Rapid Quantification of the A:B mix-ratio of a 2K Industrial OEM PU paint prior to autoclave thermal activation

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Introduction

Modern industrial paints are complex and highly engineered products. They typically contain a wide range of both organic and inorganic compounds with the cured organic polymeric binder often being the weakest link in the dry coating. These paints are applied in a multi-layered system, with each layer serving a particular primary function. Arguably the most important layer is the final clearcoat, sometimes referred to as the lacquer coat. In multi-coat systems (3-5 layer systems) it protects the lower layers from physical and environmental damage. This requires the clearcoat layer to have the supreme weather, chemical, abrasion and UV resistance, as well as high gloss.

Polyurethane(PU) formulations are often used as the clearcoat layer on a wide variety of transportation vehicles, structures and equipment. It is applied after mixing two components, labelled A & B, together. As with any two-part (2K) coating, the mix ratio of the two liquid components is critical to the final cure and performance of the coating. If the ratio is incorrect, surface wrinkling, tackiness,

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and other physical defects can result, with the long-term performance potentially compromised. Remedial action/ warranty claims are costly and their potential avoidance is discussed here using a hand-held 4300 FTIR and the external reflectance sample interface (45° specular).

In the industrial sector, automated or robotized spray guns are often used to apply paint prior to curing. Manufacturers need a quick and easy way to test whether the correct mix-ratio is being applied by the spray system to ensure the product passes subsequent QA/QC tests. An incorrect mix-ratio may result in remedial action at best and complete part scrappage at worst.

This study examined the use of a hand-held Agilent 4300 FTIR instrument (Figure 1) and a multi-variate calculation model to accurately and quickly quantify the component wet mix-ratio of a paint applied by a spray gun onto an aluminium coupon.

Figure 1. The Agilent 4300 FTIR instrument and the external reflectance sample interface, one of the many interchangeable interfaces available.

Experimental

The 2K PU used in this study was an industrial grade high-end OEM paint. It contains isocyanate blocking technology to ensure no appreciable reaction occurs in the mixed paint until the activation stoving temperature is reached or exceeded. Component B of the paint mainly contains the blocked isocyanate curative, designed to dissociate at a stoving temperature of 140 °C and then react with the polyol. Component A of the paint contains the aliphatic polyol formulation, additives and solvent. Aliphatic polyols are inherently more UV resistant than their aromatic counterparts.

As this particular paint formulation requires a stoving temperature of 140 °C, if the chassis of a vehicle is to be painted it must be free of all sundries that will not tolerate the elevated temperature. The stoving not only helps drive off the solvent but initiates a complex set of curing reactions.

A hand-held Agilent 4300 FTIR, fitted with the external reflectance sample interface (Figure 1), was used for all measurements. The interface allows the measurement of specular reflectance from the sample surface at 45° to normal. To prevent paint adhering to the instrument interface a small square of pierced sacrificial foil was placed over it. The foil was replaced for each measurement.

The external reflectance FTIR spectra of the samples were collected at 64 scans and 4 cm^{-1}, resulting in a spectral acquisition time of under 40 seconds.

First, the FTIR spectra of the two individual paint components, A and B, of the 2K PU paint were collected. Next, the spectra of the correctly mixed paint, applied to a coupon, was measured before and after the coupon received thermal stoving treatment.

Separately, the component mix ratio of the applied paint was quantified. Three more coupons were sprayed, each using a different ratio mix of the two paint components. FTIR spectra were measured at 10 sampling points per coupon. The paint component ratio mixes used are shown in Table 1. The ratios were calculated gravimetrically for higher accuracy rather than volumetrically.

Table 1. The two component paint ratio mixes that were applied to each plate.

Coupon No.	Part A	Part B
1 (Resin rich)	3.99	1
2 (Near correct ratio)	3.06	1
3 (Resin poor)	2.49	1

Results and Discussion

Measuring paint cure

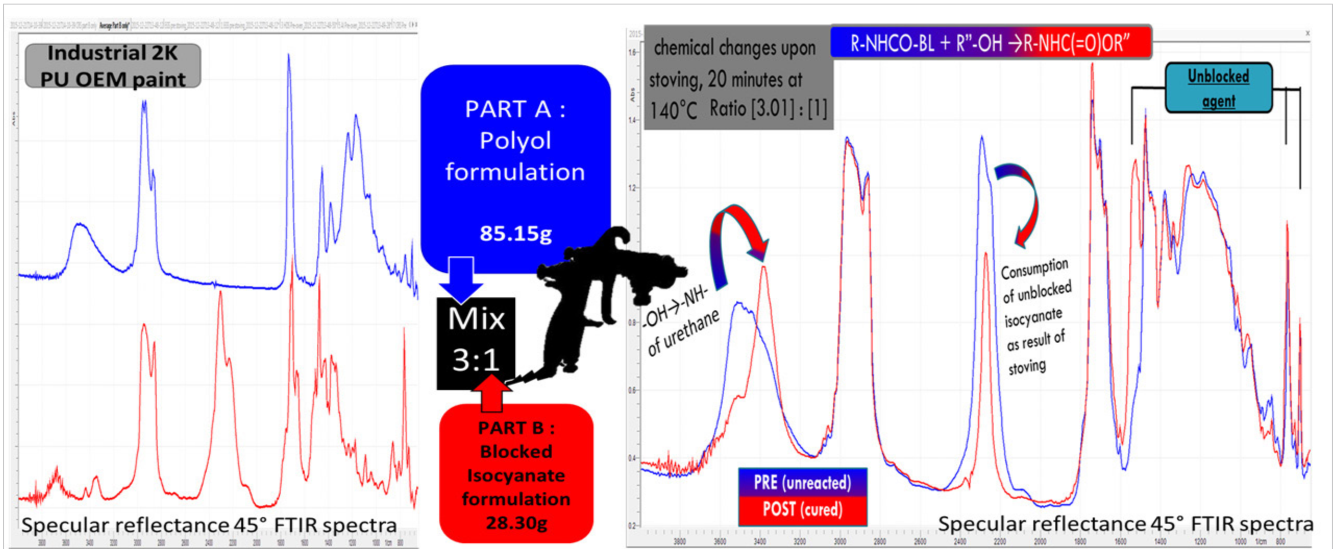

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Figure 2. FTIR spectra of the samples. Left – component A (blue) of the 2K industrial PU paint and component B (red) curative of the 2K PU. Right – pre-stoving (blue-UNCURED) and post stoving (red-CURED).

The spectra, shown in Figure 2, were collected with the external reflectance sample interface, fitted to the Agilent 4300 FTIR instrument.

The two spectra on the left of Figure 2 identify the two component matrices of the 2K PU paint. The spectra are highly detailed with more than enough spectral information for the creation of a specular reflectance library. This could then be used to ensure the right paint mixture is allocated to the correct tank. The spectra could also be used as part of QA/QC to test for storage, delivery or composition changes.

The chemical changes during cure are both measurable and abundant, as shown in Figure 2, Right. The specified 20 minutes for the primary stoving period has introduced many spectral changes that are chemical changes directly related to the curing of the paint. The three main changes are highlighted in Figure 2. These changes have great potential to be used as part of QA/QC tests to determine the degree and quality of the paint cure.

Calculating component mix ratio

Using the spectra from the three sprayed coupons (shown in Figure 3, left), a model was created to calibrate the instrument in preparation to quantify the two paint components when mixed and applied. Using eight of the ten spectra from each sprayed coupon, the calibration model was created by applying a multivariate PLS1 (partial least squares) algorithm using Microlab Expert software. This model was then incorporated into the 4300 FTIR instrument. The remaining two spectra from each plate were used to independently validate the model.

The complexity of the spectra of the paint necessitated the use of the PLS1 chemometric technique. Its use has the advantage of greater robustness than empirical models as well as higher predictive ability. Warnings can be issued if a user attempts to apply the model to a different PU paint system than the one it was created for, preventing type 1 and type 2 errors. The model can also account for intra-sample variance. Earlier attempts at simple univariate- Beer-Lambert based models were unsuccessful.

The time taken to collect all 30 spectra in Figure 3 (left) was less than 20 minutes. Twenty-four of these spectra were used to create the quantitative model, with the remaining six used to validate the model post model finalization.

The average of each Mix-Ratio set of spectra per plate is shown in Figure 3 (Right). As shown in the figure, there are distinctive differences between the spectra of the different component ratios applied to the plates when averaged.

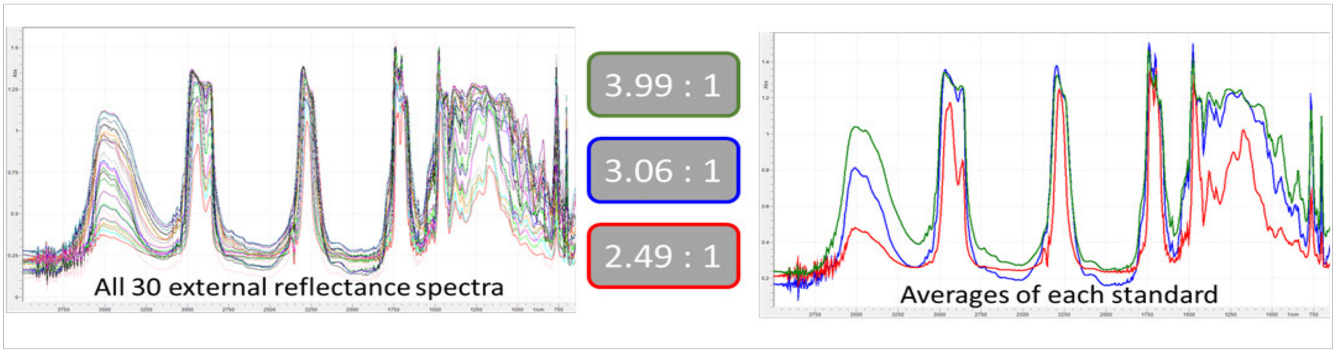

Figure 3. (Left) 3 x 10 external reflectance spectra of the three different ratios. (Right) The average of each 10 spectra, collected from the three coupons. The key to the color-coding of the spectra is shown to the left. Each individual spectra is the cumulation of 128 spectra ran at 4cm^{-1} resolution taking only 40 s per spectra.

The created PLS1 model was validated, using two randomly selected spectra of the ten obtained for each painted coupon. The model proved able to calculate the mix ratio of the applied paint to a high degree of accuracy. The actual mix ratio was plotted against the mix ratio calculated by the model, as shown on the left hand side of Figure 4. The graph shows impressive model statistics, with minimal pre-processing of a simple data mean centre resulting in excellent linearity, low calibration errors and low bias.

The right hand side of Figure 4 shows a visualisation of the model calculations. Spectra 1-10 were collected from the plate to which the paint component ratio 2.49:1 was applied. Spectra 11-20 were collected from the plate to which the paint component ratio 3.06:1 was applied and, finally spectra 21-30 were collected from the plate to which the paint component ratio 3.99:1 was applied. The ideal manufacturer's recommended ratio of this paint is 3:1 for A:B.

The PLS1 model demonstrated both excellent calibration statistics and validation statistics. Both the R and the R2 are better than 0.99 and the standard error of prediction (SEP) was very low at 0.036. This means the paint component ratio can be calculated by the model with 0.04 ratio confidence using a 6-factor PLS1 model.

The calculated paint component ratio value can be used to create a visual quality indicator to the user of the Agilent 4300 FTIR. Figure 5 shows three screen views. The one in the top left is an in-specification paint component ratio, coded green. The screen views in the top right and bottom are ratios that are critically out of specification and are displayed in red. The bottom screen view in Figure 5 also shows the critical low (low threshold) and high (high threshold) values, determined as the ideal component ratio ± 5%. These limits can be tightened or relaxed as per the paint manufacturer's recommendations or the user's specifications or experience with the product.

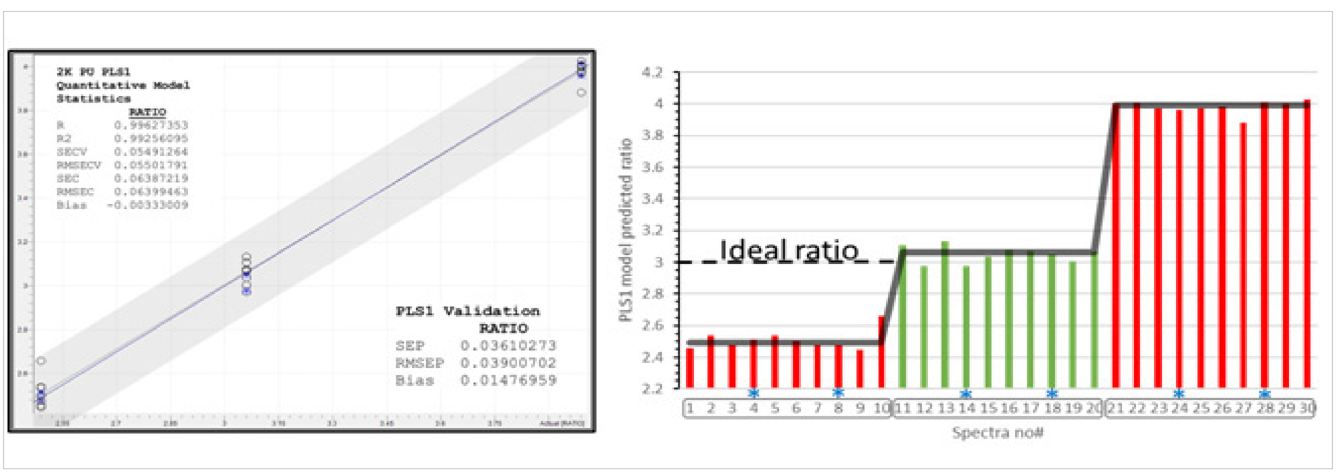

Figure 4. Left. Actual paint component ratios vs values calculated by the model. Right. The paint component ratio, calculated from 24 of the spectra collected. The asterisks (in both graphs) are the independent validation spectra that were not used to create the final model. The black dotted line indicates the ideal ratio of 3:1.

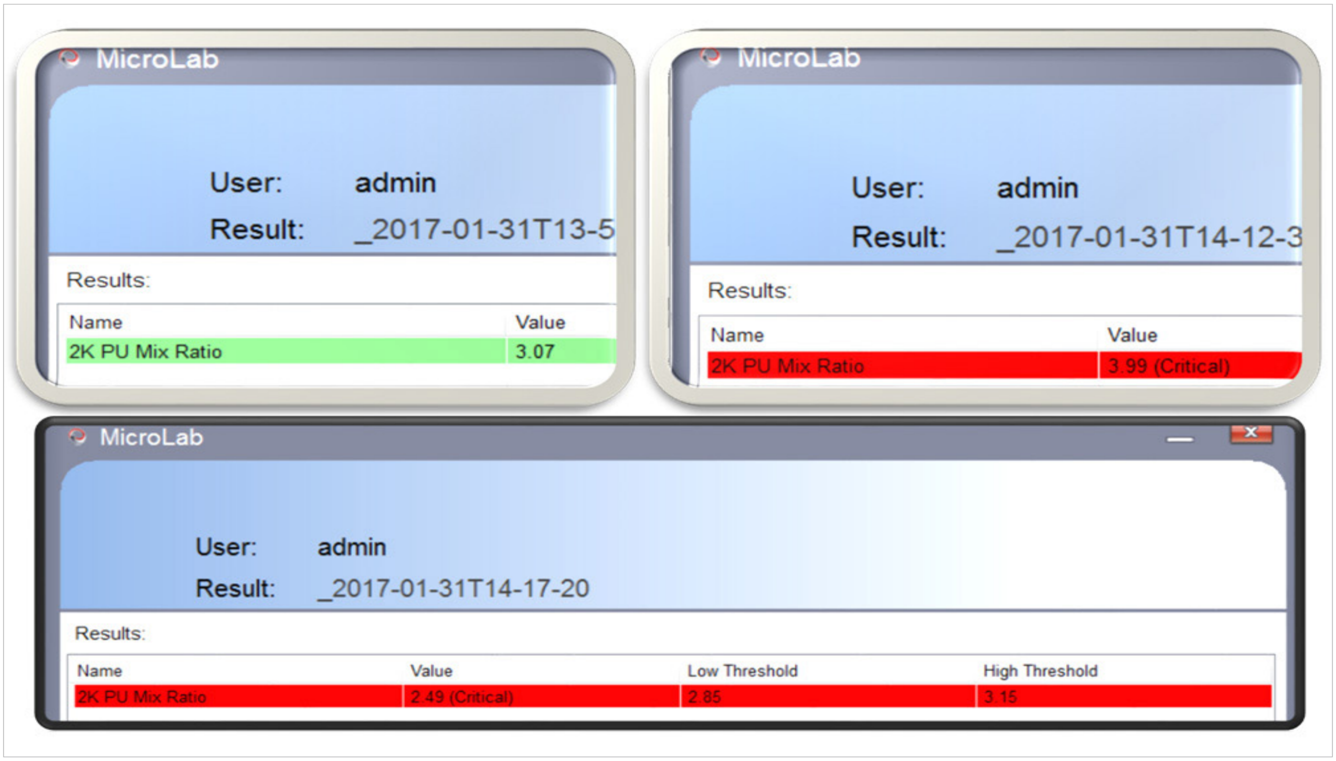

Figure 5. The visual display of the Agilent 4300 FTIR can display color-coded results, based on whether they are in or out of specification. Three example displays are shown here. (Top left). In-specification results are displayed in green. (Top right) Out of specification results highlighted in red (in this case, the resin rich sample). (Bottom) The specification limits can be adjusted in the method—this screens shows the upper and lower thresholds (flagging the resin poor sample).

Conclusion

FTIR spectra, collected with a hand-held Agilent 4300 FTIR instrument, have the potential to form the basis of a quick and accurate method of determining the cure level of a two component polyurethane paint. Spectra from the same instrument could also be used to identify paint component storage, delivery or compositional errors.

A multivariate partial least squares algorithm was used to develop a model for calculating the component ratios in a two component spray paint. Spectra collected from the paint, applied in three different ratio mixes to sample plates, was used to create and validate the model. Collection time for all the spectra needed to create the model was 20 minutes in total.

The model proved able to accurately calculate the ratio of the two paint components in the applied paint. The component ratio can be calculated by the model with 0.04 ratio confidence and has a predictive range of 2.5-4.0 for component A, where 3.0 is the ideal ratio.

The model can be incorporated into a method to be computed by the Agilent 4300 FTIR, combined with the Microlab PC software. Color-coding can be used to identify out of specification paint applications.

The combined instrument, method and user interface form a system that can quantify the as-sprayed paint component A:B ratio deposited onto a coupon in under 40 seconds. By testing the wet coating prior to painting an asset, incorrect mix-ratio application of the coating can be prevented at the point of delivery. This minimizes the risk of costly remedial action or warranty claims. The test can confirm that the paint is applied according to the manufacturer’s design specification and that the spray equipment is correctly adjusted to apply the required component ratio. Models can also be created for manually mixed 2K paints and/or other chemical formulations using the same experimental protocol.

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