An assessment of Saunderson corrections to the diffuse reflectance of paint films

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Abstract. We revise basic concepts behind the surface correction terms to the diffuse reflectance of a paint coating and its measurement with an integrating sphere. We question the validity of using the Fresnel relationships to calculate the surface reflectance terms in the case of paint films. Results of measurements on a white paint covered with an index-matched transparent slab are presented. From these results we infer the internal diffuse reflectance of the surface and obtain noticeable discrepancies from the prediction of Fresnel relationships.

1. Introduction

A paint film scatters and absorbs light incident on it. It aims to ‘hide’ any substrate on which it is applied with the smallest possible thickness and at the same time give a specific color to the reflected light. Highly scattering particles are added to paint to give the desired opacity, while optically absorbing pigments are added to give the desired color [1,2]. Paint is inhomogeneous at a scale of a few wavelengths of visible light but it is homogeneous in a macroscopic scale. The nominal color of a paint film is determined uniquely from its reflectance spectrum. To describe mathematically the reflectance of a paint film one usually divides the reflectance into a bulk reflectance and surface corrections. The surface corrections are commonly denominated as Sanderson’s corrections [3]. The bulk reflectance of a paint film is most commonly modeled using the Kubelka-Munk two flux theory [2,4,5] while the surface correction terms are usually calculated assuming a flat surface and using the Fresnel relationships for light reflection with the refractive index of the matrix material.

The KM model assumes the system is invariant under lateral translations and considers only two flux densities (watts/cm²) traveling along the axis normal to the surface: a positive flux density going from the source into the film, and a negative flux density traveling back towards the source. It is also assumed that the specific intensity is semi-isotropic at all points in space within the sample, that is, it is assumed that the specific intensity is constant on the positive and negative hemispheres. Therefore,
the specific intensity on either hemisphere is only a function of the distance to the surface. The KM model does not consider an index mismatch at air interface, although it does consider a reflectance at the film-substrate interface. Therefore the KM model may be considered as a “bulk-substrate reflectance”. In the case of a paint film the matrix material (the resin) usually has a refractive index of 1.5, and Saunderson corrections are calculated for a flat interface between refractive indices of 1.0 and 1.5. Now, while using the Fresnel relationships with the refractive index of the matrix material to calculate Saunderson correction may be a good approximation for dilute colloidal media, it may be questioned in the case of paint coatings, since the density of highly scattering particles is not small.

Practical measurements of the reflectance of paint should somehow take an average over relatively large areas of the film’s surface and over many directions of incidence and/or reflection. Measurements using integrating spheres are suitable to render average measurements of reflection properties of paint films versus the wavelength of light in a rapid and reproducible way [1-5]. There are several possible configurations that may be used with integrating spheres to characterize reflective properties of surfaces. Each configuration yields a different reflectance value. Actually when using integrating spheres the signal depends on complicated instrumental factors which results on the need of constant calibrations. Nevertheless, once having the proper calibration standard, measurements with integrating spheres are fast and precise.

The main objective of this work is to summarize the meaning and expression of the surface reflectance terms of paint films and discuss the validity of the Fresnel relationships to calculate them.

2. Reflectance formulas for a paint film

The so called diffuse-diffuse reflectance, $R_{dd}$, is one of the parameters of interest. It corresponds to illuminating the sample with perfectly diffuse light and collecting all reflected light regardless of the direction of scatter. $R_{dd}$ is given by the ratio between the reflected optical power in all directions and the incident power. It averages the reflectance over all incidence and scatter directions. By perfectly diffuse light we mean that the specific intensity (see [5]) is independent of the direction of reflection, and thus, it is semi-isotropic. Also, the so called $d:\alpha$ reflectance factor, $\tilde{R}^{d\alpha}$, has been adopted by the industry to standardize many tests on paint films $\tilde{R}^{d\alpha}$. (The symbol ~ is used here to indicate a reflectance factor.) This factor corresponds to illuminating with perfectly diffuse light the sample and measuring the reflected light at the angle $\alpha$ [1,2,6]. Usually the viewing angle $\alpha$ is small (less than 10°), and authors refers to the $d:\alpha$ reflectance factor in this case as the diffuse to near-normal viewing reflectance factor. A reflectance factor is defined as the ratio between the reflected specific intensity (also called radiance) at the viewing angle and the reflected specific intensity of a perfect diffuser illuminated in the exact same way. A perfect diffuser is lambertian and reflects all incident light. By lambertian it is meant that light is reflected with a constant specific intensity in all directions (semi-isotropically), regardless of the direction of incidence. Both, $R^{dd}$ and $\tilde{R}^{d\alpha}$ may be written in the form of a bulk reflectance with Saunderson surface corrections.

2.1 Diffuse-diffuse reflectance

Let us assume that the system is invariant under lateral translations and denote the bulk reflectance as $R_{K}$. When an incident flux density $F_i$ (W/cm²) reaches a sample, a fraction $r_e$ of it is first reflected by the air-matrix interface. The subscript $e$ stands for external reflection. A fraction $(1-r_e)$ is transmitted into the matrix and is multiply reflected between the bulk-substrate and the inside of the air-matrix interface. The inner reflectance of the air-matrix interface will be denoted as $r_i$ (where the subscript $i$ stands for internal reflectance). On each reflectance of the power flux on the air-matrix interface coming from the bulk, a fraction $(1-r_i)$ is transmitted out of the film and contributes to the net reflectance of the paint film. Adding the first reflected flux density from the front of the air-matrix interface and the transmitted fluxes coming from the multiple reflections between the bulk and the inner side of the interface gives the net reflected flux density yields,
Factorizing \((1-r)R\) gives,

\[
F' = r'F_i + (1-r')(1-r)R \left\{ 1 + R_r r' + R_r^2 r'^2 + \ldots \right\} F_i.
\]

Summing the power series in curly brackets gives the factor \(1/(1-rR)\). Dividing both sides of equation (2) by the incident flux density, \(F_i\), gives the net reflectance of the paint film. We get,

\[
R = r' + (1-r')\frac{R}{1-rR}.
\]  

This is in the general form of a Saunderson reflectance formula (with surface corrections \(r_e\) and \(r_i\)). Note that we have not yet specified the angular dependence of the specific intensity at the surface. If the incident flux is semi-isotropic, the external interface reflectance \(r_e\) corresponds to the diffuse-diffuse external reflectance of the interface which we may denote as \(r_{ed}^{dd}\). In this case, the flux transmitted inside the film just below the air-matrix interface may not be semi-isotropic due to the possible angle dependence of the transmissivity of the specific intensity (e.g. in a flat interface). However, in the case of paint films it should be safe to assume that the flux reflected from the bulk-substrate is semi-isotropic, owing to the multiple scattering inside the bulk of the paint film. In this case the coefficient \(r_i\) also correspond to the diffuse-diffuse reflectance, but from the inside of the film, \(r_{id}^{dd}\). Here also, the inner reflected flux may not be semi-isotropic, even though it is illuminated by a semi-isotropic flux, due to a possible angle-dependent reflectivity of the specific-intensity (e.g. a flat surface again).

Therefore, the fluxes that are incident to the bulk of the paint from the air-matrix interface are not, in general, semi-isotropic. Nevertheless, one usually approximates the bulk reflectance by the KM model no matter that the model supposes a semi-isotropic incident specific intensity. This is justified when the bulk of the film is highly scattering as in paint films, and thus, the positive and negative flux densities become rapidly semi-isotropic as light penetrates the bulk. We may then assume that the bulk is a lambertian reflector. Therefore, the diffuse-diffuse reflectance, \(R_{dd}\), of a paint film can be expressed as,

\[
R_{dd} = r_{ed}^{dd} + (1-r_{ed}^{dd})(1-r_{id}^{dd})\frac{R}{1-r_{id}^{dd}R}.
\]  

As already said, in the case of a flat interface the latter terms are commonly calculated with Fresnel reflection coefficients for unpolarized light \([1,2,5,7,8]\). If we suppose the refractive index of the matrix is 1.5 and that of the air is 1.0 we obtain, \(r_{ed}^{dd} \approx 0.09\) and \(r_{id}^{dd} \approx 0.6\) \([2, pp. 76]\). Also, we would expect a modest variation of these values over the visible spectrum due to the dispersion of the refractive index of the matrix material (about 4% or less).

### 2.2 The \(d: \alpha\) reflectance factor

Now, let us consider the \(d: \alpha\) reflectance factor which we denote as \(R_{d \alpha}^{dd}\). In practice, measuring this factor allows two possibilities: specular included and specular excluded measurements. By definition, the specific intensity of the incident flux density is assumed semi-isotropic as well, but we measure only the specific intensity of the reflected flux at an angle \(\alpha\) from the normal to the surface, which we will denote as \(I_(\alpha)\). By definition a reflectance factor of a sample is the ratio of the reflected specific intensity by the sample and by a perfect diffuser under the same illumination condition. Since the reflected specific intensity from a perfect diffuser is \(F_i/\pi\), regardless of the angular dependence of the
incident specific-intensity, we have that, \( \tilde{R}^{da} = I_s(\alpha)/\left(\frac{1}{2} F_i\right) \), and thus, \( I_s(\alpha) = \frac{1}{\pi} \tilde{R}^{da} F_i \). In the particular case of a semi-isotropic incident flux, we have that \( F_i = \pi I_i \) where \( I_i \) is the (angle-independent) specific intensity of the incident light. (Note that integrating \( \cos \theta \sin \theta d\theta d\phi \) over the incidence hemisphere gives the factor \( \pi \).) Thus, in this case we may write,

\[
I_s(\alpha) = \tilde{R}^{da} I_i.
\]

(5)

A first reflection of the incident flux at the air-matrix interface contributes by \( \tilde{r}^{da}_v I_i \) to the value of \( I_s(\alpha) \) where \( r^{da}_v \) is the external reflectance-factor of the interface alone and, in general, it will depend on the surface roughness. In the particular case of the interface being flat, the specific intensity reflects only specularly at the interface, and then it would appropriate to use the collimated to collimated reflectance factor \( r^{da}_v \) instead of \( \tilde{r}^{da}_v \), and we could write \( I_s(\alpha) = r^{da}_v I_i \). Actually, in this latter case \( r^{da}_v \) could also be identified as a proper reflectance instead of as a reflectance factor. Nevertheless, the interface of many paint coatings is rough, and thus for generality we should use the \( d/\alpha \) interface reflectance-factor. Another contribution to the specific intensity \( I_s(\alpha) \) comes from the flux density just below the air-matrix interface and transmitted out of the film. The specific intensity at an angle \( \alpha \) of this transmitted flux is added to the previous contribution. That is, we may write,

\[
I_s(\alpha) = \tilde{r}^{da}_v I_i + \tilde{t}^{da}_v I_i(0'),
\]

(6)

where \( I_i(0') \) is the specific intensity of the light incident on the interface from below which we assume angle-independent (semi-isotropic), and \( \tilde{t}^{da}_v \) is the appropriate transmittance factor. In analogy to the definition of a reflectance factor, the transmittance factor \( \tilde{t}^{da}_v \) is defined here as the ratio between the transmitted specific intensity in the direction of \( \alpha \) and that transmitted by a perfect lambertian diffusing screen, which in this case correspond to a screen that transmits all incident light semi-isotropically. Now, the specific intensity reflected by the bulk just below the surface is given by,

\[
F_-(0') = (1 - r^{dd}_v) R_K F_i / (1 - r^{dd}_v R_K).
\]

Here the incident flux is semi-isotropic and thus, \( F_i = \pi I_i \). Thus, the transmitted specific intensity due to \( F_-(0') \) is \( \frac{1}{\pi} \tilde{r}^{da}_v F_-(0') \) and we get,

\[
\tilde{R}^{da} = \tilde{r}^{da}_v + \tilde{t}^{da}_v \left(1 - r^{da}_v\right) \frac{R_K}{1 - r^{dd}_v R_K}.
\]

(7)

If the surface is flat, \( \tilde{t}^{da}_v \) can be seen to be equal to the collimated to collimated transmittance (or power transmissivity) \( t^{u'a}_v \) of light incident at an angle \( \alpha' \) and refracted to an angle \( \alpha \), which in turn, may be related to the collimated-to-collimated reflectance at an angle of incidence of \( \alpha' \) as [10, pp. 155]

\[
t^{u'a}_v = \left(n_1^2/n_2^2\right)[1 - r^{ua}_v] \]

where \( \alpha' \) and \( \alpha \) are related by Snell’s law (see Fig. 4a):

\[
\alpha' = \sin^{-1}(n_2 \sin \alpha / n_1).
\]

Usually the external medium is air and thus, \( n_1 = 1 \). Now, it is not difficult to see that for a flat surface, \( t^{u'a}_v = r^{ua}_v \). Also, in the case of a flat interface we have the following relation holds: \( (1 - r^{dd}_v)(n_1^2/n_2^2) = (1 - r^{dd}_v) \) [9]. Therefore we may write the \( d: \alpha \) reflectance factor when the air-matrix interface is flat as,

\[
\tilde{R}^{da} = r^{ua}_v + (1 - r^{ua}_v)(1 - r^{dd}_v) \frac{R_K}{1 - r^{dd}_v R_K},
\]

(8)

where it is implicit that \( r^{ua}_v \) is evaluated at the angle of detection \( \alpha \). This formula can be found in the literature; commonly, with out a proper explanation. In particular, a warning should be said when stating Eq. (8) to avoid possible confusions. The collimated to collimated surface reflectance term, \( r^{ua}_v \), reduces rapidly to zero when the surface roughness increases. But here \( r^{ua}_v \) is just the limit of
According to the roughness tends to zero. Actually \( r^d_{\alpha} \) is rather insensitive to roughness in comparison to \( r^o_{\alpha} \) as discussed below. In fact, many paint films do not have a noticeable specular reflection. In these cases, we cannot use the latter formula and we may have to go back to Eq. (7). We are not aware of any work showing that Eq. (7) can be put in the form of a Sauderson’s formula for all types of surface roughness. Fortunately, even non-glossy paints still have a smooth surface and the slope of the surface at any point on the surface is typically small. To some approximation we may model the illuminated surface of a paint film as a collection of flat facets, each with an area of dimensions large compared to the wavelength. In this case we may write the \( d: \alpha \) reflectance factor as,

\[
\tilde{R}^d_{\alpha} = r^o_{\alpha} + \left( 1 - r^o_{\alpha} \right) \left( 1 - r^d_{\alpha} \right) \frac{R_s}{1 - R^d_{\alpha} R_s},
\]

where the bar above \( r^o_{\alpha} \) and \( r^d_{\alpha} \) denotes taking the average over a probability density function of the surface’s slope. It is not difficult to see that for small slopes of the surface facets, the surface reflectance \( r^o_{\alpha} \) and \( r^d_{\alpha} \) do not change appreciably from their value for zero slope. Recall that the viewing angle \( \alpha \) is also supposed to be a small angle (near normal viewing) and Fresnel reflection coefficients are nearly constant for small angles of incidence. Therefore, equations (9) and (8) give basically the same result. However, here it is clear that the first surface reflectance term should not be removed when the specular reflectance is nearly zero, and actually, it keeps a value close to that for a flat surface in most non-glossy paints.

### 3. Measurements with an integrating sphere

Ideally, an integrating sphere is an empty spherical cavity with perfect diffusing inner walls. Ports are opened on the sphere walls to introduce and detect the multiply reflected light inside the sphere. For reflectance measurements another port to expose the surface of a sample is also required. The key property of an integrating sphere is that light reflected from a small surface element of the lambertian walls produces a uniform flux density on the rest of the sphere’s wall (owing to the spherical geometry) [10]. This property assures that, after the second reflection on the sphere’s inner walls of a light beam, and for subsequent reflections, the specific intensity at the sphere walls becomes semi-isotropic.

To measure the diffuse-diffuse reflectance of a sample, a photo-detector, sensitive to light coming from all directions in a hemisphere (a semi-isotropic detector), is inserted on a port on the sphere’s walls as shown on figure 1a. The optical power received by the detector is given by [11,12],

\[
P_d = \frac{\beta_1}{\beta_2 - R^d} P_0,
\]

where \( \beta_1 \) and \( \beta_2 \) are instrumental parameters. In order to measure \( R^d \) we must calibrate the sphere and determine the values of \( \beta_1 \) and \( \beta_2 \). A light trap \( (R^d = 0) \) and a calibration sample \( (R^d = R_{cal}) \) are sufficient. In this configuration the detector receives light coming from the cavity walls and from the sample. Since the latter has a much smaller area, the relative change of the detected power on changes of the diffuse reflectance of the sample can be rather small, and consequently, the signal to noise ratio is also rather small. This is probably the main reason why it is preferable to work with the \( d: \alpha \) reflectance factor instead of the diffuse-diffuse reflectance.

To measure the diffuse to specified viewing angle reflectance factor an directional detector viewing the surface of the sample at an angle \( \alpha \) (with respect to the normal of the sample’s surface) is used, as illustrated in figure 1b. The specific intensity in front of the detector’s aperture is given by,

\[
I_\alpha = \tilde{R}^o_{\alpha} I, \quad \text{where } I_\alpha \text{ is the specific intensity incident on the sample. Since the light incident on the sample is semi-isotropic (see the appendix) we have } I_\alpha = F_i / \pi, \quad \text{where } F_i \text{ is the incident flux density. Assuming } I_\alpha \text{ is constant within the reception solid-angle of the detector, } \Delta \omega_0, \text{ we have that the} \]

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detected optical power is given by, \[ P_d = a_{\text{det}} \Delta \omega_\alpha I_d(\alpha), \]
where \( a_{\text{det}} \) is the detectors area. Combining the previous equations yields,
\[
P_d = \frac{\beta_1 \tilde{R}^{\text{da}}}{\beta_2 + \tilde{R}^{\text{da}}} P_0,
\]
where \( \beta_1 = a_{\text{det}} \Delta \omega_\beta \beta_1 / \pi \). There are several commercial spectrophotometers designed to measure \( \tilde{R}^{\text{da}} \) based on Eqs. (10) and (11).

**Fig. 1:** (a) Diffuse-diffuse configuration using an isotropic detector and (b) diffuse to near normal viewing configuration using a directional detector. \( F_\text{out} \) is the flux density incident on the cavity walls and \( m \) is the diffuse-diffuse reflectance of the cavity walls.

The measurement of the \( d:\alpha \) reflectance factor allows for Specular Component Included (SCI) and Specular Component Excluded (SCE) measurements. In this case, an additional port with a lid is included in the integrating sphere. The inner side of the lid is covered with the same white diffusing coating as the rest of the interior walls of the integrating sphere. This additional port coincides with the specular image (from the sample’s surface) of the directional-detector’s cone of view (see Fig. 1b). The port may be opened for SCE measurements or closed for SCI measurements. Therefore the reflectance factor with the specular component included, \( \tilde{R}^{\text{SCSI}} \), is given, in general by Eq. (7) and by Eq. (9) for samples with smooth rough surfaces.

If the port is opened, no specularly reflected light reaches the directional detector since no light is incident to the sample from the corresponding specular direction. When the sample’s surface is perfectly flat, the specular excluded option removes the external reflection from the surface from the measurement and we must drop the first term on the RHS of Eq. (8). However, if the surface is rough, light coming from portions of the cavity wall around the specular-excluded port is reflected non-specularly at the surface and enters the directional detector. Therefore, when the surface is rough we do not entirely remove the external surface reflection. When the local slopes of a rough surface are sufficiently large, there will be no noticeable change on the detected signal when opening or closing the specular excluded-included port. Then, we may write,
\[
\tilde{R}^{\text{SCSI}} = (1 - \chi) r_\alpha^{\text{out}} + (1 - r_\alpha^{\text{out}}) \left(1 - r_\gamma^{\text{out}} \right) \frac{R_K}{1 - r_\gamma^{\text{out}} R_K},
\]
where \( \chi \) is a “gloss” factor and is defined here such that it is 1 for a flat surface (high gloss) and decreases to zero as the roughness of the surface increases (no gloss).
4. Physics of the surface reflectance terms

Up to the present day, the surface terms are almost always calculated theoretically. In some few cases it is left as free parameter and retrieved from fitting an equation to experimental data of the reflectance or reflectance factor [13,14-16]. We are not aware of any way for experimentally determining directly their value in paint films. Most authors assume that the surface terms may be calculated using Fresnel reflection coefficients for a flat interface between two transparent media [5-7,9,13-16]. When the bulk of an inhomogeneous film with an index mismatch at its surface is diluted (relatively low scattering), the Fresnel approximation is probably very good. However in highly scattering materials such as paint one may question the validity of using the Fresnel reflection coefficients to calculate the reflectance and transmittance at the surface. If one were to assign an effective refractive index to the bulk, this would have to be complex, even without absorption because of the scattering [17]. On the other hand, one may think that light traveling within the bulk correspond to inhomogeneous waves. By inhomogeneous waves here we mean that the corresponding effective wave vector is complex and its real and imaginary parts are not parallel to each other. In this case we would expect that the usual calculation of the surface reflectance may incur in noticeable errors. From a microscopic point of view we can also wonder about the role of the evanescent waves around the scattering particles and their interaction with the surface. For instance, it is well known that total internal reflection may be frustrated when interacting with the evanescent waves near the surface. We are aware of only one publication considering an effective medium [18]. However, the nature of such an effective medium and its correct use within radiative transfer models (such as the Kubelka-Munk theory) is not yet well understood. There is at least one reference where the value of the diffuse-diffuse internal reflectance, $r_{dd}$, of the surface obtained from fitting theory to experiment resulted in values clearly smaller than that predicted by the Fresnel reflectance [16]. However, the authors assumed that the light incident to the surface from within the film was not completely diffuse and therefore did not question the validity of using the Fresnel relationships. To explore this issue we designed a simple experiment to obtain some clear indication as to whether the values of $r_{dd}$ in the case of a paint film are consistent with the predictions of the Fresnel relationships for diffuse light or not.

5. Experimental evidence of deviations from Fresnel reflectance

We prepared a thin film of a non-glossy white paint. We measured the diffuse to collimated reflectance factor using a commercial spectrophotometer (Minolta 3700d). The spectrophotometer has a diffuse illumination to 8° viewing angle configuration and has the option of specular included and excluded measurements. The measured spectrum of the reflectance factors for the specular included and excluded options are plotted in Fig 2 (full and empty circles, respectively). Both curves are close to each other, which means that the gloss factor $\chi$ in this case is close to zero (reduced specular reflection due to surface roughness).

Now, in order to infer the possible values of the surface internal reflectance $r_{dd}$ for the paint film we propose the following additional measurements. The idea is to modify the surface in such a way as to assure that the surface terms are well approximated by the Fresnel reflectances. The refractive index of the matrix material of the paint is about 1.5 and if the usual calculations of the surface terms were valid we should have $r_{d8} \approx 0.04$ and $r_{dd} \approx 0.6$. To realize this we placed a glass cover-slide of refractive index of 1.5 and 100 $\mu$m thick on top of the paint film. The interface between the matrix of the film and the cover slide was erased introducing index-matching oil between the surface of the film and the cover slide. In this way the composite film corresponds to moving by 100 $\mu$m the matrix-air interface from the bulk and making sure it is flat. In principle, diffuse light leaves the bulk freely and only traveling waves reach the interface with air. Therefore, in the composite film we can indeed
suppose valid the Fresnel relationships for a flat interface between a medium of refractive index of 1.5 and air of refractive index 1.0.

\[ \begin{align*}
400 & 450 & 500 & 550 & 600 & 650 & 700 & 750 \\
76 & 78 & 80 & 82 & 84 & 86 & 88 & 90 & 92 & 94
\end{align*} \]

\[ d \alpha \] Reflectance factor

Wavelength (nm)

Paint SCI
Paint SCE
Paint + cover slide SCI
Paint + cover slide SCE

Fig. 2: Plot of the measured reflectance factors for the paint film (full and open circles for the specular included and specular excluded options, respectively) and for the composite film with an index matched cover slide on top of the paint film (full and open triangles for the specular included and specular excluded options, respectively).

Let us denote the reflectance factor of the paint film with the specular component included as \( \tilde{R} \) and that for the paint film with an index matched cover slide on top as \( \tilde{R}' \). We have,

\[
\tilde{R} = r_{e}^{dK} + (1 - r_{e}^{dK})(1 - r_{i}^{dd}) \frac{R_{K}}{1 - r_{i}^{dd} R_{K}},
\]

(13)

and

\[
\tilde{R}' = 0.04 + (1 - 0.04)(1 - 0.6) \frac{R_{K}}{1 - 0.6 \times R_{K}},
\]

(14)

From (23) we may solve for the value of the bulk reflectance, \( R_{K} \) and then use it in Eq. (22) to solve for \( r_{i}^{dd} \) in terms of \( \tilde{R}, \tilde{R}' \) and \( r_{e}^{dK} \). We get,

\[
r_{i}^{dd} = \left( \frac{\tilde{R} - r_{e}^{dK}}{(1 - r_{e}^{dK}) - R_{K}} \right) \left( \frac{\tilde{R} - r_{e}^{dK}}{(1 - r_{e}^{dK}) - 1} R_{K} \right),
\]

(15)

where \( R_{K} = (\tilde{R}' - 0.04) / (0.360 + 0.6 \times \tilde{R}') \). In Fig. 3 we plot the calculated values of \( r_{i}^{dd} \) using Eq. (15) and the experimental data in Fig. 2.
Fig. 3: Plot of the calculated values of $r_{dd}$ using Eq. (26) and the experimental data for $\tilde{R}$ and $\tilde{R}^*$ for values of $\varepsilon\delta$ of 0.0, 0.02, 0.04 and 0.06.

We can appreciate in Fig. 3 that the retrieved value of $r_{dd}$ is not very sensitive to the value assumed for $\varepsilon\delta$ within the range of acceptable values. We can see that the values of $r_{dd}$ for the paint film are clearly less than the Fresnel diffuse-reflectance for an interface between the matrix of refractive index 1.5 and air (about 0.06). We can also appreciate that it has relatively strong wavelength dependence which can not be explained by the dispersion of the refractive index of the matrix material.

6. Summary and conclusions

In this work we revised the main concepts implicated when measuring reflectance spectra of paint coatings with an integrating sphere. We revised the formulas for the diffuse-diffuse reflectance and for the $d:\alpha$ reflectance factor (diffuse to near normal viewing) of a paint film. The hypotheses behind the surface correction terms were discussed taking into account possible surface roughness in paint films. In particular, we showed that surface roughness may in general hinder the usual interpretation of the surface terms in the formula for the $d:\alpha$ reflectance factor. Although for surfaces with smooth roughness, the surface terms should not change appreciably from the case of a flat surface. Nevertheless, we also questioned the use of the Fresnel relationship to calculate the surface reflectance terms even for flat surfaces. We designed a simple experiment to infer the possible values of the inner surface reflectance and found strong discrepancies from the expected behavior from the Fresnel relationships. In particular, we obtained evidence of a strong dependence of the surface internal reflectance with the wavelength of light. Accordingly to our results a better understanding of the physics behind the reflectance of diffuse light at the interface of a highly scattering medium is necessary for modeling quantitatively the so called Saunderson corrections in the case of paint films.

Acknowledgments

We acknowledge financial support from Dirección General de Asuntos del Personal Académico from Universidad Nacional Autónoma de México through grant IN-120309 and from Consejo Nacional de Ciencia y Tecnología (México) through grant 49482-F. We are also grateful for instructive discussions with Professors Rubén G. Barrera and Eugenio R. Méndez.
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