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

Background

A search of the literature found seemingly contradictory reports of the behavior of pigments in shaken vs. non-shaken spray paints. Of the four studies reviewed, three focused on a sample set of a single color (black, red or green). Comparisons were performed using various analytical techniques (SEM, XRF, FTIR and dispersive Raman). These articles differ in concluding whether a paint shows differences in shaken vs. unshaken. Results could be due to analytical method or the color of the paint in the sample set.

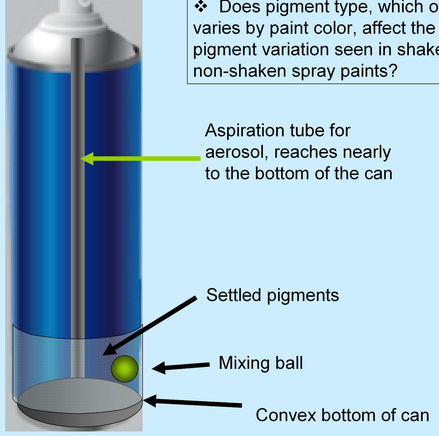
One proposed explanation [1] of the differences seen in shaken and unshaken paints is that settled pigments initially are aspirated through the tube and out the nozzle. This creates a high pigment load in the first few seconds of spraying.

As the nozzle is further depressed, a crater or vortex forms and pigments are left behind while predominantly binder is sprayed, creating a coating with a low pigment load.

After shaking, the pigment distribution is fairly uniform throughout the binder.

This explanation predicts differences in pigment load . But some studies saw no differences between shaken and unshaken results.

- ❖ Is this model valid for all spray paints or only for those with pigments that settle significantly?
- ❖ Does settling depend on pigment type?
- ❖ Does pigment type, which often varies by paint color, affect the pigment variation seen in shaken vs. non-shaken spray paints?



References and Resources

[1] Zeichner, A., Levin, N., and E. Landau
A Study of Paint Coat Characteristics Produced by Spray Paints from Shaken and Nonshaken Spray Cans. *Journal of Forensic Sciences;* (1992) Volume 37, No. 2:542-555
Our experimental procedure was adapted from this paper.

[2] Govaert, F., de Roy, G., Decruyenaere, B., and D. Ziernicki
Analysis of Black Spray Paints by Fourier Transform Infrared Spectrometry, X-Ray Fluorescence and Visible Microscopy. *Problems of Forensic Sciences;* (2001) Volume XLVII:333-339

[3] Govaert, F. and M. Bernard
Discriminating Red Spray Paints by Optical Microscopy, Fourier Transform Infrared Spectrometry and X-ray Fluorescence. *Forensic Science International;* (2004) Volume 140:61-70

[4] Buzzini, P., and G. Massonnet
A Market Study of Green Spray Paints by Fourier Transform Infrared (FTIR) and Raman Spectrometry. *science & justice* 2004, Volume 44, No. 3:123-131

Study conducted by:

Kris M. Gates (Trace & Chemistry Units)
of the Oregon State Police Portland Metro Forensic Laboratory
kris.gates@state.or.us

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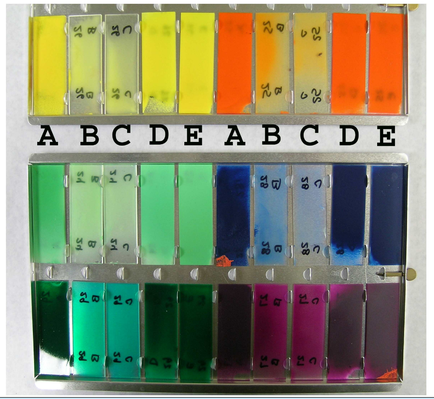
Does the type of pigment in a spray paint affect whether FTIR spectral differences are seen between samples taken from shaken and unshaken paint cans?

Procedure: Collected paint from each can onto 5 glass slides, collected at the following times:
Slides A, B, and C are collected from the unshaken can. The can is then shaken 10 times and Slide D made. Slide E is collected after the can is shaken according to manufacturer's instructions.

Time (seconds)	0-3	4-9	10-13	14-19	20-23	10 shakes	3-6	Full shaking	3-6
Slide made	A		B		C		D		E



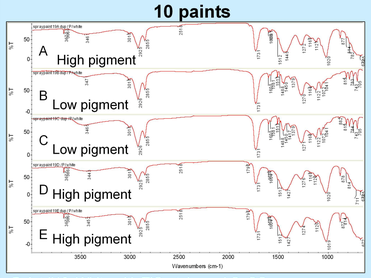
Our sample set: 25 pigmented spray paints and 3 clear spray paints:

1 2 8 12 20 3 15 16 5 14 19 9 25 31
11 18 21 22 26 24 29 23 28 17 27 CLEAN CLEAN CLEAN

FTIR Analysis and Comparison

Each spray paint slide was analyzed in duplicate at two separate laboratories using a Thermo Scientific FT-IR Continuum microscope. Samples were run in transmission mode (128 scans) and range of 4000-650 wavenumbers. The four spectra from each slide were assessed for consistency before the data from slides A-E were compared to one another to assess pigment loads of shaken and non-shaken paint cans.

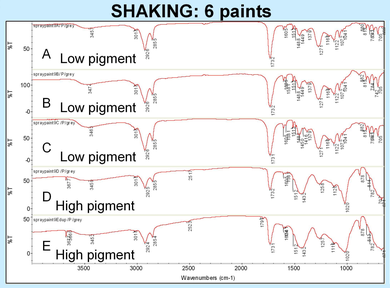
INITIAL PIGMENT BURST, THEN LOW PIGMENT LOAD UNTIL AFTER SHAKING: 10 paints



Paint #19: White with TiO_2, talc, and $CaCO_3$

Some paints behaved as predicted with the Zeichner model [1]: heavy inorganic pigments (or carbon black) are seen most in slides A (non-shaken, seconds 0-3 of spraying) and slides D and E (after shaking). Slides B and C, are visually lighter in pigment coverage on the slides and inorganic pigment peaks in the FTIR are absent or minimal. **In this group: 2, 8, 12, 17, 18, 19, 20, 22, 25, & 27**

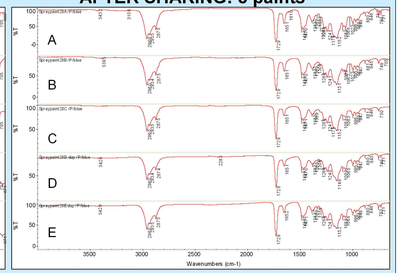
LOW PIGMENT LOAD UNTIL AFTER SHAKING: 6 paints



Paint #9: Grey primer with TiO_2, talc, and $CaCO_3$

Other spray paints showed low pigment loads in all the nonshaken slides (A, B, C). The crater/vortex around the intake tube may have formed quickly in these cans, or the aspiration tube may intake above the level of the settled pigments.
In this group: 5, 9, 14, 15, 24, & 31
Paint 16 did not fall into any of these three categories.

SIMILAR PIGMENT LOAD BEFORE & AFTER SHAKING: 8 paints

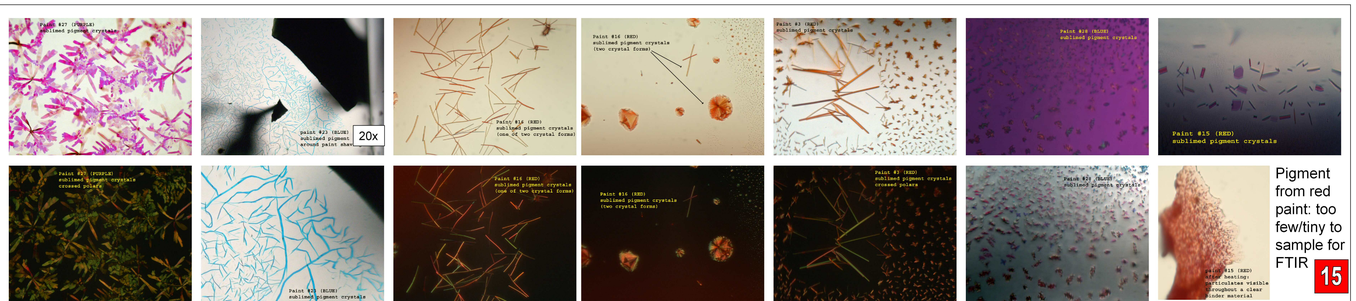


Paint #28: Blue with a pigment that sublimed

A group of spray paints showed very few differences between shaken and nonshaken FTIR data. This leads to the theory that, in these paints, the pigments did not settle. These tend to be some of the brighter paint colors, which may contain organic, rather than inorganic, pigments that have smaller particle sizes.
In this group: 1, 3, 11, 21, 23, 26, 28, & 29

Sublimation of Organic Pigments

Do those colored paints that show little pigment-settling have predominantly organic pigments rather than inorganics? Can those pigments be identified as organic by isolating them for FTIR analysis? Sublimation attempts to separate organic pigments from the paint matrix. Paint scrapings are inserted into a flat glass tube (Vitrotube) and heated over an alcohol flame. Some organic pigments will sublime and re-crystallize on the tube interior. These can then be viewed and analyzed. Crystals were observed with a compound microscope in bright field and polarized light and were reproducible.
Sublimed organic pigments were observed in 6 samples: 3 red, 2 blue, and the purple. Three of these paints had shown little settling effects (3,23,28). However, organic pigments were also isolated from paints that showed settling that could not be explained by the presence of inorganic pigments (15,16,27). Overall, brightly colored paints were most likely to contain organic pigments that sublimed.



Pigment from purple paint: FTIR hits for violet, magenta and red organic pigments **27**

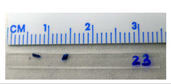
Pigment from blue paint: FTIR hits for blue organic pigments **23**

Two separate pigments from a red paint: FTIR hits for orange, scarlet and red organic pigments **16**

Pigment from red paint: FTIR hits for orange and red organic pigments **3**

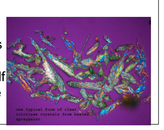
Pigment from blue paint: no solid FTIR hits **28**

Pigment from red paint: too few/tiny to sample for FTIR **15**



The technique for sublimation of organic pigments using Vitrotubes was developed by Skip Palenik of Microtrace LLC. Photomicrographs taken using 40x objective unless otherwise noted.

Also of note: Sublimed plasticizers or other additives were seen in over half the complete sample set (20x)



Conclusions

What factors determine the effects of differential pigment loads on FTIR interpretation in spray paint comparisons?

Shaken versus unshaken spray paint samples *may* appear different, both visually and in FTIR spectra. This can hamper comparisons of known and unknown paint samples in casework. By recognizing FTIR peaks due to pigment components that settle, it can be determined whether an observed difference is due to different paint sources or may instead be caused by differential pigment loads between paint samples from the same origin. This supports the practice of comparing both shaken and unshaken standards made from spray paints to questioned paint samples.

Variation in spectra due to pigment loading is most pronounced when the pigments are <u>inorganics that settle significantly</u> in unshaken paint and have numerous bands that overlap with binder peaks. The most significant of these are: <u>TALC, CLAY, OTHER SILICATES & CALCIUM CARBONATES.</u>

In our sample set, these samples showed significant FTIR differences between shaken and unshaken paints, differences that could hamper comparisons between known and questioned paints:

With Significant Pigment Settling

5	TiO_2 & $BaSO_4$	20	talc, carbon black	22	TiO_2 & talc	31	$CaCO_3$
14	TiO_2,silicates*	16	Unknown(s)	15	Unknown(s)	25	Unknown(s)
19	TiO_2 & talc	18	talc, $CaCO_3$ & carbon black	9	TiO_2, $CaCO_3$ & carbon black	27	Unknown(s) & silicates*

TITANIUM DIOXIDE can also settle significantly, but effects on the FTIR spectra are isolated to below 800 wavenumbers. Similarly, **CARBON BLACK** exhibits settling, but the sloped baseline above 1700 wavenumbers does not severely mask the FTIR fingerprint region.

These samples showed some variation of specific pigments, but FTIR comparisons were not severely hampered once these pigments were recognized.

2 8 12 **Carbon black baseline only** 17 24 **TiO_2 only**

Paint with little-to-none of the pigments listed above are less likely to show a spectral difference between shaken and non-shaken paint samples. Those paints are often brightly colored and may contain mostly organic pigments.

These samples showed minor or no variability in FTIR spectra. They do not contain talc, titanium dioxide, calcium carbonates, silica or carbon black. Primary pigments present may be organic.

Without Significant Pigment Settling

1 3 21 23 26 28 29
CLEAN CLEAN CLEAN

In some cases (paints 15, 16 and 25), pigment variation was observed but the pigment type could not be determined by FTIR. In one paint (11), TiO2 was present but little variation was observed. 11

*Silicates = clay or diatomaceous silica