Dyes and Pigments 9 (1988) 283–294

Variations in Reflectance of Pigmented Material with Particle Size and Refractive Index: An Experimental and Theoretical Study

H. S. Shah

Department of Physics, SV Regional College of Engineering and Technology, Surat–395007, India

and

K. T. Mehta

Department of Physics, MR Arts and Science College, Rajpipla–393145, India

(Received 8 July 1987; accepted 23 September 1987)

SUMMARY

The multiple-scattering technique proposed by Mudgett and Richards is the first applicable rigorous theory permitting the computations of reflectance of pigmented surfaces from the size and refractive index of pigments. The validity of this theory is established by comparing the experimental values of the reflectance of four paint samples with the theoretically predicted values. A further theoretical study on the variations in reflectance with particle size and refractive index (real and imaginary part of the refractive index) is carried out covering the range of relevance to paint technology. The study revealed that the error in the real part of the refractive index does not introduce a significant error in reflectance values. A small error in the absorption index, however, considerably changes the reflectance values and the error in particle size significantly affects the results in absorbing systems rather than in non- or weakly-absorbing systems.

1 INTRODUCTION

It is generally recognized that a multiple-scattering calculation scheme to predict precisely the reflectance of a coating would have potential use in both scientific and technological applications. The simplest scheme which is most widely used in the paint and coating industries is the Kubelka–Munk (hereafter abbreviated as K–M) two-flux theory. The prediction of reflectance using the K–M theory requires the experimental determination of the values of the K–M coefficients for each colorant.[1-3] The K–M theory is a highly simplified version of radiative transfer theory and assumes isotropic distribution of light within the paint film. This condition is not satisfied in several cases, particularly in metallic paint films where the pigment scatters light in a preferential direction and the sample exhibits geometric metamerism.[4] Deviation from isotropic distribution also occurs to some extent in thin films and in dark shades. The reflectances predicted by the K–M theory do not therefore always satisfactorily agree with experimental data.

Attempts have been made to introduce more complex theories, e.g. by Völz[5,6] and Beasley *et al.*,[7] by increasing the fluxes from two to four. The application of this theory is complex and requires the determination of several constants and this has therefore discouraged its widespread use. Mudgett and Richards have proposed a theory to include any number of fluxes.[8-10] This technique is known as the many-flux (hereafter abbreviated as M-F) or multichannel technique. The theoretical expressions of the M-F theory are highly involved, but the theoretical computations can be carried out using Standard IBM Subroutine Packages. The theory has been applied to metallic paints and the results obtained are very encouraging.[4]

The M-F technique is based on sound theoretical principles and is the first theory of this nature which can predict the reflectance of coating/paint film from fundamental characteristics of colorants, e.g. refractive index and particle size. Academically it is more attractive, but the practical determination of optical and morphological characteristics of particulate matter with great precision is difficult.[11,12] The refractive index consists of two parts, viz. the real part of the refractive index (n_{RE}) and the imaginary part of the refractive index (n_{IM}): n_{RE} is determined by the velocity of light in the medium and n_{IM} depends on the absorption characteristics of the material. The refractive index of a given material varies with the wavelengths and very few direct methods are available to determine the refractive index of particulate matter; the results obtained for the same material by different authors differ considerably.[13,14] There are several optical and non-optical methods which can be used to determine the particle size of colorants.[15] Most particulate systems are polydispersed in nature and the particle size determined by different methods gives different averages of the systems. Thus, even when all possible care is taken in the determination of the optical and morphological properties of colorants, there is likely to be some uncertainty in these values. This may thus adversely affect the values of the reflectance computed using the M-F technique, taking size and refractive index as input parameters.

The objective of this study is to assess the effect of variation of n_{RE}, n_{IM} and particle size on the reflectance computed using the M-F theory. In the first part of this paper, we have established the validity of the M-F theory by comparing the experimentally determined and theoretically predicted reflectance of four paint samples. In this case, the experimental data are compared with theoretical results only for wavelengths for which the refractive indices of the pigments are available in the literature. In the latter part of the paper, the reflectance of systems with varying size and refractive index are calculated and the sensitivity of these parameters to the final value of the reflectance is discussed.

2 MANY-FLUX THEORY

The theoretical development of turbid medium theory has resulted from the work by astrophysicists interested in understanding the passage of a light beam through a stellar atmosphere. The important calculation methods have been developed by nuclear physicists interested in calculating the neutron flux in a reactor. Research workers in the field of paint technology have adopted these methods but with a necessary simplification incorporating only the requirements of the subject. One of the important contributions in this direction have been made by Mudgett and Richards,[8-10] who have developed relatively rigorous treatment to the discrete ordinate method to account for diffuse reflectance and transmittance by dispersed media. In this approach, the light passing through the paint film is divided into a large number of channels. Each channel covers different ranges of angles from perpendicular to horizontal, as shown in Fig. 1. In half the channels light is travelling downward and in the other half upward. The change in light flux in each channel is expressed by a differential equation and there will thus be as many equations of the following form as there are channels:

$$r_i\left(\frac{\mathrm{d}F_i}{\mathrm{d}x}\right)=\sum_{i=1}^{n} S_{ij}F_i \qquad i=1,2,\ldots,n \tag{1}$$

where $r_i=1$ for $i\leq n/2$ and $r_i=-1$ for $i>n/2$. In the above, F_i represents the monochromatic flux contained within each channel i and n is the total number of channels. In propagation of light through turbid media, the differential change in flux in the channel on passing through differential thickness $\mathrm{d}x$ is decided by the increase in flux due to scattering from other channels and decrease due to absorption in the channel and scattering out of

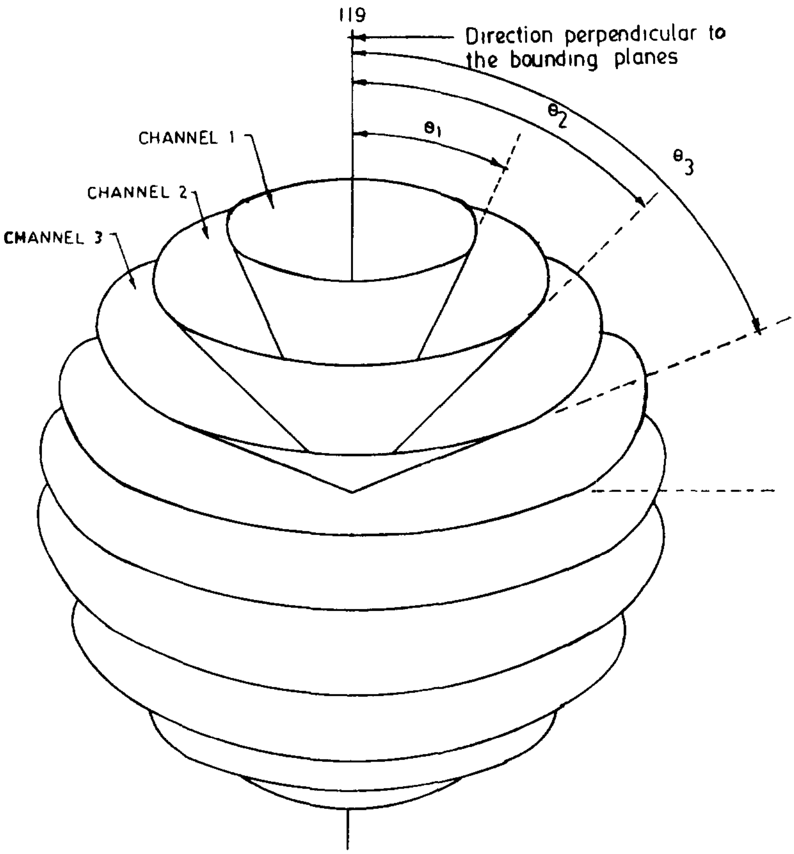

Fig. 1. The division of directions in space into channels.

the channel. Thus the coefficients S_{ij} represent the fraction of light received in the channel i due to scattering from channels j and the coefficients S_{jj} represent the fraction of loss of flux due to scattering in all other channels from channel j plus the absorption of light in channel j. The flux in each channel can be obtained by solution of eqn (1), the general solution of which is

$$F_i = \sum_{j=1}^{n} A_{ij} C_j \exp(\lambda_j x) \qquad (2)$$

where λ_j are the eigenvalues and A_{ij} are corresponding eigenvectors of the S-matrix formed by the coefficients S_{ij}. The S-matrix will be a square matrix and its size depends on the selection of the number of channels. In this present study, we have taken 26 channels, giving a 26 × 26 S-matrix. The elements of the S-matrix can be evaluated from the scattering coefficient, absorption coefficient and phase function of the particle. These parameters in turn can be determined using single-scattering theory from size and refractive index of the pigment. We have used Mie theory equations to evaluate single-scattering parameters and hence the elements of the S-matrix (ref. 9, eqns 25 and 26).

The eigenvalues and eigenvectors of the S-matrix were evaluated using standard computer subroutines HSBG, ATEIG and SIMQ in double precision from IBM System 360 Scientific Subroutine Package. The values of constants C_j depend on the conditions at the boundaries of the turbid medium. The condition at the first surface is determined by illuminating conditions and that at the second surface depends on the backing near the paint film. In the present study, we have determined the reflectance at the complete hiding of the paint film illuminated by a collimated beam of light. This is in conformity with the actual illuminating condition in the instrument used for the experimental measurements. This enables us to compare the experimentally determined values with theoretically predicted ones. The useful equations of the M-F theory, together with an explanation of various parameters and the method of computation, have been previously described in detail by us.[16]

3 EXPERIMENTAL MEASUREMENTS

For the present experimental study, we selected four paint dispersions. Two of these are chromatic paints, e.g. Phthalocyanine Green (Ph-G) and iron oxide red (Fe-R), and the other two dispersions were of titanium dioxide (TiO_2) having different average pigment sizes and which were labelled as TiO_2-A and TiO_2-B. The paint films of each dispersion were prepared on a Mylar-type polyester film using the variable paint film applicator of Gardner Instrument Division, USA. The spectral reflectance of the paint films were measured on a Shimadzu recording spectrophotometer model UV-240, which is a recording-type double-beam spectrophotometer equipped with an integrating sphere of 5 cm diameter and a microprocessor. In calibration mode, the 0% line is internally set for the desired range of the spectrum and the 100% line is set by keeping pressed white Eastman Kodak barium sulphate on the sample and specimen port.

As the paint film could not be prepared at complete hiding, the reflectances of the films were recorded by mounting the films subsequently on black and white ceramic tiles. To ensure optical contact between the Mylar and background, a drop of ethylene glycol having refractive index 1·60, almost equal to the refractive index of Mylar, was spread over the tiles. The film was mounted, rolled with a clean glass rod and the reflectance at complete hiding was then calculated using eqns (1)–(5) (ref. 17, p. 331).

The particle size in each pigment dispersion was determined by electron microscopy and light-scattering techniques.[15] The average of the particle sizes determined by both the methods was taken for theoretical computation. The absorption coefficient, scattering coefficient and phase function were computed from size and refractive index of pigments using Mie theory equations.[18] The Mie volume scattering and absorption coefficients of single scattering required for the M-F computations can be obtained using equations

$$s = \frac{3\pi}{2\lambda}\frac{Q_{sca}}{x} \qquad k = \frac{3\pi}{2\lambda}\frac{Q_{abs}}{x}$$

Here $x = 2\pi r/\lambda$ is the particle-size parameter, r is the radius of the particle and λ is the wavelength of the incident beam in the medium. The phase function data were used to estimate Legendre coefficients a_0–a_n using

$$a_l = (l + \tfrac{1}{2}) \int_0^{180} f(\theta) P_l(\cos\theta) \sin\theta \, d\theta$$

The integration can be performed using the subroutine QSF of IBM Scientific Subroutine Packages. The function $f(\theta)$ represents the angular scattering pattern of the particle, commonly known as the phase function, and it can be calculated using the Mie theory equations. These single-scattering parameters were used to compute the reflectance of the paint film using the M-F theory. The experimental and theoretical value of reflectance for all the four paint samples are compared in Table 1. The values are in good agreement and this establishes the validity of the M-F theory. Small deviations of the theoretical values from experimental ones can be accounted for as due to polydispersity in pigment sizes. Further, the refractive indices of the pigments used in the study are not measured, but have been directly taken from the literature.[13,19,20] This also affects the theoretical values of the reflectance.

TABLE 1

Comparison of Experimental and Theoretical Values of Reflectance of Paint Films

Pigment	*Radius of pigment particle (μm)*	*Wavelength (nm)*	*Relative refractive index*	*k/s*	R_∞	
					Theoretical	*Experimental*
Ph-G	0·0838	436	$1{\cdot}227 - 0{\cdot}085i$	2·3110	0·0161	0·0120
Fe-R	0·0490	436	$1{\cdot}951 - 0{\cdot}2i$	3·2182	0·0298	0·0177
TiO_2-A	0·0700	405	$2{\cdot}0687 - 0{\cdot}00014i$	0·0110	0·5930	0·5896
TiO_2-B	0·1045	546	$1{\cdot}836 - 0{\cdot}00i$	10^{-6}	0·8371	0·8416

4 COMPUTATIONAL ANALYSIS USING THE M-F THEORY

The M-F theory is based on sound theoretical principles and the data reported in the previous section demonstrate the validity of the theory in predicting reflectance from the size and relative refractive index of pigments. The results reported by Billmeyer and Carter,[4] for metallic paints using the M-F theory also confirmed the usefulness of the theory. We therefore carried out a study to analyse the effect of various parameters on the reflectance of paint film.

In the present calculation, we have used 26 fluxes to predict the reflectance of paint films. The Mie theory scattering coefficients, absorption coefficients and phase functions have been calculated using the Mie theory double precision program developed by J. V. Dave.[21] The results of the computations are given in Tables 2–8. Table 2 gives the values of reflectance

TABLE 2
Effect of Variations in n_{RE} on Reflectance for non-Absorbing Pigments having Size Parameter $x = 2$

Relative refractive index	*k/s*	*Reflectance*
$1{\cdot}227 - 0{\cdot}0i$	10^{-6}	0·8131
$1{\cdot}836 - 0{\cdot}0i$	10^{-6}	0·8089
$1{\cdot}850 - 0{\cdot}0i$	10^{-6}	0·8090
$1{\cdot}900 - 0{\cdot}0i$	10^{-6}	0·8093
$1{\cdot}950 - 0{\cdot}0i$	10^{-6}	0·8095
$1{\cdot}983 - 0{\cdot}0i$	10^{-6}	0·8095
$2{\cdot}000 - 0{\cdot}0i$	10^{-6}	0·8095
$2{\cdot}075 - 0{\cdot}0i$	10^{-6}	0·8080

TABLE 3
Effect of Variations in n_{RE} on Reflectance for Absorbing Pigments having Size Parameter $x = 1{\cdot}9$

Relative refractive index	*k/s*	*Reflectance*
$0{\cdot}933 - 0{\cdot}1i$	7·4852	0·00034
$1{\cdot}100 - 0{\cdot}1i$	7·0120	0·0012
$1{\cdot}227 - 0{\cdot}1i$	1·9609	0·0057
$1{\cdot}400 - 0{\cdot}1i$	1·5464	0·0079
$1{\cdot}500 - 0{\cdot}1i$	1·1016	0·0132
$1{\cdot}600 - 0{\cdot}1i$	0·8878	0·0168
$1{\cdot}700 - 0{\cdot}1i$	0·8619	0·0152
$1{\cdot}800 - 0{\cdot}1i$	0·9485	0·0123

TABLE 4
Effect of Variations in n_{IM} on Reflectance for Optically Soft Pigments having Size Parameter $x = 1{\cdot}26$

Relative refractive index	*k/s*	*Reflectance*
$1{\cdot}227 - 0{\cdot}001i$	0·0380	0·3875
$1{\cdot}227 - 0{\cdot}01i$	0·3800	0·1102
$1{\cdot}227 - 0{\cdot}05i$	1·9294	0·0278
$1{\cdot}227 - 0{\cdot}1i$	3·2635	0·0155
$1{\cdot}227 - 0{\cdot}15i$	4·3211	0·0122
$1{\cdot}227 - 0{\cdot}20i$	4·7028	0·0110
$1{\cdot}227 - 0{\cdot}25i$	4·7562	0·0107
$1{\cdot}227 - 0{\cdot}30i$	4·6291	0·0109
$1{\cdot}227 - 0{\cdot}35i$	4·4162	0·0113
$1{\cdot}227 - 0{\cdot}40i$	4·1697	0·0119

TABLE 5
Effect of Variations in n_{IM} on Reflectance for Optically Hard Pigments having Size Parameter $x = 2{\cdot}3$

Relative refractive index	*k/s*	*Reflectance*
$1{\cdot}951 - 0{\cdot}001i$	0·0034	0·6577
$1{\cdot}951 - 0{\cdot}01i$	0·3413	0·3338
$1{\cdot}951 - 0{\cdot}1i$	0·3182	0·0695
$1{\cdot}951 - 0{\cdot}2i$	0·5829	0·0337

TABLE 6
Effect of Variations in n_{IM} on Reflectance for Optically Hard Pigments having Size Parameter $x = 2{\cdot}07$

Relative refractive index	*k/s*	*Reflectance*
$2{\cdot}075 - 0{\cdot}001i$	0·0041	0·6426
$2{\cdot}075 - 0{\cdot}01i$	0·0398	0·3220
$2{\cdot}075 - 0{\cdot}07i$	0·2506	0·0693
$2{\cdot}075 - 0{\cdot}1i$	0·3404	0·0673

TABLE 7
Effect of Variations in Particle Size on Reflectance for $m = 1{\cdot}983 - 0{\cdot}0i$, $\lambda = 436\,\text{nm}$

Radius of particle (μm)	*Particle size parameter, x*	*k/s*	*Reflectance*
0·046 3	1·0	10^{-6}	0·835 5
0·055 5	1·2	10^{-6}	0·834 0
0·064 8	1·4	10^{-6}	0·842 5
0·074 0	1·6	10^{-6}	0·848 5
0·083 0	1·8	10^{-6}	0·844 1
0·092 5	2·0	10^{-6}	0·845 2
0·115 7	2·5	10^{-6}	0·840 0

TABLE 8
Effect of Variations in Particle Size on Reflectance for Absorbing Pigments

Refractive index and wavelength	*Radius of particle (μm)*	*Size parameter, x*	*k/s*	*Reflectance*
$m = 1{\cdot}951 - 0{\cdot}2i$	0·009 25	0·2	54·528 7	0·002 1
$\lambda = 436\,\text{nm}$	0·027 76	0·6	2·457 0	0·034 0
	0·064 77	1·4	0·608 9	0·043 3
	0·101 77	2·2	0·583 4	0·030 7
	0·138 78	3·0	0·872 8	0·019 7
$m = 2{\cdot}068\,7 - 0{\cdot}000\,14i$	0·094 5	2·2	0·011 0	0·581 0
$\lambda = 405\,\text{nm}$	0·103 1	2·4	0·011 0	0·593 1
	0·110 7	2·6	0·012 9	0·561 0
$m = 1{\cdot}227 - 0{\cdot}085i$	0·009 25	0·2	408·94	0·000 3
$\lambda = 436\,\text{nm}$	0·027 76	0·6	17·304 2	0·005 9
	0·037 01	0·8	9·043 5	0·010 8
	0·064 77	1·4	2·577 7	0·016 6
	0·092 52	2·0	1·621 6	0·006 1
	0·120 28	2·6	1·152 2	0·008 7
	0·138 78	3·0	0·999 9	0·009 3
$m = 1{\cdot}286\,7 - 0{\cdot}17i$	0·009 25	0·2	428·640 0	0·000 3
$\lambda = 436\,\text{nm}$	0·027 76	0·6	18·162 5	0·005 6
	0·064 77	1·4	2·843 1	0·013 8
	0·107 77	2·2	1·625 5	0·005 9
	0·138 78	3·0	1·210 6	0·004 5

for non-absorbing systems. The results show that a variation in refractive index from 1·227 to 2·00 does not significantly affect the reflectance values. Table 3 gives the results of variation in the real part of the refractive index for absorbing particles having a fixed value of the imaginary part of the refractive index. The results show that the reflectance increases with increase in the real part of refractive index up to 1·6 and then decreases. Tables 4–6 give the values of reflectance and k/s for a fixed value of the real part of the refractive index but different values of the imaginary part. These tables show that the reflectance changes remarkably as the system changes from a non-absorbing to even a weakly-absorbing one, this being due to the fact that optical efficiency for absorption is very high for small particles.[22] Table 7 gives the variation in reflectance with particle size for non-absorbing systems. It can be seen that as the particle size varies in the range $r = 0{\cdot}0464\,\mu m$ to $r = 0{\cdot}1157\,\mu m$ for $\lambda = 436$ nm, the reflectance values are within the range 0·83 to 0·85. Thus the small variations in particle size have negligible effect on the calculated reflectance. Table 8 shows the effect of variations in particle size on reflectance for absorbing pigments. For weakly-absorbing particles for $m = 2{\cdot}0687 - 1{\cdot}4 \times 10^{-4}i$, the reflectance values do not change significantly with particle size, but for highly absorbing systems, i.e. for $m = 1{\cdot}951 - 0{\cdot}2i$, the reflectance varies significantly with the size of pigments, initially increasing up to about $0{\cdot}07\,\mu m$ radius and then decreasing.

5 DISCUSSION

The comparison of experimental and theoretical values of reflectance establishes the applicability of the M-F technique to paint technology. The theory can be employed to predict the reflectance of the pigmented object and hence the colour with the variation in the optical and morphological characteristics of the pigment. The object of this work was to identify the parameters of which small variations may significantly affect the reflectance values, rather than to give a large amount of theoretical data. The analysis shows that the reflectance of the pigmented object is least sensitive to variation in the real part of the refractive index for non-absorbing systems. Therefore the refractive index available at the central wavelength of visible region can be used for the computation of reflectance over the entire spectrum. The same is true for weakly-absorbing systems. The amount of light reflected by the pigmented material is highly sensitive to even small changes in n_{IM}, particularly for weakly-absorbing systems. Therefore it is necessary to determine n_{IM} precisely at all wavelengths in order to predict the reflectance of the paint film and reliable methods are available for the determination of n_{IM} of pigments.[23–25] Further, in the range of size of interest to paint technology, for non-absorbing systems such as TiO_2 and $BaSO_4$, the reflectance values do not change with variation in pigment size. This is because the optical efficiency for scattering is not very sensitive to particle size in the lower range of submicron size. For moderately and highly absorbing systems, the reflectance is sensitive to change in particle size. It can thus be concluded that for chromatic pigments, a highly precise value of n_{IM} and a moderately reliable value of particle size is required in order to predict the correct value of reflectance using the M-F theory.

The work reported in this present study is of a preliminary nature and further studies on, for example, calculations of reflectance considering the polydispersity of pigments and of the reflectance of admixtures of colorants using the M-F equation are of interest. Once the reflectance prediction using M-F theory is fully established, the method can be compared with results from other systems. The M-F theory would be expected to give satisfactory results even in cases where K–M theory fails, e.g. for dark shades and for automotive paints. We hope to report studies in this respect in the future.

REFERENCES

1. F. W. Billmeyer Jr and R. L. Abrams, *J. Paint Technol.*, **45**, 23 (1973).
2. F. W. Billmeyer Jr and R. L. Abrams, *J. Paint Technol.*, **46**, 56 (1973).
3. R. G. Kuehni, *Computer colorant formulation*, Lexington, MA, Lexington Books, D. C. Health and Company (1975).
4. F. W. Billmeyer Jr and E. C. Carter, *J. Coating Technol.*, **48**, 295 (1976).
5. H. G. Völz, in *Sixth FATIPEC Congress*, p. 98, Weinheim, Verlag Chemie (1962).
6. H. G. Völz, in *Seventh FATIPEC Congress*, p. 194, Weinheim, Verlag Chemie (1964).
7. J. K. Beasley, J. T. Atkins and F. W. Billmeyer Jr, in *Electromagnetic scattering*, eds R. L. Rowell and R. S. Stein, p. 765, New York, Gordon and Breach (1967).
8. L. W. Richards, *J. Paint Technol.*, **42**, 276 (1970).
9. P. S. Mudgett and L. W. Richards, *Appl. Opt.*, **10**, 1485 (1971).
10. P. S. Mudgett and L. W. Richards, *J. Paint Technol.*, **45**, 44 (1973).
11. E. Allen, *J. Paint Technol.*, **45**, 65 (1973).
12. F. W. Billmeyer Jr, P. G. Chassaigne and J. F. Dubois, *Color Res. Appl.*, **5**, 108 (1980).
13. M. Kerker, P. S. Cheiner, D. D. Cooke and J. P. Kratohvil, *J. Colloid Interface Sci.*, **71**, 176 (1979).
14. K. V. Gehlen and H. N. Piller, *Jahrbuch Min. Geol. Beilageband*, **4**, 97 (1969).
15. K. T. Mehta and H. S. Shah, *J. Sci. Ind. Res.*, **41**, 292 (1982).
16. H. S. Shah, P. M. Vora and K. T. Mehta, *Paint India*, 21 (1984).
17. K. T. Mehta, M. C. Bhavsar, P. M. Vora and H. S. Shah, *Dyes and Pigments*, **5**, 329 (1984).
18. R. V. Desai, R. V. Mehta, H. S. Shah, J. N. Desai and D. B. Vaidya, *J. Opt.*, **3**, 17 (1974).

19. J. R. Devove, *J. Opt. Soc. Amer.*, **41**, 416 (1951).
20. A. R. Hanke, paper presented at the *Inter-Society Color Council Williamsburg Conference*, 1966.
21. J. V. Dave, IBM Type III Program 360 D-17, 4.002. Palo Alto, California, International Business Machines Center (1968).
22. F. W. Billmeyer and M. Saltzman, *Principles of colour technology*, New York, John Wiley and Sons (1981).
23. E. M. Patterson, D. A. Gillette and B. H. Stockton, *Complex index of refraction between* 300 *and* 700 *nm for Sabran aerosols*. Private communication, National Centre for Atmospheric Research (1977).
24. G. W. Grams, I. H. Blifford, D. A. Gillette Jr and P. B. Russell, *J. Appl. Meteor.*, **13**, 459 (1974).
25. C. I. Baver and R. J. Charlson, *Appl. Opt.*, **12**, 1356 (1973).