

Effect of the Continuous Medium on the Color of Discontinuous Substrates. IV. The Effect of the Refractive Index of the Continuous Medium

E. HOPE ALLEN,* D. L. FAULKNER,† G. GOLDFINGER, and R. MCGREGOR, *School of Textiles, North Carolina State University at Raleigh, Raleigh, North Carolina 27607*

Synopsis

It is known from experience that light scattering-absorbing substrates are darker when the continuous medium is water instead of air. This is due to the decrease in scattering efficiency of the scattering particles caused by the smaller value of the ratio n_1/n_2 of the refractive indices of the scattering particles ($n_1 = 1.5$ to 1.7) to that of water ($n_2 = 1.33$) as compared to that ratio when the continuous medium is air ($n_2 = 1$). Experimental evidence for this phenomenon is presented for polyester fabric viewed in air, water, and a concentrated sucrose solution. The wavelength range from 0.4 to 0.7 microns, and absolute "dry" reflectances from 0.02 to 0.7 were covered. The phenomenon cannot be adequately described with the Kubelka-Munk theory of the color of scattering-absorbing substrates.¹ Evidence is presented that at high reflectance values (0.4-0.7), the theory describes the color adequately and the results are consistent with a prediction based on a modified Mie equation for the scattering efficiency of "large" particles.^{2,3} At low reflectance values (<0.05), the Kubelka-Munk theory breaks down completely. This is consistent with the observation that this theory is not capable of predicting precisely high dye concentrations on textiles but is quite adequate for low concentrations.

INTRODUCTION

From experience one knows that light-scattering substrates such as textiles, stones, paper, or ceramics are darker when wet than when dry. It is of interest to know why this phenomenon takes place. It is also of value to be able to predict the dry color of a fabric in the wet processing stage.

Little work has been published on the color of objects when the optically continuous medium is other than air. Saunderson⁴ in 1942 recognized that the colors of various pigments were dependent upon the transparent medium in which they are viewed and reasoned that this phenomenon could be explained using a "two-constant theory" to calculate the color of opaque pigmented materials. The two constants are the absorption and scattering coefficients.

* Present address: Lehigh University, Bethlehem, Pennsylvania.

† Present address: General Electric Company, Schenectady, New York.

In studying the soiling of textiles, Prescott and Stearns⁵ measured the color of fabric stained with oil. This fabric was not immersed in oil, but merely stained. What results is a complex medium of oil and air. The authors noted that the introduction of the oil affects the scattering coefficient.

Iida⁶ in 1970 took spectrophotometric data on some wet and dry fabrics and noted that for white cotton fabrics there was a 12–14% decrease in reflectance when the fabric was immersed in water. He compared this phenomenon to the effect of antireflective coating on camera lenses. Iida briefly mentions specular reflectance of wet nonscattering substrates such as smooth stones.

In 1970, Goldfinger et al.⁷ carried out exploratory measurements on the effect of water, as a medium, on the color of light-scattering substrates. The explanation presented was that reflectance decreases when the refractive index ratio of the substrate to the medium approaches unity and thus the scattering efficiency approaches zero. This research is a continuation of that by Goldfinger et al.⁷

The simplest experimental conditions in reflectance colorimetry are those in which the sample under investigation is so thick that any increase of this thickness does not affect the results of the measurements, regardless of the background conditions.

Under these hypothetical conditions, if the ratio of the refractive indices of the fiber and the continuous medium is 1, then the sample is black regardless of the other optical properties of the substrate, since no mechanism is provided for the reflectance of light by scattering. Incidentally, under these conditions the sample would actually have to be infinitely thick.

Also, as the ratio of refractive indices deviates more and more from unity, the sample becomes less and less dark, since the scattering efficiency increases and light is back scattered having had fewer opportunities to be absorbed.

One can represent those observations as the ratio R_w/R_d of the reflectance R_w of a sample viewed in water to the reflectance R_d of the same sample viewed in air. Obviously, the value of R_w/R_d must, in most cases, be less than 1. However, this ratio is exactly 1 in the hypothetical case in which the dry fabric does not absorb any of the incident light. In that case, as long as the scattering efficiency is some finite value, all incident light is also back reflected from the wet sample and causes the ratio to be 1.

From this it follows that there exists a relationship between the lightness (Y) of a substrate and the scattering efficiency and, as a consequence, also with the ratio of the refractive indices of the optically continuous medium and the scattering particles.

This work gives experimental evidence for such an effect of the refractive index of the medium on the color of the fabric and of the magnitude of the effect at different values of the reflectance.

The system investigated is polyester fabric dyed to 14 shades ranging from black through grey to white. The lightness (Y) of these samples is:

0.716, 0.707, 0.338, 0.267, 0.169, 0.113, 0.068, 0.034, 0.026, 0.023, 0.022, 0.020, 0.019, and 0.018, respectively. The continuous medium is air with a refractive index of 1.0003 (taken to be 1, since the value in the fourth place can be disregarded), water with a refractive index of 1.33, or concentrated sucrose solution with a refractive index of 1.45.

EXPERIMENTAL

Calibration for Absolute Reflectance. Obtaining a Secondary Standard

The reflectance data as recorded on the G. E. Hardy spectrophotometer are compared to some white standard, in this case white Vitrolite. The reflectance recorded is the fraction of light reflected from the sample as compared to the Vitrolite tile. However, it is necessary to obtain absolute reflectance data because the colorimetric functions are not linear in respect to the reflectance. In this instance, $(1-R)^2/2R$ is not linear in respect to R .

An absolute calibration involves measurement of the fraction of energy reflected in the various regions of the spectrum. Such a calibration is too difficult and impractical for the requirements here. Another possibility is to compare the measured reflectance to some standard known in absolute terms.

One such standard is magnesium oxide. The absolute reflectance throughout the visible spectral range is known.⁸ Since it is difficult to prepare a perfect magnesium oxide surface, two sets of calibrations were carried out with sets of standard tiles; one involved six colored tiles which have been calibrated by the National Bureau of Standards in respect to a white Vitrolite tile, which in turn has been calibrated in respect to MgO. (The author is indebted to Burlington Industries, Mr. L. A. Graham, for the loan of the colored tiles.)

For this purpose, a calibration curve was prepared for a secondary standard by plotting the instrument reading against the known absolute values. The calibration was carried out over the visible spectrum from 0.4 micron to 0.7 micron at 0.01-micron intervals.

The absolute reflectance is

$$R_a = P \cdot V \cdot T$$

where P is the reflectance of magnesium oxide,⁸ V is the reflectance of a particular white tile with respect to magnesium oxide, and T is the reflectance of the reference with respect to that particular Vitrolite tile. These values were compared to those obtained with a Vitrolite tile of our own, which was thus made into a secondary standard. From a regression analysis on 186 pairs of points, it was found that

$$R_a = 2.0 \times 10^{-3} + 0.857R_m$$

with an estimated standard error⁹ $S_e = 5 \times 10^{-4}$ where m stands for measured. Since $\pm 1 \times 10^{-3}$ is the uncertainty of our measurement, the

value $R_a = 0.86 R_m$ was accepted as the result of these measurements. (The tile used is linear in its reflectance to ± 0.0065 between 0.4 and 0.7 micron and to ± 0.0035 between 0.46 and 0.7 micron.)

Correcting for the Positioning of the Samples

By necessity, when the fabric is immersed in a liquid medium, it must be displayed in a container because the sample ports of the G. E. Hardy spectrophotometer are in a vertical position. The holder used here was a stainless steel cell with a glass window to transmit light from the spectrophotometer (Fig. 1).

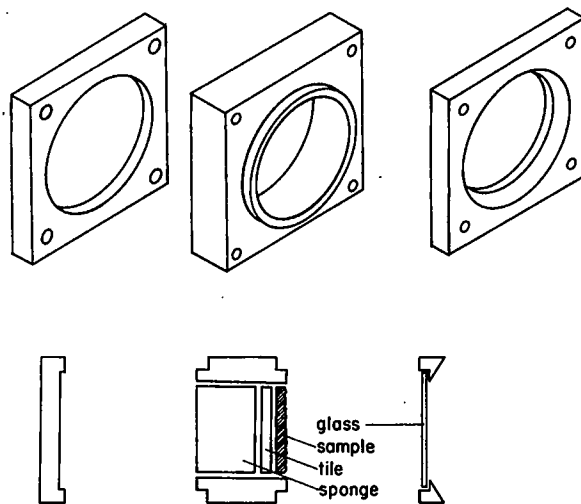


Fig. 1. Perspective and cross-sectional view of the sample cell. The immersion liquid fills the cell.

The introduction of the holder brings about two complications. First, the sample is no longer flat against the integrating sphere of the spectrophotometer but moved back (to a distance of 3.54 mm). Consequently, some of the light which should be reflected into the sphere is diffusely back-scattered by the sample and so is lost on the outside back wall of the spectrophotometer and in the sample holder.

Second, the glass window affects the light transmission through interfacial reflection which depends on the ratio of the refractive indices of the glass and the adjacent media, air, water, or sucrose solution. The effect of the glass window and the location of the sample can easily be determined by comparison if the continuous medium is air. If, however, the sample is displayed in water or sucrose solution, this is obviously not possible. Therefore, in those cases a new secondary standard was used. It consists of the known standard displayed in the sample holder, separated from the window by a 0.025-mm (0.001-in.) layer of water and sucrose solu-

tion, respectively. From these, a calibration curve was constructed which can satisfactorily be represented by

$$R_a = 0.97 \cdot R_m$$

where R_a is the absolute value of reflectance and R_m is the value obtained on the instrument using the appropriate new secondary standard.

Materials and Apparatus Used

All reflectance data were measured on a G. E. Hardy recording spectrophotometer. This instrument is equipped with an Automatic Tristimulus Integrator. The Automatic TSI calculates the color coordinates X , Y , Z and displays reflectance values continuously or in 0.005-, 0.01- and 0.02-micron intervals. All measurements were taken with black light traps to eliminate the specular component due to the glass window of the sample container.

An acceptable level of opacity was assumed when the reflectance reading in any of the media was unaffected by exchanging a white tile for a black tile as backup.

The spectrophotometer has an effective slit width of 0.01 micron \pm 20% between 0.380 and 0.700 micron. The accuracy of the wavelength scale is better than \pm 0.001 micron.

The light scattering-absorbing substrate used was polyester fabric. (Our thanks are due to National Spinning Company for supplying the dyed yarn.) Polyester was used because of its dyeability and its low hygroscopicity. However, one drawback of polyester is that it is highly birefringent, the two refractive indices, parallel and perpendicular to the fiber axis, being approximately 1.7 and 1.5.

The liquid continuous media used were water and a 63.7% sucrose solution. The refractive index of these and other liquids used was measured with the Abbe refractometer with temperature control. As a light source, the monochromator of the spectrophotometer was used.

Determination of the Dispersed Refractive Indices of the Fiber

The dispersed refractive index of the fiber was determined by the method of Freeman and Preston.¹⁰

The fiber was immersed in an oil whose refractive index was known over the visible spectral range and was approximately that of the fiber parallel or perpendicular to the fiber axis. It was viewed under 210 \times magnification with a Zeiss microscope, the fiber aligned either parallel or perpendicular, as the case may be, to the plane of polarization of the light used. The setting of the monochromator was then varied until the Becke lines disappeared. Knowing the refractive index of the oil at that wavelength furnished the information for the fiber.

Since no temperature control for the microscope stage was available, the determination was carried out at the measured ambient temperature (be-

tween 25°C and 27°C). It was assumed that the variations of the refractive index of the fiber within that temperature range are negligible. The refractive index values of the various liquids were corrected to that at the temperature as measured at the particular occasion. The data were evaluated in two ways.

The refractive indices of the sets of immersion oils were plotted on Hartman's dispersion paper. On these, the points of refractive index coincidence were marked defining a line characterizing the change of the refractive index of the fiber with wavelength.

Using Cauchy's equation¹¹

$$n = A + B 1/\lambda^2$$

the same dependance was also plotted. This equation was evaluated by a regression analysis giving

$$\text{For } n_{\perp}: A = 1.520, B = 9.039 \times 10^{-3}$$

with an estimated error⁹ $S_e = 5.9 \times 10^{-8}$

$$\text{For } n_{\parallel}: A = 1.698, B = 2.082 \times 10^{-2}, S_e = 1.5 \times 10^{-6}$$

For the evaluation perpendicular to the fiber axis, the difference between the results obtained by the two methods is zero in the third place; and for the evaluation parallel to the fiber axis, the difference is $1/2$ in the third place.¹²

Similar analyses for the liquids used in this investigation are (at 26°C):
For water:

$$A = 1.3235 \quad B = 3.113 \times 10^{-3} \quad S_e = 5.6 \times 10^{-8}$$

For 63.7% sucrose solution:

$$A = 1.4369 \quad B = 4.17 \times 10^{-3} \quad S_e = 6.6 \times 10^{-8}$$

The differences between measured and calculated values are ± 2 in the fourth place for water and for the sucrose solution.

DISCUSSION OF RESULTS

In the hypothetical case when the dry reflectance is unity and there is some finite scattering efficiency, the wet reflectance is also unity. There is no mechanism for a substrate which does not absorb any light when dry to absorb any light when wet. The incident light will penetrate to a deeper layer in the wet substrate than in the dry one. As long as there is a finite scattering efficiency and no absorption takes place, the scattering mechanism prevails and the light is eventually back-reflected from the substrate.

If one considers another hypothetical limit when the sample is absolutely black, the reflectance from the dry substrate is zero and the reflectance

from the wet substrate must also be zero. If all light incident upon the dry substrate is absorbed, then by the same mechanism all incident light upon the wet fabric must also be absorbed. Under these conditions, when the sample is absolutely black, no reduction in the ratio of the refractive index can cause any further reduction in the reflectance.

Thus a plot of "wet" against "dry" reflectance for all possible values of the refractive index ratio $n_1/n_2 > 1$ gives a monotonic curve between the points $R_w = R_d = 0$ and $R_w = R_d = 1$.

The plots for various values of n_1/n_2 can be expected to differ only in the extent of convexity toward the "dry" axis. Of course, for $n_2 = 1$, the plot is a straight line with a slope 1 and intercept 0 (Figs. 2a and 2b).

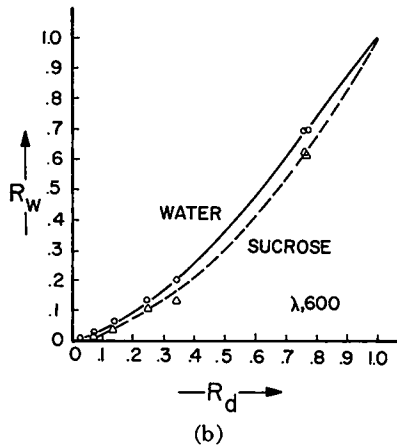
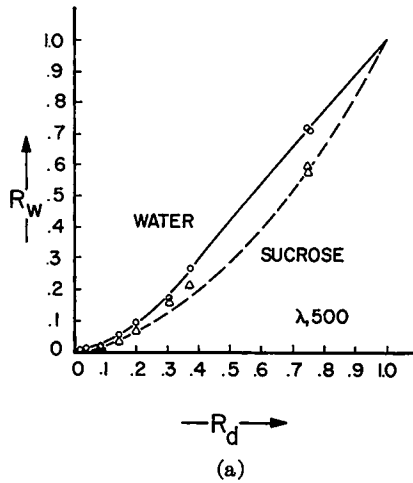


Fig. 2. "Wet" against "dry" reflectance: (a) measured at $\lambda = 0.5$ micron; (b) at $\lambda = 0.6$ micron. It can be observed that, except for the limiting cases ($R_d = R_w = 0$ or $R_d = R_w = 1$), the wet reflectance is smaller when sucrose solution rather than water is the continuous medium. The refractive index ratios are ~ 1.1 and ~ 1.2 , respectively.

Presentation of the Experimental Results

No significant conclusions can be drawn from a simple comparison of the reflectance data obtained on dry and wet samples. A more sensitive presentation of the data is necessary.

Goldfinger et al.⁴ plotted their data in the form R_w/R_d against R_d . One can predict with confidence that for $R_d = 1$, R_w/R_d is also 1, for all values of the refractive index ratio different from 1.

From experience and from consideration of the effect of the average number of scattering steps involved in reflection as a function of the scattering efficiency, one can predict that for a finite scattering efficiency and $R_d < 1$, $R_w/R_d < 1$. In the limiting case of $R_d = 0$, no prediction is possible without a reliable theory since R_w/R_d is of an indeterminate form 0/0. Goldfinger et al.⁷ claimed the value 1 for this ratio, primarily because some experimental points pointed that way.

If one plots the data in the form $(1 - R_d)/(1 - R_w)$ against R_d , then for $R_d = 0$, $(1 - R_d)/(1 - R_w) = 1$, and for all values of $R_d > 0$ it is smaller than 1.

In Figures 3a to 3d, these data are presented. It can be seen that they follow the predicted trend but also that the upswing of the plot R_w/R_d against R_d does not appear for small values of R_d as claimed by Goldfinger et al.⁷

Analysis of the Data

In a previous paper by Allen and Goldfinger,¹³ it was suggested (footnote) that all but the least reliable points used to plot R_w/R_d against R_d could be accounted for from the Kubelka-Munk theory for the reflectance of light scattering-absorbing substrates. The Kubelka-Munk theory was tested here to determine how closely it agreed with the experimental points and whether this treatment predicted a minimum in the plot of R_w/R_d against R_d .

From the Kubelka-Munk relationship for an "infinitely thick" light scattering-absorbing substrate,

$$K/S = (1 - R)^2/2R$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.

Solving for R , one gets

$$R = K/S + 1 - \sqrt{K/S(K/S + 2)} \quad (2)$$

which may be rearranged to

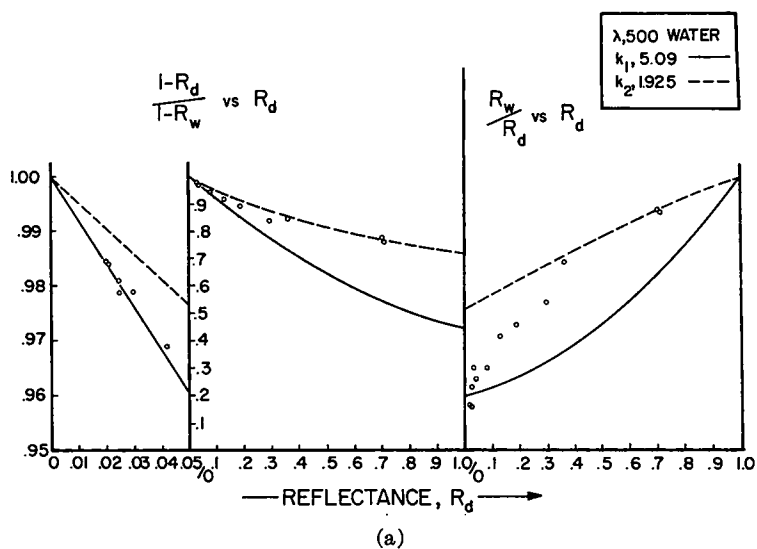
$$1 - R = \sqrt{K/S(K/S + 2)} - K/S. \quad (3)$$

For the condition when $K_d/S_d = 1$, it follows from eqs. (1) and (2) that $R = 2 - \sqrt{3} = 0.268$ and $1 - R = \sqrt{3} - 1 = 0.732$. The subscripts

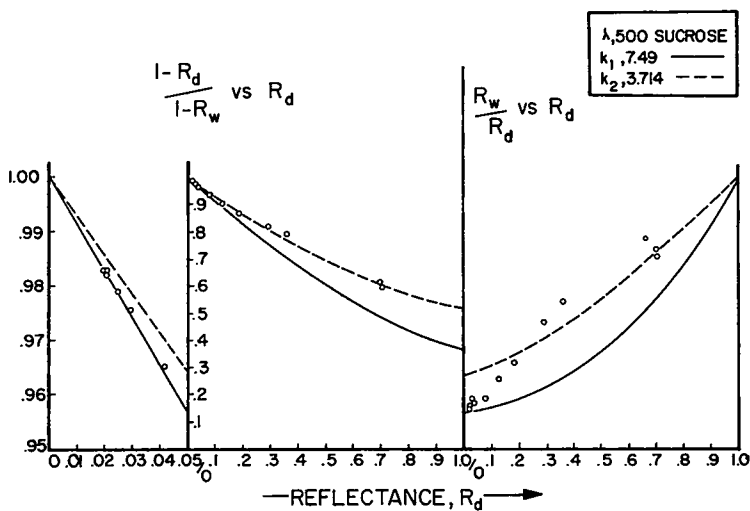
d and w are used to indicate whether the quantity refers to a sample observed in air ("dry") or in another continuous medium ("wet").

The straight-line function of the plot as shown in Figure 3 can be described as $1 - R_d/1 - R_w = 1 + b R_d$, with 1 as the intercept and b the slope. By substituting for $1 - R_d$ and R_d their values when $K/S = 1$, one obtains

$$\begin{aligned} (\sqrt{3} - 1)/(1 - R_w) &= 1 + b(2 - \sqrt{3}) \\ &= 0.732/(1 - R_w) = 1 + b(0.268). \end{aligned} \quad (4)$$



(a)



(b)

Fig. 3 (continued)

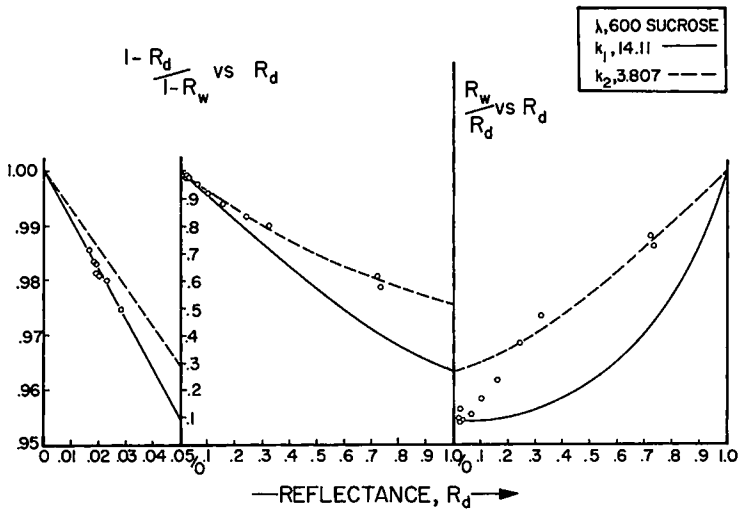
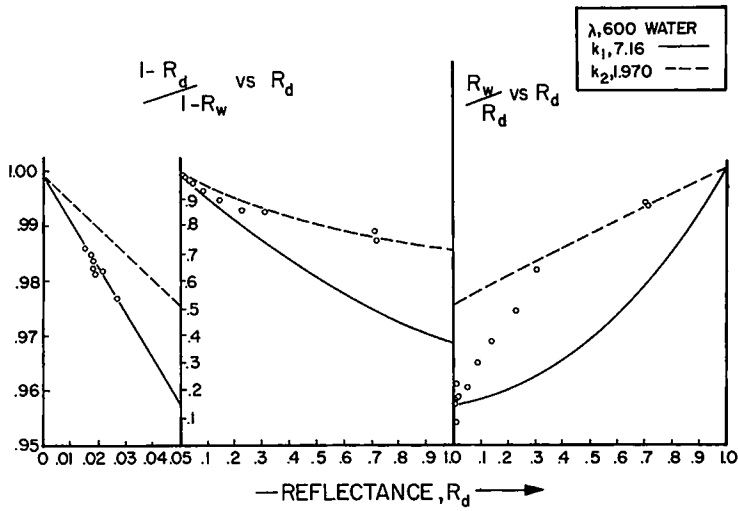


Fig. 3. Plots of $(1 - R_d)/(1 - R_w)$ and R_w/R_d vs. R_d . The lines represent values calculated assuming that the Kubelka and Munk theory holds and that K/S for a wet sample can be represented by $k(K/S)$ for a dry sample. The continuous lines are calculated from the six darkest samples ($R_d < 0.04$) and the dotted lines, from the two lightest samples ($R_d \sim 0.7$). The difference between these two possible representations are outside all possible experimental error: (3a) and (3b) results of measurements with water and sucrose at 0.5 micron; (3c) and (3d) corresponding data at 0.6 micron. It has been suggested by W. B. Prescott that one could narrow the gap between the two Kubelka-Munk predictions by applying corrections for "surface reflectance" of fibers and by ascribing to the very uncertain low-reflectance points other values, still within the range of experimental error. While this is of course so, it in no way alters our conclusions that the evidence presented indicates that the Kubelka-Munk treatment is inadequate to predict the color of textiles over the entire range of reflectance, from zero to 1.

K/S from the Kubelka-Munk relationship is often considered to be directly proportional to the concentration of colorant, C , regardless of the other prevailing conditions.

From this, one can expect $K_w/S_w = k(K_d/S_d)$, and

$$k = (K_w/S_w)(S_d/K_d) \sim S_d/S_w \quad (5)$$

since the refractive index ratio has no effect on K , the absorption coefficient.

For the condition when d , the diameter of the scattering particle, is large in respect to the wavelength of light, a condition which is certainly fulfilled with textile samples and visible light, Mie's relation^{2,3} reduces to¹⁴

$$F \approx (m^2 - 1)/(m^2 + 2) \quad (6)$$

where F is the scattering efficiency and m is the ratio of the refractive index of the scattering particles to that of the continuous medium n_1/n_2 .

Thus, one can write, from eq. (5),

$$S_d/S_w = (m_d^2 - 1)(m_w^2 + 2)/(m_d^2 + 2)(m_w^2 - 1) = k. \quad (7)$$

(By simple algebraic rearrangement the slope b and the constant k can be expressed in terms of each other.)

If the Kubelka-Munk relationship holds, and k and R_w/R_d or $(1 - R_d)/(1 - R_w)$ are calculated from the data obtained for $R < 0.04$ and $R \sim 0.7$, then the experimentally most reliable points should give within the limits of error the same plot against R_d . Figures 3a, b, c, and d and Table I show that this is not the case.

Table II shows that whereas the k_2 values calculated from the highest reflectance values are indeed proportional to S_d/S_w as calculated from the refractive indices with the aid of eq. (7), k_1 values obtained from the low reflectance values are not proportional at all.

CONCLUSIONS

The original goal of this research was to establish a theory to predict the "dry" color of a fabric from its "wet" color as a function of the refractive index of the continuous medium. The goal was not realized primarily because of the inadequacy of the Kubelka-Munk theory at low reflectance

TABLE I
Evaluation of Experimental Results (Fig. 3)^a

Wavelength, microns	n_1/n_2	$-b_1$	$-b_2$	k_1	k_2
0.5	1.110	.830	.557	7.49	3.71
0.5	1.208	.755	.325	5.09	1.92
0.6	1.103	.903	.558	14.11	3.81
0.6	1.199	.821	.333	7.16	1.97

^a n_1 = Average index of refraction of fiber; n_2 = index of refraction of continuous medium; k_1 is calculated from slope b_1 for very low values of R_d (< 0.04); b_2 is calculated from parameter k_2 for the largest values of R_d (~ 0.7).

TABLE II
Comparison of Relative Scattering Efficiencies^a

Wave-length, microns	n_1/n_2	k_1	k_2	k	k/k_1	k/k_2
0.5	1.110	7.49	3.71	4.86	.65	1.31
0.5	1.208	5.09	1.92	2.61	.52	1.36
0.6	1.103	14.11	3.81	5.07	.36	1.33
0.6	1.199	7.16	1.97	2.68	.37	1.35

^a k_1 and k_2 are determined from the low and high reflectance results, respectively; k is calculated from eq. (7). The ratios in the last two columns show that with an arbitrary correction factor (1.3), prediction might be possible for the high reflectance range, but not for the low reflectance range.

values (large colorant concentrations). However, the data at high reflectance do show that within validity of the theory prediction is possible.

One can conclude that with an adequate theory of the color of absorbing-scattering substrates,¹⁵ one will be able to predict the dry color from the wet color on the basis of the scattering efficiency of the substrate in the particular medium.

The authors wish to express their appreciation to Burlington Industries, Inc., Fieldcrest Mills, Inc., and Reeves Brothers, Inc., who supported this work through their generous financial contributions, and to National Spinning Company, who provided the polyester substrates.

This paper contains some of the information from the thesis by one of the authors (D.C.F.) submitted to the graduate school of North Carolina State University at Raleigh in partial fulfillment of the requirements for the degree of Master of Science in Textile Chemistry.

References

1. E. Hope Allen, D. L. Faulkner, G. Goldfinger, and R. McGregor, *J. Polym. Sci., Polym. Lett.*, **10**, 203 (1972).
2. G. Mie, *Ann. Physik*, **25**, 377 (1908).
3. J. R. DeVore and A. H. Pfund, *J. Opt. Soc. Amer.*, **37**, 866 (1947).
4. J. L. Saunderson, *J. Opt. Soc. Amer.*, **32**, 727 (1942).
5. W. B. Prescott and E. I. Stearns, *Text. Chem. Color.*, **1**, 64/25 (1969).
6. H. Iida, *Senryo To Yakuhin*, **15**, 3 (1970).
7. G. Goldfinger, H. S. Goldfinger, S. P. Hersh, and T. M. Leonard, *J. Polym. Sci. C*, **31**, 25 (1970).
8. National Bureau of Standards, Government Printing Office, Washington, D.C., Letter Circular LC-1017, January 1955, p. 18.
9. P. D. Lark, B. R. Craven, and R. C. I. Bosworth, *The Handling of Chemical Data*, Pergamon Press, Oxford, 1968, pp. 136-206.
10. K. Freeman and J. M. Preston, *J. Text. Inst.*, **34**, T19 (1943).
11. D. W. Tenquist, R. M. Whittle, and J. Yarwood, *University Optics*, Vol. 2, Iliffe Books, London, 1970, p. 30.
12. D. L. Faulkner and T. G. Rochow, *Microscope*, **20**, 228 (1972).
13. E. Hope Allen and G. Goldfinger, *Text. Chem. Color.*, **3**, 289/53 (1971).
14. W. W. Wandlandth and H. G. Hecht, *Reflectance Spectroscopy*, Wiley, New York, 1966, pp. 65ff.
15. E. H. Allen and G. Goldfinger, *J. Appl. Polym. Sci.*, **16**, 2973 (1972).

Received August 22, 1972