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The Physical and Chemical Characterization of Multipurpose Architectural Paint†

ABSTRACT

Paint products with more than one function, also known as multipurpose paints, have become increasingly popular in the market today. These include, but are not limited to, paint and primer in one, anti-mold and mildew, stain blocking, and hole filling. While the manufacturers of these paints suggest they increase utility, it is important that these products maintain the characteristics necessary for a good surface coating. There is no published research and little information about these new products available, which makes it challenging to determine what is being changed in the formulation. In this study, twenty-six white single layer multipurpose and non-multipurpose paint products were analyzed using a forensic analytical scheme to perform both intra-brand and inter-brand comparisons. The analytical scheme included the techniques of visual examination, stereomicroscopy, fluorescence microscopy, microchemical and microsolubility tests, Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDS). No specific characteristics or components were attributed to only the multipurpose or non-multipurpose samples as they varied across all of the brands. The largest changes were in the type and amount of filler used for the paint and primer in one products (self-priming paints). Presence of elemental zinc was one indicator of anti-mold and mildew architectural products; however, its absence did not allow exclusion from this class of products. There were 325 possible comparison pairs between all of the samples, and after performing all of the techniques, only one indistinguishable pair remained. A discrimination power of 99.69% was determined for the overall analytical scheme.

Keywords: Paint, Architectural Paint, Multipurpose, Self-priming, Discrimination Power, Analytical Scheme

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INTRODUCTION

Multipurpose architectural paints have had a drastically increased presence in the paint market. Multipurpose architectural paints include paints that have more than one function; for example, paint and primer in one products or stain blocking paint. In 2009, Behr® began this contemporary trend by releasing Behr Premium Plus Ultra® Paint & Primer in One (1) and other companies quickly followed suit. Paint producers have continued to expand their marketability by further increasing the functionality of their paint by offering products with more than one of these additional purposes, such as Glidden®'s Trio line, which is paint, primer, and hole filler in one (2).

Simultaneously, there has also been increased pressure to produce more environmentally friendly products, such as those that contain zero to low volatile organic compounds (VOCs). Volatile components are used in paint manufacturing to keep paint in liquid form until it is applied to a substrate by dissolving or dispersing paint constituents (3). The volatile components must be compatible with the paint binder to properly serve its purpose; therefore, the choice of system affects the chemistry of paint. There are increasingly more paint products on the market that combine paint's traditional task of decorating a surface with its more modern additional qualities of having low VOCs and simultaneously priming the surface, for example.

Home Depot® and J.D. Power and Associates® have awarded paint producers for their ability to create innovative paints that still provide the high quality coating desired by consumers (4,5). In 2011 alone, the percentage of consumers who bought and used paint and primer in one products (self-priming paints) increased from 12% to 17% according to J.D. Power and Associates®' U.S. Interior Paint Satisfaction Study℠ (5). Their 2012 Study showed an additional 4% increase to 21% in the purchase and use of these products (6). While this statistic was not included in their 2013 or 2014 studies, inspection of store shelves reveals almost every paint brand has a self-priming paint option. The consistent growth of public interest in the multipurpose products indicates that the paints may appear more often in forensic casework (7).

There is little information available and no published research about multipurpose architectural paints, which makes it difficult to determine what, if anything, is being changed to provide these new properties. If the paint composition has been altered, manufacturers may have changed the amount or type of fillers, pigments, and/or additives to give these effects. Variation in paint products would serve as an advantage in terms of forensic examinations. There may be compositional changes that, if detectable, allow for evidential classification as a multipurpose paint by providing additional information about the sample. Component variability may allow for quick discrimination and higher discriminating power. However, if legitimate chemistry changes are not detectable, the broadening of the paint market will not lead to an increase in discrimination power.

Due to the lack of available information, research is necessary to determine if multipurpose architectural paints have a forensically detectable change or indicator. Comparisons among paint manufacturers and product lines may elucidate any chemical consistency in the way in which the multiple purposes are achieved. White multipurpose architectural paints were physically and chemically characterized using a forensic paint analytical scheme. Multipurpose architectural paints were compared to their non-multipurpose counterparts within the same brand and line to determine if there were any significant differences. Intra-brand similarities were examined to explore the ability to classify paint as multipurpose based on specific physical and/or chemical characteristics. Additionally, interior and exterior multipurpose architectural paints from within the same brand, as available, were compared.

MATERIALS and METHODS

Twenty-six paint samples were donated or purchased from five major retail stores including Home Depot, Pleasants Hardware (Ace Hardware), Lowes, Benjamin Moore, and Sherwin Williams. White flat/matte paints were selected for evaluation to eliminate the influence of pigments used for tinting and to allow brand-to-brand comparisons. Twenty-two of the paint samples were interior coatings; four of the paint samples were exterior coatings. It should be noted, there were additional multipurpose paints available on the national market that could not be obtained for this study due to budgetary and geographic constraints (e.g., Dutch Boy).

The 12 donated samples were mechanically shaken, applied most often to wooden stir sticks, and then dried. The 14 purchased paint samples were vigorously stirred with a wooden stir stick to ensure proper mixing before applying them to glass microscope slides. All of the samples analyzed, as listed in Table 1, were single layer paint samples.

All instrumentation and chemical reagents passed daily quality assurance checks prior to use. An Olympus® SZ-11 stereomicroscope (9-55X magnification) was used to physically characterize the paint samples and to prepare samples for further testing. Paint samples were mounted in mineral oil (RI ~ 1.516) and compared side-by-side using an Olympus® BX-40 compound microscope (40-400X) equipped for fluorescence microscopy. Excitation wavelengths of 330-385 nm, 400-440 nm, 450-480 nm, and 510-550 nm were used for fluorescence microscopy.

Microchemical and microsolubility tests were performed following fluorescence microscopy. Small portions of paint were placed in a spot well plate and reactions recorded following drop-wise application of the specific chemical. Reactions, such as dissolution, effervescence, color change, swelling, and curling, were recorded while the samples were observed side-by-side. Chloroform, acetone, LeRosen, diphenylamine, toluene, concentrated nitric acid, and concentrated sulfuric acid were used. Observations were made using the stereomicroscope listed above.

Table 1: Paint Samples

Sample No.	Brand	Sample Name	Purposes	Obtained From
1	Ace	Royal® By Ace® Interior Latex Flat Wall Paint	Paint	Pleasants Hardware
2	Clark + Kensington	Paint and Primer in One Premium Interior Enamel	Paint, Primer	Ace Hardware
3	Ace	Royal® By Ace® Exterior Latex Flat House Paint	Paint	Pleasants Hardware
4	Clark + Kensington	Paint and Primer in One Premium Exterior Enamel	Paint, Primer	Pleasants Hardware
5	Benjamin Moore	Regal® Classic Premium Interior Paint	Paint	Benjamin Moore
6	Benjamin Moore	Regal® Select Premium Interior Paint & Primer Flat Finish	Paint, Primer, Mildew Resistant	Benjamin Moore
7	Benjamin Moore	ben® Premium Flat Interior Latex Paint	Paint	Benjamin Moore
8	Benjamin Moore	Aura® Waterborne Interior Paint & Primer Matte Finish	Paint, Primer	Benjamin Moore
9	Benjamin Moore	Eco Spec® WB Interior Latex Paint	Paint, Mildew Resistant	Benjamin Moore
10	Benjamin Moore	Eco Spec® WB Silver Interior Latex Paint	Paint, Mildew Resistant, Bacterial Odor Resistant	Benjamin Moore
11	Behr	Premium Plus® Interior Flat Enamel	Paint	Home Depot
12	Behr	Premium Plus Ultra Interior Paint & Primer in One	Paint, Primer	Home Depot
13	Behr	Premium Plus Ultra Interior Stain-Blocking Paint & Primer in One	Paint, Primer, Stain Blocking, Mildew Resistant	Home Depot
14	Glidden	Premium Interior Latex Paint	Paint	Home Depot
15	Glidden	DUO™ Paint + Primer Premium Paint	Paint, Primer	Home Depot
16	Glidden	Performance Edge™ 3 In 1™ Fill + Prime + Paint	Paint, Primer, Hole Filler	Home Depot
17	Olympic	Premium Interior Paint	Paint	Lowes
18	Olympic	One Interior Paint	Paint, Primer, Mildew Resistant	Lowes
19	Valspar	Ultra Premium® Interior Flat Finish	Paint, Mildew Resistant	Lowes
20	Valspar	Signature™ Paint + Primer Plus Hi-DEF® Advanced Color	Paint, Primer, Mildew Resistant	Lowes
21	Valspar	Ultra™ Paint + Primer Plus Ultimate Weather Defense	Paint, Primer, Mildew Resistant	Lowes
22	Valspar	Duramax® Paint + Primer + Ti^3 Crosslinking Technology™	Paint, Primer; Mold, Mildew, Algae Resistant	Lowes
23	Sherwin Williams	HGTV® HOME Interior Acrylic Latex - Flat	Paint	Sherwin Williams
24	Sherwin Williams	Super Paint® Interior Acrylic Latex	Paint, Primer	Sherwin Williams
25	Sherwin Williams	Duration Home® Interior Latex Matte	Paint, Anti-Microbial	Sherwin Williams
26	Zinsser	Perma White® Mold & Mildew Proof™ Interior Paint	Paint, Mold & Mildew Resistant	Benjamin Moore

For Fourier Transform infrared spectroscopy (FTIR), the paint samples were mounted on a microcompression cell with diamond windows (Spectra-Tech, Inc.). A Thermo Scientific® Nicolet 6700 FTIR coupled to a Continuμm Microscope equipped with a mercury cadmium telluride (MCT) detector was used in transmission mode (128 scans, 4 cm^{-1} resolution). Spectra were collected and visually compared based on peak locations and shapes. Spectral peaks were also used to identify paint components.

If calcium carbonate was identified as a component in a paint sample based on its FTIR spectrum, a small portion of the sample was placed in a spot well plate and one normal (1N) hydrochloric acid (HCl) was added drop-wise. Calcium carbonate, when present, can often dominate an FTIR spectrum and hide peaks from other chemical components. Addition of 1N HCl dissolved the calcium carbonate and thus reduced or removed its peaks from the spectrum (8). The samples were submerged in 1N HCl for approximately three minutes, removed and placed on a slide, and then dried under a heat lamp for 15-20 minutes. The dried samples were mounted on the microcompression cell and reanalyzed using the FTIR specified above. The resulting spectra were used to assist in peak comparisons and identifications.

Samples were mounted on carbon tape (Electron Microscopy Sciences) affixed to an aluminum stub. An Aspex® VP 2000 Scanning Electron Microscope-Energy Dispersive X-ray Spectrometer (SEM-EDS) was used to analyze the paint samples. An accelerating voltage of 25 KV was applied using variable pressure mode (0.2 torr) to avoid charging and carbon coating, and samples were viewed in the backscatter electron mode. Comparisons of elemental composition and relative peak ratios were performed and components confirmed, when possible.

Paints were physically and chemically characterized to the fullest extent possible. Each sample was examined using each test, rather than stopping analysis when discrimination was achieved. Comparisons included: multipurpose paint samples compared to its non-multipurpose counterpart within one brand; multipurpose paint samples with like functions compared between brands; and interior multipurpose paints compared to exterior multipurpose paints.

Following the specific investigation relating to their multipurpose/non-multipurpose character, each sample was compared to another regardless of original classification. Like previous discrimination studies (9,10), the number of possible comparison pairs and the power of discrimination for each technique in the analytical scheme were calculated using the following formulas:

$$\text{Number of Comparison Pairs} = \frac{n(n-1)}{2} \qquad DP = 100 \times \left[1 - \left(\frac{\#\,\text{of indistinguishable pairs}}{\#\,\text{of comparison pairs}}\right)\right]$$

where n is the number of samples and DP is the percent of pairs discriminated (9). A sample set of 26 (n = 26) resulted in 325 comparison pairs.

RESULTS and DISCUSSION

Although all the samples were white and single layered, slight differences in color, texture, or relative amount and distribution of inclusions, presumably extender pigments, were seen with the use of visual and stereomicroscopic examination. Low sample discrimination was achieved with fluorescence microscopy, most likely due to the conservative manner in which fluorescence was used to differentiate samples. Fluorescence differences are based on physical and chemical characteristics but were not associated specifically with paint components. There were no significant color differences observed with fluorescence microscopy comparisons, only intensity differences.

As microchemical and microsolubility reactions provide limited chemical information, observed reactions were used to differentiate samples rather than interpret chemical compositions. All of the samples were insoluble in acetone, chloroform, and toluene, which was the expected result as all of the samples were enamel paints. The majority of differences was seen in LeRosen and concentrated acids. LeRosen, reactive to aromatic compounds (11), caused a number of samples to change color, varying from light pink to dark red.

Components were identified via FTIR conservatively and only if the major peaks were present in the spectra. Titanium dioxide, seen as a sharp decline starting around 900 cm^{-1} leading toward a 600 cm^{-1} suppression if not for the detector cutoff, was in all 26 samples as expected, given all the samples were white. The binder was also easily identified for the majority of samples. Eighteen samples contained an acrylic binder and eight samples contained a polyvinylacetate-acrylic binder.

Some paint binders were difficult to identify as the spectrum was dominated by calcium carbonate. Following the use of HCl, calcium carbonate peaks (1445, 870, and 712 cm^{-1}) decreased in size or disappeared completely allowing the identification of the binder. A spectrum of Zinsser® Perma White® Mold & Mildew Proof™ Interior Paint, as an example, is compared to one collected following the HCl removal of calcium carbonate in Figure 1. Other than identifying the acrylic binder system in this sample, no components were identified that were not already seen before the HCl was added.

SEM-EDS, with its ability to detect minor components, was most helpful in detecting additives. These additives are typically not in high enough concentration to be detectable by FTIR or are masked by the ingredients present in much higher concentrations (12). Aluminum, silicon, and titanium were present in every spectrum but varied in amounts. Other elements, such as calcium, sodium, potassium, zinc, and magnesium, were seen in some samples and absent from others.

Multipurpose vs. Non-multipurpose

Comparing the multipurpose paints to their non-multipurpose counterparts within the same brand resulted in 11 groups for comparison. Within three of the comparison groups, there was more than one multipurpose product within the brand; each was compared to the non-multipurpose product and to each other. In total, there were 17 multipurpose paints that could be compared back to a non-multipurpose product. The samples were compared within the same brand and same line when possible.

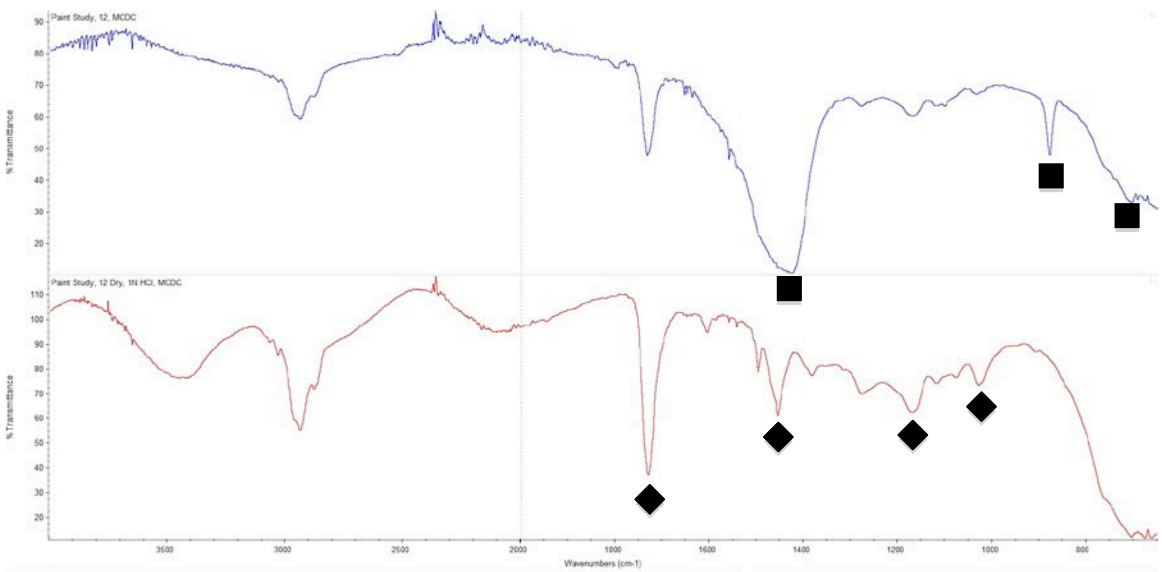

Figure 1: FTIR spectra of Zinsser® Perma White® Mold & Mildew Proof™ Interior Paint (top) and following 1N HCl addition (bottom). Calcium carbonate, whose major peaks are indicated by ■, dominates the top spectrum, but these peaks mostly disappear allowing for acrylic binder identification, whose major peaks are indicated in the bottom spectrum by ◆.

All of the multipurpose paints were distinguished from their non-multipurpose product within the same brand following the utilization of all tests. The most helpful technique for both component identification and differentiation was FTIR, though not all samples were discriminated by FTIR alone. An example of an indistinguishable pair via FTIR is shown in Figure 2. In this pair, the paint and self-priming paint could not be dissociated due to the similar peaks, shoulder positions, and sizes. On the other hand, in Figure 3, the Behr® non-multipurpose paint could be distinguished from both the self-priming and the stain-blocking, paint and primer in one paints. Discriminations by FTIR were possible for 14 sample pairs and were generally made based on peak sizes and shapes in the 1200–950 cm^{-1} region. The other common distinguishing factor was the difference seen in the binder peaks of the spectra, like those seen in Figure 4. In the top spectrum, the strong 1240 cm^{-1} peak, the ratio between the 1372 cm^{-1} and 1450 cm^{-1} peaks, and the 1170 cm^{-1} peak were all indicative of a polyvinylacetate-acrylic binder being used. An acrylic binder was identified in the bottom spectrum by the strong peak around 1170 cm^{-1}, the weaker 1236 cm^{-1} peak, the 840 cm^{-1} peak, and the ratio between the 1450 cm^{-1} and 1386 cm^{-1} peaks. Although FTIR was highly discriminating, there were no specific characteristics that allowed for classification of a sample into the non-multipurpose or multipurpose categories.

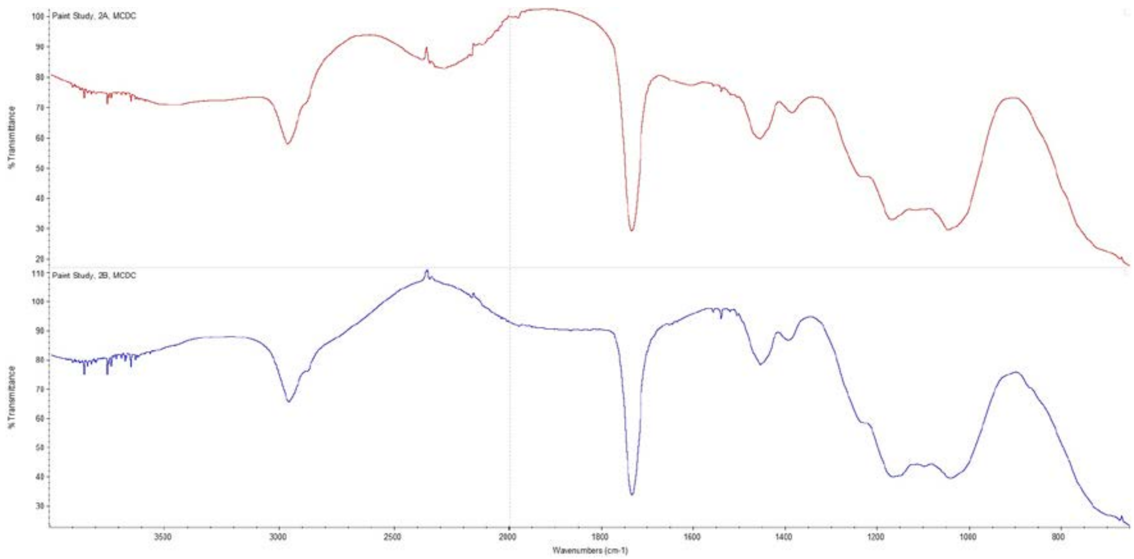

Figure 2: FTIR spectra that could not be discriminated: (top) Royal® By Ace® Exterior Latex Flat House Paint; and (bottom) Clark + Kensington™ Paint and Primer in One Premium Exterior Enamel.

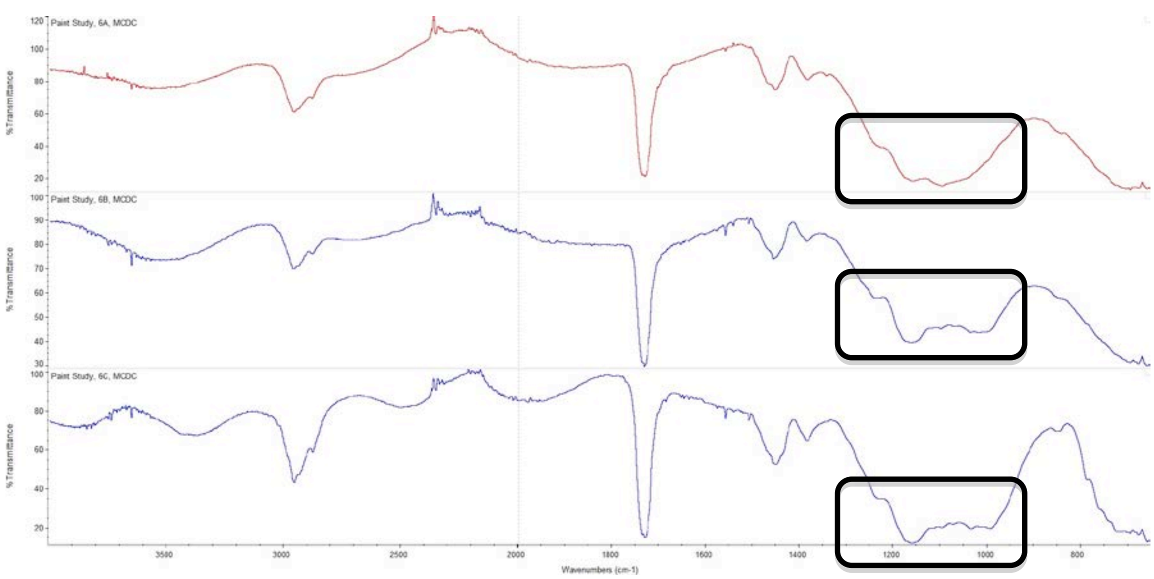

Figure 3: FTIR spectra of (top) Behr® Premium Plus® Interior Flat Enamel; (middle) Behr® Premium Plus Ultra Interior Paint & Primer in One; and (bottom) Behr® Premium Plus Ultra Interior Stain-

Blocking Paint & Primer in One. The non-multipurpose product (top spectrum) was disassociated from both multipurpose products based on peak shape differences.

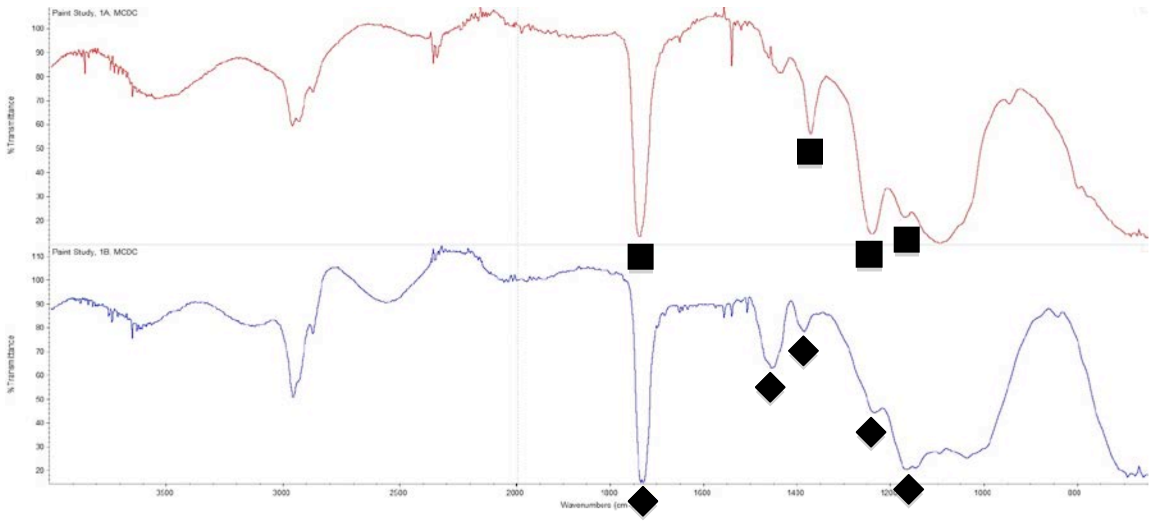

Figure 4: FTIR spectra of (top) Royal® By Ace® Interior Latex Flat Wall Paint; and (bottom) Clark + Kensington™ Paint and Primer in One Premium Interior Enamel. The top spectrum has peaks representative of polyvinylacetate-acrylic binder (indicated by ■) and the bottom spectrum has peaks representative of acrylic binder (indicated by ◆).

Using SEM-EDS alone, 11 of the multipurpose products were distinguished from their non-multipurpose counterpart. Differentiations were based on both elemental and peak ratio differences. There were no differences seen that specifically applied to the self-priming products, but zinc was detected in three of the samples that claimed to have anti-mold and mildew properties: Valspar® Ultra™ Paint + Primer Plus Ultimate Weather Defense, Valspar® Duramax® Paint + Primer Plus Ti^3 Crosslinking Technology™, and Zinsser® Perma White® Mold & Mildew Proof™ Interior Paint. Zinc was not seen in any of the other products and suggests it may indicate an anti-mold and mildew product in architectural paint applications.

Paint Ingredient Lists vs. Detectable Chemical Differences

Comparisons were made to listed product ingredients, as available. This was performed following the completion of the forensic analytical scheme to ensure that no bias was introduced into the identification of components. This was done in an attempt to identify any undetected chemical differences or components. The ingredient lists on the products, however, did not usually include the percent composition for each component. Therefore, Safety Data Sheets (SDS) were acquired to supplement the ingredient lists in order to better explain differences observed between samples. In some cases, the binder system was not listed on the SDS, but was listed on the can. Other products only included hazardous ingredients on the SDS and so other components and their percent composition were not available.

There were a wide variety of ingredients listed for each of the products; see Table 2. In general, the multipurpose products had wider percent composition ranges than the non-multipurpose products. Overall, a greater percentage of multipurpose products contained extender pigments as compared to the non-multipurpose products.

Table 2: Ingredients Listed in Non-multipurpose and Multipurpose Products. Percent compositions included were only from products that listed this information and were not known for all samples.

Ingredients	Total Number of Samples	Number of Multipurpose Products	Number of Non-multipurpose Products	Percent Composition in Multipurpose Products	Percent Composition in Non-multipurpose Products	Number of Samples Ingredient Detected in by FTIR	Number of Samples Ingredient Detected in by SEM-EDS
Titanium Dioxide	26	18	8	10-40%	10-30%	26	26
Diatomaceous Earth/Silica (Amorphous)	15	9	5	1-5%	1-5%	4	15
Nepheline Syenite	15	9	6	1-30%	1-30%	0	15
Kaolin/Clay	9	5	4	1-10%	5-10%	3	9
Limestone	8	5	3	5-30%	18-35%	5	6
Cristobalite/Silica (Crystalline)	8	7	1	0.1-5%	0.5%	1	5
Quartz	7	6	1	0.1-15%	5-10%	1	5
Proprietary Inert	5	3	2	1-5%	1-5%	0	0
Aluminum Hydroxide	4	3	1	1-5%	1-5%	0	4
Palygorskite	4	2	2	0.1-1%	0.1-1%	0	1
Zinc Oxide	3	3	0	1-5%	-	0	3
Carbon Black	3	1	2	0.1-1%	0.1-5%	0	*
Diiron Trioxide	2	1	1	5-10%	1-5%	0	0
Pumice	2	1	1	5-10%	1-5%	0	2
Barium Sulfate	1	0	1	5%	5%	0	0
Glass Oxide	1	1	0	1-5%	-	0	0
Iron Hydroxide Oxide	1	0	1	-	1-5%	0	0
Pyrithione Zinc	1	1	0	0.1-1%	-	0	0

**As samples were mounted on carbon tape, any carbon detected in the sample could not be attributed to paint components.*

In the 14 samples that had a binder listed in its ingredients, the binder was correctly identified based on the FTIR spectrum. In most cases, many of the identified fillers and pigments were confirmed as well. Titanium dioxide was present in relatively high amounts in every sample and its identification was supported by both FTIR and SEM-EDS. Diatomaceous earth was present in 50% of the multipurpose products, as was nepheline syenite. SEM-EDS was most helpful in indicating these extenders and could generally distinguish diatomaceous earth (amorphous silica), nepheline syenite (sodium potassium aluminosilicate), kaolin (aluminum silicate), and aluminum hydroxide. For example, kaolin was listed as a component in nine of the products, was seen in all nine samples by SEM-EDS, but was identified in only three of the FTIR spectra. Chemical differences seen in both the FTIR and SEM-EDS spectra were explained in some cases by the ingredient lists of the products, though it is acknowledged ingredient lists are seldom present in forensic cases. Ingredient lists, however, did not help explain aluminum to silicon ratio differences as so many of the ingredients contained some amount of these elements.

Ingredients present in lower percent compositions were more difficult to detect. For example, palygorskite (magnesium aluminum phyllosilicate) was listed as an ingredient in four samples, all of which were either Royal® by Ace® or Clark + Kensington® products, but was only detected in one of the samples by SEM-EDS. This can be explained by the percent composition range for all of those samples being 0.1-1%, mostly below the SEM-EDS 0.1% theoretical (13) and 1% more realistic (D. DeGaetano, personal communication, September 28, 2015) level of detection. Aluminum hydroxide, palygorskite, and nepheline syenite were not identified in any of the samples by FTIR. Aluminum hydroxide and palygorskite were present in concentrations less than 5%, but nepheline syenite was usually present in greater than 5% composition. A broad peak in the 1100-1000 cm^{-1} region suggested the presence of nepheline syenite, but its other characteristic peaks in the 800-300 cm^{-1} range were either hidden by titanium dioxide or beyond the range of the detector (650 cm^{-1} cutoff). The majority of the samples had broad peaks in the range of 1100-1000 cm^{-1}. In this region, it was common to see peaks for silicon dioxide, diatomaceous earth, amorphous silica, and nepheline syenite (14), all commonly present in white architectural paint. Low levels of potassium and sodium, along with the aluminum and silicon peaks in the samples, as detected by SEM-EDS, were speculated to be due to the presence of the nepheline syenite in the paint and were confirmed by the ingredients list on the paints. All of the samples with nepheline syenite listed as an ingredient had the associated elements detected by SEM-EDS.

Zinc oxide, known to have antimicrobial properties (15), and pyrithione zinc were present in anti-mold and mildew products only. Zinc was detectable by SEM-EDS in three samples containing zinc oxide, but not in the one sample containing pyrithione zinc most likely due to the percent concentration. A magnified image of Valspar® Duramax® Paint + Primer Plus Ti^3 Crosslinking Technology™ is shown in Figure 5 as well as the spectrum of one of the bright spots in the samples. Out of the 11 anti-mildew and mold products, four products contained zinc. Other components listed in this table such as diiron trioxide and barium sulfate, though listed in higher concentrations than that detectable by SEM-EDS, remained unrevealed by this technique. Diiron trioxide, barium sulfate, and pumice were only listed in two products each. For all three of these ingredients, they were present in one multipurpose and one non-multipurpose product that were part of an inter-brand pair. For example, the diiron trioxide was only listed in the Royal® By Ace® Exterior Latex Flat House Paint and Clark + Kensington™ Paint and Primer in One Premium Exterior Enamel.

Interestingly, examination of Glidden's 3 in 1 paint (fill + prime + paint) revealed a different texture than any of the other samples. There appeared to be small glass beads dispersed throughout the paint. While these beads were not isolated and identified due to their fragility, it is thought that these were most likely glass oxide based on the product's list of ingredients. Silicon dioxide was not identified in the FTIR spectra, however, the percent concentration of glass oxide present was consistent with being less than the detectable concentration by FTIR. This sample's texture was so different from others, as seen in Figure 6, that it was easily distinguishable with each analytical technique.

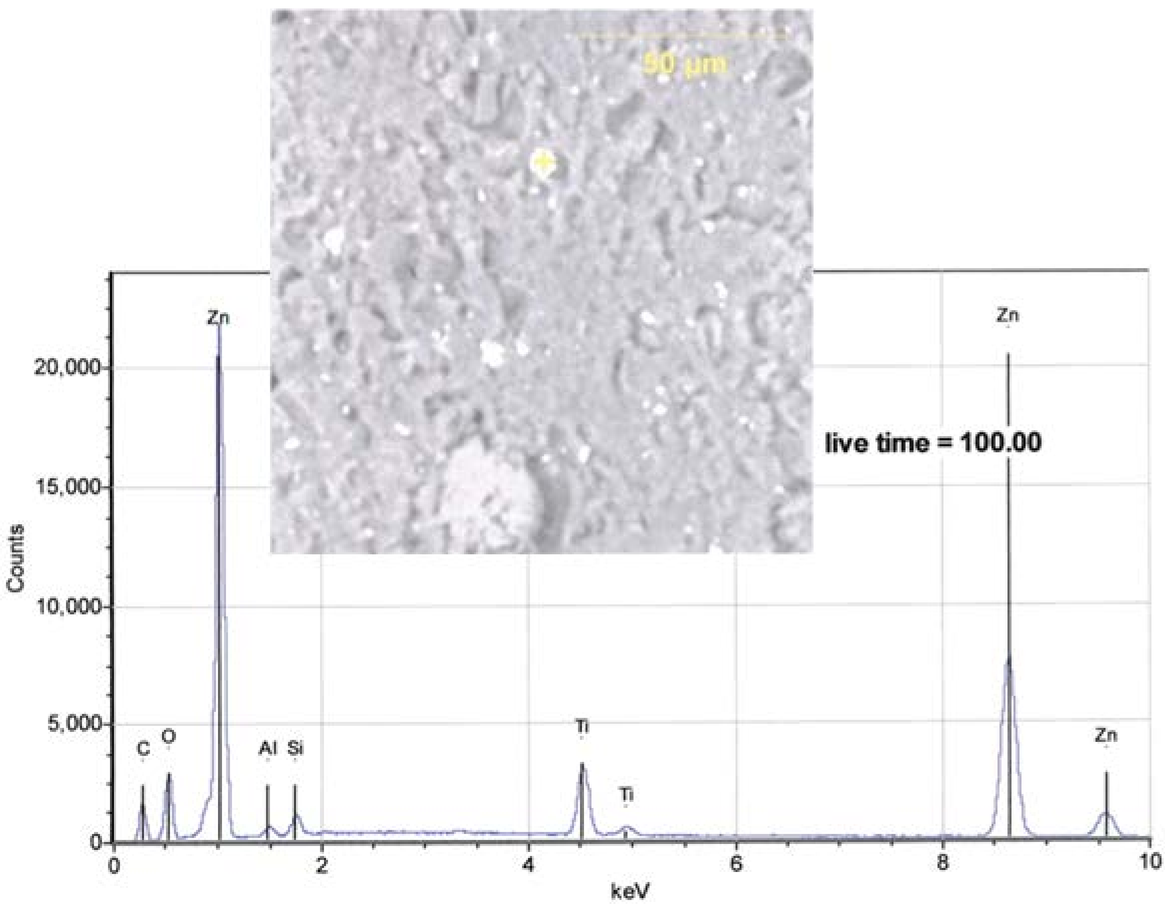

Figure 5: SEM-EDS image (top) at a display magnification of 662X and spectrum (bottom) of Valspar® Duramax® Paint + Primer Plus Ti³ Crosslinking Technology™.

The concentration of calcium displayed the greatest variability between samples. This was attributed to limestone (calcium carbonate), which was listed as an ingredient for eight of the samples but was only seen in five with FTIR and six with SEM-EDS. Five additional samples contained calcium as seen in their SEM-EDS spectra, but the calcium could not be attributed to any of the ingredients listed on the SDS. Contamination could not account for the calcium presence as a new blade was used for each sample. The calcium could be due to proprietary inerts or the presence of unlisted ingredients that have low concentrations.

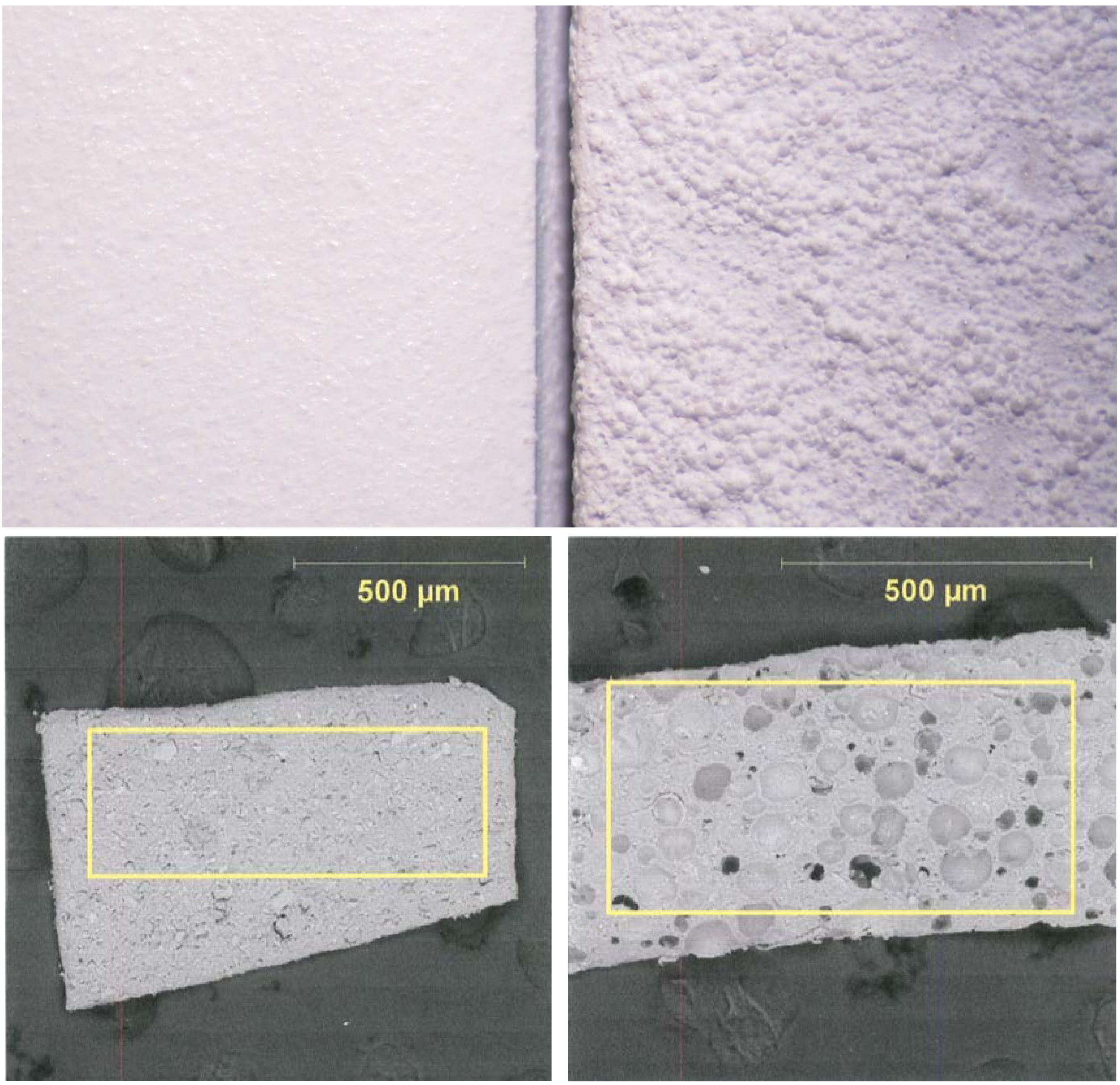

Figure 6: Stereomicroscopic (top left: ~13X) and SEM-EDS (bottom left: 75X) images of Glidden® Premium Interior Latex Paint (non-multipurpose); and Stereomicroscopic (top right: ~13X) and SEM-EDS (bottom right: 100X) images of Glidden® Performance Edge™ 3 In 1™ Fill + Prime + Paint

Between the non-multipurpose and self-priming products, there were no consistent changes across brands based on the listed ingredients. Each brand altered their product differently to give the paint priming properties. This variation prevented classification as self-priming multipurpose. For the anti-mold and mildew paints, zinc compounds were present in a few of the multipurpose samples, which indicated that some of the brands may be using similar compounds to add these properties. The presence of zinc compounds may indicate an anti-mold and mildew paint if architectural, but zinc's absence does not exclude the paint from that multipurpose family of paints.

Multipurpose vs. Multipurpose vs. Non-multipurpose

In order to determine if brands were altering their paints in the same way, multipurpose paints of the same type were compared to each other as well. In total, there were 18 multipurpose products analyzed in this study, 12 of which were self-priming products and 11 were anti-mold, mildew, and microbial resistant. Six of the multipurpose products were paint, primer, and anti-mold/mildew or microbial resistant. Only one product purported to be paint, primer, and hole filler in one.

There was a large amount of variation between the self-priming products across brands. While varied, differences between the non-multipurpose and self-priming paints overlapped across some of the brands. One of the differences was to vary the binder system. Based on FTIR spectra, Olympic® used a different binder system for the multipurpose product (acrylic) and non-multipurpose product (polyvinylacetate-acrylic). Along with the Olympic® products, Clark + Kensington®, Sherwin Williams®, and Benjamin Moore® self-priming products had the acrylic binder peaks identified whereas the non-multipurpose equivalents had polyvinylacetate-acrylic binder systems identified by FTIR. In all four cases, it was noted that the acrylic binder was consistently used for the self-priming products.

Another difference was changing the type or amount of extender pigments used. Changes were primarily seen in the concentration of calcium carbonate (e.g., limestone) or silicon-containing compounds (e.g., talc, kaolin, diatomaceous earth). FTIR and SEM-EDS detected the presence of calcium carbonate and calcium, respectively, in the Glidden® paint and primer in one, as shown in Figures 7 and 8. While the addition of calcium carbonate may not have been the only change made to create Glidden's self-priming paint, it was the largest change detected. On the other hand, Sherwin Williams® paint and primer in one product had no calcium detected in its FTIR or SEM-EDS spectra. The self-priming paint had a dominant amount of silicon present whereas the non-multipurpose paint had a large amount of calcium present, as seen in Figure 9.

In the Benjamin Moore® products, FTIR and SEM-EDS data supported an increase in calcium carbonate in the self-priming products from the concentration present in their non-multipurpose products; see Figures 10 and 11 for the SEM-EDS data. Limestone was listed for both the non-multipurpose paint and self-priming product ingredients, but the ingredient lists reflected lower percent compositions than that of their non-multipurpose counterpart. There is an additional slight decrease in aluminum and silicon seen in one of the Benjamin Moore paint pairs; see Figure 10. Kaolin is listed as present in 3-7% composition in the non-multipurpose paint and is not listed as an ingredient for the self-priming paint. Kaolin was not identified in either paint's FTIR spectrum but their SEM-EDS spectra indicated aluminum and silicon in both. Therefore, what was seen in the data was not always consistent with the product ingredient lists.

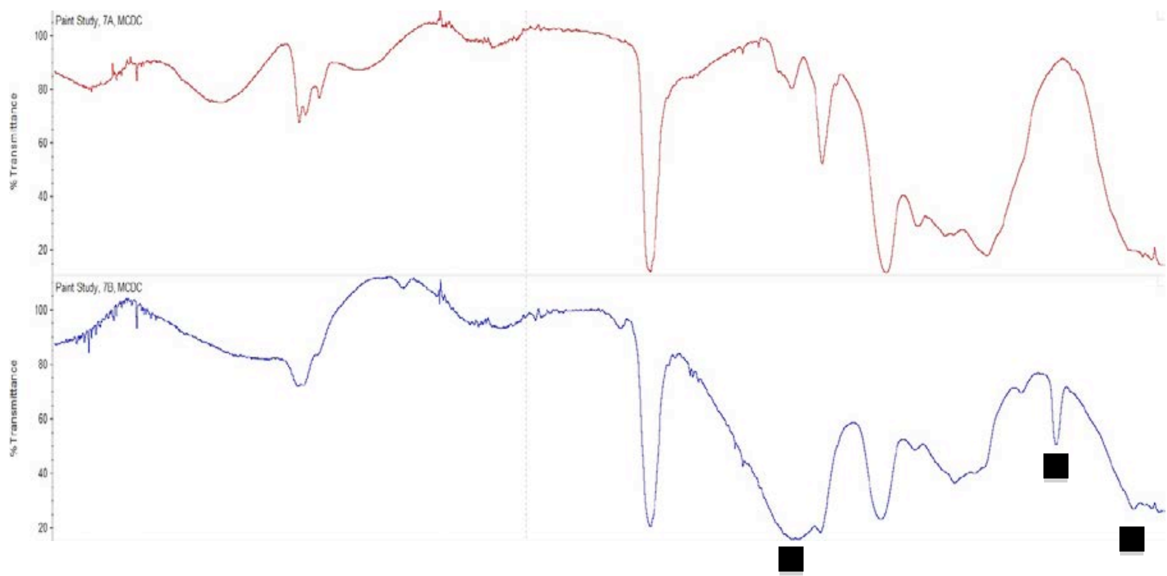

Figure 7: FTIR spectra of (top) Glidden® Premium Interior Latex Paint; and (bottom) Glidden® DUO™ Paint + Primer Premium Paint. These products were disassociated due to the calcium carbonate peaks in the bottom spectrum as indicated by ■.

Only two multipurpose samples could not be differentiated from one another: Behr® Premium Plus Ultra Interior Paint & Primer in One and Behr® Premium Plus Ultra Interior Stain-Blocking Paint & Primer in One. While these self-priming products were distinguishable from their non-multipurpose counterpart, they could not be distinguished from each other by FTIR (Figure 3), SEM-EDS (Figure 12), or any other technique used in this study. After comparison of the SDS of these two self-priming products, the ingredient lists including the percent compositions, were determined to be exactly the same. Although the company issued a press release on the stain-blocking product formula (16), the new product was being sold in the same shelf location at a particular store as the original self-priming product. The self-priming product had been completely replaced with the stain-blocking self-priming product. From the physical and chemical characterization performed in this study and the research done on the products, the self-priming and stain-blocking self-priming products were found to be indistinguishable though it may be a limitation of the analytical scheme.

Even though the alterations used to create the self-priming products varied across the brands, there was some consistency in the types of compounds being changed. In most cases, calcium carbonate, silicate compounds, or silica was changed in concentration and in some cases, the binder system was changed. Ultimately, due to the variation, there were no specific characteristics that would allow classification as a self-priming product.

Interior vs. Exterior Multipurpose Paints

There were four exterior paints analyzed in this study and three of them were multipurpose products. Throughout the analytical scheme, there were no observations that led to the distinction of interior vs. exterior, though likely due to such a limited number of comparisons. All interior vs. exterior product comparisons resulted in discriminations. Out of the four pairs of intra-brand interior and exterior products, only the Royal® by Ace® had differences in their binder systems. Polyvinylacetate-acrylic was identified in the interior product's FTIR spectrum whereas acrylic was seen in the exterior product. The Clark + Kensington™ and Valspar® products were all determined to have acrylic binder.

While ingredient lists indicated some concentration differences of minor components, not all of these components were detectable. Diiron trioxide, for example, was a listed ingredient in the Royal® by Ace® exterior product and Clark + Kensington™ Paint and Primer in One Premium Exterior Enamel, but there was no indication of iron in either SEM-EDS spectrum. Nepheline syenite, on the other hand, a minor component in the Royal® by Ace® exterior product, was indicated via SEM-EDS. The Clark + Kensington™ products were dissociated due to silicon peak heights and a small magnesium peak in the interior product's SEM-EDS spectrum. The magnesium may be attributable to palygorskite, though unlikely as it is listed at a concentration of less than 1%. Palygorskite was also listed in the exterior product's SDS at the same concentration but was not detected in its SEM-EDS spectrum.

In the two Valspar® exterior products, both claiming to be mildew resistant, zinc was detected using SEM-EDS. The only non-multipurpose Valspar® product analyzed in this study was an interior product and both this product and the multipurpose interior product were differentiated from the exterior products based on the identification of zinc in the exterior products' SEM-EDS spectra as well as the identification of kaolin and quartz in the interior non-multipurpose product's FTIR spectrum. Quartz was listed in the Valspar® Ultra™ Paint + Primer Plus Ultimate Weather Defense's ingredient list but in too low of a concentration to be detected by FTIR. There were low levels of potassium in both of the exterior products' SEM-EDS spectra and low levels of sodium and potassium in the interior products' spectra that could not be attributed to anything in the ingredient lists other than a "proprietary nonhazardous ingredient". The Valspar® interior and exterior products were completely dissociated from each other using FTIR, but the exterior products were not dissociated using SEM-EDS.

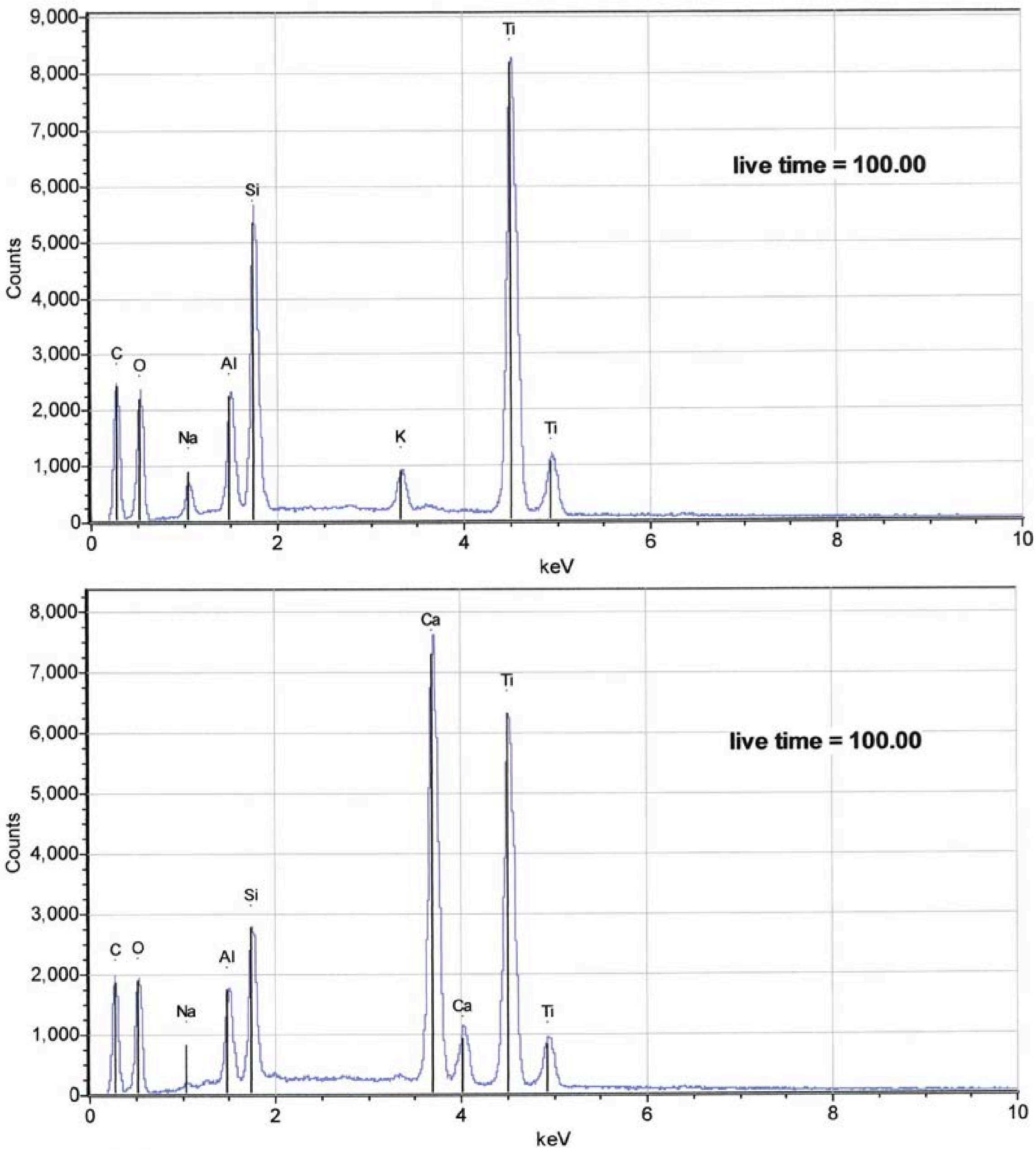

Figure 8: SEM-EDS spectra of (top) Glidden® Premium Interior Latex Paint; and (bottom) Glidden® DUO™ Paint + Primer Premium Paint.

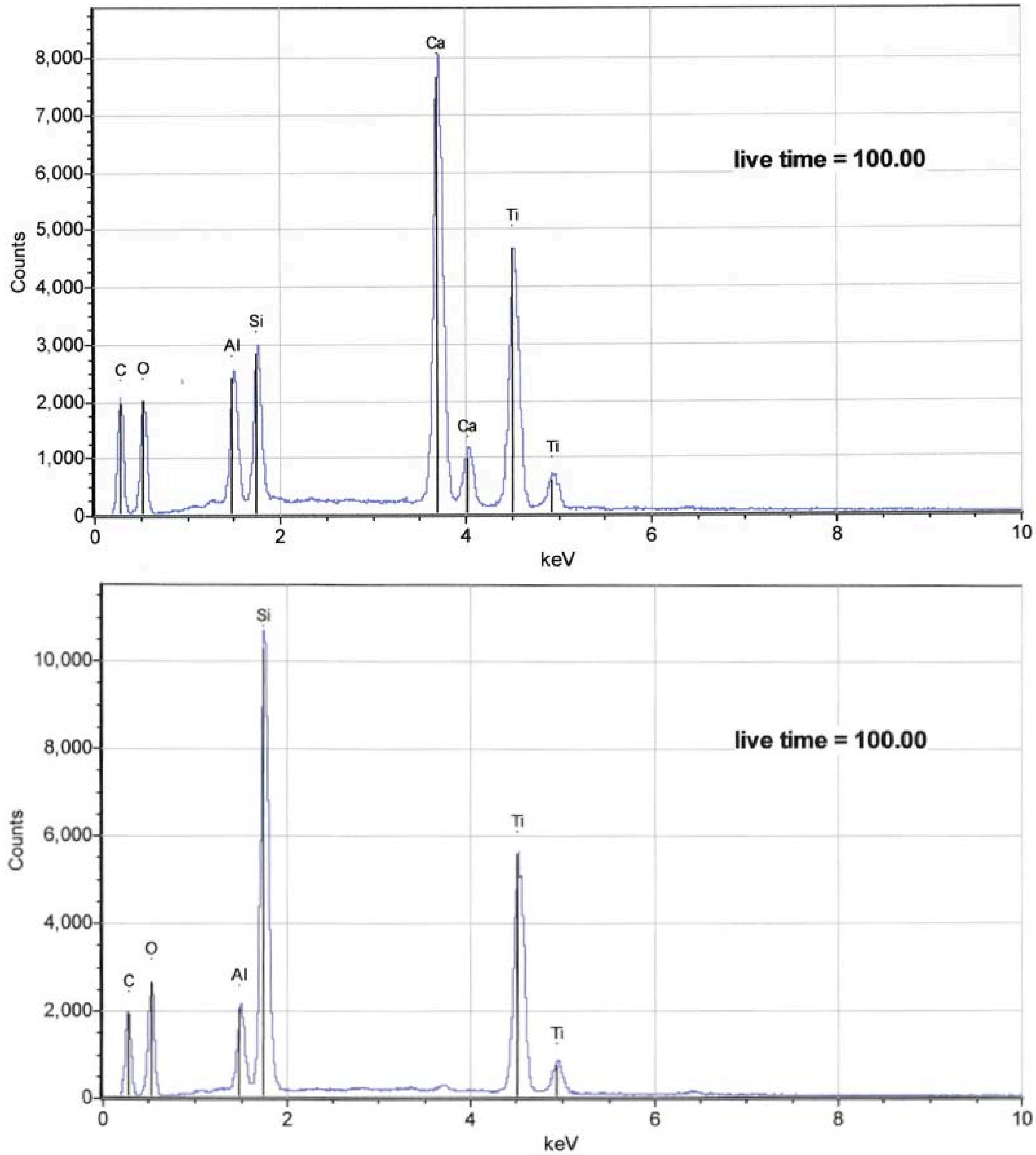

Figure 9: SEM-EDS spectra of (top) HGTV® HOME by Sherwin-Williams® Interior Paint; and (bottom) Sherwin-Williams® SuperPaint® Paint and Primer in One Interior Acrylic Latex.

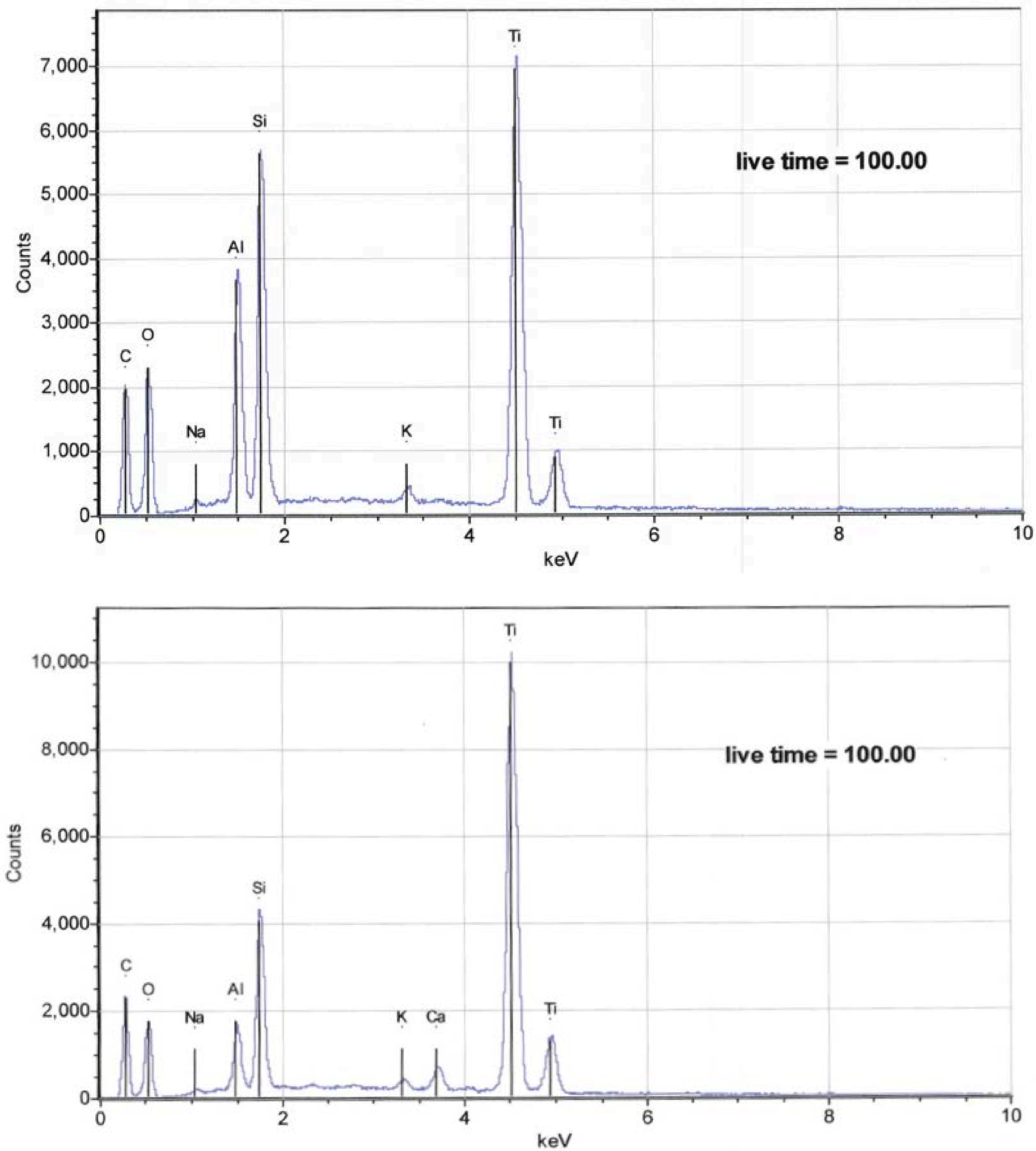

Figure 10: SEM-EDS spectra of (top) Benjamin Moore ben® Premium Flat Interior Latex Paint; and (bottom) Benjamin Moore Aura® Waterborne Interior Paint & Primer Matte Finish.

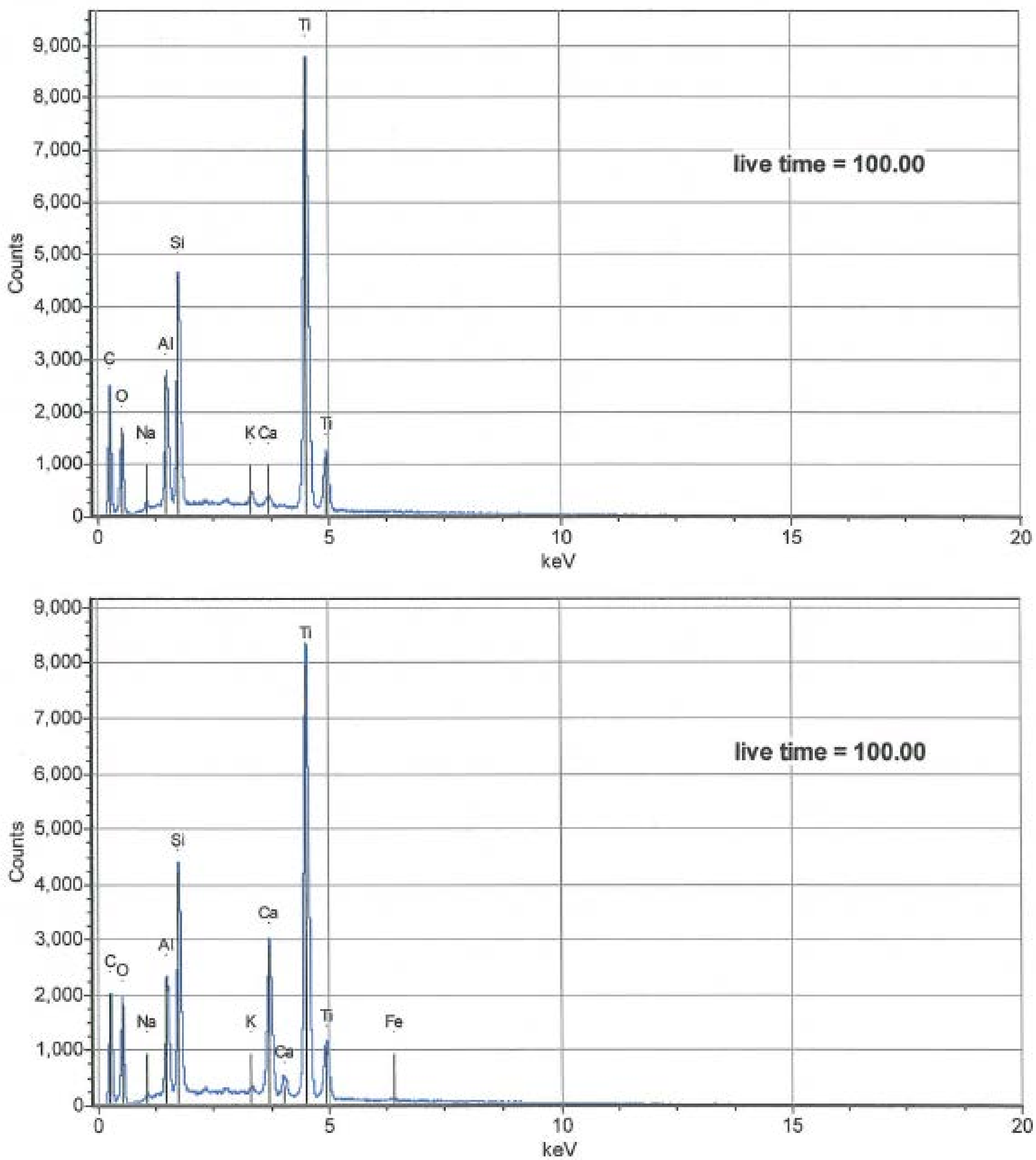

Figure 11: SEM-EDS spectra of (top) Benjamin Moore Regal® Classic Interior Flat Paint and (bottom) Benjamin Moore Regal® Select Premium Interior Paint and Primer Flat Finish.

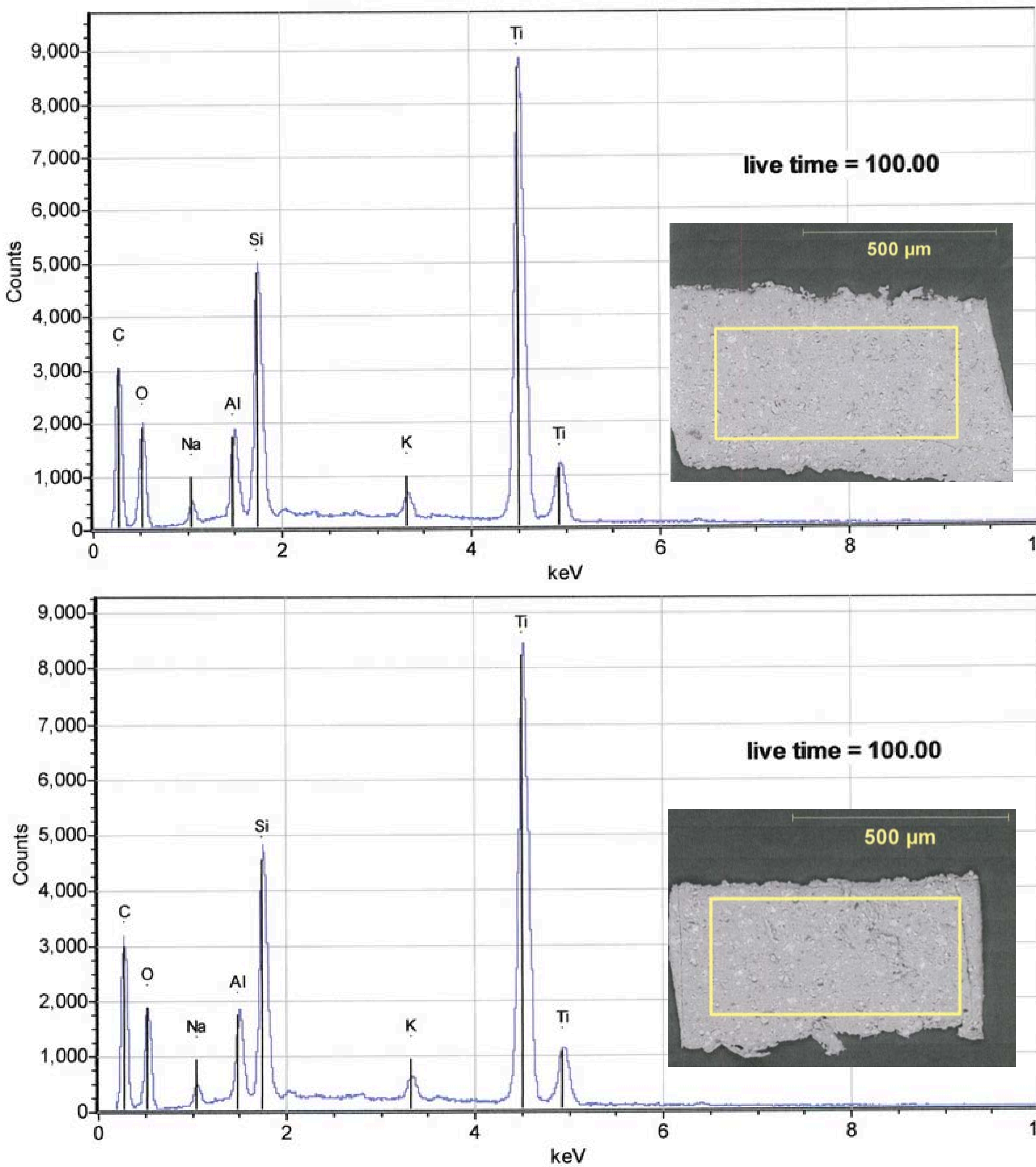

Figure 12: SEM-EDS spectra of (top) Behr® Premium Plus Ultra Interior Paint & Primer in One; and (bottom) Behr® Premium Plus Ultra Interior Stain-Blocking Paint & Primer in One. The respective SEM-EDS images for each sample are shown within the spectra. These were the only two multipurpose paints that were indistinguishable from one another throughout all testing.

Discrimination Ability

Various discrimination studies have been performed on paint samples that have been randomly selected from a given population (17). A recent example is a discrimination study performed on single layer white architectural paints (10). Additional discrimination studies have been performed on paint samples that were not randomly selected, but where the samples represent "worst case scenarios" as they are likely difficult to discriminate (17). The 26 white architectural paint samples used for this study were evaluated similarly to these previous discrimination studies. While these samples were neither randomly selected nor represent a "worst case scenario", the results obtained in their comparison were used to determine any consistency in obtained discrimination.

The discrimination power for each technique was calculated before evaluating the analytical scheme as a whole; see Table 3. In the 2013 Wright et al. architectural paint study, FTIR was evaluated individually to determine its discrimination power. It was calculated to be 94.45% (10), which is in line with the discrimination power of FTIR achieved in this study (95.38%). Of note, their study included more comparison pairs (1225 vs. 325). The overall discrimination process is shown in Figure 13. After performing all of the techniques on the samples, only the Behr® Premium Plus Ultra Interior Paint & Primer in One and the Behr® Premium Plus Ultra Interior Stain-Blocking Paint & Primer in One could not be distinguished. There may be differences between these sample formulations but they could not be identified using this analytical scheme. The discrimination power of this analytical scheme was determined to be 99.69%. This was compared to the discrimination power achieved in the Wright et al. single layer white architectural paint study, which was 99.35%. It should be noted their analytical scheme included FTIR, visual and microscopic examination, SEM-EDS, and pyrolysis gas chromatography – mass spectrometry (pyGC-MS) (10), which differed slightly from what was used in this study. Differences included the use of microchemical and microsolubility tests and lack of pyrolysis as no pyrolysis instrument was available. Additionally, their study was based on 50 samples run in triplicate by different analysts, which decreases both bias and variation (10). White architectural paints, especially single layered, were thought to be one of the toughest types of paint samples to differentiate in a forensic laboratory. This study supports others that a high discrimination power is achievable for white single layered paints when a thorough analytical scheme is employed.

Table 3: Discrimination power of each technique as well as the number of sample groups, number of groups which contain only one sample, and number of samples in the largest group.

Technique	Discrimination Power	# of Groups	# of 1-sample groups	Largest Group Size
Visual & Microscopic Analysis	60.92%	5	2	15
Fluorescence Microscopy	70.46%	7	4	13
Microchemical & Microsolubility Tests	89.23%	12	7	7
FTIR	95.38%	18	14	5
SEM-EDS	97.54%	20	16	3
Total Analytical Scheme	99.69%	25	24	2

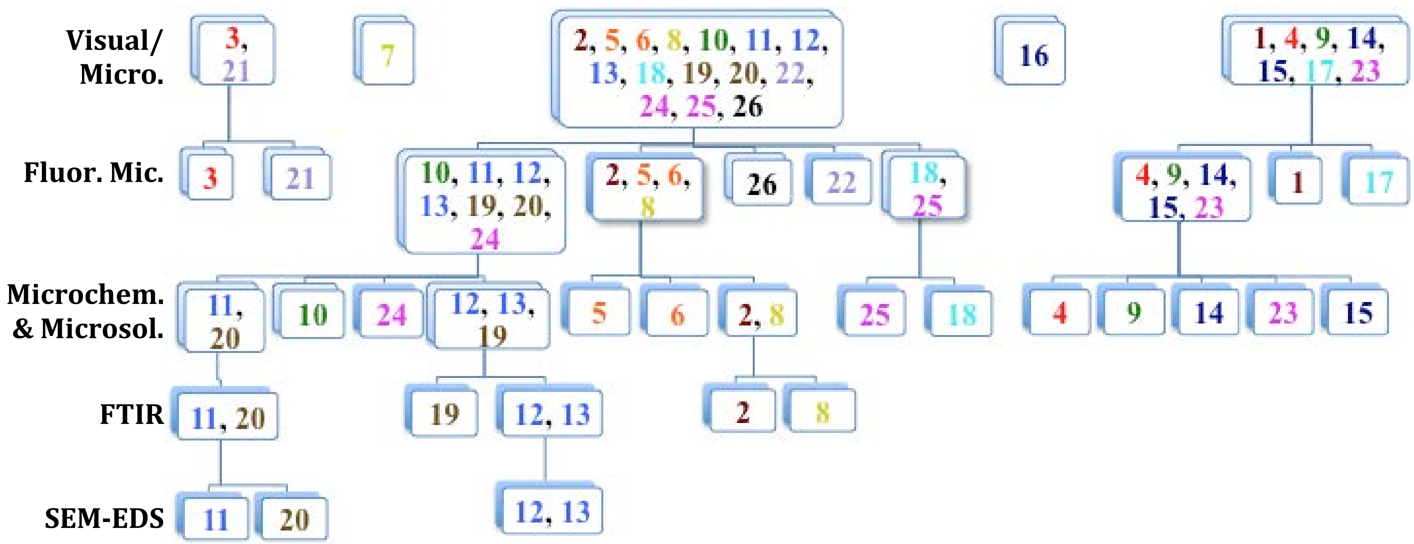

Figure 13: Overall Analytical Scheme Discrimination of Paint Samples. The intra-brand comparison samples are shown in the same color.

CONCLUSION

Multipurpose and non-multipurpose architectural paints were compared within a single brand and between brands in order to determine what differences, if any, could be seen using a forensic analytical scheme. Differences were seen in the majority of the comparison samples; however, no attribute allowed for class recognition in terms of multipurpose or non-multipurpose. Even though the self-priming products showed no consistent changes across the brands, the variation in how the multiple purposes were achieved broadens the ability to discriminate architectural paint samples. The possibility to detect minor elemental zinc in paint suggests anti-mold and mildew additives may be possible to recognize, but is not definitive. SEM-EDS proved critical in detecting these additives. There were no characteristics or components that were specific to distinguish interior from exterior paints, however, there were not a sufficient number of comparison samples to develop a general conclusion. Although the samples could not be classified into the multipurpose, non-multipurpose, interior, or exterior categories, a high discrimination ability was demonstrated between all of the products.

Using the analytical scheme in this study, the compositions of all of the multipurpose products were determined to be different from those of their non-multipurpose counterparts. The differences could be attributed to the ingredients listed on the products or their SDS for the most part, but not all of the ingredients were detected by the techniques in the analytical scheme, even though some of them were listed in percent concentrations above the level of detection for the techniques used. There were indeed chemical differences seen between the multipurpose and non-multipurpose products.

The samples were also treated as independent samples and each compared to another regardless of their multipurpose or non-multipurpose class to establish a discrimination power for the entire analytical scheme. After performing all of the techniques and determining individual discrimination powers, one indistinguishable pair remained, resulting in a very high power of discrimination for the analytical scheme as a whole. This showed that the overall analytical scheme, rather than individual techniques, was the strongest resource to distinguish architectural paint evidence for forensic examiners.

FUTURE WORK

This work would benefit from increasing the number of samples analyzed. Additional samples outside of the authors' geographical area and the inclusion of newer products made commercially available since this work was undertaken could further help elucidate if any trends develop in how these multipurpose paints are formulated. Additionally, with more samples, the use of Raman spectroscopy or pyrolysis techniques may further assist in component identification and/or sample discrimination.

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