Intra-sample vs. Inter-sample Variability in Architectural Paint

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Abstract

The aim of this project was to determine whether any intersample variations between architectural paint products of the same brand could be established. Different batches of the same product were analysed to test whether they could be distinguished.

Samples analysed included batches of white paint manufactured over several months and red and blue colour samples. Samples were analysed by microscopy, microspectrophotometry (MSP), Fourier Transform Infra-Red (FTIR) and micro-XRF. Pyrolysis-GC/MS was also used to analyse a subset of the samples. The samples were compared by visual inspection of the data and by multivariate techniques for the complex data sets resulting from micro-XRF.

The results showed that, at the brand level, the techniques tested were highly discriminatory. However, the variations within a single batch were equal to or greater than the variations between batches of a single product. There was no consistently successful technique for distinguishing between batches of the same product; nor was the overall analysis scheme sufficiently discriminating.

These results suggest that when significant differences are observed between architectural paint samples it is strong evidence that the samples did not come from the same source. If no significant variations are found, they are probably of the same brand. In this case, the analyst will require national market data to assess the defence hypothesis and the strength of the evidence.

Introduction

Paint is ubiquitous in modern life and readily transferred by contact. It is commonly found at crime scenes. One of the questions which often arises is "what is the chance of a coincidental match with paint comparison evidence" (defence hypothesis)?

Several topics need to be investigated to answer this question. Firstly, can the investigator discriminate between different brands of paint? Secondly, what is the type of paint and how common is it in the general population? If the paint is a common type, can the investigator discriminate within the brand (batch discrimination)? Finally, are there any post-manufacturing points of discrimination (eg: tinting, blending)?

Aims

The first aim of this work was to test samples of architectural paint from a single batch, to assess instrumental precision and intra-sample variation. Secondly, different architectural paints were compared using standard forensic techniques to assess the discriminating power of the techniques. Finally, different batches of the same architectural paint were tested using standard forensic techniques to assess discriminating power.

Previous studies

Almost all previous paint significance studies have focused on automobile paint. Cousins *et al.* (1984) tested intersample variations in automobile paint by microspectrophotometry [1]. Massonnet undertook an in-depth study of grey metallic automotive paints [2]. Stoecklein and Becker conducted a review of forensic procedures, focused on automobile paint databases [3]. Govaert and Bernard studied spray paints by microscopy, FTIR and micro-XRF [4]. Thorburn-Burns and Doolan used Pyrolysis GC/MS and FTIR for the analysis of automobile paint [5]. Although the techniques applied are the same, architectural paint is chemically different to automobile paint and, more importantly, it generally presents less variation due to the fact that it is often mono-layered.

Methods and Materials

Each sample was thoroughly mixed, applied to a microscope slide and allowed to dry for one week before analysis.

Methods for forensic comparison of architectural paint were chosen based on the FBI Paint Comparison Guidelines [6]. The methods were: microscopic examination, including comparison microscope; microspectrophotometer, covering the UV and visible regions; Fourier transform infrared spectroscopy; micro-X-ray fluorescence and pyrolysis GC/MS for selected samples.

Samples – White

Five batches of Dulux Wash & Wear (acrylic) were sourced from the manufacturer. A further nine batches of Dulux Wash & Wear were sourced from retail in Sydney and Canberra. Batch manufacture dates ranged from 2003 – 2005. Two batches of each of the following white paints were sourced from retail: Dulux Weather Shield, gloss white; Dulux Professional Acrylic Primer, undercoat; Berger Gold Label Satin, acrylic white base; Dulux Spring, acrylic white base and Dulux Professional, flat acrylic.

Samples – Tinting

Two batches of Dulux Colour Solutions, untinted, were sourced from retail. Ten batches of Dulux Colour Solutions, tinted High Blue (shade P35H3), were sourced from various retail outlets. Eleven batches of Dulux Colour Solutions, tinted Young Salmon (shade P04H3), were sourced from various retail outlets.

Results

Microscopic examination. Samples were examined under direct lighting, at magnifications ranging from 63 – 320X. Characteristics examined were colour, surface texture, gloss and fluorescence. No inter-batch variations were found for any product. The four interior white topcoats were

indistinguishable. All other products were distinguished from each other and from the interior white topcoats.

Microspectrophotometer. White samples were examined in the UV region (240 – 420nm). No inter-batch variations were found for any product. The technique was useful for distinguishing samples which are not vivid white (primers). Tinted samples were examined in the visible region (380 – 800nm). One red sample was distinguished from the other batches of red paint, apparently due to a tinting error (Figure 1).

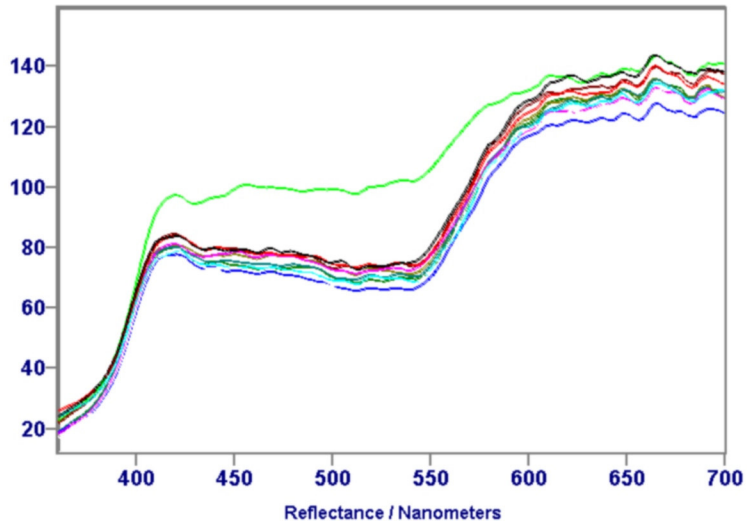

Figure 1: MSP spectra of all 12 red-tinted samples

Infrared examination. No inter-batch variations were found for any product. All of the white products were distinguished from each other. The tinted samples were distinguished from the white products. The red and blue tinted samples were indistinguishable from each other. The major components in all samples were identified as methacrylate and titanium dioxide. Minor components in various products included acrylate, styrene and calcium carbonate (Figure 2).

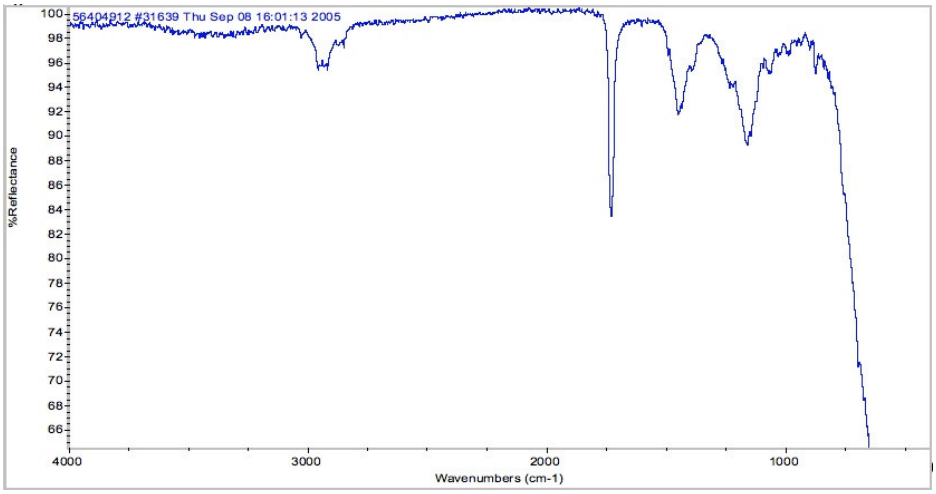

Figure 2: FTIR spectrum of white acrylic topcoat

X-ray Fluorescence examination. All of the products were distinguished from each other on visual inspection of the data. One red batch was distinguished from the other red batches – this was the same batch distinguished by MSP. The two primer undercoat batches were distinguished without detailed statistical analysis. No other batches of any product were distinguished.

MicroPyrolysis GC/MS examination. Pyrolysis GC/MS was carried out on the 14 batches of Dulux Wash & Wear. One batch was distinguished from all others by the presence of a major peak in the chromatogram. Mass spectrometry identified the peak as *d*-limonene – this chemical is not part of the paint formulation (Figure 3, peak at 7.81 minutes). This means that there was possible contamination of the manufacturing process or of the precursor chemicals.

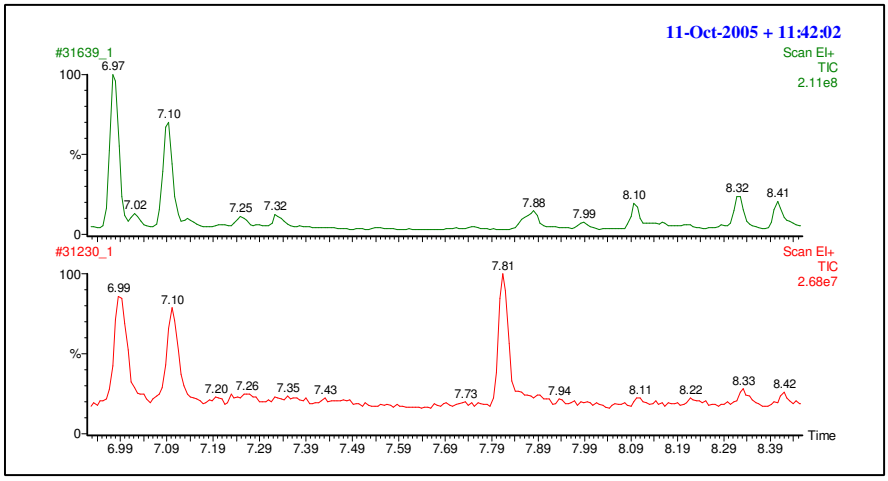

Figure 3: PyGC/MS of two samples from different Wash & Wear batches, showing discrimination due to d-limonene peak at 7.81 minutes

Conclusion/Discussion

The overall results for all products and batches are shown in Table 1. At the brand level, the standard examinations are highly discriminatory for architectural paint. There was no consistently successful technique to distinguish batches of the same product. A manufacturing defect or other unusual circumstance was required to produce batch variations. Tinting proved to be highly reproducible across multiple retail outlets, with only one tinted batch out of 21 distinguished due to a tinting error.

This study did not consider quantitative analysis, which is rarely undertaken in routine analysis. In addition, ageing effects were not assessed in this project. These two considerations may provide significant discrimination between batches of a product, increasing the strength of the evidence for indistinguishable samples.

Table 1: Summary of examinations

Product Type	No. of Batches	Samples Discrimated
"Wash and Wear 101 Advanced", acrylic, low sheen, white	14	One batch differentiated by pyrolysis GC/MS
"Spring", low sheen, acrylic white base	2	No discrimination between batches
"Weather Shield x10", gloss white	2	No discrimination between batches
"Professional Acrylic Primer Undercoat"	2	The two batches were separated by MSP and by XRF analysis
"Berger, Gold label Satin", acrylic white base	2	No discrimination between batches
"Professional", flat acrylic in white base	2	No discrimination between batches
"Colour Solutions", *"High Blue"*, Chip 297, Shade P35H3	10	No discrimination between batches
"Colour Solutions", *"Young Salmon"*, Chip 70, Shade P04H3	11	One batch discriminated by MSP and by XRF analysis
"Colour Solutions", untinted (white)	2	No discrimination between batches

The results of this study support the following conclusions:

If two samples of architectural paint are distinguished by the standard forensic casework techniques (i.e. meaningful differences were found), they are from different sources.

If two samples of architectural paint are indistinguishable (i.e. no meaningful differences were found), they are probably of the same brand and make (and tint, where applicable).

It is not possible to distinguish architectural paint at the batch level, using standard qualitative forensic analysis techniques.

If two samples are indistinguishable, the analyst will need national market data to assess the defence hypothesis and the strength of the evidence. Quantitative analysis and examination of the ageing effect could be considered as they may discriminate the samples further.

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References:

Cousins D.R., Platoni C.R. and Russell L.W., The variation in the colour of paint on individual vehicles, *Forensic Science International*, Volume 24, Issue 3, 1984, Pages 197-203.

Massonnet, G., Les peintures automobiles en criminalistique, PhD, University of Lausanne, 1996.

Stocklein, W. and Becker, S., *Paint and Class, A Review: 1998 – 2001*, 13th INTERPOL Forensic Science Symposium, October 2001.

Govaert, F. and Bernard, M., Discriminating red spray paints by optical microscopy, Fourier transform infrared spectroscopy and X-ray fluorescence, *Forensic Science International*, 2004, Volume. 140, Pages 61 – 70.

Thorburn-Burns, D., and Doolan, K.P., A comparison of pyrolysis-gas chromatography-mass spectrometry and Fourier transform infrared spectroscopy for the characterisation of automotive paint samples, *Analytica Chemica acta*, 2005. Volume. 539, Pages. 145 – 155.

Scientific Working Group on Materials Analysis, (SWGMAT), Forensic Paint Analysis and Comparison Guidelines, U.S. Department of Justice, Federal Bureau of Investigation, *Forensic Science Communications*, July 1999, Volume. 1, No. 2.