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Discrimination of Retail Black Spray Paints

ABSTRACT: Household black spray paints are occasionally encountered in forensic investigations involving homicide, sexual assault, stalking, motor vehicle hit and run, terrorist activity, and property crime. Comparisons of questioned material with known samples employ well established procedures including microscopy, Fourier Transform infrared microspectrometry, scanning electron microscopy in conjunction with energy dispersive X-ray spectrometry, pyrolysis gas chromatography, and UV-Vis microspectrophotometry. This study evaluates the discrimination power of a series of four of these techniques on a sample set of seventy-one black household spray paints acquired at retail stores in the United States. One of each different type of product encountered was included in the sample set providing a product, not a population, survey. The results corroborate the conclusions reached in similar published European studies of black, red, and green spray paints.

KEYWORDS: Forensic, Comparisons, Paint, Spray Paint, Discrimination Study

Household black spray paints are occasionally encountered in forensic investigations involving homicide, sexual assault, stalking, motor vehicle hit and run, terrorist activity, and property crime. Typically, it is requested that a cured paint sample found at the scene (questioned sample) be compared to the paint contained in a can of spray paint discovered in the possession of a suspect (known sample) in an effort to determine if they are alike. In doing so, the known sample must be in the same form as the questioned material; hence, samples of sprayed paint from the can are permitted to cure prior to comparison. Comparisons employ well established procedures including microscopy, Fourier Transform infrared microspectrometry, scanning electron microscopy in conjunction with energy dispersive X-ray spectrometry, pyrolysis gas chromatography, and UV-Vis microspectrophotometry (1). If the samples are found to be different it is concluded that the two could not have had a common origin. If they are found to be indistinguishable it is concluded that the paint from the scene could have originated from the known can of spray paint.[2] The question then becomes, how many

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[2] The U.S. Supreme Court's Daubert ruling (Daubert v. Merrell Dow Pharmaceuticals, Inc. (1993) 509 U.S. 579, 589) requires testability of the principle using the scientific method. They state that

other sources of spray paint could be like that found at the scene? Although a large sampling of randomly acquired spray paints would be ideal to answer this question; it is difficult, if not impossible, to acquire such a sample set ensuring that it is representative of the true population. Alternatively, many forensic scientists employ product discrimination studies to provide some evaluation of the evidential significance of the comparison results.

This project undertakes such a task, evaluating the discrimination power of a series of four analytical techniques on a sample set of seventy-one black household spray paints acquired at retail stores in the United States in 2001. One of each different type of product encountered was included in the sample set. Black spray paints were chosen as a worst case scenario due to their common occurrence and the absence of coloring pigments that would only improve discrimination capability. The paints were acquired at retail stores in the central Florida area, including Ace Hardware, Home Depot, K-Mart, Lowes, Sears, Scotty's, True Value Hardware, and Wal-Mart. Samples of cured paint were prepared from each and they were initially inter-compared by Fourier Transform infrared spectrometry (FTIR). This approach was taken considering the widespread availability of the technique, the fact that binder and extender pigment classification information is acquired simultaneously, it is a relatively rapid method, and it requires minimal training compared to microscopy. In that several analysts were each working with a different subset of the samples at the same time, it also provided a simple means for initial inter-comparison of the entire sample set. Spray paints that were indistinguishable by infrared spectrometry were then compared by stereomicroscopy and brightfield/polarized light compound microscopy (PLM). Paints still indistinguishable were compared by scanning electron microscopy - energy dispersive x-ray spectrometry (SEM-EDS) and finally pyrolysis gas chromatography (PyGC). SEM-EDS analysis was performed prior to PyGC since household paint deposits encountered in casework are typically quite thin and limited in sample quantity. SEM-EDS analysis requires far less sample than PyGC, especially when performing replicate analyses to assess heterogeneity.

"scientific methodology today is based on generating hypotheses and testing them to see if they can be falsified; indeed this methodology is what distinguishes science from other fields of human inquiry." In forensic paint examinations, an original hypothesis that the two materials are different and could not have a common origin is adopted. The samples are then subjected to comparisons using a series of reliable highly discriminating techniques in an effort to falsify the null hypothesis that the samples are alike and could have originated from the same source. If the samples prove to be different, the null hypothesis is falsified and the original hypothesis must be accepted; that is, the questioned sample could not have originated from the known can of spray paint. If the samples prove to be indistinguishable, the null hypothesis is not falsified and it must be concluded that the samples could have a common origin.

Although it has been reported that some discrimination can be achieved using UV-Vis microspectrophotometry (MSP) on black automotive paints (2), it was not employed in this analytical sequence for two reasons. First, black household spray paints are almost always pigmented with carbon black, offering little ultra-violet or visible spectral data. Much more discriminating information can be acquired by assessing the pigment's distribution and particle size. Secondly, as mentioned before, household paint deposits encountered in casework typically are quite thin, have uneven layer thickness, and do not lend themselves to detailed comparison by MSP using controlled sample preparation methods, such as the recommended technique of microtomy (3, 4).

Similar studies have been reported in Europe dealing with black, red and green spray paints (4, 5, 6). Considering the samples used in this study were acquired in the same approximate time frame as those in the European studies, the project would either corroborate those results for the spray paint population in the United States or demonstrate a different discrimination potential due to the number of manufacturers, types of products, or compositional differences.

SAMPLES AND METHODS OF ANALYSIS

Seventy-one new cans of spray paint were purchased from local hardware and home improvement stores in 2001. The products were chosen to not only include different brands but also different finish types, such as flat, satin, gloss, and hammered. Records of their type and retail outlet are listed in Table 1. Samples were sprayed onto three-by-five inch metal test panels following one minute of vigorous shaking. After initial application outdoors in the sunlight, they were air dried for a minimum of one month indoors at room temperature (25 °C) prior to sampling. Thin peels were taken for analysis from the cured paint using a number 11 scalpel blade being careful to not cut down to the metal substrate.

Fourier Transform Infrared Microspectrometry (FTIR)

Samples were analyzed as thin peels compressed either with the beveled edge of a scalpel blade or a roller bearing and then laid on the surface of 0.5 mm thick silver chloride discs. Analysis was performed in the transmission mode on either a Nicolet Nexus 670 FTIR in conjunction with a Continuum microscope accessory using a 15X Cassegrain objective and condenser, 4 cm^{-1} resolution, MCTB detector (4000 to 450 cm^{-1}) or on a Bio-Rad FTS-40 in conjunction with a UMA-300 microscope accessory using a 36X Cassegrain objective, 4 cm^{-1} resolution, MCTB detector (4000 to 450 cm^{-1}). Both instruments were purged with dry carbon dioxide free air.

Table 1: Black Spray Paint Samples

Manufacturer listed on can	Brand Name	Product Code	Finish	Retail Outlet	Description of Use
Dutch Boy /Sherwin-Williams	Fresh Look	Black 3751	Satin	K-Mart	Acrylic Enamel - Interior/Exterior
Dutch Boy Sherwin-Williams	Fresh & Easy	Black FE501	Gloss	K-Mart	Interior/Exterior Enamel
Dutch Boy/Sherwin-Williams	Fresh Look	Black 3727	Flat	K-Mart	Acrylic Enamel - Interior/Exterior
Dutch Boy/Sherwin-Williams	Fresh Look	Black 3726	Gloss	K-Mart	Acrylic Enamel - Interior/Exterior
Dutch Boy/Sherwin-Williams	Fresh Look	Black 3614	Satin	K-Mart	Interior/Exterior - Controls Rust
Dutch Boy/Sherwin-Williams	Fresh Look	Black 3600	Gloss	K-Mart	Interior/Exterior - Controls Rust
Dutch Boy/Sherwin-Williams	Fresh Look	Black 3604	Flat	K-Mart	Interior/Exterior - Controls Rust
Dutch Boy/Sherwin-Williams	Fresh Look	Black S3671		K-Mart	High-Temp
General Paint & Manufacturing Co	X-O Rust	Black XO-2	Gloss	True Value	Interior/Exterior Enamel
General Paint & Manufacturing Co	X-O Rust	Black XO-19	Flat	True Value	Interior/Exterior Enamel
Manufactured f/Ace Hardware	Ace	Black 17004	Gloss	Ace Hardware	Interior/Exterior Premium Enamel
Manufactured f/Ace Hardware	Ace	Wrought Iron Black 17003	Flat	Ace Hardware	Interior/Exterior Premium Enamel
Manufactured f/Ace Hardware	Ace	Black 1010016	Flat	Ace Hardware	Indoor/Outdoor Enamel - Rust Stop
Manufactured f/Ace Hardware	Ace	Black 17072	Gloss	Ace Hardware	Indoor/Outdoor Enamel - Rust Stop
Manufactured f/Ace Hardware	Ace	Black 17073	Satin Flat	Ace Hardware	Indoor/Outdoor Enamel - Rust Stop
Manufactured f/Ace Hardware	Ace	Barbecue Black 1010065		Ace Hardware	Barbecue Black 1000 * Rust Stop
Manufactured f/Ace Hardware	Ace	Black 11920	Gloss	Ace Hardware	Epoxy Enamel
Manufactured f/Ace Hardware	Ace	Black 17065	Gloss	Ace Hardware	Heat Resistant
Manufactured f/Ace Hardware	Ace	Black 17067	Flat	Ace Hardware	Heat Resistant
Manufactured f/Ace Hardware	Ace	Black 17029	Flat	Ace Hardware	Instant Drying Lacquer
Manufactured f/Ace Hardware	Ace	Black 17028	Gloss	Ace Hardware	Instant Drying Lacquer
Manufactured f/Scotty's	WOW	Black 77008	Gloss	Scotty's	Interior/Exterior Enamel
Roc Sales Inc.	Quick Color	Black J2853	Flat	Home Depot	All Purpose Enamel
Roc Sales Inc.	Quick Color	Black J2851	Gloss	Home Depot	All Purpose Enamel

Table 1: Black Spray Paint Samples (continued)

Manufacturer listed on can	Brand Name	Product Code	Finish	Retail Outlet	Description of Use
Rust-oleum Corp.	Rust-oleum Professional	Black 7578	Flat	Lowe's	High Performance Enamel
Rust-oleum Corp.	Rust-oleum Professional	Black 7579	Gloss	Lowe's	High Performance Enamel
Rust-oleum Corp.	Premium Rust-oleum	Black V7779	Gloss	Lowe's	Gloss Protective Enamel/Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	Black 7776	Flat	Lowe's	Flat Protective Enamel/Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	Black 7250	Metallic	Lowe's	Indoor/Outdoor - Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	Black 7215	Hammered	Lowe's	Metal Finish/Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	BAR-B-QUE Black 7778		Lowe's	High Heat Enamel/Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	Black 7777	Satin	Lowe's	Protective Enamel/Stops Rust
Rust-oleum Corp.	Premium Rust-oleum	Black 7220	Textured	Lowe's	Indoor/Outdoor - Metal Surfaces
Rust-oleum Corp.	American Accents	Canyon black 7946	Satin	Lowe's	Smooth Finish - Ideal for Wood
Rust-oleum Corp.	Painter's Touch	Black 1976	Flat	Home Depot	Multi-Purpose - Indoor/Outdoor
Rust-oleum Corp.	Painter's Touch	Black 1974	Semi-Gloss	Home Depot	Multi-Purpose - Indoor/Outdoor
Rust-oleum Corp.	Painter's Touch	Black 1909		Home Depot	Vinyl & Fabric
Rust-oleum Corp.	Painter's Touch	Black 1913		Home Depot	Chalk Board
Rust-oleum Corp.	Rust-oleum Specialty	Black 1905	Gloss	Home Depot	Lacquer High Lustre Coating
Rust-oleum Corp.	America's Finest	Black HD2879 830	Gloss	Home Depot	All Purpose - Interior/Exterior
Rust-oleum Corp.	America's Finest	Black HD2876	Ultra Flat	Home Depot	All Purpose - Interior/Exterior
Rust-oleum Corp.	Rust-oleum	Black 7886	Gloss	Home Depot	Appliance Epoxy Ultra Hard Enamel
Rust-oleum Corp.	Premium Rust-oleum	Black 7798	Semi-Gloss	K-Mart	Protective Enamel - Stops Rust
Sears Laboratory	Sears Best	Black 30 16724	Flat	Sears	Interior/Exterior - Anti-Rust Enamel
Sears Laboratory	Sears Best	Black 30 66368	Gloss	Sears	Interior/Exterior - Anti-Rust Enamel
Sears Laboratory	Sears Best	Black 30 16718	Gloss	Sears	General Purpose Enamel
Sears Laboratory	Sears Best	Black 30 66028	Gloss	Sears	Polyurethane High Gloss Enamel
Sears Laboratory	Sears Best	Black 30 66098	Satin Flat	Sears	Polyurethane Satin Flat Enamel

Table 1: Black Spray Paint Samples (continued)

Manufacturer listed on can	Brand Name	Product Code	Finish	Retail Outlet	Description of Use
Sherwin-Williams	Krylon	Black 1602	Ultra Flat	Lowe's	Interior/Exterior
Sherwin-Williams	Krylon	Black 1613	Semi-Flat	Lowe's	Interior/Exterior
Sherwin-Williams	Krylon	Black 1601	High-Gloss	Lowe's	Interior/Exterior
Sherwin-Williams	Krylon	Black 303	Flat	Lowe's	Epoxy Enamel - Indoor/Outdoor
Sherwin-Williams	Red Devil	BBQ Black RDHT0700		Lowe's	Interior/Exterior - Hi-Temp
Sherwin-Williams	Decrolon	Black HNH1105	Gloss	Lowe's	Enamel - Interior/Exterior
Sherwin-Williams	Decrolon	Black HNH1107	Flat	Lowe's	Interior/Exterior Enamel
Sherwin-Williams	Color Works	Black CW01023	Satin	Wal-Mart	Interior/Exterior
Sherwin-Williams	Color Works	Black CW01025	Gloss	Wal-Mart	Interior/Exterior
Sherwin-Williams	Krylon Living Color	Black 7210	Gloss	K-Mart	Latex Enamel
Sherwin-Williams	Krylon	BBQ Black 1618		K-Mart	BBQ & Stove
Sherwin-Williams	Krylon	Black 3206		Sears	Appliance Epoxy
Sherwin-Williams	Red Devil	Black RDGP0101	Gloss	Scotty's	Interior/Exterior Enamel
Sherwin-Williams	Red Devil	Black RDGP0103	Flat	Scotty's	Interior/Exterior Enamel
Sherwin-Williams	Krylon	Black 7030	Gloss	Scotty's	Indoor/Outdoor Lacquer
Sherwin-Williams	Krylon	Black RTA9218	Flat	Scotty's	Rust Tough Enamel
Sherwin-Williams	NOW	Wrought Iron Black 21211	Flat	Ace Hardware	Interior/Exterior
Sherwin-Williams	NOW	Black 21213	Gloss	Ace Hardware	Interior/Exterior
Valspar Corp.	One & Only	Black 05917	Flat	Lowe's	Multi-Purpose - Interior/Exterior
Wal * Mart	Color Place	Black 21004	Flat	Wal-Mart	Rust Control - Spray Enamel
Wal * Mart	Color Place	Black 21008	Gloss	Wal-Mart	Rust Control - Spray Enamel
Wal * Mart	Color Place	Black 20004	Flat	Wal-Mart	Indoor/Outdoor
Wal * Mart	Color Place	Black 20008	Gloss	Wal-Mart	Indoor/Outdoor

Light Microscopy

Samples were compared side by side under Nikon SMZ-2B stereomicroscopes (0.6X to 40X magnification) with oblique lighting supplied by 100 watt quartz-halogen light sources employing bifurcated fiber optic light guides. This permitted assessment of gloss and texture (i.e., soft, brittle, flexible, rigid). When necessary, thin sections mounted on cover-slipped microscope slides using Norland Type 61 optical adhesive

were also compared side by side on a Leitz Diaplan brightfield/polarized light compound comparison microscope (100X to 400X magnification) equipped with 100 watt quartz-halogen light sources and Variolum light homogenizers for color balancing. This permitted assessment of extender pigment type, distribution, and grain size as well as carbon black pigment distribution (i.e., homogeneous or agglomerated).

Scanning Electron Microscopy in conjunction with Energy Dispersive X-ray Spectrometry (SEM-EDS)

Samples were mounted on pyrolytic carbon planchets as thick peels using Duro-Tak adhesive. The sample mounts were then carbon evaporation coated using a Pelco CC-7A carbon coater employing carbon rods. Specimens were subsequently analyzed on a Leica-Cambridge S360 scanning electron microscope under high vacuum using a 20KV beam potential, zero degree specimen tilt, and an EDAX, Inc. energy dispersive x-ray spectrometer, beryllium windowed, 25 micro-second time constant, dead time of approximately 35 percent, a Mn Ka resolution of approximately 132 eV, and count times of approximately 600 live seconds.

Pyrolysis Gas Chromatography (PyGC)

Samples were mounted in a quartz tube and placed into the inductively heated platinum coil probe of a Chemical Data Systems Model 1000 Pyroprobe. The probe was inserted into a universal pyrolysis interface held at 150 °C attached to the injection port of an Agilent 5890 gas chromatograph. They were pyrolyzed at a final temperature of 750 °C held for 20 seconds employing the ramp off function of the Model 1000 Pyroprobe. The gas chromatograph was equipped with a split/splitless capillary column inlet held at 225 °C leading into two fused silica capillary columns via a “Y” quartz effluent splitter located in the chromatograph’s oven. The inlet was run in the split mode with a 1 to 10 ratio. Five ml/min nitrogen carrier gas was directed into the pyroprobe interface and 20 ml/min into the gas chromatograph injector, with a 1 ml/min septum purge. The one capillary column is a high polarity 25 m x 0.32 mm FFAP (nitroterephthalic acid modified polyethylene glycol) coated with a one micron film thickness (Quadrex, Corp., PO Box 3881, Woodbridge, CT) and the other is a low polarity 30 m x 0.32 mm SPB-1 (polydimethylsiloxane) also coated with a one micron film thickness (Supelco, Supelco Park, Bellefonte, PA). The oven was run at 50 °C for one minute, then ramped at 6 °C per minute to 100 °C, then at 8 °C per minute to 140 °C, then at 16 °C per minute to 220 °C where it was held for 15.67 minutes, producing a total run time of 35 minutes. Dual flame ionization detectors at 250 °C were used to detect the effluents from the respective columns. Nitrogen make-up gas was used in the detectors and they were operated using a column compensated corrected baseline.

RESULTS AND DISCUSSION

Infrared spectroscopy is expected to be sensitive to a variety of differences found in these types of paint. It should demonstrate differences in binder types, not only within general binder classes but also some variations within a given binder class. The types of general binder classes encountered in the sample set are listed in Table 2. Alkyds were by far the most common and a combination of resins was not unusual. Classification is not always straightforward, as in the infrared spectrum depicted in Figure 1. Is it a nitrocellulose lacquer plasticized with an ortho-phthalate plasticizer or is it an ortho-phthalate alkyd modified with nitrocellulose as a hardener? Even inspection of the methyl/methylene stretch region (3000-2800 cm^{-1}) is not diagnostic considering both the alkyd and the phthalate plasticizer will have strong absorptions in this region. In fact, the dilemma is solved with a simple solvent test.

Table 2: General Binder Classes	
BINDER TYPES	MODIFIERS
Acrylic lacquers	Styrene
Acrylic enamels	Vinyl toluene
Nitrocellulose lacquers	Urethane
Alkyd enamels	
Epoxy enamels	

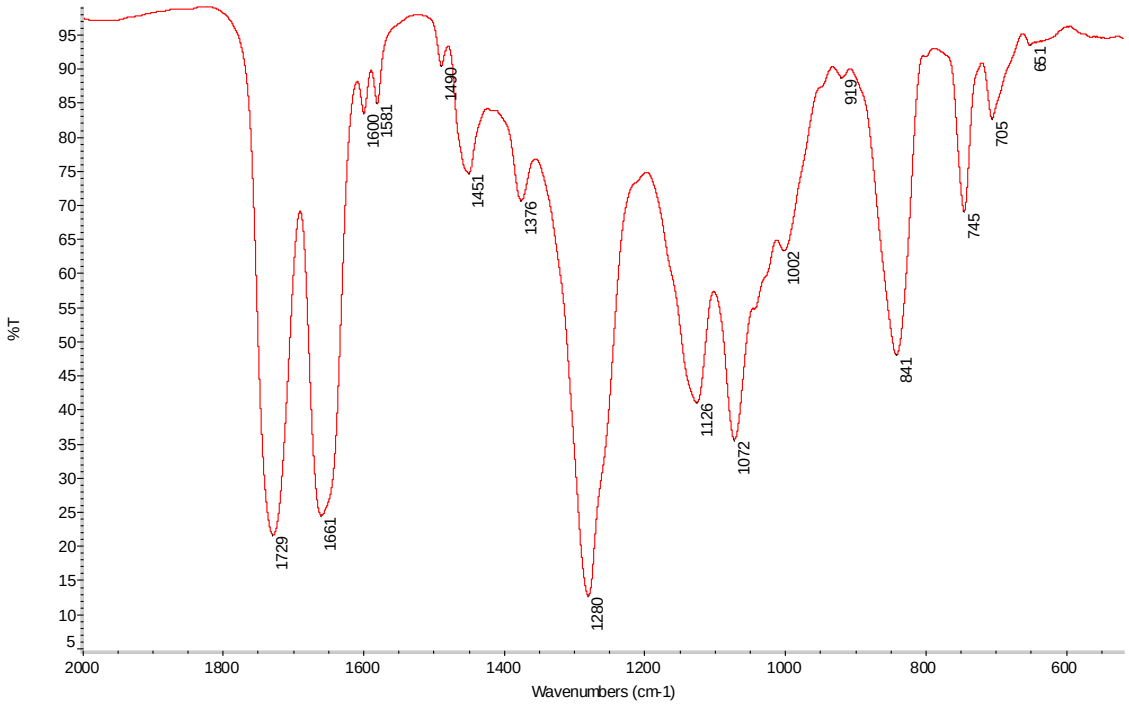

Figure 1 FTIR spectrum of Ace Hardware black 17028 spray paint depicting the fingerprint region of the spectrum most helpful for recognizing the binder class.

The plasticized nitrocellulose lacquer will be soluble in acetone while the modified alkyd enamel will not. It is interesting to note that even though this paint's label indicates it is

an instant drying lacquer, it is insoluble in acetone. An example of variations within a binder class is depicted in Figure 2. Both Figure 2a and 2b are ortho-phthalate alkyds; however, Figure 2a is an epoxy modified alkyd (see arrows at 1510 cm^{-1} and 832 cm^{-1} for the epoxy) while Figure 2b is not. The marked broad absorption band at 1168 cm^{-1} in Figure 2a also suggests acrylic modification may be present, unlike in Figure 2b.

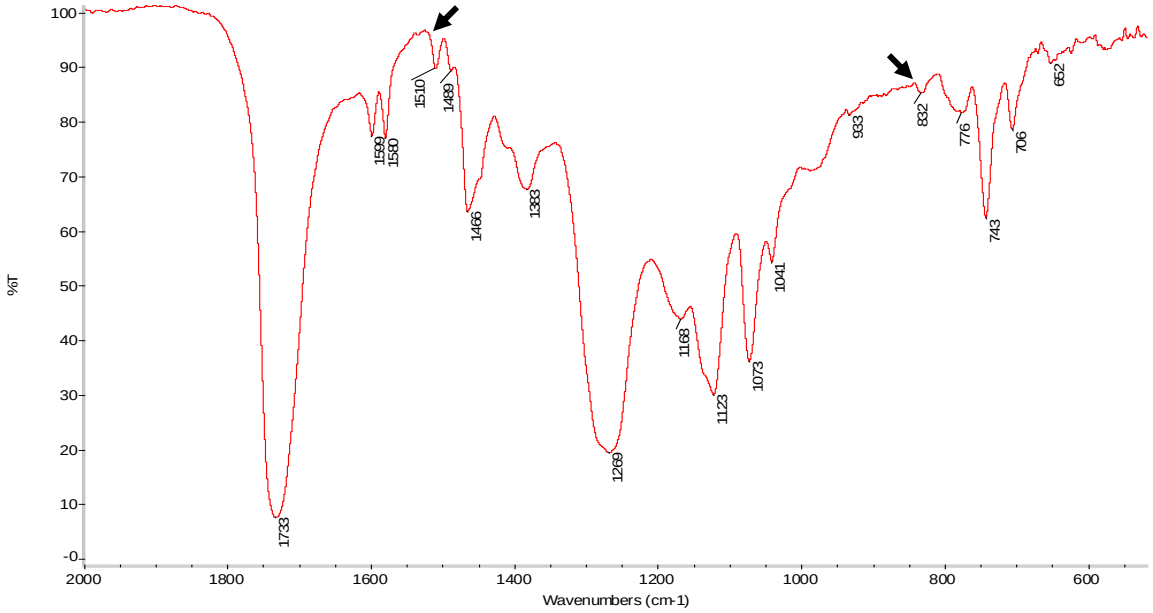

Figure 2a: Epoxy modified ortho-phthalate alkyd enamel (Rust-oleum black gloss #7886)

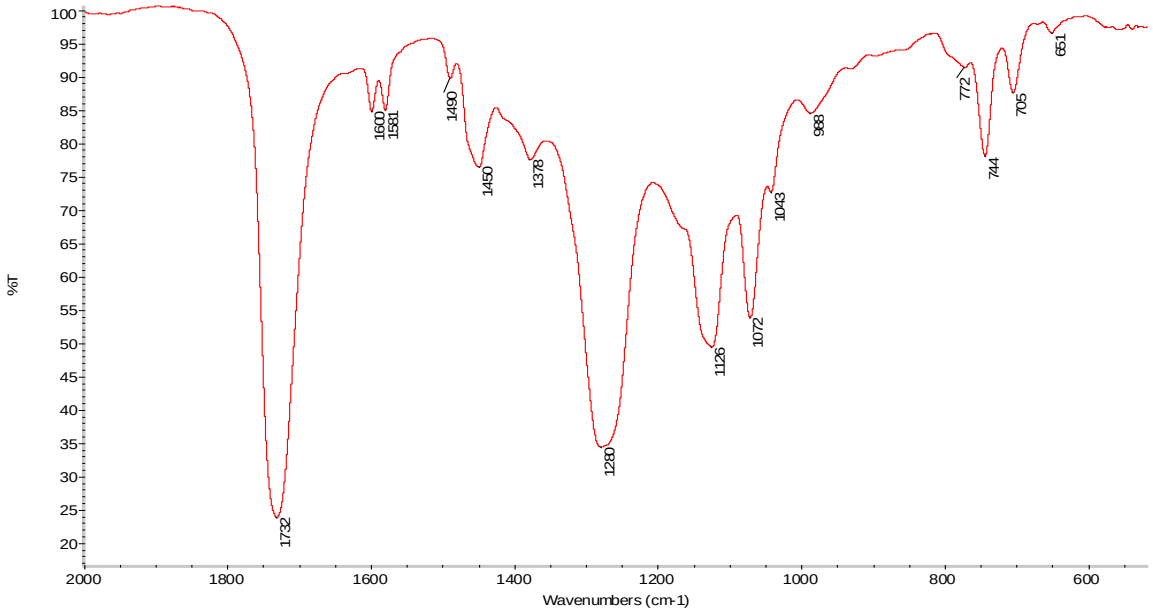

Figure 2b: Ortho-phthalate alkyd enamel (General Paint and Manufacturing X-O rust XO2 gloss black)

Infrared spectroscopy should also demonstrate differences in extender pigment types and concentrations. Figure 3 gives an example of a combination of extender pigment types with differing relative concentrations. Both Figure 3a and 3b are acrylic-alkyds with barium sulfate and talc extender pigments, but Figure 3a has barium sulfate (indicated by "B") in a higher concentration relative to talc (indicated by "T") and Figure 3b is just the opposite. Figure 4 demonstrates an example of a difference in clay extender pigment concentration.

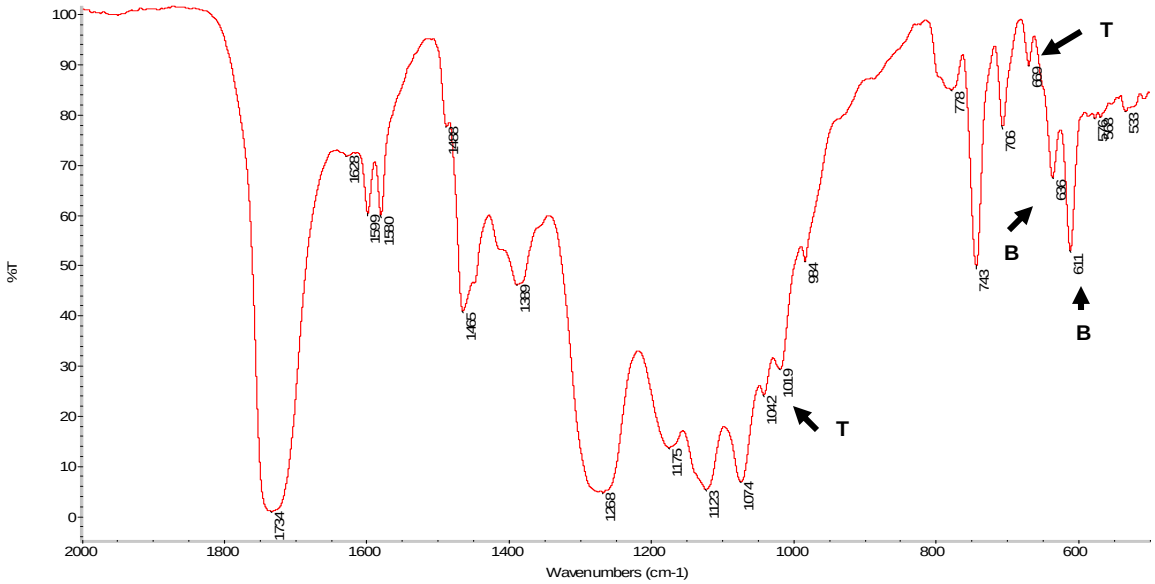

Figure 3a Rust-oleum black V7779 gloss – acrylic-alkyd enamel with barium sulfate and talc

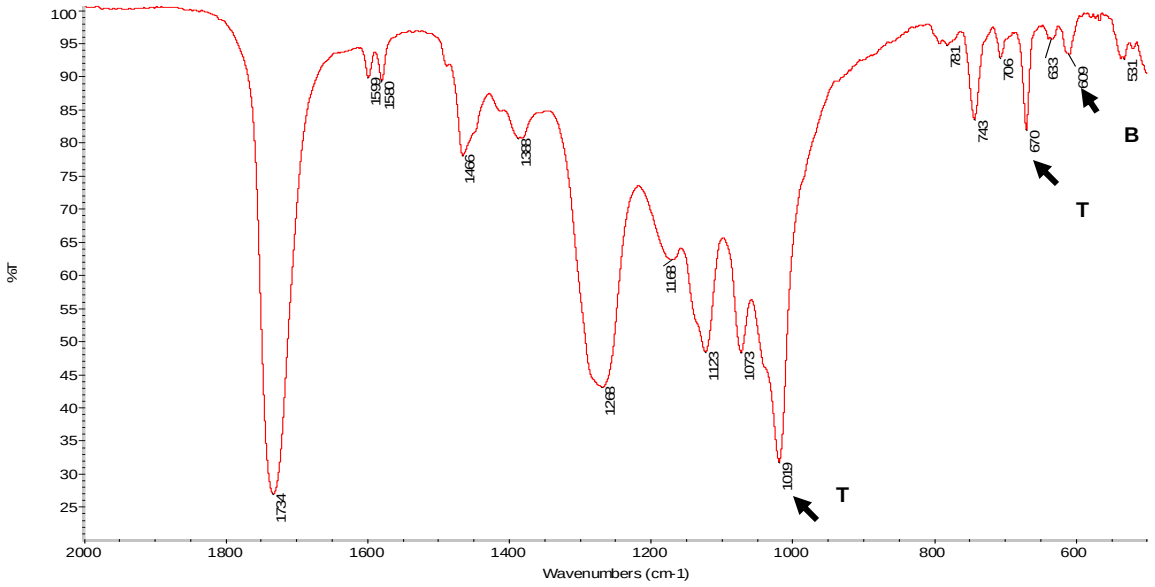

Figure 3b Premium Rust-oleum black 7798 semi-gloss – acrylic-alkyd enamel with barium sulfate and talc

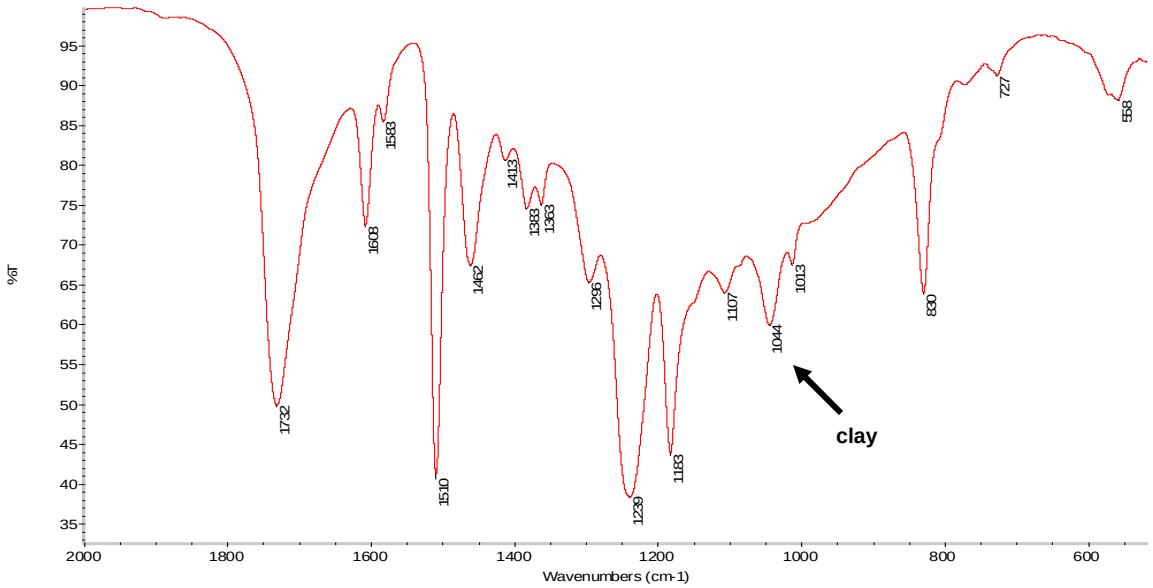

Figure 4a Sherwin-Williams Krylon Black 3206 - epoxy enamel with clay

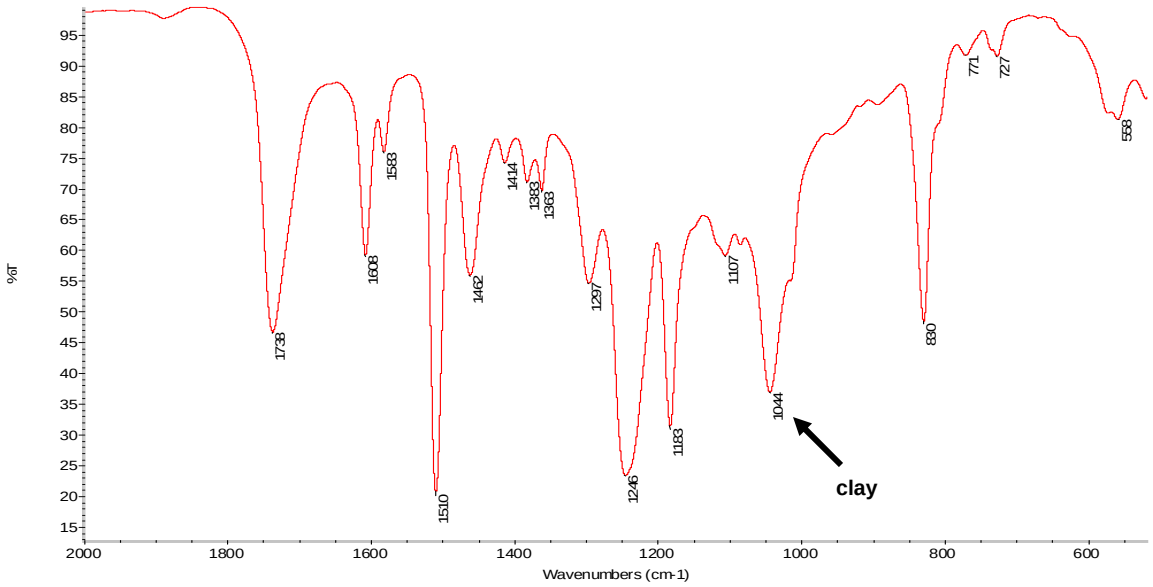

Figure 4b Ace Hardware Gloss Black 11920 - epoxy enamel with clay

Inter-comparison of the infrared spectra was undertaken using a spectral library approach. Spectra were collected on replicate samples of each spray paint. One Absorbance spectrum was selected from the replicate set and entered into a user library (Nicolet Omnic search software). Following baseline correction, each of the seventy-one entries was searched for corresponding spectra in the library using a Euclidean algorithm. The top ten "hits" were visually compared for pattern correspondence. Variations in peak intensities resulting from sample thickness variations were considered a correspondence. The indistinguishable sets were reviewed to assure that all spectra falling into a group based on visual inspection of both their percent

Transmittance and Absorbance spectra were also reflected in each group's spectral search hit lists. Finally, all hit list pairs having high correlation indices but discriminated on visual comparisons were reviewed to assure that the observed differences were reproducible in the replicate sample spectra.

The results demonstrate that only 23 pairs out of a possible 2,485 pairs are indistinguishable by infrared spectroscopy. That equates to a discrimination power of 99.1 percent for this one technique alone. The indistinguishable groups are listed in Table 3. It is not uncommon to find second party vendors along with major manufacturers listed in a given group. As might be expected, it would appear that the major paint manufacturers produce the product marketed under the second party vendor's label. This is most certainly not unusual and can be seen in other product markets, such as tapes.

Table 3 Indistinguishable groups following FTIR comparisons

GROUP 1 – Dutch Boy/Sherwin Williams Fresh Look Black 53671 – Sherwin-Williams Red Devil Barbecue Black RDHT0700 – Ace Hardware Flat Black 17067 – Ace Hardware Barbecue Black 1010065
GROUP 2 – Sherwin-Williams Decrolon Gloss Black HNH1105 – Sherwin-Williams NOW Gloss Black 21213 – Wal-Mart Color Place Gloss Black 20008 – Scotty's WOW Gloss Black 77008
GROUP 3 – Sherwin-Williams Color Works Gloss Black CW01025 – Dutch Boy/Sherwin-Williams Fresh and Easy Gloss Black FE501 – Ace Hardware Gloss Black 17004 – Sears Best Gloss Black 3016718
GROUP 4 – Sherwin-Williams Krylon High Gloss Black 1601 – Sherwin-Williams Krylon Lacquer Gloss Black 7030
GROUP 5 – Rust-oleum Professional Gloss Black 7579 – Premium Rust-oleum Textured Black 7220

Table 3 Indistinguishable groups following FTIR comparisons (continued)
GROUP 6 – Dutch Boy/Sherwin-Williams Fresh Look Flat Black 3604 – Wal-Mart Color Place Flat Black 21004
GROUP 7 – Dutch Boy/Sherwin-Williams Fresh Look Flat Black 3727 – Ace Hardware Wrought Iron Flat Black 17003
GROUP 8 – Premium Rust-oleum Hammered Black 7215 – Roc Sales Inc. Quick Color Gloss Black J2851

The 23 indistinguishable pairs were then subjected to microscopic comparisons. Stereomicroscopy and polarized light microscopy discriminate between two of the 23 pairs. They are listed in Table 4. Both pairs have different finish (gloss) types, as indicated by their names. The one pair is hammered black versus gloss black and the other pair is gloss black versus textured black. One can see a slight apparent difference in the barium sulfate concentrations in the Figure 5 pair (635 cm^{-1} and 611 cm^{-1}); however, there is no apparent extender pigment difference in the Figure 6 pair. That is understandable since the appearance of the hammered finish is achieved by pigment flocculation, not an addition of extender pigment (7, 8). Many of the pairs originally discriminated by infrared spectroscopy would have also been easily differentiated by microscopy had that technique been employed as the initial step.

Table 4 Pairs indistinguishable by FTIR but differentiated by microscopy
PAIR 1 – Premium Rust-oleum Hammered Black 7215 – Roc Sales Inc. Quick Color Gloss Black J2851
PAIR 2 – Rust-oleum Professional Gloss Black 7579 – Premium Rust-oleum Textured Black 7220

The remaining 21 indistinguishable pairs were then subjected to SEM-EDS analyses. These comparisons distinguished between an additional 5 pairs that are listed in Table 5, leaving 16 pairs undifferentiated. PyGC results differentiate between an additional two pairs listed in Table 6, leaving 14 indistinguishable pairs. The fourteen pairs consist of two groups of four and two groups of two; specifically, Groups 2, 3 and

7 listed in Table 3, along with the two Ace Hardware paints in Group 1. Three of the four groups contain apparent second party vendors. The final discrimination power for the 2,485 pairs is 99.4 percent.

Figure 5a Rust-oleum Professional Gloss Black 7579

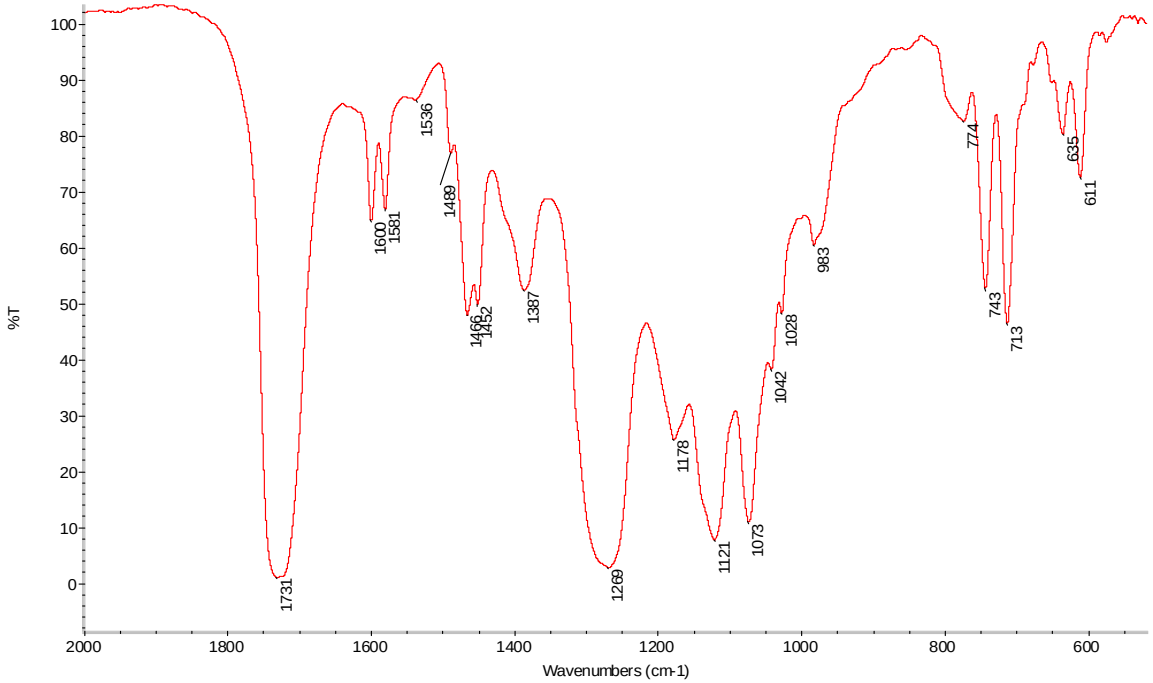

Figure 5b Premium Rust-oleum Textured Black 7220

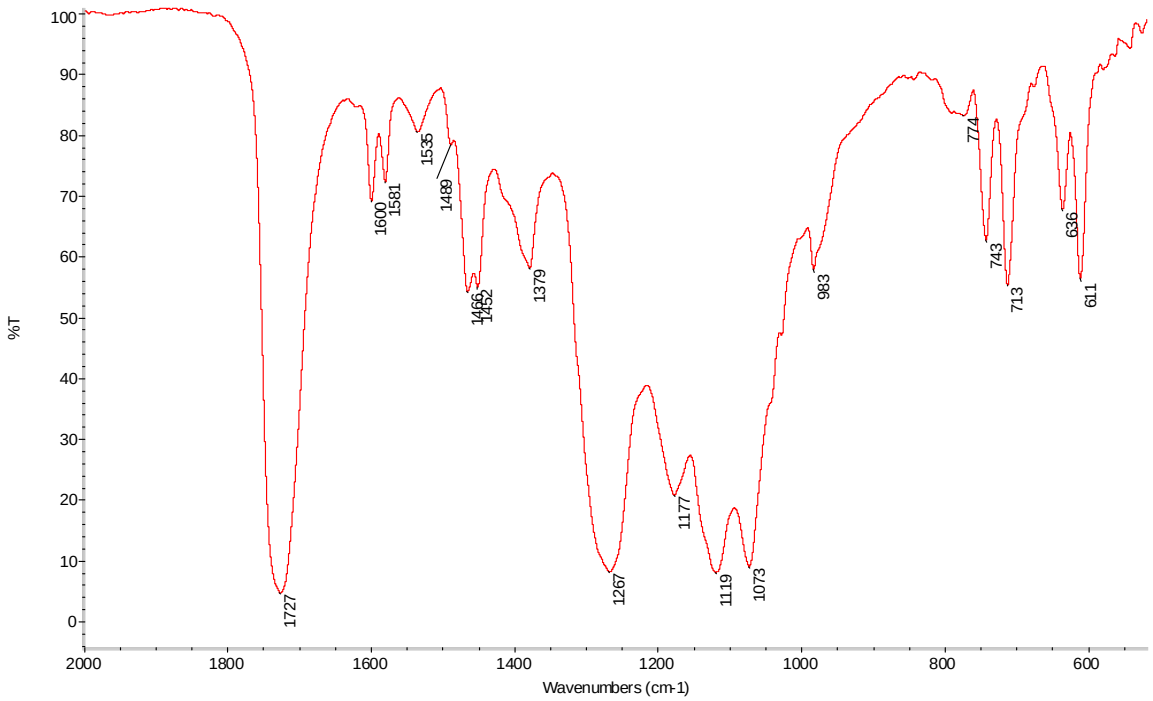

Figure 6a Premium Rust-oleum Hammered Black 7215

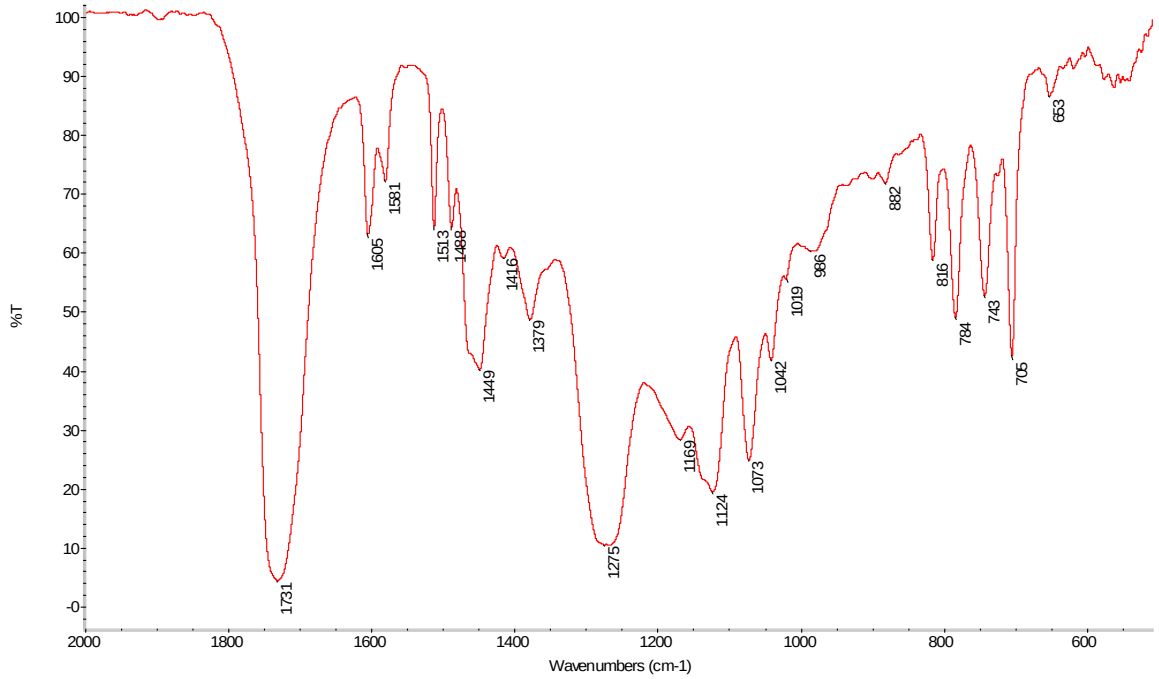

Figure 6b Roc Sales Inc. Quick Color Gloss Black J2851

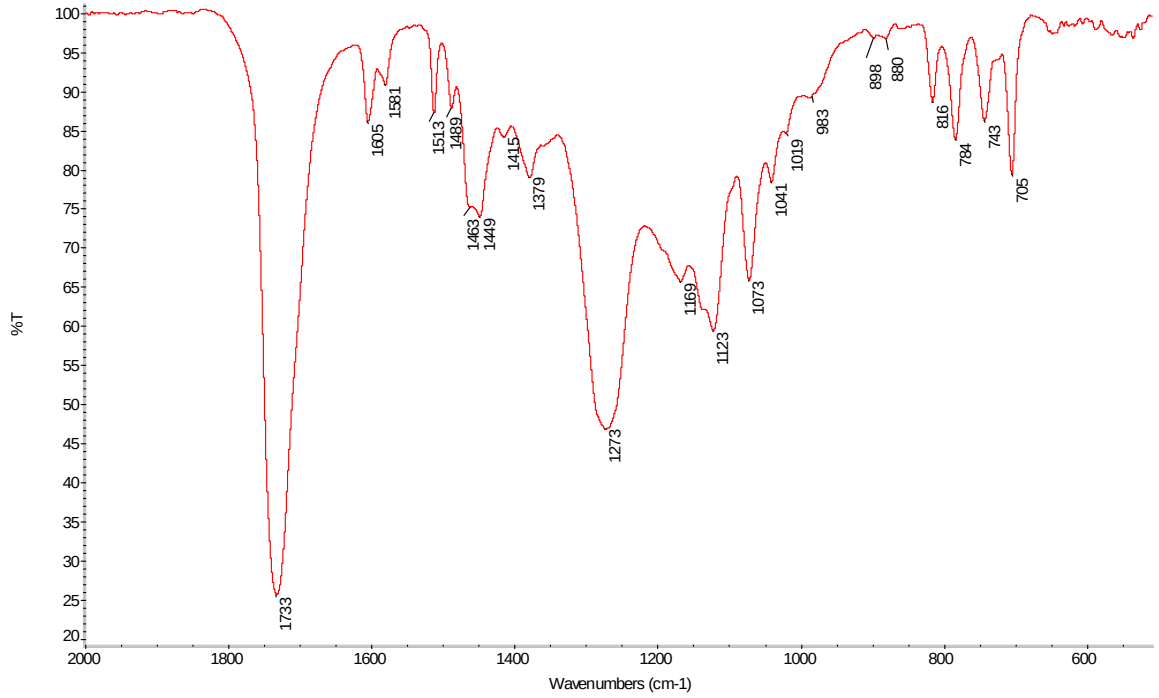

Table 5 Pairs indistinguishable by FTIR and microscopy but differentiated by SEM-EDS
PAIR 1 (differentiated by Ti to Cl ratios) – Sherwin-Williams Krylon High Gloss Black 1601 – Sherwin-Williams Krylon Lacquer Gloss Black 7030
PAIR 2 (differentiated by K to Ca ratios) – Sherwin-Williams Red Devil BBQ Black RDHT0700 – Dutch Boy/Sherwin-Williams Fresh Look Black 53671
PAIR 3 (differentiated by K to Ca ratios) – Sherwin-Williams Red Devil BBQ Black RDHT0700 – Manufactured for Ace Hardware Ace Barbecue Black 1010065
PAIR 4 (differentiated by K to Ca ratios) – Sherwin-Williams Red Devil BBQ Black RDHT0700 – Manufactured for Ace Hardware Ace Black 17067
PAIR 5 (differentiated by P to Ca ratios) – Dutch Boy/Sherwin-Williams Fresh Look Black 3604 – Wal-Mart Color Place Black 21004

Table 6 Pairs indistinguishable by FTIR, microscopy, and SEM-EDS but differentiated by PyGC
PAIR 1 – Dutch Boy/Sherwin-Williams Fresh Look Black 53671 – Ace Hardware Barbecue Black 1010065
PAIR 2 – Dutch Boy/Sherwin-Williams Fresh Look Black 53671 – Ace Hardware Flat Black 17067

CONCLUSION

This study employed ideal laboratory-prepared samples. Actual casework samples involving spray paint deposits often suffer from sample size or condition constraints that would reduce this level of discrimination. For example, it is impossible to control the degree of mixing of paint prior to spraying in casework questioned samples. This can have some effect on the semi-quantitative comparison of pigments (6, 9). However, if a sample is reasonably homogeneous it is believed the results of this study

approximate the discrimination power since a majority of the techniques used permit the analysis of very small samples along with replicate analyses to assess heterogeneity. Comparable results were observed when comparing the results of this study with those of its European counterparts. Govaert, et. al. (2001) reported a high degree of discrimination amongst black spray paints, although they did not quantify it. Govaert and Bernard (2004) reported a discrimination power of 98.8 percent in their study of red spray paints and Buzzini and Massonnet (2004) reported that 98 percent of the possible pairs in their study of green spray paints were discriminated using just a combination of FTIR and Raman spectrometry. It is fair to conclude that the discrimination power between spray paints using an analytical scheme such as that described in ASTM E1610-02 (1) is high.

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