Dyes and Pigments 5 (1984) 329–340

Estimation of the Kubelka–Munk Scattering Coefficient from Single Particle Scattering Parameters

K. T. Mehta

Department of Physics, M.R. Arts and Science College,
Rajpipla 393 145, India

M. C. Bhavsar, P. M. Vora and H. S. Shah

Department of Physics, S.V.R. College of Eng. and Tech.,
Surat 395 007, India

(Received: 25 June, 1983)

SUMMARY

Computer colour matching of paints is based on the determination of the Kubelka–Munk absorption (K) *and scattering coefficients* (S) *of pigments.* K *and* S *are sensitive to particle size in the range of sizes employed in paint technology. The K–M theory does not provide any guidelines for the correction of the values of* K *and* S *with a change in particle size. On the other hand the Mie theory linear scattering coefficient can be calculated from a knowledge of size and refractive index of the pigment. A number of relations correlating the K–M scattering coefficient and the linear scattering coefficient have been proposed in the literature. Attempts are made to estimate the K–M scattering coefficient using a relation suggested by Mudgett and Richards and to make a comparison with experimental values. The Mie theory equations being complex, simplified equations applicable to pigment sizes for the calculation of Mie theory parameters are proposed. The viability of the simplified equations has been established by comparing the results with those obtained using the full Mie equations.*

The K–M scattering coefficient for titanium dioxide pigments has been determined from reflectance measurements. The particle size of titanium

Dyes and Pigments 0143-7208/84/$03·00

dioxide has been determined by a light scattering method. The K–M scattering coefficient calculated from the linear scattering coefficient obtained using the simplified expressions agrees with experimental results. This suggests a method for the correction of the values of K *and* S *with changes in pigment particle size.*

1. INTRODUCTION

Determination of Kubelka–Munk (K–M) scattering and absorption coefficients is of vital importance in determining colour recipe formulae in the paint, paper, plastics and textile industries. The K–M scattering and absorption coefficients are empirical and have no firm theoretical basis, and the justification of the K–M equations is based only on their widespread use and practical utility. The scattering and absorption coefficients introduced in the K–M equations are determined only from experimentally measured parameters.[1] No relation is provided in the K–M theory for the determination of theoretical values of these coefficients from the basic optical and morphological properties of the colorants.

Colour recipe formulae are determined from characteristic values of these coefficients determined in the laboratory by separate calibration experiments. The results of calibration experiments give correct colorant formulations in so far as the pigments used for colouration are exactly identical to those used for calibration. However, the colorants supplied by different manufacturers or by the same manufacturer at different times may have the same chemical properties but the morphological properties (size, size distribution and shape) and the optical properties (scattering and absorption coefficients) may not be exactly identical. Under such circumstances the colour recipe formula, determined once, may not continue to give identical results. The K–M theory does not provide guidelines to correct the values of the scattering and absorption coefficients of the colorants to allow for any change in particle size.[2]

On the other hand, the Mie theory describes the scattering and absorption of light by a single colorant particle or a dyed fibre-element. The Mie theory enables the calculation of scattering and absorption coefficients (also called linear coefficients) from the knowledge of particle size and refractive index. Though the scattering and absorption coefficients described by the Mie and K–M theories are not exactly identical, each of them appears to depend on the scattering pattern exhibited by the particle.[3] Attempts have been made to correlate the coefficients described by these two theories. It is reported that, as the incident light is diffused within the paint film, the effective path length is more than the geometrical thickness of the film, and hence the K–M absorption coefficient (K) is greater than the linear absorption coefficient (k). It has been shown that for an isotropic distribution of scattered light within the sample, the K–M absorption coefficient is twice the linear absorption coefficient.[4] Kubelka initially assumed that the K–M scattering coefficient (S) is equal to twice the linear scattering coefficient (s), for perfectly diffused light. According to Gate, $S = 0{\cdot}75s$.[5] Some authors also suggested that since S represents isotropic scattering of isotropic fluxes, $S = 0{\cdot}5s$. Purely on theoretical grounds, Mudgett and Richards[6] have obtained a relation between the parameters described by the two theories as $S = 0{\cdot}75s(1 - a_1/3)$. Here a_1 is a Legendre coefficient which can be determined from a knowledge of the size and refractive index of the particle using involved expressions available elsewhere in the literature.[7,8]

The purpose of the present study has been to determine S from s using the theoretical expression given by Mudgett and Richards and to compare the values with experimental results. Simplified expressions, covering the range of particle sizes employed in colour technology, to determine Legendre coefficients and linear scattering coefficient are also given in this paper.

2. EQUATIONS

$$R_t = \frac{R - k_1}{1 - k_1 - k_2(1 - R)} \tag{1}$$

$$R_{ot} = \frac{R_o - k_1}{1 - k_1 - k_2(1 - R_o)} \tag{2}$$

$$R_{gt} = \frac{R_g - k_1}{1 - k_1 - k_2(1 - R_g)} \tag{3}$$

$$a = \frac{1}{2}\left[R_t + \frac{R_{ot} - R_t + R_{gt}}{R_{ot}R_{gt}}\right] \tag{4}$$

$$R_{\infty t} = a - [a^2 - 1]^{1/2} \tag{5}$$

$$S=\frac{2\cdot303}{d}\,\frac{R_{\infty t}}{1-R^2_{\infty t}}\log\frac{R_{\infty t}[1-R_{ot}R_{\infty t}]}{R_{\infty t}-R_{ot}} \tag{6}$$

$$\frac{\tau}{c}=24\pi^3\left[\frac{m^2-1}{m^2+2}\right]^2\frac{V}{\rho\lambda^4} \tag{7}$$

$$\frac{\tau}{c}=\frac{3\pi}{2\rho\lambda}\,\frac{Q_{\mathrm{sca}}}{X} \tag{8}$$

$$Q_{\mathrm{sca}}=\frac{2}{X^2}\sum_{n=1}^{\infty}(2n+1)[|a_n|^2+|b_n|^2] \tag{9}$$

$$\overline{\cos\theta}=\frac{4}{X^2Q_{\mathrm{sca}}}\sum_{n=1}^{\infty}\left[\frac{n(n+2)}{n+1}R_e(a_na^*_{n+1}+b_nb^*_{n+1})+\frac{2n+1}{n(n+1)}R_e(a_nb^*_n)\right] \tag{10}$$

$$s=\frac{0\cdot75Q_{\mathrm{sca}}}{r} \tag{11}$$

$$\frac{S}{s}=0\cdot75(1-a_1/3) \tag{12}$$

$$a_1=3\overline{\cos\theta} \tag{13}$$

$$\frac{S}{s}=0\cdot75(1-\overline{\cos\theta}) \tag{14}$$

$$\begin{aligned}Q_{\mathrm{sca}}=\frac{8X^4}{3}\left(\frac{m^2-1}{m^2+2}\right)^2\Bigg[1+\tfrac{6}{5}X^2\left(\frac{m^2-2}{m^2+2}\right)\\+X^4\left\{\frac{3}{175}\times\left(\frac{m^6+41m^4-284m^2+284}{(m^2+2)^2}\right)+\frac{1}{900}\left(\frac{m^2+2}{2m^2+3}\right)^2\right.\\\left.\times[15+(2m^2+3)^2]\right\}\Bigg]\end{aligned} \tag{15}$$

$$\overline{\cos\theta}=\frac{X^2}{15}\,\frac{(m^2+3)(m^2+2)}{2m^2+3} \tag{16}$$

$$a_1=\frac{0\cdot2X^2(m^2+3)(m^2+2)}{2m^3+3} \tag{17}$$

K = K–M absorption coefficient.
S = K–M scattering coefficient.
k = Mie volume absorption coefficient.
s = Mie volume scattering coefficient.
R = reflectance of sample with white background.
R_o = reflectance of sample with black background.
R_g = reflectance of white background.
R_t, R_{ot} and R_{gt} = respective reflectance values of R, R_o and R_g duly corrected for internal reflection using the Saunderson equation.
k_1 = external reflection coefficient of the first surface of the material for collimated light given by the equation $k_1 = (m - 1)^2/(m + 1)^2$.[9]
k_2 = internal reflection coefficient of the first surface of the material for diffuse light which is taken as 0·60.[9]
$R_{\infty t}$ = reflectance of a layer of the material for infinite thickness.
d = film thickness.
Q_{sca} = linear Mie scattering coefficient.
$\overline{\cos\theta}$ = asymmetry factor.
a_1 = first Legendre coefficient.
$X = 2\pi r/\lambda$ where r is the radius of the particle and λ is the wavelength of the incident beam in the medium.
m = relative refractive index of the particle.
V = volume of the particle.
τ = optical density.
τ/c = specific turbidity.
c = concentration of the sample.
ρ = density of the dispersed material.

3. EXPERIMENTAL

3.1. Determination of K–M scattering coefficient

Titanium dioxide (rutile) pigment dispersed in linseed oil with 26% pigment mass concentration (PMP) supplied by Goodlass Nerolac Company was used in the present study. The dispersions with pigment mass concentrations 0·5, 1·0, 4·0 and 26·0% were prepared using additional vehicle supplied by the company. The paint films at incomplete hiding with thickness varying from 40 to 200 μm were drawn on a Mylar

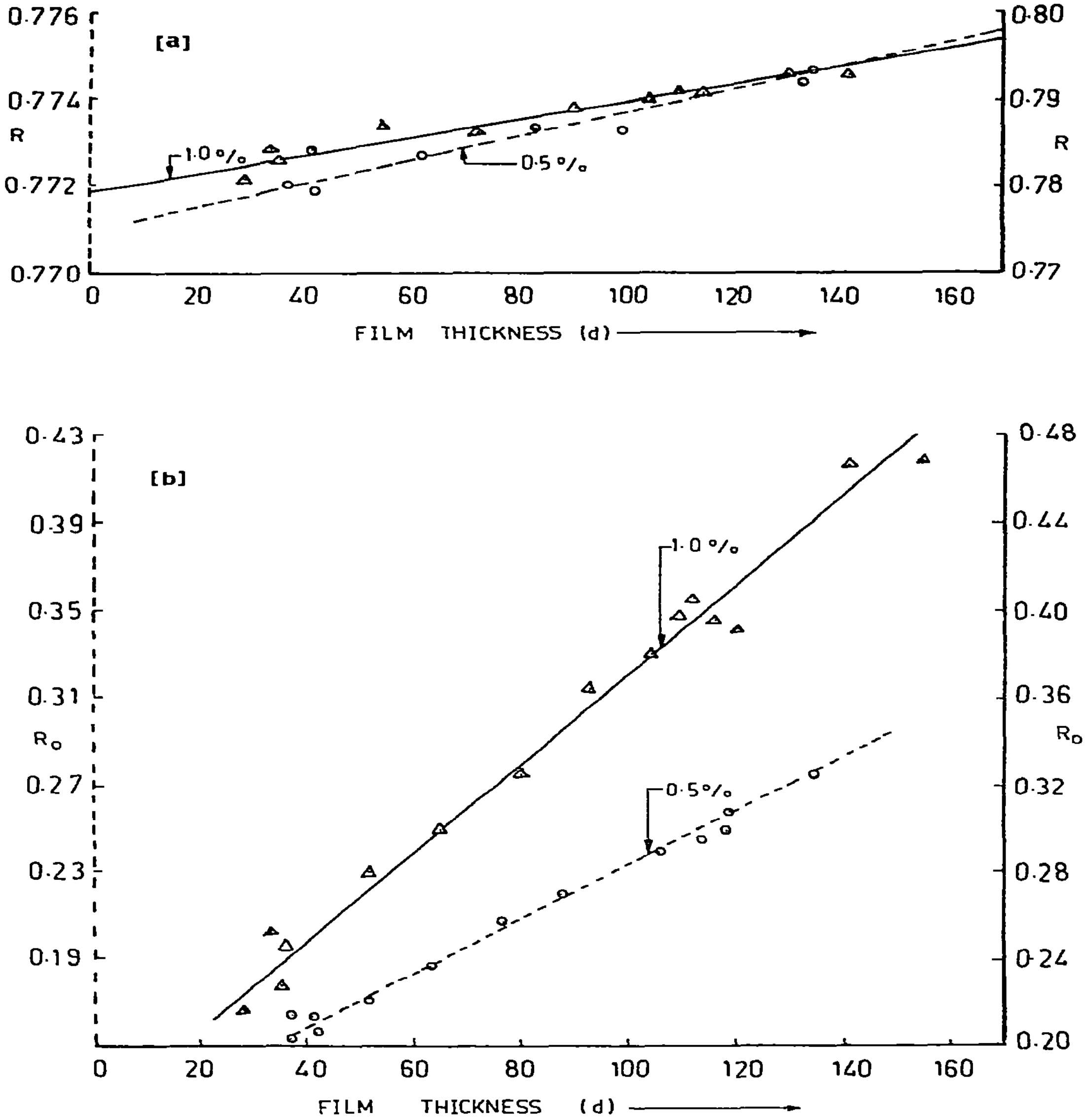

Fig. 1. Plot versus film thickness (μm) of (a) R and (b) R_0, for concentrations 0·5 and 1%.

type polyester film using a variable paint film applicator obtained from Gardner Instrument Division, USA. The paint films were dried at 60 °C for 24 h in a hot air oven. Each paint film was visually examined and a piece 30 × 30 mm having uniform thickness was taken for the observations. This film was further allowed to dry at room temperature for 48 h before measurements were made.

The spectral reflectance of the paint film was measured using a Shimadzu recording spectrophotometer model UV-240, which is a double-beam spectrophotometer equipped with an integrating sphere of 5 cm diameter and a microprocessor. The equipment employs normal/diffuse illumination/viewing conditions. The 0 % and 100 % lines were set in the equipment before recording the observations. Reflectance of the paint films was measured by mounting the film on white and black ceramic tiles. A drop of ethylene glycol was placed over a tile and the film was mounted and rolled using a clean glass roller. This ensured good optical contact between the tile and film and avoided unwanted reflection due to the formation of an air film. The reflectance values R and R_0 of paint films mounted on a white and a black tile respectively were recorded.

The paint samples were weighed using a semimicro balance with sensitivity 0·1 mg. The thickness of the paint films was determined from the area and density of paint film. As an approximation, the density of paint film was taken to be that of the vehicle. The graph of R and R_0 versus thickness of paint films were plotted as shown in Fig. 1 and the experimental data were interpolated at any desired thickness. The interpolated values of R and R_0 were then corrected for internal reflection due to refractive index discontinuity at the boundary of the film, using the Saunderson equation.[10] The K–M scattering coefficient per unit volume

TABLE 1
Experimental Values of K–M Scattering Coefficient for TiO_2

Concentration of pigments in paint film (% PVC)	*K–M volume scattering coefficient for $\lambda = 560\,nm$*	*Percentage of standard deviation*
0·1190	55 194	5·62
0·2381	60 936	4·97
0·9523	68 148	7·62
6·1904	72 938	8·21

Average $S = 64\,304\,cm^{-1}$.

of pigment was then calculated for 10 paint films of different thicknesses for each concentration using eqns. (4)–(6). The average value of the K–M scattering coefficient for each concentration was determined, and these values were then converted to the K–M volume scattering coefficients by multiplying by the ratio of the density of the pigment to the density of the paint film. This also took care of the error introduced in paint film thickness measurement due to the assumption that the density of the paint film equalled that of the vehicle. The density of rutile titanium dioxide is 4·2 and the density of the paint film measured experimentally was 0·975 g cm^{-3}. The K–M volume scattering coefficients thus calculated are given in Table 1.

3.2. Particle size measurement

Light scattering method

Particle size of titanium dioxide pigment was determined using two different methods based on light scattering techniques.[11] A dilute sample of titanium dioxide was prepared by dispersing a known quantity of titanium dioxide pigments in analytical grade toluene. The dispersion was stirred thoroughly using a mechanical stirrer to break down the pigment into individual particles. The dispersion was then diluted to various known concentrations. The spectral transmission of these samples was then measured using the Shimadzu spectrophotometer.

In first method, the graph of τ/c versus c was plotted. It was linear. The value of τ/c corresponding to infinite dilution was determined by extrapolating the graph to intersect the τ/c axis. This value of τ/c was substituted in eqn (7), and the particle volume (V) was determined. Assuming the pigments to be spherical, the radius of the particle was determined. In second method, the value of Q_{sca}/X was calculated using eqn. (8). The theoretical plot of Q_{sca}/X vs. X for X ranging from 0·2(0·2)10 and for $m = 1{\cdot}836$ was computed using the Mie equation on an IBM 360.[12] From the theoretical plot of Q_{sca}/X vs. X, values of X corresponding to experimental values of Q_{sca}/X were read, and hence the particle radius was determined. The results of particle size determination are given in Table 2.

Electron microscopy

As an additional check for particle size measurements, the electron micrographs of titanium dioxide pigments were recorded. They showed

TABLE 2
Particle Size Estimation in Titanium Dioxide Dispersion

Wavelength (nm)	*Radius of pigment from turbidity graph (μm)*	*Radius determined from Q_{sca}/X vs. X curve*
546	0·072	0·074 μm
580	0·078	0·078 μm
	Average radius = 0·075 μm	

that titanium dioxide particles are polydisperse in size. Measurements made on several electron micrographs showed that the radii of titanium dioxide pigments vary from 0·07 to 0·14 μm giving an average value of 0·1 μm.

In the present study we have used the average particle size determined by the light scattering method, as the measurements are made *in situ* and the probability of measuring aggregates is small.

4. THEORETICAL

Single scattering coefficients can be calculated using the Mie theory. The efficiency factor for scattering is defined by eqn. (9) in which a_n and b_n are functions of refractive index and particle size. The expressions describing a_n and b_n are extremely complicated, containing Bessel functions and their derivatives.[13] Computation of the asymmetry factor $\overline{\cos\theta}$ is equally involved, as seen in eqn. (10). The computations can be carried out easily using Mie theory IBM subroutines.[12] Thus comparison of the experimental value of S with the computed value using eqns. (9)–(12) is highly involved and expensive.

In paint technology, one deals with pigments of size parameter up to $X \approx 2$, i.e. $2r = 0{\cdot}35$ μm at $\lambda = 560$ nm, the centre wavelength of the visible spectrum. In this case it is possible to employ approximate equations[14,15] valid for this range of particle sizes, in place of the complicated Mie equations, The simplified expressions for Q_{sca} and $\overline{\cos\theta}$ are given in eqns (15) and (16). The K–M scattering coefficient S is first calculated using the Mie theory for relative refractive index, $m = 1{\cdot}54$, and size parameter, $X = 0{\cdot}2(0{\cdot}2)1{\cdot}6$, and then compared with the value calculated using the simplified equations. Thus the validity of approximate equations can be established for the present study and then they can be applied to actual cases for which experimental data are recorded. The values of s, $\overline{\cos\theta}$ and S calculated by means of the Mie equations using the IBM 360 for $m = 1{\cdot}54$ and $X = 0{\cdot}2(0{\cdot}2)1{\cdot}6$ are compared in Table 3 with the parameters calculated using the simplified equations. The results indicate that the values of s, $\overline{\cos\theta}$ and S computed using the simplified expressions agree well with those calculated using the Mie theory. Therefore it appears justifiable to use the simplified equations to calculate these parameters.

TABLE 3
Comparison of Scattering Coefficients Computed Using Mie Theory and Approximate Equations (for $m = 1{\cdot}54$, $\lambda = 560$ nm, and refractive index of medium = 1)

X	r (μm)	s_{Mie}	$s_{approx.}$	$\overline{\cos\theta}_{Mie}$	$\overline{\cos\theta}_{approx}$	S^a	S^b
0·2	0·0178	177·67	177·66	0·008 06	0·008 09	132·18	132·17
0·4	0·0357	1 430·71	1 431·09	0·031 98	0·032 35	1 038·71	1 038·59
0·6	0·0535	4 866·14	4 880·13	0·071 41	0·072 78	3 388·98	3 393·70
0·8	0·0713	11 398·84	11 566·63	0·127 15	0·129 39	7 462·08	7 552·49
1·0	0·0891	21 051·30	22 051·40	0·203 01	0·202 18	12 583·30	13 194·83
1·2	0·107	32 235·00	35 526·00	0·306 85	0·291 14	16 756·00	18 887·00
1·4	0·125	43 489·00	48 417·00	0·442 50	0·396 27	18 184·00	21 923·00
1·6	0·143	57 307·00	52 262·00	0·573 41	0·517 58	18 334·00	18 909·00

[a] K–M scattering coefficient calculated using Mie theory equations.
[b] K–M scattering coefficient calculated using eqns (15), (16).

The refractive index of titanium dioxide for $\lambda = 546$ nm is 1·836 and for $\lambda = 577$ nm it is 1·813.[16] Thus there is not much variation in the refractive index of TiO_2 in this range of the spectrum. Consequently the K–M volume scattering coefficient has been calculated for $m = 1{\cdot}813$ using eqn. (14). The values of s and $\overline{\cos\theta}$ calculated for titanium dioxide using eqns (15) and (16) are 161 475·9 and 0·362 29. These give the K–M volume scattering coefficient S as 77 231·5. This value is comparable to the experimentally determined value, 64 304.

The experimental value of the K–M volume scattering coefficient and that calculated from the single scattering parameter do not agree closely but they have the same order of magnitude. The difference between the two values of S may be due to other uncertainties in the experimental measurements as described below.

(1) The Mie scattering coefficient changes significantly with particle size in the size range $X = 1$–4 (ref. 15, p. 177). Electron micrograph data show that titanium dioxide particles are polydisperse in size. The radii of particles range from 0·07 to 0·14 μm. Therefore the scattering coefficient calculated using the size determined by the light scattering method will differ from actual values.

(2) The thickness of paint film is determined from the weight of paint film of known area. This method of measurement of film thickness may lead to uncertainty by about 10% due to non-uniformity in thickness. This may subsequently affect the experimental value of S.

5. CONCLUSION

The K–M theory makes possible the calculation of the reflectance and hence the tristimulus values of colour from a knowledge of K–M scattering and absorption coefficients of pigments. The theory does not provide any method for the calculation of K and S from the basic parameters of the colorants. On the other hand the Mie scattering theory provides a method for the calculation of the linear scattering and absorption coefficients of colorant from a knowledge of their size and refractive index. The thrust of this work has been to explore the possibility of correlating the K–M scattering coefficients with the basic parameters of the colorants, rather than to give large amounts of data. Much modern colour technology is now based on computer colour matching requiring knowledge of K and S of the colorants and it is very important to know the variation of these factors with the particle size of the colorant. The present study indicates that it is possible to correlate the K–M scattering coefficient with the particle size through the Mie scattering parameter. It is suggested that the use of the simplified equations rather than complicated Mie equations is better for applications to paint technology.

REFERENCES

1. G. Kortüm, *Reflectance spectroscopy*, translated by J. Lohr, p. 112. New York, Springer-Verlag (1969).
2. E. Allen, *Colour 77*, p. 153. New York, Troy (1977).

3. P. S. Mudgett and L. W. Richards, *J. Paint Technol.*, **45**, 44 (1973).
4. P. Kubelka and F. Munk, *I. Tech. Physik*, **12**, 593 (1931).
5. L. F. Gate, *Appl. Opt.*, **13**, 236 (1974).
6. P. S. Mudgett and L. W. Richards, *Appl. Opt.*, **10**, 1485 (1971).
7. C. M. Chu and S. W. Churchill, *J. Opt. Soc. Amer.*, **45**, 958 (1955).
8. G. C. Clark, C. M. Chu, and S. W. Churchill, *J. Opt. Soc. Amer.*, **47**, 81 (1957).
9. F. W. Billmeyer, Jr, and D. H. Alman, *J. Color and Appearance*, **2**(1), 36 (1973).
10. J. L. Saunderson, *J. Opt. Soc. Amer.*, **32**, 727 (1942).
11. K. T. Mehta and H. S. Shah, *J. Scient Ind. Res.*, **41**, 292 (1982).
12. J. V. Dave, *IBM Type III Program 360 D-17.4.002*, International Business Machines Center, Palo, California, USA (1968).
13. R. V. Desai, R. V. Mehta, H. S. Shah, J. N. Desai and D. B. Vaidya, *J. Opt.*, 3, 17 (1974).
14. R. Penndorf, *J. Opt. Soc. Amer.*, **52**, 797 (1962).
15. H. C. Van de Hulst, *Light scattering by small particles*. New York, John Wiley and Sons (1957).
16. J. R. DeVore, *J. Opt. Soc. Amer.*, **41**, 416 (1951).