Radiation-transfer Calculations for the Diffuse Reflectance from Pigmented Coatings

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Abstract

We use a numerical solution of radiation transfer equations to calculate the diffuse reflectance of a pigmented film composed by a transparent pigment embedded in a latex resin. We introduce in the calculation experimentally determined values for the optical absorption of the resin as well as for the particle size distribution of the pigment, and analyze the sensitivity of the diffuse reflectance to the different parameters of the model.

Introduction

The optical appearance of pigmented coatings can be partly described and measured through its diffuse reflectance, that is, the fraction of light reflected in all different directions. The spectral dependence of the diffuse reflectance can be measured in a spectrophotometer with an integrating sphere that collects all the light reflected from the sample, with either a diffuse or collimated incidence. The lack of a full understanding of how this diffuse reflectance depends on the geometrical and optical parameters that describe the system has been one of the main obstacles for a rational and optimized formulation of paints, as far as optical properties are concerned.

From the electromagnetic point of view the source of this lack of understanding comes from the difficulties that arise for finding an adequate treatment for the multiple scattering of light within the pigmented film. Although the problem of multiple scattering in colloidal and granular systems has a long history, and many different approaches have been devised and models with different degrees of sophistication have been tested [1, 2], the interaction of light in paint films has very particular features. For example, high-quality white paints require of non-absorbing pigments with a large scattering power and high volume concentrations embedded in a transparent matrix.

Our main objective here is to analyze if a radiation-transfer approach for the multiple scattering of light can provide a useful and quantitative tool for the prediction and understanding of the above-mentioned dependence. There have been also many attempts to carry out this same analysis, and one of the problems that has been always faced is the lack of reliable information about the precise value of several parameters of the model. In this sense a discrepancy between the theoretical predictions and the reflectance measurements does not yield a clear hint about the sources of disagreement. For this reason and in order to characterize the pigmented films as precise as possible we choose here a very simple system that consists of only TiO_2 rutile crystallites (pigment) embedded in a transparent latex resin (matrix)**. We will call this system *simplex*.

In a previous study on *simplex* [4], a consistency test was proposed in order to trace back, as well as possible, the sources of disagreement between theory and experiment, even when the value of some of the parameters of the model were either inaccessible or poorly known. In this study [4], *simplex* films with a thickness of around 100 microns were prepared over a black substrate. The diffuse reflectance of each was measured as a function of the incident wavelength in the optical range (400–700 microns) and these spectra were then inverted by fitting the spectral dependence of the model parameters, using the simple two-flux radiation-transfer approach devised by an improved version of Kubelka-Munk (KM) [5]. Some of these parameters should, for example, be independent of the thickness of the film and others should depend linearly on the volume filling fraction of the pigment. The inversion procedure was then repeated using reflectance spectra measured on samples with different thicknesses and different pigment filling fractions. Therefore, a lack of consistency in the spectral dependence of the parameters fitted in this way could be taken as an indication that the KM approach itself might not be adequate. The KM approach considers the existence of only two fluxes, one going down the film and another going back up. The scattering and absorption properties of the colloidal particles are described in terms of two phenomenological parameters, usually denoted as S and K, respectively. In Ref. [4] the pigment was taken as a collection of identical non-absorbing spheres randomly located and the main results of the analysis

were the following: (i) the resin cannot be regarded as completely transparent (nonabsorbing) because a small absorption coefficient was definitely required to fit the experimental data, (ii) the KM approach is not adequate either in optically thin films with nonabsorbing pigments or in the spectral region where the absorption of the pigment is significant.

In this work we heal some of the problems and shortcomings that were present in Ref. [2] by (i) using the full numerical solution of the radiation-transfer equations, known as the discrete ordinate method (DOM) or the N-flux method, and (ii) by incorporating actual measurements of the particle size distribution of the pigment and the absorption of the resin. We also perform a careful analysis of the sensitivity of the diffuse reflectance on different relevant parameters of the model with some surprising results, concerning the effects of agglomerates and the optical absorption of the resin.

Model

By direct observation of the TiO_2 crystallites using electron microscopy and taking into account their random orientation within the film, we conclude that it is possible to regard them as a collection of spheres with a definite size distribution. The size distribution was obtained directly from an assortment of electron micrographs, taking care in distinguishing the size of the individual crystallites in case of agglomerates. The size distribution obtained in this way was fitted to a log normal distribution of radius a, that is,

$$D(a, a_0, \sigma) = (1/\sqrt{2\pi} a \log \sigma) \exp \left[- \left(\log (a/a_0) / \sqrt{2} \log \sigma \right)^2 \right] \quad (1)$$

with $a_0 = 0.11\ \mu m$ and $\sigma = 1.34$.

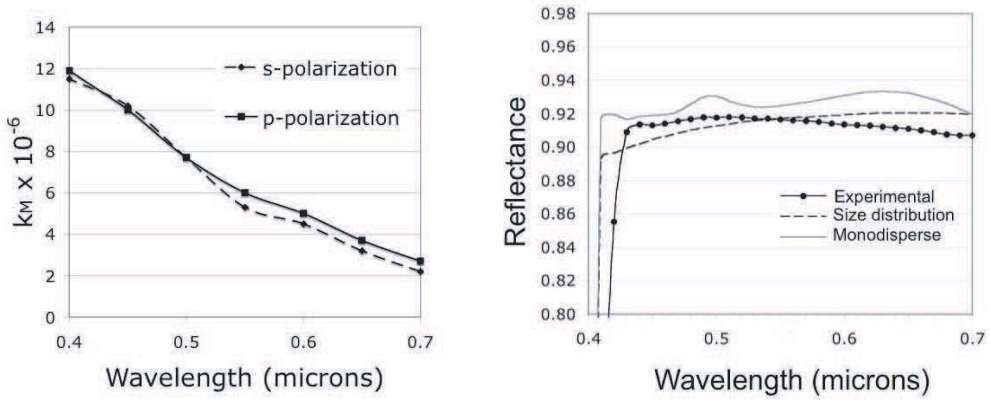
The coating can be then modeled as a collection of TiO_2 spheres randomly located (with a uniform and isotropic probability density) within an otherwise homogeneous matrix with plane parallel interfaces. We will consider that the film is located on top of a black (totally absorbing) substrate and is illuminated from air across the other interface. The spectral dependence of the complex index of refraction of TiO_2 is taken from the literature [6], the real part lies between about 3.2 at the blue side and about 2.6 at the red side of the optical spectrum, the imaginary part is essentially zero up to about 400 nm were the uv absorption peak starts to rise. The spectral dependence of the complex index of refraction of the resin was measured using an attenuated-total-reflection technique in a prism configuration. The real part lies between about 1.53 at the blue side and about 1.48 at the red side of the spectrum. We show in Fig. 1a the imaginary part k_M of the index of refraction when measured with s- and p- polarization. Here, note the consistency of the measurements with two different polarizations and that the magnitude of k_M lies between 5×10^{-6} and 2×10^{-5}. It is important to point out that, although the magnitude of k_M is quite small, the overall effect in the decrease of the diffuse reflectance is considerable (a few percent) and can be explained by recalling that multiple scattering enlarges the actual "path" of the scattered (diffuse) beam, enhancing in this way the absorption due to the matrix. Explicit calculations show that, in this case, the decrease in reflectance due to the matrix absorption can be as large as 8% (!), definitely a considerable amount.

The treatment of the multiple scattering of light within the film is performed through the numerical solution of the radiation-transfer equations, and we analyze the case when the system is illuminated with diffuse light, that is, light coming with equal probability from all possible directions. Taking the z-axis perpendicular to the interfaces of the film, and owing to the symmetry properties of the system the direction of a light beam is given by its azimuthal angle only.

Thus one can take as elements of volume thin sheets of width dz and describe the scattering and absorption process in these sheets by first constructing channels as the directions between two cones with adjacent azimuthal angles, and labeling them by $i = 1, ...n$. Thus at each element of volume the flux in channel i is increased by the scattering process that takes flux from channel j to channel i, and it is decreased by absorption within the element of volume and the process that scatters flux away from channel i. Therefore, the equations for the balance of flux F_i within channel i look like

$$\frac{dF_i}{dz} = \sum_{j=1}^{n} S_{ij} F_j, \quad i = 1, ...n. \quad (2)$$

Here, for $i \neq j$ the coefficients S_{ij} describe the scattering from channel j into channel i, and can be calculated from the angular distribution of scattered light. If one assumes independent scattering these coefficients can be



(a) (b)

Figure 1: (a) Spectral dependence of the imaginary part of the index of the resin for p- and s- polarizations. (b) Spectral dependence of the diffuse reflectance of a simplex film. Here the dots represents the experimental measurements, the continuous and dashed lines represent our calculation for a mono- and poly-dispersed systems, respectively. The values of the parameters are given in the text.

calculated using Mie theory [7]. Thus, these coefficients are given in terms of the relative index of refraction between the pigment and the resin, the wavelength of the incident light and the radius of the spheres. For $i = j$, the coefficient S_{ii} describe the total scattering from channel i to all other channels, plus the absorption within channel i. The absorption from the pigment is proportional to the absorption cross section, that can be also calculated from Mie theory [7]. The *absorption* of the matrix (resin) can be accounted for by adding into the coefficient S_{ii} a term that accounts for the absorption of a continuous material (matrix) that occupies the volume left out by the spheres, that is, a term proportional to $2(1-f)\,4\pi k_M/\lambda$, where f is the volume filling fraction of the spheres and k_M is the imaginary part of the resin refractive index.

The general solution of Eq. (2) can be written as

$$F_i = \sum_{j=1}^{n} A_{ij} C_j \, \exp[\lambda_j z] \quad i = 1, 2, ... \tag{3}$$

where λ_j are the eigenvalues of matrix S_{ij} and A_{ij} is a matrix formed by the eigenvectors of S_{ij}, while the C_j's are constants to be determined through the boundary conditions at the interfaces.

The boundary condition at the illuminated interface ($z = 0$) can be written as

$$\sum_{j=1}^{n} C_j (A_{ij} - r_i A_{n+1-i,j}) = D_i \tag{4}$$

where D_i is the flux entering into the film in channel i at $z = 0$, and $n+1-i$ is the channel corresponding to the specularly reflected beam with respect to channel i, and r_i is the internal reflectance, that is, the reflectance from the interior of the film at the film-air interface. The internal reflectance r_i can be calculated using Fresnel's relations for the reflection amplitudes and then averaging over all the angles of incidence. Therefore, r_i is a function of the index of refraction of the matrix. At the other boundary there is a black substrate, thus $F_i(z = h) = 0$, where h is the thickness of the film. As the integrating sphere of the spectrophotometer (Minolta CM-3700d) sends the entire incident flux F_0 back into the sample, $\sum_{i=1}^{n} D_i = F_0$.

The diffuse reflectance R is finally calculated by adding up, at $z = 0$, the flux F_i traveling along all channels that send light back into air. Putting all this together one can see that $R(a_0, \sigma, f, h, \lambda, \tilde{n}_S, \tilde{n}_M)$ is a function of 9 parameters, where $\tilde{n}_S$ and $\tilde{n}_M$ are the complex indices of refraction of the spheres and the matrix, respectively. In Fig.1b we show the experimental spectral dependence of the diffuse reflectance of a *simplex* film of thickness $h = 93\ \mu m$ and $f = 0.20$, together with the results of calculations for two different cases: one for a monodispersed pigment with $a = 0.11\ \mu m$ and the other with a pigment with lognormal size distribution with the parameters reported above, that is, $a_0 = 0.11\ \mu m$ and $\sigma = 1.34$. One can see that the effect of the size distribution is to smooth out the profile of the curve. On the other hand, the calculation for the case of the polydispersed system

describes the experimental values "quite reasonably", especially when one takes into account that there are no adjustable parameters in the calculation. The decrease of the reflectance at the blue side of the spectrum is definitely due to the absorption of the pigment. The lack of agreement for the precise wavelength at which the pigment starts to absorb should come from the difference between the reported imaginary part of the index of refraction of TiO_2 and the one of the actual crystallites, that are commercially produced with a thin coating that prevents uv degradation. We also presume that the difference of about 2% at the red side of the spectrum should come from a small absorption of the actual pigment. Therefore, it would be extremely interesting (though challenging) to design and perform optical absorption measurements directly on the crystallites.

Finally, we performed similar calculations of the diffuse reflectance by keeping f fixed but appropriately increasing the value of σ and a_0 in the lognormal size-distribution of the pigment, with the idea of simulating an agglomeration effect. Surprisingly enough we found a negligible change in the reflectance for a wide range of "reasonable" values of a_0 and σ. This means that for such a high value of the pigment filling fraction, the presence of agglomerates is actually neither relevant nor important, at least compared to the changes in the diffuse reflectance resulting from changes in k_M as small as 10^{-6}. In order to have a direct evidence of this we prepared *simplex* samples with different amounts of dispersant in order to provoke pigment agglomeration (confirmed by scanning electron microscopy), and we found that the diffuse reflectance did not suffer any appreciable change, in agreement with the results of our calculations.

Conclusion

A multi-flux radiation transfer model was used to predict the most sensitive parameters in the diffuse reflectance of pigmented white coatings. The absorption of the matrix was shown to be the most critical factor. In contrast, the effects of pigment aggregation are shown to be secondary in these systems. The modelling had the benefit of including precise resin absorption measurements as well as the size distribution of the pigment particles.

**The TiO_2 used is a commercial grade pigment for paint from Kerr McGee. The latex used is a vinyl-versatic emulsion manufactured by the mexican paint company Comex.

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