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# The Effect of Pigment Type on Pigment Variation due to Differential Mixing in Spray Paints

## ABSTRACT

A multi-colored set of twenty-eight spray paints was examined to explore FT-IR spectral differences caused by the differential mixing of binder and pigment components. Trends in differential settling of pigments based on their type (organic versus inorganic) were noted and resulted in recommendations for avoiding false exclusions in casework. In addition, a technique for sublimation of organic pigments from spray paints for isolation and analysis by FT-IR is described.

Keywords: Paint, Spray Paint, FT-IR, Pigments, Heterogeneity, Sublimation

## INTRODUCTION

Paint comparisons performed in the forensic setting typically involve either vehicle paints or architectural coatings. Spray paint, however, is another possibility and this paint type poses unique challenges to the paint examiner due to its method of application. The pigments, binder polymers, and other components in vehicle paints and architectural paints are usually fairly well-mixed before the paint is applied to a surface. Aerosol spray paints used during a crime may be applied in any state, ranging from well-mixed to completely unmixed. This affects both the visible color and chemical composition of the spray paint coating. In addition, samples of vehicle and architectural paint are most often collected and submitted for comparison as dry paint samples. In contrast, known (reference) spray paints are typically seized and submitted as aerosol cans that contain wet paint, meaning that the paint examiner must take into account the mixed/unmixed possibilities when comparing that known paint to any questioned paint samples. Failure to do so may result in a false determination that two paints could not have shared a common source, when in fact observed differences are due only to variation in mixing of the paints at the time of application.

A review of the literature found seemingly contradictory reports of the behavior of pigments in shaken versus non-shaken spray paints. Of the four previously conducted studies[1-4], three focused on a sample set of a single color (black, red or green).

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Comparisons of coatings produced by shaken spray paint cans versus unshaken cans were performed using various analytical techniques: scanning electron microscopy in conjunction with energy dispersive X-ray spectrometry (SEM-EDS), X-ray fluorescence spectrometry (XRF), Fourier-Transform infrared spectroscopy (FT-IR) and dispersive Raman spectroscopy. The authors differ in their conclusions regarding whether paint from shaken versus unshaken cans shows significant differences. The contradictory results could be due to either the analytical technique, the color of the paint in the specific sample set, or a combination of factors.

Paints typically contain a liquid portion composed of polymer-based binders and volatile solvents and solid particulates of pigments. One proposed explanation(1) of the differences seen in shaken and unshaken spray paints is that in unshaken paints, settled pigments accumulate at the bottom of the can. See Figure 1. When the spray nozzle is depressed, these pigments are initially aspirated through the intake tube and out the nozzle. This creates a paint coating with a high pigment load in the first few seconds of spraying. As spraying continues, a crater or vortex forms around the lower end of the intake tube and settled pigments are left behind in the can while predominantly liquid binder is sprayed, creating a coating with a low pigment load. This could mean that the paint coatings created at different times by a single can of spray paint may vary greatly

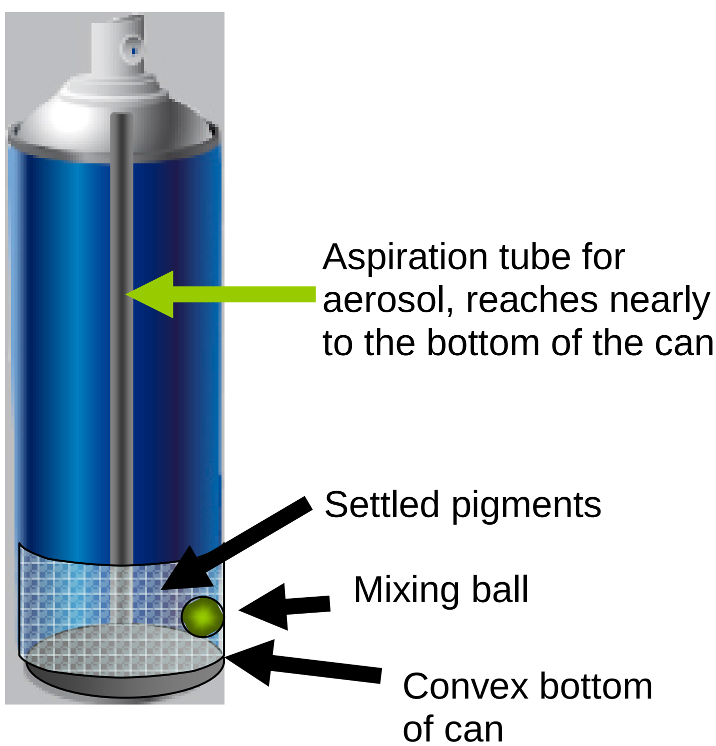



*Figure 1: Interior of a typical spray paint can, unshaken state*

in both visible color and chemical composition. If, on the other hand, the paint has been mixed by sufficient shaking, the pigment distribution is fairly uniform throughout the binder. This proposed "Zeichner" model predicts differences in pigment load when comparing shaken and unshaken paint samples. Zeichner's study included two cans of blue paint (of the same type), and one can each of black, white, grey and gold. X-ray radiographic images were taken to document the settling of pigments within the can and settling experiments were conducted with intake tubes and fine sand. Zeichner's observed pigment behavior could be explained by his proposed model. However, other published studies report no differences between shaken and unshaken results. This led to the hypothesis that perhaps the type of pigment could be the factor that determines whether this pigment-settling model holds true for a given spray paint sample. This work evaluates that hypothesis.

## EXPERIMENTAL

The experimental procedure is based on methods described in the article: *A Study of Paint Coat Characteristics Produced by Spray Cans from Shaken and Nonshaken Spray Paints* by Zeichner, A., et al. (1)

Thirty-one cans of aerosol-type spray paints were acquired from local hardware and home improvement stores. A variety of colors, brands, and gloss-levels were chosen, comprising a sample set of 25 pigmented paints and three clear coats. Three of the 31 cans (cans 6, 13, and 30) ran dry or had a nozzle malfunction and were not included in the study. See Table 1 for paint set details.

Each can of spray paint was left undisturbed for a minimum of 24 hours prior to sample collection. Five slides (A-E) were used to collect paint from each of the cans, holding the slides approximately 30 cm from the spray can nozzle. The first three slides were collected from the unshaken can. A stopwatch was started at the same time the spray nozzle was first depressed. Glass slide A was collected from time 0-3 seconds, and then removed from the paint stream. The clock continued to run as the paint was sprayed, and then slide B was put into the stream from time 10-13 seconds, and then slide C was in the stream between 20-23 seconds. In other words, the paint was sprayed for a continuous 23 seconds, during which slides were collected at three intervals of three seconds apiece.

The can was then shaken 10 times and sprayed once again. Slide D was collected from 3-6 seconds during this spray time. Next, the can was shaken thoroughly according to the label's directions. For most paints, this meant shaking for 1-2 minutes after the mixing ball was heard to move freely. One can (#4) did not have an audible mixing ball

*Table 1: Paint Sample Set Information*

| CAN # | COLOR | TYPE | DETAILS |
|---|---|---|---|
| 1 | Metallic Gold | Enamel | Krylon (Sherwin-Williams) #1701 Bright Gold |
| 2 | Black | Fast-Drying Enamel | ColorWorks (Illinois-Bronze Paint Co) with Busan-11-M1 rust- and mold-inhibitor |
| 3 | Red | High Gloss | Krylon (Sherwin-Williams) #2108 Banner Red |
| 4 | Clear | Acrylic Gloss | Krylon (Sherwin-Williams) #1301 Crystal Clear Gloss |
| 5 | White | Gloss | Brite Touch (Borden Inc.) B-10 Gloss White |
| 7 | Clear | UV resistant | Rust-oleum Clear Top Coat #7902830 Matte Clear |
| 8 | Black | Body Shop Paint Acrylic Lacquer | Plasti-kote #1020 Black |
| 9 | Grey | Sandable Primer | Rust-oleum #1980 Gray Primer |
| 10 | Clear | Hi-Gloss Lacquer | Valspar #65064 Clear Gloss |
| 11 | Beige | Gloss | Krylon (Sherwin-Williams) #2504 Khaki Gloss (Beige) |
| 12 | Black | Flat Ultra Enamel | Valspar #165951 Flat Black |
| 14 | White | Enamel Gloss | Rust-oleum Painter's Touch #1992 Gloss White |
| 15 | Red | Hobby/Craft Paint | Krylon (Short Cuts) SCS-033 Red Pepper |
| 16 | Red | Interior-Exterior | Krylon #2108 Banner Red Gloss |
| 17 | Pale Pink | Enamel Satin | Krylon (Satin Touch) #3526 Simply Pink |
| 18 | Brown | Primer | Rust-oleum #7769 Rusty Metal Primer |
| 19 | White | Fast Dry Interior/Exterior | Rust-oleum (America's Finest) HD2890 Flat White |
| 20 | Black | Fast Dry Enamel | ColorPlace #20004812 Flat Black |
| 21 | Brown | Ultra Enamel | Valspar (American Tradition) #165926 Java Brown Satin |
| 22 | Yellow | Fast Drying | Rust-oleum (American Accents) #7932830 Summer Squash |
| 23 | Blue | Enamel Gloss | Valspar Interior/Exterior #65031 Royal Blue |
| 24 | Pale Green | Satin | Valspar Interior/Exterior #65082 Summer Leaf |
| 25 | Orange | Gloss | Valspar Interior/Exterior #65018 Orange |
| 26 | Yellow | for Plastic | Valspar Plastic Paint Interior/Exterior #68108 Yellow |
| 27 | Purple | Flat Enamel | Valspar Interior/Exterior #65087 Black Plum |
| 28 | Blue | for Plastic | Valspar Plastic Paint Interior/Exterior #68106 Royal Blue |
| 29 | Green | Gloss | Valspar Interior/Exterior #65035 Lawn Green |
| 31 | Alert Orange | Upside-down Marking Paint | ACE Solvent-Based 1017565/1015765B APWA Alert Orange |

and was therefore shaken for approximately two minutes. The nozzle was depressed, and again, slide E was collected from 3-6 seconds during this spray time. Diagrammatically, the sampling sequence for each can was as follows:

| Time (seconds) | Spraying started | 0-3 | 4-9 | 10-13 | 14-19 | 20-23 | Spraying stopped | 10 shakes | 0-2 | 3-6 | Spraying stopped | Full shaking | 0-2 | 3-6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sampling | | A | | B | | C | | | | D | | | | E |

The slides were allowed to air dry outside in the sun at ambient temperature (about 75 degrees F) for approximately 90 minutes before bringing them inside for storage.


*Figure 2 Slide sets for samples 24-29. Note the visible difference in pigment concentrations between slides A/D/E vs. B/C.*

Each glass slide was scored along its length's midline and broken in half. Half of each slide became the Portland Metro Laboratory sample and the other half went to the Springfield Laboratory for analysis via FT-IR. The two FT-IR microscope systems in these labs are equivalent except for the lack of a purge on the Springfield instrument. The area of sampling for FT-IR on each half-slide was along the scored/broken edge, in the approximate middle of the slide's width. In each lab, duplicate samples were run from each slide, for a minimum of four data collections per original glass slide.

Collection of spray paint data was performed using the Thermo Scientific Nicolet Continuμm Infrared Microscope attachment to a 6700 FT-IR. Paints were analyzed as thin peels in transmission mode from 650 to 4000 wavenumbers, with a minimum of 128 scans, atop either a salt plate or one half of a diamond compression cell. Data was collected between July 2010 and April 2011.

Comparisons made between duplicate samples collected in each lab and among the four total samples collected from both lab locations showed little variation in overall data between the two instruments or between duplicate samplings of the same slide in a particular lab. Variations noted were the presence/absence of the $CO_2$ absorbance, variation in data quality due to sample thickness/opacity that affected baselines and noise, and minor variations caused by pigments in samples that appeared visibly heterogeneous, such as the metallic gold with effect flakes in a clear binder. Therefore, data from Portland (using an instrument equipped with the purge system) has been used for display purposes and to draw overall conclusions. Spectral evaluation of FT-IR data allowed identification of peaks indicative of specific pigment types.

## RESULTS AND DISCUSSION

FT-IR spectra were evaluated for trends in variation between the unshaken paint (slides A, B and C) and the paint after shaking (slides D and E). Few differences were observed between slides D (sprayed after 10 shakes) and E (sprayed after complete shaking). The behaviors of the paints were grouped into three main categories. These groups were then assessed for features such as pigment type and paint color. The pigments primarily observed were inorganic extender pigments such as talc, clays, titanium dioxide ($TiO_2$), and carbonates (such as calcium carbonate, $CaCO_3$), as well as organic carbon black. Organic pigments responsible for paint coloration were not identified individually, but were generally recognized by numerous sharp peaks within the infrared fingerprint region. Settling of these organic pigments was particularly noted in one orange and both red paints. Although this study did not identify any inorganic coloring pigments, this could be explored by examining larger color sets.

Group 1 behaved as predicted by the Zeichner model: heavy extender pigment-loading was seen primarily in slide A (non-shaken, seconds 0-3 of spraying) and slides D and E (after shaking). Slides B and C were visually lighter in pigment coverage on the slides and common inorganic extender pigment peaks were absent or minimal in the FT-IR spectra. Ten samples were in this group: 2, 8, 12, 17, 18, 19, 20, 22, 25, & 27. This sample set included: all four black samples, and one each of orange, yellow, brown, pale pink, white and purple. Comparisons of shaken and non-shaken paint applications from these cans could lead an unaware examiner to a false exclusion due to the significant infrared spectral differences.

The six paints in Group 2 also showed evidence of extender pigment settling when analyzed via FT-IR. However, these spray paints showed low pigment loads in all the unshaken slides (A, B, and C). In this group: 5, 9, 14, 15, 24, & 31. These were: two white samples, a grey, a red, a pale green, and a road-marking paint in bright orange. Paint 16 (red) showed signs of pigment settling, but did not fall neatly into Group 1 or 2.

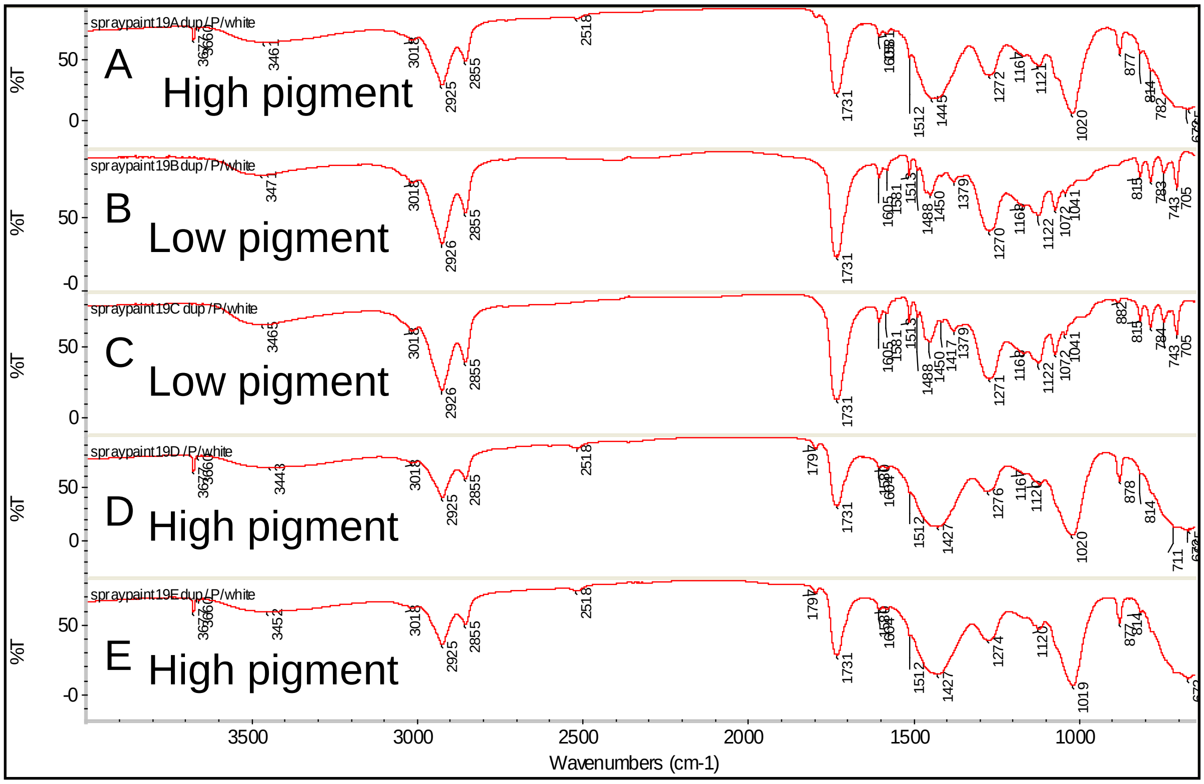



*Figure 3 Group 1 Example: Paint #19: White with $TiO_2$ (Broad 700-600 $cm^{-1}$), talc (3677 $cm^{-1}$, 1018 $cm^{-1}$), and $CaCO_3$ (1799 $cm^{-1}$, 1420 $cm^{-1}$)*

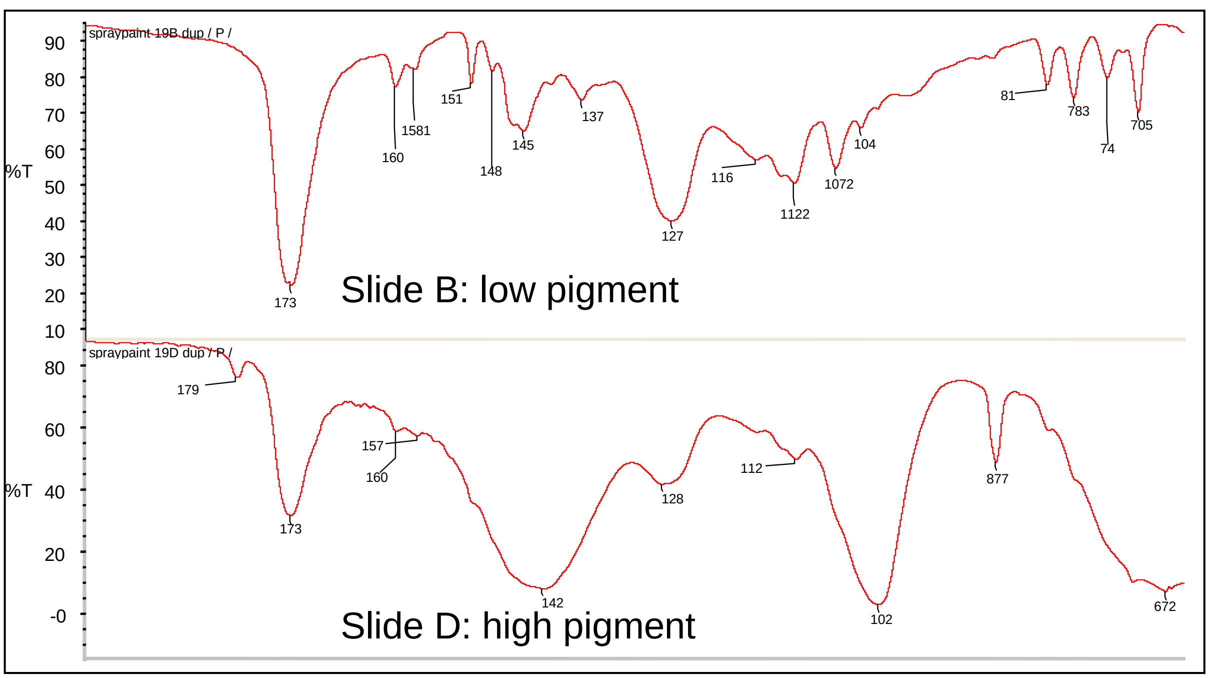



*Figure 4 Fingerprint regions: Paint 19 white: Slide B (unshaken) vs. D (shaken). Would you think these were from the same paint source?*

These results were interesting in that the visual appearance of the unshaken samples (slides A, B, and C) were not necessarily consistently light in visual appearance. For example, Paint 24 slide A appeared fairly green to the eye and much darker than slides B and C, but the spectral data for slide A exhibited only a fraction of the substantial titanium dioxide contribution detected in slides D and E. The crater/vortex around the intake tube may have formed quickly in these cans, or the lower end of the aspiration tube may have been above the level of the settled pigments. It is possible that the extender pigments, those that add to the paint's opacity, may settle differently than the coloring pigments which are responsible for some of the paint's visible hue. Another possible explanation is that some settling pigments in these paints may not be readily detected by the FT-IR methods used here.

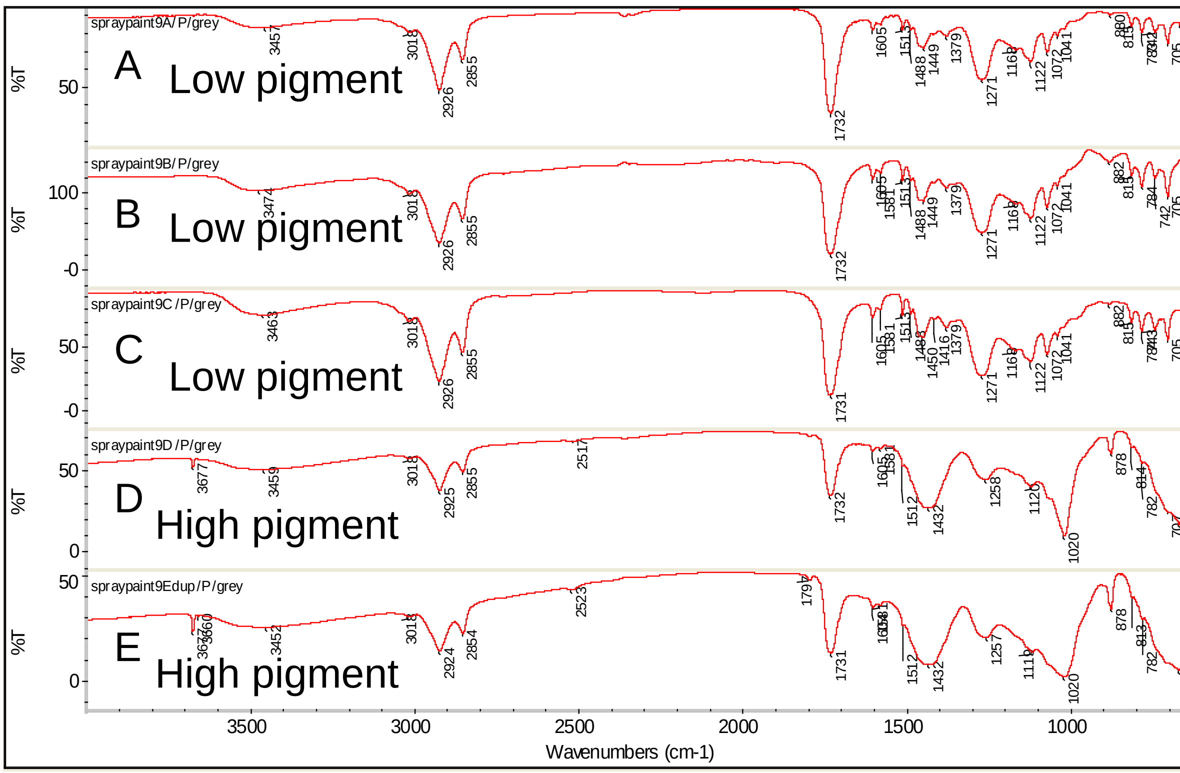



*Figure 5 Group 2 Example: Paint #9: Grey primer with $TiO_2$, talc, and $CaCO_3$*

The third group included eight pigmented paints and the three clear coatings. These spray paints showed very few spectral differences between shaken and unshaken FT-IR data. This suggested that, in these paints, the pigments detected by FT-IR did not settle differentially. In other words, if multiple pigments were present in a paint can, they all settled to a similar degree rather than separating into strata of more-settled and less-settled pigment types. Similar to Group 2, the pigment density clearly differed on the various slides (see obvious color/opacity differences visible in paint sets 26, 28, and 29 in Figure 2); however, within Group 3 the pigments detected by FT-IR did not vary from slide to slide. These samples tended to be some of the brighter paint colors, which may contain organic rather than inorganic pigments that have smaller particle sizes or particles of lesser density. In this group: 1, 3, 11, 21, 23, 26, 28, 29 and the three clear-coat samples. These included: both blue samples, a metallic gold, one yellow, one brown, one red, one beige and a deep green. The metallic gold is somewhat of an anomaly. Although the metallic flake pigment may be settling, settling could not be determined by transmission FT-IR since that technique only collects data from the clear binder material and not the opaque metallic flake.

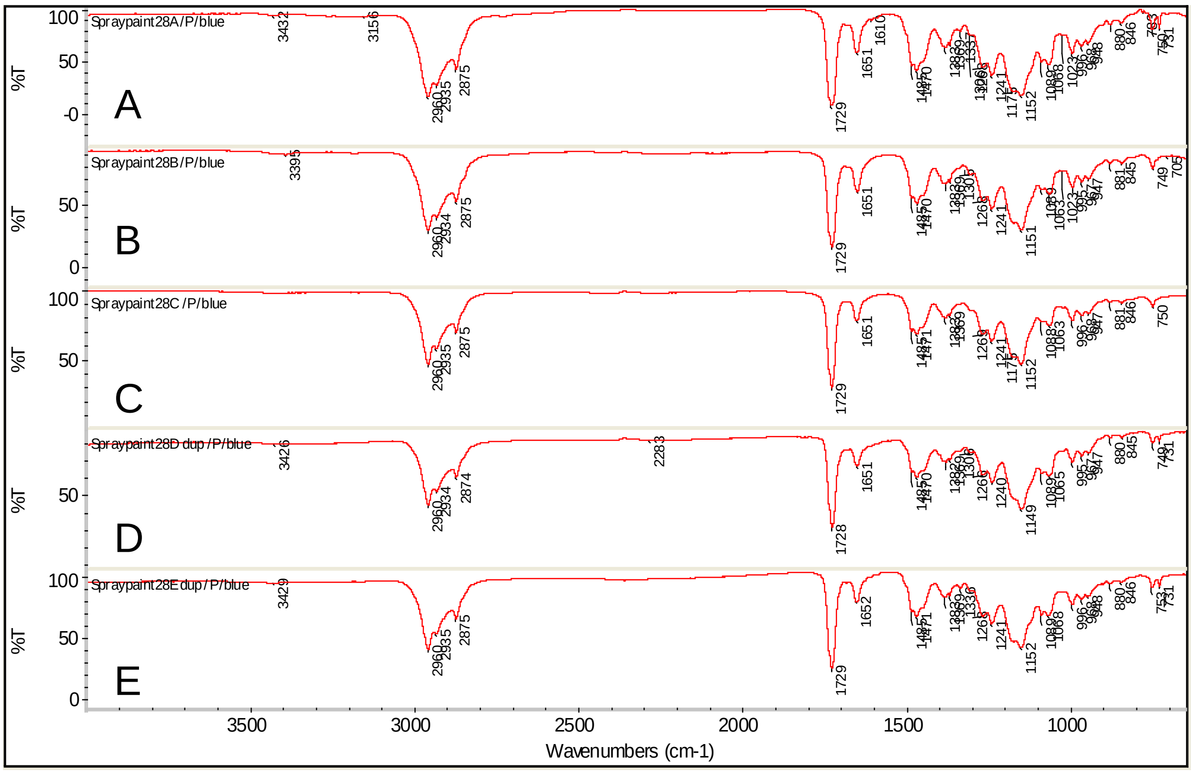



*Figure 6 Group 3 Example: Paint #28: Blue—no inorganic pigments identified; no difference in settling behavior observed as pigment variation in slides A-E*

*Summaries*

Groups 1 & 2:

- Pigment settling attributed to the presence of relatively more dense inorganic pigments or carbon black seen in the IR spectra. Falling into these groups were: all four black samples, all three white samples, the grey, one orange, one yellow, a pale pink and pale green, a purple, and a brown.
- Based on the observation of spectral peaks not readily attributable to a binder class, additional pigments of an organic type may also be present.

- Pigment settling attributed to unidentified organic pigments was seen in both reds and the orange sample. These pigments contributed multiple sharp peaks to the spectral fingerprint regions.
- Muted colors (white, black, grey, pastel shades) tend to fall within these groups, although some bright colors are seen here as well. Bright colors may have a combination of inorganic and organic pigments.
- Due to the wavenumber region of carbon black absorbance (seen as a sloping baseline at the higher wavenumbers), this pigment did not significantly interfere with comparisons of peaks in the fingerprint regions of the spectra. The presence or absence of other settling-prone pigments may mask or reveal peaks in the so-called fingerprint region, making interpretation and comparison difficult.

Group 3:

- Little-to-no IR spectral differences across the A-E slide set were observed for these paints. Therefore, no differential pigment settling was suspected based upon the FT-IR data.
- These paints do not contain talc, titanium dioxide, calcium carbonates, silica or carbon black. The primary pigments present may be organic and either less prone to differential settling or not detected by FT-IR. Paint 11 (beige) does have titanium dioxide but little pigment variation was observed; all slides showed a heavy pigment load.
- Colors are more likely to be bright and/or deeply colored, including both blue samples, a deep green, a red, a yellow, and a brown. Metallic gold is also included here due to the examination technique.
- Clear coatings also fall within this group. These were included in the study to determine if binder-mixing was also a factor in FT-IR comparisons. No slide-to-slide binder differences were observed that could be attributed to mixing.

*Further examination of possible organic pigments*

Inorganic pigments such as talc are readily identifiable by their characteristic and relatively simple FT-IR patterns, and carbon black is often recognized as the cause of a sloping baseline at higher wavenumbers. However, organic pigments may produce much more complicated spectra that may not easily be distinguished from the polymer binder or not detectable by FT-IR. Due to the large number of possible organic pigments and the complexities with in situ identification, definitive identification of the pigment may be impossible.

However, in order to investigate if organic pigments were indeed present in the spray paints in this study, each paint sample was tested to see if pigment crystals would sublime from the paint matrix and could thereby be isolated for microscopy and FT-IR analysis. The technique for sublimation of organic pigments using Vitrotubes[5] was developed by Skip Palenik of Microtrace LLC. Paint scrapings were inserted into a flat glass tube (Vitrotube) and heated briefly over an alcohol flame. Metal tongs were used to grip the tubing near the opening at the heated end to act as a heat-sink and provide a region suitable for crystallization. Some organic pigments will sublime and re-crystallize on the tube interior. These colored crystals can then be viewed and analyzed. Crystals were observed with bright field and polarized light microscopy and their formation was found to be reproducible. Samples were carefully collected from the Vitrotube interior and analyzed via FT-IR.

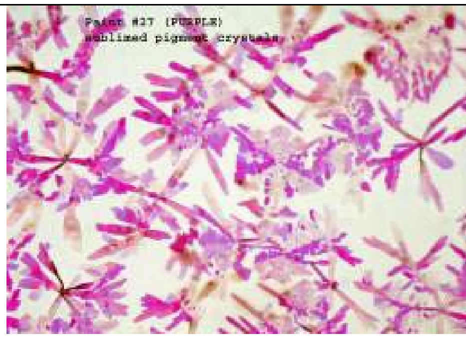
Sublimed organic pigments were observed in six samples: all three red paints, both blue samples, and the purple. See Figure 7. Brightly-colored paints were most likely to contain organic pigments that sublimed. Among this sample set, this was confined to those in the red-purple-blue color family. No pigment sublimation was seen with the yellow, orange, or green samples.

Generally, library database searches of the colored pigment crystals seen in the subliming samples produced best-hit search results for organic pigments in the same color range as the visible color of the crystals. (This laboratory system does not possess any specialized searchable pigment libraries.) There was too little of one crystal type to permit FT-IR analysis, and another produced no useful search results. However, sublimation was considered a promising technique for isolation and examination of organic pigments within some spray paint matrices. Further exploration of this technique using other types of paints may prove it to be a useful tool in paint comparisons where organic pigments are present. If identification rather than comparison of pigments are the goal, it must also be ensured that heating of the pigments by this method does not alter their crystalline form.

In addition to the colored sublimed crystals in six paints, over half of the samples produced clear crystals of various forms. Several of these were analyzed via FT-IR and determined to be some kind of plasticizer.

## CONCLUSIONS

The behavior of paint pigments in relation to the amount of mixing prior to application varies. Much of this variation can be attributed to the presence or absence of carbon black or inorganic extender pigments such as titanium dioxide, talc, silicates, and calcium carbonates. If these pigments are present, they tend to create variable pigment-loading: higher in shaken paints and generally lower in unshaken paints. For the forensic scientist, this variation may appear as significant differences in visible hue or in large differences in FT-IR spectral data that could be misinterpreted as paints




*Paint 27 (purple paint, violet crystal)*


*Paint 23 (blue paint, blue crystal)*


*Paint 28 (blue paint, red crystal)*


*Paint 16 (red paint, red-orange crystals: two forms)*


*Paint 3 (red paint, red-orange crystal)*


*Paint 15 (red paint, magenta crystal)*


*Clear crystals indicative of plasticizer compounds; some form of these seen in over half of the sample set. Shown in bright field and crossed-polarized light at 200x magnification.*

*Figure 7 Examples of sublimed crystals from spray paints. Unless otherwise noted, photomicrographs are at 400x magnification, bright field, on a Leica DMLB2 microscope.*

coming from different origins. Although less of a factor for the comparison of FT-IR spectral data of paints not containing the pigments listed above, some color intensity variation was seen in other paint samples in this study.

Organic pigments, when present, do not appear to settle differentially in unmixed paints in a manner that creates spectral differences. However, they may be combined with inorganic pigments that settle differently, potentially creating variable mixtures of pigments throughout the spraying process. Color alone cannot determine whether differential settling of pigments will be a problem with paint comparisons. Organic pigments that are not detected by FT-IR may also be a cause for these variations. Other analytical techniques that are more sensitive to these pigments would be of value in observing the impact of pigment settling. Using FT-IR, a more objective indication of potential settling-induced complication is afforded by those pigments known to be prone to settling-induced variation: talc, titanium dioxide, calcium carbonates, silicates, and, to a lesser degree, carbon black.

The heterogeneity of all paint types is a normal consideration for paint analysts, but the extremes seen in spray paint analysis merit special precautions. To avoid false exclusions, comparison standards from spray paint cans should be taken from the can in both unshaken and shaken states. These will enable the examiner to assess the full range of variation possible from a known spray paint and will increase the accuracy of determinations of questioned paints' possible association with it. This assessment is much improved when an analyst can determine which peaks are attributed to the binder, which should not vary with mixing, and those which come from the pigments themselves. Although elemental analysis was not included in this study, the same recommendation would apply for XRF or SEM-EDS analysis and comparisons of spray paints.

These overall findings for heterogeneity in spray paint related to shaking times are in agreement with trends recently described by Muehlethaler et.al.[(6)] in research conducted with FT-IR and Raman, but on a more limited subset of colors: red, green and blue paints.

**ACKNOWLEDGEMENTS**

This researcher thanks Kaylon Wells for assistance with slide preparation, Adam Fleischer and Shane Harlson for assistance with data collection via FT-IR, Rhonda Banks for research consultation, advice and review of this article, and Melissa Simons for article review. Thanks also to the Oregon State Police Forensic Services Division for providing the time and support required for this research.

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5. Vitrotube source information: phone 973-402-1443 (New Jersey, USA) http://www.vitrocom.com/products/view/3530-050 Rectangular capillary tubing of borosilicate glass. Dimensions: 50mm long x 3mm-wide opening x 0.3mm-high opening. Tube of 31, $19 (Jan 2012)

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