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Comparison of Experimental and Theoretical Study of Diffuse Reflectance of Highly Scattering Particulate Systems

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Abstract

Diffuse reflectance of titanium dioxide pigment dispersion is measured in visible region for wavelengths 400(20)700 nm. Kubelka-Munk absorption and scattering coefficients are determined using two constant K-M theory. Average particle size in pigment dispersion is determined by light scattering method. Complex refractive indices of pigment are determined using particle model theory. Scattering and absorption coefficients are computed for all wavelengths using Mie theory equations. K-M coefficients are determined from Mie coefficients using appropriate formulae. Diffuse reflectance values are calculated from theoretical values of K-M coefficients. Theoretical and experimental values of reflectance agree well. The colour difference evaluated from two reflectance curves is 1.28 CIELAB units.

Key words : K-M absorption and scattering coefficients, spectral reflectance

Introduction

Kubelka-Munk theory (hereafter abbreviated as K-M theory) is used to study multiple scattering media. K-M equation is obtained on certain assumptions but the theoretical expressions give moderately good results, even though all assumptions are not ideally observed (Billmeyer & Abrams 1973), K-M theoretical expressions are derived on the physical model that light flux inside the medium is divided into two channels, one going downwards and other in upward direction (Kortum 1969; Kubelka 1948). The rate of change of flux in each channel is assumed to be proportional to two empirical constants K and S. These constants are known as K-M absorption and scattering coefficients. The K-M theory coefficients are to be determined experimentally only. No theoretical relations are provided by the theory, to determine these coefficients from size and refractive index of pigment.

The above fact was also realized by Kubelka and he has proposed that the K-M coefficients may exhibit correlation with the extinction coefficients of single scattering. Many authors have proposed various relations between K-M coefficients and single scattering coefficients (Kubelka 1948; Mitton, Vejnsoka & Frederick 1962; Harding, Golding & Morgell 1960; Brockes 1964, Buttignol 1968; Brossman 1974). The research workers in the field have studied the relation between K-M and single scattering parameters for two or three selected wavelengths. The correlation between the theoretical and experimental values of K-M coefficients and their effect on reflectance has not been reported so far. The ultimate objective of establishing the relations between K-M and single scattering coefficients is to use the same for predicting reflectance spectra from size and refractive index of particles. In this paper, we have estimated K-M absorption and scattering coefficients of titanium dioxide pigment dispersion from size and refractive index of pigment for wavelengths 400(20)700 nm of interest for colour calculations. These data are then used to determine the spectral reflectance curve of the sample. Overall performance of the relation is studied by determining CIELAB colour difference between the experimentally measured and theoretically predicted diffuse reflectance spectra. Average particle size and complex refractive index of the sample used were determined using appropriate method.

Experiment

Sample Preparation

Rutile titanium dioxide dispersion supplied by Goodlass Nerolac company with 26 percent weight concentration was used for the present study. Pigment dispersion were diluted to .003 percent concentration by weight using the vehicle supplied by the company. Paint films were prepared as drawdowns at incomplete hiding on 75 microns thick 'Mylar" polyester film using Gardner Variable Paint Film Applicator. Paint films were determined by weighing square piece of film of 50 cm^2 area cut using a steel template and razor blade.

Measurement

The paint films prepared at incomplete hiding on transparent 'Mylar' were subsequently mounted on a black and white ceramic tile with a few drops of ethylene glycol on tile. A cylindrical rubber roller was rolled over the film to ensure firm optical contact between 'Mylar' and tile, thus eliminating any air gap between them. The diffuse reflectance measurements of paint film for wavelengths 400(20)700 nm were recorded on Shimadzu double beam spectrophotometer model UV-VIS 240 equipped with integrating sphere.

Calculations

The experimentally measured reflectance were used to calculate the reflectance of paint film at infinite thickness using following equation

$$R_\infty = a - b \quad (1)$$

$$\text{here} \quad a = 0.5\left[R + \frac{R_0 - R + R_g}{R_0 R_g}\right] \quad (2)$$

$$\text{and} \quad b = (a^2 - 1)^{1/2} \quad (3)$$

R_∞ is the reflectance of the paint film at complete hiding. R_0 and R being reflectance of paint film on black and white background R_g being the reflectance on white background. All experimentally measured values of reflectance used in above equations were corrected for surface reflection using Saunderson relations (Saunderson 1942)

$$R_t = \frac{R_m - k_1}{1 - k_1 - k_2(1 - R_m)} \quad (4)$$

here R_m and R_t are measured and corrected values of reflectance. The corrected values are often called as internal reflectance factors that would be measured inside the film. Here k_1 and k_2 are Fresnel reflection coefficients and can be determined using equation available else where.

Experimental values of K-M scattering coefficients were determined using Equations (Kortum 1969)

$$S = \frac{2.303}{d}\frac{R_\infty}{1 - R_\infty^2} log \frac{R_\infty[1 - R_0 R_\infty]}{R_\infty - R_0} \quad (5)$$

K-M absorption coefficients were then determined using Equation

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (6)$$

Normalized values of K and S were calculated by dividing experimental values by the concentration of paint samples used for experimental measurements. These values are used to compare with corresponding theoretical values obtained using single scattering parameters.

Determination of Size and Refractive Index

Evaluation of single scattering parameters requires the knowledge of size and refractive index of pigments. In the present study, the average particle size in titanium dioxide, pigment dispersion was determined using light scattering method described in the previous publication (Mehta et al.1984; Shah & Gandhi 1989) from this department. Average particle diameter was determined as 0.15 micron.

Optical characterization of particle is determined by its complex refractive index, $m = n - in'$. In the present study we have taken values of n for titanium dioxide for the available wavelengths and the values for desired wavelengths are interpolated by fitting the polynomial equation to the available data. The results are shown in Fig. 1 as a plot of refractive index V_s wavelength.

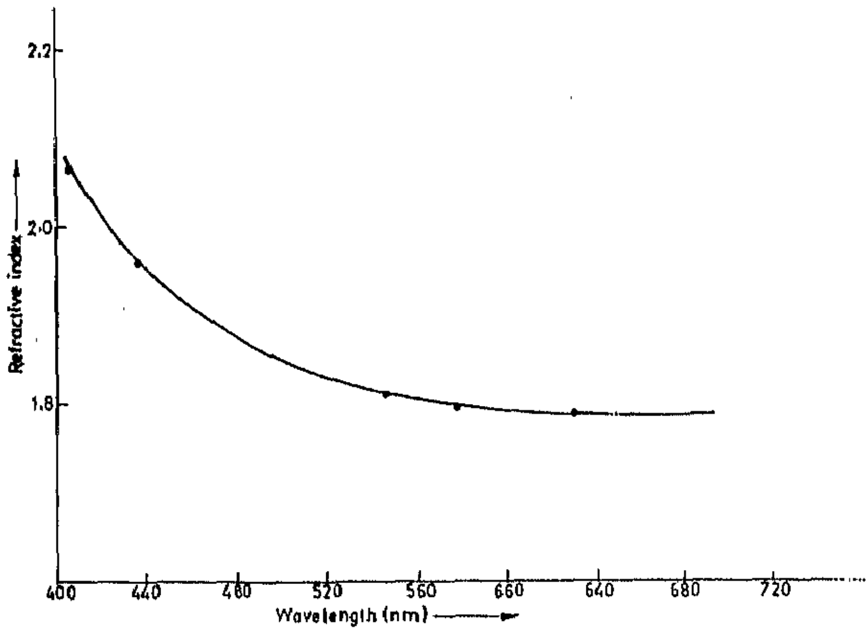

Figure 1. Change of refractive index of pigments for wavelengths 400-700 nm.

n' varies with wavelength. The data for n' of titanium dioxide are not available in literature. Different methods are proposed to determine n' of particulate system. We have used the expression proposed on the basis of particle model theory of diffuse reflectance. According to the method, values of n' are determined for wavelengths 400(20) 700 nm using expression

$$n' = \frac{k\lambda}{4\pi} \tag{7}$$

and

k is determined from equation,

$$k = \frac{3A}{2dn^2} \tag{8}$$

where d is diameter of particle, n is real part of refractive index and A is represented by following equation

$$A = 1 - [\frac{2R_\infty}{1 + R_\infty^2}] \tag{9}$$

Computation of Single Scattering Parameters

Single scattering parameters *e.g.* coefficients for extinction and phase function depend on particle size and complex refractive index of material of the particle. In the present study we have computed single scattering parameters using rigorous Mie theory expressions-employing computer subroutines established by Dave. Linear scattering coefficients k and s are related to Mie efficiency parameters by relations

$$K = \frac{3\pi}{2\lambda}\frac{Q_{abs}}{x} \quad \text{and} \quad S = \frac{3\pi}{2\lambda}\frac{Q_{sca}}{x} \tag{10}$$

where x is particle size parameter and is expressed as ratio of particle circumference to wavelength of light in respective medium.

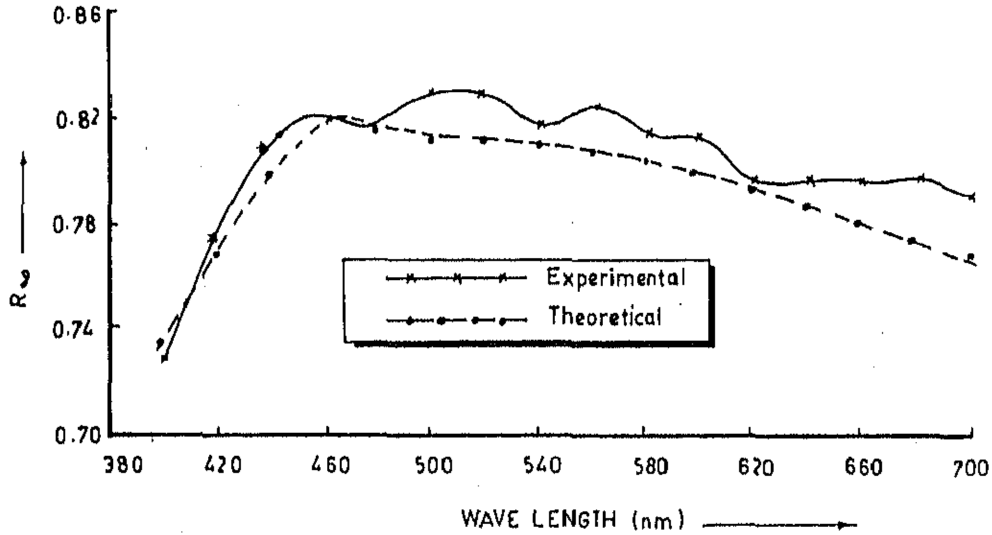

Figure 2. Reflectance of the paint film at complete hiding.

Results

The plot of R_∞ vs λ is shown in Fig. 2. Values of K-M coefficients were determined using Equations (5) and (6) for all sixteen wavelengths. These values are then converted to normalized K-M coefficient. Experimental values of K and S are graphically shown in Figs. 3 and 4.

K-M coefficients are determined by using Equations

$$S = 0.75s \tag{11}$$

and

$$S = 0.75s\left[1 - \frac{a_1}{3}\right] \tag{12}$$

where a_1 is normalized Legendre coefficient and s can be calculated using Equation (10). Values of K-M scattering coefficients determined using both the Equations are plotted in Fig. (4). The present study shows that K-M coefficients determined by relation $S = 0.75s$ overall agree reasonably well with experimental results. Therefore these values are used for futher calculations.

We have used the theoretically predicted values of K-M coefficients to evaluate the

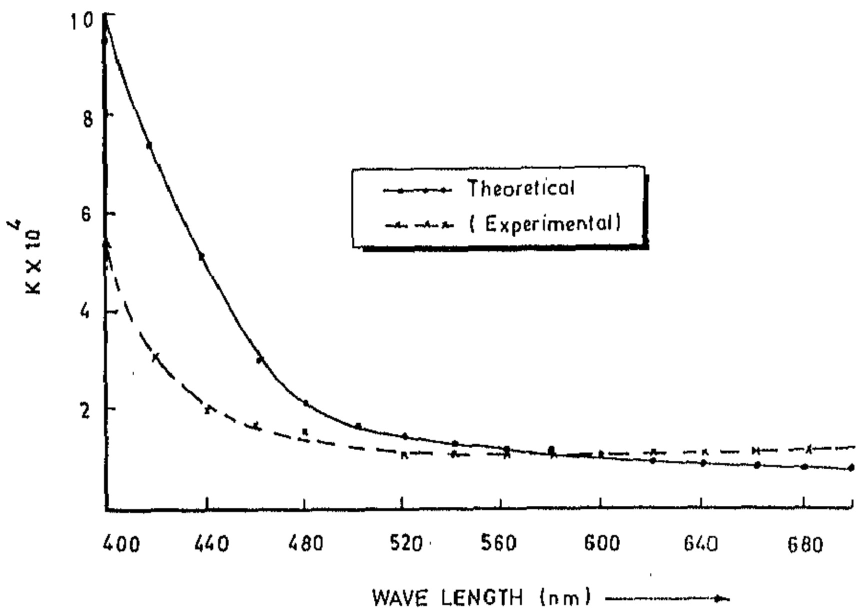

Figure 3. K-M absorption coefficient vs wavelength.

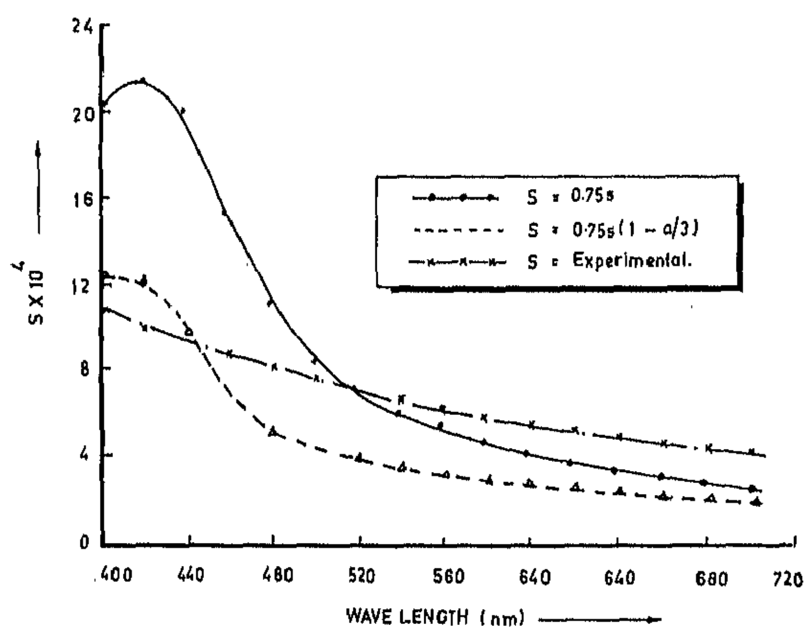

Figure 4. K-M scattering coefficient vs wavelength.

colourimetric curve of titanium dioxide using the well known K-M relation

$$R = 1 + \frac{K}{S} - [(\frac{K}{S})^2 + 2(\frac{K}{S})]^{1/2} \tag{13}$$

The values of reflectance are shown by points in Fig.2. The comparison of experimental and theoretical results show that the colourimetric curve predicted using the present theoretical technique agree satisfactory with the experimental curve. The colour difference between the experimental and predicted curve turns out to be 1.28 CIELAB units.

Discussion

In this work, for the first time, we have examined the possibility of predicting colourimetric curve of paint film from size and refractive index of pigment. The result shows that there is only fare correlation between experimental and theoretical values of K-M coefficients for entire spectral region but the reflectance values agree fairly well. The colour difference from two colourimetric curves turns out to be 1.28. CIELAB units which is within the accepted tolerance limit for practical purposes.

In the present study we have used the paint films prepared using highly diluted dispersion and therefore isotropic distribution of scattered light in the medium is not expected. This is the reason why $S = 0.75s$ works well instead of equation $S = 0.75s(1 - a_1/3)$.

The work reported in this paper is a result of our preliminary attempts to predict colourimetric curves of pigment dispersion from the fundamental optical and morphological characteristics of pigments. This work may not be of practical use for the enormous colour matching computations carried out by industrial organization. At the sme time the theoretical technique will be useful for any pigment industries to determine optimum size and size distribution of pigments to achieve the highest tinting strength and surface covering power. Extensive study in this topic is yet required to establish the method to correlate K-M coefficient with single scattering parameter under varied experimental conditions.

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