Mix Ratio Identification in Industrially Significant Two-Part Coating Systems Using the Agilent 4300 Handheld FTIR

Application Note

Quality Control in Coatings

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Introduction

Protective coatings are commonly applied to automobiles, aircrafts, ships, railways, furniture, bridges, concretes, architectural constituents, industrial installations, and many other products that we encounter on a daily basis. Coating application in many of these products is primarily implemented to provide protection against harsh environments such as UV light, extreme temperatures, acid, alkali, salt, water, and so forth, and to improve the aesthetic appearance of finished products.

A wide variety of coating formulations exist in the market; their use depends on the performance requirement of the final product. Coatings may be applied to the products as a primer basecoat, a mid-coat, or as the topcoat. For example, polyurethane coating is applied on top of epoxy primer coating to prevent the discoloration of epoxy from UV and to provide the specified color and sheen.

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Many of these coatings are packaged and supplied by the manufacturers as two-part systems, also known as two-pack or 2K. Coatings are also supplied as either single pack (1K) or even tri-pack (3K) systems. Two-part systems commonly consist of a reactive resin and a separate curing agent or hardener.

Manufacturers recommend proper mixing ratios of coating system components, either by volume or weight, before application to the product. To ensure the desired characteristics of the coating on the substrate, it is important to stay within the tolerated variability allowed by the mixing ratio. For some sensitive coating systems, small deviation from the recommended ratio will adversely affect performance.

Similarly, an incorrect mixing ratio can lead to product defects and irregularities. The effects of off-ratio mixing may not be readily apparent, but may show up after time, possibly leading to decreased coating performance or even premature coating failure depending on the degree of mixing error and the component. Cure agent-rich mixtures result in higher strength but also reduced impact resistance and higher probability of brittle failure, whereas resin-rich mixtures result in low strength. Both will affect the longevity of coatings on the product due to reduced performance, and can exhibit discoloration, inconsistent patchy gloss, blooming, cracking, and poor intercoat adhesion or stickiness.

This application note demonstrates that the Agilent 4300 Handheld FTIR system is highly effective for determining the mix ratio of two popular two-part coating systems: an epoxy primer and a polyurethane (PU) top coat. In addition, a simple two-coat system with epoxy as primer and PU as a top coat was also modeled. The mid-IR technique is ideal for monitoring the mix ratio because the components involved in each coating have their own distinctive spectra related to their chemical makeup and the degree of final cure. Furthermore, because of its exceptional portability and performance, the 4300 Handheld FTIR accomplishes this analysis wherever it is required. The method-driven, intuitive software and user interface enable users of widely varied experience to get rapid, highly accurate results.

Methods and Materials

Two-part marine grade epoxy and two-part polyester polyol saturated, aliphatic urethane coatings were obtained commercially. The recommended mixing ratio for the base (resin component) and the reactor (curing agent/hardener) was 1:1 by volume for epoxy and 2:1 by weight for polyurethane coating. A series of calibration and validation samples were generated by mixing the two-part coating system at the correct ratio as well as incorrectly (Table 1).

Table 1. Calibration and validation samples used for measuring mix ratio of two-part coating systems. The recommended mix ratio is highlighted in green.

	Polyurethane				Epoxy				Polyurethane on epoxy			
	Weight in grams								Weight in grams			
Steel panel	Part A	Part B	Actual ratio A/B	Target ratio A:B	Part A mL	Part B mL	Actual ratio A/B	Target ratio A:B	Part A	Part B	Actual ratio A/B	Target ratio A:B
Calibration sample												
1	10.50	2.22	4.72	2:0.40	17.05	8.83	1.93	1:0.5	11.93	2.82	4.24	2:0.45
2	10.20	2.70	3.78	2:0.55	14.95	11.23	1.33	1:0.75	10.00	3.36	2.98	2:0.65
3	10.21	3.34	3.06	2:0.65	15.28	15.33	1.00	1:1	10.85	3.96	2.74	2:0.75
4	11.06	5.63	1.96	2:1	17.40	21.61	0.80	1:1.25	7.59	3.78	2.01	2:1
5	10.15	5.86	1.73	2:1.15	9.56	14.47	0.66	1:1.50	11.03	6.74	1.64	2:1.20
6	10.23	7.07	1.45	2:1.35	14.33	25.19	0.57	1:1.75	9.17	6.58	1.39	2:1.45
7	10.38	9.36	1.11	2:1.80	11.74	23.38	0.50	1:2	7.22	6.78	1.06	2:1.9
Validation sample												
8	10.14	8.17	1.24	2:1.6	13.85	8.71	1.59	1:0.6	8.49	7.86	1.08	2:1.85
9	10.15	4.53	2.24	2:0.9	15.01	12.77	1.18	1:0.85	9.84	5.74	1.71	2:1.20
10	10.54	3.93	2.68	2:0.75	13.92	18.73	0.74	1:1.35	9.07	2.79	3.25	2:0.60

For both the polyurethane and epoxy coating systems, component B (curing agent) was varied to obtain different mix ratio compositions. The components were mixed and applied to the steel substrate within the pot life (working life) of the mixture. All other application conditions, such as induction time, temperature, substrate cleanliness, and dry time, were followed as specified by the manufacturer for each coating. Three types of coated coupons were prepared: polyurethane, epoxy, and polyurethane on top of epoxy.

The 4300 Handheld FTIR spectrometer with external and diffuse reflectance sampling interfaces was used for measuring the mix ratio of coating systems painted on a steel panel. The measurement was taken after the paint was left to air-dry overnight. Each spectrum was a result of 64 co-added scans at 4 cm^{-1} resolution, yielding a total measurement time of 26 seconds. The measured spectral range was 4,000–650 cm^{-1}. Five different spots were analyzed on each painted steel panel at each mix ratio. A calibration model based on Partial Least Squares (PLS) regression was developed using the mean centering and multiplicative scatter correction as the preprocessing algorithm.

Results and Discussion

Figure 1 shows the PLS calibration plots showing the actual versus predicated value for each coating mix ratio. The minimum number of factors yielding a correlation coefficient of R^2 greater than 0.99 was chosen for each calibration plot; 5, 6, and 4 factors were required for polyurethane, epoxy, and polyurethane on top of epoxy coatings, respectively. The number of factors used in each model also ensured the higher prediction accuracy on the validation sample, as shown in Table 2.

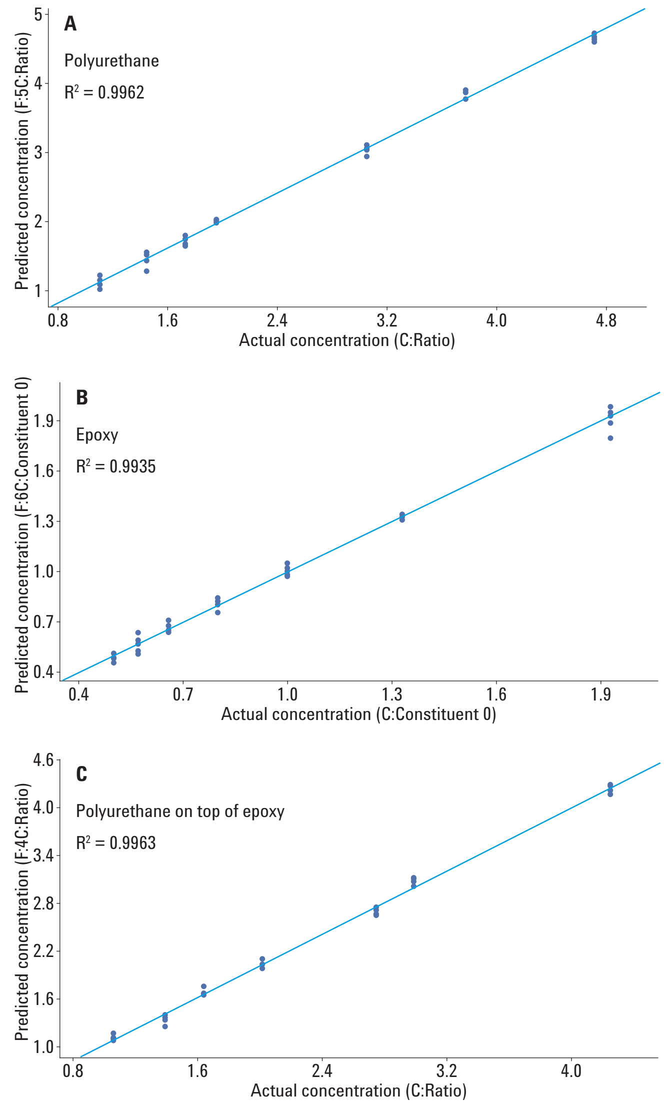

Figure 1. Calibration model obtained for different mix ratios of two-part coating systems (polyurethane, epoxy, and polyurethane on top of epoxy), developed using the PLS algorithm.

Table 2. Predicted mix ratio of validation samples using the PLS model for each coating.

Polyurethane			**Epoxy**			**Polyurethane on Epoxy**		
Actual	**Predicted[1]**	**% Difference**	**Actual**	**Predicted[1]**	**% Difference**	**Actual**	**Predicted[1]**	**% Difference**
1.24	1.24 ± 0.2	0.17	1.59	1.65 ± 0.16	3.77	1.71	1.65 ± 0.04	3.51
2.24	2.21 ± 0.04	1.34	1.18	1.21 ± 0.02	2.54	1.08	1.13 ± 0.04	4.63
2.68	2.46 ± 0.02	8.21	0.74	0.74 ± 0.02	0.41	3.25	3.24 ± 0.16	0.31
Average % error		3.24		2.24		2.82		

[1] Average value of five measurements taken on five different spots of the steel substrate panel ± two standard deviations.

Figure 2 shows the spectral region used to build the calibration model for the polyurethane coating system. Since the amount of component B (curing agent) was varied, the spectral band in the region ~2,100–2,400 cm^{-1} due to aliphatic polyisocyanate moiety was altered (Figure 2). The band intensity positively correlated with the increase in component B (that is, with the decrease in mix ratio).

Figure 3 shows the spectral region used to build the PLS calibration model for the epoxy coating system. Notable bands and spectral features that correlate with the mix ratio are in the 1,650–2,200 cm^{-1} and 1,600–800 cm^{-1} regions.

Although only measurements made using the external reflectance sampling interface are shown here, the diffuse reflectance interface yielded similar results. For example, the average percent error on mix ratio prediction of validation samples for polyurethane, epoxy, and polyurethane on top of epoxy were 3.24, 2.24, and 2.82, respectively (Table 2) using the external reflectance interface, whereas the average error was 4.83, 4.82, and 0.81, respectively, for the same samples when the diffuse reflectance interface was used.

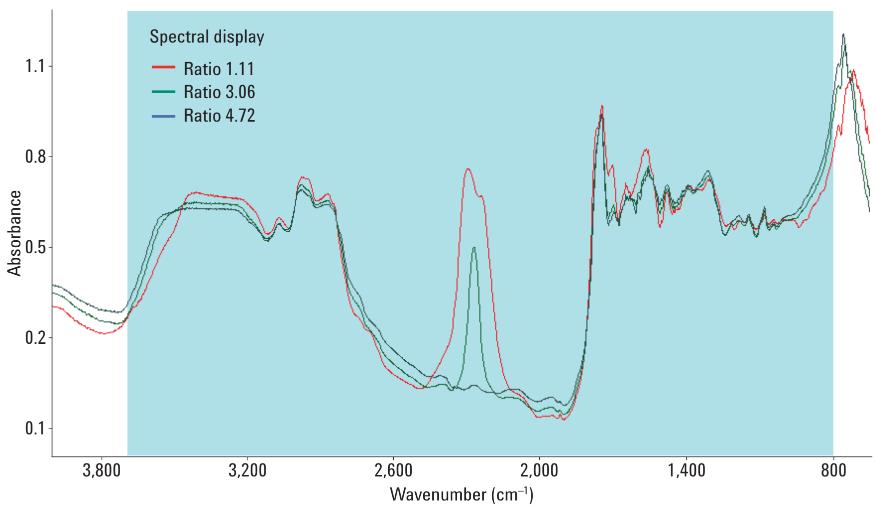

Figure 2. External reflectance IR spectra of three different mix ratios of polyurethane coating. The region highlighted in blue was used for the PLS calibration model.

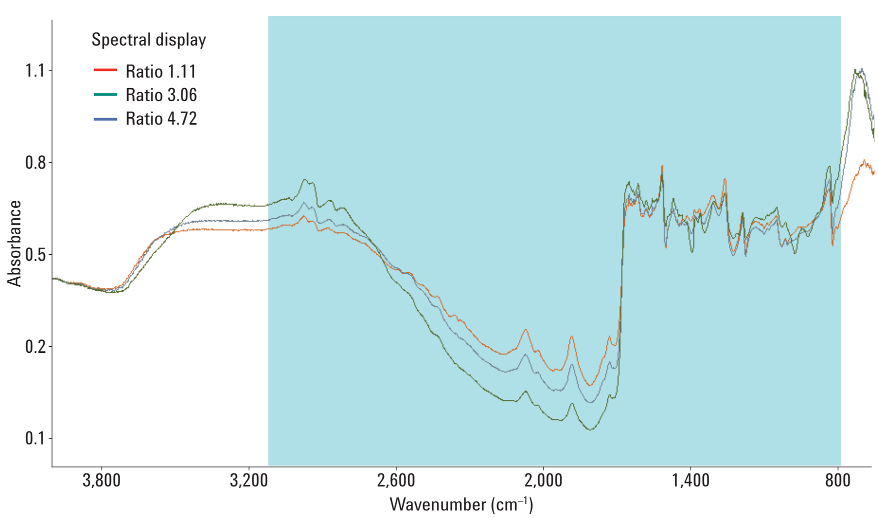

Figure 3. External reflectance IR spectra of three different mix ratios of epoxy coating. The region highlighted in blue was used for the PLS calibration model.

Conclusion

This project shows that the Agilent 4300 Handheld FTIR successfully identifies the mix ratio in 2K coatings and in a two-coat system. The instrument and accessory used here can be easily extended to identification of the mix ratio in other formulations, or the degree of cure for single- or two-component cure systems.

Excellent results are obtained using either the diffuse or external reflectance sample interfaces, depending on the coating system formulation and the painted substrate. For coating finishes on reflective metal surfaces such as steel or aluminum, the external reflectance sample interface is the better choice; for coatings with higher amounts of fillers or those applied to surfaces with minimal light reflection, the diffuse reflectance sample interface is the preferred approach.

The 4300 Handheld FTIR enables virtually instantaneous determination of the mixing ratio, helping to ensure that coatings meet their performance specifications and longevity requirements. Furthermore, the portable, handheld system enables these determinations where and when needed, whether in a laboratory environment or at the physical site where the coating is in use.

Agilent 4300 Handheld FTIR

Lightweight: At 2.2 kg (4.8 lb), the 4300 Handheld FTIR is ideal for mid-IR measurements in the lab, out of the lab, wherever and whenever needed.

Balanced: With a center of gravity located at the handle, the system is comfortable to use with less physical strain, allowing for more accurate and precise measurements.

Rapid scanning: Scan large surface areas in less time. With the optional MCT detector, the 4300 Handheld FTIR enables measurements to be made more rapidly.

Nondestructive: No need to excise a sample for later analysis in a lab—this handheld spectrometer is brought to the object or surface to be measured.

Immediate results: Focus on the measurement locations of greatest importance. At-site analysis lets you make decisions in real-time.

Intuitive: Easy-to-use software guides less experienced personnel to actionable results faster. Preprogrammed methods powered by advanced mathematical models, and advanced reporting features all function automatically behind the scenes.

The 4300 Handheld FTIR comes with the choice of interchangeable, permanently aligned sample interfaces. Two sampling interfaces are used in this application:

1. **External reflectance interface**
   - Allows the analysis of films and coatings on reflective metal surfaces such as aluminum or steel
   - Used for the analysis of smooth, opaque samples where infrared light reflects off the surface
2. **Diffuse reflectance interface**
   - Used when sample reflects little light
   - Provides excellent results for a wide variety of samples, including surface coatings with higher amount of fillers

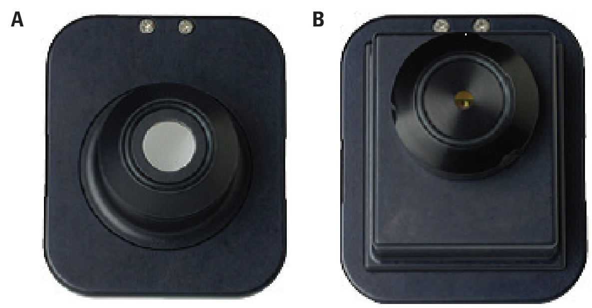

Figure 4. A) External reflectance interface and B) diffuse reflectance interface for the Agilent 4300 Handheld FTIR.

For More Information

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