

## FT-IR Spectrometry

## Authors

Dale C. Mann, BS

Keith G. Cline, PE

MDE, Inc  
700 S. Industrial Way  
Seattle, WA 98108

## Confirmation of the Presence of Styrene Butadiene Resin (SBR) Polymer in Drywall Primer Applications.

A combination of Fourier Transform Infrared (FT-IR) Spectrometry and Thermogravimetric Analysis (TGA) was used to distinguish and identify styrene butadiene from polyvinyl acrylic resin-based interior latex primers and paints. A wide range of standard mixtures of the two resins were analyzed and the relative percentages of the two accurately estimated using the two methods. The isolation techniques and analytical methods of analysis were developed to verify the composition of primer/texture/paint applications used on interior condominium walls.

### Introduction

Over the past several years, architects and developers of condominium housing projects in western Washington have begun to utilize the Washington State's Energy Code<sup>1</sup> allowing a rated vapor barrier primer/paint to replace the traditional polyethylene plastic sheeting or Kraft-backed insulation bats historically used in the construction to achieve the required water vapor perm rating of 1.0 or less. Building specifications for the interior wall finish called for the application of a vapor barrier rated primer followed by the normal decorative paint/top coat.

A literature review of many major paint distributors of interior vapor barrier primers shows the resin in the vapor barrier primers is a styrene butadiene rubber (SBR) formulation. This formulation is quite different from the normal drywall primer, polyvinyl acrylic (PVA). Litigation involving the perceived lack of a SBR primer on interior drywall surfaces soon led MDE Forensic Laboratories to develop methods to positively identify the presence/absence of an SBR primer after a PVA top coat was also applied to the walls.

## Laboratory Methods

Cross sections of the texture, primer and paint applied to the interior of the drywall were prepared by mounting specimens in acrylic and polishing. Examination of these samples showed the presence of a primer layer applied to the drywall, followed by a texture and finally the decorative top coat paint. The primer layer exhibited an average dry film thickness that met all manufacturers' specifications, regardless of the potential resin formulation of the primer.

### Fourier Transform Infrared Spectrometry

The decorative top coat and texture were physically separated from the primer layer. The primer layer and uppermost layer of drywall paper were peeled off and ultrasonically extracted using a 50/50 mixture of tetrahydrofuran/methylene chloride solvent mixture. The solvent was evaporated to dryness and the isolated primer resin analyzed using FT-IR<sup>2,3</sup>.

FT-IR results for pure SBR and PVA resins are shown in Figure 1. The predominant absorbances for an SBR resin, resulting from the styrene content, are at 700 and 730  $\text{cm}^{-1}$ . Figure 2 illustrates some typical results from the extracted condominium primer layers. Many of these did not yield pure SBR spectra, however absorbances typically due to styrene were readily detected in all extractions. The primary absorbances in these spectra appeared to be due to the co-extracted presence of a quantity of PVA resin. Note that a PVA resin decorative top coat was originally present on each sample.

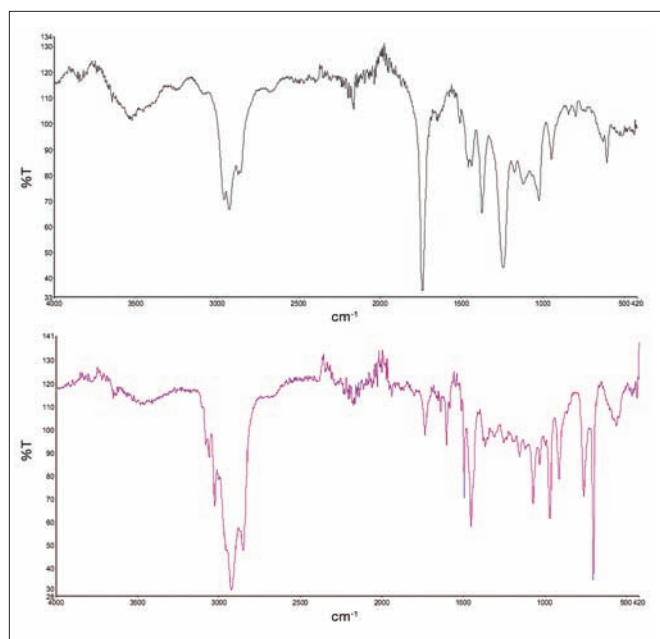


Figure 1. FT-IR comparison of a pure PVA resin (top) and a pure SBR resin (bottom).

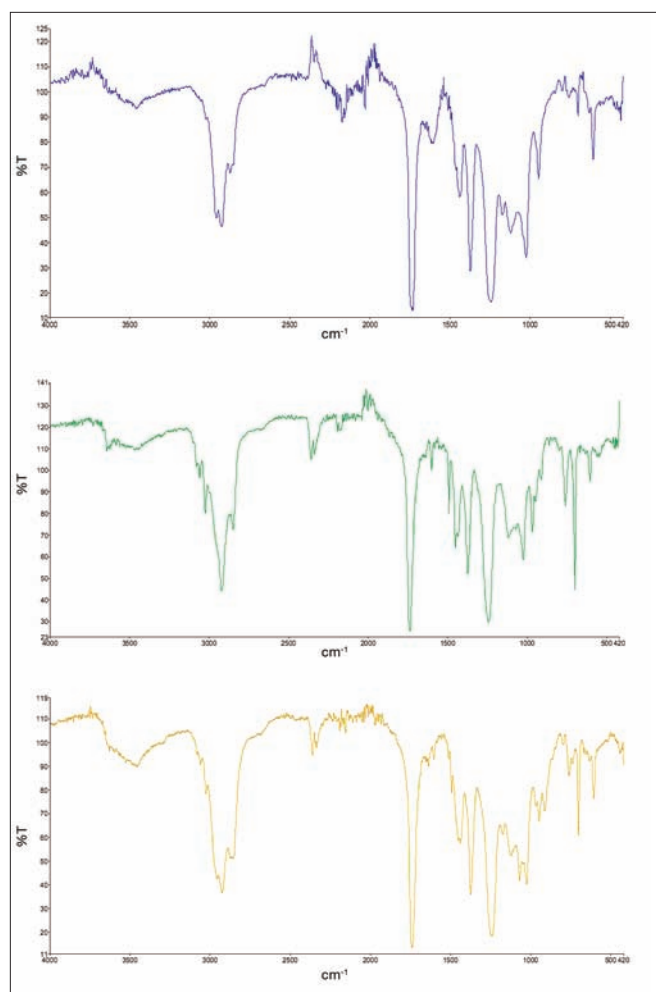


Figure 2. Examples of three "typical" FT-IR results from the solvent extraction of isolated primer layers from three separate condominium units. Note the lack of a definitive SBR spectra but the presence of a styrene absorption at 700  $\text{cm}^{-1}$ .

### Thermogravimetric Analysis

Resins extracted from both PVA and SBR formulated paints were analyzed using TGA<sup>4,5,6</sup>. The samples were analyzed using nitrogen gas and a temperature program of 25-600  $^{\circ}\text{C}$  with a 20  $^{\circ}\text{C}/\text{min}$  ramp. This temperature program caused the complete pyrolysis of the paint resin samples. Evaluation of the data showed distinctly different slopes in the weight loss versus temperature curves. The first derivative of these curves was used to identify the inflection points. The temperatures of these inflection points were found to be 350  $^{\circ}\text{C}$  for the PVA resin and 425  $^{\circ}\text{C}$  for the SBR resin. Figure 3 illustrates the first order weight loss curve and the first derivative of that curve for both pure SBR and PVA resins.

### Pyrolysis Gas Chromatography/Mass Spectrometry

Pyrolysis GC/MS methodology was also investigated as a means of verifying the presence of SBR by using the presence of styrene. However, it was found that small amounts of styrene were produced during the pyrolysis of PVA resin. This artifact and the desire to use available instrumentation led us to not pursue this methodology.

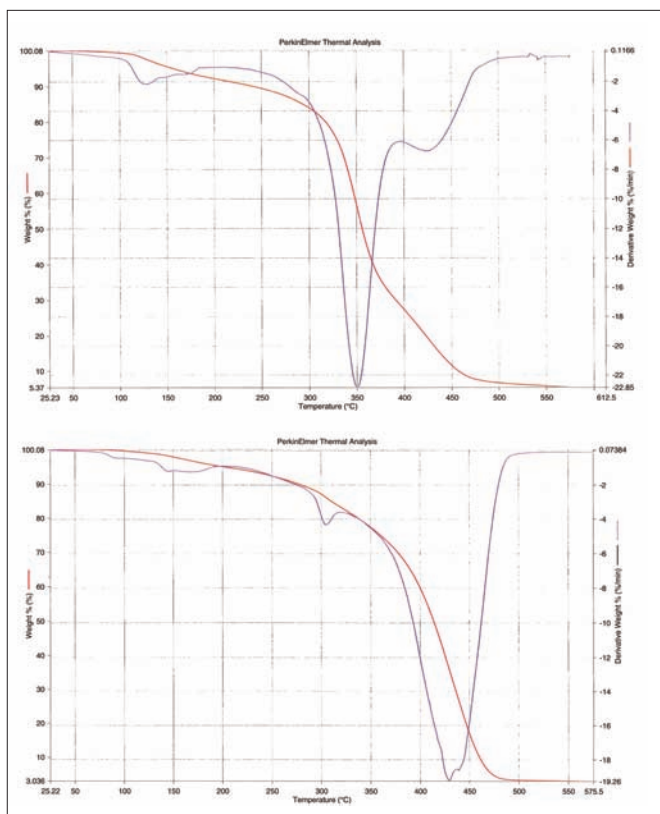


Figure 3. TGA comparison of a pure PVA resin (top) and a pure SBR resin (bottom). The weight loss vs. temperature is shown in blue and the 1st derivative of that curve is shown in red.

## Analysis of Standard Mixtures

Pure SBR and PVA resins were extracted from exemplar primer and paint products. The purity of the resulting evaporated extracts was evaluated using FT-IR and TGA. Mixtures of the two were made by adding a weighed amount of each resin, dissolving in solvent to homogenize and dried for analysis.

The standard mixtures were 0%, 10%, 30%, 50%, 70%, 90% and 100% of SBR resin in PVA. These mixtures were analyzed using both FT-IR and TGA. The ratio of the peak height at 700  $\text{cm}^{-1}$  (the styrene absorption for the SBR) to the 1740  $\text{cm}^{-1}$  (the carbonyl adsorption for the PVA) was used to estimate the relative amounts of the two resins. Figure 4 illustrates typical FT-IR results and Figure 5 depicts the resulting calibration curve.

The standard mixtures were likewise analyzed using TGA. The ratio of the peak heights of the second derivative plots at 425  $^{\circ}\text{C}$  (for the SBR) to the 350  $^{\circ}\text{C}$  (for the PVA) was used to estimate the relative amounts of the two resins in the mixture. Figure 6 illustrates typical TGA 1st derivative plots and Figure 7 depicts the resulting calibration curve using the log of the ratio of the peak heights of these curves.

## Subject Samples

Samples isolated for the several condominium projects evaluated during the course of the investigations yielded a wide range of FT-IR and TGA results. In some instances, a SBR was easily and cleanly confirmed by both analytical methods. In other condominium projects evidence of SBR was much less pronounced. Figures 2 and 8 depict the range of FT-IR and TGA results for some of these investigations.

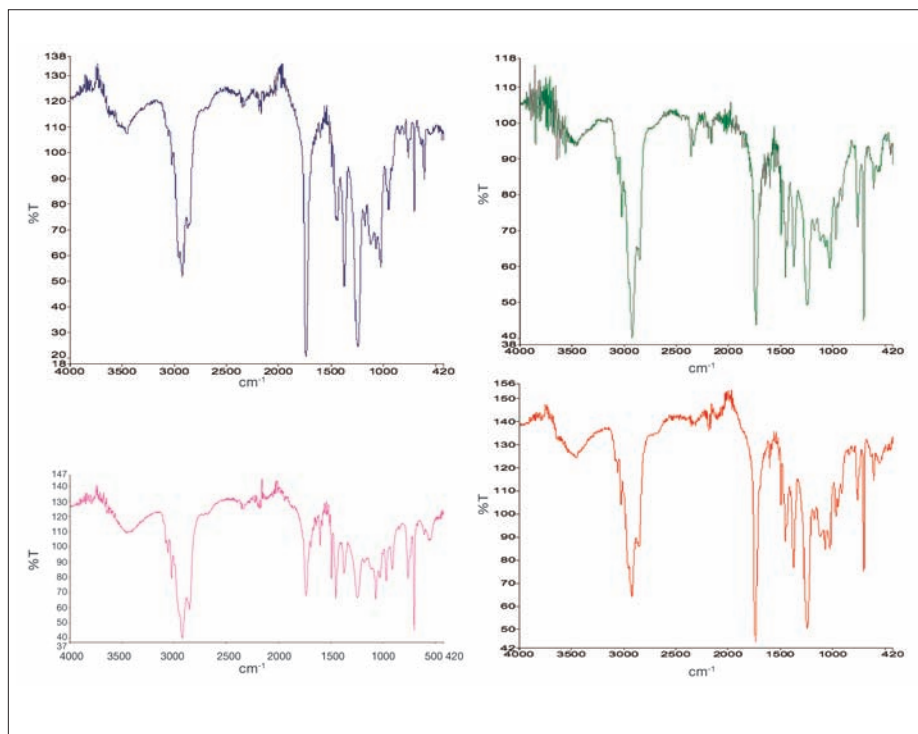


Figure 4. FT-IR comparison of standard mixtures of SBR and PVA resins. From top to bottom, the SBR/PVA ratios are 90/10 (blue), 70/30 (red), 50/50 (green), and 10/90 (brown).

Some “contamination” of the physically isolated primer layer by the overlying PVA paint was expected due to the difficulty of mechanically separating the coating layers during sample preparation. This was particularly true when the primer and paint had been applied without an intervening layer of texture. For some projects only low relative concentrations of SBR were calculated, even when it was thought a “clean” isolation of the primer layer was performed.

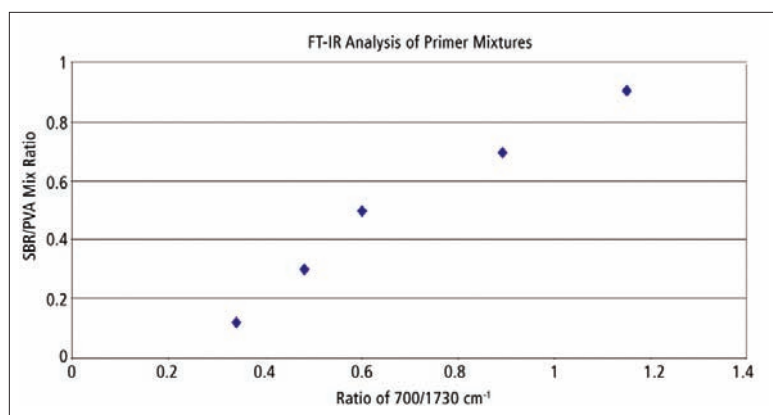


Figure 5. Calibration curve for the FT-IR analysis of standard mixtures of SBR and PVA. Peak height ratios are the SBR/styrene absorbance at 700  $\text{cm}^{-1}$  divided by the PVA/carbonyl absorbance at 1732  $\text{cm}^{-1}$ .

As laboratory work progressed during these investigations, many of the locally available drywall primers (both vapor barrier products and traditional drywall primers) were analyzed. Though not clearly specified on product labels or in the product technical data sheets, it became apparent during the laboratory analysis that many primers labeled as vapor barrier products were actually a blend of SBR and PVA resins. At least one manufacturer alluded to this in their product information. Figures 9 and 10 depict the FT-IR and TGA results for a variety of exemplar vapor barrier primers.

Calculation of the relative amount of SBR to PVA in the analyzed exemplar primers showed a range from 100% SBR to 20% SBR. In one condominium project, the calculated SBR in the isolated primer layer never exceeded 20%. The primer that was later confirmed to have been used as the vapor barrier was a blended resin containing only 20% SBR. This information was only confirmed after the laboratory results were used as motivation to persuade the manufacturer to release their formulation.

## Summary

The combination of FT-IR and TGA analysis of vapor barrier primers is a powerful analytical method useful for confirming the presence/absence of a styrene butadiene resin in the primer. A semi-quantitative estimate of the relative amount of the SBR compared to the more traditionally used PVA resin is possible.

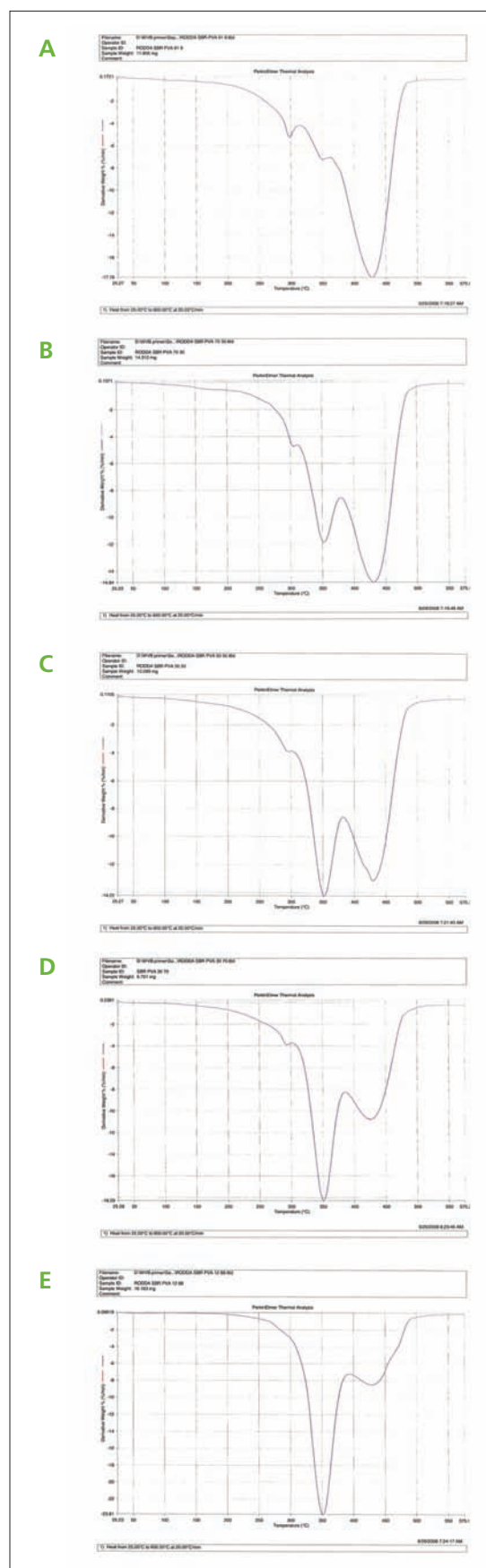


Figure 6. TGA comparison (using 1st derivative of weight loss curve) of standard mixtures of SBR and PVA resins. From top to bottom, the SBR/PVA ratios are 90/10 (A), 70/30 (B), 50/50 (C), 30/70 (D) and 10/90 (E).

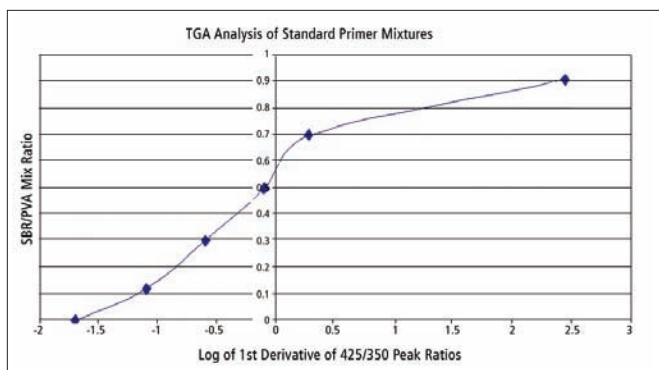


Figure 7. Calibration curve for the TGA analysis of standard mixtures of SBR and PVA. Calculated ratios are the SBR/1st derivative peak height at 425 °C divided by the PVA/1st derivative peak height at 350 °C.

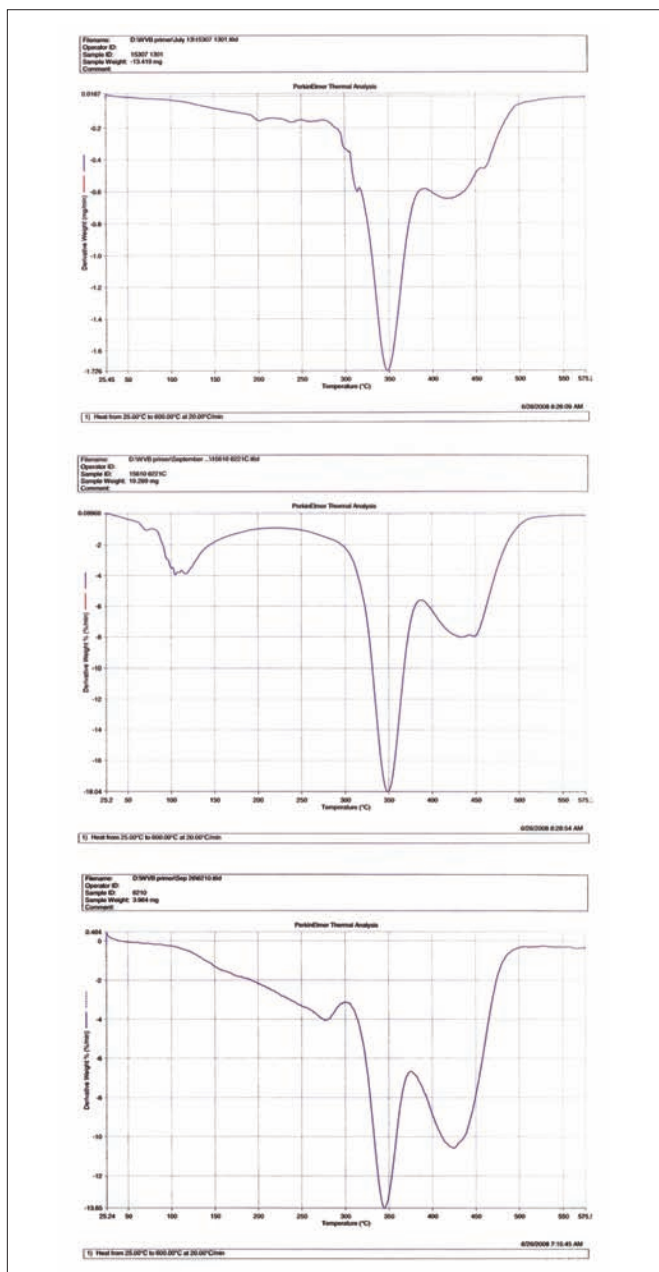


Figure 8. Examples of three "typical" TGA 1st derivative results from the solvent extraction of isolated primer layers from three separate condominium units.

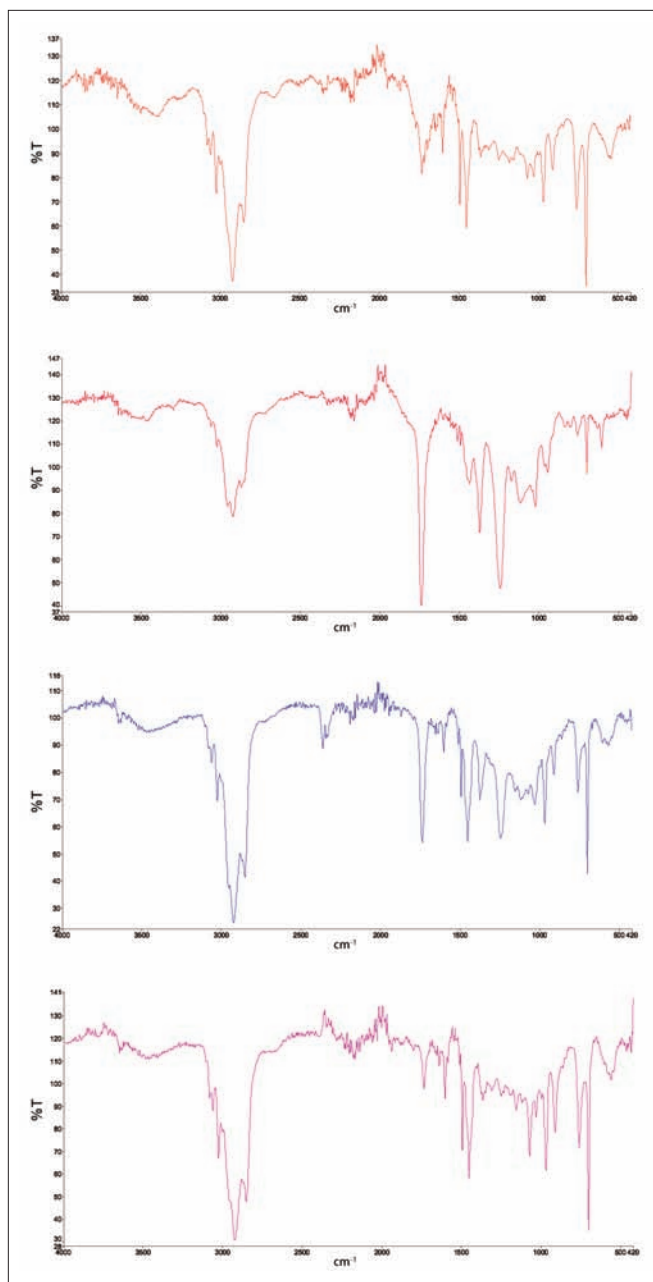


Figure 9. FT-IR spectra of four different brands of vapor barrier primer. Each is a mixture of SBR and PVA resins.

## References

1. Washington State Energy Code, 502.1.6.1-4, 1994.
2. ASTM® D3168-85 (2005) Standard Practice for Qualitative Identification of Polymers in Emulsion Paints, 2005.
3. Kolske, Joseph V. Paint and Coating Testing Manual, Chapter 75:850-852, 1995.
4. Earnst, C.M, Ed. The Compositional Analysis by Thermogravimetry, STP 977, ASTM®, 1988.
5. ASTM® E1131-03 Standard Test Method for Compositional Analysis by Thermogravimetry, 2003.
6. ASTM® E2008-06 Standard Test Method for Volatility Rate by Thermogravimetry, 2006.

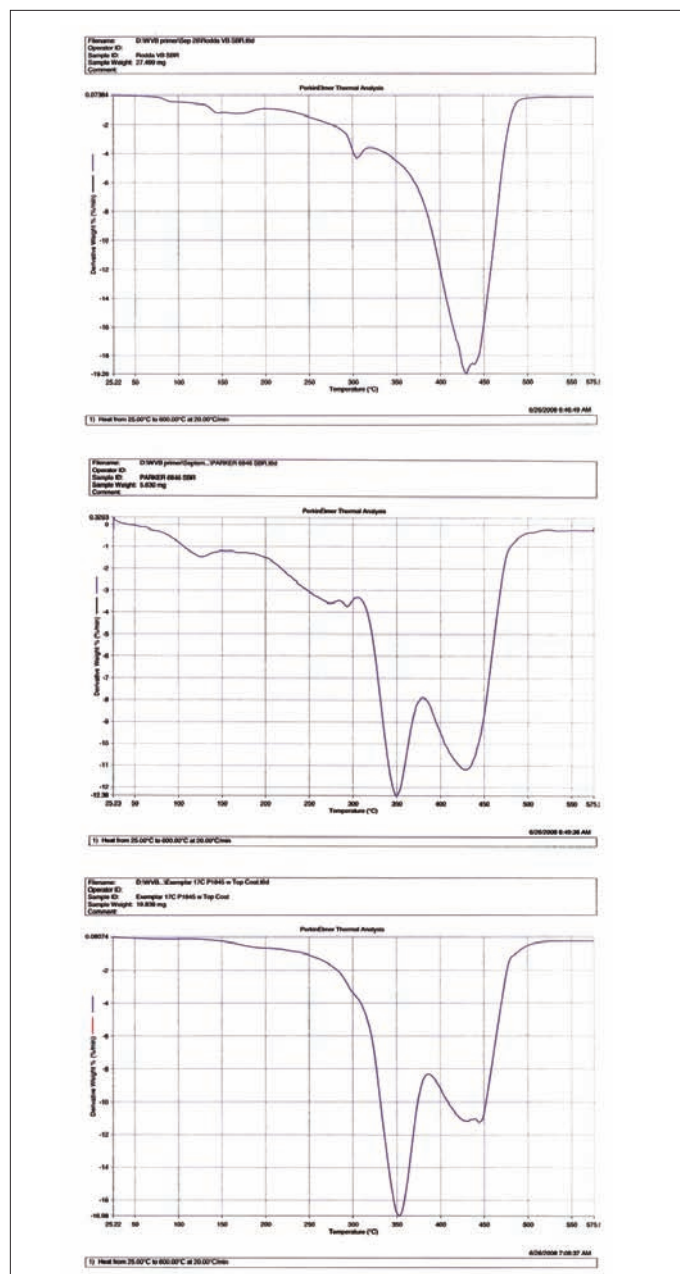


Figure 10. TGA 1st derivative curves of three different brands of vapor barrier primer. Each is a mixture of SBR and PVA resins.