Advantages of Multi-Flux Methods for Relating the Colour Appearance of a Material to its Composition and Structure

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Colour & Appearance of Paint

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Introduction

Relatively simple theories, such as the Schuster-Kubelka-Munk theory [1] are often used to relate the colour appearance of a material to its composition. These types of theory are able to predict well the colour properties of conventionally pigmented materials that are uniform in composition. The most common practical application is in computer-based systems of formulation prediction used as an aid when colour matching inks, paints and other types of surface coating.

The paper describes some of the limitations of the simple theories and suggests changes that have the potential for application to a wider range of materials. The principle suggestion is a more versatile method of taking into account the range of paths and directions that the light beams can follow as they interact with the material.

Interaction of light with a material

The four types of interaction that need to be considered when light is incident on the surface of a material are illustrated by Figure 1.

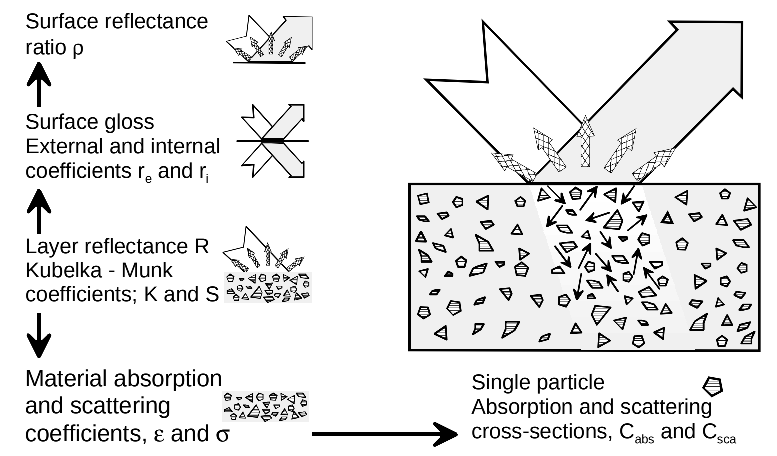

Figure 1: Linking the material absorption and scattering coefficients to the reflectance of a coating layer.

The first type of interaction occurs at the air-to-coating boundary. The refractive index changes at the boundary, n = 1.0 for air and n = 1.5 is a representative value for a polymeric coating material. The change results in partial reflection of the light that is incident on the boundary. The light reflected at the air-to-coating boundary may be seen as gloss by the observer, it adds to the light that is reflected by the body of the material and may be included in the light detected by a colour-measuring instrument. The fractional amount of light reflected (r_e) and transmitted (t_e) at the air-to-coating boundary depends on the angles at which the light strikes the surface. At normal incidence on an optically flat boundary (glossy) about 4% of the incident light is reflected. Around 9% of light with a diffuse range of incident directions is reflected by an air-to-coating boundary [2].

The second type of interaction that occurs is with the components of the body of the material. The light energy can be absorbed and converted to heat or be scattered in direction by the components that make up the body of the coating. The ability of a component to absorb light is characterised by the absorption extinction coefficient (ε) with units of m^{-2}. The coefficient determines the fraction (ε dX) of a collimated beam of light that is absorbed as it travels through a thin layer of the material of thickness dX. The corresponding ability of a component to scatter light is characterised by the scattering extinction coefficient (σ) with units of m^{-2}.

The extinction coefficients of a material are determined from the properties of the components by adding together contributions according to their volume fraction. For example, consider the absorption extinction coefficient of a coating material (ε_m) containing a white pigment ($\varepsilon_w = V_w\hat{\varepsilon}_w$) and a coloured pigment ($\varepsilon_p = V_p\hat{\varepsilon}_p$) distributed within a binding medium ($\varepsilon_b = V_b\hat{\varepsilon}_b$), then

Equation 1: $\varepsilon_m = V_b\hat{\varepsilon}_b + V_w\hat{\varepsilon}_w + V_p\hat{\varepsilon}_p$, and $\sigma_m = V_b\hat{\sigma}_b + V_w\hat{\sigma}_w + V_p\hat{\sigma}_p$

Where V is the volume fraction of the component, $\hat{\varepsilon}$ $\hat{\sigma}$ are the "per unit volume" extinction coefficients and the subscripts m, b, w and p denote the material, the binding medium, the white pigment and the coloured pigment respectively.

The reflectance (R_0), transmittance (T_0) and absorptance ($A_0 = 1 - R_0 - T_0$) of the layer of coating material can be related to the extinction coefficients, however in order to do this assumptions need to be made about the angular distribution of the light travelling within the material. The accuracy of these assumptions has a strong influence on the reliability of the prediction of the optical properties of the composite material.

A third type of interaction, present when the coating layer is semi-transparent, is the reflection of the light transmitted through the layer by the underlying substrate. The term R_g is commonly used to represent the fraction of the incident light that is reflected by the substrate. The value is determined by the properties of the substrate material, however it is influenced by the nature of the boundary between the substrate, the nature of the coating layer and by the angular distribution of the light that is incident on the boundary.

The fourth interaction concerns the transfer of the light that is within the body of the material to and from the outside of the material. This light undergoes partial reflection (r) and transmission (t) by the coating-to-air boundary. For example around 60% of light with a diffuse range of incident directions is reflected at a coating-to-air boundary [2].

Reflectance of the composite material

The overall reflectance ratio of the composite material (ρ) is determined in two steps. In the first step, illustrated in Figure 2, the Stokes method is used to determine the net reflectance of two layers from the properties of each layer.

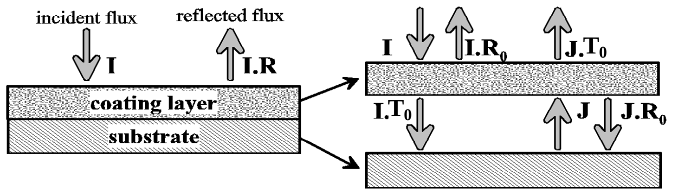

Figure 2: Imagined splitting of the composite to relate the reflectance (R) to the properties of the components

The body reflectance (R) of the composite material is related to the substrate reflectance (R_g) and the properties of the layer (R_0, T_0) by the equation:

Equation 2: $$R = R_0 + \frac{T_0^2 . R_g}{1 - R_0 . R_g}$$

The second step takes into account the effect of the air-to-coating boundary; the Stokes method is again used to relate the "external" reflectance of the material (ρ) to the body reflectance R and the partial reflectance (r) and transmittance (t) of the boundary. The subscripts "e" and "i" in Equation 3 denote values for transfer across the air-to-coating boundary and for transfer across the coating-to-air boundary respectively.

Equation 3: $$\rho = r_e + \frac{t_e . t_i . R}{1 - r_i . R}$$

Two flux model of light interaction in a layer

The Schuster-Kubelka-Munk theory is often used to determine the layer properties R_0 and T_0. The theory assumes that there is a diffuse angular distribution of light intensity within a light scattering material. The light energy flow within a material is treated by splitting into an upwards travelling flux (J) and a downwards travelling flux (I), as illustrated in Figure 3.

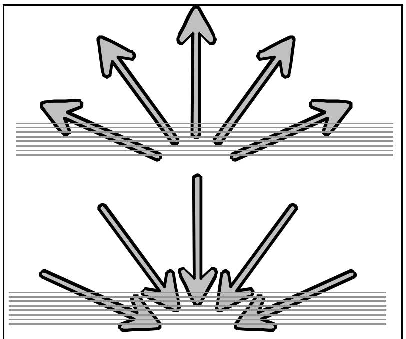
Figure 3: Two diffuse fluxes

The absorption coefficient (K) and the scattering coefficient (S) for each energy flux are defined in the following way.

K.dX. The fractional amount of power lost from a flux by absorption as it passes through a thickness dx of material.

S.dX The fractional amount of power lost from a flux by scattering as it passes through a thickness dx of material.

The optical properties of the coating layer of thickness D, in terms of the reflectance (R_0), transmittance (T_0) and absorptance (A_0) are related to K and S by the equations

Equation 4 $$R_0 = R_\infty \left(\frac{1 - e^{-Z}}{1 - R_\infty^2 e^{-2Z}} \right), \; T_0 = \left(1 - R_\infty^2\right)\left(\frac{e^{-Z}}{1 - R_\infty^2 e^{-2Z}} \right), \; A_0 = 1 - R_0 - T_0$$

and $$Z = D\sqrt{K(K+2S)}\,,\ R_\infty = \left(1+\frac{K}{S}\right) - \sqrt{\left(1+\frac{K}{S}\right)^2 - 1}$$

The flux coefficients K and S may be related to the extinction coefficients ε and σ by considering the average distance travelled by light within the flux compared to the net movement along the flux direction. For example, when the flux moves through a distance dX, the light within the flux travelling along a direction at an angle θ to the flux direction will move through the longer distance $dX/\cos(\theta)$. The ratio of the average distance travelled by light within the flux to the distance moved by the flux is known as the path-length-gain factor of the flux (g). In the case of diffuse light, the gain factor is g = 2.0, so that:

Equation 5 $K = g\,\varepsilon = 2\,\varepsilon$, $S = (g\,\sigma)/2 = \sigma$

In deriving the relationships shown in Equation 4, the path-length-gain factor is assumed to be the same for both the down-flux and the up-flux and to stay constant as the light flux travels through the layer.

The assumptions of the two-flux model are reasonably satisfied by a conventionally pigmented coating layer on a diffusely reflecting substrate, such as card or paper, which is illuminated by diffuse light. However they are not satisfied in several other circumstances, for example when a collimated beam of light illuminates the surface. Under these conditions the gain factor “g” for the down-flux is not a constant. The value is initially 1.0 at the illuminated surface and increases with distance into the layer as the down-flux is progressively scattered into a wider range of directions. The simple two-flux theory, which assumes constant “g”, will not provide an accurate prediction of the colour properties under these illumination conditions.

Multi-flux model of light interaction in a layer

There have been several suggestions for optical models that use three or more fluxes of light energy. A major disadvantage of moving away from the two-flux concept is that the mathematical complexity increases dramatically and the equations obtained are, in most cases, so complex that they have limited practical value.

One version of a three-flux theory [3, 4] is a simple extension to the two-flux theory that introduces the concept of an incident flux and two interacted fluxes. A simple illustration of the concept is shown in Figure 4.

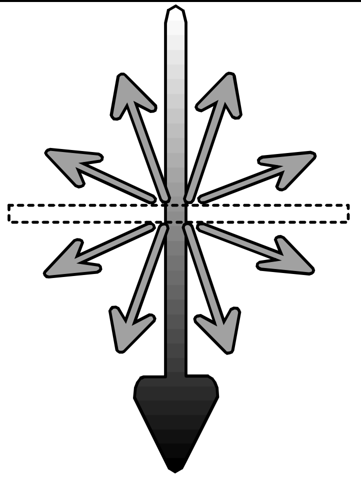

Figure 4: Three flux model, an “incident” flux is scattered into a down and an up “interacted” flux.

At the top surface of the material, the incident flux (i) contains all of the light that illuminates the surface. The incident flux loses energy by absorption and by scattering as it travels through the layer. The light scattered from (i) as it travels through the layer is transferred partly into the "down" interacted flux (I) and partly into the "up" interacted flux J.

The absorption and scattering coefficients for the incident flux are "*k*" and "*s*" respectively and they are related to ε and σ through the path-length-gain factor (g_{in}) in a similar way to Equation 5.

Equation 6 $\quad k = g_{in}\,\varepsilon, \qquad s = (g_{in}\,\sigma)/2$

The angular distribution of intensity within the incident flux (i) is determined by the nature of the illumination, which could be a collimated beam of light ($g_{in} = 1.0$) or it could be a diffuse flux of light ($g_{in} = 2.0$). The change in energy as the flux passes through a thin layer of the material (dX) is given by

Equation 7 $\quad \mathrm{di}(\mathrm{X}) = -(k + 2s)\,\mathrm{i}(\mathrm{X})\,\mathrm{dX}$

Each of the interacted fluxes gains energy from the light scattered from the incident flux (i) and can lose energy by absorption and by scattering. The light energy lost by scattering from one interacted flux is gained by the other interacted flux. The changes in energy as the interacted fluxes pass through a thin layer of the material (dX) are given by

Equation 8
$$\mathrm{dI}(\mathrm{X}) = [-(\mathrm{K}+\mathrm{S})\mathrm{I}(\mathrm{X}) + \mathrm{S}\mathrm{J}(\mathrm{X}) + s\,\mathrm{i}(\mathrm{X})]\mathrm{dX}$$
$$\mathrm{dJ}(\mathrm{X}) = -[-(\mathrm{K}+\mathrm{S})\mathrm{J}(\mathrm{X}) + \mathrm{S}\mathrm{I}(\mathrm{X}) + s\,\mathrm{i}(\mathrm{X})]\mathrm{dX}$$

Results and discussion

The simplest expressions derived from the three-flux model concerns the reflectance of an opaque layer of the coating material and these are shown in Equation 9.

Equation 9
$$\mathrm{R}_\infty = \frac{\alpha\left(\sqrt{\mathrm{K}(\mathrm{K}+2\mathrm{S})} - \mathrm{K}\right)}{\alpha\sqrt{\mathrm{K}(\mathrm{K}+2\mathrm{S})} + \mathrm{K}}, \text{ where } \alpha = \frac{g_{in}}{g}$$
and
$$\frac{\mathrm{K}}{\mathrm{S}} = \left[\frac{(1-\mathrm{R}_\infty)^2}{2\mathrm{R}_\infty}\right]\left(\frac{1}{\mathrm{C}_0 + \mathrm{C}_1\mathrm{R}_\infty}\right), \text{ where } \mathrm{C}_0 = \frac{1+\alpha}{2\alpha} \text{ and } \mathrm{C}_1 = \frac{1-\alpha^2}{4\alpha^2}$$

The accuracy of prediction this version of the three flux model can be determined by comparison of predicted values with the exact reflectance values determined by Giovanelli [5]. Giovanelli's values for the reflectance from the surface of an opaque, conventionally pigmented material illuminated by a collimated beam of light are compared in Table 1 with those predicted by the two-flux and by the three-flux theories.

Table 1 and Figure 5 show that the predictions of the two-flux model are over 10% in error in the middle part of the reflectance range. The error is reduced at low and high reflectance, as shown by Figure 5. In contrast the three flux model, with gain factor values of g_{in} = 1.0 and g = 2.0, has a prediction error of less than 1% throughout the range.

The results for a second example material are shown in Figure 6. The three flux method has been used to model the metallic reflectance and diffuse reflectance of a polished metallic surface coated with various thicknesses of a conventionally pigmented material.

Table 1: Exact [5] and predicted reflectance values for an opaque layer illuminated with collimated light.

ε/σ	Exact	Prediction	
	% Refl.	Two flux	Three flux
0.0050	81.7	86.8	81.4
0.0256	64.1	72.7	64.0
0.111	41.5	51.9	41.9
0.429	20.9	29.2	21.6
1.000	11.5	17.2	12.1
2.333	5.7	8.9	6.1

The surface is modelled for illumination by a collimated beam of light at near to normal incidence and the reflectance is determined at two viewing angles, the specular angle and an off-specular angle. The metallic surface modelled has a reflectance of %R = 90.0 and the coating material has absorption and scattering extinction coefficients that correspond to medium grey appearance as an opaque layer (%R_{opq} = 50.0).

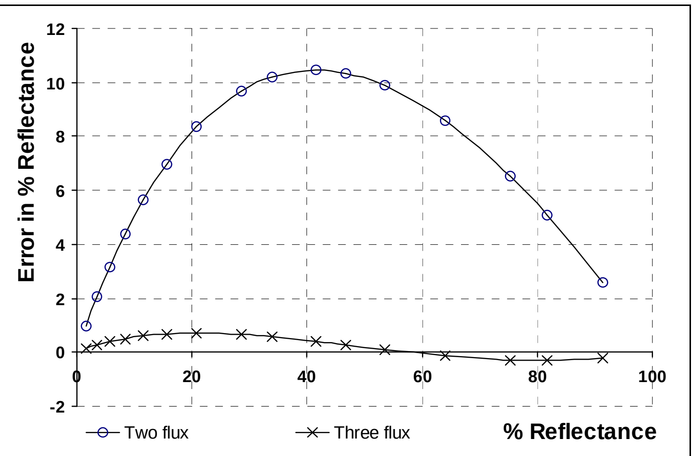

Figure 5: Error in prediction of the reflectance of an opaque layer illuminated by a collimated beam of light

The variation in the reflectance of the surface, when viewed at the specular angle is shown as “%R Metallic” in Figure 6. The amount of light reflected at the specular angle, decreases very rapidly as the coating thickness is increased. At this viewing angle the appearance would change from a bright metallic glare to a diffuse, mid-grey solid-colour.

The appearance of the surface when viewed at an off-specular angle is determined by the amount of diffuse light that leaves the surface of the material, expressed as “% R Diffuse” in Figure 6. The light removed from

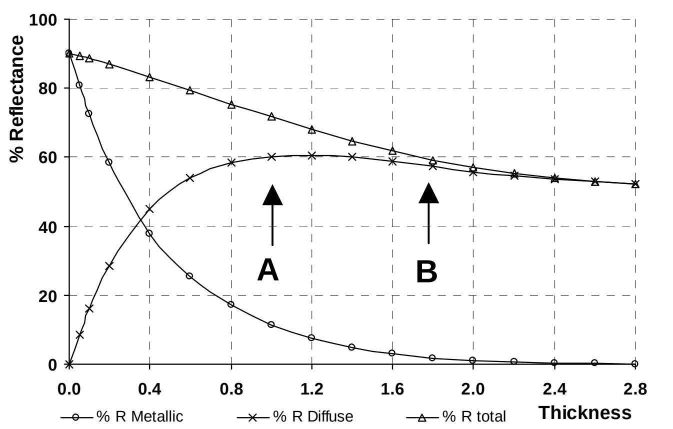

Figure 6: Modelled reflectance of a metallic surface (%R = 90) coated with various thicknesses of a conventionally pigmented material (%R_{opq} = 50)

the collimated incident beam by scattering will be transferred partly into the diffuse down-flux and partly into the diffuse up-flux. The figure shows that the diffuse reflectance increases rapidly as the layer thickness is increased, reaches a maximum, and then decreases steadily to the opaque layer reflectance.

When viewed at an off-specular angle, the surface will initially appear dark for thin coating layers, and then increase in lightness towards mid-grey as the thickness is increased. It is interesting to note that the panel coated with a middle thickness coating (point A in Figure 6) is predicted to be noticeably lighter, when viewed at an off-specular angle, than that of the thick coated panel (point B in Figure 6).

Multi-flux models can be used for purposes other than the prediction of the colour of materials; an example is the prediction of the total energy flux density at various positions within the coating layer. The energy flux density has a direct influence on the solidification rate of radiation cured coating materials [3].

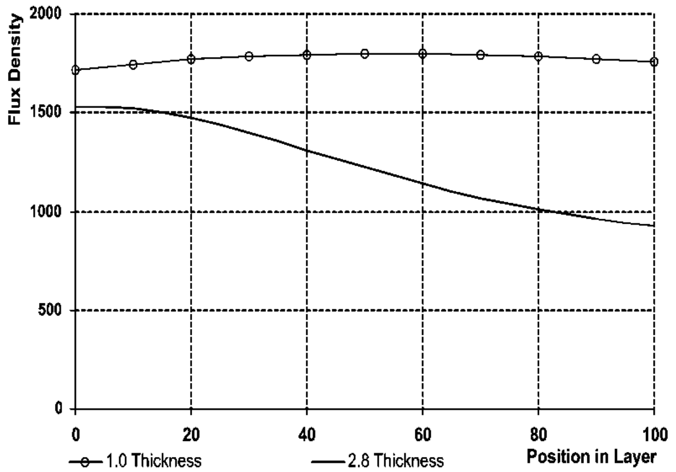

Figure 7: Energy flux density at positions in the layer

The results for the prediction of flux density by the multi-flux model for two of the thickness values shown in Figure 6 are shown in Figure 7. Note that at a thickness of 1.0 unit, the flux density is almost constant throughout the layer. Whereas at a thickness of 2.8 unit there is a significant reduction (60%) in energy density with distance from the top layer, giving an indication of the change in cure-time that might be needed for a through cure of a coating of this thickness.

Conclusions

The method of use of three-flux optical model for predicting the reflectance properties of opaque materials and of semi-transparent coatings on substrates has been explored.

An improved accuracy of prediction of reflectance of an opaque material has been demonstrated for the three-flux model compared to the conventional two-flux (Schuster-Kubelka-Munk) model.

The results have demonstrated the use of the three-flux method for modelling the appearance of coatings applied to metallic-appearance substrates.

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