Optical Properties of Coatings. Effect of Pigment Concentration

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The ability to calculate the bidirectional reflectance and transmittance of an irradiated layer of monodisperse matrix-suspended pigment particles, using only rigorous scatter theory, system physical properties, and *no* empirical constants, has been experimentally verified on water suspensions of polystyrene spheres of diameter 0.102–0.530μ, wavelengths 0.436 and 0.546μ, pigment volume fraction $1.3 \times 10^{-6} - 0.295$, optical thickness 0.01–3211, when the clearance between particles exceeds both 0.3 wavelength and 0.4 particle diameter. At closer spacing non-interfering-particle scatter theory is still valid provided an empirically determined "scatter efficiency" is used. Some practical implications of the results of close packing are presented.

Nomenclature

b = fraction of radiation in backward direction
c = clearance between particles ($=\delta$-d)
C = geometrical particle cross section
d = particle diameter
K_s = scattering coefficient per unit volume ($=1.5$ PVC X_s/d)
L = slab thickness
PVC = pigment volume concentration or volume fraction
R_D = diffuse component of hemispherical reflectance
T = hemispherical transmittance
T_D = diffuse component of hemispherical transmittance
X_s = scattering efficiency
X_{se} = effective scattering efficiency
δ = center-to-center distance between particles calculated assuming a regular rhombohedral array
θ = angle between scattered and incident beam
λ = wavelength of light in vacuo
τ = optical thickness in mean free paths, $\tau_1 = K_sL$

Introduction

THE need for imparting special optical properties such as directional or wavelength selectivity to pigment coatings emphasizes the significance of being able to use pure theory to determine the best choice of refractive index, absorption coefficient, size, and spacing of the pigment particles and thickness of the matrix in which the particles are to be suspended. When the particle separation is sufficient to eliminate particle interaction, the polar diagram of the transmitted and reflected radiation can be calculated from multiple scatter superimposed on Mie scatter, with excellent agreement between theory and experimental measurements[1–3]; but for close packed systems pure theory is unavailable and past practice has been to substitute approximations such as two-flux theory and to obtain experimentally determined constants to describe the gross performance of a pigment layer. This paper reviews the progress that has been made towards the theoretical prediction of the properties of pigment suspensions. It first reports the results of careful comparison of experimental angle-dependent transmission and reflection with calculations based on pure theory, for layers of open space particles in a matrix, to supplement results in an earlier publication[2]; it then presents an empirical relation for determining the effect of close spacing on the effective scatter cross section of particles; finally, it illustrates the application of the results in calculating the effect of pigment loading on the transmission of coatings. The empirical correlation developed for predicting the effect of close spacing permits the use of theory—with no adjustable constants—to calculate the bidirectional reflectance and transmittance of layers of close packed spheres or other particles for which the single scatter diagrams are available.

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Single Scatter

The polar diagram of single scatter by particles may be obtained either from measurements on thin layers of dilute suspensions or, for spheres and a few other geometrical shapes, from solutions of the Maxwell equations. The predictions of the latter have been tested extensively, frequently with polystyrene lattices with narrow size distributions.[2,4] For pigment particles, such as titanium dioxide, a fair approximation to the single-scatter diagrams may be obtained by assigning the particles an equivalent spherical diameter and using the Mie equations.[5]

Multiple Scatter for Open-Spaced Particles

The ability to predict the properties of particle suspensions from theory without the use of any adjustable parameters has been tested on very well-defined polystyrene particle suspensions, and excellent agreement has been obtained between theory and experiment.[1–3] Additional results are shown in Figs. 1, 2, and 3, where experimental data points are compared with theory. Figure 1 represents the components of polarization and their sum for the bidirectional reflectance and transmittance at 0.436μ for 0.530μ polystyrene latex spheres confined in a cell formed by parallel microscope slides, for normal incidence. The lower and upper halves of the figure correspond to different particle concentrations. The values for

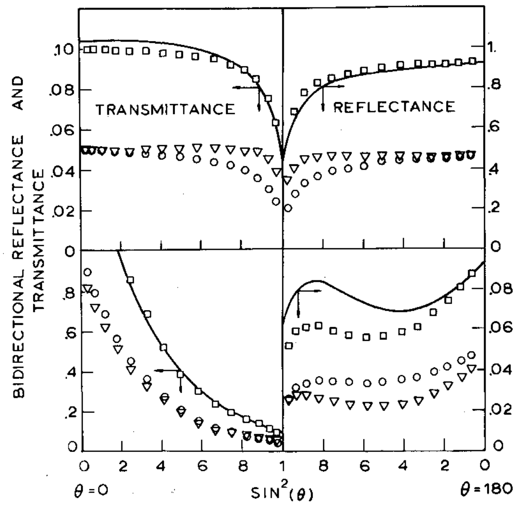

Fig. 1 Components of polarization of bidirectional reflectance and transmittance of polystyrene latex spheres. $L = 0.147$ cm, $\lambda = 0.436\mu$, $d = 0.530\mu$. Data points represent experimental values, solid lines theory. Key: triangles, parallel components; circles, perpendicular component; squares, total value (components added). Top plots: PVC = 2.8×10^{-2}, $\tau_1 = 215.9$; bottom plot: PVC = 1.4×10^{-4}, $\tau_1 = 1.09$.

the perpendicular component of polarization are seen to exceed those for the parallel component over a range of angles, as would be expected from consideration of the single scatter diagram of the particles. As the optical thickness increases the difference between the two components of polarization decreases and, ultimately, reverses sign as a consequence of the differences in reflectance for the two components at the bounding glass slides. The solid lines on Fig. 1 are calculated bidirectional reflectance and transmittance obtained from the solution of the transport equation by the method of discrete ordinates or discrete conical sheets, with allowance for all complicating factors with the exception of polarization effects.[2] Figure 2 is a sample from the data, for two values of PVC (the particle volume concentration or volume fraction

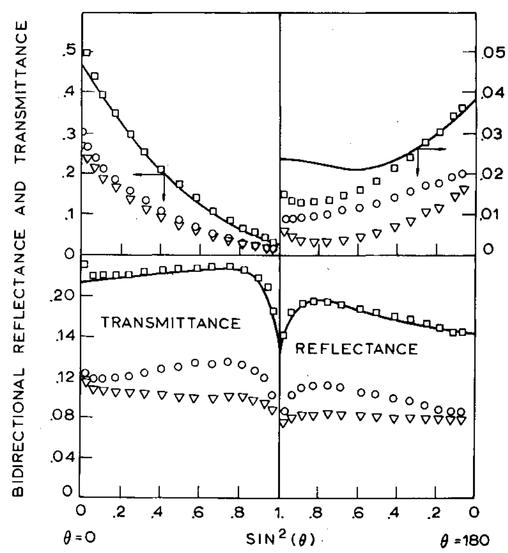

Fig. 2 Components of polarization of bidirectional reflectance and transmittance of polystyrene latex spheres; $L = 0.147$ cm. Data points represent experimental values, solid lines theory. Key: triangles, parallel component; circles, perpendicular component; squares, total value (components added). Top plots: sphere diameter = 0.530μ, $\lambda = 0.546\mu$, PVC = 5.2×10^{-5}, $\tau_1 = 0.247$, $\pi d/\lambda$ 3.05. Bottom plots: sphere diameter = 0.106μ, $\lambda = 0.436\mu$, PVC = 6.7×10^{-4}, $\tau_1 = 0.537$, $\pi d/\lambda = 0.764$.

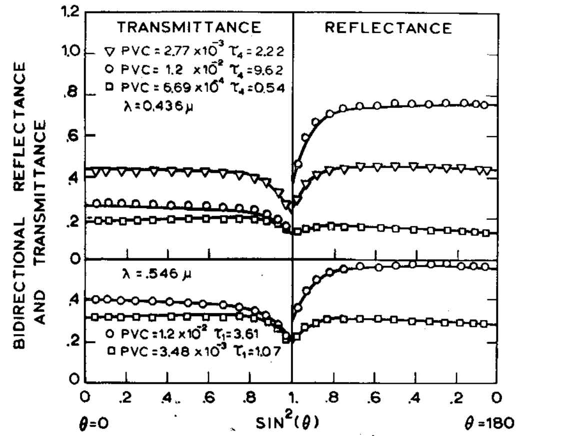

Fig. 3 Bidirectional reflectance and transmittance as a function of PVC of 0.106μ polystyrene spheres, $L = 0.147$ cm. Data points represent experimental results, solid lines theory.

occupied by particles), two particle sizes, and two wavelengths. The agreement between the calculated and measured values is good except for the reflectance at low optical thickness and large angle. (This discrepancy is due to loss through the side walls of the test cell). Figure 3 shows comparisons of measured bidirectional transmittances and reflectances (sum of two components of polarization, but omitting the spike of direct or unscattered radiation) for 0.106μ particles at two wavelengths and several optical thicknesses. Note that, except at large angles, the reflectance and the diffuse component of transmittance are Lambertian (values constant as angle varies), and that the diffuse component of transmittance, for $\lambda = 0.436\mu$, passes through a maximum as optical thickness τ_1 is increased. Integration of the reflected and transmitted radiation, exclusive of the unscattered reflected and transmitted beams concentrated in spikes along $\theta = 0°$ and 180°, yields the values shown in Fig. 4 where again excellent agreement is found between measured (data points) and calculated values (solid lines). The results in Figs. 1–4 support the conclusions in Ref. 2 that, for coatings of particles far enough apart to be treated as independent scatterers, the radiative properties can be accurately predicted from theory without the introduction of any adjustable parameters, and that adequate results are obtained without making allowance for polarization effects.

Multiple Scatter in Close-Packed Systems

As the value of the center-to-center distance δ between particles.¶ Approaches either the particle diameter or the wavelength of interest, the particles can no longer be treated as independent point scatterers. Rigorous analysis of the close-packed particle system is presently impractical and a semi-empirical approach was therefore adopted. Previous investigators[6–8] had determined the concentrations at which interference became significant but had left unresolved the extent to which departure from noninteraction between particles was due to spacing measured in particle diameters or spacing measured in wavelengths. Accordingly, a series of experiments were designed with different size monodisperse polystyrene particles, different wavelengths, and different particle concentrations in order to cover the critical range of combinations of clearance/wavelength (c/λ) and clearance diameter (c/d). Since the multiple Mie scatter solutions had been experimentally verified at large interparticle spacing, any departure of measured transmittances and reflec-

¶ The center-to-center distance δ used here is that based on regular rhombohedral array, for which $\delta/d = [\pi/3(2)^{1/2}]^{1/3}/(\text{PVC})^{1/3} \cong 0.905/(\text{PVC})^{1/3}$.

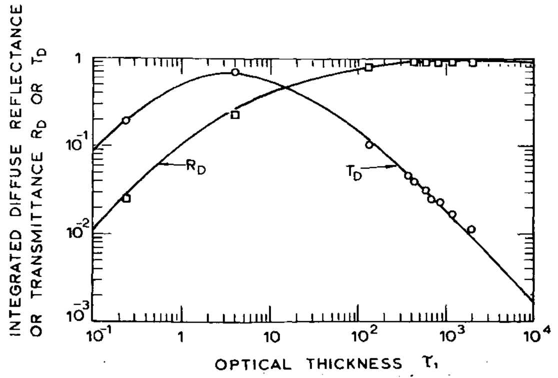

Fig. 4 Integrated diffuse reflectance and transmittance as a function of optical thickness: $d = 0.530\mu$, $\lambda = 0.546\mu$. Data points experimental, solid lines theoretical.

tances from calculated values was an indication of interaction between particles. A small sample of the data is presented in Fig. 5, which shows that, when the particle volume concentration is as high as 0.2195 ($\delta/d = 1.5$) and the wavelength/diameter ratio is as high as 0.436/0.102, the data are no longer in agreement with theory based on noninterfering particles, and that the disagreement is worse when the ratio of particle clearance, (δ-d) or c, to wavelength λ is 0.093 (top figures) than when it is 0.117 (bottom). Use of a markedly smaller wavelength/diameter ratio (0.436/0.53) produced no departure from open-pack theory even at the higher PVC of 0.29. The detailed results on the effect of close-packing will be the subject of a later publication.

Results on multiple scatter provided the basis for another simplification. The calculated and observed distributions of scattered intensity were remarkably smooth, e.g., Fig. 3. This evidence of diffusion of the radiation suggested that the calculated values would be insensitive to the detailed angular distribution of the scatter diagram or phase function, and that consequences of interaction could therefore be accounted for by redefining an effective scatter coefficient, leaving the phase function unchanged.

Representative results are shown in Fig. 6, where the reciprocal of the total transmittance is plotted vs optical thickness. The solid line is calculated from theory,** and is a fair approximation of the data points obtained with a PVC of

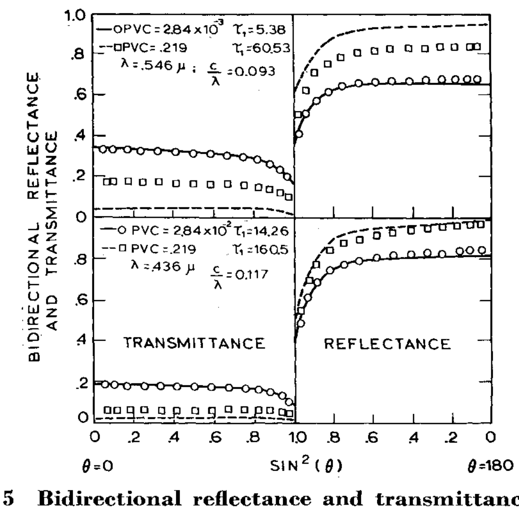

Fig. 5 Bidirectional reflectance and transmittance as a function of PVC of 0.102μ polystyrene spheres. Data points represent experimental results, drawn lines theory, based on assumption of noninterference.

** The two-flux approximation[9] also yields a straight line on the coordinates of Fig. 6, but the constants must be obtained empirically.

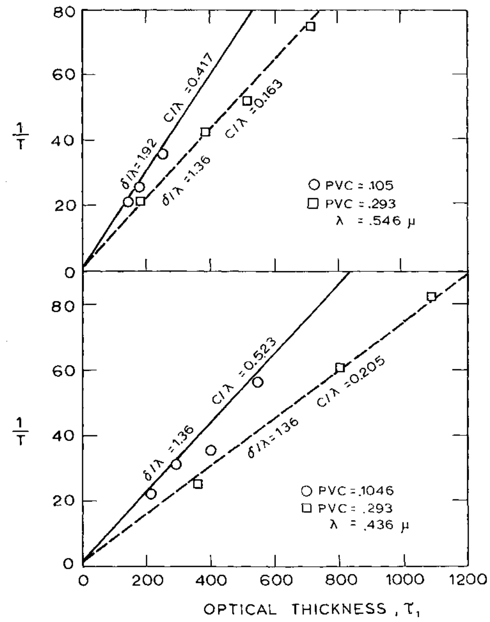

Fig. 6 Comparison of theory with measurements on polystyrene spheres 0.248μ in diameter. Continuous lines are based on multiple scatter of noninterfering particles.

0.105. As the PVC is increased to 0.293 the data points depart significantly from the solid lines and are best correlated by the dashed lines shown. Since the optical thickness τ_1 is the product of layer thickness by number concentration by effective scatter cross section CX_s, where C is the true cross-section and X_s is the scatter efficiency, it is clear that the dashed line could be forced to coincide with the solid by calculating the abscissa τ_1 using an effective scatter efficiency X_{se} (ratio of effective scatter cross section to projected area) in place of the true value X_s calculated from the Mie equation. It is fortunate that the points at high PVC's lie—unexpectedly—on a straight line, as this permits the definition of an effective scatter efficiency which is independent of τ_1. Extensive data[10] on the effect of close spacing has shown that the interference correlated primarily with the ratio of the clearance between particles and the wavelength, (δ-d)/λ, and that for the most concentrated solutions studied (PVC = 0.3) no interference was noted provided the clearance/wavelength

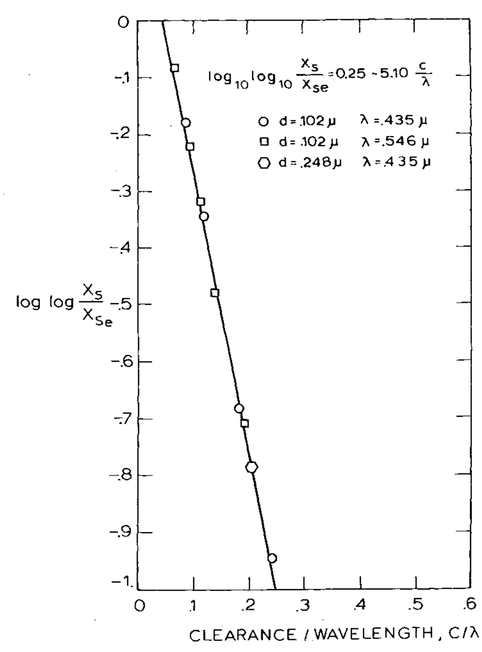

Fig. 7 X_s/X_{se} correlation plot.

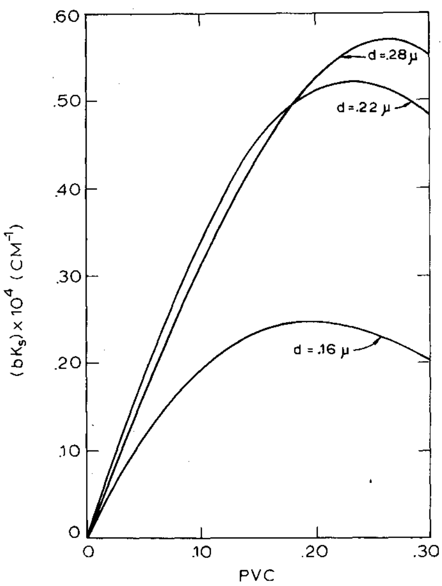

Fig. 8 Variation in backscattering coefficient per unit volume of TiO_2 paint film as a function of PVC. Refractive index of vehicle equals 1.5; $\lambda = 0.55\mu$.

ratio was large. The data on the ratio of effective scatter cross-section to that calculated from the Mie equations has been correlated; see Fig. 7. The equation of the line obtained is

$$\log_{10}\log_{10}(X_s/X_{se}) = 0.25 - 5.1\ c/\lambda$$

for (c/λ)'s greater than 0.069. The measured values of X_{se}/X_s varied from 0.15 at c/λ of 0.069 to 1.0 at large c/λ's and exceeded 0.95 for c/λ's greater than 0.37. Extrapolation of the above correlation to a c/λ of zero yields a value for X_{se}/X_s of 0.0165 but there is no experimental basis for this value or any theoretical expectation that an asymptotic value should exist.

The correlation on the effect of interparticle spacing on scatter cross section has been derived for monodisperse, spherical, nonabsorbing particles, with a refractive index ratio of particles to medium of 1.20. Further experimentation is needed to establish the effects of absorption, nonsphericity, polydispersity, and refractive index. In the absence of additional data, however, the above correlation should provide a useful estimate of interference effects. It should be noted that the importance of clearance-to-wavelength as a correlating parameter was not recognized by Harding et al.,[8] and the relation they recommend does not adequately correlate the data of the present study.

Practical Applications

For pigment suspensions which can be described as an assembly of Mie scatterers, the optical properties can be calculated from pure theory with no empirical constants if the correlation for the effect of close-spacing is accepted. Another use of the results is in optimization of the formulation of optical coatings. For example, let the problem be the selection of particle size and pigment concentration for a particular application of a thin coating of titanium dioxide particles suspended in an alkyd resin. For comparative purposes it is sufficient to determine the back scattering coefficient per unit volume. This is given by

$$bK_s = b(N/V)(\pi d^2/4)X_{se}$$

where b is the back-scatter fraction N/V the number of particles per unit volume, $(\pi d^2/4)$ the projected area of a particle, and X_{se} the effective scatter efficiency. The latter can be obtained from the scatter efficiency X_s calculated from the Mie equations and the value of X_{se}/X_s calculated from the correlation presented in the preceding section. The value of b, the back-scatter fraction, is obtained as the slope of the straight line obtained when $(1/T - 1)$, where T is the total transmittance calculated rigorously for the particles of interest, is plotted vs the optical thickness τ_1. (Examples of the linearity of $1/T$ vs τ_1 are found in Fig. 6. The intercept will differ from 1.0 by small amounts when interface reflection is taken into account.) It should be noted that the value of b so obtained will differ significantly from the back-scatter fraction for single scatter.[11]

The values of bK_s calculated assuming that TiO_2 particles are monodisperse spheres with a refractive index relative to the alkyd resin of 1.75 are shown in Fig. 8 for particle diameters of 0.16, 0.22, and 0.28μ and for a wavelength of 0.55μ. At low PVC's bK_s is directly proportional to PVC, with the 0.22μ particles having the highest hiding power. As the PVC increases to the concentrations at which $(\delta - d)/\lambda$ falls below 0.4, the scatter efficiency decreases, and the line of bK_s vs PVC develops some curvature. Ultimately a point is reached at which further increase in pigment concentration actually causes the hiding power (as measured by bK_s) to decrease. The PVC at which interference effects become noticeable increases with particle size, causing the values of bK_s for 0.22μ and 0.28μ to cross over. The value of the correction factor for interaction between particles should be evident; without it Fig. 8 would have consisted of three straight lines, tangent to the curves at the origin. Furthermore, the conclusions agree qualitatively with the results of previous investigators[12,13] working with TiO_2 system.

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