architectural paints include acrylic, alkyds, urethane, vinyl resins, styrene-butadiene, and epoxy. Again, the impact of the increased regulations and the environmental bearing of the paints are driving a change from oil-based to more water-based paints that have fewer toxic effects. The use of toxic heavy metals such as lead, which was used for many years, have also been phased out over the years. The big enhancement regarding the increased weatherability of exterior paints has also be a focal point for many paint manufactures, this has correspondingly driven large research and development into the field of paint manufacture and durability including the overall performance of these paints in different climates.

1.7 Paint Examination

Stereomicroscopy and light microscopy

The very first part of any paint examination, in most cases, should be the documentation of the physical characteristics, followed by an attempt to demonstrate a jigsaw fit of the edges or a fit of any surface striations between the questioned and known samples before moving onto any chemical testing [6]. This first preliminary examination is generally performed by magnification of 5-40 X on a stereomicroscope to observe the overall appearance of the sample

and to ascertain that it is in fact a paint item that is submitted for analysis and/or comparison [15]. The typical features that are noted when using this type of technique is the overall colour of the paint, if there are any irregularities on the surface of the paint, the general layer structure that is present and to take the measurement of the paint thickness. If there are any unexplained differences between the known and the questioned paint sample that are noted during this initial stage, then they can be ruled out has having a common source [13].

If more analysis of the paint is needed after the first optical stage, then polarized light microscopy can be used to allow for more a detailed examination of the paint's colour, any visual effects present in the sample, and the extender pigments [13]. Florescence microscopy using bright and dark field illumination of the paint samples can provide further features to examine, such as characterization of the pigments and additives, and these are often viewed at a higher magnification and with excitation wavelength of 365nm [15].

Microspectrophotometry (MSP)

Colour is one of the most important characteristics of paint. One of the first steps that is undertaken in forensic investigation is the determination and comparison of colour [24]. As forensic paint samples are frequently small, it is often difficult to determine the colour by eye. MSP allows for an objective measurement of colour, as opposed to the subjective results of visual colour comparison [24]. Microspectrophotometry colour measurements of the paint samples are measured in reflectance or transmittance mode to calculate the tristimulus values or the CIE colour coordinates [25]. The results are then evaluated by a spectral comparison or by using the colour differences in CIELAB units [25]. The main advantage of this technique is that it offers a non-destructive approach to the characterisation of vehicle and architectural paint in forensic examination [26, 27].

The colour measurements from different areas of an object change as a result of the environmental conditions such as exposure to certain chemicals and ultraviolet radiation [15]. Vehicles can be discriminated based on the varying decrease of UV-absorbance concentration over time [15]. This idea has been hypothesised by several previous studies and authors, its proof was tested and demonstrated in chapter 4

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectrometry is routinely employed in paint examinations [11, 28-30]. It is probably the most utilised method for pigment identification in forensic laboratories [31]. It is one of the

most encountered instruments in forensic laboratories and can be used in a variety of different evidence types. It is sensitive to molecular structure, therefore, can provide rich information on the chemical composition of a paint sample (i.e. resins, fillers and main inorganic pigments present) [24]. It can also provide molecular structure information on both organic and inorganic constituents of multicomponent mixtures such as paint layers.

Samples can be directly analysed on a cross-section of the paint chip, which is embedded in a resin, or without prior separation of the paint layers if the reflection technique is being used. When evaluating the FTIR spectra, the important aspects of comparison are the location, relative intensity, and shape of the absorption bands [13]. The chemical changes that can occur with UV degradation due to weathering can also be monitored by FTIR and used in the comparison of paints [15]. This technique was utilised in the weathering and clear coat research. FTIR spectroscopy can be applied both, to help identify probable sources of paint through use of databases, such as PDQ database, and to comparing samples from different sources to determine if they have a common origin [30].

FTIR spectroscopy can be applied both to help identify possible sources of paint through use of databases, such as the Paint Data Query (PDQ) database, which was developed by forensic scientists in Canada and used all over the world to provide forensic scientists with an up-to-date library of the chemical composition and variety of different paint samples. FTIR is very useful in comparing samples taken from different sources to determine if they have a common origin [30]. Samples can be directly analysed on a cross-section of the paint chip [24], without prior separation of the paint if the reflection technique is being used [11]. The paint samples can be analysed without destructive preparation or if required they can be sampled and sandwiched in mounted medium that can allow for very thin cross sections of the paint to be taken. These thin cross sections can then be viewed under the microscope, figure 1 below, and the thin layers of the paint can be analysed separately.

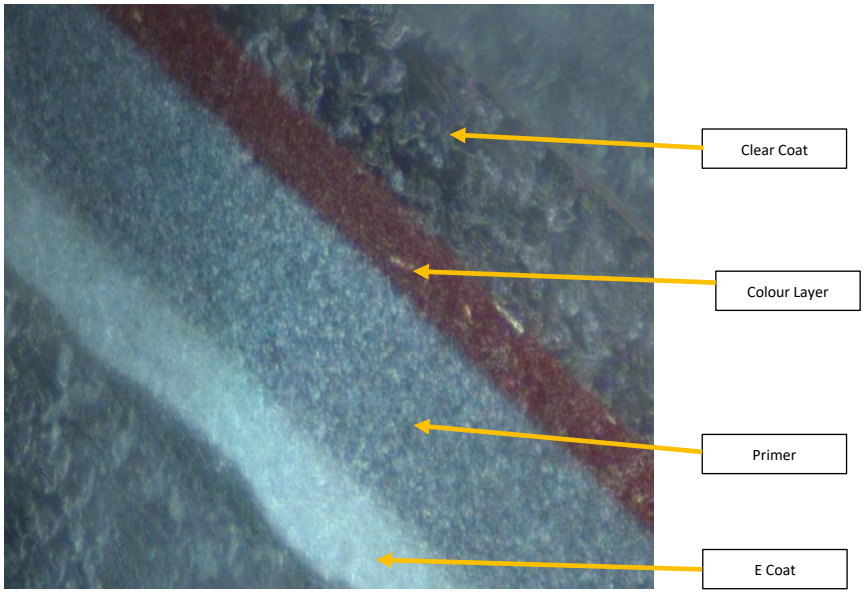


Figure 1:Visual layer structure of vehicle paint viewed under a stereomicroscope at 30 x magnification

Raman Spectroscopy

The theory of Raman spectroscopy has been around since the 1920's, however, only in the past few decades has it become a reliable and commercially available instrument [11]. Raman spectroscopy has been applied in many paint examinations to inform the user about the pigment content of the examined samples and in many cases it can assist in identifying any differentiation between paint samples that are of the same colour [24]. It is a complementary technique to IR spectroscopy and can be used in the identification of the main organic or inorganic pigments that are present in a paint sample [15]. Raman spectroscopy provides reliable and detailed information about the pigments [11, 32-37]. The benefit of pigment identification is that it can provide a fast initial screening of the trace (faster than infrared spectroscopy) or it can potentially provide additional evidentiary significance to the comparison of two paints in a full analysis [31]. This analytical technique is fast becoming a widely accepted tool in the examination of paint traces within forensic laboratories and is the focus of several recent research topics.

The drawback of using this technique is that it can sometimes make meaningful analysis of the spectrum difficult [11]. This is mainly linked to an intense background signal [31]. The Raman instrumentation measures the inelastic scattering of light, depending on the vibrational modes of non-polar bonds of a molecule when excited by an intensive light source to the fluorescence effects, sample heating leading to thermal degradation, or even pyrolysis, or photochemical reactions [11]. The fluorescence effects may often be lessened by changing the wavelength of

the laser, photobleaching the sample or utilisation of metal colloids (surface enhanced resonance Raman spectroscopy techniques) [11]. There are several different laser wavelengths that are available for Raman depending on the type of instrument that is to be used and the colour of the pigment that is to be analysed. For example: The near IR lasers are useful for the analysis of red, orange, yellow, brown, and violet pigments and the visible lasers can be applied for the detection of blue and green pigments [15].

Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS)

Analytical pyrolysis has been used by forensic scientists since the early 1970s to characterise a wide range of traces from the crime scene evidence [38]. The pyrolysis products of a sample are detected and identified by coupling the pyrolysis unit to a gas chromatography or a mass spectrometer or a combination of both [38]. The mixture is further analysed by the MS component which results in a signal displayed as the total ion chromatograph (TIC). This chromatogram is then used to compare between the questioned and known paint specimens [13]. Py-GC/MS generally gives good discrimination, involves minimal sample manipulation and generates reliable, reproducible results, and is able to detect very small quantities of material [38]. It is often used to examine the polymeric portion of paint by thermally degrading the polymer resulting in a complex mixture which is then separated by the GC component [13]. Py-GC/MS is usually the preferred method for analysis, as the data that it provides a reliable identification and comparison of the analytes, the results are easy to interpret, and the technique is very cost effective [38]. Other benefits of this technique is that it commonly offers good discrimination, involves minimal manipulation of the sample, generates reliable and reproducible results and it is able to work with very small quantities of material [38].

Py-GC/MS is a valuable technique in the forensic examination of paint that is often promoted for its ability to differentiate and identify paint samples that are indistinguishable by FTIR spectroscopy [39, 40]. It has been shown with previous research to be capable of categorising clear coats through library searching of the chromatogram and spectra or by visual inspection alone [41]. This technique can also provide additional information about additives and impurities in a sample [15]. However, not all forensic laboratories utilise this technique, as it can often be a time-consuming process and difficult with smaller sample-size. It is a destructive technique and therefore other techniques should be considered before its use.

Scanning Electron Microscopy/ Energy Dispersive Spectrometer (SEM/EDS) and X-Ray Fluorescence Spectrometry (XRF)

These two scientific techniques are used in the determination and comparison of the elemental composition of a specimen. They are both the methods of choice for the identification of inorganic components of pigments and extenders, however XRF is more sensitive to lower atomic weight elements commonly found in extenders [15]. Although organic pigments cannot be identified, their presence can be indicated by the presence of some elements such as chlorine, bromine, nickel, manganese, and copper [15].

For SEM/EDS, paint samples can be analysed by either secondary (SE) or backscatter electrons (BSE). They can provide general information of the morphology and the layer structure of the paint specimen. The advantage of SEM/EDS is that even very small paint samples, often too small for other analytical techniques, can be analysed [15]. However, caution must be given as the paint that is being analysed might not be a true accurate representative sample of all the pigments contained in the whole paint item [50]. It is advised that the microtome sections be carbon coated to prevent electrical charging of the sample during the analysis [15].

1.8 The degradation mechanisms of paint

The degradation of paint can occur as a result of a number of factors. Some of these can include:

- The poor preparation and/ or application of the paint to the substrate.
- Atmospheric effects.
- The structural defects that maybe present in the paint film.
- The stresses that can occur between the bond and the substrate.
- And corrosion [42].

The types of failures of paint coatings, typically of surface preparation and application problems can include:

- Cracking, chalking and alligatoring,
- Peeling, flaking and delamination,
- Rusting,
- Lifting and wrinkling,

- Failures around the weld areas,
- Edge failures
- And pinholing [42].

The primary factors aiding in degradation are thermal, mechanical, radiant, and chemical in nature [42]. The method of degradation can involve depolymerization, generally triggeredby heating, splitting out of constituents in the polymer, chain scission, crosslinking,oxidation, and hydrolysis [42]. The most damaging weather component for paint, is the exposure to ultraviolet (UV) radiation. This exposure can cause embrittlement, fading, surface cracking, and chalking. After the direct exposure to sunlight for a period of years, most polymers and paints will exhibit reduced impact resistance, lower overall performance, and a change in their appearance [42].

1.9 Evaluation and Reporting of Paint Evidence

The crucial objective that the forensic scientist brings to any case is the interpretation of the trace observations. This step is often referred to as "evaluation"[43]. Experience of the forensic scientist is very important, however the scientist should, as far as possible, be able to rationalise the opinion that is presented [43]. It is also important that the forensic scientist communicate their findings effectively [43].

Evaluative reporting is one of the most widely used approaches to assist in the correct assessment of forensic evidence and it is a useful way to deal with uncertainty and provides a balanced approach to interpretation [44]. This approach relies on the Bayesian model that deals with the presentation of the probability theory to reasoning under uncertainty [45]. The model reveals the vital importance of the likelihood ratio, the formulation of which crystallises three key rules for the interpretation of forensic science evidence:

1. Interpretation of scientific evidence is carried out within a framework of circumstances. The interpretation depends on the structure and content of the framework.
2. Interpretation is only meaningful when two or more competing propositions are addressed.
3. The role of the forensic scientist is to consider the probability of the evidence given the propositions that are addressed [43].

Adherence to these rules will serve to promote logical reasoning and clarity of thought [43].

In this approach, it is vital to consider the probability of the evidence given each of the two propositions [43]. In general, the prosecution's proposition (Hp) is the explanation that is put forward by the prosecution and the defence's proposition (Hd) in the explanation that is put forward by the defence. It is widely accepted that the forensic scientist should consider at least a pair of competing hypotheses, in the context habitually denoted Hp and Hd, to illustrate their findings given the facts relating to the case [45]. The Likehood Ratio (LR) is the ratio of the probabilities of the scientific evidence (E) given the two opposing propositions and any relevant other information (I) [46].

When calculating the likelihood ratio there is always a numerator and a denominator. The numerator is variable relative to the transfer and persistence trends. The denominator is highly dependent on how likely it is to find the similar results by chance. If the forensic scientist deems the evidence to be more plausible given the prosecution proposition is true than if the defence proposition is true then the prosecution proposition will be supported [43].Or it can be the other way around. In both cases the extent of the support depends on the magnitude of the likelihood ratio [43]. The level of support that is offered for one proposition over the other will vary depends on the amount and type of information that is present.

$$LR = \frac{Pr(E/ Hp, I)}{Pr(E/ Hd, I)}$$

The likelihood ratio, is based on interpretation of obtained data in the context of two contrasting hypotheses, i.e.: Hp mostly associated with prosecutor, who typically states that the collected specimen (trace) and the comparison sample come from the same object, and the alternative hypothesis, Hd, which describes the defence statement that the collected specimen comes from some other sources [47]. The support given for one proposition over another will vary given the amount of information that is present. Calculation of LR values allows obtaining information which hypothesis is supported by the data and suggests how strong this support is. If the probability of the findings favours the prosecution's proposition, the likelihood ratio will be greater than one. On the other hand, if the probability of the findings favours the defence's proposition, the likelihood ratio will be less than one [44]. It is important to note that a neutral result is not the same as inconclusive, an LR of 1 simply means that the probabilities of both propositions are both equal [44]. The evidence neither supports either proposition [46]. An advantage of the LR approach is taking into consideration possible sources of uncertainty like within-object variability related to e.g. inhomogeneity of the analysed sample as well as between-object variability, which takes into

account the information about variation of measurements of characteristics between various samples in the relevant population.
When interpreting paint evidence, the paint, the number of layers, the colour of the paint layers and the chemical composition of the paint are all taken into consideration [46]. The data that was collected in survey 1 that is presented in Chapter 2, can be used when calculating the likelihood ratio at the source level. For example, if paint from a vehicle that was used in robbery was transferred to a carpark pillar that was located outside the shop. Then if a vehicle that was suspected of being used in the robbery was later seized and paint samples from the car were taken and sent for forensic analysis with the paint that was colled from the carpark pillar. The resulting paint analysis showed that the paint collected from the carpark pillar is in agreement with the paint collected from the suspected vehicle. In order to fairly assess the evidence and calculate the likelihood ration, we need to consider both the prosecution's and defence's view. The prosecution's view is that the paint on the stationary post is from the suspect vehicle. The defence's view is that the paint on the stationary post is not from the suspect vehicle but from some other unrelated painted object.

The colour of the suspected vehicle and the paint collected from the pillar was orange, then using the results from survey 1, a greater strength can be placed on the interpretation of the paint evidence due to a lower likelihood that orange paint transfer would be found by chance on such surfaces. On the other hand if the paint transfers were blue in colour, the evidential value would be lower due to a higher chance of blue paint transfer being found by chance. However, neither the shade nor the chemical composition of the paint is taken into consideration with this case example. If this is known then the evidential value of the paints may be increased. Nevertheless, the results from this survey provide the examiner with valuable data that can be used to assist in determining the evidential value of paint evidence in certain circumstances.

The interpretation of the evidence is highly dependent on the questions that are being asked, and that these questions can exist at different levels. The hierarchy of proposition has been developed to better formalised the levels of the questions. The hierarchy of propositions is the level at which the propositions (hypotheses) are aimed [46]. These hypotheses are formulated from the case information that are provided and are mutually exclusive in the context of the case, they cannot occur at the same time, and can be modified or refined once new

information is obtained throughout the case developments [44]. The highest level in this hierarchy is the offence level, which addresses the guilt or innocence of the suspect [44].

. The hierarchy of propositions is the level at which the propositions (hypotheses) are aimed [46]. These hypotheses are formulated from the case information that are provided and are mutually exclusive in the context of the case, they cannot occur at the same time, and can be modified or refined once new information is obtained throughout the case developments [44]. The highest level in this hierarchy is the offence level, which addresses the guilt or innocence of the suspect [44]. This is for the courts to decide, not for the forensic scientist to determine [46]. Below this sits activity level, where propositions focus on how the evidence arose. Source level propositions centres on where the evidence came from. Activity level propositions look at how the evidence came about. An example of this is the foreign paint that was found on the suspect's crowbar got there due to the them prying open the door that was painted [46]. Source level propositions are concerned with what was the source of the paint evidence and not about how it got there. For example, the sample of paint that was taken from the scene matches that from a suspect's vehicle [46]. The development of the hierarchy propositions will vary depending on the type of evidence and what is the main goal [46]. For most evidence types, propositions are derived at source level, although, in paint evidence, activity level propositions may be obtained [46]. Forensic scientists typically report on source level propositions, however, they may find that activity level propositions are more appropriate in some cases [44, 46].

Forensic scientists most often report on source level propositions (where did the paint trace come from, what vehicle or tool?), but they may also find that activity level (how did the paint trace get there, resulting from what action?) propositions are more relevant in some cases [44]. As the propositions will necessarily change between the two levels, the assessment of the probabilities of the findings will change, potentially resulting in different strengths of the findings between activity and source level [44]. A paint related example of hierarchy propositions would be, the finding of consistent ten-layered, multi-coloured paint fragments between two paint sources would provide a much higher level of support for a common source level than finding of single-layered white paint fragments [44].

Evaluative reporting utilizes the forensic scientist's own knowledge and experience combined with the available, and relevant information to correctly evaluate the probability of the findings in light of two competing propositions that are formed to overall aid the Court [44]. It highlights

the clear path of logic that was undertaken by the forensic scientist in order to form their conclusion, and this transparency of thinking aids not only the forensic scientist but also helps the court in following and evaluating the expert's testimony. [44].

The forensic scientists would normally prepare a report to support the justifications for their final decision. The report would explain the whole process, including the information that was received regarding the evidence and the methods that were used to form the propositions, the available case items, the analyses that carried out on them, any observations that were made, the methods of evaluation and the conclusions drawn from it. Any assumptions that are made during the evaluative processes should be made clear in the report [44].

When documenting the analyses and reporting the results it is important that the forensic scientist conveys the nature of the information that was used to evaluate the findings of the report. The information that is used to evaluate the paint evidence may include the results of the empirical research, databases, surveys that have been conducted or the forensic scientist's own experience and knowledge [44].

The research that was conducted and presented here, helps to fill the gaps, as detailed in the section below, in the background information relating to vehicle and architectural paint. The gaps include having little to no up-to-date data that can be used by the forensic scientist when evaluating the paint traces, also, a lot of the data that has been collected already has been from a number of different countries, where the colour and types of vehicles and paint may differ which could affect the evidential value calculations that the forensic scientist may use when reporting the results of their finding. Also, the conducting of the natural weathering studies has helped to improve the calculation and understanding of the evidential value of both vehicle and architectural paint by identifying the changes that can occur to paint due to exposure to the climate and how these changes can be used to help identify and compare paint traces in a forensic examination. The key reasons behind the need for the surveys and research are identified below and the main aims and objectives are listed and made clear.

1.10 The Current Challenges with Paint Analysis

Even with the advancements and implementation of new technology, the interpretation and evaluation of routine paint analysis still remains problematic for forensic scientists [7]. Potential limitations and issues that may arise when determining the correct evidential value of paint evidence can be linked to the lack of empirical data that are necessary to achieve the

evaluative step. This lack of data for many areas of forensic science was central to the criticisms in the 2009 National Academy of Science (NAS) report on forensic science [48]. The surveys and weathering studies that were conducted with this research, help to improve the forensic evaluation of the paint traces by adding more up-to-date data and more importantly, data that is more relevant to the Australian statistics. In order to determine the probability of the paint evidence at the activity level, studies on the background, transfer and persistence of paint, like those that are presented in chapter 2, are needed [46]. The natural weathering studies that were conducted in the Sydney, Australian environment, not only identify the chemical and physical changes that occur to vehicle and architectural paint, but it helped demonstrate that these acquired additional characteristic changes could be used when comparing paint traces to improve the overall strength and evaluation of the evidential value of the paint.

Over the past 20 years there have been a number of surveys published on vehicle colours, largely from the United States and Canada. A survey published by McDermott et al. [49], which was undertaken in Ireland, examined at not only the colours of the vehicles, but also noted the damage that was observed and explored the use of this data within forensic paint interpretation. Despite this work and that of which has been conducted by others [5, 39, 50-53], there have been no published vehicle paint surveys that have been conducted within Australia, and notably, there are limited data published worldwide on the specific presence of vehicle paint that has been transferred onto stationary objects. This important and key background information is currently lacking and no such survey data available that has been collected from within Australia. This is the main motivation behind the development and implementation of the two surveys that are presented in chapter 2, it was envisioned that they would help to improve and allow for more relevant data to be utlised when evaluating the paint cases.

Moving on to the research regarding the weathering of vehicle paint, previous forensic centred research has focused on the ability to discriminate the clear coat layers based on the polymer chemistry. A few forensic research papers have analysed clear coat samples using Microspectrophotometry (MSP) and Fourier Transform Infrared Spectroscopy (FTIR), looking for both; the type of UV screening chemicals that are used, and also the photo-oxidation index, to help discriminate between the samples. Even though some of the researchers considered the possible effects of ageing due to weathering of the clear coat layer, they did not fully consider the benefit that it could have on the evidential value when analysing the UV screening chemical profiles within the clear coat layer. This was explored for the clear coat layer of different types

of vehicle paints, including paint samples that were taken from both covered and uncovered areas on the vehicle, the findings and possible forensic implications are presented in chapter 3.

With regard to architectural paint research, previous studies that were focus on the discrimination of architectural paint have been conducted on fresh and unweathered paint samples. A number of these studies mentioned the need to assess the impact that ageing will have on the architectural samples. It has been hypothesised that the effects of weathering will change the chemical profile of architectural paint samples and that it may provide a changed and unique pattern that will allow them to be further distinguished from other architectural paint samples. This theory and the lacking information in this area have been addressed and is covered in chapter 4.

1.11 Aims and Objectives the Research Project

The aims and objectives of this research project are:

- To provide more geographically relevant and up to-date data relating to vehicle paint colours, and.
- To investigate how the natural climate can create additional acquired characteristics that can be utilised when assessing and evaluating the evidential value of both vehicle and architectural paint.

These above aims are the central foundations of this thesis, with each chapter introducing the background and presenting the research that was conducted to help achieve these aims. We begin this accomplishment with chapter 1 which gives a brief background and understanding of vehicle and architectural paint, followed by discussion of some of the most widely used forensic analysis techniques and evaluation of paint traces as well as the current challenges with paint evidence.

The second chapter is centred around the two surveys that were performed on vehicle paint colours on the roads and also on stationary objects and walls within the Sydney, Australia region. The information collected from these two surveys helps to satisfy one of the first aims of the project, by not only providing recently updated information but also more relevant data relating to the Australian location. The data from these surveys can therefore be used to improve the evaluation of the evidential value of paint traces, especially in the Australian climate.

In the remaining chapters, chapter 3 looks at the weathering effect on the clear coat layer and if vehicles can be identified by the weathering profile that is created with the different weathering exposures. This clear coat research helps to answer the second aim of the project and provides additional characteristics that can be evaluated and compared which will also lead to improved interpretation of the evidential value of the paint evidence. To help back up the vital results from the clear coat and other weathering studies, an intra-sample variation study was developed and undertaken to help show that any variations in the analysis of the paint samples was due to the effects of weathering degradation and not because of the internal variations with the different areas that were sampled.

Chapter 4 focuses on the natural weathering changes that can occur to water-based and oil-based white architectural paint over a three-year period in the Sydney metropolitan, Australian climate. The results from this study were evaluated and assessed for the forensic implications that these changes may have on the paint traces and consequently on the interpretation of the evidence and ultimately on the evaluation of the evidential value of the paint. The added information that these natural weathering studies have produced can provide the forensic scientist with more unique characteristics that can be compared and assessed and can ultimately increase the strength of evidence when comparing two paint samples.

The final two chapters of this project summarise and evaluate the findings of the background surveys and weathering studies, with a recap on how they help to improve the interpretation of the evidential value of paint. The final section of Chapter 6 outlines the need for further work and highlights any gaps that may still be present in paint research.

Chapter 2: Surveys of Vehicle Colour Frequency and the Transfer of Vehicle Paints to Stationary Objects in Sydney, Australia

The work described in this chapter was published in Forensic Science International: *Jackson F, Buford J, Maynard P, Roux C. Surveys of vehicle colour frequency and the transfer of vehicle paints to stationary objects in Sydney, Australia. Forensic Science International. 2015; 248: 124-128.*

2.1 Abstract

The interpretation of vehicle paint evidence in forensic casework hinges on several factors including the type of paint, colour, number of layers, and background information. Vehicle colour surveys are an important source of information for the forensic paint examiner when interpreting the level of significance of a paint transfer between vehicles involved in a collision or smears of vehicle paint left at the scene. The two surveys that are to be presented investigated (i) the frequency of the colour of vehicles observed on both a motorway and suburban roads in Western Sydney and (ii) the frequency of different vehicle paint colours transferred to car park pillars and walls from five different car parks within North West Sydney, Australia.

In the first survey, the highest frequency of vehicle colours recorded were white, grey, black, and blue. The second survey resulted in very similar findings with the four most seen colours across the five car parks being blue, white, red, and silver. The results in the second survey consider the potential for anomalies within the data due to the use of painted service vehicles used within the car parks, such as trolleys and trailers. Interestingly, the results from both surveys were very similar to previous vehicle colour surveys that have been conducted and corresponded to the vehicle colour registration data obtained from the NSW Roads and Maritime Service (RMS) website. The results from these two surveys provide up to date statistics that can provide the forensic paint examiner with valuable background data when assessing the significance of vehicle paint micro traces in casework.

2.2 Introduction

The work that is presented in this chapter not only adds valuable background data relating to vehicle paint, which was highlighted in the previous chapter as much needed, but it also provides a good foundation to the forensic evaluation of the evidential value of paint evidence. This chapter as well as the chapters following, help to improve and enhance the evaluation of the evidential value of paint analysis, which is the end goal of this research study.

Crime scene examiners frequently encounter paint specimens during casework, these can often play important roles in investigations and prosecutions [6]. Paint has considerable potential as a source of evidence as a means of establishing association between people, places or things [7]. Traces of paint can be recovered in many cases such as road accidents, burglaries, acts of vandalism and, in a more general way, in every situation where a painted object is involved in a criminal action [9]. The interpretation of transferred paint findings however, remains problematic for forensic scientists [7]. Potential limitations and issues that may arise when determining the accurate evidential value of paint evidence have been identified and raised in previous research and a number of reports [7, 13, 51, 54]. It is through increasing the knowledge and data relating to paint evidence with the help of surveys and conducting research, that these concerns and issues can be resolved. This was the main idea and basis for conducting these surveys, as they would not only provide more up to date data, but they would also contain more relevant statistics of the occurrences in the Australian climate that can be used when evaluating the value of vehicle paint evidence and allow for the correct understanding and outcome of the evidence to be made by the courts.

Foreign paint on a surface can be used for investigations and court proceedings as it can indicate to a greater or lesser degree of certainty that contact of some kind had occurred between the surfaces in question [7]. For paint transfer to occur, there are two related requirements: proximity and an action of some kind [7]. If a vehicle hits a stationary object with enough force, paint from the vehicle will be transferred to the stationary object. A transfer of paint from the stationary object to the vehicle may also occur. If both transfers occur this is called a two-way transfer and can be of high evidential significance. The paint that is transferred can be examined and compared to discriminate and evaluate if similarities are identified. This is the main objective of most vehicle paint examinations carried out in a forensic laboratory. As stated by Holden [54], the evidential value of paint depends on such

factors as type of paint, unusual pigments and the probability of another vehicle of the same colour/model being at the scene at the same time as the suspect vehicle.

Let us suppose that a vehicle was involved in the ram raid of a shop front. During this ram raid, paint from the vehicle was transferred onto a stationary post located outside the shop. A vehicle suspected of being used in this incident was later seized by police and paint trace taken from the vehicle and the stationary post was collected for forensic analysis. Results show that the paint collected from the stationary post is not differentiable from the paint collected from the suspected vehicle. To fairly assess the evidence, we need to consider both the prosecution's and defence's view. The prosecution's view is that the paint on the stationary post is from the suspected vehicle. The defence's view is that the paint on the stationary post is not from the suspected vehicle but from some other vehicle. These two opposing views of the evidence are used when assessing the evaluation of the evidence and are commonly used to determine the likelihood ratio that are commonly utilised within the courts. To assist with the forensic interpretation of this type of evidence, these two surveys aim to examine the background frequency of vehicle paint colours on the road and also on stationary objects. This will provide forensic experts with the data to better evaluate the eventual value of the evidence of motor vehicle paint cases.

Over the past 20 years there have been a number of surveys published on vehicle colours from the United States and Canada [50, 52, 55]. A survey published by McDermott et al. [49], undertaken in Ireland, examined at not only vehicle colours but also noted damage to the vehicles and investigated the use of this data in forensic paint interpretation. Despite this, there is no published survey conducted within Australia and limited data published on the specific presence of vehicle paint that has been transferred onto stationary objects. This type of background information on vehicle paint colours is currently lacking, with no such data available within Australia.

2.3 Method

The first survey, (i), was conducted on both a busy motorway and a suburban road in Western Sydney counting the colour of passing vehicles. To assist with the survey, a mobile application was developed that could be downloaded and readily used on iPhone/iPads or other smart devices. The application listed a chosen set of vehicle paint colours, Figure 2, that were based

on the colours used in the survey by McDermott et al. [49]. This would allow for the findings from this survey to be easily compared to that in McDermott et al.



Figure 2:Colour counter application and chosen colours for survey (i)

The survey was undertaken using the chosen application and counting passing vehicles on the motorway and suburban road within an hour timeframe. Cars, Utility vehicles and vans were included in the survey, but trucks, public transport or emergency vehicles were excluded. The results that were collected during the survey were emailed via the application and results collated for the overall survey.

The second survey, (ii), conducted on vehicle paint colours left on car park pillars and bollards was undertaken in the North West region of Sydney involving a total of five car parks. Permission was sought from the car park owners before conducting the surveys. The surveys were conducted early in the morning and finishing before 10 am, when traffic in the car parks would be at a minimum. Yellow safety vests were worn while performing the surveys to reduce the risk of injury and accidents occurring in the car parks. The surveys were undertaken with the assistance of a qualified forensic paint examiner.

The survey was performed using the same colour counter application as for the first survey; however, a few additional colours were added to the application to increase the overall colour range. A rubber classification was added to allow for differentiation of black paint and black rubber smears (note: rubber also included smears left by bumpers and side mirrors) (Figure 3).



Figure 3: Colour counter app and chosen colours for survey (ii).

Samples of black paint and black rubber were taken from the car parks for possible future examination to positively identify their composition. Other paint samples that were easily removed from the stationary objects without causing damage to the car park walls were taken for possible chemical analysis later.

Using the application downloaded on an iPad, each pillar was examined at the bottom half of the pillar at a height that would correspond to the level at which most vehicles would leave a mark. A handheld torch was used to provide better illumination of the smears in dark areas of the underground car parks. The different vehicle paint colours that were seen were counted using the application by tapping on the corresponding colour on the screen. Colours that appeared more than once on a single bollard/ pillar were carefully examined to make sure that they did not appear to come from the same incident. Samples of rubber or vehicle paint were removed by scalpel or carefully by hand and placed into a small plastic container and labelled with their location and colour. Each survey was performed on one level or designated area in the car parks. Once a level or area was completed the results obtained were finalised and a summary of the results was displayed on the application (Figure 4).



Figure 4: Results shown in app.

2.4 Results and Discussion

A total of 5374 vehicles were counted in survey (i), 4687 vehicles over a one-hour period on the busy motorway and a further 687 vehicles were counted on the suburban road. The results collected from the two locations were collated, table 1, and compared to the findings from the 1999 McDermott survey and three other surveys that were carried out in the US and Canada in the 1980s, table 2 [49-51, 53].

Table 1: Results from survey (i).

Colour	Suburban Road (%)	Western Sydney Motorway (%)
Black	15.4	13.0
Red	8.3	7.9
White	27.9	32.0
Blue	12.5	12.4
Grey	28.5	24.8
Green	2.0	4.2
Orange	1.5	0.6
Yellow	2.8	2.5
Brown	1.2	2.1
Violet	0.0	0.5

Comparison of the results from the McDermott [49] and survey i) show that, in both surveys, yellow, orange, violet and brown coloured vehicles are the least common colours whilst grey appears more frequently. Red was more common in the McDermott's survey, whereas white appeared more frequently in survey (i). The higher amount of white in survey (i) could be attributed to the time and location that the survey was conducted. Which was on a busy motorway during work hours where a large number of the vehicles were commercial white vans and utility vehicles.

The top five vehicle colours of survey (i) were found to be the same as that in the McDermott survey [49], albeit in a different order. The colours red, grey, and blue were common in the top five of all of the surveys compared, white featured in all of the surveys except for one [9-11, 13]. It is interesting to note that high number of brown vehicles that are present in the US and

Canada surveys. As these surveys were undertaken in the 1980s this could be due to the fashionable colour of brown vehicles during these times.

Table 2: Top 5 colours from each survey.

Survey	Vancouver 1984	Calgary 1982	Regina 1982	Regina 1984	Halifax 1984	New Brunswick 1988	6 States US and Florida 1981	McDermott 1999	Western Sydney Motorway 2012	Suburban Road 2012
Colour	Blue	Blue	Blue	Blue	Blue	Blue	Blue	Red	White	Grey
	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Grey	Grey	White
	Grey	White	Green	White	Grey	Grey	Green	Blue	Black	Black
	White	Grey	Red	Grey	Red	Red	White	White	Blue	Blue
	Red	Red/ Green	Grey	Red/ Green	White	Green	Red	Black	Red	Red

On the completion of survey (ii), a total of 1359 vehicle paint smears were observed on the pillars and walls that were surveyed in the five car parks. The amount and height of these smears varied depending on the location within the car park. Figure 5 illustrates the type of smears that were observed on the pillars in the survey. In figure 6, three different vehicle paint colours are visible on the single pillar, white at the top of the image, blue below the white and a small amount of red in the middle of the blue paint. Up to five different colours were recorded from a single pillar.

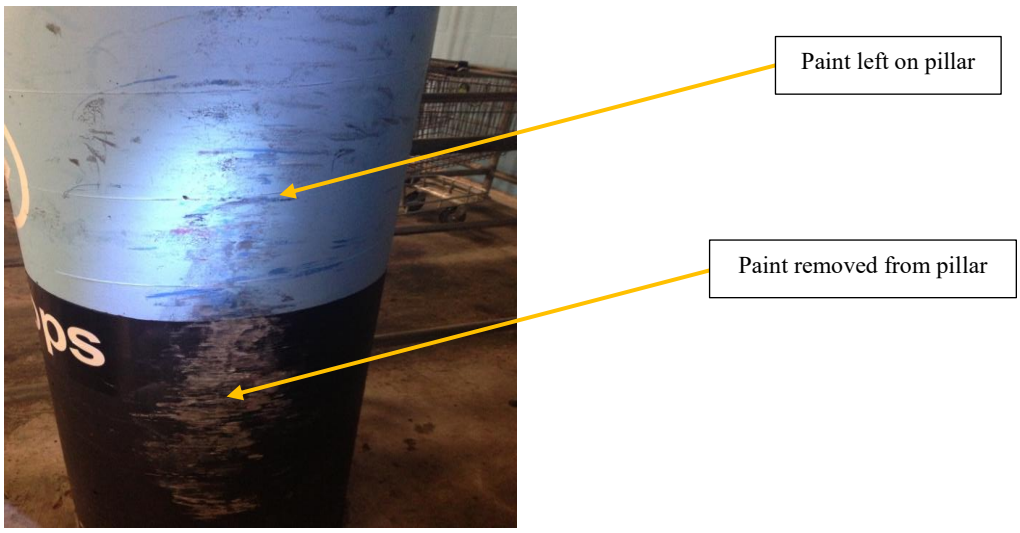


Figure 5: Paint smears transferred to pillar

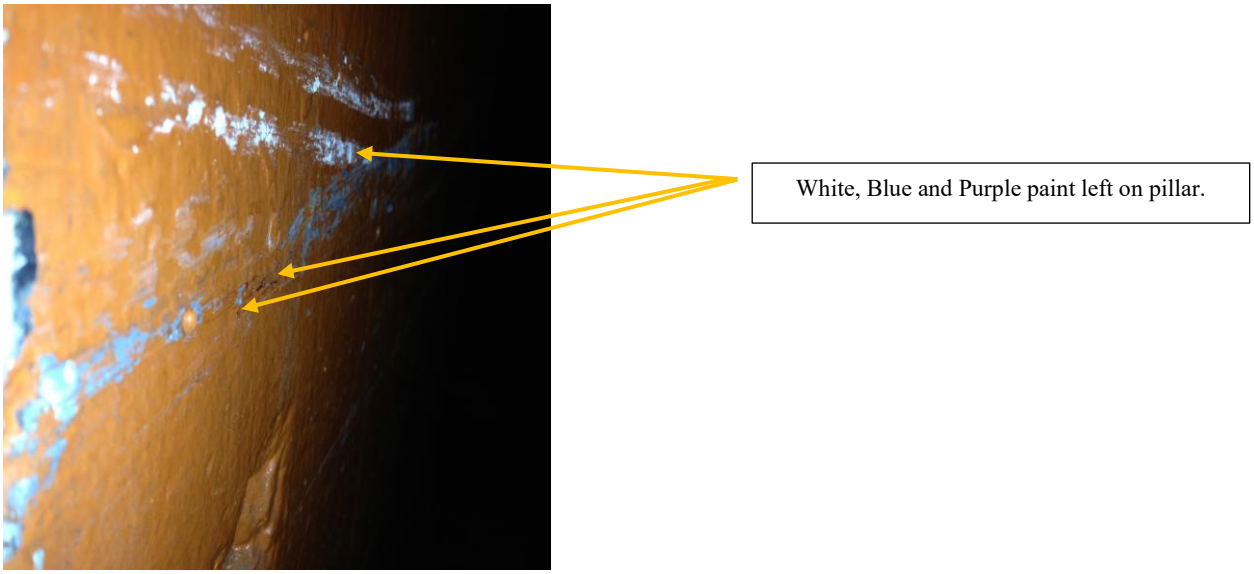


Figure 6: Three different paint colours observed on pillar.

The results obtained from all five car parks were entered into an Excel spreadsheet to assist in the comparison. From the results, Table 3, apart from rubber, blue and red were the most common vehicle colour traces that were seen on the walls and pillars. White and silver vehicle paint was also frequently seen, with a higher number of black and green noted to three of the car parks. The higher number of recorded green and yellow traces on pillars to two of the car parks may be attributed to painted service vehicles and trolleys that are used within these car parks. On several occasions, blue and yellow painted trailers were observed to be in use in these car parks to collect the trolleys from the designated trolley bays and around the car park itself. A few of the trolleys were observed to be coated with a plastic coating that was green in colour and could easily be removed and deposited on the walls and pillars of the car parks, these marks were discounted when they were observed.

Table 3: Results collected from surveys with the top four colours highlighted for each vehicle park.

Colour	Car Park 1 (%)	Car Park 2 (%)	Car Park 3 (%)	Car Park 4 (%)	Car Park 5 (%)
Black	5.5	6.0	1.8	3.2	0.7
Red	13.5	17.3	18.0	8.6	17.6
White	9.6	1.5	10.4	9.6	5.1
Blue	22.1	22.6	13.1	16.6	21.0
Grey	0.7	1.5	0.3	2.1	0.0
Silver	9.1	16.5	8.5	16.6	8.5
Green	1.7	5.3	17.7	5.9	10.8
Orange	0.0	0.0	0.3	0.0	0.7
Yellow	2.2	4.5	11.6	3.7	5.1
Brown	2.9	0.0	2.7	0.0	2.4
Purple	1.0	0.0	0.6	0.5	0.3
Rubber	31.7	24.8	14.9	33.2	27.8

Another possible anomaly was detected in one car park with a higher number of silver vehicle paint transfers recorded than the other four car parks. However, during the survey it was noticed that a higher number of silver painted vehicles were present in the car park and this anomaly may have attributed to a higher number of silver vehicle paint transfers.

Within this same car park, it was also noted that in some areas more paint had been removed from the pillars than that being deposited onto the pillars itself by the vehicles (Figure 7). A reason for this may be due to the soft malleable nature of the paint on these pillars which may have made it more likely that the coating was removed during forceful contact rather than vehicle paint being deposited. In this case it could be expected that the paint from the pillars would be found on the vehicle coating itself.



Figure 7: Paint removed from pilar.

Finally, the results obtained from both survey (i) and (ii) were then compared to the online data relating to the vehicle paint colours of registered vehicle published on the New South Wales (NSW) Roads and Maritime Services (RMS) website that are published quarterly. The data for all four quarters in 2011, 2012 and 2013 were tabulated and compared with results from the earlier vehicle paint colour survey conducted in Ireland [49] (Table 4).

Table 4: Comparison of data from the RMS website and Ireland surveys.

Colour	RMS 2013 (%)	RMS 2012 (%)	RMS 2011 (%)	Ireland (%)
Black	9.7	9.3	8.7	8.8
Red	10.9	11.3	11.7	25.1
White	23.1	23.3	23.5	12.7
Blue	14.7	15	15.2	15.7
Grey	8.4	7.9	7.3	18.7
Silver	22.5	22.5	22.1	-
Green	5.2	5.8	6.6	9.8
Orange	0.5	0.4	0.4	0.5
Yellow	3.1	3.3	3.4	0.7
Brown	1.3	0.7	0.7	5.8
Purple	0.5	0.5	0.5	1.1

It can be seen from the above data in tables 1, 3 and 4 that white and blue were the most observed vehicle colours. Silver and red vehicle colours were also commonly represented and made up the top four colours with white and blue. It should be noted that with the survey (i) and the Ireland survey, silver and grey colours were not recorded separately resulting in a higher number of grey colours recorded and thus allowing grey to represent one of the four top vehicle colours for these two surveys. Furthermore, in survey (i), black was more common than in any of the other compared surveys and outnumbers red in the top four. Nevertheless, the general pattern in all the compared surveys and data from RMS website remained consistent with the most common colours. On the other end of the scale, the least common colours observed comprised of purple, orange, and brown.

Overall, the most frequent colours are seen to be consistent over all the compared surveys and the data from the NSW RMS website. This takes into consideration the potential anomalies within the data from painted service vehicles and trolleys used in the surveyed car parks. What is most significant when comparing these results is that the data collected from the NSW RMS website show an overall agreement with the vehicle colour surveys, suggesting that this data can be used confidently in the interpretation of vehicle paint within NSW at least.

Nevertheless, the undertaking of these two vehicle paint surveys remains an important factor when interpreting the evidential value of vehicle paint as they demonstrate at the trace level the significance of vehicle paint colours that are transferred on to stationary objects. It also provides the courts with confidence that the most recent data available has been used for the interpretation. Surveys of these types provide the examiner with valuable data to assist the courts in determining the evidential value of paint examinations in certain circumstances.

Let us go back to the previously mentioned case scenario regarding the ram raid of a shop front. Now given that the colour of the suspected vehicle and the paint collected from the stationary post is orange, using the results from this survey, a greater strength can be placed on the interpretation of the paint evidence due to a high likelihood ratio that would be expected with a low frequency colour such as orange. On the other hand, if the paint colours were blue, no substantial value can be added, and a much lower likelihood ratio would be expected with a high frequency colour such as blue.

2.5 Conclusion

Even though survey (i) was limited to a motorway and suburban road in Western Sydney and survey (ii) was limited to only five car parks within Sydney region of NSW, the data collected was able to establish that there was a strong pattern in the most frequently seen colours on the roads and also on stationary objects. Both surveys demonstrated that white, blue, red, and silver were the four most common colours while purple, orange and brown were the least common colours noted. As a result, these surveys add valuable information on vehicle paint colours and assists with providing background data on the occurrence of certain vehicle paint colours on stationary objects. The data collected from these surveys can be utilised in the calculation of the likelihood ratio and when determining the correct evidential value of the paint evidence and its significance in forensic cases.

Furthermore, the results from the two surveys of vehicle colour frequency and the transfer of vehicle paints to stationary objects established that the most frequent colours were highly comparable to previous conducted surveys [49-51, 53], and data from the NSW RMS website. A significant finding was the similarity between the data that is published quarterly on the NSW RMS website and the data that was collected from both surveys. As a result, it may be suggested that the regularly updated data on the NSW RMS website could be used when interpreting vehicle paint evidence in NSW only.

Although the above findings help to fill in the gaps and add greatly needed data on the significance of vehicle paint evidence, additional surveys need to be conducted in order to maintain the background data on vehicle paint and improve the interpretation of this type of trace evidence.

Chapter 3: An Investigation into the Identification of Vehicles from the Analysis of the Automotive Clear Coat Layer

3.1 Abstract

Clear coats on automotive paint systems are designed to protect the appearance of the coloured base coat, from any environmental damage. One potential source of damage is ultra-violet (UV) radiation from sunlight; exposure to UV radiation can quickly degrade paint systems. To prevent this from occurring, clear coats may contain one or more screening chemicals such as UV Absorbers (UVAs) and Hindered Amine Light Stabilizers (HALS), that can inhibit the effect of the UV radiation on the coating. Nevertheless, even with this form of protection, the clear coats will still degrade over time. The UVAs that are used to help protect the clear coats can undergo photodegradation themselves and therefore lose their effectiveness over weathering exposure [56]. The subsequent weathering degradation that occurs can be seen as a 'profile' within the clear coat layer, such that the concentration of the UVAs and HALS will increase with depth within the layer. Smith et al. [56] conducted a study that demonstrated that the concentration of the UVA was depleted from the surface inward creating a gradient through the thickness of the clear coat through the weathering timeline. Therefore, the outer layer of the clear coat will have the lowest concentrations and the inner layers that are the furthest away from the weathering conditions, will have the highest concentrations. This may be due to the diffusion of the UVAs from the clearcoat into the underlying layers [56]

To test this hypothesis, 52 vehicle paint samples, that were collected from an earlier study that was conducted in New Zealand, together with an additional 30 vehicle paint samples that were collected within Australia were utilised. The paint sample from New Zealand included samples that were taken from different areas of the same vehicle. The advantage of the different sample locations was that it helped to compare the varied weathering degradation effects on different vehicle substrates, covered areas versus exposed areas (e.g., bonnet vs. bumper of car).

The paint samples were mounted along with a reference clear coat sample and then thin cross sections were taken and these were then analysed using UV microspectrophotometry, Fourier transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy. The results from all three of the analysis techniques were compared and the data were treated with principal

component analysis (PCA) software, Unscrambler X 10.3. The statistical analysis assisted in demonstrating the weathering changes that occurred over the 12-month period of the weathering exposure and in sense in the paint samples that were already exposed previously. The results from this study demonstrated that vehicles and even panels on the same vehicle can be differentiated by using the distinct profiles of the UV screening chemicals that are produced within the clear coat layers due to weathering.

3.2 Introduction

Automotive coatings generally consist of a multi-layer system of typically 3 layers: clear coat, basecoat, and primer [1]. The main function of the clear coat is to ensure both the overall appearance of the topcoat paint and to protect the underlying layers from the damaging effects of the harmful UV radiation of the sun and other environmental factors. This exceptional protection mechanism of the clear coat layer is usually attributable to the addition of additives to help minimise the effects of UV radiation. Automotive clear coat layers are generally around 30-40 μm thick and usually contain at least an ultraviolet light absorber additive (UVAs) with some also containing a hindered amine light stabiliser (HALS). UVAs prevent the weathering degradation by filtering out the UV energy and converting it into harmless levels of heat that can be released, figure 8 below.

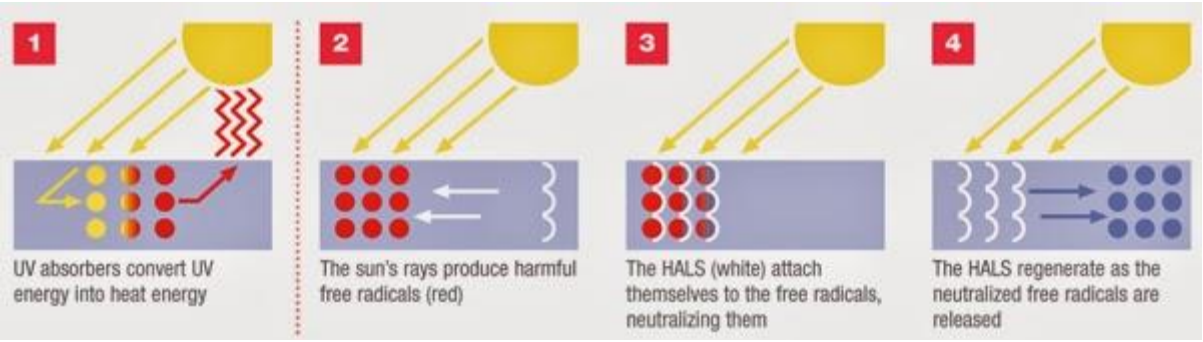


Figure 8: Effects of UV absorbers and Hals on UV radiation.

Types of UVAs are Benzophenone (BP), Benzotriazole (BTZ) and Hydroxyphenyltriazine (HPT). HALS are an increasingly important sub-group of stabilizers; they are very effective against both the heat and light induced degradation of the polymers. They act as radical scavengers to inhibit the degradation processes that can result from the photo-oxidative breakdown of the binders. Although, this protection that is offered by the UVAs is not permanent, as they themselves can undergo photodegradation and lose their effectiveness during the weathering processes [2].

Aside from the important role of providing resistance to weathering; the clear coat layer also provides gloss, hardness, physical protection from road debris and resistance to attack from solvents and chemicals [3]. Visible changes to the appearance of the coating system usually occur only after a significant period when the damage has accumulated enough to show macroscopic details such as gloss loss and micro-cracking [4]. However, these chemical, physical, and mechanical changes can be monitored and measured much earlier.

There have been numerous changes and advancement in the technology of the clear coat industry over the years; this has included the addition of a clear coat layer to the general coating system and changes to the general chemical formulations that are currently used [1]. These changes have come about mostly due to the need for improvements in the formulation and protection the clear coat can offer against the harsh conditions [1]. Also, improved regulations regarding the environmental impact of the chemicals that are used in the clear coats, have brought about modifications to make sure they will adhere to the latest regulations. The overall improvements in paint technology have produced clear coats that are not only of a higher quality, but which are also able to withstand harsher conditions and that will protect the underlying paint and substrate for longer periods [1].

Previous forensic based research has focused on the ability to discriminate the clear coat layers based on the polymer chemistry. A few forensic research papers have analysed clear coat samples using a microspectrophotometer (MSP) and Fourier Transform Infrared Spectroscopy (FTIR), looking for both; the type of UV screening chemicals used and the photo-oxidation index to help discriminate the samples [57]. Although some of the researchers considered the effects of ageing due to weathering could have on the clear coat layer, they did not fully contemplate the benefit that these changes could possibly have on the evaluation of the evidential value the clear coat layer. The intention of this research was to verify that vehicle panels from both within and between vehicles could be differentiated due to the diverse exposure periods of the clear coat layers. The overall aim of this study is to determine whether vehicles and even different panels on the same vehicle can be differentiated based upon the profiles of the UV screening chemicals within the clear coat layers. To accomplish this, a multi-technique sequence was utilised to evaluate the vehicle clear coat chemistry. One of the techniques was UV microspectroscopy, which was employed to measure the UVA content in the clear coat layer of the paints. FTIR and μ-Raman spectroscopy were other techniques that were employed to detect any shift in the chemical profile and/or intensity.

The information that could be collected with these different techniques is very useful when comparing known and questioned paint specimens which may have originated from slightly different areas on the same vehicle. For example, a paint sample that originated from the roof of a vehicle will have a different UVA profile to a paint sample that originated from inside the side panel of the same vehicle. The sample from the roof of the vehicle will have a more weathered degradation as it is exposed to the harmful effect of the sun more than a panel which does not get as much sun exposure. Therefore, it may be determined what area on the vehicle, the source, the paint sample originated from and help provide more evidence as to what happened. This can help to provide information that can be used when calculating a activity level proposition.
These results will provide the forensic examiner with the ability to improve the evaluation of the evidential value of paint by allowing another level of discrimination between samples.

3.3 Method

Samples

Samples were taken from 50 New Zealand vehicle paint samples that already had exposure to the environment for several years. The vehicle type included 19 different car manufacturers with the manufacture years, ranging from 1988 to 2006. The paint samples were taken from more than one location on the vehicle, with most of the paint samples taken from the bonnet, side panel, or the roof. A few of these samples also included areas that were covered and had no or very little exposure to environmental conditions, such as under the bonnet.

In addition to the 50 New Zealand paint samples and to increase the chemical variation of the clear coats, an extra 30 vehicle paint samples were acquired and analysed. These vehicle paint samples, from both Australian and European vehicle manufacturers were collected within Australia by a number of different forensic laboratories that submitted sections of known paint samples to the Victorian Police Forensic Services Department (VPFSD). These samples were added to the Paint Data Query (PDQ) world-wide sample collection which was initially set up by the Royal Canadian Mounted Police (RCMP) [3]. The PDQ database is an international automotive paint database that is used by forensic scientists in laboratories located in 24 countries [3]. The data base is predominantly used to assist in the calculations of how unique a paint system is and can be a valuable source to help forensic scientists to stay up to date on the latest trends and new formulations that appear in the paint industry [3].

The vehicle paint samples that were received were approximately 20 cm X 10 cm in size and included a metal substrate. The details of each paint sample including the make, model, colour, and year of manufacture were recorded. The dates of manufacture of the samples ranged from 2004-2012, with the bulk of the samples from 2012. To help minimise any previous weathering degradation, the samples that were selected for the study were from the most recent date of manufacture to the commencement of the study, which was the 2012 samples.

Exposure of samples

As the chosen paint samples that were obtained from Victoria Police had little to no exposure to the environment before they were collected, they needed to be exposed to controlled weathering conditions so it was possible to study the changes that would occur as a result. To achieve this, an area on the roof of one of the science buildings at UTS was arranged that would allow for the samples to be kept in constant sunlight and to avoid any shadowing or reduced sunlight exposure.

Sub-samples were taken from the paints before they were exposed to the weathering conditions and again at 3 monthly intervals for 12 months. Once the small sub-samples were collected at the determined time intervals, the sampled area was marked and covered with a weatherproof sealant that would stop any water getting into the exposed layers and increasing and alter the weathering process. After the sub-samples were taken and the area was sealed over, the paints were replaced in the same positions that they had been removed from. The sub-sampled paints were stored and kept in a dark cupboard away from any further exposure to UV light.

Sample preparation

The sub-sampled paints were all embedded using a UV light curing resin, Technovit® 2000 LC. This resin is based on methacrylate and is cured under a blue light using a Technovit® 2000 LC Technotray CU unit. Layers of a clear coat film were added to either side of the paint samples during the embedding stage. The clear coat layer was used as a reference film. It was an acrylic resin with a known UVA concentration absorbance. The clear coat film that was used as the reference film was obtained from a smash repairer who sprayed the clear coat film onto a sheet of stainless steel. This clear coat was never exposed to the environment and was stored in a dark place to prevent any weathering.

Thin cross sections of the mounted paint samples together with the reference films were cut using a Leica RM2145 rotary microtome equipped with a sharp titanium carbide blade. Different cross section thicknesses of 3 µm, 10 µm and 30 µm were chosen for the three different analytical techniques. Once the thin cross sections were cut, they were placed between two glass slides and secured together to help keep them flat. These were then stored away from direct sun or any artificial light.

Instruments

The UV measurements were performed using a Craic 20/20 PV MSP equipped with a 36-x objective, with the aperture set to 5 x 5 µm. A spectrum was collected from a 250–450 µm range with measurements taken from:

- the outer area of the clear coat,
- middle layer, and
- inner area of the clear coats,

See figure 9 below for a visual representation of the areas that were measured.

UV measurements were also collected from the reference film before and after the vehicle paint sample. The measurements of the reference allowed the actual cross-section thickness of the sample to be calculated and normalised to a thickness of 10 µm.

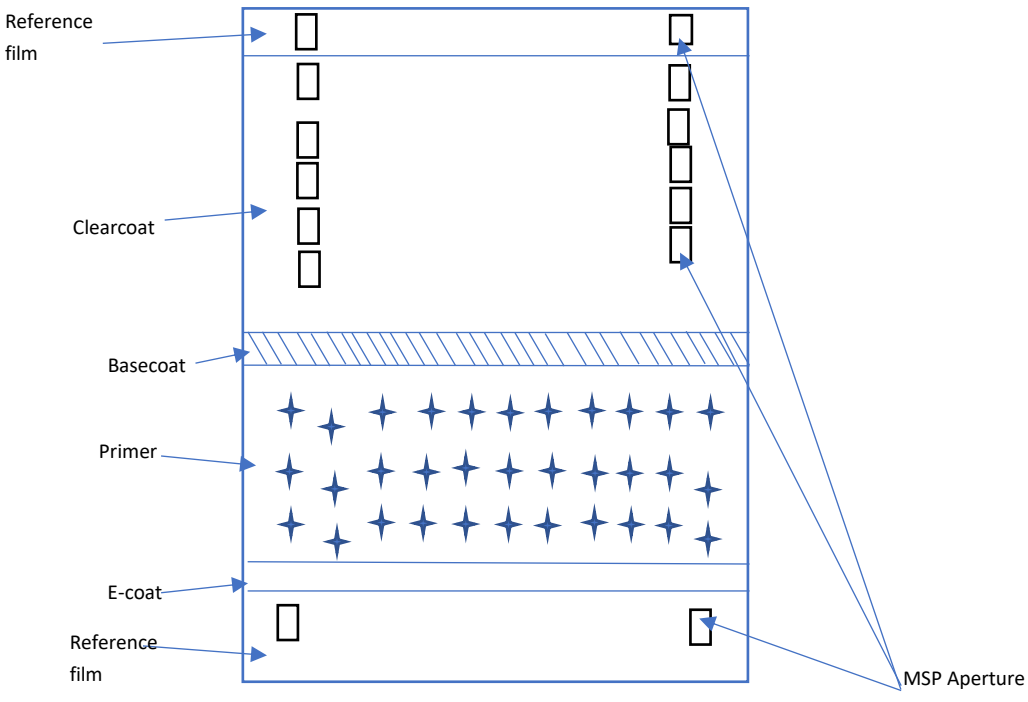


Figure 9: MSP areas measured along the vehicle paint sample including the reference films.

The FTIR measurements were performed using a Nicolet 6700 FTIR spectrometer coupled with a Nicolet Continuum FTIR Microscope from Thermo Fisher Scientific. A 15 x Infinity Reflachromat objective, a Mercury Cadmium Telluride (MCT/A) detector and OMNIC 8.3 software were used in all experiments. The paint samples were analysed in transmission mode on a micro-compression cell with a diamond window. The measurement parameters that were used included:

- 4.0 cm^{-1} resolution,
- 64 co-added spectra, and
- 4000-650 cm^{-1} range.

The Raman measurements were performed on a Renishaw inVia Raman microscope with a 50-x objective. A 785 nm Renishaw NIR diode was used for all samples, with parameters of:

- 2 accumulations,
- 10 s integration time, and
- a range of 200-2000 cm^{-1}.

Measurements were taken throughout the clear coat sample, including the outer, middle, and inner layers similarly to the measurements that were taken for the MSP experiments.

Pre-processing

Principle Components Analysis (PCA) using the Unscrambler X 10.3 (Camo software), was used to help reprocess the samples and to reduce the dataset. This was applied to all the clear coat samples to help visualise of any clusters or separations that were formed to get a better understanding on what was occurring. The pre-treatments were systematically applied to the spectra, this involved using:

- a Savitzky-Golay algorithm,
- 1st derivative
- 12-point correction to the data

These pre-treatments were applied before the final analysis was conducted.

3.4 Results and discussion

Even before any of the analytical data was entered into the Unscrambler software and compared, there were clear differences within the clear coat layers of the samples from New Zealand that included samples that were from covered and uncovered areas of the same car when the MSP data was graphed, see figures 10 and 11 below. The UVA concentrations were increasing within the clear coat layer. The outer layer of the clear coat, which had the most exposure to the weathering conditions and degradation was seen to have the lowest UVA concentrations. As the measurements moved inwards towards the inner layers of the clear coat layer the UVA concentrations increased. The samples that were taken from areas that were covered, showed the least variance in the UVA concentrations throughout the entire depth of the clear coat layer. This was to be expected as they were covered and would have fewer effects from the harmful UV degradation effects of the sun as they were covered and would have had minimal to no exposure to the weathering conditions.

This highlights the concept that was mentioned previously that the effects of weathering will degrade the clear coats more predominantly from the outside layer to the inside layer of the clear coats. This type of degradation pattern could be seen as a profile and will be different even from the same vehicle but between paint that is taken from a panel that is covered or that is not exposed to the same amount of UV radiation as other panels on the vehicle, such as under the bonnet or inside the boot of a car, compared to paint that is taken from an area that has full exposure to the harmful weathering climate, such as the roof.

This was demonstrated with the MSP measurements that were taken from the two areas on the clear coat that were from the outside layer of the clear coat and the area that was furthest away from the UV radiation, the inside layer of the clear coat. The inside layer of the clear coat which had protection from the weathering degradation climate with the outer and middle layers of the clear coat acting as barriers to the harmful UV radiation. The pattern which is created from the outside layers towards the inside layers of the clear coat is seen as a depth of field characteristic that will be distinct on different areas on the same vehicle. This is a significant discovery and will therefore need further research into the area to help support and better evaluate its potential of providing more acquired characterises that can be used to better compare the paint. This would then help to improve the evaluation of the evidential value.

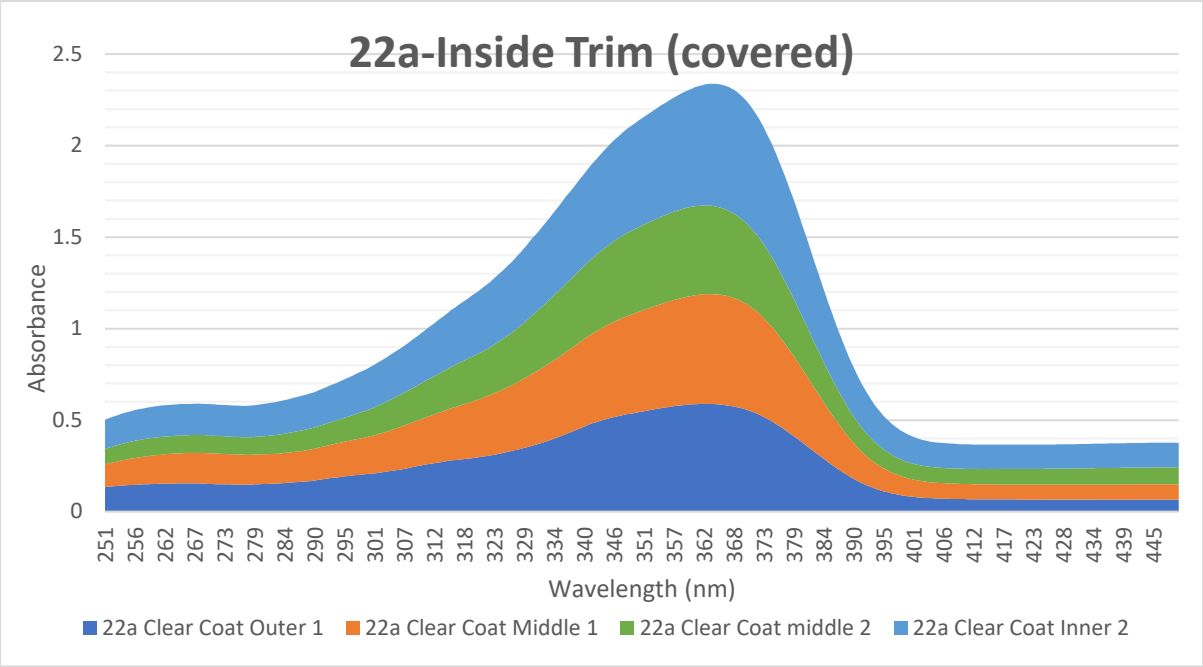


Figure 10: MSP measurements for the New Zealand sample 22a from the door trim, covered.

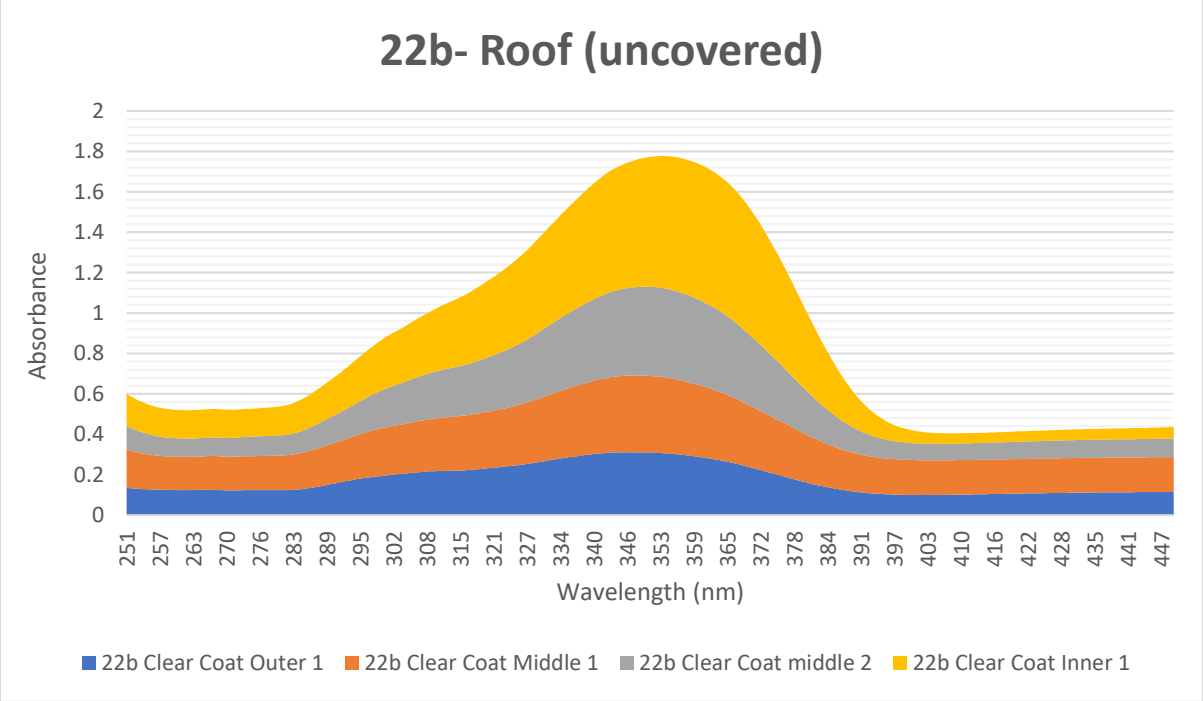
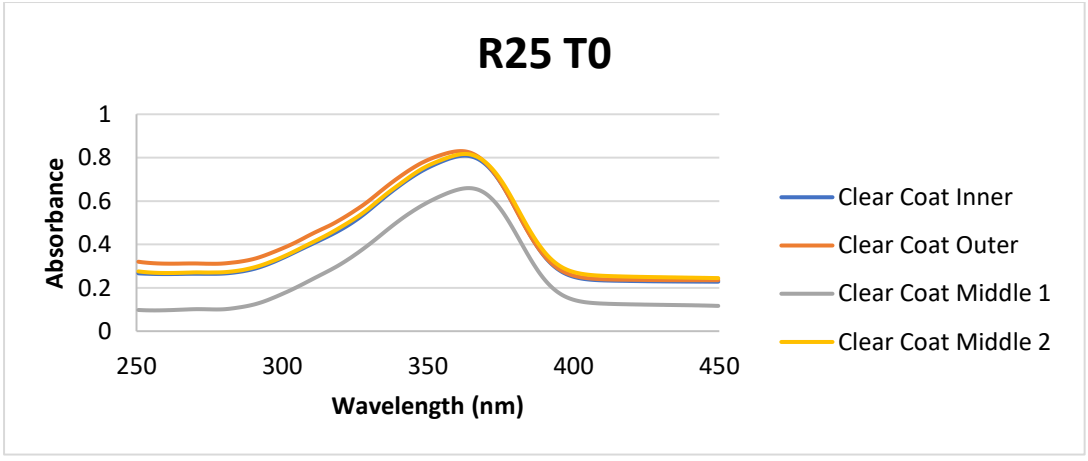


Figure 11: MSP measurements for the New Zealand paint sample 22b from the roof, uncovered.

The results from the other vehicle paint samples, that were obtained from Victoria Police, and were exposed to the weathering climate, showed that the degradation of the UV screening chemicals increased with the length of time the paints were exposed. The MSP measurements were also graphed which enabled the clear differences to be visualised, see figures 12 and 13 below. There was an obvious difference from the measurements that were taken before

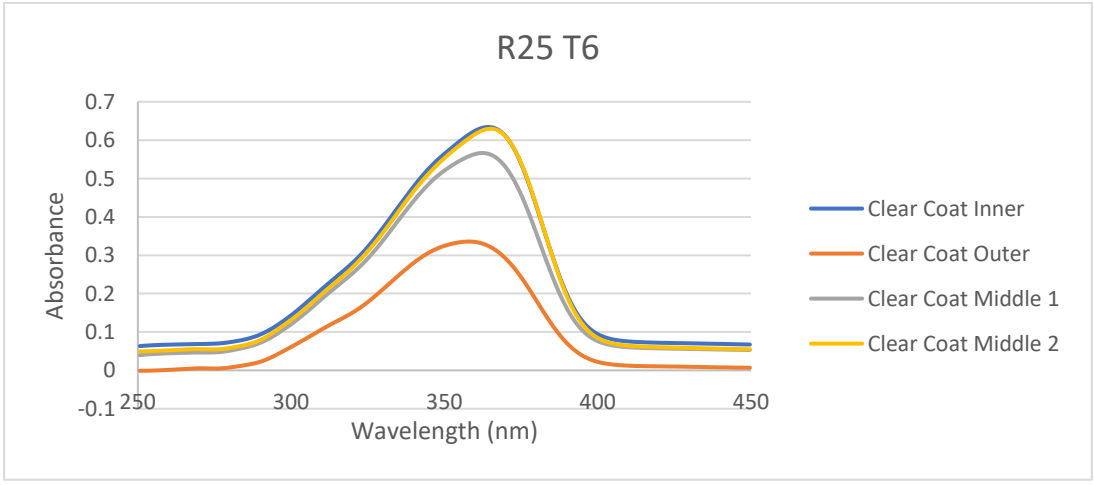
weathering to those even after only 3 or 6 months of weathering. Therefore, the results from all the samples emphases the need for the known and questioned paint samples to be taken at the same time and from similar locations to avoid any discrepancies that may reduce or affect the interpretation and the strength of evidence that is given to the paint samples.

One of the aims for this area of the study was to determine if vehicles could be discriminated based upon the profiles of the UV screening chemicals within the clear coat layers. This has been demonstrated and shown that not only different vehicles can be discriminated, but also different panels on the same vehicle. These findings have not only strengthened the discriminating power of the analysis by adding more comparable features that can be assessed and differentiated, but it has also improved the evaluation of the evidential value of paint evidence by potentially allowing an activity level statement to be applied.



3

Figure 12: MSP measurements for the paint sample R25 before weathering exposure.



4

Figure 13: MSP measurements for the paint sample R25 after 6 months of weathering exposure.

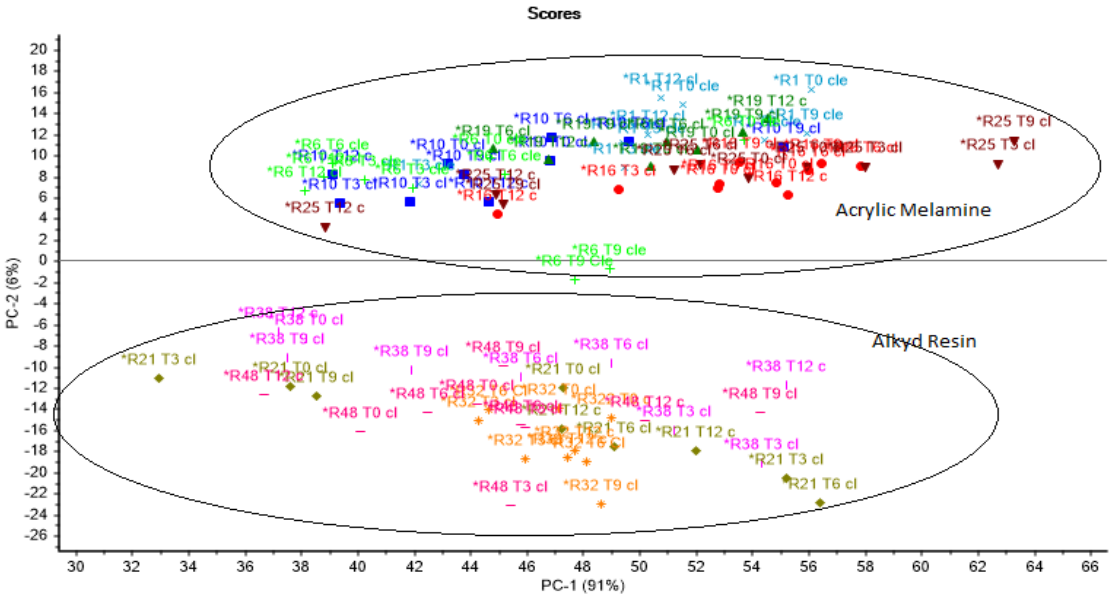


Figure 14: PCA plot of the FTIR results of the clear coat of 10 vehicle samples at T0-T12.

The PCA results that were calculated and plotted, were very useful in separating not only the different vehicles that were present in the study, but it also helped to group the different resin types between the different clear coats that were present according to their chemical properties, figure 14 above. From the above PCA plots, figure 14, it can be seen that the acrylic melamine and alkyd resin clear coats both formed separate groups. This was mainly due to the different chemical foundations of the two clear coat groups. Further to this, there was even separation of the same clear coats at different exposure lengths. For example, it can be seen in the PCA plot above, figure 14, that sample R25 showed separation after only 3 months of weathering. However, the biggest separation was seen after 12 months exposure to the weathering conditions, which had the biggest change in the PC1 axis. These results showed that vehicle paint samples from the same sources could be separated and differentiated due to different weathering exposures.

3.5 Conclusion

The results from this study showed that there was a clear differentiation between the paint samples that were taken from different locations of the same vehicle. Furthermore, when a comparison of the unweathered paint samples to the same paint after they had been exposed to the harsh weathering climate and undergone the weathering degradation, differences could be seen between the samples. This helped to highlight the importance for care to be taken when comparing clear coats from different panels.

The results from this study have not only backed up the research that has been conducted previously on the clear coat chemistry and the knowledge that changes can be seen within the clear coat layers, but it has gone further to identify the increased discrimination power that changes can have due to the weathering of the UV chemicals in the clear coats can have on the overall evidential value of paint. It has also however, highlighted the possible issues and challenges that may arise when analysing samples that have been collected at different times, as they may not have undergone the same weathering changes. The weathering features of the paint samples are not often picked up in the routine analysis of paint in many forensic laboratories. This may mislead the scientist and confuse the overall findings of the paint examination. On the other hand, if the weathering effect is recognised, it may also be used to provide further points of comparison and to individual characteristics which could be utilised to provide a higher value of evidence than the often-reported source level of paint evidence.

This study allow vehicles to be differentiated based on the environmental degradation history of the clear coat chemistry of the paint. Although, with more research and further studies into this area can more information and true understanding of the significance of the analysis of the clear coat layer be truly known. Yet, the research that has been presented in this study will be of great benefit to the forensic community and it may also assist with the evidence that is presented in court as it can help to clarify and improve the strength of evidence that is being applied to the paint evidence that is present.

3.6 Intra-Sample Variation

Before we can move onto a more in-depth assessment of the weathering changes that have occurred above in this study, an important question needed to be addressed: *what if these chemical changes that are being measured and recorded are actually from the chemical variations in the paint due to different areas that have been sampled, and not actually because of natural weathering degradation that can occur over time*? To help verify if this was in actually occurring, a small intra-sample study was undertaken. This involved taking small sub-samples of paint from slightly different areas of the same panel and analysed using MSP and the results tested with PCA.

3.7 Intra-Sample Variation Study Method

Overall, there were 3 vehicle manufacturers that were chosen for the study. From each of the chosen vehicles, a small sub-sample, 1 x 1 cm, was taken from the original paint panel. These sub-samples were taken at 3-monthly intervals over a 12-month period.

The sub-samples of the paint that were collected over this time period were mounted in a mould with a mounting resin, Technovit brand, then very thin cross sections of the mounted samples were cut using a microtome, with a sharp tungsten carbide blade attached. The thin cross sections of the samples were then analysed by MSP. The MSP data was examined, and results tested using a model called analysis of variance (ANOVA) to test for any significant changes or variance within the same sample. This was done for both for the clear coat and the colour layer of the selected vehicle paint samples.

3.8 Results and Discussion

For the MSP data that was collected for each paint sample, please see appendix 1.

The overall results from this intra-sample variation survey showed there was no significant variations that could be detected with the MSP measurements that were collected from within the same sample over the chosen time intervals.

3.9 Intra-Sample Variation Study Conclusion

The results that were collected from the three different vehicle manufacturers and over the 12-month period, backed up the hypothesis that the changes were not because of internal sample variation with no differences being detected from within the same paint sample. Therefore, it can be understood that any of the changes that are recorded and documented from the paint samples are from actually external factors, e.g., weathering degradation, and not from any internal reasons or influences, like variations in the paint foundations.

Chapter 4: Physical and Chemical Changes of Water and Oil Based Architectural Paints Due to Weathering in the Sydney, Australian Climate And their Implications in Forensic Science.

4.1 Abstract

The weathering deterioration of architectural paint is predominantly due to the environmental effects of solar radiation, temperature, humidity, and pollution. These can have a pronounced effect on not only the performance and appearance of the paint systems, but also in a forensic context when comparing weathered paint specimens to other specimens that have not been exposed to the weather.

The aim of this study was to investigate and record the changes that can occur due to weathering on eight architectural paint samples; six water-based and two oil-based paints, over a three-year period in the Australian climate in the Sydney Metropolitan area, to verify if the changes that occur due to weathering can be used to improve the forensic evaluation of the paints. These weather effects are believed to bring about changes to the paints that can ultimately separate them chemically from other visually similar paints. This added information can provide the forensic scientist with more information about the paints and can ultimately increase the strength of evidence when comparing two paint samples. Subsamples approximately 1-2 cm sections of the full layers of the paint layer samples were collected periodically over the three-year period and analysed using microscope-Raman spectroscopy and a 785 nm laser. The results collected were treated and analysed by principal component analysis (PCA) using the Unscrambler software X.

The oil-based and water-based samples were easily separated using PCA analysis, even after three years of weathering. Changes were seen in the first oil-based sample with separate cluster groups forming between the different time periods after PCA analysis. A group of the other samples also showed similar changes over the three-year weathering period.

4.2 Introduction

Comparing specimens taken from the crime scene to control samples to characterise paint traces is an important aspect of casework in forensic science [58]. Comparing microtraces is one of the first steps that is undertaken forensic analysis not only to determine if two samples have a common origin but also what happened and to determine a possible source [8]. The forensic scientist will do this while examining the evidence and documenting the microtraces to characterise the sample and use this information when comparing it to other microtraces.

Determining if there is a connection and/or activity relating to the specimen is the main objective as a forensic examiner. Paint traces can come in the form or single layer or multilayer fragments, chips, smears, or even small droplets. White architectural paint is often encountered as forensic traces in the laboratory as it is widely used as a protective coating for doors, window frames, and internal woodwork.

Architectural paints consist of four main components: a binder, the pigment/ extender, the solvent/liquid system to aid in paint application, and additives, which include de-foamers and anti-corrosion substances [14, 59]. The paint systems are generally divided in to either oil-based (organic solvent-borne coatings) or water-based (waterborne coatings) depending on the solvents they use. Oil-based paints are soluble in organic solvents and are generally made of alkyd, epoxy, varnish, lacquer and polyurethane resins [60]. Water-based paints involve two types of technology: an emulsion or latex system and a system based on water-soluble resin [60]. Water-based paints are more desired since they are more environmentally friendly. The pigments have two functions: to be decorative and to be protective. They provide colour, opacity, coverage, protect the binder from weathering, improve the strength and adhesion of the paint film, and can also control gloss [59]. A common pigment used in all white architectural paint is titanium dioxide (TiO_2) mainly in the form of rutile [59]. The range of different architectural paints come in gloss, semigloss, and flat [60]. Gloss paint is a hard, mark-resistant film that is easily cleaned and reflects the light [60]. The binder to pigment ratio is higher than semi-gloss paint [60]. Semi-gloss paints have a bit more pigment than gloss film paint, and therefore cause the light to be reflected in slightly different directions. Calcium carbonate is added to help reduce the surface gloss of paints [58].

Paint that is applied to external finishes is subjected to a variety of environmental factors that can degrade the paint and reduce its useful lifespan [61]. It is important to protect the wood surface when exposed to the environment, especially if it is for an extended period. Atmospheric agents can lead to a loss of the timber's natural colour, build-up of dirt and growth of fungi on the wood surface [62]. It is therefore important to protect the wood surface with an appropriate coating. The weathering deterioration of paint is predominantly due to the environmental effects of solar radiation, temperature, humidity, and pollution [63]. These weathering agents bring about deterioration in chemical, physical and mechanical properties of the paints, causing eventual failure of the protective property of the coating. The exposure of the paint to UV radiation can initiate the photochemical degradation of the polymers [62]. Paints with the addition of a UV absorber can minimise the degradation of the wood by ultraviolet radiation [62]. In outdoor weathering, many factors can simultaneously influence the ageing and degradation of the paint. The effects of UV radiation, heat and moisture can cause changes in the chemical structure of macromolecules, thus influencing the physical properties of a coating, and ultimately leading to its failure (cracking, gloss loss, blistering, etc.) and a reduction of its life-time [57]. The effects of weathering bring about deterioration in chemical, physical and mechanical properties of the paints, causing eventual failure of the protective property of the coating [64].

A wide range of techniques, such as microscopic, FTIR, GC/MS can be utilised in the examination and analysis of paint samples that are collected as forensic microtraces. One of the specialised techniques is Raman spectroscopy, which offers a non-destructive and rapid way of obtaining information on the organic and inorganic pigments and extenders present in a paint sample. Raman spectroscopy not only provides discrimination, but it is also a faster and less consumptive method than FTIR [31]. Raman spectroscopy is a valuable analytical technique which can provide information on not only the organic and inorganic pigments, but some of the extenders that are present in the sample as well. The analytical technique can allow the samples to be studied *in situ* and with no to minimal preparation. Fluorescence, however, still remains a limitation with paint and other samples [31].

The examination of architectural paint by Raman spectroscopy has been evaluated and compared to other previously utilised techniques such as FTIR and py-GC/MS. Often its use

is thought as only "complementary" to infrared spectroscopy [31], but with increasing development and affordability, Raman spectroscopy can now be seen as stand-alone method in evaluation and discrimination of paint evidence. The paper by Zieba-Palus *et al*. [65] explored the application of both infrared and Raman spectroscopy in examination of paint microtraces. They found both techniques in combination, to be an interesting analytical tool for forensic paint analysis. The use of micro-Raman spectroscopy was also investigated by Buzzini *et al.* [9], where the effectiveness of micro-Raman analysis was evaluated in different case studies. These case studies demonstrate that this technique was invaluable when it came to analysing tiny paint smears on a substrate without much sample preparation and interference from their support. Further work by Kendix *et al*. [66] investigated the potential combination of micro-Raman spectroscopy and SEM-EDS.

In-depth research on the examination and discrimination of household paints has been conducted using Raman spectroscopy as well as other techniques [58, 67-69]. Many of these studies focused on the differentiation of the paints due to difference in the pigment and manufacture additives. The two-part study by Bell *et al*. [67, 68] on the forensic analysis of architectural paint, demonstrate the advantages of Raman spectroscopy over the established FT-IR methods by allowing further discrimination of resins and white paint samples. Stewart *et al*. [58] demonstrated the ability to chemically map the cross-section of multilayered white paint chips with the use of lateral scanning Raman spectroscopy. This produced data with high evidential value. The work conducted by Wright *et al*. [69], although not using Raman, involved the analysis and discrimination of 964 architectural paint samples using FTIR, SEM and Py-GC/MS. At the end of the examination sequence, all the random pairs were distinguishable.

These previous studies focusing on the discrimination of architectural paint have been conducted on fresh and unweathered paint samples. A number of studies have mentioned the need to assess the influence that ageing can have on the architectural samples. This was conducted and evaluated in the present work. This research was designed to study and assess the effects of weathering on eight architectural paint samples: six water-based and two oil-based paints, over a three-year period in the Australian climate in the Sydney Metropolitan area. The test was performed in natural outdoor conditions over a three-year period. It was

suspected that the effects of weathering would change the chemical profile of the architectural paint samples and may provide a distinguishing pattern allowing them to be further differentiated from other architectural samples. This would in turn lead to improved evaluation of the evidential value when comparing questioned and known samples. The changes that are caused by weathering could also mislead forensic investigations when comparing questioned and known samples and when comparing questioned samples to data from reference databases. The Raman spectra of the weathered paint samples may not be indifferentiable to the original manufacture coating [70, 71].

4.3 Materials and methods

Wood

The design for this part of the experiment followed the Standard Practice for Selecting Wood Substrates for Weathering Evaluations of Architectural Coatings D7787/D7787M-13 **[72]**. One large single plank of pine wood was purchased from the local hardware store and cut into approximately 21 cm long pieces. The use of a single piece of pine wood ensured that any variation found within the samples would be a result from the paint itself and not due to influence from the wood substrates. The pieces of pine wood were carefully selected to ensure that no defects were present that could affect the results.

The thickness of each panel was 1.8 cm which was well within the recommended panel thickness according to the ASTM standard.

Paints and preparation of the samples

The colour of the architectural paint samples were all white exterior paints except for the first sample which was an oil-based interior semi-gloss paint. This was chosen as it would show possible accelerated weathering effects compared to the exterior paints that are designed to withstand the outdoor climate for many years. A comparison of the performance of oil-based versus water-based paints was also included with the use of two oil-based paint samples. Paints from three different brands were purchased and a gloss or low sheen version of each brand was selected.

The individual wood panels were first painted with Dulux Precoat 100% acrylic primer, which is the recommended first step before applying any paint, a pink tint added to assist with visualisation of the topcoat when analysing the microtome samples. Two coats of the primer were applied and left to dry for 48 hours prior to the topcoat paints being applied. The topcoats were also applied using a two-coat system. The same application and drying method were followed for each of the paint samples. The wooden panels were given individual numbers to assist with identification of the paint that was used, these numbers and corresponding brand and paint types are listed in table 5 below.

Table 4: Individual sample IDs and brand and type of paints.

Sample ID	Paint Brand	Sheen	Type of paint
A1	**Dulux super enamel- semi gloss**	**Semi**	**Enamel Oil-based**
A2	**Dulux super enamel- high gloss**	**High**	
A3	**British paints 4 seasons exterior- gloss**	**Gloss**	**100% acrylic water-based**
A4	**British paints 4 seasons exterior - low sheen**	**Low**	
A5	**Taubmans sun proof exterior- gloss**	**Gloss**	
A6	**Taubmans sun proof exterior - low sheen**	**Low**	
A7	**Dulux weather shield- gloss**	**Gloss**	
A8	**Dulux weather shield - low sheen**	**Low**	

Weathering and sample collection

The weathering and sampling of the selected paints were performed following the ASTM Standard Practice for Conducting Exterior Exposure Tests of Paints on Wood D1006/D1006M-13 [73]. The painted panels were weathered naturally on a roof, under the natural weather conditions that were experienced within Sydney, Australia. The ability to use natural outdoor weathering provides more accurate results compared to the use of accelerated testing, which can give rise to incorrect and different deterioration mechanisms that are not encountered during normal weathering of paint.

The samples were mounted to a wooden frame covered with metal mesh, using strong magnets to allow easy removal for regular sampling (Figure 15). The frame and mesh ensured that the samples were off the ground and prevented any pooling of water around the panels during heavy rainfall. The panels were placed on a slight angle of 5 degrees and positioned in direct sunlight, avoiding any areas of shadow or protection from natural climate conditions.

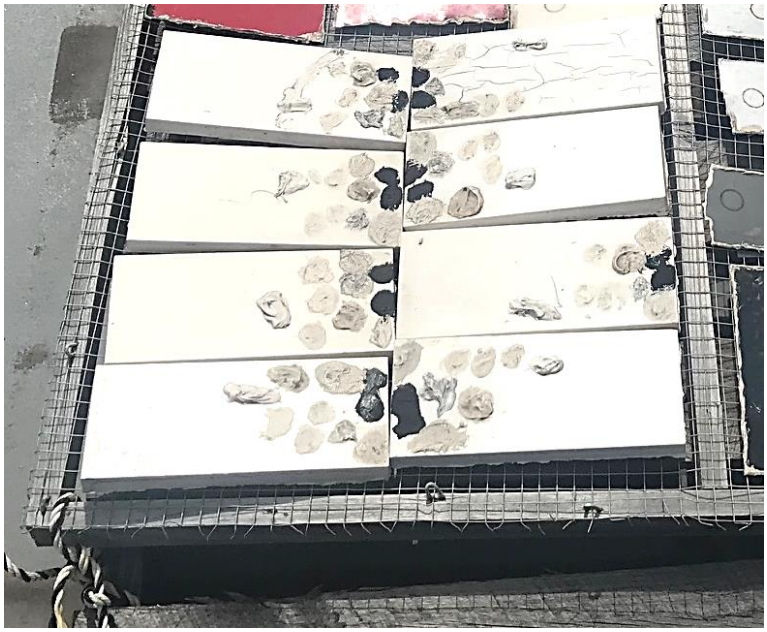


Figure 15: Image of architectural paint samples on roof during weathering exposure.

A small (5 x 5 mm) sample was collected from each panel prior to the start of the weathering exposure and then every three months for the first two years, and every six months for the final year. The paint samples were removed from the wooden panels using a clean metal scalpel, making sure the full layer structure of the paint sample had been removed. The removed paint sections were stored in a dark cardboard folder, away from heat and any sunlight prior to examination.

Sample Preparation

The paint samples were each embedded using a UV curing resin, Technovit® 2000 LC, and cured under blue light using the Technovit® 2000 LC Technotray CU unit. Very thin cross-sections of the embedded paint samples were cut using a Leica RM2145 rotary microtome fitted with a titanium carbide blade. A cross-section thickness of 30 µm was chosen for the Raman measurements. An image of the cross-section of one of the samples can be seen below

in Figure 16. The cut sections were carefully removed from the blade and placed between two glass slides and again stored away from direct sun in a dark cardboard folder before they were analysed.

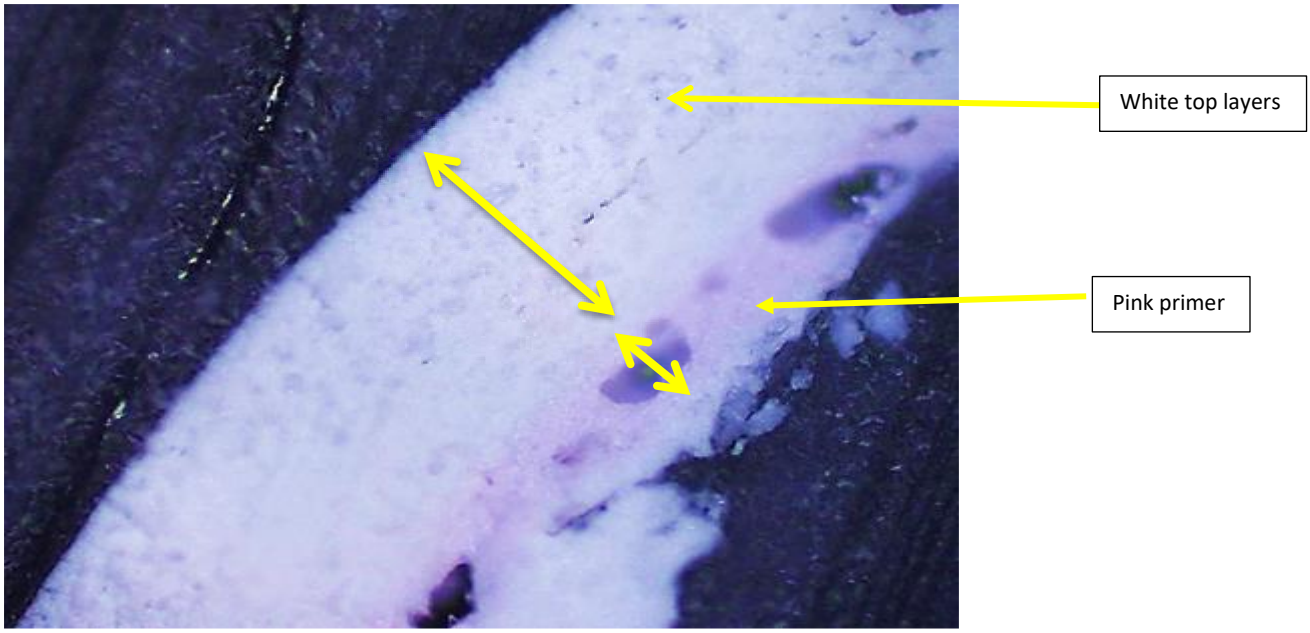


Figure 16: Cross section of a white architectural paint sample, showing the primer (pink layer) and topcoat layers (white layers).

Measurements of Environmental Conditions

The record of weather conditions during the three-year study was obtained from the Australian Bureau of Meteorology website (http://www.bom.gov.au/). The Sydney Observatory weather station, located 1.2 km away from the sample location, was chosen as it was the weather data point. The overall averages for minimum and maximum temperature ranges, total rainfall, and average UV index were calculated for each sampling time period during the three years. The following weather information was recorded for this location (Figure 17):

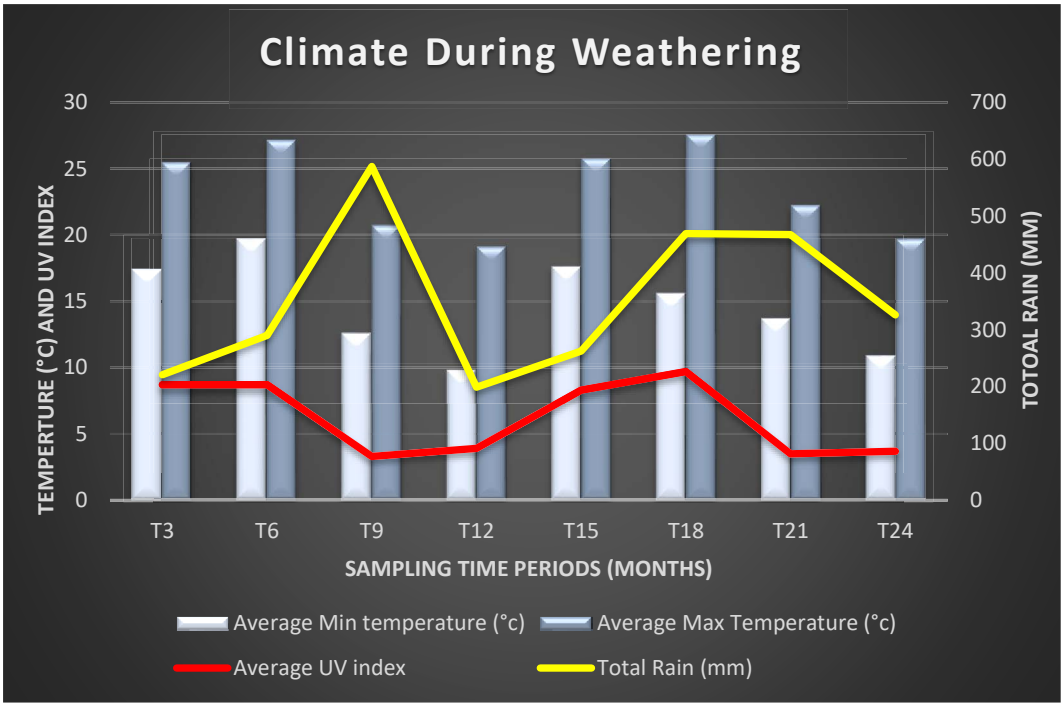


Figure 17: Climate measurements recorded during sample weathering time periods.

Visual examination

The paint samples that were prepared and exposed to the natural weathering climate, were viewed and checked regularly during the 3-year period of the weathering study for any changes and degradation affects that were occurring. This involved both examination by the human eye and under magnification of up to 50x using stereomicroscopes. The condition of the paint was recorded into a notebook and photographs were taken of any significant or noteworthy findings. The visual condition of the paint samples, during (at 3-6 monthly intervals) and again after the study was concluded (after the 3 years).

Raman Spectroscopy

Raman measurements were performed using a Renishaw inVia Raman microscope with a 50-x objective and a DM 2500 M Leica Microscope. The 785 nm Renishaw NIR diode laser was used for all samples. This was found to give the best spectral results for the white paint samples with minimal interference or fluorescence issues. The research conducted by Bell et al. [59], found that the 785 nm excitation gave excellent spectra with low levels of background interferences. The measurements were performed using the 30 µm cross sections of the paints

in situ on glass slides without any sample preparation. The same parameters were used for all the samples and throughout the whole three-year time period, which included: 5 accumulations, 10 s integration time, grating 1200 lines/ mm, a range of 200 - 2000 cm^{-1} and laser power of 1%. During method development, higher laser powers were tested, however, it was found that not all paint samples were able to be analysed using a higher laser power. One impact of the reduced laser power was greater background noise This was significantly reduced by increasing the number of accumulations to 5. Having multiple accumulations helps to improve the signal of a weak peak without saturating stronger peaks. Even though the extension of the spectral range to 4000 cm^{-1} could possibly show CH bands from the binder, it was decided to limit the range to 200-2000 cm^{-1} to avoid fluorescence and shift in the baseline which is known to occur beyond 2500 cm^{-1}.

Measurements were taken throughout layers of the topcoat including the outside, middle and inner area of the layers and were repeated along a different section of the paint sample. A total of six measurements were taken from each paint sample and for all the eleven different weathering time periods. Raman spectroscopy imaging of paint cross-sections is a more effective evaluation of the degradation process as it ensures less data misinterpretation and gives a full depth profile of the paint system [63].

Statistical Analysis

For the initial analysis of the results and ease of numbers into other platforms, as well as general data entry to input into the statistical software later, Microsoft Excel 2016 was used. Statistical treatments were performed using Unscrambler X (Camo software) version 10.3 using the imported Excel data. Pre-treatments were systematically applied to all spectra, using Savitzky-Golay algorithm, 1st derivative 12-point correction, and then normalised to the rutile peaks that were found in all of the white paints. First derivative spectra were generated to avoid any possible human error that can occur when manually subtracting baseline from each spectrum individually. Multiplicative scatter correction was performed to help compensate for any spectral effects in the data. The variables were then truncated to 750-1900 cm^{-1}, the area of interest and where the most spectral changes would occur. Principle component analyses were cross-validated, and data mean centred.

4.4 Results and Discussion

Visual Examination

It has been established that the effects of weathering can bring about deterioration to the chemical, physical and mechanical properties of paints, which can lead to the eventual failure of the protective property of the paint system [64]. Absorption of UV light can cause chain scission which leads to decomposition of the polymer. The chemical reactions that are taking place during this process influence the physical properties of coatings and ultimately may lead to cracking, gloss loss and blistering [64]. This effect was confirmed for the eight architectural paint samples selected for this study that were exposed to natural weathering conditions. Visual changes were observed for both the oil-based (A1-A2), and water-based paints (A3-A8), see figure 18 below.

Two oil-based paints were selected from the same manufacturer. The first was an interior only paint and the other sample was designed for both interior and exterior use. The interior only oil-based paint, A1, was included as it was anticipated that it would show a higher rate of deterioration than the exterior paints. Interior paints are not designed to withstand the harsh outdoor conditions and will generally demonstrate the harmful effects of weathering more rapidly as they have no, or very little UV absorbers compared to those intended for outdoor use. This was clearly confirmed, with significant visual changes to the surface of the paint in the form of widespread cracking along the top and sides of the panel after just 24 months and with further cracks appearing after 36 months of exposure, shown in Figure 4. The paint surface also became very brittle and difficult to sample at the quarterly and half yearly sampling intervals, resulting in only very small flakes of paint coming off when using a scalpel to remove the paint layers. This may be a result of the oxidation of the styrene-butadiene copolymer found in emulsion coatings that are used in interior architectural paints, which causes the film to become brittle [60]. In contrast to this, the A2 sample, with a high gloss finish and designed for both interior and exterior surfaces, showed no signs of cracking and the gloss and colour of the paint remained unchanged throughout the three-year period. In addition, the paint layers were able to be removed more easily and smoothly than the A1 sample.

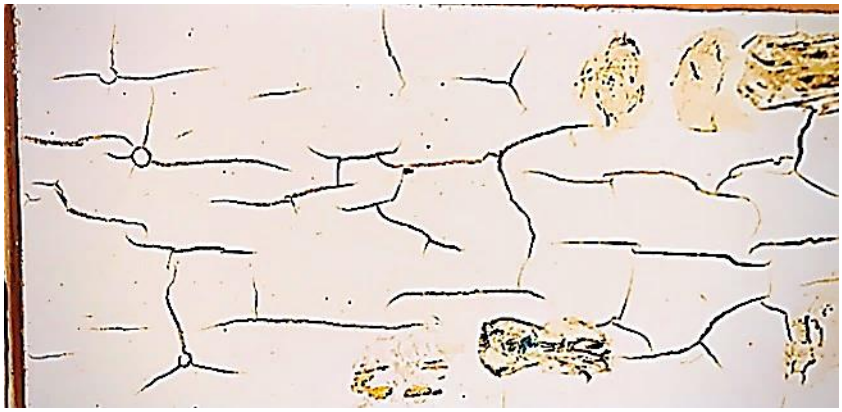


Figure 18: Cracks on the surface of sample A1, 1.5 X magnification.

The water-based samples, A3-A8, showed no signs of cracking on the paint surface during the three years of exposure. Semi-gloss/low-sheen and high gloss paints were chosen for each of the three paint manufacturers. The high-gloss paints all fared better than the semi-gloss/low-sheen paints, which all appeared dull and off-white in colour after 36 months of exposure to the outdoor climate. It is known that paints with a higher gloss retain their sheen for longer than low-sheen or semi-gloss paints. The loss of gloss and chalking effects are due to the loss of binder as volatile products and leaching of soluble products which proceed most rapidly at the exposed surface of the paint [64].

Raman Spectroscopic Analysis

The Raman spectra of the eight architectural paints were analysed for the 36-month weathering period. The bands where the most changes occurred for both the oil-based and water-based samples were identified and the assignments for these bands are shown in Table 4.5. As expected, there was a noticeable difference in the Raman spectra of the oil-based and water-based-samples before weathering, allowing for easy discrimination between the two different paint systems. The oil-based paints, A1 and A2, contained a larger phthalate band at 1041 cm^{-1} and a higher aromatic band at 1599 cm^{-1}. The water-based paints, A3-A8, contained a doublet at 862 and 820 cm^{-1} that was not seen in the oil-based paints, also there was a small aromatic CH deformation band at 1031 cm^{-1}, and a larger CH_2 scissor band at 1449 cm^{-1}.

Table 5: Assignments of the main bands observed in the Raman Spectrum of the architectural paint samples.

WAVENUMBER (CM^{-1})	ASSIGNMENT
610	Rutile
1001	Styrene
1041	Phthalate
1086	Calcium carbonate
1096	Dolomite
1301	CH_2 twist
1449	CH_2 scissor
1599	Aromatic
1730	Carbonyl, C=O

Weathering of paint is brought about by the detrimental chain-scission and cross-linking reactions in the paint film. This can cause erosion and weakening in the mechanical compatibility with the substrate, by undermining adhesion and leading to destruction of the film-substrate integrity [64]. The degradation of acrylic and styrene polymers proceeds predominantly by chain-scission depolymerisation reactions [64]. These can form corresponding monomers as degradation products, leading to new bands or an increase in existing peaks. Overall, a decrease in intensities of the Raman bands was seen in this weathering study with a few small increases also noted, indicating pronounced chemical changes within the architectural paints.

The Raman spectra of sample A1 showed a substantial decrease after 12 months and total disappearance of the styrene band at 1002 cm^{-1} after 36 months. The calcium carbonate band at 1086 cm^{-1} also decreased after 12 months and the band totally disappeared after 36 months. In contrast, there was a noticeable increase of the phthalate band at 1041 cm^{-1}. The Raman spectra before weathering, showed three bands at 996, 1041 and 1086 cm^{-1}, whereas the spectra after just 30 months of weathering showed only one band at 1041 cm^{-1}, see Figure 5 for illustration. Bell *et al* [59] found that the intensities of phthalate 1041 and carbonyl 1730 cm^{-1} bands are strongly correlated, so this behaviour is consistent with the well-known degradation mechanism of oil-based paint coatings. Similar findings were observed with the other oil-based paint A2, with the disappearance of the styrene band at 1002 cm^{-1} and slight increase of the phthalate band at 1041 cm^{-1}. A2 did not contain a calcium carbonate band at 1086 cm^{-1}.

Changes were also seen within the water-based paints. Sample A3 had a total disappearance of the calcium carbonate peak at 1086 cm^{-1} and an increase in the phthalate peak at 1041 cm^{-1}. Sample A5 showed an increase in 1002 cm^{-1} and 1440 cm^{-1} CH_2 scissor bands and the 1730 cm^{-1} carbonyl band. Sample A7 showed major changes to the styrene band at 1002 cm^{-1} and calcium carbonate at 1089 cm^{-1}. An increase in the calcium carbonate 1089 cm^{-1} band and slight decrease in styrene at 1002 cm^{-1} was noted for A8.

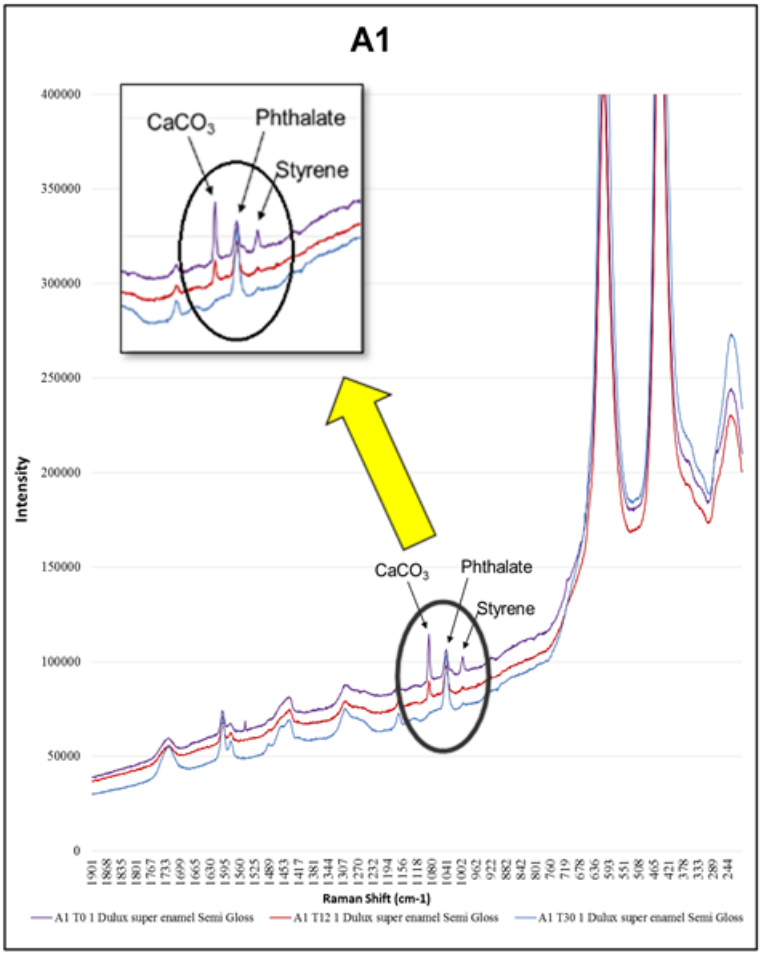


Figure 19: Changes in the intensities of the styrene, calcium carbonate and phthalate peaks of A1 sample after 12 and 30 months of weathering.

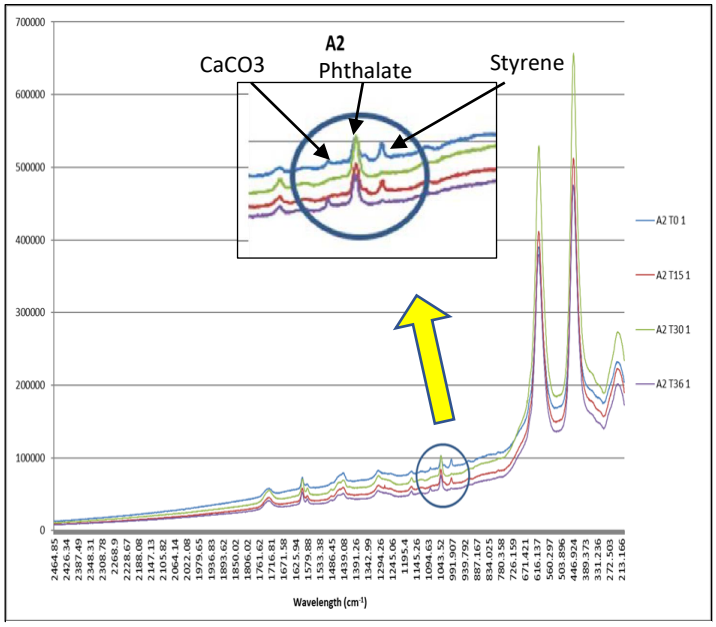


Figure 20: Similar changes seen to the the styrene, calcium carbonate and phthalate peaks for the A2 samples after 15, 30 and 36 months of weathering.

Principal Component Analysis

Principal component analysis (PCA) was carried out on the architectural paint samples to determine if there may be any initial differences between the samples and during the entire 36-month time period that the samples were exposed. The PCA results before the start of the weathering process, labelled T0, already showed a clear separation of the oil-based and water-based paints. This is due to the significant discriminating features of the two types of paints with clear differences in the functional peaks between the oil and water-based paints.

The PCA of the water-based samples did not show a significant separation at T0. After 12 months, sample A8 was seen to form a separate group from the rest of the water-based samples (Figure 20) This separation of A8 remained throughout the rest of the weathering time period.

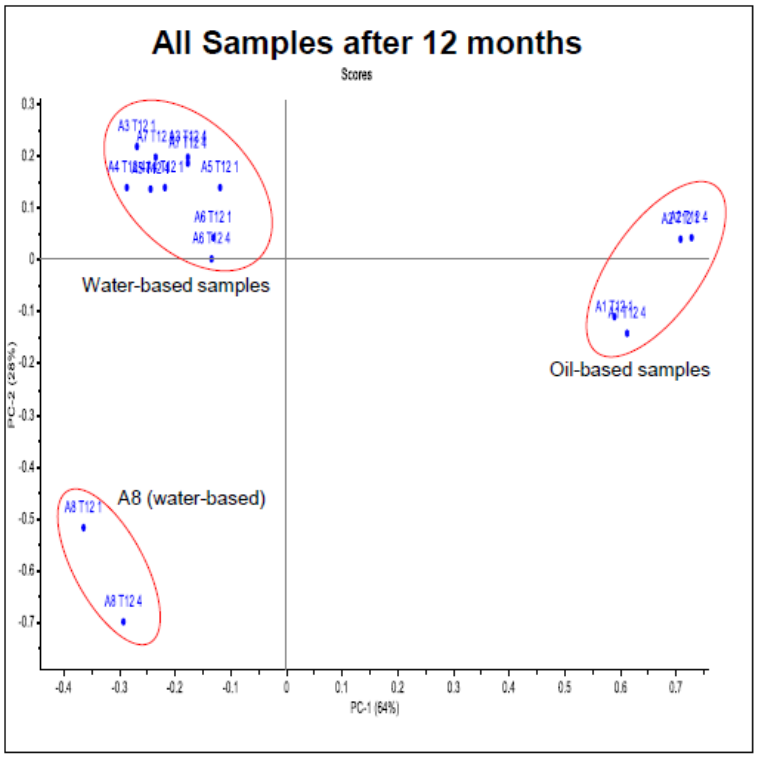


Figure 21: All samples after 12 months of weathering.

Sample A2 showed noticeable separation after only 9 months, see figure 22 below. The changes continued throughout the 36-month exposure with another cluster forming at 12-24 months and again at 30 and 26 months. This demonstrates the continual chemical changes that occurred to the paint sample during exposure to the natural environment. It was interesting to note that the cluster at 36 months was to the right of the PCA plot and not as it was expected to be on the far

left closer to the 30 months cluster. This could be due to the change in the calcium carbonate and the styrene peak intensities that were noted to occur after 30 months of weathering.

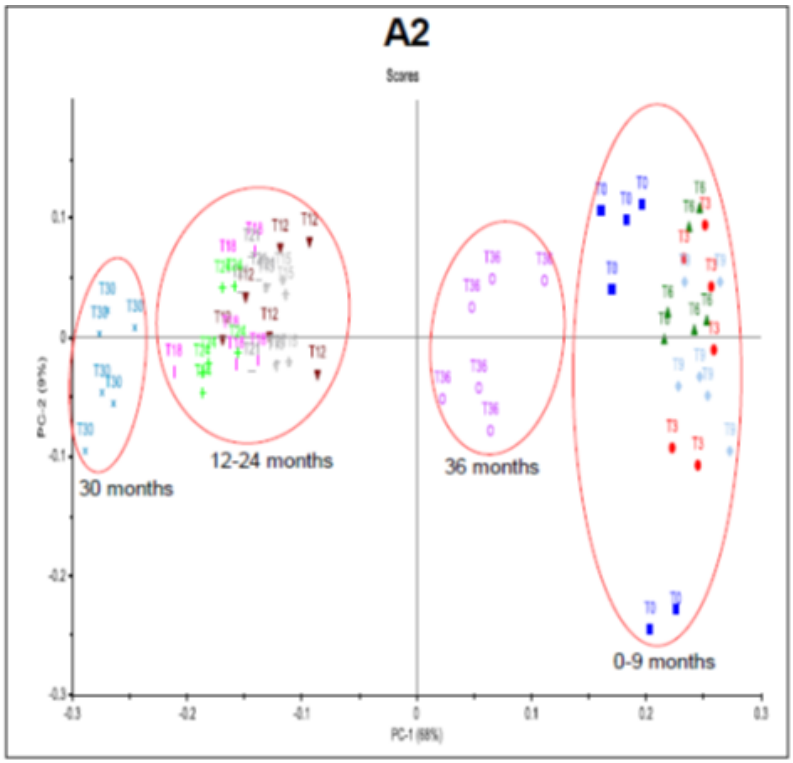


Figure 22: Sample A2 showing separate PCA clusters after 12, 30 and 36 months of weathering.

Photodegradation is known to be a surface effect, with degradation taking place mainly in the top layer of a coating [8]. However, the PCAs of all the paint samples for this study demonstrated that the effects of weathering occurred throughout the paint layers with the analysis of the outer, middle, and inner layers all demonstrating changes and forming close clusters together. This was in contrast to the results in chapter 3 which demonstrated that the outer layers of the clear coats showed greater variance and weathering degradation than the inner layers.

4.5 Conclusion

The aim of this study was to investigate the effects of weathering on architectural paint samples and determine if these effects provide a distinguishing pattern which will allow them to be further differentiated from other architectural samples. This was demonstrated by the results of the weathered selected 8 white architectural paint samples, as a number of the physical and

chemical profiles were found to be altered by the effects of weathering. Prior to the paints being exposed to the natural climate and outdoor conditions, there was a clear spectral difference between the water-based and the oil-based architectural paint samples. This was to be expected and was mainly due to the clear differences in the chemical properties of the two different paint systems. More unexpected and significant changes were seen across all the paint samples after a period of 12-months of weathering, more notable within the water-based samples.

The gloss, water-based white paint samples showed fewer visual degradation changes than the low sheen samples. Overall, the interior oil-based paint samples showed the most visual changes with widespread surface cracking during the 3-year exposure. These visual changes were not surprising, and it was generally expected as paints that are manufactured for interior use are not designed to be exposed to the harsh outdoor weathering conditions. This is predominantly because they do not contain UV inhibitors and other chemical filters that can stop or slow down the weathering effects from the natural outdoor environment. After the three years of exposure to the outdoor Sydney climate, and the examination of the spectral data followed by PCA allowed for a clear understanding as to the extent of the chemical changes and the differences that had occurred due to the weathering degradation of the architectural paints.

These unique weathering results are of great benefit to the forensic science community in that they add more characteristics that can be examined when assessing painted objects. It is also important to note that these distinctive changes may mislead forensic scientists when evaluating questioned to known paint samples that have not been weathered, even if they are the same paint but just not exposed to the same conditions. For example, a car that has left a paint smear on a wall during a hit and run or a ram raid incident. A suspect vehicle has been found but it has been months or years later. The paint that was left behind at the scene may show spectral differences to the paint taken from the suspect's vehicle, but they would be as a result of the different weathering exposure intervals. Also, when conducting database searches using relevant reference paint databases. The added information and characteristics of the paint allows for a higher discriminating power and improved evaluation of the evidential value of the evidence to be applied to the paint sample. This study was only limited to white architectural paints and a handful of the brands that are available. To obtain more insight and

to help discriminate other paint samples, the addition of vehicle paint as well as expanding the architectural paint samples is needed.

Chapter 5: General Discussion

This research project set out to answer the aims and objects that were identified earlier in an attempt to improve the evaluation of the evidential value of vehicle and architectural paint. To do this, a number of questions were raised at the beginning of the project, the first one was, *can the evaluation of the evidential value of paint be improved with the addition of up-to-date surveys to provide the forensic examiners with more accurate data and add strength to the analysis of the paint specimens?* This question was answered by conducting a survey of the most common vehicle colour that was seen on the roads within western Sydney, as well as the most common colours that are found on stationary objects within car parks around the same area. The first survey resulted in the top four colours to be red, blue, black, and white. The second survey that was conducted on stationary objects in different car parks was found to have similar colours occupying the top four most seen colours. When the results from both these surveys were compared to previously conducted surveys in other countries, some similarity was seen but more notably, it highlighted some differences in the colours that were recorded and the important need to conduct surveys that are more relevant to Australia and more recent, as it was found that the general trend of the vehicle colours did changed over time and varied from continent to continent. Therefore, if a forensic scientist was analysing samples that were purple in colour, which was found to be one of the least common vehicle colours, then they can add more evidential strength to the overall findings. On other hand if they had paint that was red in colour, then a lower evidential strength would be applied and it would improve the defence's likelihood ratio, as it was recorded to be one of the most common colours that were seen on the roads. This survey also showed a good correspondence to the official road authority colour data. This finding is promising because it indicates that such a survey may not need to be repeated often as official data could be considered as a proxy that is fit for purpose.

The second question that was raised was, *can the environmental weathering effects on the paint samples, generate additional acquired characteristics that can be used when comparing paint traces?*

This question was addressed through research that involved analysing clear coats from both the New Zealand and Australian paint samples. The results from this study established that it was possible to not only distinguish paint samples from different vehicles, but it was even possible to separate them between panels of the same vehicle based on the analysis of the UV

screening chemicals in the clear coats. It was found that the degradation pattern of these particular chemicals was not only different between the vehicles, but they produced different characteristic profiles on the panels that were exposed to the harsh UV radiation, compared to those that were not exposed to the same conditions.

An example of this in a criminal setting could be- let us say there was a hit and run accident, and paint was left behind and examined with paint specimens that were taken from a suspected vehicle that was involved, the forensic scientist could not only provide results to demonstrate that the suspected car was the one that left behind the paint samples, but the results could potentially be used determine which particular panel or area on the car the paint came from. However, further research is still needed in this area to gain increased understanding and proof that this occurs in different paint to verify the full potential of this research.

The results and findings that were discovered from the work that was conducted with this research project, ultimately allowed for the evaluation of the evidential value to be improved by the addition of more up to date and geographically relevant background paint survey data as well as more added comparative features which form as a result of the effects of weathering on both vehicle and architectural paint. These observed findings help the forensic scientist to provide the correct evaluation of the evidential value to the paint evidence that is being analysed.

The weathering studies showed that there are a number of physical and chemical changes that can occur to both to vehicle and architectural paint over time. Moreover, not all the paint was affected the same way or at the same rate and it was found to be dependent on the amount of exposure to the harmful UV radiation that the paint had received. This has resulted in the overall improvement in the strength and evidential value that can be given to the paint evidence as it has been demonstrated with the findings from this research project. The results have shown that even paint of the same type (colour, brand, manufacture, and year) could be distinguished from each other because of the differences in the UV concentrations that were measured in the clear coat study. This would not only point to the vehicle as being the source of the paint sample, but it could also indicate what panel or area of the vehicle the paint sample came from. This would then offer support for an increase in the evidentiary value, as it would provide not only source level evidence but also higher .

The results from the intra-sample variation study helped to verify that the results of the weathering studies were actually caused by the natural weathering degradation of the paints and not from any internal sampling variations that may be present. This was an important study to perform as it provided the necessary evidence to prove that the changes that were being recorded in the samples were actually from the UV degradation of the chemical composition of the paints. It also demonstrated the sampling techniques that were used, and the instrumental analysis of the samples were appropriate and did not cause the measurement discrepancies. These two surveys answered the first question that was asked with this research project as the data helped to increase and add strength to the evidential value of the paint samples.

The next part of this research project, in chapter 4, centred on the weathering of 8 oil-based and water-based architectural paint in the Sydney, Australian climate. This study came about as there have been a number of studies involving architectural paints over the years, however, there has been little to no research data that has looked into the effects of weathering on these types of paints. Previous work by Roux *et. al*.[74] highlighted the need for the ageing effects of architectural paint to be explored as it would help to provide an increase to the strength of evidence for samples that are indistinguishable. This was the main idea behind this work and to help fill the gap and the understanding of the weathering changes that occur on architectural paints. The research that was conducted on the weathering of architectural paints established that the oil-based and water-based architectural paints that were used were able to be analytically separated even before the exposure to the outdoor weathering effects, which was not surprising given the chemical variation that are already present in the paints. The use of both interior and exterior oil-based paints allowed for further differences to be established, with the interior paint showing the most visual and chemical changes with the weathering effects compared to the interior paints that have UV chemical filters and inbuild protection from the UV radiation. The results were not all that surprising as the paints that were manufactured for interior use only, all showed the weathering degradation effects sooner and to a larger extent, than the paints that were designed to withstand the harsh outdoor exposure. This study also helped to demonstrate the value and importance of conducting natural weathering tests as opposed to accelerated and artificial tests that may not be able to replicate what actually happens in the real climate.

Overall, the research that was conducted into the natural effects of weathering and the results that were observed to both the vehicle and architectural paints have not only provided the

scientist with increased data to offer a stronger evidential value to the paint evidence they may examine, but it has also equipped them with the information and means to offer a stronger evidential value. This could be a result of an activity level weight of the paint evidence as opposed to only a source level being applied due to the panel or area of the paint being determined by examining and matching or demonstrating differences in the weathering profiles of the paint samples that are being analysed. This higher strength of the evidence can be applied as it has been identified with this research, that not all paint will undergo the same weathering changes. This was even demonstrated with paints of the same chemical makeup. The main differences were found between the paints that were fully exposed to the harsh environmental conditions, such as the paint from the roof and bonnet of the vehicle, compared to those that were covered and had less exposure to these same conditions, such as under the bonnet or in the boot of the vehicles. The absorbance of the UV chemicals that were present in the clear coats was measured and graphed which helped to make clear, the differences that were seen to occur between the layers of the clear coat that were on the outside and had more exposure to the harmful UV radiation compared to the layers that were the closest to the colour layers and would have less exposure. These differences can therefore be compared for paint samples that are suspected to be from the same vehicle and if they are found to follow similar weathering degradation profile and pattern then the forensic scientist may possibly then be able to determine what side of the vehicle or from which panel the paint sample had originated from.

Similarly, the changes that were observed to the white architectural paint samples, proved that various weathering degradation changes can occur in the same paint after different exposure times to the same weathering conditions. This has highlighted the importance of collecting both known and questioned paint specimens at the same time to help avoid any mistakes or misinterpretations being made with the forensic analysis of the paint samples due to differences in the weathering profiles that can be found. These significant results have also given support for increased likelihood ratio calculations being made, as paint that is collected from one side of the house that has full exposure to the harmful UV radiation will have a different physical and chemical weathering degradation patter to that of paint that is from an area of the house that is in full shade. Therefore, the paint samples from the two separate areas of the same house will both possess different weathering characteristics that can be measured and evaluated. A knowledgeable forensic scientist may then use this information to evaluate the weathering profiles of the paint specimens and verify that the sample in question, did in fact come from

the same area of the house that the known paint sample was taken from. Their overall evaluation of the paint evidence will then be increased as they can provide activity level instead of only source level strength to the paint evidence.

In contrast to this, the results can also support the defence's hypothesis, that the paint is not from the object or the vehicle in question, but from some other source. If there are enough physical and chemical weathering differences that cannot be easily explained, then it may show support for the theory that the questioned paint is from another source or area on the same object or vehicle, even though they may share some chemical similarities. These weathering differences could then result in a LR of <1 which would indicate support for the defence hypothesis over the prosection hypothesis.

Furthermore, if any differentiable paint traces are found during the analysis it will reduce the numerator in the LR calculation, and the more differentiable paint traces that are discovered, the stronger the impact, ie the LR of non-differentiable microtraces decreases. On the other hand, the more variable the population information is (the results that were collected from the study into the weathering effects of architectural paint), the more the denominator is reduced, i.e. the LR of the non-differentiable paint traces increases.

Chapter 6: Overall Conclusion and Future Work

The results from the diverse research design of this project have both; added more up to-date data, compared to the previously conducted surveys and studies focusing on paint. It has also provided data which is more relevant to the Australian climate and cases by conducting background surveys in Sydney, Australian. From the results of the surveys that were conducted and presented in chapter 2, aided in the increased calculations of the likelihood ratio to be made. Therefore, if a forensic scientist was analysing samples that were of a colour that was least commonly found, then they can add more evidential strength to the overall findings. On other hand if they had paint that was a colour which was most commonly found, then a lower evidential strength would be applied to the overall findings of the paint evidence. The research involving the effects of weathering on clear coats and architectural paints both help to not only discriminate between different paints but also within the same type of painted object and allow for possible point of contact or the areas/area from which the paint samples originated from to be verified, using the varied weathering patterns that were shown to occur on the different panels of the same vehicle. This helps to support a higher weighted evaluation of the evidence to be made, as it may can support the forensic scientist to offer a higher level of evaluation. This research may also help to reduce and eliminate any uncertainties that the scientist and courts may have. By providing increased data and additional acquired characteristics that can be analysed and compared, it can reduce the inclusion of possible false paint sources that can skew the overall findings which may provide false assumptions to the forensic scientist and the police which may then lead to wrongful outcomes in the courts.

The results and findings that were made clear from the work that was conducted with this research project, ultimately allowed for the evaluation of the evidential value of vehicle and architectural paint to be improved. This was not only achieved by the addition of more up to date and more geographically relevant, Australian based data, but also with the addition of more comparative features that can be utilised during the forensic examination of paint. These acquired and additional characteristics form as a result of the effects of weathering on both vehicle and architectural paint. The results and findings from the paint surveys and the weathering studies that were conducted during this research project, all help give the forensic scientist the correct and relevant information that they can draw on to provide the correct evaluation of the evidential value to the paint evidence that is being analysed.

This research project has in turn, also given the investigators and the courts greater understanding and confidence that the correct assessment of the facts has been made by providing improved and additional data that can be drawn on by the forensic scientist when comparing and evaluating paint evidence. Furthermore, the results from this research project not only cover, but they also help fill the gaps in the knowledge and understanding of the chemical data and changes that occur to paint evidence. An example of this is with the weathering studies that were conducted in Chapters 3 and 4.

Still, further work and more research is needed to increase and keep updating the background knowledge of paint evidence so that the best available data can be used when evaluating the evidential value of paint. The correct use of the data collected from this research project and further research with respect to the LR framework must also be further examined to gain the full understanding and benefits from the presented results. The results that were collected during this research study can also be used to give more weight to the calculation of the likelihood ratio by increasing or decreasing the LR calculation. This effect is explained above in chapter 5, where any differentiable microtraces that are found and with the increased information from the background studies that were conducted, will affect the numerator or the denominator (defence or the prosecution theory) when the forensic scientist is calculating the LR of the given scenario. Only with further background studies can the calculation of the likelihood ratio be kept accurate with the most relevant and up to date data being used.

Likewise, as the weathering studies that were presented here were very useful, they were limited to only a small number of paint samples and over a short time period. More information could ultimately be obtained with the addition of more paint samples, both from additional vehicle and architectural samples and conducted over a longer period of time .and also adding to the type (different vehicle and architectural brands). The increased number of paint samples that are tested will help to increase the areas that have yet to be covered and to expand on the knowledge regarding the weathering effects that can occur on a wider variety of paints and under different conditions. This will not only offer invaluable insights to the degradation effects on different paints, but it can also cultivate more characteristics that can be measured and utilised in the comparison of paint samples.

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Appendix 1

The table below shows the MSP results that were measuredfor the paint samples that were included in the intra-sample variation study. The MS measurements were taken at time 0 before any exposure to the weathering climate and included three different areas of the same paint panel and the measurements were taken in duplicate for each area. This process was repeated at 3,6,9 and 12-month intervals on the same paint panels in order to gauge whether any significant variation was occurring within same sample due to the different areas being sampled and not due to the weathering degradation effects.

		Paint Sample					
		R19 #1		R19 #2		R19 #3	
		MSP Measurement					
		1	2	1	2	1	2
MSP Wavenumber (nm)	250.65	0.7437	0.7469	0.7437	0.7469	0.7437	0.7469
	251.45	0.7582	0.7492	0.7582	0.7492	0.7582	0.7492
	252.25	0.7711	0.7512	0.7711	0.7512	0.7711	0.7512
	253.85	0.7926	0.7543	0.7926	0.7543	0.7926	0.7543
	254.66	0.8013	0.7555	0.8013	0.7555	0.8013	0.7555
	255.46	0.8089	0.7564	0.8089	0.7564	0.8089	0.7564
	256.26	0.8152	0.7571	0.8152	0.7571	0.8152	0.7571
	257.86	0.8247	0.7579	0.8247	0.7579	0.8247	0.7579
	258.66	0.828	0.7581	0.828	0.7581	0.828	0.7581
	259.46	0.8305	0.7581	0.8305	0.7581	0.8305	0.7581
	260.27	0.8321	0.758	0.8321	0.758	0.8321	0.758
	261.87	0.8332	0.7576	0.8332	0.7576	0.8332	0.7576
	262.67	0.8329	0.7573	0.8329	0.7573	0.8329	0.7573
	263.47	0.832	0.7569	0.832	0.7569	0.832	0.7569
	264.27	0.8307	0.7566	0.8307	0.7566	0.8307	0.7566
	265.87	0.8271	0.7559	0.8271	0.7559	0.8271	0.7559
	266.67	0.8249	0.7556	0.8249	0.7556	0.8249	0.7556
	267.47	0.8226	0.7554	0.8226	0.7554	0.8226	0.7554
	268.27	0.8201	0.7557	0.8201	0.7557	0.8201	0.7557
	269.87	0.8156	0.7565	0.8156	0.7565	0.8156	0.7565
	270.68	0.8141	0.7572	0.8141	0.7572	0.8141	0.7572
	271.48	0.8133	0.7585	0.8133	0.7585	0.8133	0.7585
	272.28	0.8132	0.7604	0.8132	0.7604	0.8132	0.7604

	273.88	0.815	0.7636	0.815	0.7636	0.815	0.7636
	274.68	0.8164	0.7645	0.8164	0.7645	0.8164	0.7645
	275.48	0.8184	0.7653	0.8184	0.7653	0.8184	0.7653
	276.27	0.8206	0.7659	0.8206	0.7659	0.8206	0.7659
	277.87	0.8245	0.7675	0.8245	0.7675	0.8245	0.7675
	278.67	0.826	0.7686	0.826	0.7686	0.826	0.7686
	279.47	0.8271	0.7699	0.8271	0.7699	0.8271	0.7699
	280.27	0.8282	0.7712	0.8282	0.7712	0.8282	0.7712
	281.87	0.8306	0.7744	0.8306	0.7744	0.8306	0.7744
	282.67	0.8319	0.7762	0.8319	0.7762	0.8319	0.7762
	283.47	0.8341	0.7789	0.8341	0.7789	0.8341	0.7789
	284.27	0.8369	0.7822	0.8369	0.7822	0.8369	0.7822
	285.87	0.8449	0.7898	0.8449	0.7898	0.8449	0.7898
	286.66	0.8503	0.7935	0.8503	0.7935	0.8503	0.7935
	287.46	0.8563	0.7973	0.8563	0.7973	0.8563	0.7973
	288.26	0.8627	0.8007	0.8627	0.8007	0.8627	0.8007
	289.86	0.8755	0.8063	0.8755	0.8063	0.8755	0.8063
	290.66	0.8813	0.8088	0.8813	0.8088	0.8813	0.8088
	291.46	0.8867	0.812	0.8867	0.812	0.8867	0.812
	292.25	0.8916	0.8153	0.8916	0.8153	0.8916	0.8153
	293.85	0.9001	0.8232	0.9001	0.8232	0.9001	0.8232
	294.65	0.9038	0.828	0.9038	0.828	0.9038	0.828
	295.45	0.9071	0.8336	0.9071	0.8336	0.9071	0.8336
	296.24	0.9106	0.8395	0.9106	0.8395	0.9106	0.8395
	297.84	0.9187	0.8532	0.9187	0.8532	0.9187	0.8532
	298.64	0.9237	0.8609	0.9237	0.8609	0.9237	0.8609
	299.44	0.9291	0.8689	0.9291	0.8689	0.9291	0.8689
	300.23	0.9346	0.8763	0.9346	0.8763	0.9346	0.8763
	301.83	0.9466	0.8902	0.9466	0.8902	0.9466	0.8902
	302.63	0.9532	0.8965	0.9532	0.8965	0.9532	0.8965
	303.42	0.9602	0.9024	0.9602	0.9024	0.9602	0.9024
	304.22	0.9674	0.9081	0.9674	0.9081	0.9674	0.9081
	305.81	0.9807	0.919	0.9807	0.919	0.9807	0.919
	306.61	0.987	0.9242	0.987	0.9242	0.987	0.9242
	307.41	0.9925	0.9296	0.9925	0.9296	0.9925	0.9296
	308.2	0.998	0.9355	0.998	0.9355	0.998	0.9355
	309	1.0038	0.9423	1.0038	0.9423	1.0038	0.9423
	310.59	1.0157	0.9576	1.0157	0.9576	1.0157	0.9576

311.39	1.0223	0.966	1.0223	0.966	1.0223	0.966
312.98	1.0366	0.9835	1.0366	0.9835	1.0366	0.9835
313.78	1.0451	0.9923	1.0451	0.9923	1.0451	0.9923
314.58	1.0535	1.001	1.0535	1.001	1.0535	1.001
315.37	1.062	1.0093	1.062	1.0093	1.062	1.0093
316.96	1.0811	1.0256	1.0811	1.0256	1.0811	1.0256
317.76	1.0912	1.0328	1.0912	1.0328	1.0912	1.0328
318.56	1.1014	1.0394	1.1014	1.0394	1.1014	1.0394
319.35	1.111	1.0459	1.111	1.0459	1.111	1.0459
320.94	1.1283	1.0586	1.1283	1.0586	1.1283	1.0586
321.74	1.1359	1.0648	1.1359	1.0648	1.1359	1.0648
322.53	1.143	1.0714	1.143	1.0714	1.143	1.0714
323.33	1.15	1.0788	1.15	1.0788	1.15	1.0788
324.92	1.1646	1.0956	1.1646	1.0956	1.1646	1.0956
325.72	1.172	1.1046	1.172	1.1046	1.172	1.1046
326.51	1.1792	1.1141	1.1792	1.1141	1.1792	1.1141
327.31	1.1866	1.1238	1.1866	1.1238	1.1866	1.1238
328.9	1.2025	1.1437	1.2025	1.1437	1.2025	1.1437
329.69	1.2112	1.1533	1.2112	1.1533	1.2112	1.1533
330.49	1.2199	1.1626	1.2199	1.1626	1.2199	1.1626
331.28	1.2287	1.1713	1.2287	1.1713	1.2287	1.1713
332.87	1.2461	1.1877	1.2461	1.1877	1.2461	1.1877
333.66	1.2545	1.1954	1.2545	1.1954	1.2545	1.1954
334.46	1.2629	1.203	1.2629	1.203	1.2629	1.203
335.25	1.2715	1.2106	1.2715	1.2106	1.2715	1.2106
336.84	1.2886	1.2264	1.2886	1.2264	1.2886	1.2264
337.64	1.297	1.2348	1.297	1.2348	1.297	1.2348
338.43	1.3053	1.2438	1.3053	1.2438	1.3053	1.2438
339.22	1.3137	1.2532	1.3137	1.2532	1.3137	1.2532
340.81	1.3303	1.2729	1.3303	1.2729	1.3303	1.2729
341.6	1.3387	1.2823	1.3387	1.2823	1.3387	1.2823
342.4	1.347	1.2915	1.347	1.2915	1.347	1.2915
343.99	1.3638	1.3083	1.3638	1.3083	1.3638	1.3083
344.78	1.372	1.3157	1.372	1.3157	1.372	1.3157
345.57	1.38	1.3225	1.38	1.3225	1.38	1.3225
346.37	1.3878	1.3286	1.3878	1.3286	1.3878	1.3286
347.95	1.4016	1.3388	1.4016	1.3388	1.4016	1.3388
348.75	1.408	1.3433	1.408	1.3433	1.408	1.3433

	349.54	1.4143	1.3475	1.4143	1.3475	1.4143	1.3475
	350.33	1.4203	1.3516	1.4203	1.3516	1.4203	1.3516
	351.92	1.4315	1.3596	1.4315	1.3596	1.4315	1.3596
	352.71	1.4364	1.3639	1.4364	1.3639	1.4364	1.3639
	353.5	1.4409	1.368	1.4409	1.368	1.4409	1.368
	354.29	1.4451	1.372	1.4451	1.372	1.4451	1.372
	355.88	1.4535	1.3799	1.4535	1.3799	1.4535	1.3799
	356.67	1.4582	1.3839	1.4582	1.3839	1.4582	1.3839
	357.46	1.4627	1.3877	1.4627	1.3877	1.4627	1.3877
	358.26	1.4668	1.3913	1.4668	1.3913	1.4668	1.3913
	359.84	1.4745	1.3984	1.4745	1.3984	1.4745	1.3984
	360.63	1.4782	1.4017	1.4782	1.4017	1.4782	1.4017
	361.42	1.4814	1.4048	1.4814	1.4048	1.4814	1.4048
	362.22	1.4845	1.4078	1.4845	1.4078	1.4845	1.4078
	363.8	1.49	1.4137	1.49	1.4137	1.49	1.4137
	364.59	1.492	1.4163	1.492	1.4163	1.492	1.4163
	365.38	1.4935	1.4186	1.4935	1.4186	1.4935	1.4186
	366.97	1.495	1.4216	1.495	1.4216	1.495	1.4216
	367.76	1.495	1.4222	1.495	1.4222	1.495	1.4222
	368.55	1.4944	1.4221	1.4944	1.4221	1.4944	1.4221
	369.34	1.4931	1.4211	1.4931	1.4211	1.4931	1.4211
	370.13	1.491	1.4191	1.491	1.4191	1.491	1.4191
	371.71	1.4847	1.4118	1.4847	1.4118	1.4847	1.4118
	372.5	1.48	1.4059	1.48	1.4059	1.48	1.4059
	373.29	1.4744	1.3984	1.4744	1.3984	1.4744	1.3984
	374.87	1.4593	1.3786	1.4593	1.3786	1.4593	1.3786
	375.67	1.4502	1.3668	1.4502	1.3668	1.4502	1.3668
	376.46	1.44	1.3537	1.44	1.3537	1.44	1.3537
	377.25	1.4286	1.3394	1.4286	1.3394	1.4286	1.3394
	378.83	1.4026	1.3075	1.4026	1.3075	1.4026	1.3075
	379.62	1.3882	1.2901	1.3882	1.2901	1.3882	1.2901
	380.41	1.3731	1.2719	1.3731	1.2719	1.3731	1.2719
	381.99	1.3411	1.2339	1.3411	1.2339	1.3411	1.2339
	382.78	1.3245	1.2142	1.3245	1.2142	1.3245	1.2142
	383.57	1.3076	1.1941	1.3076	1.1941	1.3076	1.1941
	384.36	1.2906	1.1738	1.2906	1.1738	1.2906	1.1738
	385.94	1.2558	1.1326	1.2558	1.1326	1.2558	1.1326
	386.73	1.2386	1.112	1.2386	1.112	1.2386	1.112

	387.51	1.2216	1.0916	1.2216	1.0916	1.2216	1.0916
	389.88	1.1729	1.0335	1.1729	1.0335	1.1729	1.0335
	390.67	1.1577	1.0157	1.1577	1.0157	1.1577	1.0157
	391.46	1.1432	0.9989	1.1432	0.9989	1.1432	0.9989
	392.25	1.1295	0.9831	1.1295	0.9831	1.1295	0.9831
	393.83	1.1045	0.9545	1.1045	0.9545	1.1045	0.9545
	394.62	1.0933	0.9417	1.0933	0.9417	1.0933	0.9417
	395.41	1.0829	0.9299	1.0829	0.9299	1.0829	0.9299
	396.98	1.0645	0.909	1.0645	0.909	1.0645	0.909
	397.77	1.0564	0.8997	1.0564	0.8997	1.0564	0.8997
	398.56	1.0491	0.8912	1.0491	0.8912	1.0491	0.8912
	399.35	1.0425	0.8835	1.0425	0.8835	1.0425	0.8835
	400.92	1.0313	0.8701	1.0313	0.8701	1.0313	0.8701
	401.71	1.0267	0.8643	1.0267	0.8643	1.0267	0.8643
	402.5	1.0225	0.8592	1.0225	0.8592	1.0225	0.8592
	403.29	1.0189	0.8546	1.0189	0.8546	1.0189	0.8546
	404.86	1.013	0.847	1.013	0.847	1.013	0.847
	405.65	1.0107	0.8439	1.0107	0.8439	1.0107	0.8439
	406.44	1.0086	0.8411	1.0086	0.8411	1.0086	0.8411
	407.23	1.0068	0.8386	1.0068	0.8386	1.0068	0.8386
	408.8	1.0036	0.8343	1.0036	0.8343	1.0036	0.8343
	409.59	1.0022	0.8323	1.0022	0.8323	1.0022	0.8323
	410.38	1.0008	0.8305	1.0008	0.8305	1.0008	0.8305
	411.95	0.9982	0.827	0.9982	0.827	0.9982	0.827
	412.74	0.9969	0.8254	0.9969	0.8254	0.9969	0.8254
	413.52	0.9958	0.8238	0.9958	0.8238	0.9958	0.8238
	414.31	0.9946	0.8223	0.9946	0.8223	0.9946	0.8223
	415.88	0.9924	0.8195	0.9924	0.8195	0.9924	0.8195
	416.67	0.9913	0.8182	0.9913	0.8182	0.9913	0.8182
	417.46	0.9904	0.817	0.9904	0.817	0.9904	0.817
	418.24	0.9895	0.8158	0.9895	0.8158	0.9895	0.8158
	419.82	0.9877	0.8136	0.9877	0.8136	0.9877	0.8136
	420.6	0.9868	0.8125	0.9868	0.8125	0.9868	0.8125
	421.39	0.9859	0.8114	0.9859	0.8114	0.9859	0.8114
	422.96	0.9837	0.8091	0.9837	0.8091	0.9837	0.8091
	423.75	0.9825	0.8078	0.9825	0.8078	0.9825	0.8078
	424.53	0.9812	0.8064	0.9812	0.8064	0.9812	0.8064
	425.32	0.9797	0.8048	0.9797	0.8048	0.9797	0.8048

	426.89	0.9762	0.8013	0.9762	0.8013	0.9762	0.8013
	427.68	0.9743	0.7994	0.9743	0.7994	0.9743	0.7994
	428.46	0.9722	0.7974	0.9722	0.7974	0.9722	0.7974
	429.25	0.9701	0.7953	0.9701	0.7953	0.9701	0.7953
	430.82	0.9655	0.7909	0.9655	0.7909	0.9655	0.7909
	431.6	0.963	0.7887	0.963	0.7887	0.963	0.7887
	432.39	0.9606	0.7865	0.9606	0.7865	0.9606	0.7865
	433.96	0.9554	0.7819	0.9554	0.7819	0.9554	0.7819
	434.74	0.9528	0.7796	0.9528	0.7796	0.9528	0.7796
	435.53	0.9501	0.7773	0.9501	0.7773	0.9501	0.7773
	436.31	0.9474	0.775	0.9474	0.775	0.9474	0.775
	437.88	0.9418	0.7704	0.9418	0.7704	0.9418	0.7704
	438.67	0.9391	0.768	0.9391	0.768	0.9391	0.768
	439.45	0.9363	0.7657	0.9363	0.7657	0.9363	0.7657
	440.24	0.9335	0.7635	0.9335	0.7635	0.9335	0.7635
	441.81	0.9279	0.759	0.9279	0.759	0.9279	0.759
	442.59	0.9251	0.7568	0.9251	0.7568	0.9251	0.7568
	443.37	0.9224	0.7546	0.9224	0.7546	0.9224	0.7546
	444.94	0.917	0.7504	0.917	0.7504	0.917	0.7504
	445.73	0.9143	0.7484	0.9143	0.7484	0.9143	0.7484
	446.51	0.9117	0.7465	0.9117	0.7465	0.9117	0.7465
	447.29	0.9092	0.7446	0.9092	0.7446	0.9092	0.7446
	448.86	0.9043	0.741	0.9043	0.741	0.9043	0.741
	449.64	0.9019	0.7393	0.9019	0.7393	0.9019	0.7393

Appendix 2

Raman, FTIR spectra and PCA plots for some of the archectrural and vehicle paint samples, demonstrating the spectiral changes that occurred during the weathering exposures.

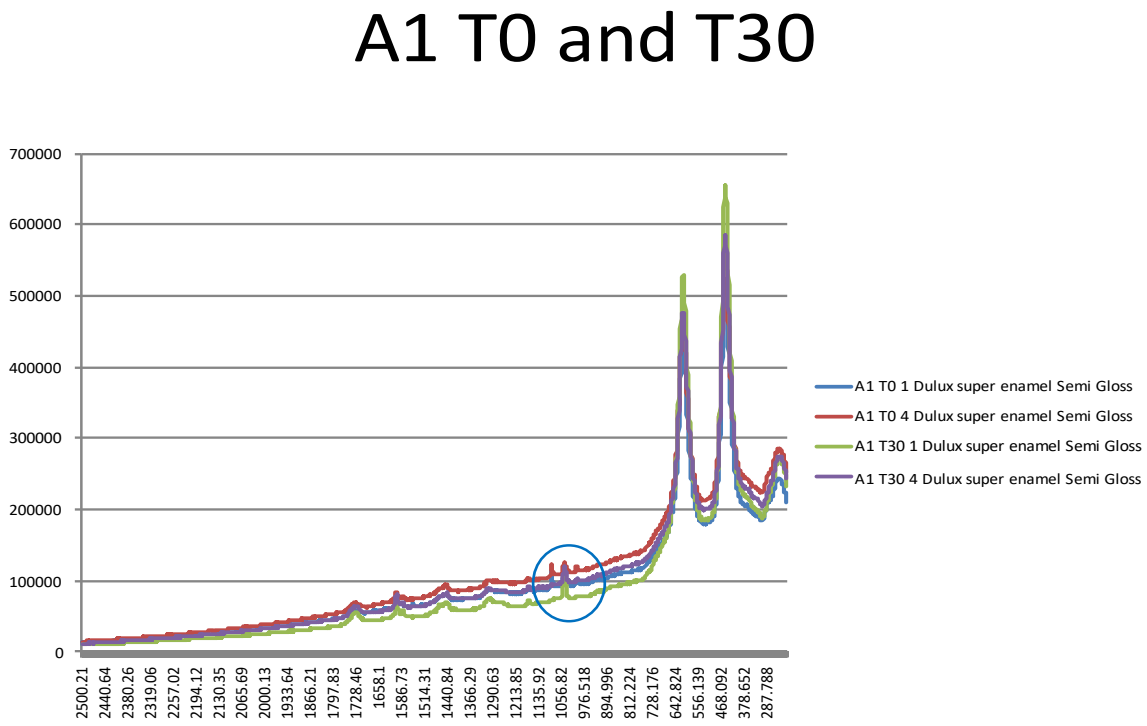


Figure 23: Raman spectra for the archectrural paint sample A1 before weatheing and after 30 months of weathering, highlighting the specrtural changes that have occurred.

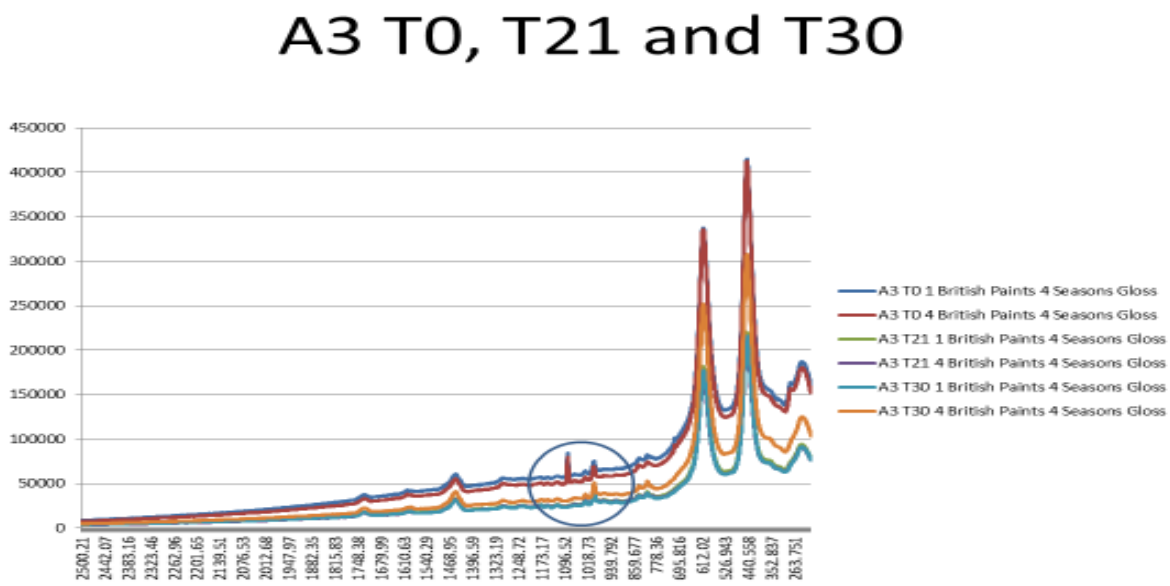


Figure 24: Raman spectra for archectrural paint sample A3 before weathering, at 21 and 30 months of weathering, highlighting the specrtural changes that have occurred.

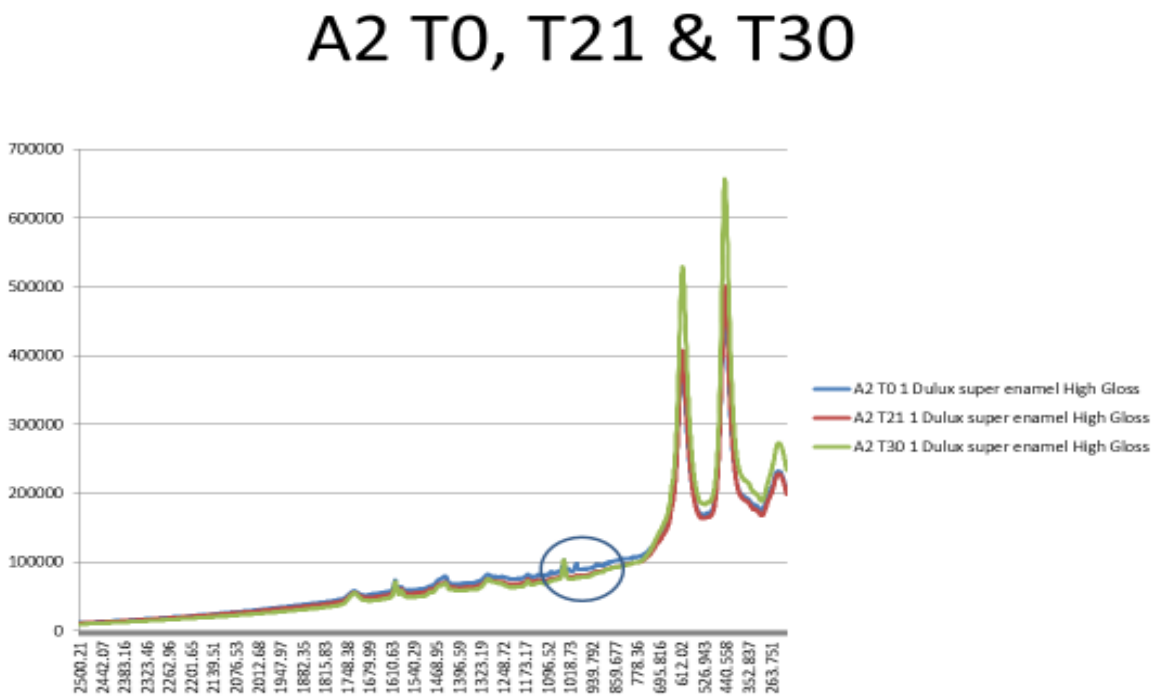


Figure 25: Raman spectra for the archectrural paint sample A2 before weathering, at 21 and 30 months of weathering exposure, highlighting the specrtural changes that have occurred.

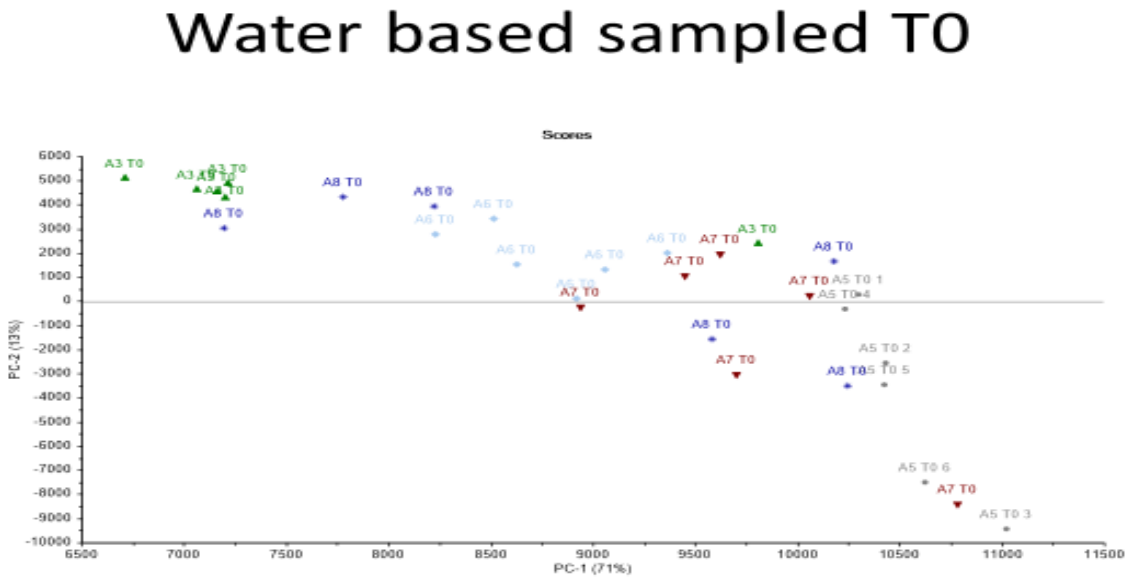


Figure 26: All of the water-based archectural paint samples before weathering, no clear separation seen.

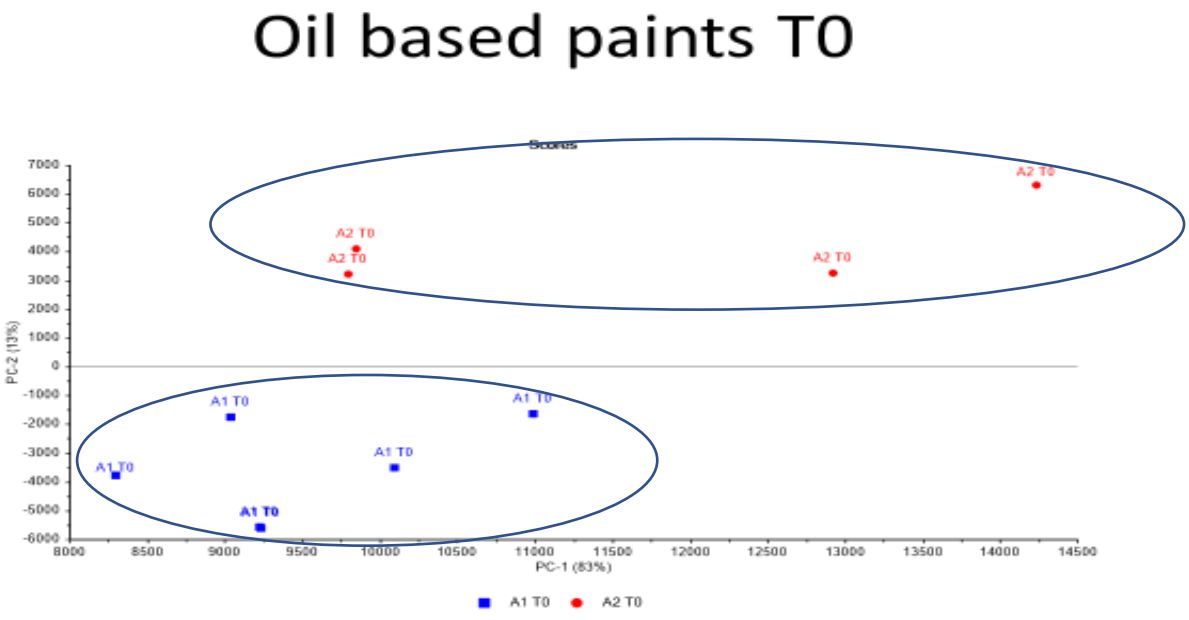


Figure 27: PCA plot of the two oil-based archectural paint samples before weathering, showing already a clear separation between the two samples.

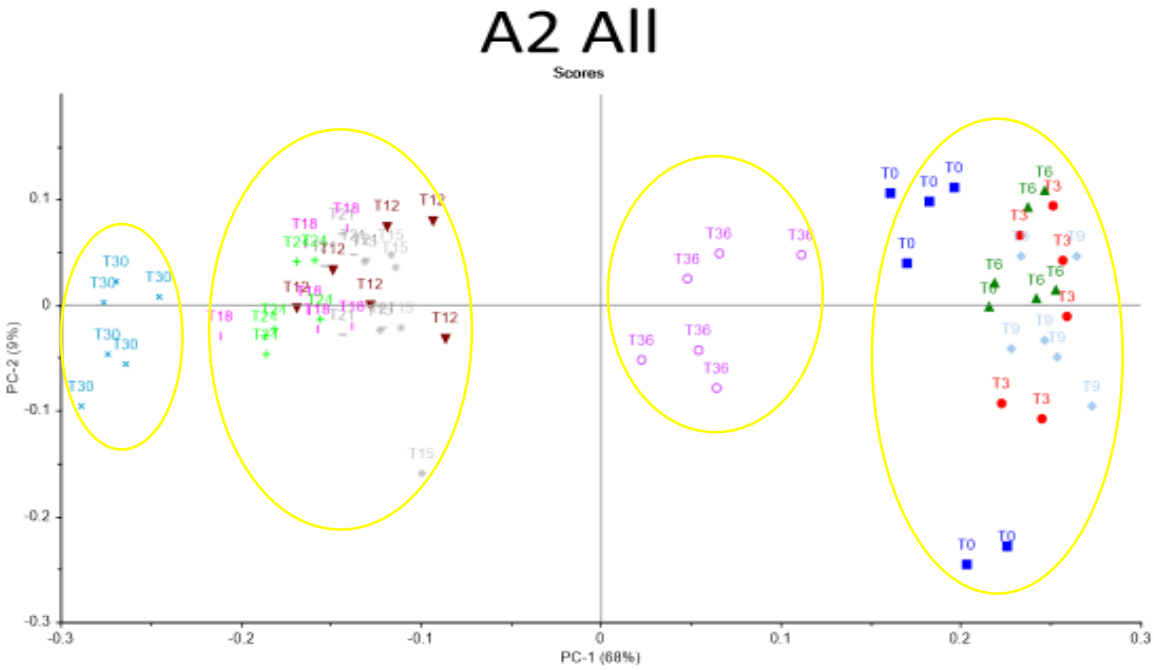


Figure 28: PCA polt of the raman spectra results for the archectural paint sample A2 for the first 36 months of weathering overladed.

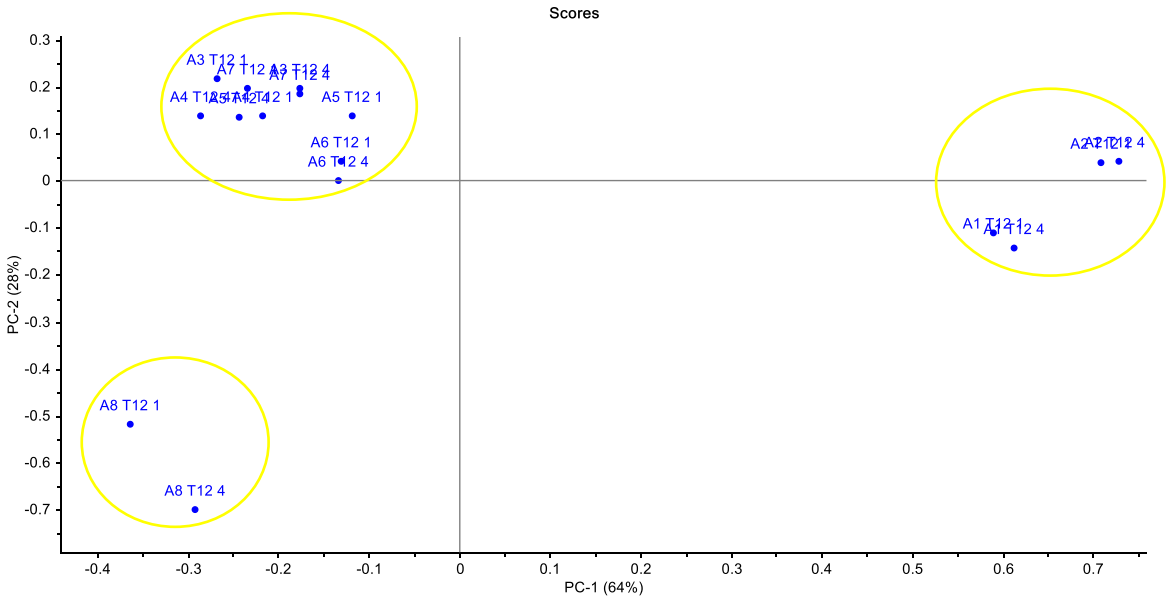


Figure 29: PCA plot showing the clear eparation of archectural paint sample A8 from the other water-based paint samples after 12 months of weathering.

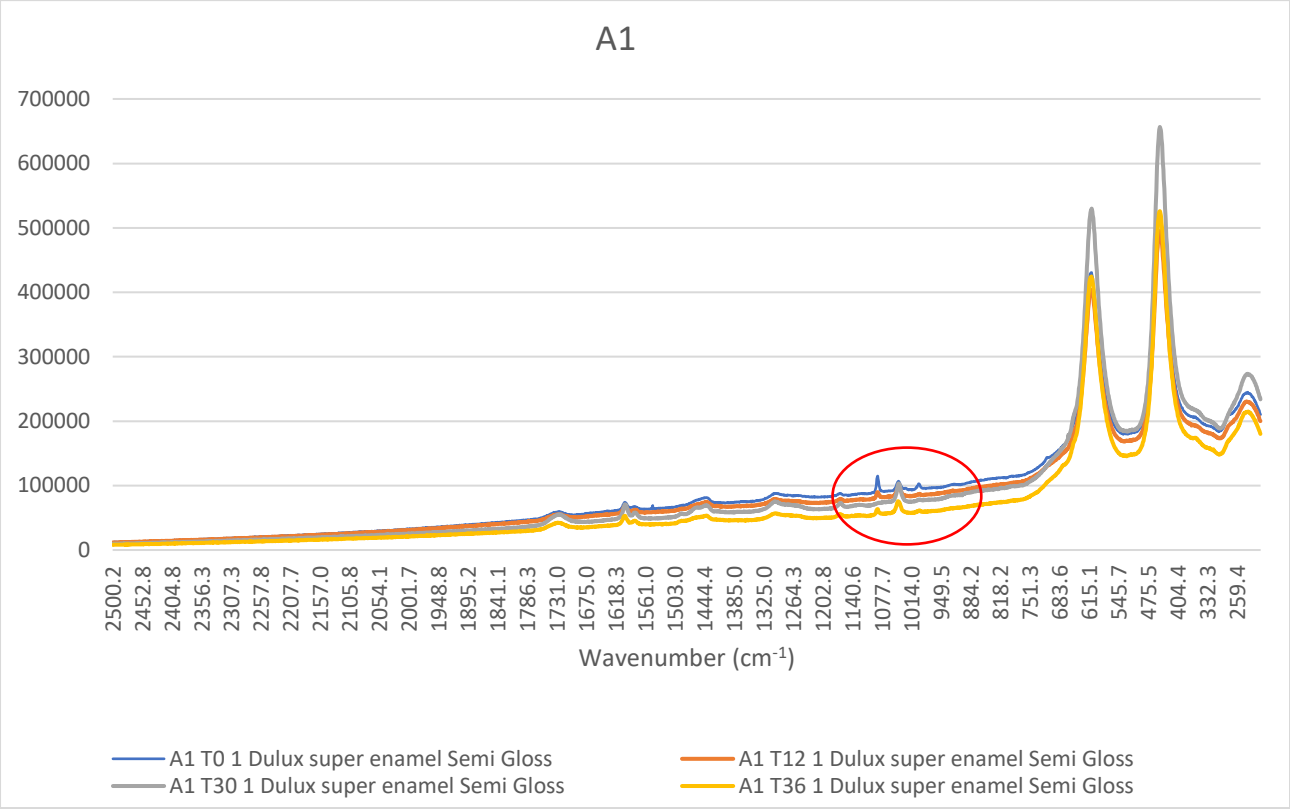


Figure 30: Raman spectra of archectrural paint sample A1 before weathering and after 12, 30 and 36 months of weathering.

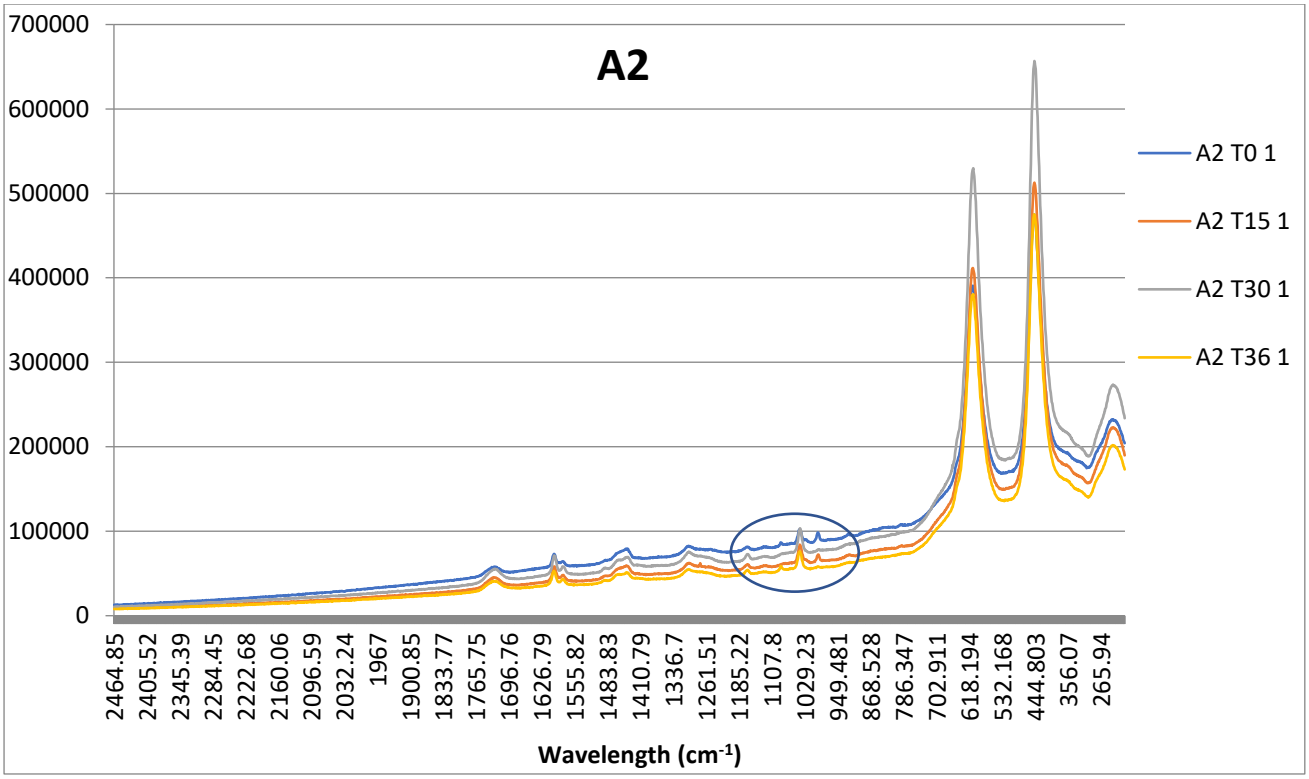


Figure 31: Raman spectra of archectrural paint sample A2 before weathering and after 12, 15, 30 and 36 months of weathering.

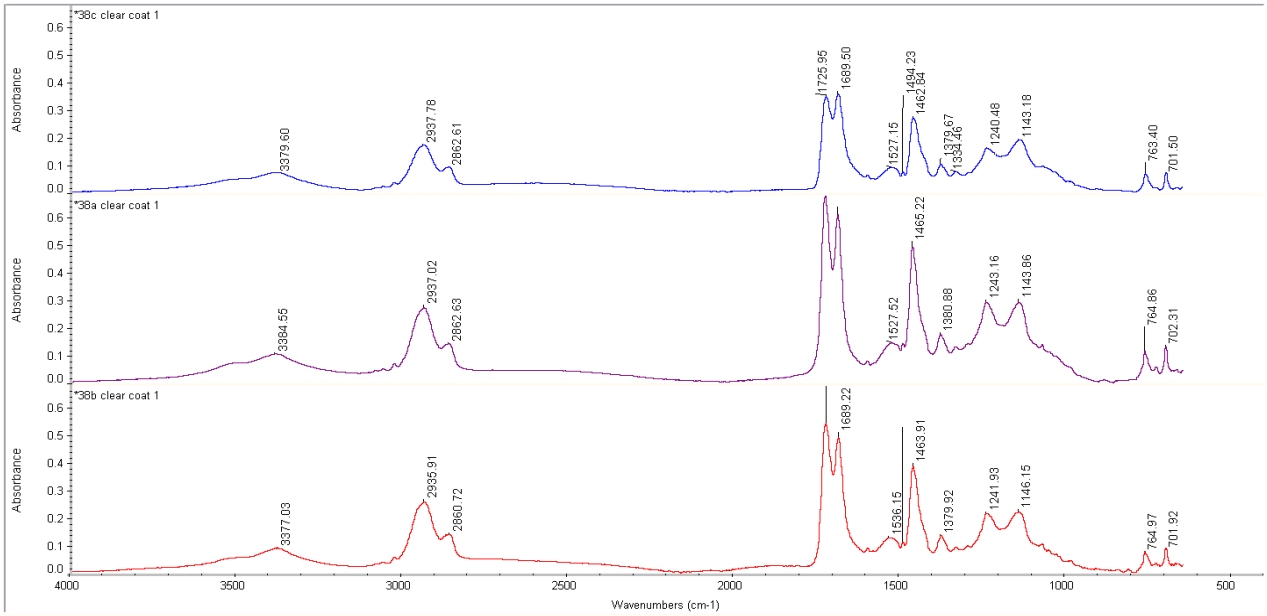


Figure 32: FTIR absorbance spectra from different locations on the same vehicle.

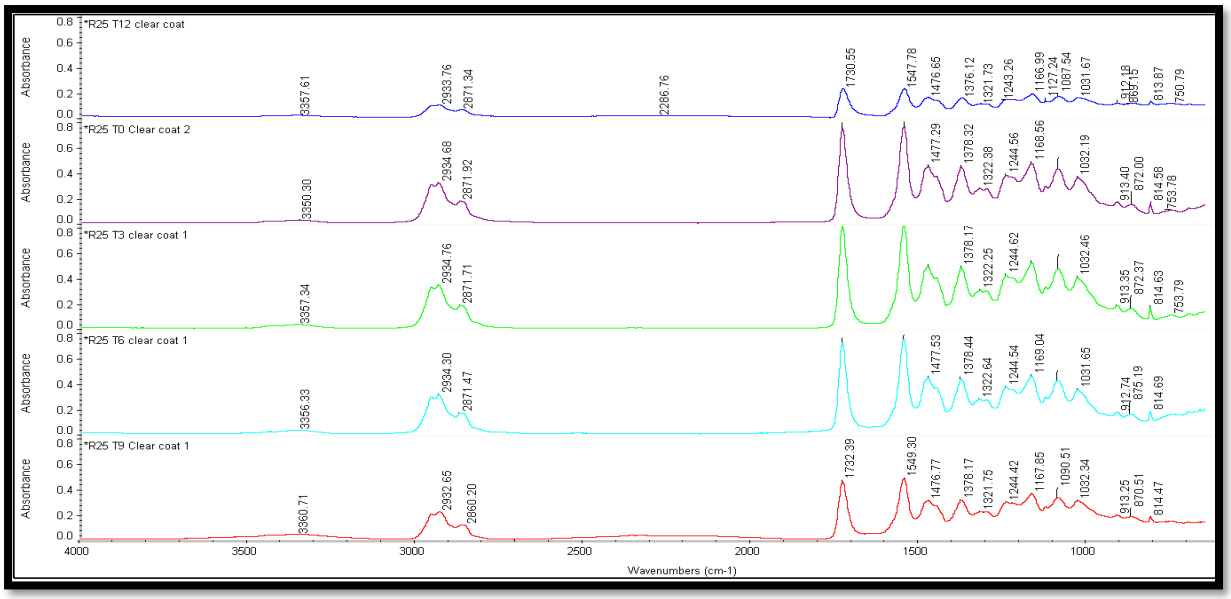


Figure 33: Changes to the FTIR spectra of the same vehicle paint sample, R25 at before weathering, T0, and at 3-12 months of westhering.

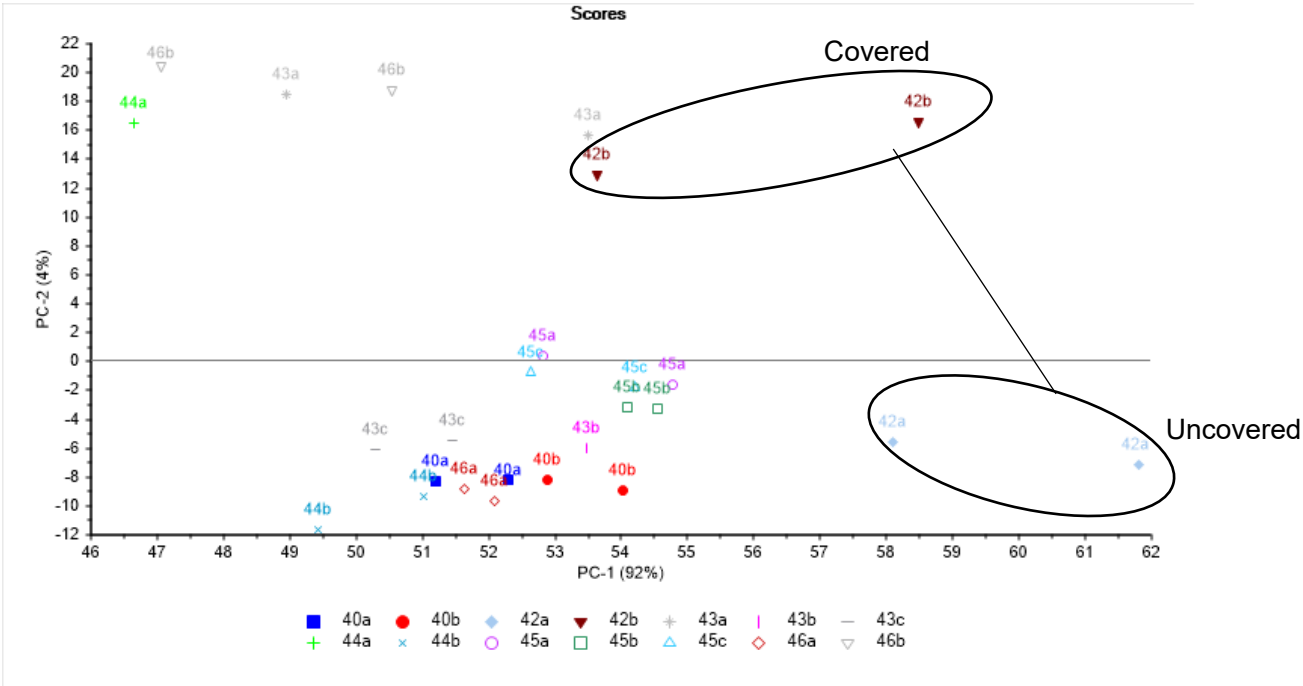


Figure 34: PCA plot of some of the vehicle paint samples from different locations on the same vehicle that were analysed.