Visible spectral dependence of the scattering and absorption coefficients of pigmented coatings from inversion of diffuse reflectance spectra

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A spectral-projected gradient method and an extension of the Kubelka–Munk theory are applied to obtain the relevant parameters of the theory from measured diffuse reflectance spectra of pigmented samples illuminated with visible diffuse radiation. The initial estimate of the spectral dependence of the parameters, required by a recursive spectral-projected gradient method, was obtained by use of direct measurements and up-to-date theoretical estimates. We then tested the consistency of the Kubelka–Munk theory by repeating the procedure with samples of different thicknesses. © 2002 Optical Society of America

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1. Introduction

When we consider optical properties of particulate coatings, for example, pigmented polymers used in the paint industry[1] or selective absorbing coatings utilized in photothermal conversion systems,[2] it is desirable to know the spectral dependence of the effective scattering and absorption coefficients that characterize a batch of samples of interest according to some specific application. Then the optical response of the particulate coatings can be modeled and their performance can be evaluated. The main problem found in the modeling of this type of system is the adequate treatment of the multiple-scattering phenomenon that is due to the presence of the particulate inclusions. Perhaps the simplest approach to the treatment of multiple scattering of light by randomly located inclusions is the Kubelka–Munk theory (KMT). With the KMT diffuse light illuminates one side of the film, and the flux of scattered light is regarded as an average flux that travels in only two directions perpendicular to the film: the forward and the backward directions. For this reason the KMT is also known as a two-flux theory. The film is then characterized by two phenomenological parameters: S describes the effective scattering and K accounts for absorption. Under certain assumptions these two parameters can be calculated within the framework of the Lorenz–Mie theory.[3] Although the KMT is extremely simple, it can be extended to model realistic situations to provide a clear and powerful tool for evaluation of some of the optical properties of particulate thick films. This is especially true in areas such as the coating industry, in which the main interest relies more on the behavior of angular-integrated diffuse reflectance than on specific features of its angular pattern. Nevertheless, the lack of understanding of the applicability conditions and limitations of the KMT, as well as the lack of guiding criteria for the proper choice of values of some of its parameters, often limit utilization of the conclusions extracted from analysis of the data.

Here we concentrate our attention on the optical performance of white-paint coatings composed of a collection of particulate inclusions of a transparent pigment embedded in an otherwise homogeneous polymeric matrix. Our objective is evaluation and interpretation of the spectral dependence in the visible range of the angular-integrated diffuse reflectance (AIDR) by use of a model based on the KMT. In the original formulation of the KMT the partial reflections of diffuse radiation at the coating–air interface were not considered. However, inclusion of

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their effects in the overall reflectance and transmittance of the film is relatively straightforward. But this requires the introduction of a new set of parameters: the reflection coefficients of the diffuse radiation[4] at the front interface. In principle, given the indices of refraction of the matrix and the substrate, these coefficients could be calculated if we assumed, for example, that the angular distribution of the impinging radiation is isotropic and we then performed an angular average of the Fresnel reflection coefficients. There are, however, cases in which some of these coefficients can be neither calculated nor measured such as the diffuse reflection coefficient at the coating–substrate interface when the substrate is a diffuse scatterer, for example, white paper. There is also no general agreement in relation to the index of refraction that should be used in the calculation of these reflection coefficients. Should one use the index of refraction of a plain matrix or rather an effective index of refraction that takes into account the presence of inclusions?

A slight absorption in the matrix is also a source of conceptual and practical problems. In this case the concepts of scattering and absorption cross sections have to be either changed or at least interpreted differently.[5,6] It has also been argued[5] that in this case the splitting of extinction in scattering plus absorption is no longer valid, and the correct way to proceed in practical calculations is still an open question. Let us recall that an imaginary part of the order of 10^{-4} in the index of refraction of the matrix can reduce the overall reflectance of the coating by approximately 5%. This reduction is of the utmost importance when one evaluates, for example, the optical performance of a white-paint coating.

In summary, we have a simple theory based on certain general assumptions and with a collection of phenomenological parameters whose estimation is not always straightforward. Also, a lack of agreement in the prediction of the AIDR with actual measurements might simply mean that the choice of parameter values was not the correct one. An obvious alternative to this procedure is inversion of the AIDR data to adjust the parameter values required by theory to the experimental data. The main problem in this procedure is that the values so obtained are not unique, either because the spectral reflectance data are not enough to determine the spectral behavior of all relevant parameters or simply because the inversion problem does not have a unique solution.

Here we propose a systematic procedure to tackle this problem by use of a projected gradient method that allows the simultaneous adjustment of values of an ample collection of parameters. First, we model our system as an extension of the KMT and perform the best possible estimation of all the parameters required for calculation of the AIDR spectrum. We refer to this selection of parameters as the first approximation. We then use this first approximation as the initial input in a projected gradient method to adjust the parameter values to the measured values of the AIDR spectrum of a film with a given thickness. This method uses a recurrence algorithm that provides a set of values that gives the best adjustment to the experimental data. We refer to this set as the retrieved values. Finally, to check the validity of the general assumptions on which the extended KMT is based, we repeat the procedure with films of different thicknesses. Since parameters S and K, as well as the matrix absorption and the reflection coefficients at the front interface should be independent of the thickness of the sample, any difference between the retrieved values of these parameters in samples with a different thickness should indicate the existence of some inconsistencies within the model.

The paper is organized as follows: in Section 2 we briefly review the extended KMT. In Section 3 we describe the preparation of the samples, the measurements of the AIDR spectra of rutile-pigmented polymer coatings, and the procedure to determine the set of parameter values required as a first approximation in the inversion of the extended KMT. In Section 4 we summarize the procedure followed in spectral-projected gradient methods (SPGMs) and report and analyze the results obtained for the spectral dependence of the parameters. Finally, we devote Section 5 to our conclusions.

2. Extended Kubelka–Munk Theory

With the KMT it is assumed that film is illuminated by diffuse light at the air–coating interface, so this is the first requirement for measurements of the AIDR spectra for rigorous application of the KMT to the analysis of the data.[7–9] Second, the diffuse scattered light travels in only two directions perpendicular to the interface, so each of the two fluxes can be regarded as the angular average over each hemisphere. If one further assumes that (i) the intensity of the diffuse radiation that propagates through the coating is always isotropic and (ii) the independent scattering approximation is valid, then both S and K can be determined in terms of the corresponding scattering C_{sca} and absorption C_{abs} cross sections of the pigments. It is not straightforward to establish the limits of validity of these approximations with precision. Nevertheless, there are length scales in the problem that can serve as a guide, for example, wavelength λ of the incident radiation, the (average) size a_0 of the inclusions, the mean-free path l of the photons, the typical separation r_0 among inclusions, and thickness h of the film. The dimensionless quantity $x \equiv 2\pi n_M a_0/\lambda$, where n_M is the refractive index of the matrix, is known as the size parameter. Although the isotropy of the diffuse radiation is not guaranteed by establishment of the photon-diffusion regime, the establishment of this regime is a necessary condition for randomization of scattered light, and this implies $h \gg l$; so the coating should be thick enough to allow all possible multiple-scattering events that would ensure randomization of the photon-scattering process. Also, the validity of an independent scattering approximation requires $(2\pi/\lambda)r_0 \gg 1$, so the concentration of inclusions within the film cannot be too

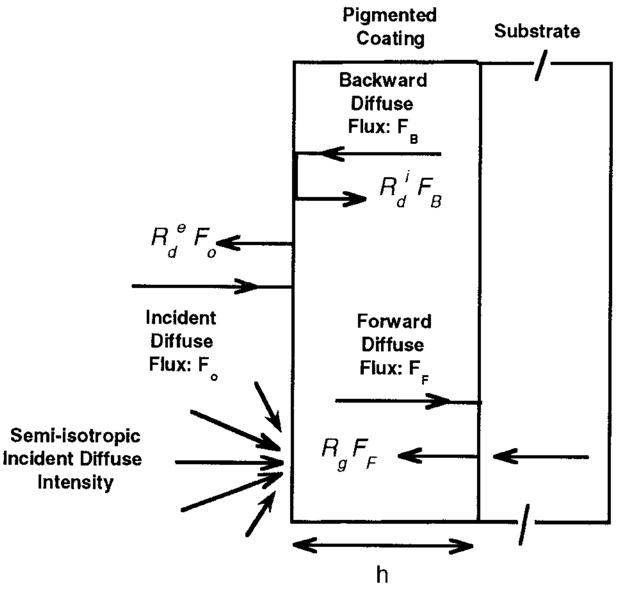

Fig. 1. Diagram of a pigmented coating on a thick substrate, illuminated with semi-isotropic diffuse radiation. Partial reflection of the external (internal backward) diffuse radiation is described by the reflection coefficient $R_d^{\,e}$ ($R_d^{\,i}$). R_g describes the partial reflection of forward diffuse radiation at the backcoated interface.

large. Taking $l = 1/n_0(C_{\text{sca}} + C_{\text{abs}})$, where n_0 is the number density of inclusions, C_{sca} and C_{abs} are the pigment scattering and absorption cross sections, respectively, and $r_0 = (3/4\pi n_0)^{1/3}$, the above two inequalities can be written as $h \gg 1/(s + k)$ and $f^{1/3} \ll x$. Here $f = n_0 V_p$ is the filling fraction of the inclusions, V_p is the (average) volume of the particulate inclusions, $s = fC_{\text{sca}}/V_p$ and $k = fC_{\text{abs}}/V_p$; thus $1/s$ and $1/k$ are the scattering and absorption mean-free paths, respectively. Actually there is some empirical evidence[10] that, for a system that consists of small ($\sim$0.25 μm) inclusions of rutile in resin, the independent scattering approximation starts to break down for filling fractions larger than 0.10.

Under these assumptions one can write explicit expressions for the scattering and absorption coefficients S and K, and here we choose the ones given by Ishimaru,[11] that is, $S = 2(1 - \sigma_d^{(i)})s$ and $K = 2k$, where $\sigma_d^{(i)}$, the forward-scattering ratio, is the fraction of power scattered by any of the pigment inclusions in the forward hemisphere, under the assumption that semi-isotropic incident radiation impinges over each of them. The partial reflection of the incident and backward internal diffuse radiation at the air–coating interface can be taken into account in terms of the diffuse reflection coefficients $R_d^{\,e}$ and $R_d^{\,i}$, respectively[12] (see Fig. 1). In terms of these coefficients, diffuse reflectance R of a pigmented coating of thickness h, illuminated with semi-isotropic diffuse radiation, becomes

$$R = R_d^{\,e} + \frac{(1 - R_d^{\,i})(1 - R_d^{\,e})R_{\text{KM}}}{1 - R_d^{\,i}R_{\text{KM}}}, \tag{1}$$

where R_{KM} is the Kubelka–Munk reflectance given by

$$R_{\text{KM}} = \frac{1 - R_g\left[1 + \dfrac{K}{S} - b\ \coth(bSh)\right]}{1 + \dfrac{K}{S} + b\ \coth(bSh) - R_g}. \tag{2}$$

Here $b = \sqrt{K(K + 2S)}/S$, and R_g is a diffuse reflection coefficient defined as the ratio of the diffuse flux reflected from the coating–substrate interface over the incident flux that impinges upon it. Diffuse reflectance R is defined as the quotient of the backward flux at the air side of the air–coating interface over the (diffuse) incident flux. R depends on λ, and since the backward flux corresponds to an angular average over the corresponding backhemisphere, R is identified as the AIDR. Sometimes the KMT has been erroneously applied under collimated illumination[13] or by neglect of the external and internal reflections at the front interface.[14] Finally, an additional problem arises with the white-pigmented coatings treated here. The problem is that the matrix is a resin with a slight absorption in the visible range, and, as mentioned before, the rigorous treatment of this problem is not an easy task. Here we adopt a simple approach that incorporates the absorption coefficient α of the matrix into absorption parameter K. Therefore, analysis of the reflectance data of pigmented films, with the extended KMT, can be done first by determination of the following seven parameters: S, K, $R_d^{\,e}$, $R_d^{\,i}$, R_g, α, and h, and then by calculation of reflectance R with the aid of Eqs. (1) and (2). The results of these calculations should then be compared with experimental measurements.

3. First Approximation

The system we consider here is a particulate film composed of a pigment that consists of small, TiO_2 (rutile) crystallites embedded in a polymeric resin. The rutile crystallites are first dispersed in water with the aid of small amounts of a chemical dispersing agent (Orotan 1124) and mechanical shear stress. After the rutile is dispersed, the emulsion of resin and water is added, and then it is deposited over a flat black board with an applicator that furnishes a film with a well-defined thickness. Then it dries at room temperature for 24 h until the resin coalesces to form a homogeneous solid matrix. The thickness of the film and the AIDR spectrum were then measured with a Minolta CM3700 spectrophotometer with an integrating sphere and diffuse incident illumination. The coatings were prepared such that the filling fraction f of the pigment in the dried film was 0.20, which assumes that all the water evaporates during the drying process and that no air voids are left in the dried resin. A typical AIDR spectrum is shown in Fig. 2.

We now compare the measured diffuse reflectance spectrum with the one computed with Eqs. (1) and (2). Since this calculation requires the values of the

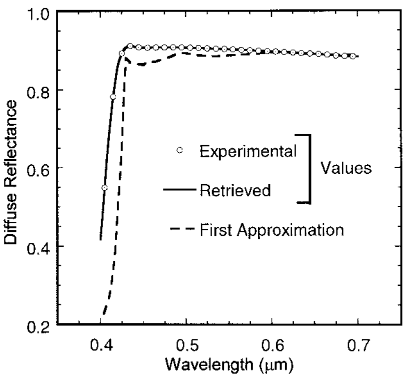

Fig. 2. Experimental, first approximation, and retrieved diffuse reflectance spectra R of a 48-μm-thick titanium dioxide (rutile-) pigmented polymer coating illuminated with visible diffuse radiation. The mean pigment radius a is equal to 0.15 μm and the filling fraction is equal to 0.20. The retrieved values were obtained after 1612 iterations.

seven parameters mentioned above, we first obtained the best possible estimate for the values of these parameters either by calculation or by measurement. We then calculated the corresponding reflectance spectrum using Eqs. (1) and (2); these values of the parameters and the reflectance are what we refer to as the first approximation, which we use later as the initial values in a recurrent SPGM.

We start the evaluation of the first approximation by determining S and K. Parameters S and K are given by $S = 2\,[1 - \sigma_d^{(i)}]\, s$ and $K = 2k$. We first assume that the pigment inclusions are identical spherical particles with a radius a given by the mean size of the crystallites. Here we used $a = 0.15$ μm, which is the value reported by the manufacturer. With the assumption of a spherical shape one can then use the framework provided by the Lorenz–Mie theory[3] to compute the cross sections C_{sca} and C_{abs}, as well as the forward-scattering ratio $\sigma_d^{(i)}$. This calculation requires the refractive indices of the matrix and the pigment. The spectral values of the refractive index for rutile $n_p(\lambda)$ were taken from the literature.[15,16] The real part of $n_p(\lambda)$ is large and around 2.8 at the red side of the visible spectrum and increases to approximately 3.0 on the blue side. The imaginary part has a distinctive feature that is zero (no absorption) in most of the visible range with an absorption peak that starts growing for $\lambda < 0.42$ μm and develops fully in the near UV. The real part of the refractive index of the resin was measured at $\lambda = 0.56$ μm, giving $n_M = 1.5$, and it is assumed that this value does not change at other wavelengths in the visible range. The scattering and absorption cross sections C_{sca} and C_{abs} as well as the forward-scattering ratio $\sigma_d^{(i)}$ were calculated with $n_M = 1.5$. The spectral dependence of S is shown in Fig. 3(a) for $h = 48$ μm, labeled first approximation. The calculation of C_{sca}, C_{abs}, and $\sigma_d^{(i)}$ also provide information about the size and spectral dependence of the extinction mean-free path $l = 1/(s + k)$. We found that l lies between 0.31 and 0.46 μm, confirming the validity of the inequality $h \gg l$ for $h = 48$ μm.

The absorption of the matrix is incorporated into the absorption coefficient K by use of an extremely simple approach. In this approach one considers that the absorption coefficient K contains two contributions: a contribution k from the pigment and an additional contribution $(1 - f)\alpha$ from the matrix, both of which are combined by the following mixing rule: $K \rightarrow 2[k + (1 - f)\alpha]$. Here $\alpha = 4\pi k_M/\lambda$ is the absorption coefficient of the matrix and k_M is the imaginary part of its index of refraction. This mixing rule, although it has not been formally justified, is commonly used in many applications of the radiative transfer theory to incorporate the absorption of the matrix.[17] Our estimation is that α should be of the order of 10^{-3}, and we simply took $k_M = \alpha\lambda/4\pi \approx 10^{-4}$ over the whole visible spectral range. The estimation for this value of α was obtained from measurements of the reflectance in thick samples, together with the relation $R_\infty \approx 1 - \sqrt{2K/S}$ for $K/S \ll 1$, provided by the KMT. Here R_∞ is the reflectance of a sample with infinite thickness, but in practice it can be identified with a thickness such that there is no more significant increase in R as the thickness increases. In the spectral range where the pigment is

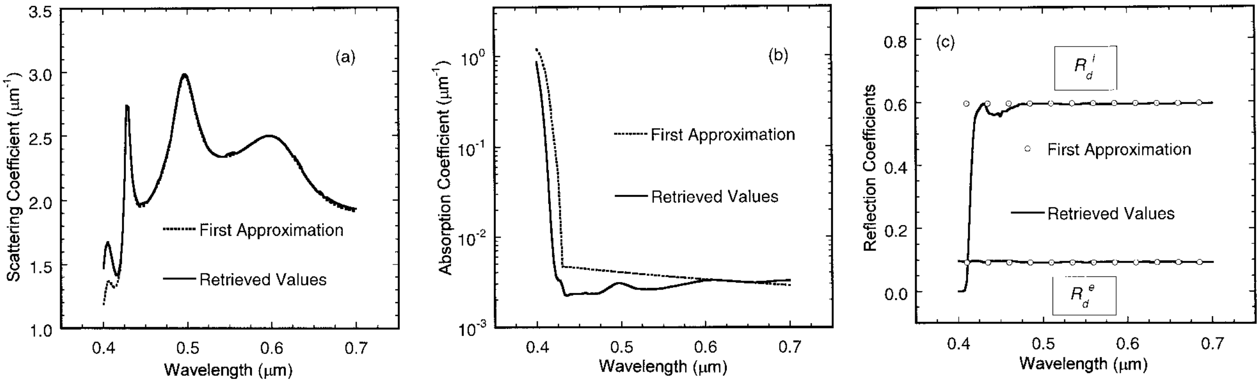

Fig. 3. Spectral dependence of the approximated and the retrieved values of (a) scattering coefficient S, (b) absorption coefficient K, (c) external and internal diffuse reflection coefficients R_d^e and R_d^i, respectively, for the film whose diffuse reflectance spectrum is displayed in Fig. 2.

completely transparent ($K = 0$) and there are no other sources of absorption, one should obtain $R_\infty = 1$. Therefore, any decrement of the measured reflectance in thick samples from the value $R = 1$ implies an absorption, which we have attributed to the matrix,[18] and is determined by the expression $R \approx 1 - 2\sqrt{(1 - f)\alpha/S}$, in accordance with our proposed mixing rule. A direct measurement of the spectral dependence of the absorption coefficient of the matrix would be extremely helpful. In Fig. 3(b) we show the spectral dependence of K for $h = 48$ μm, labeled first approximation. The sharp increase of K below ~0.42 μm is associated with the absorption of the pigment, whereas the value around 0.003 μm^{-1} in the rest of the spectrum comes completely from the absorption in the matrix.

We realize that a better evaluation of parameters S and K can be obtained if reliable information about the particle size and shape distribution of the crystallites were readily available. In that case, a more realistic value of S and K could be obtained by performing an average of C_{sca}, C_{abs}, and $\sigma_d^{(i)}$ over the size distribution of the crystallites. A further and possibly important improvement would also be to take into account the effects of aggregation of the crystallites. Aggregation affects not only the size distribution of the pigment but also its scattering power; the scattering cross section of a cluster of crystallites might differ from the one that corresponds to a single sphere of the same volume. However, precise measurements of the particle size distribution of inclusions in concentrated samples, by use of light- or ultrasound-scattering techniques, are just starting to become available; whereas more direct techniques, such as scanning transmission electron microscopy, still lacks sufficient statistical information to yield representative results. Nevertheless, any effort to incorporate the effects of the size distribution of the crystallites and clusters on their scattering and absorption properties would be welcomed by researchers.

We now determine the reflection coefficients at the front interface. First we assume that the interface is absolutely flat and illuminated with unpolarized isotropic radiation. We computed the diffuse reflection coefficients R_d^e and R_d^i from the refractive index of matrix n_M by performing an angular average over an isotropic incident radiation of the Fresnel reflectance $|r(\theta)|^2 = (1/2)[|r^{\text{TE}}(\theta)|^2 + |r^{\text{TM}}(\theta)|^2]$. Here r^{TE} and r^{TM} are the Fresnel reflection amplitudes for tranverse-electric and transverse-magnetic polarizations. We performed these calculations by taking $n_M = 1.5 + i \times 10^{-4}$ over the whole spectral range of interest and obtained $R_d^e = 0.09$ and $R_d^i = 0.60$. Since it is assumed that n_M has no spectral dependence, R_d^e and R_d^i have no spectral dependence either.

The choice of index of refraction of the sole matrix n_M to calculate R_d^e and R_d^i might not be strictly correct, because one neglects the contribution of the coherent component of the reflected light at the air–coating interface that is due to the presence of inclusions. Even in the absence of the matrix one could expect that an incident beam would be specularly reflected because of the presence of pigment inclusions within the slab region. This coherent component of the reflected light is the result of the constructive interference of the light scattered by the pigment inclusions, and this constructive interference occurs only in the specular direction. But the interference phenomenon is not included in the realm of radiative transfer theories, because in these theories one deals with intensities rather than with amplitudes and phases of the propagating electromagnetic field. For example, in the original KMT[7] form, R_d^e and R_d^i are equal to zero in the absence of a matrix. A possible way to include the effects of the coherent reflectance by the inclusions is to introduce an effective index of refraction n_{eff} instead of n_M into the calculation of R_d^e and R_d^i. Nevertheless there are no reliable expressions for n_{eff} in the case in which the size of the inclusions in concentrated samples is of the same order of magnitude as the wavelength of the incident radiation. Furthermore, Bohren[19] has pointed out that in the case of large inclusions the concept of an effective index of refraction has to be revised, and he proposed that it is necessary to introduce effective dielectric and magnetic responses ϵ_{eff} and μ_{eff}, such that $n_{\text{eff}} = \sqrt{\epsilon_{\text{eff}}\mu_{\text{eff}}}$. He also derives explicit expressions for ϵ_{eff} and μ_{eff} for the case of normal incidence in the dilute limit. Here we used the procedure proposed in Ref. 14, which can be regarded as an extension of Bohren's ideas for concentrated samples without satisfactory results. We believe that the proper way to calculate the contribution of the coherent component of the reflected beam is still not well established, although valuable efforts have been made to solve this problem by use of analytic wave theory of multiple scattering together with the T-matrix formalism.[17] Nevertheless, it seems that, according to the results obtained below, the effects of coherent reflectance should not be too large.

Calculation of the diffuse reflection coefficient R_g at the coating–substrate interface depends on the physical nature of the substrate, and, as mentioned above, if the substrate is a diffuse scatterer, the calculation would require a model for the optical properties of the diffuse scatterer itself. To avoid these additional complications, here we deal with only white-pigmented coatings deposited over a black substrate, thus we use $R_g = 0$.

The next parameter to be determined is thickness h of the coating that was measured directly with an electromagnetic device (Elcometer 345 coating thickness gauge). The measurement was performed as the difference between two measurements: first, one measures the thickness of the board upon which the film is to be deposited (≈350 μm); and second, one measures the board with the deposited dried film. The thickness of the film was obtained as the difference between these two measurements. The statistical uncertainty, which is the difference between two measurements, is slightly rough with regard to the thickness of the deposited film. We reduced this uncertainty to approximately 6% by averaging a series of measurements taken within the exact same area at which we measured the reflectance (a few square centimeters).

The seven parameters so determined were introduced into Eqs. (1) and (2) yielding the spectral behavior of the reflectance shown in Fig. 2 and labeled first approximation. In this spectrum the thickness of the film is $h = 48$ μm and the filling fraction f is 0.20. The large values of diffuse reflectance over the visible spectrum are due to the high scattering efficiency of rutile, and the edge around $\lambda = 0.42$ μm is due to its absorption. We refer to this edge as the absorption edge. Even though the general agreement of the first approximation and the measured reflectance spectrum can be considered as satisfactory, as seen in Fig. 2, some significant discrepancies can be found below the absorption edge at approximately 40%. The origin of these discrepancies might be from a lack of information and experimental uncertainties in the determination of some of the parameters. For example, significant differences can arise owing to differences between the actual values of the refractive indices in the samples and the values taken from the literature. It is well known that the optical constants of a thin film are influenced by the deposition conditions and similar behavior might be expected in relation to the growing conditions of the small pigment particles. Another source for the discrepancies might be the validity of the KMT itself. At this point we must choose from all these possibilities those that we believe might be the most significant. So first we assume that the KMT is adequate and we then invert the reflectance data to adjust the values of the parameters to the measured spectra.

4. Inversion of the Reflectance Data

We now perform the inversion of the reflectance data for the adjustment of the parameters required by the KMT by using the SPGM. Using this method one can calculate the values of parameters S, K, $R_d^{\,e}$, and $R_d^{\,i}$, which lead to the measured diffuse reflectance spectrum when we use the values obtained above (the first approximation) as the initial set of values in a recurring process. This is an attractive option to determine improved parameter values because, if the KMT is consistent, it can overcome some of the uncertainties mentioned above in the calculation of the first approximation. The method is based on minimization of the function

$$F = \sum_{i=1}^{N} |R_{\exp}(\lambda_i) - R[S(\lambda_i), K(\lambda_i), R_d^{\,e}(\lambda_i), R_d^{\,i}(\lambda_i), \lambda_i, h]|^2, \quad (3)$$

where N is the number of wavelengths that specify the measured diffuse reflectance spectrum. Note that we have also included thickness h in the parameter list and that h has no subindex i because it does not depend on λ. The value of h is allowed to adjust to the measured spectra, but only within the uncertainties given by its measurement (approximately 6%). We consider F as a function of vector $\mathbf{Z}$, whose $4N + 1$ components are

$$Z_i = \begin{cases} S(\lambda_i), & i = 1, 2, \ldots, N \\ \mathbf{K}(\lambda_i), & i = N+1, N+2, \ldots, 2N \\ \mathbf{R}_d^{\,e}(\lambda_i), & i = 2N+1, 2N+2, \ldots, 3N \\ R_d^{\,i}(\lambda_i), & i = 3N+1, 3N+2, \ldots, 4N \\ h, & i = 4N+1 \end{cases}. \quad (4)$$

The basic purpose for use of the SPGM is to calculate this vector in such a way that $F[\mathbf{Z}] \le \epsilon_1$, with ϵ_1 as small as possible for $\|\mathbf{g}(\mathbf{Z})\| \le \epsilon_2$, where $\mathbf{g}(\mathbf{Z})$ is the vector gradient of the function $F[\mathbf{Z}]$, with ϵ_2 as a previously defined numerical tolerance. For our computations we used $\epsilon_2 = 10^{-5}$. Conjugate gradient methods are suitable to solve this optimization problem.[20] In these methods the desired vector $\mathbf{Z}$ is approached from an initial $\mathbf{Z}^{(0)}$ value according to the formula $\mathbf{Z}^{(m+1)} = \mathbf{Z}^{(m)} - \alpha_m \mathbf{g}_m$, with the step-length function defined as

$$\alpha_m = \frac{[Z^{(m)} - Z^{(m-1)}]^t [Z^{(m)} - Z^{(m-1)}]}{[Z^{(m)} - Z^{(m-1)}]^t [g_m - g_{m-1}]}, \quad (5)$$

where $\mathbf{g}[\mathbf{Z}^{(m)}] = \mathbf{g}_m$ is the gradient of function F, $[\ldots]^t$ denotes transpose, and $m = 0, 1, 2 \ldots$ until the numerical tolerance criterion is satisfied or until some maximum number of iterations is reached. The order of the current numerical approximation is specified by m. In our application the $\mathbf{Z}^{(0)}$ vector is what we call the first approximation, and it was computed as described above.

Several conjugate gradient approaches have been devised[21,22] that depend on the method followed to compute recursively the step-length function α_m. In particular we apply the SPGM as devised by Raydan,[23] who combined the approach of Barzilai and Borwein[24] to compute the step length given by Eq. (5) and the nonmonotone line search devised by Grippo *et al.*[25]: the current approximation of $\mathbf{Z}$ is accepted if

$$F[\mathbf{Z}^{(m+1)}] \le F[\mathbf{Z}^{(m-j)}] + \gamma[g(\mathbf{Z}^{(m)})]^t \cdot [\mathbf{Z}^{(m+1)} - \mathbf{Z}^{(m)}]$$

with $j = 0, 1, 2, \ldots, L$, where L is a positive integer and γ is a small positive number. Otherwise the α_m value can be recalculated by use of two safeguarded parameters σ_1 and σ_2 with $0 < \sigma_1 < \sigma_2 < 1$ and quadratic interpolation to generate a new α_m value contained between $\sigma_1 \cdot \alpha_m$ and $\sigma_2 \cdot \alpha_m$. Typical values of L and γ are, respectively, 10 and 10^{-4}. The values of σ_1 and σ_2 were set to 0.1 and 0.9, respectively. The computational efficiency of this approach has recently been compared with that of other standard methods.[26] Applications of this SPGM have been devised to obtain, for example, the refractive index and the extinction coefficient of thin films.[27,28]

The SPGM briefly summarized in the previous paragraphs has been used to obtain the spectral dependence of S, K, $R_d^{\,e}$, and $R_d^{\,i}$ from diffuse reflectance

Table 1. Performance of the SPGM on Four Rutile-Pigmented Coatings

Sample Thickness (μm)	Number of Iterations	F	$\Delta R_d{}^i$	ΔS (μm^{-1})	ΔK (μm^{-1})	Δh (μm)
25	884	8.4×10^{-10}	7.0×10^{-3}	3.9×10^{-3}	1.0×10^{-3}	4.7×10^{-6}
48	1638	8.1×10^{-10}	6.7×10^{-3}	5.1×10^{-3}	9.7×10^{-4}	2.4×10^{-5}
59	1649	8.0×10^{-10}	7.8×10^{-3}	4.9×10^{-2}	1.0×10^{-3}	1.0×10^{-5}
84	1218	9.2×10^{-10}	2.0×10^{-3}	1.8×10^{-3}	4.9×10^{-4}	1.9×10^{-5}

data by use of $N = 121$ values obtained from the interpolation of 30 equally spaced measurements contained in the visible spectral range. Since h does not depend on λ and the method requires the evaluation of $\partial R(\lambda)/\partial h$ for a fixed λ, we arbitrarily chose any value of λ to calculate the retrieved values of h and the spectral dependence of the rest of the parameters. Then we repeated the procedure N times, and each time we chose a different value of λ for the calculation of $\partial R(\lambda)/\partial h$. Then we calculated the average value of each parameter S, K, $R_d{}^e$, $R_d{}^i$, and h over the N generated spectra and the standard deviations ΔS, ΔK, $\Delta R_d{}^e$, $\Delta R_d{}^i$, and Δh. The values reported as the retrieved values of S, K, $R_d{}^e$, $R_d{}^i$, and h correspond to these averages. Also, one can restrict the search for values of each parameter between a minimum and a maximum value. We performed calculations for coatings with four different thicknesses of $h = 25$, 48, 59, and 84 μm. The minimum and maximum values for h were chosen as the measured value $\pm 6\%$, which approximately corresponds to the experimental uncertainty. The retrieved values for h did not show any significant difference with respect to the measured values introduced in the first approximation, yielding a Δh always less than 2.5×10^{-5} (see Table 1). Also, we did not add upper and lower realistic bounds to the search for values of S and K. The search values for $R_d{}^i$ were restricted to between 0 and 1. The values of $R_d{}^e$ were restricted to between 0.085 and 0.095. These two values are an estimate of the changes in $R_d{}^e$ that are due to uncertainties in the value of n_M taken between $1.4 \le n_M \le 1.6$. There is also more confidence in the values of the first approximation for $R_d{}^e$ than the corresponding values for $R_d{}^i$ because, in external reflection, the air side of the interface is illuminated with isotropic radiation, whereas in internal reflection the matrix side of the interface is illuminated by diffuse radiation that suffers a highly anisotropic reflection that is due to the existence of a critical angle. Now, since the calculation of $R_d{}^e$ and $R_d{}^i$ in the first approximation assumes isotropic incidence, this assumption would certainly hold for $R_d{}^e$ although it would be uncertain for $R_d{}^i$.

Figure 2 depicts the retrieved values obtained for the reflectance $R(\lambda)$ from the SPGM procedure, and one can see that there is excellent agreement between these retrieved values and the experiment. Here the thickness of the coating is 48 μm and the number of iterations in the recurrent process is 1612. We recall that the filling fraction of the rutile inclusions is 0.20, and that they are regarded as small spheres with a mean radius $a = 0.15$ μm. The dashed curves in Figs. 2 and 3 correspond to the first approximation specifying the $\mathbf{Z}^{(0)}$ vector. As seen in Fig. 3(a) the approximate and retrieved values of S are close to each other above the absorption edge, with slightly larger values at the blue side of the visible spectral range.

In Fig. 3(b) one can see that, for absorption coefficient K, there are also no significant differences between the retrieved values and the first approximation in the region where intrinsic absorption comes from the matrix; the retrieved values lie below the first approximation on the blue side of the spectrum and slightly above on the red side. Below the absorption edge, the retrieved values of K lie significantly below the first approximation. The smaller retrieved values of K below the intrinsic absorption edge of the pigments explain the larger measured diffuse reflectance values as compared with the initial approximated values. Although these results are somewhat satisfactory, it would be worthwhile to consider a more rigorous way to include the absorption in the matrix or at least to justify the mixing rule used here. This could be done, for example, by use of some of the extended versions of the Lorenz–Mie theory for spherical particles immersed in absorbing media.[29]

In Fig. 3(c) we show the retrieved values of $R_d{}^e$ and $R_d{}^i$ as well as the values that correspond to the first approximation. One can also see that the retrieved values of the external diffuse reflectance $R_d{}^e$ are close to those of the first approximation and with negligible spectral dependence. The agreement between the $R_d{}^i$ retrieved values and the first approximation is not as good; the retrieved values are much the same as those that correspond to the first approximation, with slight variations at the blue side of the spectrum and a sharp decrease below the absorption edge. Some of the spectral dependence that appears in $R_d{}^i$ might come from the spectral dependence of the effective index of refraction which should be used instead of n_M or, in general, from a better treatment of the coherent reflectance at the air–coating interface. The sharp decrease in the retrieved values of $R_d{}^i$ below the absorption edge means that less radiation is reflected into the coating and, consequently, more radiation emerges from the coating to contribute to its total diffuse reflectance, as demanded by the larger values of R given by the measurements. This effect might also be influenced by the angular distri-

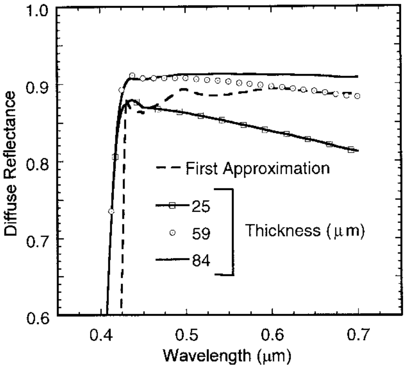

Fig. 4. Diffuse reflectance spectra of three pigmented coatings at thicknesses listed in the figure. The dashed curve corresponds to the first approximation of the diffuse reflectance for the thicker coating.

bution of propagating diffuse radiation intensity close to the inner side of the coating–air interface.

We now investigate another aspect of the inversion problem: the consistency of the KMT. If the KMT is to be consistent, the retrieved values of $S(\lambda)$ and $K(\lambda)$ should be independent of the thickness of the sample, because they are assumed to be intrinsic properties of the composition and geometry of the coating. We repeated the process mentioned above for a sample with $h = 48$ μm for another three samples with the same pigment size ($a = 0.15$ μm) and the same filling fraction ($f = 0.20$) but with three different thickness values, one thinner $h = 25$ μm, and the other two thicker, $h = 59$ and 84 μm. The agreement between the retrieved values of the reflectance in these three samples and the diffuse reflectance measurements was as good as that in Fig. 2 and will not be shown here. Figure 4 depicts the measured diffuse reflectance spectra that corresponds to these coatings as well as the first approximation for the thicker film. The first approximation of the diffuse reflectance is almost insensitive to the thickness of the coatings considered in Fig. 4.

In Fig. 5 we display the first approximation and the retrieved values of $S(\lambda)$, $K(\lambda)$, and $R_d^{\,i}(\lambda)$ for three pigmented samples ($h = 25$, 59, and 84 μm). Obviously, the first approximation is independent of thickness. The corresponding values of ΔS, ΔK, $\Delta R_d^{\,i}$, and ΔH are not significantly different from those obtained before and are also listed in Table 1, together with the values that correspond to the number of iterations. It is obvious that the general trends mentioned above and shown in Fig. 3 with regard to the spectral dependence of the retrieved values for the coating with $h = 48$ μm are also displayed for the coatings with $h = 25$, 59, and 84 μm. The major difference is in the absorption coefficient K, where the thinner coating shows significantly more absorption than the first approximation and the retrieved values of the other three coatings. These larger K values of thinner films for wavelengths larger than 0.42 μm explain the lower values of the measured diffuse reflectance in comparison with the values of the first approximation, as seen in Fig. 4. According to the results depicted in Fig. 5(c), for the thicker coating the internal reflection coefficient has a somewhat lower value than the one specified in the first approximation over the spectral range for which there is no absorption from the pigment. The measured diffuse reflectance values corresponding to this coating (see Fig. 4) are somewhat larger than those given by the first approximation.

To explain the disagreement between the first approximation and the retrieved values of $S(\lambda)$, $K(\lambda)$, and especially $R_d^{\,i}(\lambda)$ in the blue part of the spectrum, one might conclude that the propagating diffuse radiation intensity should be nonisotropic. Vargas recently showed[30] that the KMT can be applied under nonisotropic conditions provided that the effective scattering and absorption coefficients are given by

$$S \rightarrow \langle S\rangle = \xi(1-\sigma)s, \quad K \rightarrow \langle K\rangle = \xi k, \qquad (6)$$

where ξ is the geometric average value of the isotropy factor and σ is the arithmetic average value for the forward-scattering ratio. These averages were obtained from the values that correspond to forward and backward diffuse radiation intensities, which differ when there is anisotropy in the angular distribution of the diffuse scattered radiation. For perfectly isotropic diffuse radiation $S \rightarrow S^{(i)} = 2(1-\sigma_d^{(i)})s$ and

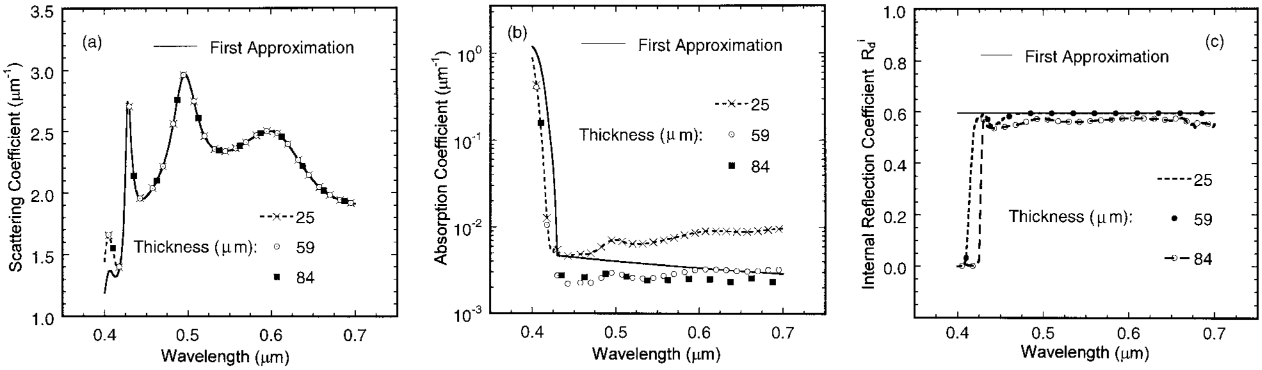

Fig. 5. Visible spectral dependence of (a) scattering coefficients S, (b) absorption coefficients K, (c) internal reflection coefficient $R_d^{\,i}$ for three TiO_2-pigmented coatings at thicknesses listed in the figure, as obtained with the SPGM.

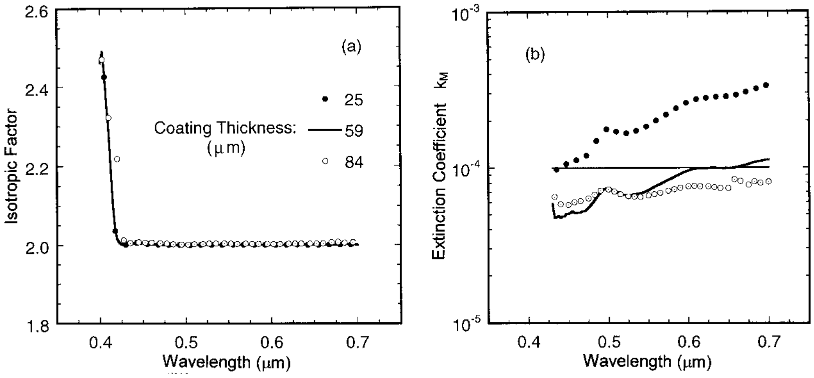

Fig. 6. Spectral dependence of (a) mean isotropy factor ξ that characterizes the angular distribution of the diffuse radiation intensity that propagates through rutile TiO_2-pigmented polymer coatings at thicknesses listed in the figure, and (b) extinction coefficient k_M of the matrix at the spectral region in which the pigments do not absorb. The thin solid curve in Fig. 5(b) corresponds to the initial estimated value.

$K \rightarrow K^{(i)} = 2k$ with $\xi = 2$. By taking into account that typically $\sigma_d{}^{(i)} \cong \sigma$, from Eqs. (6) one obtains

$$\xi \cong 2\left[\frac{\langle S\rangle}{S^{(i)}}\right], \qquad (7)$$

where $\langle S\rangle$ is calculated with the SPGM. In this way, the deviations observed in the spectral dependence of the effective scattering coefficient can be used to obtain the corresponding spectral dependence of the isotropic factor. We are not aware of previous experimental measurements to obtain the spectral behavior of the isotropic factor, usually denoted as the average crossing or average path-length parameter.

Figure 6(a) displays the wavelength dependence of the isotropic factor for pigmented coatings whose optical properties were considered previously in Fig. 5. As can be seen in Fig. 6(a), below 0.42 μm the isotropic factor increases to values greater than 2.0 as λ decreases, implying an increase in the degree of anisotropy in the angular distribution of the propagating diffuse radiation intensity. This is in fact in agreement with the lower values obtained for the retrieved internal reflection coefficient $R_d{}^i$, in comparison with the values that correspond to the first approximation. Furthermore, one can even qualify the type of anisotropy because values larger than 2.0 imply that there is more radiation that travels parallel to the interfaces than perpendicular to them, whereas for values smaller than 2.0 the reverse is true. However, it is important to note that in Eqs. (6) and (7) one assumes that ξ and $\sigma_d{}^{(i)}$ are independent of the spatial location within the film, and this might not be necessarily true. For example, one could expect that the degree of anisotropy would differ closer to the boundaries than in the middle of the film. From another point of view, one can regard the values of ξ and $\sigma_d{}^{(i)}$ in Eqs. (6) and (7) to be either some kind of spatial average of the corresponding spatially dependent quantities or to correspond to values at some specific locations. Here an analysis of the angular distribution of the intensity by use of, for example, the discrete ordinate eigenanalysis (*N*-flux) method[17] would be extremely valuable.

Another fact yet to be explained is the overall slight increased absorption displayed by the matrix in the case of a thinner sample ($h = 25$ μm). For wavelengths larger than 0.42 μm only the matrix contributes to the absorption. Then the discrepancies between $K^{(i)} = 2(1 - f)(4\pi k_M{}^{(i)}/\lambda)$ and $\langle K\rangle = \xi(1 - f)(4\pi k_M/\lambda)$ can be used to estimate the correct values for the imaginary part of the matrix refractive index $[k_M]$ in the spectral region where there is no absorption from the pigments:

$$k_M = \left(\frac{2}{\xi}\right)\left(\frac{\langle K\rangle}{K^{(i)}}\right)k_M{}^{(i)}, \qquad (8)$$

where $k_M{}^{(i)}$ is the imaginary part of the matrix refractive index initially estimated. As seen in Fig. 6(b) only the thinner sample shows an increased absorption of the matrix material. It would be difficult to explain this fact if we argued that the effect was due to anisotropy of diffuse scattering. One should bear in mind that larger uncertainties have been reported as a result of measurements of the reflectance and the thickness of a thinner sample. It would probably be convenient to take more precise measurements on a collection of thin samples.

5. Conclusion

A spectral projected gradient method (SPGM) has been applied to invert measured diffuse reflectance spectra of thick titanium dioxide pigmented coatings on black substrates illuminated with semi-isotropic diffuse radiation. The approach has been successfully implemented in samples of four different thicknesses to obtain the spectral dependence of (i) the effective scattering and absorption coefficients of the coatings, (ii) the external and internal diffuse reflection coefficients, (iii) the isotropic factor, and (iv) the extinction coefficient of the polymer matrix. The Lorenz–Mie theory and Fresnel relations were used to obtain the first approximation required by the SPGM. The spectral dependence of the retrieved values of the SPGM agrees quite well above the absorption edge of the pigment with the values that correspond to the first approximation. We conclude that some of the differences between the retrieved and the first approximation values in this region of the spectrum might be clarified if we included an effective index of refraction, a better treatment of the absorption of the matrix, or if we performed more precise measurements on thin samples. Below the absorption edge, the agreement between the retrieved and the first approximation values is not as good, and we have explored the influence in this disagreement of the assumption of isotropy of the diffuse intensity. We have done this through calculation of the spectral dependence of the isotropic factor. We found that anisotropy of the diffuse intensity increases sharply below the absorption edge, and we conclude that a more detailed study of the angular distribution of the diffuse radiation in this spectral region would be necessary. However, during the different stages in the development of this study, we also pointed out that there are still several types of problem and conceptual difficulties that should be addressed before a reliable, precise, and physically sound model of the interaction of light with granular thick films is generated.

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