A METHOD TO CREATE AN AUTOMOTIVE PAINT DATABASE

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Abstract

An automotive paint database in forensic science is mostly useful for case investigation, especially for hit-and-run accidents and for case linkage when the same brand of paint is used. In this study a model of paint database was created from X-ray diffraction patterns using the MATCH! phase identification program.

Each X-ray diffraction pattern was converted to a peak data. The resulting peak data were then accumulated to form a database which could be used to identify paint chips or particles. The program identifies an unknown by comparing peak positions (2θ) and relative intensities (I/I_0) with those of reference diffractograms in the database.

***Key word*:** Forensic science, Automotive paints, X-ray diffraction, phase identification software

Introduction

Basically the roles of paint coating are decoration and essential protection. Paint applications are generally house decorative, automotive, and industries.

Paint components generally comprise of 4 parts. First film-formers hold all ingredients in the paint system. Secondly, pigments provide varied color to decorate and protect both the inner paint layer and the substrate surface. If pigments do not provide colors, they are used as extenders which are necessary for physical property improvement such as adhesion, ease of sanding and film strength. Thirdly, liquids are mostly used as solvent for polymer dissolving and to adjust the consistency. Additives are the last base ingredient for improving chemical and physical properties, for example flow ability, and compatibility (Turner, 1967).

Automobile surfaces need both of beauty and corrosive protection. In a car coating, paints are commonly applied three layers. The inner most layer, the primer, is essential to give good adhesion, anticorrosion and smoothness. At the same time, it provides full hiding of the substrate before the topcoat layer is applied. The next outer layer is the topcoat which gives desired appearance. The outer most layer is the clear coat which gives a glossy appearance (Zeno *et al.*, 1994; Caddy, 2001).

In road accidents, such as a hit-and- run, the offenders sometimes leave the victims irresponsibly in the scene. Nevertheless, paint evidence from the offenders' cars probably remain on the damaged car, the victim's clothes, or sometimes even on the wounds on the victims' bodies. Hence, the duty of the forensic scientist is to examine and identify paint trace evidence for case investigation (Buzzini *et al.*, 2004).

Paint flake examination using the topcoat layer is significant in terms of giving a better view on the color of the suspect's car (Gelder *et al.*, 2005). This result will be used as preliminary information for linking other evidences.

In daily working, an early step of paint identification is to compare control paint and the collected paint visually and by using low power visible light microscopy. If they match in color, chemical compositions will be examined further.

X-ray diffraction is a widely used technique in paint integrative examination because it could reveal crystalline materials in paint composition such as pigments, extenders. Generally, X-ray diffraction is used with dry paint flake as it could differentiate paint evidence when visual comparison cannot. Mostly X-ray diffraction is a tool for identifying crystalline pigments in paint film (Rendle 2003; Lomax, 2010).

In identifying powders, X-ray diffraction is used in technique used in characterization and standardization of crystalline pigments in paint industry. The peak positions (2θ) and relative intensities (I/I_0) of each pigment are characteristic and are therefore collected for making an in-house library (Debnath *et al.*, 2006). Creating a paint database from known sources is necessary for forensic analysis since it could provide useful preliminary information such as the manufacturer, and sellers (Buzzini 2004).

When working with the database, a management software is necessary for handling a large amount of data and the software must provide searching and matching of the unknown samples. The analytical result can then be presented in terms of simple statistic matching (Rendle 2003, 2004).

In this study the main purpose is to develop a method to create an automotive paint database of 160 Samples from Nippon Paint Company. In order to examine paint samples, X-ray diffraction technique is employed. All diffractograms were collected as phase pattern to create an automotive paint database using the MATCH! Phase identification program.

Experimental

Instrumentation

X-ray diffraction analysis was performed on a Bruker AXS D8 X-Ray diffractometer employing $CuK\alpha_1$ (λ = 1.54056 Å) radiation which is a common radiation source for polycrystalline materials. In this experiment, small amount samples were desirable, furthermore zero back ground plate silicon wafer was used as sample holder. Baseline correction and smoothing were done by using the *DIFFRAC^{plus} EVA* program.

Materials

160 automotive topcoat paint samples were supplied by Nippon Paint Company. These were: 10 black samples, 42 blue samples, 11 gold samples, 11 grey samples, 34 green samples, 2 orange samples, 1 pink sample, 19 red samples, 17 sliver samples, 10 white samples, and 3 yellow samples. Each paint had been sprayed on a metal sheet and each paint was scraped from the sheet for X-ray examination.

Database software

The MATCH! phase identification software version 10.1a is an easy-to-use database software for phase identification. It is useful for handling large X-ray powder diffraction data. To serve the aim of this study, the MATCH! program was employed for transforming diffractograms of automotive paints into peak profile as characteristic of each sample. The resulting was then built up to form a database which could be used to identify paint chips or particles. The program identifies the unknown paint sample by comparing peak positions (2θ) and relative intensities (I/I_0) with reference diffractograms in the database and given result in form of Figure of Merit (FoM).

Method

Initially, each automotive paint sample from the metal sheet was scraped in the form of paint flakes and laid on a zero background silicon wafer. Subsequently the sample was examined by using X-ray diffractometer, the resulting diffractogram being characteristic of each paint sample. In creating an automotive paint database, raw file (*.raw) of sample diffractogram (**Fig.1**) was imported to the MATCH! phase identification software.

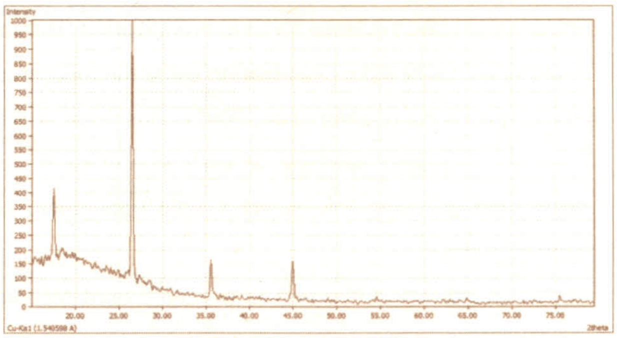

Fig.1 An example of diffractogram of automotive paint sample.

The next step was processing of the raw data which included information on peak position (2θ) and integrated intensities (**Fig.2**). The diffractogram was saved in the peak data (*.dif) format as the fingerprint of each automotive paint sample.

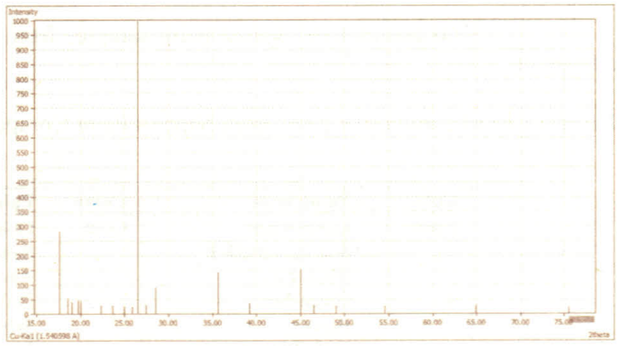

Fig.2 Informative peak data converted from diffractogram.

When creating an automotive database (**Fig.3**), the peak data (*.dif) was taken into the database through to user database manager mode. Then, the user database was obtained.

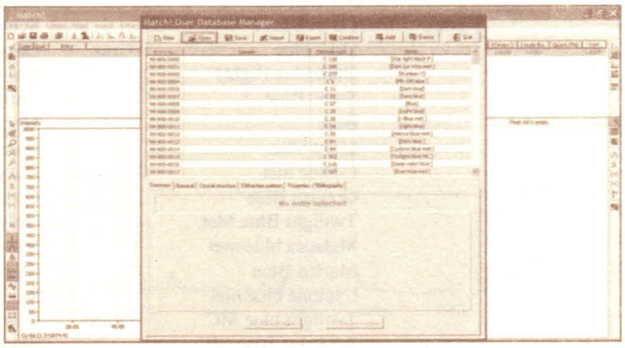

Fig.3 List of automotive paint sample in the model database.

This program provides an essential unknown sample matching mode by comparing the diffractogram of unknown sample to the reference patterns in the database (**Fig.4**). Subsequently, the MATCH! program expresses the result of matching in the form of Figure of Merit (FoM). This function of the program is useful for forensic science analysis such as matching unknown automotive paint samples from road accidents to the reference patterns in the database.

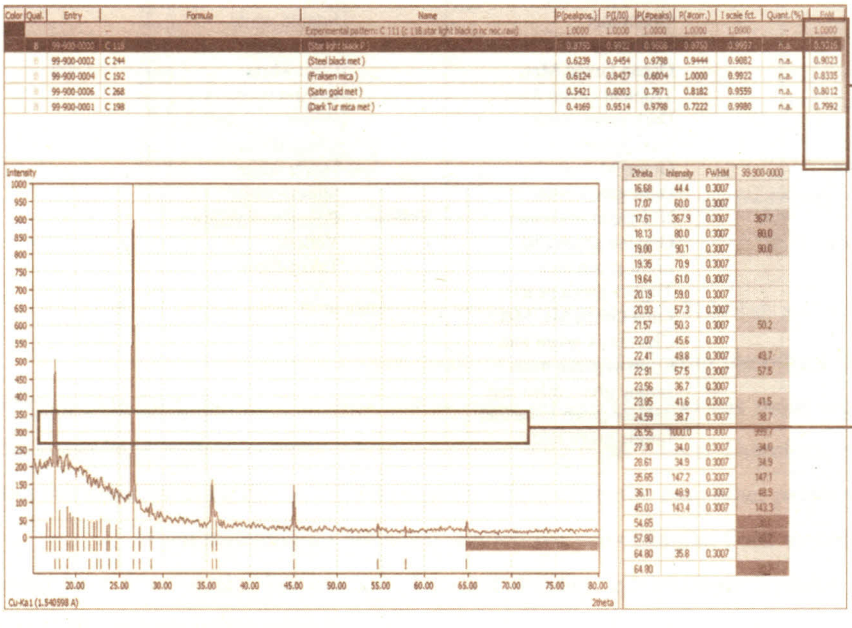

Figure of Merit (FoM) result of matching, if diffractograms are similar, FoM will be close to 1 but if they are different, FoM will be close to 0.

Upper vertical blue lines from diffractogram of paint sample and lower vertical red lines from reference pattern in this model database is used for matching by MATCH! program.

Fig.4 The comparison of sample with the reference patterns in the database.

Results and discussion

160 automotive topcoat paint samples from Nippon Paint Company (Table 1) were examined by X-ray diffraction.

Table 1 List of automotive paint from Nippon Paint Company in this study

Color	Paint name	Color	Paint name	Color	Paint name
Black	Lamp Black	Gold	Gold met	Red	Milno Red
	Star light black P		Sand gold		Light vermillion
	Black Met		Amethyst M		Red
	Green-Met.		Fraksen mica		Wine Red
	Black		Wheat beige met		Signal Red
	Dark Tur mica met		Lynx gold met		Rasbery red
	Sparkling Black Met.		Sahara beige met		Monaco Red
	Steel black met		Sunlight gold met		Palmp Red
	Ebony Black		Sahara gold mica met		Nifty Red
	M-steen		Fraser beige		Inza red
Blue	PB-190 blue		Sebring met		Brown met
	Dark blue	Gray	Grey		Canberry Red
	Dark blue (light)		Brownish gray		Taxi red
	Sonic Blue		Dark Grey		Super red
	Blue		Magma gray		Foxfire red mica
	Light blue		Blue gray met		Flash Red Met.
	L-Blue met		Hazy gray met		Flaming red
	Grayish Blue		Golden gray mica		Red
	Twilight Blue Met.		Grayish brown met		Vivid Red
	Malacca blue met		Meteor gray met	Silver	Silver 4ogue met
	Marien Blue´		Light quartz gray met		Grace Silver met
	Cyclone blue met		Misty gray met		Titanium silver
	Twilight blue MC	Green	Glory gray		Satin silver met
	Aquerius Blue MC		Smoke gray		Silver met
	Deep violet blue		Y.S. Green		Sky silver met
	Blue mica met		PC Green		Vogue silver met
	Dark blue pearl met		Green		Hilight silver
	Dark Blue Met.		Green met		Crytal silver met
	Marine Blue Met.		Light green		Silver grey met
	Marine blue met		Hanover Green Met.		Seyfert silver
	Ingenerate blue		Green mica		Bluish silver
	Blue M		Tahition Green Met.		Sun beam silver met
	Taxi blue		Cypress green mica		Sun beam silver met
	Purple mica		New blue green mica		Bluish silver met
	Dark blue mica		Spruce green met		Golden silver met
	Light blue met		Dusk green mica		Silver
	Blue		Thyme green	White	Frost white
	Medium blue met		Green pearl met		Pearl
	Turquoise mica		Green met		Sophia white
	Andaman blue		Furisco green		Clear white
	Purple		Ocean Green Met.		Cool white
	Nares blue met		Tropical Green Met.		Crystal white
	Sihouette blue		Dark green mica		White
	Nautical blue met		Taxi green		Clean white
	Dynastic Blue Met.		Green M opal		Dover white
	Sapphire Blue		Dark green mica		Shinny white
	Iris blue		Nid green mica met	Yellow	Permanent yellow
	Sapphire blue mica		Grayish green met		Yellow
	Pastel blue		Light green met		Taxi yellow
	Rigid blue		Timber green pearl		
	Horizon blue		Luna Green MC Met.		
	F-series blue		Chamonix green met		
Orange	Racing Orange		Cypress green mica		
	Orange yellow		Jungle green mica met		
Pink	Pink		Heater green mica met		
			Jungle green mica		

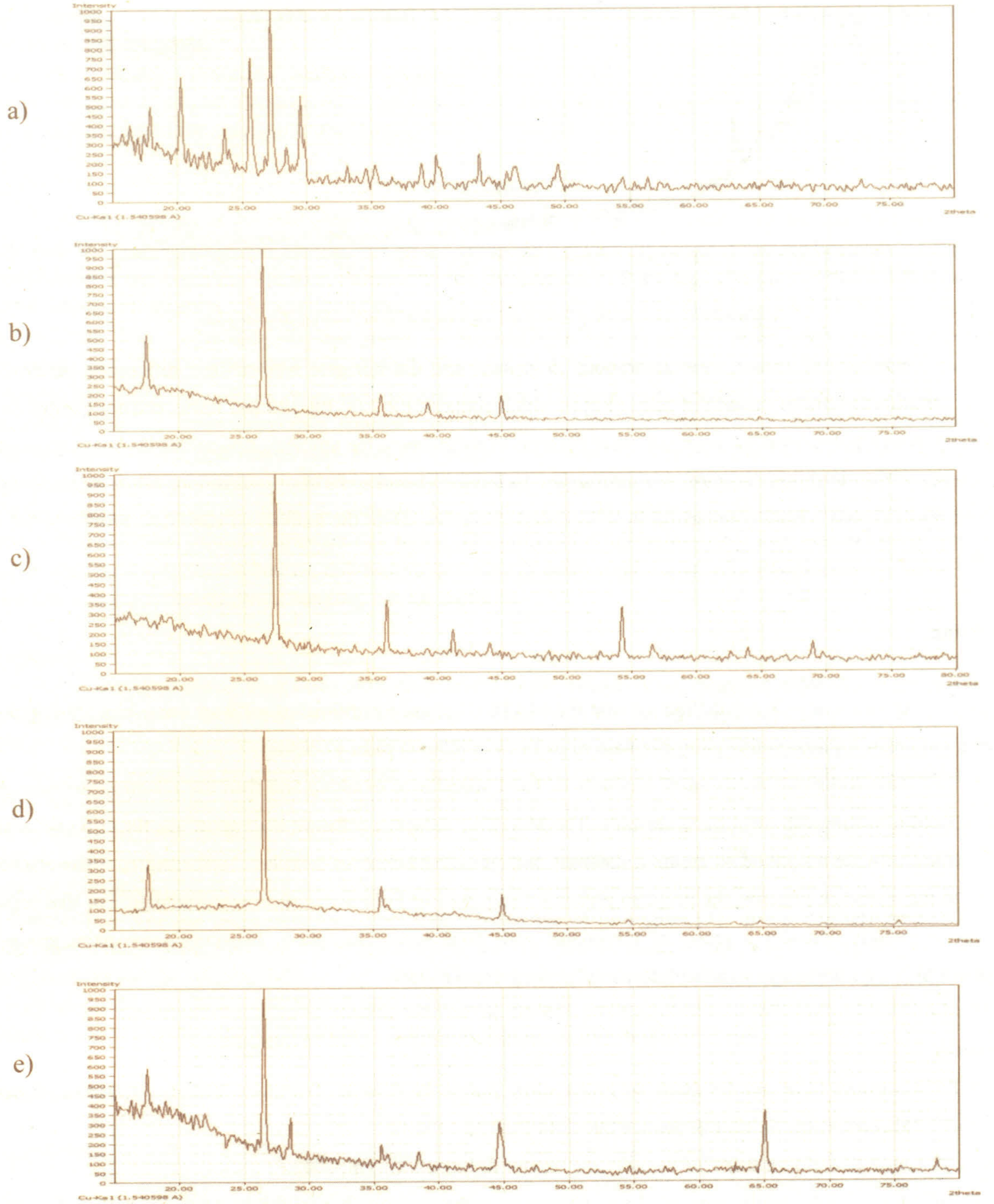

Fig.5 Example diffractogram from varous color samples: a) Orange yellow b) Sunlight gold met c) Inza red d) Pink e) Sun beam silver met.

Most paint sample groups could be distinguished from the others since their pigment compositions were different (**Fig.5**). Especially, orange yellow paint sample (**Fig.5a**) has more peaks in the diffraction pattern and the peaks also have higher intensity when comparing with other colors. Therefore, creating fingerprint as a phase pattern from this color by using the MATCH! program is slightly better than other paints which have fewer peaks.

When matching an unknown automotive paint sample, FoM would also be high. The other paint groups mostly have fewer peaks. For example, Inza red (**Fig.5c**), exhibits only 5 peaks. As a result, matching of an unknown paint to this pattern is less reliable.

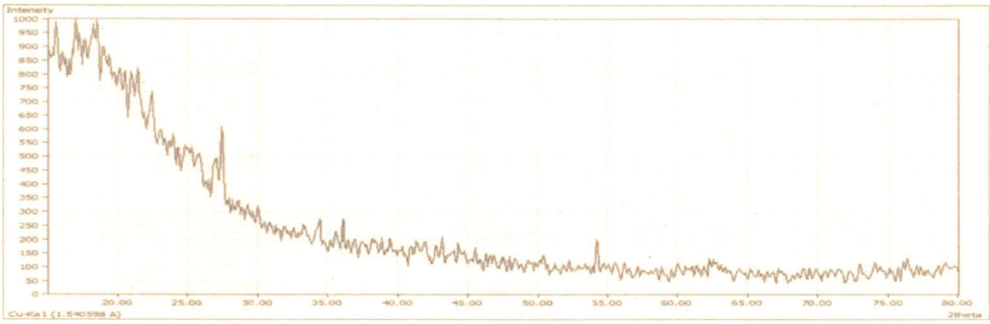

Fig.6 Amorphous pattern of Palmp red paint sample do not express distinct peak.

Some paint groups were amorphous to X-Rays and did not give well defined diffraction patterns. For example, amorphous pattern Palmp red paint (**Fig.6**) which contains PR 221, PR 170 and rutile, did not exhibit distinct peaks even though polycrystalline pigment were present. In these cases, the amount of pigments in paint compositions may not reach the detection limit of this diffraction technique (Lomax, 2010). In addition, when considering the matching result (FoM), visual comparison is still needed to narrow down the number of candidate groups in the FoM column.

Conclusion

In this study, X-ray diffraction and the MATCH! phase identification software were brought together in an attempt to create an automotive paint database of paint from Nippon paint Company.

This technique needs small amounts of paint samples to examine and then the resulting diffractograms could be used to distinguish most paint samples. The MATCH! database software is of great use for Forensic analysis since it could provide a method to create a database for matching unknown samples. Furthermore, when comparing samples to the reference patterns, the program presents a sequence of FoM scores for each candidate. For that reason it is useful to initially consider a group of candidates with FoM score close to 1. However some paint groups are amorphous to X-rays and may be difficult to identify using this database.

References

Buzzini P, Massonnet G. *A market study of green spray paints by Fourier Transform Infrared (FTIR) and Raman Spectroscopy*. Science & Justice 2004; 44(3): 123 - 131.

Caddy B. *Forensic Examination of Glass and Paint*: Taylor & Francis Group; 2001.

Debnath NC, Vaidya SA. *Application of X-ray diffraction technique for characterization of pigments and control of paints quality*. Progress in Organic Coatings 2006; 56: 159-168.

Gelder JD, Vandenabeele P, Govaert F, Moens L. *Forensic analysis of automotive paints by Raman spectroscopy*. Journal of Raman Spectroscopy 2005; 36: 1059-1067.

Lomax SQ. *The application of x-ray powder diffraction for the analysis of synthetic organic pigments. Part 2: artists' paints*. J Coat Technol Res 2010; 7(3): 325-330.

Rendle DF. *X-ray diffraction in forensic science*. The Rigaku, 2003; Vol. 19 No.2 & Vol. 20 No.1

Rendle DF. *DATABASE USE IN FORENSIC ANALYSIS*. Crystallography Reviews, 2004; 10(1): 23-28.

Turner GPA. *Introduction to PAINT CHEMISTRY*: Cox & Wyman; 1967.

Zeno W. Wick Jr, Jones FN, Pappas SP. *Organic Coating: Science and Technology*: John Wiley & Sons; 1994.