Using Beer's Law to Model
Percent Transmittance of Multilayer Composite Coatings

By **Don Campbell** and
Antonette St. Pierre
BASF Corporation

Transmission of light through automotive topcoat and primer layers can lead to degradation of the underlying electrocoat layer and to topcoat delamination. To protect against this, it is critical that transmission of both ultraviolet wavelengths and certain visible wavelengths be effectively blocked by the topcoat and primer layers. The clearcoat, basecoat, and primer each have their own role and combine to protect against light transmission. The transmittance of these combined layers is typically measured by the Integrating Sphere UV-Visible Spectrophotometer. It would both simplify measurement of the topcoat systems and allow better system modeling if these layers could be measured separately and combined using Beer's Law to obtain the transmittance of the total topcoat system. Although some automotive pigments function by reflecting or scattering, we demonstrate here that log-linear models similar to Beer's Law for absorption can still be used to combine these layers and interpolate the effect of individual layer thickness on the total topcoat transmittance.

INTRODUCTION

Measurement of light transmission through automotive topcoats and primers has been practiced for many years. In the 1980s, the integrating sphere spectrophotometer was introduced to accurately measure the total transmittance of systems where the transmission depends on the angle of the incident light.[1]

Basecoats (or color coats) that contain reflective aluminum flake pigment are a common example of such a system. Most measurements now use the integrating sphere geometry.

Many manufacturers have some form of UV transmittance specifications, and these can cover individual layers or even the complete system of primer (if used) plus basecoat and clearcoat. Furthermore, some manufacturers have now extended these specifications to include high energy visible light up to 500 nm since learning that some electrocoats can experience photodegradation even at these lower energies.

It is also known that the thickness of individual layers can be difficult to control precisely over a complex shape such as an automobile, but transmission depends critically upon the thickness of each layer. Some manufacturers use transmittance specifications targeted at less-than-nominal layer thickness to protect against the possibility of an individual layer being thinner than desired. However, over-engineering and wasted cost can occur without a good model to predict the overall transmittance of the system based upon the contribution of individual layers.

The basecoat and primer layers are especially critical for protection against low-energy UV light and high-energy visible light where the clearcoat's UV absorber cannot function. This critical function of the basecoat's pigmentation must be reconciled with the desire to create attractive and stylish new colors annually and with minimal time to market. In addition, the primer layer is now often not baked before application of the basecoat layer as part of an energy saving integrated layering process.

Certain colors, such as blue, allow transmission of high energy visible light by their very nature. In other cases, such as white pearl colors, high transmittance across a wide range of wavelengths results from the desire for a very bright, or "clean" white. In addition, such pearlescent colors often have two color coats making the total system transmittance more complicated. The possibility for the thickness of each layer to vary

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independently in painting makes the robust design of these colors difficult.

It would therefore be desirable to be able to measure each layer independently and then combine the layers mathematically. Beer's law might also be used to interpolate or extrapolate the effect of varied thickness for individual layers on the total system transmittance.

However, many of the pigments used in automotive coatings do not function by absorption where Beer's law has been shown to apply. Examples of such pigments include aluminum flake pigments that reflect light and titanium dioxide (TiO_2) and other opaque pigments that scatter light. The use of Beer's law is further complicated by the use of the integrating sphere spectrophotometer where transmission is averaged over many angles of incidence, and, hence, many pathlengths through the film.

We set out to determine if the absorbance (log transmittance) as measured by an integrating sphere spectrophotometer of coatings with absorbing, reflecting, or scattering pigments was linearly proportional to the layer thickness.

$$\log(T)_{\lambda,\text{film thickness}} = A = \varepsilon_{\lambda}(\text{absorbance/film thickness})*\text{film thickness}$$

$$\log(T) = \log(\text{transmittance}) = A(\text{absorbance}) = \log(\%T)-2$$

We also wanted to determine whether the absorbance of individual layers could be added to obtain the total system absorbance as logically inferred from Beer's law.

$$A_{\text{topcoat},\lambda} = A_{\text{primer},\lambda} + A_{\text{basecoat(s)},\lambda} + A_{\text{clearcoat},\lambda}$$

EXPERIMENTAL

A Varians Cary 4G UV-Visible Spectrophotometer with a Labsphere DRA-CA-5500 Integrating Sphere Reflectance Accessory and Cary WinUV Scan Application Software was used in this experiment. Coatings are placed in a slide with the outside painted surface toward the light source. Percent transmission for the coatings was measured every 10 nm from 290 nm to 800 nm. Each coating was analyzed at several thicknesses. This data was entered into a spreadsheet for manipulation. Modeled data was converted back into percent transmittance because this is the unit used by many manufacturers in coatings specifications.

The primers used in this study are waterborne primers from BASF Coatings and are used in integrated processes. The basecoats are also waterborne for use in integrated processes. The clearcoat is a two-component isocyanate clearcoat. All coatings are available from BASF Coatings in Southfield, MI.

Coating layers were spray applied either individually or as part of a multilayer composite to Tedlar film. Film thicknesses were measured by an Elcometer film thickness gauge over steel. Coating layers can be easily removed from the Tedlar film for measurement of transmittance.

RESULTS AND DISCUSSION

The first coating measured was the clearcoat. Since its absorption is due primarily to UV absorbing dyes, which should obey Beer's law, it provides an opportunity to evaluate any effects from the Integrating Sphere optics and reflection. As with all of the coatings, the logarithm of the percent transmittance is plotted against film thickness at several wavelengths to check for linearity (*Figure* 1). The slope at all wavelengths is then used to model the full transmittance curve at one of the measured thicknesses and compared to the actual measurements (*Figure* 2).

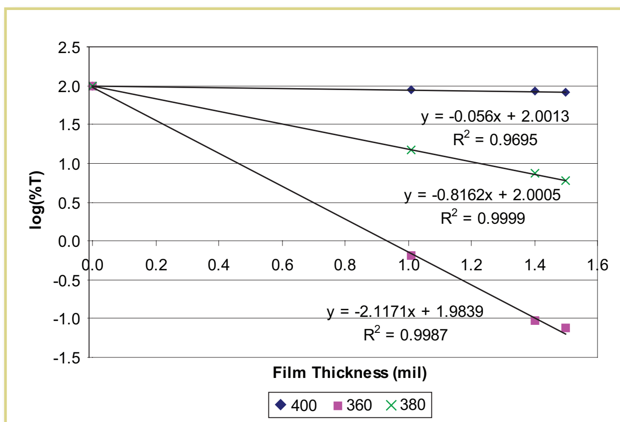

Figure 1—Linearity plot of absorbance versus film thickness for clearcoat with UV absorber.

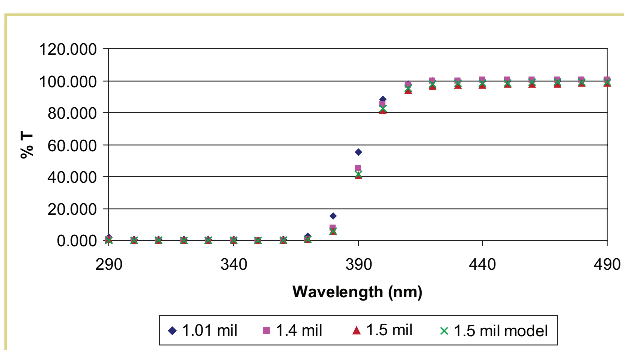

Figure 2—UV-Visible spectrum for clearcoat—modeled and actual at various film thicknesses.

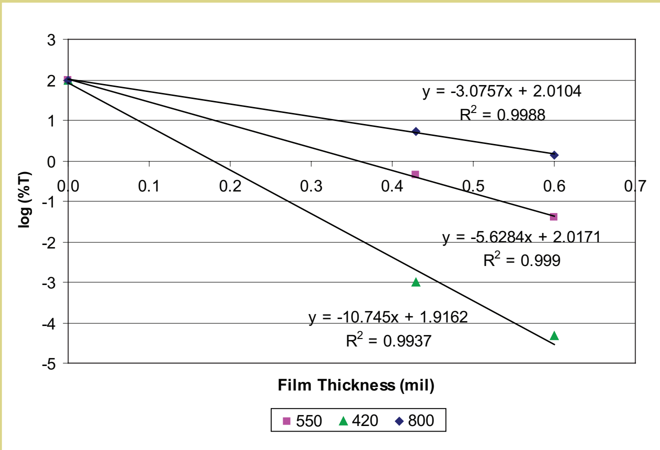

Figure 3—Linearity plot of absorbance versus film thickness for basecoat with black pigment (absorption only).

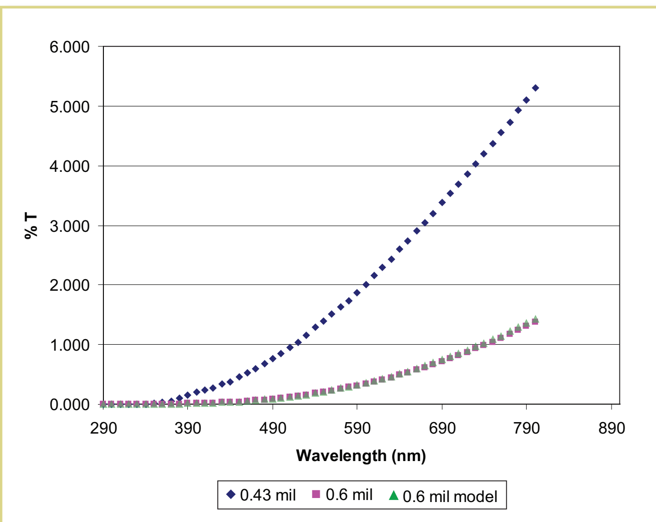

Figure 4—UV-Visible spectrum for black basecoat—modeled and actual at various film thicknesses.

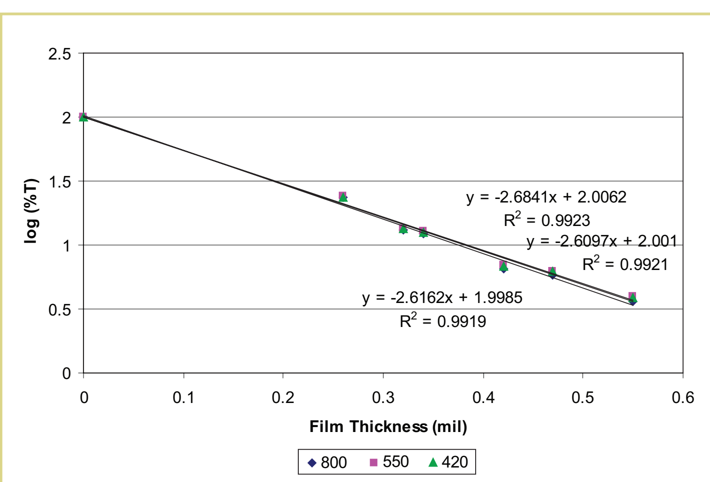

Figure 5—Linearity plot of absorbance versus film thickness for basecoat with aluminum flake pigment (reflection only).

Good linearity is observed, and the data intersects 100% Transmittance (log (%T)=2) at zero film thickness.

For those wishing to create modeled transmittance curves, this can be done easily from the absorbance and film thickness data using the LINEST function for columns of data. Remember the addition of 2.0 before converting back to percent transmittance.

In reviewing the data and slopes in areas of very strong absorption, it is apparent that accuracy of the measurements below 0.1% transmittance is limited. For example, at 320 nm, the measurement for percent transmittance at 2.0 mil of clearcoat was actually slightly higher than that measured at 1.5 mil of clearcoat. Therefore, for purposes of determining the extinction coefficients, it is best to use film thicknesses where the percent transmittance is not much less than 0.10%.

It is also necessary to take the greatest care in measuring the film thicknesses. Multiple measurements were averaged for each thickness and the film thickness gauge was calibrated immediately prior to measuring the films.

As seen here, the percent transmittance at 1.5 mil of clearcoat is modeled well across the spectrum. Likewise, good linearity and modeling are seen with the black basecoat in *Figures* 3 and 4.

Figures 5 and 6 show the same results for a silver metallic basecoat using only reflective aluminum flake pigments. Again, good linearity is seen with 100% transmittance at zero film thickness. Also, the modeled transmittance values match those measured across the spectrum.

We now evaluate white and near-white primers and basecoats to determine whether the model can be extended to pigments that function by light scattering. *Figures* 7 and 8 show good linearity and good predictive modeling for a white primer system.

However, when a white basecoat with higher brightness than the primer was evaluated (L=90 for the basecoat vs L=84 for the primer), the conventional Beer's law relationship did not apply. As seen in *Figure* 9, the absorbance is still linear in the film build range that was measured, but the line does not intercept 100% transmittance at zero film. Rather, it appears that the film has a higher extinction coefficient at thin films and that the extinction coefficient has a lower value at thicker films.

To verify this effect, a model white coating was prepared with only TiO_2 pigment (scattering pigment only). A second coating was prepared like the first but with a small amount of carbon black added (scattering plus absorbing pigments). The linearity of these two coatings is shown in *Figure* 10. It confirms the greater nonlinearity at thin films for the coating containing only TiO_2; that is, the intercept value for the TiO_2-only film is further below 2.0.

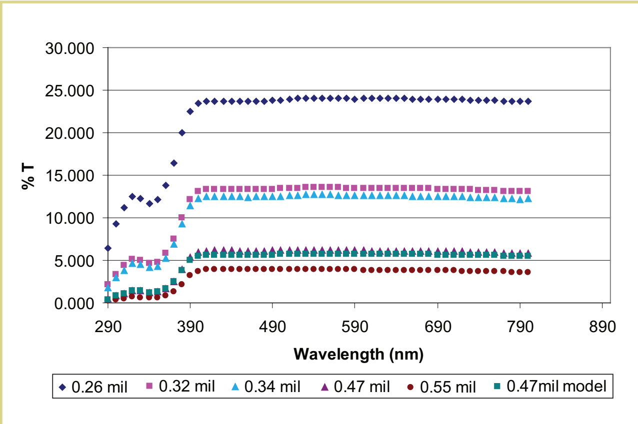

Figure 6—UV-Visible spectrum for silver basecoat—modeled and actual at various film thicknesses.

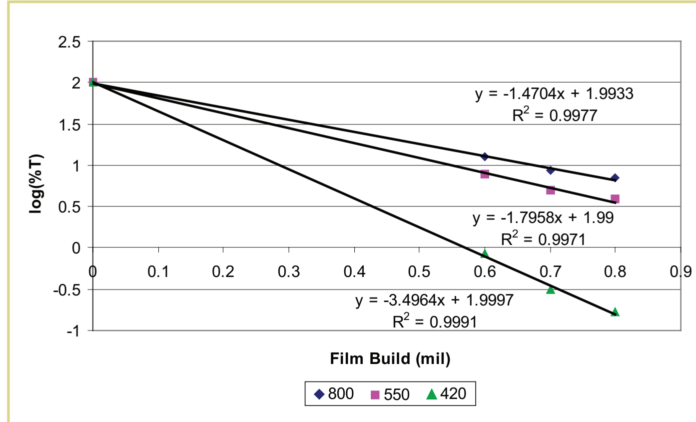

Figure 7—Linearity plot of absorbance versus film thickness for primer with white and black pigment (scattering plus some absorption).

To understand this effect, we considered the nature of light scattering compared to light absorption. A schematic is shown in *Figure* 11. For pigment of high refractive index and with a diameter much greater than the wavelength of the incident light, the incident light is scattered equally in all directions.

Applying this to a coating layer containing scattering pigments affords an explanation of the observed nonlinearity. From the schematic in *Figure* 12, it can be seen that, for pigment particles near to the surface, light scattered out of the film can leave the film without interference. However, for particles deeper into the film, light that is scattered "out" of the film can strike another pigment particle and be scattered back "in" to the film.

The introduction of absorbing pigments would result in the possibility of absorption before backscattering could occur. This would decrease the nonlinear effect as is demonstrated with the addition of black pigment in *Figure* 10. This phenomenon is also consistent with the weak and peculiar substrate hiding characteristics of white coatings.

Due to the difficulty of preparing continuous films at low thickness and the difficulty of handling such thin films, the transition from this high to low extinction coefficient was not measured directly by the authors, but is logically inferred from the data. Indeed, the precise point of transition will depend upon several factors including the pigment loading level (PVC) and the particle size of the scattering pigment.

Nonetheless, it is critical to note that the absorption was linear over the practical operating range of film thicknesses for all of the coatings studied. Thus for the bright basecoat shown in *Figure* 9, a model with the introduction of an intercept other than zero absorbance at zero film was used to successfully predict the transmittance curve for the white basecoat (*Figure* 13).

$$\log(T)_{\lambda,\text{film thickness}} = \varepsilon_{\lambda} * \text{film thickness} + \text{constant(intercept)}$$

For those wishing to model the transmittance curves, this is done by using the SUM(LINEST(),{}) function for each wavelength.

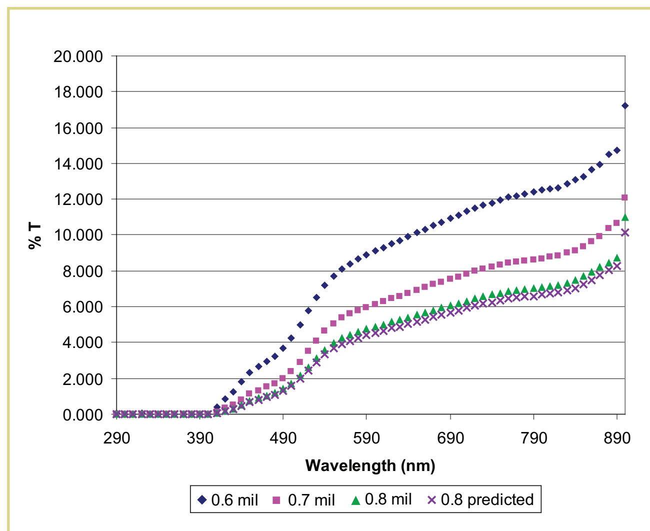

Figure 8—UV-Visible spectrum for white primer—modeled and actual at various film thicknesses.

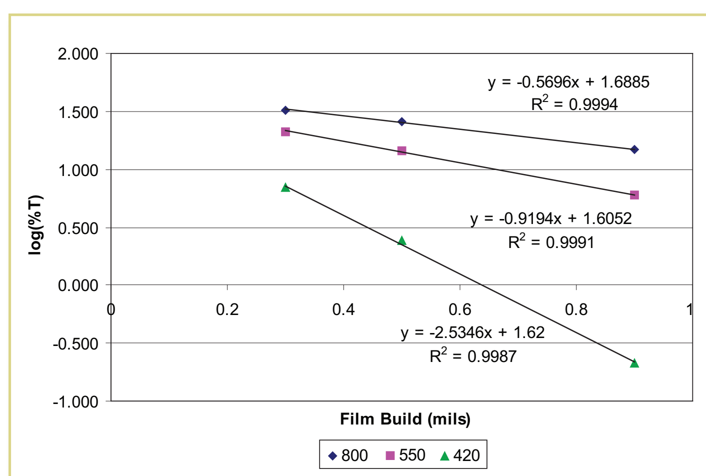

Figure 9—Linearity plot of absorbance versus film thickness for basecoat with white pigment (scattering only).

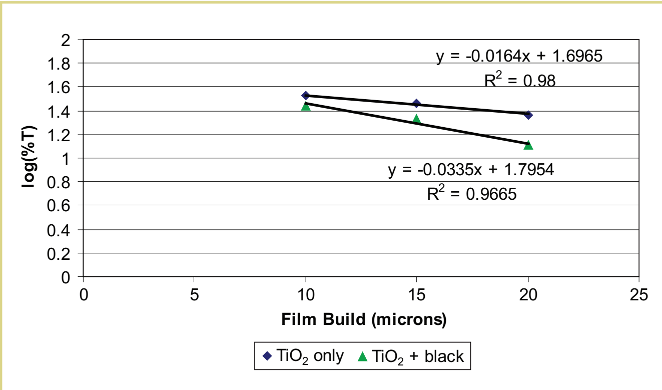

Figure 10—Linearity plot of absorbance versus film thickness for primer with white and black pigment compared to white pigment only.

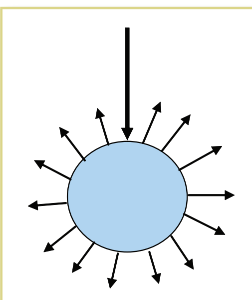

Figure 11—Scattering by opaque pigments—pigment diameter > wavelength of light.

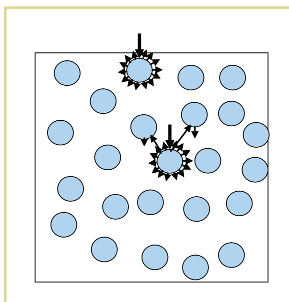

Figure 12—Scattering of pigment particles in film showing the effect of the particle's location within the film.

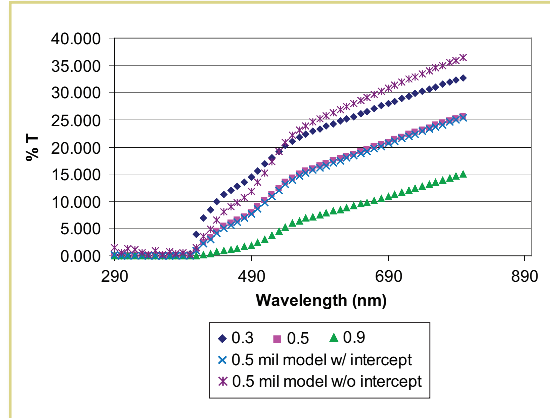

Figure 13—UV-Visible spectrum of white basecoat—actual at various film thicknesses and modeled with and without intercept.

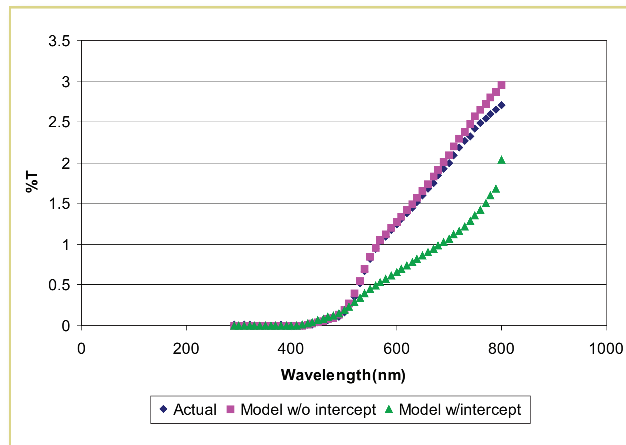

Figure 14—UV-Visible spectrum of white pearl tricoat. Primer, groundcoat, midcoat, and clearcoat are modeled and added using Beer's law. Groundcoat is modeled both with and without an intercept.

This amended model can be used only if the scattering layer is the uppermost pigmented layer in the multilayer composite coating. However, the white basecoat shown here is actually a white groundcoat that is used below a mica-containing midcoat in a "white pearl"-type composite. Thus, even scattering at the surface of the groundcoat might be reflected back into the film by the mica pigments in the midcoat.

To evaluate this effect, we sprayed the complete layering of this white pearl composite coating including primer, groundcoat, midcoat, and clearcoat (0.7, 0.7, 0.4, and 2.3 mil, respectively). We then modeled this composite with a nonzero intercept for the groundcoat and with a zero intercept (no intercept) groundcoat. The transmittance curves for the measured composite and for the two models are shown in *Figure* 14.

As is seen, the model with the zero intercept for the groundcoat layer best predicts the measured transmittance. This supports the effect of backscattering (or back-reflection) from the midcoat layer. It also demonstrates that the absorbance of even complex multilayer composite coatings can be modeled using the sum of the individual layer absorbances.

CONCLUSIONS

Linearity of film thickness and absorbance has been demonstrated for a variety of automotive topcoats in accordance with Beer's Law. A clearcoat and basecoats containing absorbing or reflecting pigments have shown linearity over the entire film thickness range. Basecoats that contain exclusively scattering pigments, such as titanium dioxide, show nonlinear behavior at low film thicknesses, but then reach a point of linear behavior within their normal operating range of film thickness. It has also been demonstrated that absorbance can be measured for individual layers of a multilayer composite coating and then added to obtain the total absorbance for the multilayer composite. CT

References

1. Jacquez, J.A., McKeehan, W., Huss, J., Dimtroff, J.M., and Kuppenheim, H.F., "Integrating sphere for the measurement of reflectance with the Beckman Model DR recording spectrophotometer," *J. Opt. Soc. America,* 45, 971–975, (1955).

AUTHORS

Don Campbell and **Antonette St. Pierre**, BASF Corporation, Southfield, MI.