Reflectance spectroscopy from TiO2 particles embedded in polyurethane

Gudla, Visweswara Chakravarthy; Canulescu, Stela; Johansen, Villads Egede; Schou, Jørgen; Ambat, Rajan

Link back to DTU Orbit

Reflectance spectroscopy from TiO$_2$ particles embedded in polyurethane

Chakravarthy G.V., Stela Canulescu, Villads Johansen, Jørgen Schou, Rajan Ambat,
Technical University of Denmark, Kongens Lyngby, 2800 Denmark

Summary

This paper presents the results of a physical simulation carried out using TiO2-Polyurethane composite coating on bright aluminium surface to understand the light scattering effect for designing white surfaces. Polyurethane matrix is selected due to the matching refractive index (1.7) with Al$_2$O$_3$ layer on anodized aluminium surfaces. Three different TiO$_2$ particle distributions were dispersed in polyurethane and spin coated onto high gloss and caustic etched aluminium substrates. Reflectance spectra of TiO$_2$-polyurethane films of various concentrations were analysed using an integrating sphere. The results show that the TiO$_2$-polyurethane coatings have a high diffuse reflectance as a result of multiple scattering from TiO$_2$ particles. Diffuse reflectance spectra of TiO$_2$ containing films vary weakly with particle concentration and reach a steady state value at a concentration of 0.75 wt.%. Using the Kubelka Munk two-stream model, the scattering and absorption coefficient of the TiO$_2$ particles embedded in polyurethane was determined. These studies can serve on understanding the fundamental requirements for generating a bright and white decorative anodized aluminium surface.

1. Introduction

Anodization has been extensively applied for surface finishing of aluminium components to improve the corrosion resistance, adhesion of further paint systems and aesthetics in architectural, decorative and automobile related applications [1]. The anodized layer is usually transparent to visible light and contains nano sized pores which can be filled with a variety of dyes to impart a wide range of colours to the surface [2]. Most of the dyes used for this purpose are organic in nature and are prone to degradation over a period of time when exposed to sun light [3]. Nearly all colours including black can be imparted to anodized aluminium, but achieving a bright white anodized aluminium surface has not been achieved to date. The dye molecules used for colouring anodized aluminium are in the nanometer scale and are smaller than the pore size in the anodized layer, whereas traditional white pigments are bigger. Also, the mechanism behind colouring of anodized layer is selective absorption of certain wavelengths and reflectance of other wavelengths in visible light by dye molecules. On the other hand white appearance requires no absorption of incident light in the visible range by the anodized layer. Thus it is not possible to achieve white anodized aluminium with glossy appearance by using conventional dyeing techniques. For the anodized layer to provide effective scattering of light it needs to be tailored and one approach is incorporation of high refractive index particles in the anodized layer. TiO$_2$ in rutile phase has a refractive index of 2.6 – 2.9 and is widely used as a white pigment in paints [4]. Also, it is stable to UV radiation and does not degrade when exposed to sun light. Thus the use of TiO$_2$ for achieving white anodized aluminium surfaces is very promising and needs a fundamental understanding to achieve the required optical properties.

In this paper we study multiple scattering of light from TiO_2 particles embedded in a transparent medium, i.e. polyurethane which mimics anodized aluminium. Scattering and absorption coefficients are calculated using Kubelka-Munk two stream model for different particle size distributions and the optimal film thickness is computed. The effect of particle size distribution and concentration are experimentally investigated along with that of surface condition by using TiO_2-polyurethane coatings on aluminium. Our studies can serve as a model for understanding the interaction of light with scattering particles in anodized aluminium and facilitate designing of anodized surfaces that are bright, white and glossy.

2. Experimental

2.1. Materials & Methods

Aluminium substrates having high specular reflectance (high gloss) were obtained in cold rolled condition from Alcan Rolled Products, Germany. A polyurethane clear coat based on acrylic resin (Sigmavar WS Satin) was obtained from Sigma coatings, the Netherlands. TiO_2 particles in rutile phase were obtained in three different size distributions from DuPont Titanium Technologies, Belgium. The aluminium substrates were subjected to ultrasonic etching in 10 wt. % NaOH at 60 °C for 10 min followed by demineralised water rinsing. The etched substrates were then desmutted in HNO_3 followed by demineralised water rinsing. Polyurethane-TiO_2 dispersions with varying amount of TiO_2 (0.5, 1, 1.5, and 2 wt. %) were prepared by ultrasonic dispersion for 15 min. Coatings were deposited on high gloss and etched aluminium substrates using a spin coater (Model WS-650Sz, Laurell Technologies Corporation, USA). Coating thickness of approx. 10 μm was employed as most of the decorative anodizing use an anodized layer thickness of around 10–15 μm [1]. After spin coating the samples were dried in warm air. Nomenclature used for the samples is given in table 1.

Table 1: Nomenclature used for the samples.

Substrate		TiO_2 powder		Reflectance	
Type	Designation	Type	Designation	Type	Designation
Aluminium – High Gloss	**HG**	D50 – 320 nm	**a**	Total	**T**
Aluminium – Caustic Etched	**CE**	D50 – 390 nm	**b**	Diffuse	**D**
		D50 – 500 nm	**c**		

A sample termed as 'HG-a-0.5' would mean that the coating contained 0.5 wt. % TiO_2 of size distribution 'a' in polyurethane over a high gloss aluminium substrate. Samples coated with polyurethane containing no TiO_2 were named as HG-PU-Ref and CE-PU-Ref. Samples without any coating were named as HG-Ref and CE-Ref.

2.2. Spectrophotometry

Optical appearance of the sample was analysed using an integrating sphere spectrophotometer setup. The samples were illuminated with light from a Deuterium-Tungsten halogen light source (DH 2000, Ocean optics), 8° incidence. Reflected light from the samples was collected and analysed for diffuse and total reflectance using a spectrometer (QE 65000, Ocean Optics). The wavelength range analysed was 350 – 750 nm and was integrated over a period of 4 s. The specular reflectance spectra were obtained by subtracting the diffuse component from total reflectance. The total and diffuse reflectance spectra were termed as 'T' and 'D' for each sample respectively.

2.3. Characterization

The surface topography and roughness of the aluminium substrates in high gloss and etched condition was measured using an atomic force microscope (Bruker Multimode 8). A silicon tip (Nanosensors SSS-NCH) with a tip radius of < 2 nm was used in tapping mode. The scan range was 100 x 100 μm. Morphology of the TiO_2 powder was observed using scanning electron microscopy (Model Quanta 200 ESEM FEG, FEI). Particle size analysis was performed on the TiO_2 powders using laser diffraction particle size analyser (Malvern Mastersizer 3000) coupled with a wet dispersion unit (Malvern Hydro SM).

3. Theory and Simulation

3.1. Mie theory

In order to determine the maximum scattering efficiency of light from TiO_2 particles in polyurethane and thus which particle distribution can be expected to scatter most white, the S and K Kubelka-Munk parameters [5] have been determined. The Kubelka-Munk equation, in many cases is a rough estimate compared to more complex models [6]. However, the Kubelka-Munk coefficients can give a good indication of the overall scattering properties of materials. Since S and K are heuristic parameters, there exists many ways of defining them, one method for spherical particles is as below [7],

$$S = \frac{3}{4} f \frac{C_{sca}(1-g)}{V_p} \quad (1); \qquad K = 2f \frac{C_{abs}}{V_p} \quad (2)$$

where C_{sca}, C_{abs} are the particle's scattering and absorption cross section respectively, f is the volume fraction of the particles in the matrix, g is the so-called asymmetry parameter [8]. Inherit in these expressions are (among others) that the particles acts as single scatters (they are optically far from each other), their size is in the Mie regime (which is controlled by the 3/4 fraction), and that there is no depth (z) dependence on their scattering effect like seen in e.g. Vargas and Niklasson [9]. To be able to take size distribution of the particles into account, we generalize the parameter calculation in (1, 2) using the same procedure as in Auger et al. (2003), which gives the average coefficients:

$$< K >= 2f \frac{\int_0^\infty C_{abs}(r)N_p(r)dr}{\int_0^\infty V_p(r)N_p(r)dr} \quad (3); \qquad < S >= f \frac{3}{4} \frac{\int_0^\infty C_{sca}(r)(1-g(r))N_p(r)dr}{\int_0^\infty V_p(r)N_p(r)dr} \quad (4)$$

where r is the particle radius, and N_p is the normalized particle distribution, meaning that

$$\int_0^\infty N_p(r)dr = 1 \qquad (5)$$

The size distribution of each TiO_2 powder obtained from particle size analysis was fitted to a lognormal distribution which is a normal choice of distribution fit [10]. The lognormal distribution is given by:

$$N_p(r) = \frac{1}{r\beta\sqrt{2\pi}} e^{-(\ln(x)-\alpha)^2/(2\beta^2)} \qquad (6)$$

where the two parameters α, β can be found from the mean particle size $\bar{r}$ and its variance σ^2 as $\beta^2 = \ln(1 + \sigma^2/\bar{r}^2)$ and $\alpha = \ln(\bar{r}) - \frac{1}{2}\beta^2$. Calculations were carried

out for wavelengths in the range 350–750 nm using the tabulated values for the optical constants of TiO$_2$ from the literature with linear interpolation applied at wavelengths for which values were not available. The optical constants as a function of wavelength for polyurethane in which the TiO$_2$ particles are embedded were taken from ellipsometric measurements (not shown here). The real index n_{medium} of polyurethane ranges from 1.645 at λ = 350 nm to 1.579 at λ = 750 nm, and its extinction coefficient k_{medium} is below 0.001 all wavelengths. The scattering S and absorption coefficients K of TiO$_2$ embedded in polyurethane calculated using Mie theory are shown in Fig. 1. The S, K parameters were calculated for three size distributions corresponding to TiO$_2$ powders a, b and c for a concentration of TiO$_2$ in polyurethane of 0.5 wt. %.
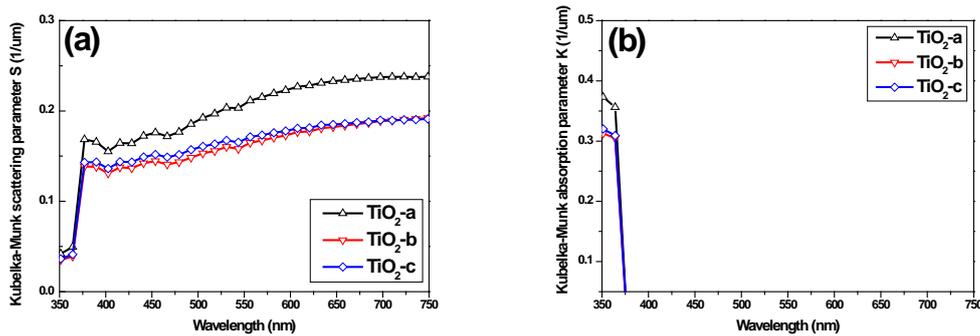
Figure 1: Kubelka Munk (a) scattering coefficients S and (b) absorption coefficient K for coatings of 0.5 wt. % TiO$_2$-polyurethane and for three particle distributions. TiO$_2$ powders a, b and c having median size of 320 nm, 390 nm and 500 nm respectively.

3.2. Selection of distribution by calculations of scattering parameters

By using the freely available multiple spheres scattering tools, MSTM [11] and the optical properties of TiO$_2$ [4], all parameters needed to find S and K are present, and the results from these calculations can be seen in **Fig. 1**. From this it can be seen that the scattering efficiency, which is proportional to S, is best for the size distribution of TiO$_2$-a powders, and that powders b and c seem to have similar scattering properties. The absorption efficiency, which is proportional to K, is mostly controlled by the optical properties of TiO$_2$ that is, its wavelength dependent absorption.

3.3. Estimation of film thickness and concentration

The diffuse reflectance using Kubelka-Munk theory [6] (and ignoring interface reflections) is

$$R = \frac{1 - R_g[a - b\coth(bSh)]}{a + b\coth(bSh) - R_g}$$

where $a = (S + K)/S$, $b = \sqrt{a^2 - 1}$, h is the thickness of the film, and R$_g$ is the diffuse reflectance of the backing substrate. Since S is proportional to the volume concentration, f, all other parameters are independent on that, it is seen how varying either volume concentration or film height by a factor has the same effect. Therefore it is enough to vary one of those parameters to study the change in either height or concentration. In **Fig. 2** a study of change in film height is seen. R$_g$ has been set to 80% for aluminium. It follows from here that a layer in the order of 100 μm is needed to obtain close to full coverage or 50 μm for a volume fraction of f = 0.1.
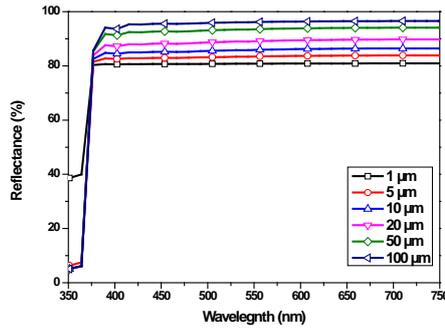
Figure 2: Diffuse reflectance for films of different thicknesses.
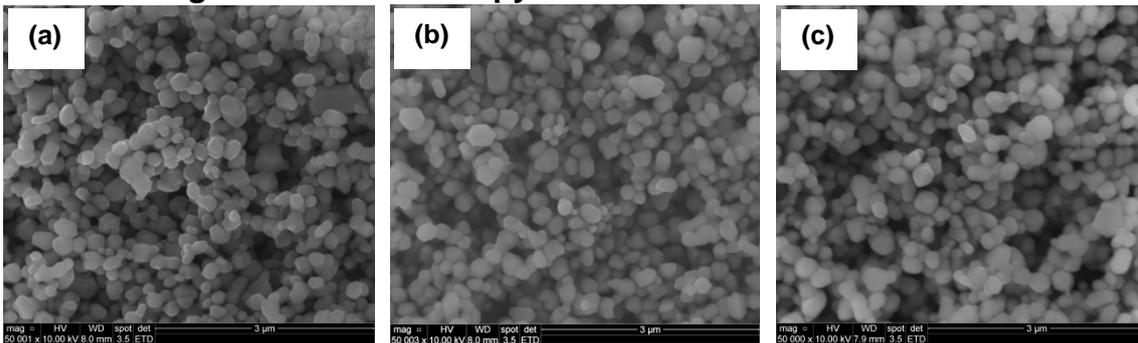
4. Results

4.1. Scanning electron microscopy

Figure 3: SEM micrographs of (a) TiO_2 powders-a, (b) TiO_2 powders-b and (c) TiO_2 powders-c.

The SEM images of the TiO_2 powders used for preparing the composite coatings are shown in Fig. 3. It can be seen that the particles are spherical in shape and have a homogenous morphology. The size distribution (D_{50} value) was measured to be 320, 390, and 500 nm for powders a, b, and c respectively.
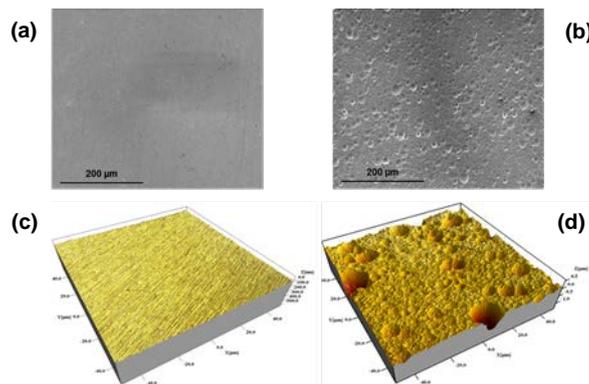
4.2. Surface morphology of aluminium

Figure 4: SEM micrographs of (a) high gloss aluminium, (b) caustic etched aluminium and AFM surface topography images of (c) high gloss aluminium and (d) caustic etched aluminium.

The surface of the high gloss aluminium substrate as shown in the SEM and AFM images (Fig. 4 (a) & (c)) shows a typical rolled surface appearance. The caustic etched aluminium surface (Fig. 4 (b) & (d)) shows a homogenous attack by the etching agent which has resulted in the formation of pits on the surface. Area roughness (Sa, measured from AFM images) of the high gloss substrate was measured to be 8 nm which after caustic etching treatment increased to a value of 158 nm.

4.3. Spectrophotometry

4.3.1. Coatings without TiO₂
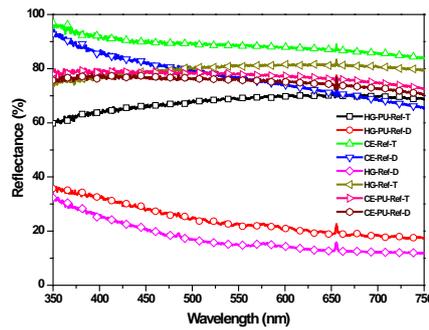
Figure 5: Reflectance spectra of aluminium substrates and polyurethane coatings without TiO₂ (T-total reflectance, D-diffuse reflectance).

The high gloss aluminium substrate has a total reflectance value (Fig. 5) of about 80%. Upon etching this value increases to 95%. The diffuse reflectance of high gloss aluminium is about 20% which shows the highly specular nature of these substrates. Caustic etching increases the diffuse reflectance value to just below 80%. The total and diffuse reflectance of high gloss substrates after being coated with polyurethane containing no TiO₂ is 60% and 30% indicating that it reduces the total and also the specular while increasing the diffuse reflectance. Polyurethane coating on caustic etched substrates reduces the total reflectance value to 80%, but does not affect the diffuse reflectance value considerably. The difference between diffuse reflectance of caustic etched and polyurethane coated caustic etched samples can be seen at lower wavelengths where the absorption due to polyurethane is prominent.
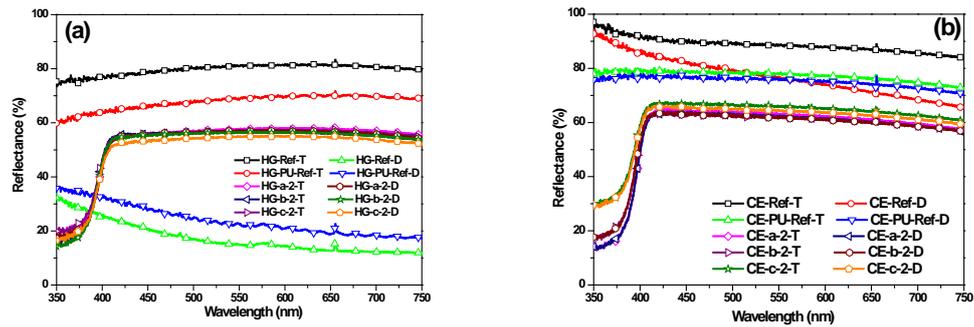
4.3.2. Coatings with TiO₂
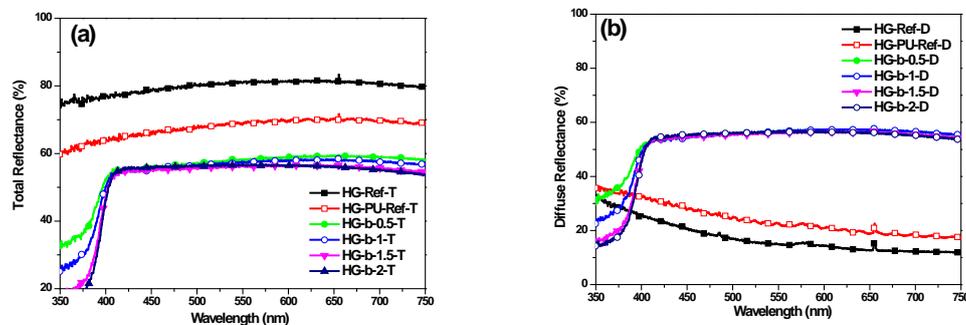
Figure 6: (a) Total and (b) Diffuse reflectance spectra from polyurethane coatings of TiO₂ powders 'b' on high gloss aluminium substrates.

The total reflectance spectra of TiO₂ powder with size distribution 'b' is shown in Fig. 6 (a). The value for total reflectance shows a decreasing trend with increasing TiO₂ powder content. The decrease in total reflectance value from 0.5 wt. % to 2 wt. % TiO₂ is from 55% to 50%. The diffuse reflectance (Fig. 6 (b)) on the other hand is not affected considerably upon increasing the TiO₂ content. It can be seen that the value for total and diffuse reflectance is about the same implying that the specular component is minimal and the samples have a completely diffuse appearance.
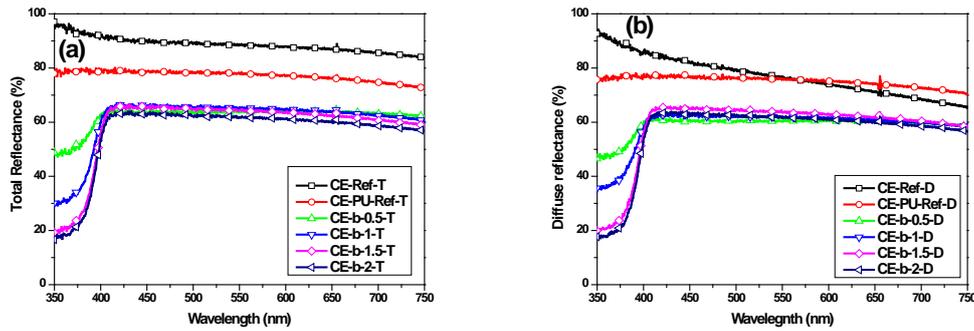
Figure 7: (a) Total and (b) Diffuse reflectance spectra from polyurethane coatings of TiO_2 powders 'b' on caustic etched aluminium substrates.

The total reflectance spectra for caustic etched substrates coated with polyurethane containing different amounts of TiO_2 powders of size distribution 'b' are shown in figure(Fig. 7 (a)). The reflectance value decreases with increasing TiO_2 content and the difference is about 5%. Compared to total reflectance from the high gloss substrates of the similar composition, the reflectance value is higher by a value of 10%. The diffuse reflectance (Fig. 7 (b)) for these coatings is also higher than the corresponding high gloss samples by a value of 10%. The specular component is almost zero implying that the samples are completely diffuse in appearance.

Figure 8: Comparative reflectance spectra from coatings of TiO_2 powder a, b and c at a concentration of 2 wt. % on (a) high gloss and (b) caustic etched aluminium substrates.

Fig. 8 (a) compares the total and diffuse reflectance of the three types of TiO_2 powder coatings at 2 wt. % on high gloss aluminium substrates. The total as well as diffuse reflectance value is the highest for the powders with size distribution 'a'. The total and diffuse reflectance of samples with TiO_2 powders 'b' and 'c' are also nearly the same, but have a higher specular component when compared to the TiO_2 powder 'a'. The total and diffuse reflectance for all the powders at 2 wt. % concentration on the caustic etched samples is shown in Fig. 8 (b). The value for total and diffuse reflectance is highest for powder 'c' and lowest for powder 'b'. But the specular reflectance value is the lowest for powder 'b' and hence they are the most diffuse of the caustic etched samples.

5.   Discussion

The theoretical calculations show that the best scattering is achieved when the TiO_2 powders used in the coating are in the size range of 320 nm (median size). The extent of scattering also increases with increasing thickness, but an anodized layer of 100 µm is not feasible for decorative applications. Lower film thicknesses would

require more scattering particles implying an increased particle concentration. The diffuse and specular component can also be tailored to achieve required level of white and glossy appearance. The reflectance spectra from three different kinds of TiO_2 powders shows that the caustic etching of aluminium substrates increases the diffuse and total reflectance value, and decrease the specular reflectance. Anodization of such a surface when containing high refractive index particles would give a diffuse appearance due to the surface roughness and also a bright appearance due to enhanced scattering. Among the three different TiO_2 powders used, the powders with size distribution 'a' provide the highest reflectance values for high gloss substrates at a concentration of 2 wt. %, which agree with the theoretical calculations. For caustic etched substrates the total and diffuse reflectance is highest for the powders with size distribution 'c' at a concentration of 2 wt. %, but the most diffuse appearance with no specular component is for the samples from powder 'b'. Further work is under progress and will be the focus of a more detailed journal paper.

Conclusions

Caustic etching of aluminium improves the diffuse reflectance of the substrates. Increase in light scattering particles like TiO_2 powders decreases the specular reflectance thus making the surface appear more diffuse. The particle size distribution for achieving the maximum diffuse reflectance is 2 wt. % for TiO_2 with a refractive index of 2.7 in the given polyurethane matrix.

Acknowledgements

6.   References

[1].   S. Wernick, R. Pinner and P.G. Sheasby, The Surface Treatment and Finishing of Aluminium and its Alloys, Finishing Association, Teddington, 1987.

[2].   Charles A. Grubbs, Metal Finishing, Volume 105, Issue 10, 2007, Pages 397–412.

[3].   Sheasby P.G., The weathering of anodized aluminium, Conference Aluminium 2000, Modena, mars 1990.

[4].   Winkler, Jochen (2003), Titanium dioxide, Vincentz Verlag, Hannover.

[5].   Kubelka, P. and F. Munk (1931), An article on optics of paint layers, Z. tech, Physik 31 (1930), 1–16.

[6].   Vargas, W. E. and G. A. Niklasson (1997a, August), Applicability conditions of the Kubelka-Munk theory, Applied optics 36 (22), 5580–6.

[7].   Auger, J.C., R. G. Barrera, and B. Stout (2003, June), Scattering efficiency of clusters composed by aggregated spheres, Journal of Quantitative Spectroscopy and Radiative Transfer 79-80, 521–531.

[8].   Craig F. Bohren, D. R. H. (1983), Absorption and Scattering of Light by Small Particles. Wiley.

[9].   Vargas, W. E. and G. A. Niklasson (1997b, September). Generalized method for evaluating scattering parameters used in radiative transfer models, Journal of the Optical Society of America A 14 (9), 2243.

[10].   Liao, C.-M., Y.H. Chiang, C.P. Chio (2009, February), Assessing the airborne titanium dioxide nanoparticle-related exposure hazard at workplace, Journal of hazardous materials 162 (1), 57–65.

[11].   http://www.eng.auburn.edu/users/dmckwski/scatcodes/