Notes on Integrating Sphere Paint

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This informal document is a collection of notes and references about commercial integrating sphere paint and similar diffuse reflectance materials.

1 Overview of the coating problem

Diffuse reflectors are important in many applications. Diffuse coatings, for example, can be used to trap light inside solar cells, in order to improve their efficiency. Most diffuse reflectance coatings seem to be based on compressed barium sulfate powder. The most widespread (and studied) diffuse coating seems to be "6080" paint for integrating spheres, which has been sold by various manufacturers over time (Kodak, Eastman, Munsell, and now Labsphere).

High-quality diffuse reflectors are often assumed to be ideal Lambertian diffusors, and are modeled by only a single parameter, the diffuse reflectance ρ ($\lesssim 1$). This is a standard practice, for example, with integrating spheres [1], and it is also a common approach for integrating-sphere detectors, whether modeled by a ray-tracing [2] or a "photon gas" approach [3]. This model is also used for light-trapping enhancement of solar cells [4].

Unfortunately, these materials seem to have been exclusively characterized for reflection into air or vacuum ($\rho = \rho_{\mathrm{air}}$), and so there seems to be a lack of information about their use as coatings, for reflection inside other media, such as glass or acrylic. As a result, it is not even clear whether it is appropriate to model them as ideal Lambertian diffusers when used as coatings. If they do behave as ideal diffusers, then in the simplest case of diffuse illumination, one would just expect the reflectivity ρ to be effectively modified by the refractive index of the target medium [3, 4] (and a similar effect if the medium is between paint and air [5]). If they do not behave as ideal diffusers, then the paint-media interface has to be modeled. Unfortunately, it is not clear how to extend the more detailed models traditionally used for 6080 paint to account for a target media other than air (see Section 3). "Full" modeling of highly turbid, random media with interfaces is very difficult (e.g., [6]). Perhaps, in practice, roughening of the paint-media interface could be used to recover a more ideal diffusor behavior [4].

For example, consider 6080 paint applied to glass. Figs. 1 and 2 demonstrate a few properties for reflection inside glass (Pyrex or N-BK7) off of a flat interface with Labsphere 6080 paint. In Fig. 1, the interface is illuminated by a collimated green laser beam. Fig. 1(left) shows multiple rings due to total internal reflection off of a parallel glass-air interface, which demonstrates that 6080 does reflect the laser light in a diffusive manner. Fig. 1(right) shows that, in addition to diffuse-like reflection, there is still specular reflection from the flat 6080-glass interface. This is not the case for a typical 6080 surface in air, perhaps due to surface roughness. Fig. 2 shows that a flat 6080-glass interface is not Lambertian, since it undergoes a gradual transition towards total internal reflection with increasing incidence. In contrast, an ideal Lambertian surface should appear "white" at all angles of incidence, and give no specular reflection. External illumination with a green laser pointer shows that this total internal reflection is frustrated, likely

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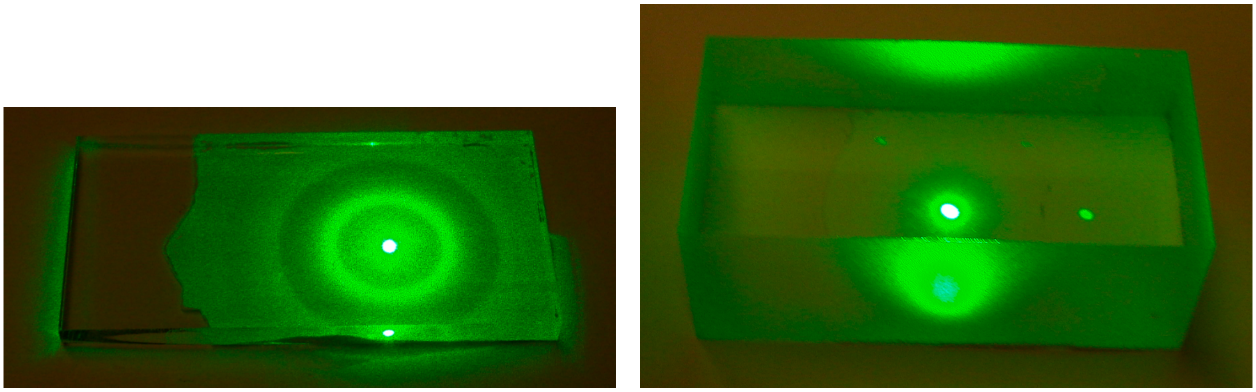

Figure 1: Reflection of a green laser pointer inside Pyrex glass, off of a rear interface with Labsphere 6080 paint. (Left) Multiple rings from total internal reflection at the front Pyrex-air interface. The Pyrex block is 1" × 2" in size and 0.125" thick, with polished sides. The ring radii are multiples of about 6 mm. (Right) Specular reflection of a tilted laser beam off the rear Pyrex-6080 interface. The Pyrex block is 1" × 2" in size and 0.75" thick, with ground sides.

because the paint is a heterogeneous (porous) media. Therefore, 6080 paint does not simply act as an ideal diffuser when used to reflect light inside glass.

One potentially elegant way to model an interface with a diffuse coating would be to use a complex refractive index for the diffuse material. Complex refractive indices have been measured for highly turbid media [7]. Perhaps such an approach could be appropriate for high-quality diffuse reflectors. As far as we know, no one has explored this for 6080 paint, and effective complex refractive indices have not been measured for other high-quality diffuse reflectors. However, an effective, real refractive index has been measured (by finding a Brewster's angle in air) for pressed barium sulfate powder, to be around 1.415, which is a little less than that of typical glass [8]. That measurement, together with Figs. 1 and 2, provides some support for this idea. 6080 paint would be an ideal candidate for such study, because of its long history and widespread use. It would be very convenient if 6080 paint could be described by a complex refractive index. Even if it cannot be described by a complex index, it would be interesting to know why. Such knowledge would be important to understand how diffusors work as coatings for internal reflection inside media other than air. For example, this should be important for light-trapping enhancement of solar cells or for integrating-sphere detectors with internal liners (e.g., glass or plastic inner coatings or containers). It could even be useful for standard integrating spheres, which can suffer from internal specular reflection [9, 10].

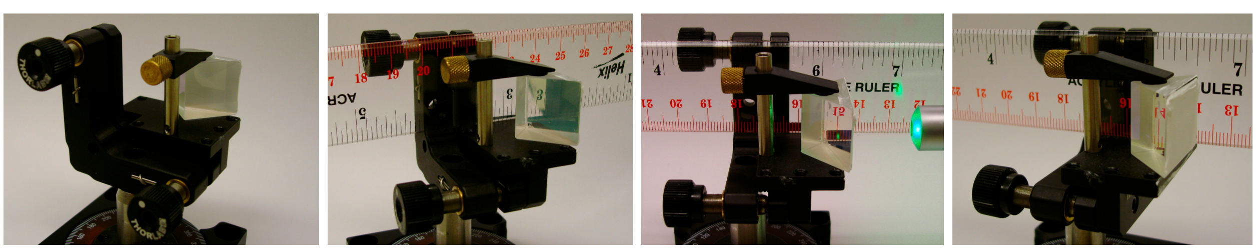

Figure 2: Gradual transition to total internal reflection for the hypotenuse of an N-BK7 right-angle prism (Thorlabs PS908L-B) coated with Labsphere 6080 paint. Illumination with a green laser pointer demonstrates frustration of the total internal reflection for an angle of incidence of roughly 45° with an external prism face, which corresponds to a angle of incidence with the hypotenuse of roughly 73° inside the prism.

2 Information about diffuse reflectance coatings

2.1 Labsphere 6080 white reflectance coating (Eastman/Kodak/Munsell 6080)

Labsphere's 6080 paint is a "cost-effective, near-Lambertian coating for diffuse reflectance applications" that is "ideal for use in integrating spheres, reflectance spectrophotometers, sphere photomemeters, lamp housings, display backlight reflectors, optical components and other applications that call for diffuse illumination or reflectance" [11]. It has a diffuse reflectance in air (ρ_{air}) between 95-98% for wavelengths between 300 to 1200 nm. The paint is made of barium sulfate ($BaSO_4$) particles suspended in a polyvinyl alcohol (PVA) binder. For reference, the density of barium sulfate is 4.5 g/cm^3, and of PVA is 1.19-1.31 g/cm^3. The (real) refractive index of barium sulfate is 1.64, and of PVA is 1.50. The paint is sold diluted in ethanol, and must be applied by airbrush. The optimal thickness is stated as $0.5 - 0.6$ mm, and its instructions say that additional thickness does not increase reflectance.

Labsphere will not give out specific details about the paint (which are trade secrets). However, they do admit (via email) that their 6080 paint is the same as the "6080" variants sold in the past by Kodak, Eastman, and Munsell (whom Labsphere purchased). Luckily, there are old journal articles about the reflectance of barium sulfate and the Eastman white reflectance coating. According to Ref. [12] (whose authors were from Eastman), the optimal particle diameter is roughly $0.3 - 3.0$ μm and the sizes of most of the particles in the old Eastman white reflectance paint are between roughly $0.05 - 3.0$ μm. The ratio of PVA:$BaSO_4$ in the paint is states as 1:100 "by parts," which was chosen to optimize the tradeoff of reduced performance for enhanced mechanical strength due to the PVA binder.

It is unclear exactly how packed the particles are, or how much the PVA binder fills the voids between particles. Both likely depend on how the paint is applied. However, we can estimate the packing density from details about powdered samples. Pressed powder layers of barium sulfate without a binder make a better reflector than the paint (perhaps due to index matching effects from the binder). An estimate for an optimal powder packing density is 2.3 g/cm^3 [12]. This corresponds to a volume packing fraction of about 51% for barium sulfate powder, which agrees with a report of 52% in Ref. [8]. For comparison, a BCC crystal has 68% volume fraction, so the powder is very tightly packed, perhaps as tightly as possible while retaining a random structure.

We can estimate the degree that the PVA fills voids between particles using this packing fraction. If the 1:100 "by parts" ratio is by volume, then assuming the particles in the paint are as closely packed as in the pressed powder, then the volume fraction for the PVA is 1/100 that of the particles, or 0.51%. Therefore, the PVA doesn't fill the space between particles. If the 1:100 "by parts" ratio is by mass, then the ratio of volumes is about 1:375 leading to a packing fraction of about 0.14%, so the PVA still cannot fill the voids. Therefore, it seems safe to guess that the PVA does not completely fill the space between particles, and that the remaining void is filled with ambient air. However, this is still just a guess.

Kubelka-Munk coefficients have been measured for 6080 paint, see Ref. [13]. Ref. [14] provides a comparison of different models for 6080 paint (or binder-less versions). An effective (real) refractive index has been measured as $n_{\text{p}} = 1.419, 1.415, 1.420$ at $700, 800, 1000$ nm for a pressed barium sulfate powder with volume fraction 0.52 [8].

2.2 Labsphere proprietary Spectraflect and Duraflect coatings

Labsphere also has a proprietary barium sulfate coating, Spectraflect, that they use on their own products or apply to parts sent to them [15]. They also have another (not $BaSO_4$ based?) coating, Duraflect, intended for more harsh conditions [16]. When contacted by email, Labsphere says that they are doing more and more coatings on glass and acrylics for customers in LED lighting R&D and solar cell applications.

2.3 Labsphere Spectralon

Labsphere's Spectralon is a commercial reflectance material, not a coating, and it has the highest known diffuse reflectance of any coating or material in the UV-VIS-NIR range (typically $\rho_{\text{air}} > 99\%$). It is a sintered

PTFE thermoplastic similar to Teflon. The index of refraction of Spectralon should be similar to that of Teflon, which is roughly 1.35. Labsphere will machine Spectralon into custom shapes, so I guess that a custom form-fitting piece could be glued into optical contact in order to act as a "coating." I do not think that Spectralon has internal voids, so it is not a porous or heterogeneous material like the $BaSO_4$ coatings.

3 Traditional models for 6080 paint

6080 paint is a highly reflective, diffusely reflecting, random (turbid), and heterogeneous (porous) media. The study of scattering by such materials is an enormous field with a vast history (e.g., [17]), so there are numerous models and applications. Random media are still a subject of much modern physics research [6]. Unfortunately, 6080 paint is a difficult, special case for three reason: (1) it is densely-packed (the particles touch), (2) it is a strong multiple-scatterer, and (3) the particle size is of the same order as the wavelength of light that are of interest. Here is a list of traditional models for 6080 paint and similar materials:

Radiative Transfer (RT) When applicable, the equations of RT give a complete description of the interaction of light with a scattering and absorbing medium. Solutions usually require numerical evaluation. Seems to always assumes sparse, infinitesimal independent scatterers. I have only found one paper that attempts to extend RT to closely-packed media [18]. An example application to ceramics for computer vision is Ref. [19].

Kubelka-Munk (KM) Theory Phenomenological "2-flux" theory that is an approximate solution to RT for diffuse light [17, 20]. This is the most commonly used theory, since its results are simple. There are numerous N-flux variants ("discrete-ordinates" method?) and modifications, the most common being the so-called 4-flux theory. For results with 6080 paint, see Ref. [13].

Photon Diffusion Models Approximate solution to RT for low absorption and strong scattering. Unclear if accurate near material boundary, and has difficulty with boundary conditions. Long history starting with neutron scattering. [One issue I've noticed is there may be a boundary layer of the energy density at the surface (shows up in Monte Carlo with plane wave illumination), which I think could be recovered if you use an inhomogeneous driving force, but which paint-modelers don't seem to account for.] Complexity varies widely; see Refs. [17, 14].

Monte Carlo (MC) Well, what can't be modeled with MC? The paint can be modeled as a strong, isotropically scattering material. For example, see Ref. [21]. [Note boundary layer comment above.]

Ref. [14] provides a comparison of RT, KM, and diffusion model results for 6080 paint (or binder-less versions), all of which agree for near unity albedo. However, it's unclear how these models would account for diffuse reflection into a medium with a refractive index that isn't the same as air. First off, the KM theory only has one parameter, the ratio of scattering to absorption coefficients, and being phenomenological, an interface would have to be artificially introduced. Likewise, diffusion models seem to only have scattering and absorption constants, and no explicit material index. Adding an interface shouldn't change these coefficients, unless they were incorrectly measured (with respect to an index mismatch). Thus the diffusion model seems to say the reflectivity wouldn't care about an interface at all. RT seems to have an index (see [19]), but it assumes sparsely packed particles and the solutions are numerical. Of course, I could be missing something.

There is a large literature of reflection and shading models used in computer graphics to render various surfaces, with might be useful to explore (e.g., [19]).

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