A SURVEY OF VEHICLE TOPCOAT COLOUR FREQUENCY AND CHEMICAL PROFILING OF PAINT CHIPS FOR FORENSIC COMPARISON

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by

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LIST OF ABBREVIATIONS & SYMBOLS

ATR	Attenuated Total Reflectance
DAC	Diamond Anvil Cell
FTIR	Fourier Transform Infrared
PCA	Principal component analysis
PLM	Polarised light microscopy
PyGC-MS	Pyrolysis gas chromatography - mass spectrometry
SEM-EDS	Scanning electron microscopy - energy dispersive X-ray spectroscopy
XRD	X-ray powder diffraction
PC	Principal Compaund
%	Percent

TINJAUAN KEKERAPAN WARNA PADA PERMUKAAN ATAS KENDERAAN DAN PEMPROFILIN KIMIA SERPIHAN CAT UNTUK PERBANDINGAN FORENSIK

ABSTRAK

Pemeriksaan forensik ke atas bahan bukti berkaitan dengan cat yang dikumpul daripada siasatan tempat kejadian boleh digunakan untuk menghubung kait antara individu, objek dan/atau tempat. Kajian ini bertujuan untuk mengkaji kekerapan warna pada pemukaan atas kenderaan dan pemprofilan kimia serpihan cat untuk perbandingan forensik. Fasa pertama kajian ini melibatkan tinjauan warna permukaan atas kenderaan di dua kawasan dalam satu hari serta hari yang berlainan. Kemudian, fasa kedua melibatkan analisis sampel serpihan cat diperoleh dari pelbagai bahagian pada kenderaan yang sama serta kenderaan berlainan yang mempunyai warna permukaan atas yang sama dengan menggunakan Spektroskopi Inframerah Fourier Transformasi-Pantulan Keseluruhan Dikecilkan (ATR-FTIR). Tinjauan menunjukkan bahawa warna putih, hitam dan kelabu terang merupakan warna atas permukaan kenderaan yang paling biasa dijumpai di kawasan penyelidikan iaitu di Johor Bahru. Dua kenderaan bewarna kelabu terang dan dua kenderaan bewarna putih dipilih untuk sampel tanpa mengambil kira jenama kenderaan untuk dianalisis. Spektroskopi ATR-FTIR telah berjaya menghasilkan profil bagi serpihan cat yang diuji dalam kajian ini. Profil ATR-FTIR yang dikumpulkan dari kereta yang sama menunjukkan profil yang serupa dan ditempatkan secara berdekatan dalam plot skor. Sebaliknya, serpihan cat yang dikumpul dari kereta yang berlainan mungkin mempunyai profil yang berbeza. Hasil daripada kajian ini, adalah ditunjukkan bahawa penentuan warna permukaan atas oleh saksi atau mangsa terutamanya berkaitan

dengan kes kemalangan kenderaan harus ditafsirkan dengan teliti untuk membantu siasatan dan soal siasat forensik. Adalah disarankan juga agar maklumat berkenaan warna kenderaan dapat berfungsi sebagai petujuk awal bagi pasukan penyiasat dalam mengesan kenderaan tersebut. Serpihan cat juga sangat berguna untuk membezakan sumber bahan bukti forensik.

A SURVEY OF VEHICLE TOPCOAT COLOUR FREQUENCY AND CHEMICAL PROFILING OF PAINT CHIPS FOR FORENSIC COMPARISON

ABSTRACT

Forensic examination of car paint related evidence collected from a crime scene could be used to link between people, objects and/or places. This study was aimed to investigate the vehicle topcoat colour frequency and the chemical profiling of paint chips for forensic comparison. The first phase of the study involved a survey of the vehicle topcoat colour in two areas within a day and with different days. Subsequently, the second phase involved analysis of paint chip samples obtained from the varying parts of the same car and different cars carrying the same topcoat colour using Attenuated Total Reflectance-Fourier Infrared (ATR-FTIR) spectroscopy. The survey showed that white, black, and light gray colours were the most common encountered vehicle topcoat colours in the research area, namely in Johor Bahru. Two vehicles with light gray colour and two vehicles of white colour are chosen for sampling regardless its brand for analysis. ATR-FTIR spectroscopy result had successfully generated the profiles of the paint chips tested in this study. It was found that the ATR-FTIR profiles collected from the same car were shown to be very similar and located closely in the score plot. On the other hand, paint chips collected from different cars could have different profiles. From this study, it was noted that the topcoat colour determination by witness or victim, particularly related to vehicular accidents, shall be interpreted carefully to assist the forensic investigation and interrogation. It was also suggested that the colour information of a vehicle could serve as an initial lead for investigative team in tracing the vehicle. Paint chip samples were also very useful to differentiate the source of forensic evidence

CHAPTER 1

INTRODUCTION

1.1 Introduction

Paints are materials applied on the surface of any substrate covering wood, metals, plastics as well as many other composite substances. Generally, they have two important roles, namely, to protect and to decorate a substrate. The former role is to shield the substrate from external insults such as ultraviolet radiation, chemical reaction, moisture, atmospheric pollutants, *etc*. On the other hand, the latter gives the desire coatings on a substrate, as well as to disguise inferior construction or conceal imperfection (Rayland, 2012).

Paint is a complex mixture, consisting of three main components, namely the pigment, binder, and solvent (Bently, 2001; Rayland, 2012). Pigment provides colour and opacity. Usually, they are finely ground, inorganic or organic, insoluble, and dispersed particles suspended in the binder and solvent system (Milczarek, 2006; Bently, 2001). Note that extender is also included as pigment. Extender is commonly used in primers and primer surfacers to enhance film properties, as well as to determine the filling and sanding properties of paint film.

Binder appears as non-volatile portion of liquid vehicle within a paint that contributes to its adhesive and cohesive properties. Using binders, the pigment particles are binder together, and allow the paint attached to the substrate. Lastly, solvent acts as vehicle during manufacturing and application, carrying paint particles to be adhered to a desired surface.

During application of paint on a surface and subsequent period of curing, solvents evaporate leaving the solid coating (Ryland, 1979; Ryland, 1981). The use of different solvents could also produce different surface effects. Other than the three main components, modifier is added in small amount into the formulation to improve the properties of the paint. Such modifiers can act as driers, corrosion inhibitors, catalysts, ultraviolet absorbers, plasticizers, as well as various other substances to improve performance of the paints (Bently, 2001; Rayland, 2012).

There are two types of paint systems, known as decorative and automotive systems, respectively. Automotive paint system would have more than four layers of paintings, depending on the desired effects. Automotive paint is very important particularly during an investigation of cases such as hit-and-run accident, vehicle crash and death accident, burglary, assault and murder (Candy, 2001).

'On-the-road' of automotive paint survey is very important in providing accurate information on the actual vehicle topcoat colors distribution at a particular area for better understand the evidential value of the paint or vehicle topcoat colour (Buckle *et al.*, 1987). Furthermore, examination of the paint flakes collected at different point of a vehicle would also aid in describing if the topcoat color is uniformly distributed within a vehicle, and further supported through forensic examination (Gothard, 1976). Therefore, this study will be conducted in two phase which are:

- Phase 1: Obtaining the recent data of topcoat colour of vehicle in different locations in Johor Bahru namely: the E2, Lebuhraya Utara Selatan and Lebuhraya Senai, Senai-Johor Bahru.

- Phase 2: Chemical analysis of the paint flakes obtained from the same vehicle but different parts of the vehicle (intra-vehicle examination) and different vehicles (inter-vehicle colour examination).

1.2 Problem Statement

During a trial, investigative officers or forensic scientists are often required to explain the evidential value of questioned paint evidence recovered from a vehicular accident, including its colour (Buckle *et al.*, 1987). In certain vehicle accidents, particularly hit-and-run, investigative team would look for information alleged by the witness/victim to begin investigation. In many instances, the colour of vehicles could provide important investigative lead, but the descriptions based on perception of witnesses. A recent "on-the-road" data on topcoat colours distribution is important to reflect the actual colour distribution of vehicles used in particular area.

The number of vehicles on-the-road in Malaysia is showing an increasing trend in accordance to the increased national population. Based on the statistics released by the Malaysian government, the total registration of new passenger vehicles, excluding those commercial transport is increasing year by year (Ministry Transport of Malaysia, 2018). With an increasing trend, the investigation of vehicle related incidents or crimes are getting challenging. In Malaysia, all vehicle either private or commercial vehicle will register the vehicle follow the prefix or code that represent the state of registration. Malaysian registration plate is display at the front and rear of vehicle according to the law. Unfortunately, the prefix or code is not necessarily followed the state. The vehicle owner able to have the registration plate of other states although the vehicle is purchased from different states. Study showed that only 48.5% to 54.4% of vehicle population are locally registered either by the local resident or people originated from other placed and the rested of vehicle population is mixed registered from another place (Lee *et al.*, 2019). Since the vehicle purchase in particular state might not be used in that state, the database on the vehicle topcoat colour might also be varied as compared to the actual distribution on the road. Surveys and compilations of vehicle colour distributions generalised as topcoat colour (Bentley, 2001) have been conducted to assess the probative value of a vehicle's colour in supporting forensic conclusions (Abdullah *et al.*, 2014; Lee and Sandercock, 2011; Stone *et al.*, 1991; Volpe *et al.*, 1988; Buckle *et al.*, 1987; Ryland *et al.*, 1981). Any lack of accuracy in describing the colour perceived by a witness, especially if there are two or more witnesses, would impact credibility during cross-examination (Croucher, 2003). Therefore, the survey of topcoat colour distribution may support forensic expert during the trial especially on established the probative meaning of evidential value of automotive paint. This study is an alternative to reflect the vehicle topcoat colour distribution which is very important for forensic investigation and interrogation.

Painted surfaces could be found in almost every crime scene and playing important role to assist the vehicular related incidents. During the occurrence of a crime, paint related evidence can be transferred from one place to another whenever there is contact between two surfaces. Subsequently, analysis of such evidence can greatly contribute to the details of a crime, and the modus operandi of that crime. As the paint formulations are specific to the purpose and application of the paint, forensic examination of paint related evidence collected from a crime scene could be used to link between people, objects and/or places. In fact, the examination commonly involves the comparison of questioned samples recovered from a crime scene with the reference samples taken from the known source. Therefore, chemical profiling of the topcoat colour is very important to identify difference and similarity of intra-vehicle colour and inter-vehicle colour of most frequent colour present on-the-road. Interpretation of scientific evidence is very crucial to avoid confusion, misunderstanding and miscarriages of justice. Moreover, forensic scientist must explain the finding clearly and unambiguously to ensure other participant in criminal justice system understand scientific evidence (Newstead *et al*., 2010; Rudram *et al.*, 1995).

1.3 Aim and Objective

The aim of this study is to survey the vehicle topcoat frequency and the chemical profile of the paint chips for forensic comparison. The specific objectives are:

i. To obtain the “on-the-road” data to reflect the actual colour distribution of vehicles used in the research area.
ii. To compare the data for the current study with previously published data.
iii. To compare the intra-vehicle colour and inter-vehicle colour paint chips through Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR).

1.4 Significance of Study

The outcome of this study could provide the data of the most topcoat colour distributed in that particular area. Indirectly, the information on the colour determined during forensic investigation used to suggest the evidential value of that colour. Examination of the paint flakes collected at different point of a vehicle would also aid in describing if the paint color is uniformly distributed within a vehicle. The chemical profile could determine whether the same vehicle would be the same or different at different part or area of the vehicle. In addition, the determination will provide same or different chemical profiles. This further support the forensic examination in order to justify if an unknown sample could provide important clue during forensic investigation to relate the questioned and known paint chips.

CHAPTER 2

LITERATURE REVIEW

2.1 Paint System

A paint system is a multi-layer system carrying adhesive, anti-corrosive, resistance to atmospheric and environmental insults, and barrier properties in addition to the desired colour and appearance. Such system is not possible to be achieved by a single layer of paint, but attainable by multiple layers of paints applied on one surface. Typically, there are two types of paint systems, known as decorative and automotive systems, respectively. Table 2.1 demonstrates these two paint systems with their layers. Decorative paint system could have three different types of paints applied layer by layer on a substrate. Comparatively, automotive paint system would have more than four layers of paintings, depending on the desired effects (Bentley, 2001)

Table 2. 1: Decorative and automotive paint system (Bently, 2001)

Decorative paint system	**Automotive paint system**	
	Solid colour	**Metallic colour**
Gloss coat	Topcoat	Clearcoat Metallic base coat
Undercoat	Primer surfacer Cathodic electrocoat primer	
Primer	Pre-treatment	
Substrate (e.g. Wood)	***Substrate (e.g. Steel)***	

In general, both decorative and automotive paint systems are similar which involve multiple layers of paint but with slightly different nomenclature. The primer coat in both systems functions to adhere to the respective substrates and make the substrates more receptive to the paint systems. In automotive paint system, corrosive protection is achieved by adding anticorrosive in the paint formulation as electrocoat primer which coloured from black to grey. This is important due to the corrosive nature of the substrate, especially upon exposure to air and moisture. Undercoats and primer surfacers act to provide opacity or hiding effect to the substrate, and subsequently ensure a smooth base for the topcoat. Such paints are highly pigmented, appeared as light grey for lighter coloured cars and red oxide for darker cars. Lastly, gloss coat at the top layer provides colour to the paint system through pigment. Basecoat/clearcoat system, on the other hand, provides the metallic automotive refinish system through aluminum or mica platelets and a layer of clear unpigmented acrylic- or polyurethane-based varnish to improve gloss, durability, and appearance of a vehicle (Bently, 2001; Pfanstiehl, 1998).

2.2 Forensic Analysis of Paint Related Evidence

Through forensic comparison, the similarities in appearance, layer sequence, size, shape, thickness, or some other physical or chemical features of paint related evidence from both questioned and reference samples could conclude a common origin. On the contrary, the presence of significant observed difference might suggest the different sources of paint related evidence. In general, strength of the conclusion highly depends on the type and number of corresponding features in the evidence. In other words, the more layers of paint present in an evidence, the less likely it is to be encountered with another source of paint with the same characteristics based on the layer sequence and components. Such comparison is mandatory during forensic investigation in criminal cases involving the transfer of paint related samples, but only possible when comparable samples are available to forensic investigators and analysts.

In cases where possible source of a paint evidence is unknown or in the absence of comparable samples, forensic comparison using known and questioned samples become impossible. However, a paint sample is not only useful in linking a questioned source to a known sample. Paint related evidence could also contribute to generate important information for forensic investigation of a case. For example, determination of the makes, models, and years of manufacture of the motor vehicles is possible from paint collected from the crime scene or a hit-and-run accident. Since the different paint manufacturers tend to utilise different components in their products, it requires a knowledge of paint formulations and processes, the paint standards, as well as availability of colour databases to gain the details of the paint evidence, especially without a known source. As a result, there are literally thousands of paint formulations worldwide.

As paint related evidence could provide important information in solving a crime, the appropriate and accurate forensic analysis must be carried out on such evidence. ASTM International has published several consensus standard guidelines on paint and analysis of paint samples, including

- Forensic Paint Analysis and Comparison (ASTM E1610-2014)
- Infrared Spectroscopy in Forensic Paint Examinations (ASTM E2937-13)
- Scanning Electron Microscopy/X-ray Spectrometry in Forensic Paint Examinations (ASTM E2809-13)
- Microspectrophotometry and Color Measurement in Forensic Paint Analysis (ASTM E2808-11)

Additionally, Scientific Working Group for Materials Analysis (SWG-MAT) had also published a standard guide involving the uses of Pyrolysis GC and Pyrolysis GC-MS in forensic paint examinations. According to all the standard guidelines, they described that one can deduce whether two samples in question are like one another through a thorough analytical scheme on various physical and chemical features. Analysis and examination of paint related evidence are complimentary by using different analytical techniques, including stereomicroscopy, polarised light Microscopy (PLM), fourier transform infrared (FTIR) spectroscopy, pyrolysis gas chromatography-mass spectrometry (PyGC-MS), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), UV-Vis microspectrophotometry (MSP), and X-ray powder diffraction.

2.2.1 Stereomicroscopy

Stereomicroscopy is routinely used in the first step of examination in the analytical scheme of paint analysis. Simply examining and identifying the outermost layers and any possible layer sequence of the paint related evidence could provide clue on the type of paint. When two paint samples with several layers can be matched up, they are most likely coming from a common source. In forensic analysis, the most individualised paint evidence consists of a fractured edge flake that can be matched to an area of another piece of paint flake. When chips of paint containing several layers are recovered from a crime scene, examination of the colour, as well as the number, sequence and thickness of each layer becomes of great importance. Such surface texture and colour layer sequence can be compared through macroscopic examination. In certain instances, paint sample processing is required in which the individual layers of the paint related evidence need to be carefully separated with a scalpel or a microtome to make precise cuts of the layers (Thornton, 2002).

A stereomicroscopic with fiber optic tungsten filament illumination, more specifically to reflect the light source against a neutral grey background, is a recommended method for the examination of microscopic sample like paint. The Munsell coordinate system, standard colour chart DIN 6164, the natural colour system and Methuen Handbook of colour are designed to classify colour in three-dimension colour space which enable them to be given labels or coordinate on the colour of a paint sample. Note also that none of the colour system mentioned is suitable for colour determination of special-effect paints that form a high percentage of automotive paint. It was recommended that the colour collection distribution by main paint producers and manufacturers to describe and classify car paint colour. In fact, such determination method was successfully proven by the forensic communities.

Locke *et al.* (1986) described how the Johne and Reilhofer ER10 spectrocolorimeter can be used for the rapid construction of a data collection of motor vehicle paint colours. Colour measurements of a number of solid and metallic vehicle colours, taken from the ICI Colour Book and plates supplied by manufacturers, were recorded using this instrument and compared with results from a Nanospec 10S microspectrophotometer. The ER10 was also used to record data from motor vehicles of the corresponding colour. The results demonstrate the compatibility of the colour data obtained using the two instruments and hence the feasibility of constructing a data bank to assist in the identification of vehicle paints of unknown origin. It was noted that the different types of printing applied on the vehicle by the manufacturers on various vehicle had challenged the forensic analysis due to difficulty in assigning the paint colour, particularly on very small piece of sample for accurate comparison in addition to introduction of over 200 new colours each year (Locke *et al.*, 1986).

2.2.2 Polarised light microscopy (PLM)

PLM uses incident and transmitted light to examine paint samples and allows up to ×1000 magnification (Thornton, 2002). Using PLM, the plane-polarised light in incident light/bright field and fluorescence can determine the particle form in such sample, particularly the crystalline materials including majority of the pigments. The specific effect pigments such as metal and pearl can be accomplished. It also allows the examination of layers of paint samples, as well as the measurement of the thickness and uniformity of each layer. Usually, the morphology and physico-chemical features of coloured pigments and extenders in the composition of paint were observed in magnification ranging between 250× and 1000× in transmitted light/bright or light/dark field. Only a small-sized paint sample, at approximately 3 μm section which had been embedded to surface resin parallel or perpendicular, is needed for the analysis. Subsequently, the paint sample could also subject to fluorescence microscopy at an excitation wavelength of 365 nm (Rayland, 2012).

2.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

Microspectrometry is used to record the reflectance spectra diffused by the paint sample, providing a mathematical measure in form of chromaticity co-ordinate and tristimulus (Mazzeo *et al*., 2007). In other words, the reflectance or transmittance spectra from the suspect and control samples was measured, and the tristimulus values or colour coordinates was calculated. Using FTIR microspectroscopy, the infrared radiation can be absorbed to yield a spectrum that is characteristic to that paint sample. It can be used to examine the organic components of binders and pigments present in the sample, as well as to classify the various types of general binders. All of the components of paint produce infrared absorptions, and infrared spectroscopy is one of the main tools used by both the coatings chemist and the forensic analyst to determine the overall composition of paint. The binders that are used can be identified by these means, as well as the pigments that are present in high concentrations (Rayland & Suzuki, 2012).

The two main sampling accessories that are used with FTIR spectrometers to obtain paint spectra are the diamond anvil cell (DAC) with the infrared microscope and attenuated total reflectance (ATR). The DAC requires much larger samples than can be analyzed with the infrared microscope, one of the main advantages of this accessory is that when used on an extended-range FTIR spectrometer, the lower frequency absorptions of the sample can be observed. Paint samples are simply pressed against an ATR element, which is a refractive infrared-transparent material such as zinc selenide or diamond. ATR has a very shallow penetration depth that is proportional to wavelength, so ATR spectra have stronger relative intensities for the lower frequency absorptions than those of transmission spectra. An ATR objective of an infrared microscope also provides the best means to analyze paint smears that are too thin to be physically removed from the substrate (Rayland & Suzuki, 2012) .

The FTIR profiles generated could aid in determination whether there is any significant difference exist between known and question samples. In most circumstances, the technique is capable of distinguishing between paint samples even the two samples are appearing as same colour through visual and microscopic examination (Zięba-Palus *et al.*, 2013; Toda *et al.*, 2012).

FTIR has its advantages in detecting simultaneously all frequency of a sample, enhancing the speed and sensitivity. The signal-to-noise ratio can be further improved by implementing greater throughput energy and utilising a laser for calibration of the position of the moving mirror. Different profiles of 500 paint flakes were evidenced by physical examination dan chemical analysis using infrared, emission spectrographic and pyrolysis GC by Gothard (1976).

The characterization of paint become more difficult because there is various pigment and additives are added to the coating. An acrylic, amino, alkyd, nitro, and polyurethane paints are popular automotive coatings. Several instrument used to characterised an eleven-layer of paint samples are Fourier-transform infrared spectroscopy, Raman spectroscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy (Rui Chen *et al.*, 2015). In recent 2019, Abdul Malek *et al*, 2019 had also investigated the composition of topcoat layers recovered from the vehicle using a combination of ATR-FTIR imaging and SEM/EDX (Gothard, 1976; Abdul Malek *et al.*, 2019).

One of the more challenging aspects of forensic paint comparison is the assessment of the significance of the findings. Edmondstone *et al*. (2004) conduct the study to assess the distinctiveness of automotive paints in order to determine their evidential value. The total of 260 set of the automotive paint was collected from the damage cars and has been compared to each other by visual observation, optical microscopy and ATR-FTIR spectroscopy analysis. The study found that only one out of 33,670 sample pair comparisons could not be differentiated using standard examination techniques. The one indistinguishable pair came from cars of the same make and model manufactured in the same year in the same assembly plant and only the differentiation is based on topcoat colour and chemical analysis of the topcoat only. This result of the study provides the forensic paint examiner with the information that can be used to assess the evidential value of the automotive paint (Edmondstone *et al.,* 2004). Study by Ryland, *et al*. (2000), found that FTIR is the effective tools for discriminate the major automotive paint manufacturer' formulation types which currently used in original finished.

Jungang *et al.*, 2016 conduct the study to analysed 52 automotive coating samples by using FTIR and Raman Spectroscopy spesifically. Compounds with Ti, Fe, Cu, Pb, and Cr are often added to coatings as pigments or additives. FTIR used to identify the resin and additives found on the automotive paint, while Raman microscopy is more powerful in detecting additives and pigments. This paper suggested it is more effective using these two techniques in combination for identification than using them separately. The analysis of automotive coatings is important for forensic scientists. The results in this study reveal that these two non-destructive methods can be used in combination and can effectively identify different paint samples for environmental or forensic purpose (Jungang *et al.*, 2016).

2.2.4 Pyrolysis gas chromatography - mass spectrometry (PyGC-MS)

Pyrolysis is the thermal fragmentation of a substance in an inert atmosphere. The pyrolytic process produces molecular fragments which are usually characteristic of the composition of original macromolecular material. Its advantages for forensic examinations are both absorbing and rewarding. The pyrolysis products have been detected and identified by coupling the pyrolysis unit to a gas chromatograph or a mass spectrometer or a combination of both instruments as in PyGC-MS. PyGC-MS is able to produce reliable data, allowing the comparison of analytes. PyGC and PyGC-MS provide also good discrimination, involve minimal sample manipulation and able to detect very small quantities of materials.

As paint commonly appears in solid form, PyGC can be used to determine its composition. Through pyrolysis, a sample is heated into vapour, followed by breaking up the chemical bonds of micromolecules in binder to decompose into smaller and volatile fragments. Subsequently, the vapourised sample is injected into a GC to separate the components at controlled condition of temperature, heating rate and time. The result chromatogram could be identified through molecular weight determination using mass spectrometry, comparison between the library and the chemical fingerprint of reference samples. PyGC is known as a powerful technique for identification and discrimination of polymers in surface coating. Therefore, this method can identify the additives in the composition of the paint, including the coalescing agents, organic pigment, and flow promoters. In 2013, Muehlethaler *et al*. had successfully analysed paint samples using the technique and determined the different composition among the samples (Muehlethaler *et al.*, 2013) Minimum trace sample of 10 µg is neccesary to identified monomer in biding system but posibility of identification some additive or pigment and offered improved discrimination of chemically similar paint (Burke *et al.*,1985; Fakuda, 1985; Cassista *et al.*, 1994). However, it is important to note that the technique is destructive in nature, requiring sample preparation step and time-consuming, as well as proper planning and selection of analytical method due to limited samples available for forensic investigation (Muehlethaler *et al.*, 2013).

2.2.5 Scanning electron microscopy - energy dispersive X-ray spectroscopy

Scanning Electron Microscopy-Energy Dispersive X-Ray Spectrometry (SEM–EDS) is a commonly used method for elemental analysis. Study by Rui Chen *et al.*, 2015 conclude that Scanning electron microscopy-energy dispersive X-ray spectroscopy offered rapid and accurate elemental analysis, and provided confirmation of the infrared and Raman results. Interaction of SEM beam with the sample creates X-rays that are detected and identified by the energy dispersive X-ray spectrometer. Being non-destructive, the technique can analyse small, large, as well as multi-layered paint fragments. Carrying the ability to detect wide range of element on the periodic table, it had been used to examine the elemental composition of a paint sample, layer by layer. This technique distinguished two paint samples based on their different elemental compositions. Additionally, it helps in identifying and comparing the pigments in each layer of the paint (Henson, 2001).

Scanning Electron Microscopy-Energy-Dispersive X-Ray Spectrometry SEM–EDS is the main method used in U.S forensic science laboratories for elemental analysis of paint evidence (Henson *et al.*, 2001; Ryland *et al*, 2006). As described in previous section, pigments and extenders are contained in the composition of paint. In automotive industries, the compositions are varied and therefore contributing to different elemental profiles. For examples, the most common white pigment might be contained non-toxic titanium dioxide (TiO_2) as compared to some lead-based predecessors. Decorative pigments, also known as effect pigments, are added to coatings to achieve a glittery or flamboyant appearance. Aluminum metal flake had traditionally been used to put the metallic appearance in an automotive finishing coat, and recently slowly substituted by water-borne coatings (Henson, 2001).

2.2.6 X-ray powder diffraction (XRD)

X-ray powder diffraction is useful to identify any microcrystalline components in paint samples. Complex examination of artwork (painting and sculptures), car paint (fragment and abrasions analysis), analysis and comparison of lacquer system of industry had been reported utilizing this technique. For traffic accident cases, the types of pigment of vehicle such as the effect, plate-like, or colour-variable pigment can be identified for comparison of various paint samples. Paint samples examined by X-ray diffraction are typically small fragments that are mounted on the tip of a drawn glass capillary tube using a petroleum jelly or other non-crystalline adhesive (Kotrlý, 2006; Henson, 2001)

2.3 Pigment and Colour

Colour of a paint system is contributed by the pigments. To function as pigments and to provide opacity, the particles must be able to scatter light and of optimum size.

With different refractive index of the pigment as compared to that of the resin, the particles scatter light. These pigment particles are crystalline solid appearing in shapes such as cubic, rectangular, needle-like, and other flat shapes which can reflect light. As described in previous section, pigments can be natural inorganic, synthetic inorganic and synthetic organic that provide different colours that desired by the manufacturers. Selection of pigments would be decided by intended effects by the products, including

- brilliance and clarity of hue - the most attractive and cleanest colours can be achieved with organic pigments.
- white and black colour paints - titanium dioxide is the purest white pigment while the inorganic carbon is most jet black.
- non-bleeding pigments - inorganic compounds less likely to soluble in organic solvents, while most organics are very insoluble, but some could have certain solubility in stronger solvents.
- lightfastness - inorganic compounds are more resistant from ultraviolet light exposure.
- heat stability - inorganic pigments and very few organic compounds are stable at high temperature without decomposition.
- anti-corrosion - all inorganics are anti-corrosives.
- ultraviolet absorption - titanium dioxide and fine iron oxide can block ultraviolet radiation.
- reflective effect - metallic aluminium and treated mica in platelet form give reflective effect.

In between decorative and automotive paints, organic pigments are preferable in the former as characteristics such as ultimate colour fastness and heat stability are not needed. On the other hand, inorganics are used in the latter which requires very high standard quality of paint. Recently, usage of environmental toxic inorganics, particularly lead and chromate, had been restricted and banned in both the decorative and automotive markets. It is important to note that the formulations of paints, especially the pigments, had been changed over time with the recent derived paint which varies the colours across a spectrum by observation angle. In fact, all the paints should have optimum pigment loading to achieve the desired colouring effect (Rayland, 2012).

2.4 Vehicular Statistics in Malaysia

The number of vehicles on-the-road in Malaysia are showing an increasing trend, in accordance to the increased national population. Based on the statistics released by the Malaysian government, the total registration of new passenger vehicles, excluding those commercial transport had been risen to 533,202 units in 2018 from 514,675 unit in 2017. In other words, a 3.6% growth was recorded, and these figures are expected to continual increase. Between the same year, the registration for commercial vehicles in 2018 was also increased by 5.7% or 3,562 unit, totaling at 65,512 in 2018 (Malaysian Automotive Association, 2019). In term of average daily traffics in Malaysia, it was reported that the total number of vehicles on-the-road was slightly greater in 2018 as demonstrated in Table 2.2. From the statistics the state of Selangor continues to be the state with the greatest number of vehicles on the road. By comparison, Kuala Lumpur would have the most crowded traffic with the large volume of vehicle in relative to the comparative smaller area in territory.

Table 2. 2: Average daily car in State of Malaysia (Ministry Transport of Malaysia, 2018)

No	**Location**	**Year**	
		2018	**2017**
1	Selangor	410719	412155
2	**Johor**	**396318**	**399150**
3	Kuala Lumpur	274773	278523
4	Perak	244988	240881
5	Pulau Pinang	138714	13606
6	Negeri Sembilan	124239	122779
7	Pahang	121142	119102
8	Kelantan	95872	93978
9	Terengganu	94608	94450
10	Sabah	80478	78299
11	Kedah	79277	78166
12	Sarawak	76689	75716
13	Melaka	44227	42566
14	Perlis	30216	33233
	Total	**2212260**	**2082604**

With an increasing trend, the investigation of vehicle related incidents or crimes are getting more challenging. Traffic accidents had been reported every day in the mass media, indicating the seriousness of these incidents to the publics and the society. Traffic accidents can cause physical, financial, and mental effects towards the personnel involved in the incident. More severely, they could lead to injuries, paralysis and even death. Table 2.3 demonstrates the statistics of death cause by road accident in Malaysia. Although a slight decrease was noticed in 2018 as compared to 2017, the impact of traffic accidents should not be overlooked.

Table 2. 3: The statistics of death cause by road accident in Malaysia (Ministry Transport of Malaysia, 2018)

No	**State**	**Year**	
		2018	**2017**
1	Selangor	1,046	1,087
2	**Johor**	**977**	**1,067**
3	Perak	693	711
4	Kedah	509	560
5	Pahang	485	485
6	Kelantan	420	442
7	Pulau Pinang	390	401
8	Negeri Sembilan	362	370
9	Sarawak	333	408
10	Sabah	310	351
11	Terengganu	275	330
12	Kuala Lumpur	229	236
13	Melaka	191	230
14	Perlis	64	62
	Total	**6,284**	**6,740**

In fact, with comparing the number of vehicles on the road with the occurrence of the accident, it was found that the possibility of having a vehicular accident could be higher when the road is occupied with greater volume of vehicle.

2.5 Forensic Significance of Vehicle Colour Determination

Investigation of crime related vehicle become more challenging due to the increasing of the vehicle presented on the road of Malaysia. As described in previous sections, forensic comparison of at least two paint samples enables the possible determination of whether they are of common sources. Additionally, forensic analysis can narrow down a vehicular paint sample to the make, model, and to certain extent the year of a car. Prior to forensic analysis, witnesses who had observed the happening of a vehicular incident are usually required to provide a testimony to describe the incident. This colour information of a vehicle could serve as an initial lead for investigative team in tracing the vehicle (Croucher, 2003).

2.5.1. Vehicular topcoat colour distribution

The cases involve vehicle such as 'hit-and-run' cases, snatch theft and burglary required the statement of the witness, the colour of vehicles could provide important investigative lead. In certain vehicle accidents, particularly hit-and-run, investigative team would look for information alleged by the witness/victim to begin investigation. Therefore, the vehicular colour distribution in particular area and 'on-the-road' data collection is important in order for a forensic scientist provide the opinion evidence on paints that came from vehicle accident and other crime related vehicle (Buckle *et al*., 1987; Abdullah *et al.*, 2014).

Tippet *et al*. (1968), Gothard (1976) and Rayland *et al*. (1979) were among the earliest conducted the survey of topcoat colour at South Wales, New South Wales of Australia, and USA, respectively. Tippet *et al*. (1968) also examined the paint chip samples collected from houses or building other than vehicles alone. The two thousand samples were then classified according to the layer and colour code which consist of eight colours, namely black, blue, brown, cream, green, gray, red, and yellow. The paint chips from the building were found to be more random on topcoat highly depending on owner interest, availability, cost and how often the owner repainted the building (Milczarek *et* *al.*, 2006). In contrast, the vehicles usually follow a definite sequence of the layer and thickness depending on car manufacturer (Candy, 2001).

Gothard (1976) conducted a survey by randomly collecting 500 vehicles from motor vehicle insurance company's yard of "write-off" vehicle as a sample by considering that these would be reasonably representative of cars on the road and should not contain preponderance of older vehicle. Generally, car manufacture coat their vehicles in distinctive ways in regard to topcoat system, types and number of undercoats. The examination technique by using IR absorption have been shown capable to differentiating all but four of the 500 samples. These were two pairs from vehicles of similar make, model, and colour. All refinished vehicle were easily differentiated. The author concludes that there was no significant different of car population in New South Wales from those of most areas in Australia therefore that the results should reflect the general population of the cars (Gothard, 1976). This may or may not true for other country because vehicle distribution may be determine by consumer preference and marketing strategy of manufacturer. Same study suggested to be conducted at other area (Gothard, 1976).

Rayland *et al*. (1979) collected 200 paint chip specimens from three salvage yards in Philadelphia, Pennsylvania, USA to evaluate the evidential value of automobile paint chips by study the frequency of occurrence of automobile topcoat colour (Ryland, 1979). Rayland *et al*. 1981 conducted an extensive automotive topcoat colour survey involving 43,000 vehicles in six eastern states in United State involving the moving vehicle and static vehicle (parking lots). The system of 28 colours was used to provide greater differentiation in distribution of vehicle topcoat colour as purpose to give effective assessment of the probative value of a colour. The study also contributes the classification