Color Prediction of Absorbing–Scattering Fibers Dyed with a Colorant Mixture

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ABSTRACT: An extension of the Allen and Goldfinger model of the prediction of the color of absorbing–scattering fibers to the case of a colorant mixture has been proposed. Using this approach, the spectral reflectance of an array of dyed polyester fibers with a colorant mixture are calculated from spectral absorbance measurements of the colorant. The results are compared to those calculated by applying Kubelka–Munk analysis on the predicted reflectances of each of the colorant mixture's components. The predicted spectral reflectances coincide well with those measured experimentally. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1165–1172, 1997

Key words: reflectance; absorbance; color prediction; dyes; fibers

INTRODUCTION

The color of a fabric is the stimulus sensation produced as a result of the composition of a light radiation incident on it, the reflection or transmission components making up the incident light dependent on its wavelength. Color discrimination and recognition problems occur in a wide variety of industries, notably in the dying process of the textile industry. The prediction of the color of textile substrates necessitates information on the optical properties of the system, such as the refractive index of the fiber, coefficient of absorption of the dye, dye concentration and distribution, as well as on its geometry and dimensions.

In 1931, Kubelka and Munk[1] gave a treatment of the color of a system that simultaneously absorbs and scatters light. The Kubelka–Munk theory and the prediction of reflectance were studied in detail by Nobbs.[2] Preston and Tsien[3] proposed a model in which they considered a pile of parallel plates, in which each plate represents a layer of fabric and had the thickness of one fiber diameter. Neglecting all multiple reflections within the pile, they obtained their relation for the ratio of the light reflected by the dyed fiber to that by the undyed fiber. Satisfactory prediction based on this treatment could not be obtained.

In 1972, Allen and Goldfinger[4] proposed a model by which the color of dyed fabrics can be predicted using the properties of the geometry of the fabric, the distribution of the dye in the fiber, and the refractive indices of the continuous medium and the fibers. They expanded later[5] with their treatment, taking into account the effect of an inhomogenety of dye distribution. Sokkar et al.[6] expanded this model further, taking into account the effect of optical anisotropy of fibers and dispersion. Using this approach, the scattered reflectance based on the shape of the spectral transmission curve of the dyed fiber polymer and its refractive index can be calculated. Sokkar et al.[7] assumed a model of isotropic cylindrical fibers of skin-core structure in a parallel array to calculate the spectral reflectance of samples dyed with ring dye and with uniform dye.

In this work, we propose a model based on the model of Allen and Goldfinger,[4] and its extension proposed by Sokkar et al.,[6] to treat a polymer fiber dyed with a mixture of colorants.

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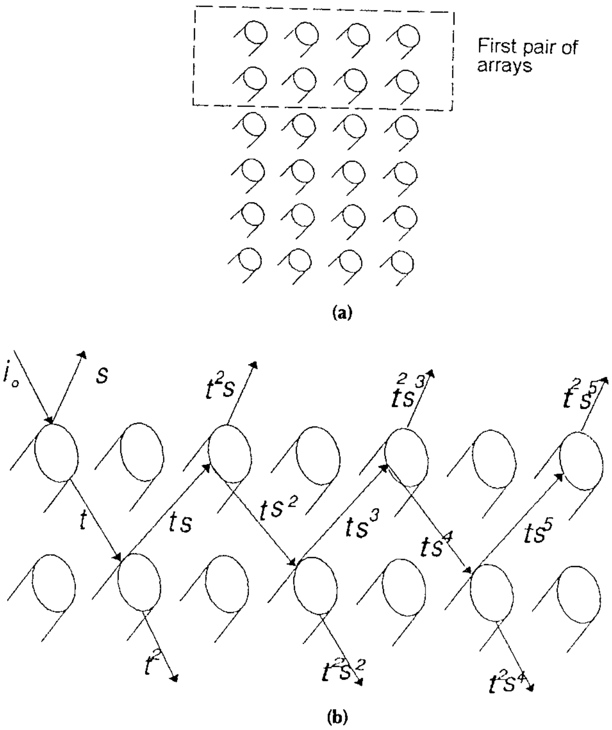


Figure 1 (a) Cross section through a model of dyed cylindrical fiber. (b) Representation of grouping of the first pair of absorbing–scattering arrays.

MATHEMATICAL TREATMENT

The effect of mixture colorant on the color of absorbing–scattering fibers can be calculated by extending the model of prediction of the color of absorbing–scattering substrates[4] to the case of a colorant mixture.

The fabric is represented by a parallel bundle of cylindrical fibers that are optically homogeneous and large in diameter compared to the wavelength of light. The fibers are dyed in this case with a mixture of colorants. These dyed fibers are considered widely separated so that the light incident on a fiber is not influenced by its neighbors.

Figure 1(a) shows the cross section through a model of dyed fabric consisting of a number of distinct layers of infinitely wide arrays of anisotropic cylindrical fibers. We consider the events taking place on the first pair of absorbing–scattering arrays [Fig. 1(b)]. Supposing a light of intensity i_o incident on the first array, a scattered fraction s has its direction reversed, and a fraction t is refracted in the general direction of incidence and will be permitted to continue through the layer. On encountering the second array, a fraction t is again refracted in the general direction of incidence, a fraction s has its direction reversed, and a fraction a will be absorbed so that

$$t + s + a = 1$$

The total light intensity transmitted through the first pair of arrays is given by

$$T_1 = t^2 + t^2s^2 + t^2s^4 + \cdots .$$

Setting $M = t/s$, then

$$T_1 = t^2/(1 - s^2)$$
$$= M^2(1 - a)^2/[(1 + M)^2 - (1 - a)^2] \quad (1)$$

That reflected by the same pair of arrays is

$$R_1 = s + t^2s + t^2s^3 + t^2s^5 + \cdots$$
$$= (1 - a)(1 + T_1)/(1 + M) \quad (2)$$

Following the detailed calculations given by Sokkar et al.,[6] the intensities transmitted and reflected by a pile of cylindrical arrays can be defined in general, as follows:

$$T_N = T_{N-1}^2/(1 - R_{N-1}^2) \quad (3)$$

and

$$R_N = R_{N-1}(1 + T_N) \quad (4)$$

where the subscript N refers to the $2n^{\text{th}}$ layer of dyed fabric. In order to determine R_N in eq. (4), the quantities a and M must be calculated.

DETERMINATION OF THE QUANTITIES *a* AND *M*

Figure 2 shows a cross section through a dyed fiber and the path of reflected and refracted light. The length of the path traveled by reflected light l_p is given by

$$l_p = 2\sqrt{1 - (d^2/n^2)}$$

where the radius of the circle representing a cross section is taken equal to one, n is the refractive index of the fiber, and d is the distance from the y-axis (see Fig. 2). The fraction of light transmitted through the dyed fiber between the point of internal refraction and first internal reflection is

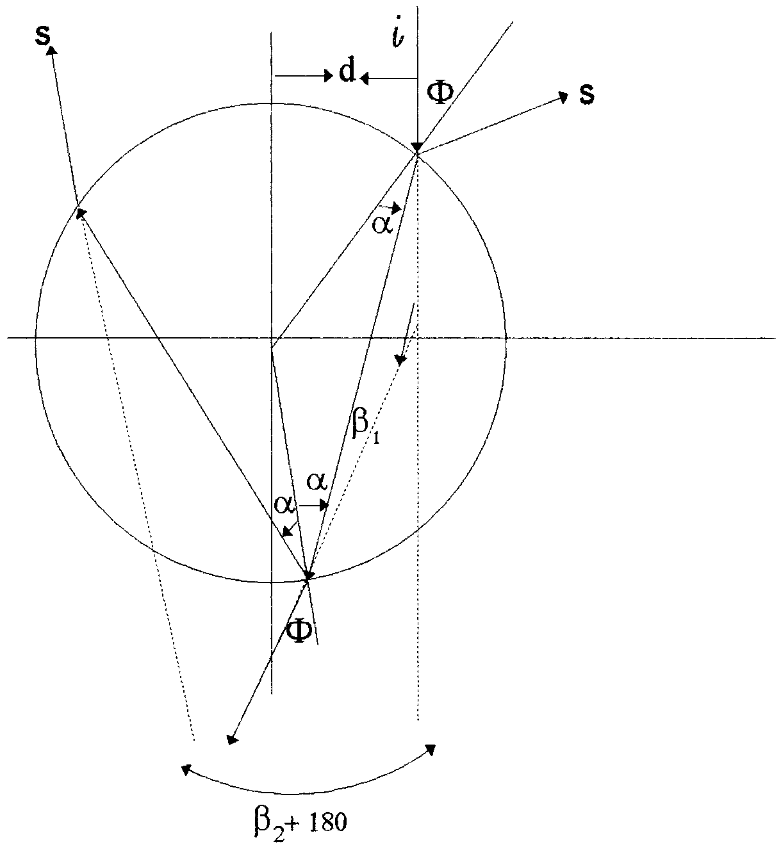


Figure 2 Cross section through a fiber showing the different light reflections and refractions.

$$\alpha = 10^{-2c\varepsilon\sqrt{1-(d^2/n^2)}} \tag{5}$$

where $c\varepsilon$ is the product of the concentration of the colorant and its coefficient of absorption per unit length.

In case of mixture colorant, if the concentration of the m^{th} constituent colorant in the mixture is c_m, then the fraction α for the resultant mixture is given as

$$\alpha = 10^{-\Sigma 2c_m\varepsilon_m\sqrt{1-(d^2/n^2)}}$$

For three colorants mixture, the value of α is

$$\alpha = 10^{-2(c_1\varepsilon_1+c_2\varepsilon_2+c_3\varepsilon_3)\sqrt{1-(d^2/n^2)}} \tag{6}$$

When the light first fell on the fabric, $(1-\rho)\alpha$ of the light is transmitted, where ρ is the Fresnel reflection factor, and $(1-\rho)-(1-\rho)\alpha = (1-\rho)(1-\alpha)$ is absorbed. Through the second path, the transmitted fraction is $(1-\rho)\alpha\rho$, and, of course, $(1-\rho)\alpha\rho(1-\alpha)$ is absorbed. In a third step, $(1-\rho)\alpha^2\rho^2(1-\alpha)$ is absorbed, and so on, over an infinite number of steps. The value of a can be calculated from

$$\begin{aligned} a &= (1-\rho)(1-\alpha) + (1-\rho)(1-\alpha)\alpha\rho \\ &\quad + (1-\rho)(1-\alpha)\alpha^2\rho^2 + \cdots \\ &= (1-\rho)(1-\alpha)/(1-\alpha\rho) \end{aligned} \tag{7}$$

where the Fresnel reflection ρ has two different values, for parallel $(\rho^{\parallel})$ and for perpendicular $(\rho^{\perp})$ polarization components of radiation on anisotropic dyed fiber, given by[6]

$$\rho^{\parallel} = \frac{(1-d^2)^{1/2} - (n^{\parallel 2} - \mathrm{d}^2)^{1/2}}{(1-d^2)^{1/2} + (n^{\parallel 2} - d^2)^{1/2}}$$

$$\rho^{\perp} = \frac{n^{\perp 2}(1-d^2)^{1/2} - (n^{\perp 2} - d^2)^{1/2}}{n^{\perp 2}(1-d^2)^{1/2} + (n^{\perp 2} - d^2)^{1/2}}$$

where $n^{\parallel}$ and $n^{\perp}$ are the refractive indices of the dyed fiber for light vibrating parallel and perpendicular to the fiber axis, respectively.

The quantity M in eq. (1) is obtained by determining for each angle of incidence and for each step of refraction whether the general direction of the flux is downward or upward.[4]

$$M = t/s = \frac{\rho_{0.707 \le d \le 1} + (1-\rho)^2 \Sigma \alpha^m \rho^{m-1}_{\cos \beta_m(-)}}{\rho_{0 \le d \le 0.707} + (1-\rho)^2 \Sigma \alpha^m \rho^{m-1}_{\cos \beta_m(+)}} \quad (8)$$

where β is an auxiliary quantity used to determine the direction of the refracted radiation in the fiber (see Fig. 2). The quantities β_1 and β_N are given by

$$\cos \beta_1 = -(1 - 2d^2)(1 - 2d^2/n^2) - 4d^2/n[(1 - d^2)(1 - d^2/n^2)]^{1/2}$$

$$\cos \beta_N = \cos \beta_{N-1}(2d^2/n^2 - 1) - \sin \beta_{N-1}(2d/n)(1 - d^2/n^2)^{1/2}$$

Throughout the calculations, a numerical integration is carried out for the values of a, calculated from $d = 0$ to 1 [eq. (7)]. Substituting for a and M back into eqs. (1) and (2), the reflectance R of anisotropic substrate can be calculated[6] as follows:

$$R = (R_N^{\parallel} + R_N^{\perp})/2 \quad (9)$$

where the numerical summation of $R_N^{\parallel}$ and $R_N^{\perp}$ values are extended to

$$T_N^{\parallel} < 10^{-6} R_N^{\parallel} \text{ and } T_N^{\perp} < 10^{-6} R_N^{\perp}$$

As the refractive index is wavelength-dependent, the spectral reflectance could be calculated using the Cauchy's dispersion formula, as follows:

$$n = \mathrm{A} + \mathrm{B}/\lambda^2 \quad (10)$$

where A and B are constants to be determined.

The reflectance of fibers dyed with a colorant mixture may generally be calculated using eq. (9), which includes the value of α from eq. (5). This calculation may, moreover, be deduced from eqs. (9) and (5) for each colorant[6] and for their mixture (by addition) using Kubelka–Munk function.[1]

EXPERIMENTAL WORK

Samples Preparation

Three samples of dyestuffs (Terasil red R, Disperse yellow C-3G, and Novester blue CB2) were prepared at definite concentrations. The dye powder was completely dissolved in a solution of 95 : 5% of acetone and glashian acetic acid. Colorant mixtures of two and three of these dyestuffs with different concentrations are also prepared (see Table I). Polyester fibers of the same diameter were then dyed with each of these dyestuffs, as well as with their mixtures, using the standard dyeing procedure applied in the dyeing industry.

Spectrophotometric Measurements

The spectral absorption of each of these basic dyestuffs and their mixtures were measured using UV-3101PC double beam spectrophotometer from Schimadzu, Japan. The spectral reflectance of the mixture dyed fibers were also measured. Diffuse reflection measurements were carried out using the 60 mm diameter integrating sphere attachment.

The spectrophotometer is linked to a personal computer to command the switching and rotation of the gratings, the radiation sources and detectors, as well as the acquisition of data. Slit widths or signal amplification gain is also controlled automatically to adjust the base and the 100% levels before any series of measurements.

Initial tests were carried out to determine the best position of the bundle of fibers and its thickness. The fibers were thread over a special support without introducing any tensile strength on the fibers in a plane perpendicular to the light beam with the fiber axis oriented in the plane of incidence of the instrument beam. The optimum thickness of the bundle is searched by increasing gradually the thickness of a layer while measuring its reflectivity each time until no more increase in the overall reflectivity of the fibers is noticed. The thickness is then just sufficient to hide the fiber's support, and this does not contribute to the reflectivity value.

Interferometric Measurements

The diameter and the refractive index of the substrate and dyed fibers were determined using the Pluta double beam interfering microscope.[8,9] Figure 3(a,b) shows microinterferograms of totally

Table I Colorants Used and Their Concentrations

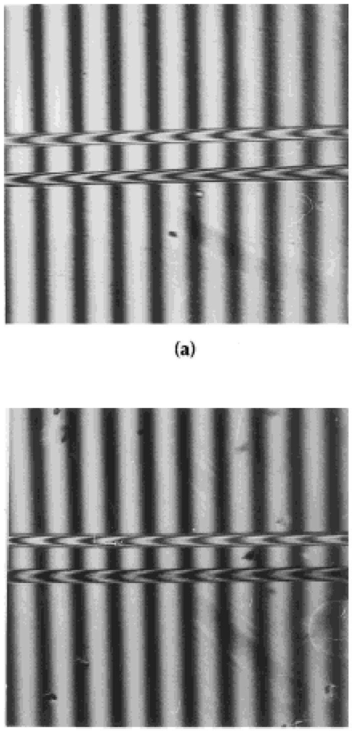
Sample No.	Dyestuff	Concentration (%)
1	Terasil red R	.010
	+ Disperse yellow C-3G	.020
2	Novester blue CB2	.013
	+ Terasil red R	.015
3	Terasil red R	.016
	+ Disperse yellow C-3G	.014
	+ Novester blue CB2	.011
4	Disperse yellow C-3G	1.15
	+ Terasil red R	.46
5	Terasil red R	1.5
	+ Novester blue CB2	1.35
6	Disperse yellow C-3G	.84
	+ Novester blue CB2	1.35

duplicated images of a polyester fiber dyed with a colorant mixture of Terasil red and Disperse yellow [Fig. 3(a)] and of Novester blue and Terasil red [Fig. 3(b)]. The wavelength of the monochromatic light used is $\lambda = 546$ nm, and the refractive index of the immersion liquid is $n_L = 1.656$ at 26°C.

The refractive indices n'' and $n^{\perp}$ of each fiber were determined at two wavelengths (546 and 591 nm) with the electric vector of the incident light parallel and perpendicular to the fiber axis, respectively, using the following formula[10]:

$$n_a = n_L + \frac{\lambda z_a}{Mht_a}$$

where n_L is the refractive index of the immersion liquid, λ is the wavelength of the light used, z_a is the interference fringe shift inside the dyed fiber, M is the magnification, h is the interfering spacing, and t_a is the thickness of the fiber. The refractive index at any wavelength in the measured range was then determined using Cauchy's equation [eq. (10)]. The Cauchy's constants are given in Table II.



(a)

(b)

Figure 3 Totally duplicated images using the Pluta interference microscope with monochromatic light of wavelength 546 nm, of fibers dyed with (a) Terasil red and Disperse yellow and (b) Novester blue and Terasil red.

RESULTS AND DISCUSSION

Figure 4(a) shows the spectral absorbance of the Terasil red R dye (dotted curve) and the Disperse yellow C-3G dye (dashed curve). The spectral absorbance of their mixture is also shown (solid curve). Figure 4(b) shows the same for another recipe of a mixture of Terasil red R and Novester

Table II Cauchy's Constants of the Dyed Fibers

Sample No.	Dyeing Material	A''	$A^{\perp}$	$B^{\parallel}$ (nm)^2	$B^{\perp}$ (nm)^2
1	Terasil red R	1.704	1.446	23796	18823
2	Novester blue CB2	1.727	1.452	8350	20556
3	Disperse yellow C-3G	1.716	1.465	9023	15712
4	Terasil red R + Novester blue CB2	1.715	1.449	16073	19690
5	Disperse yellow C-3G + Terasil red R	1.710	1.456	16410	17268
6	Terasil red R + Disperse yellow C-3G + Novester blue CB2	1.716	01.44	13723	18364

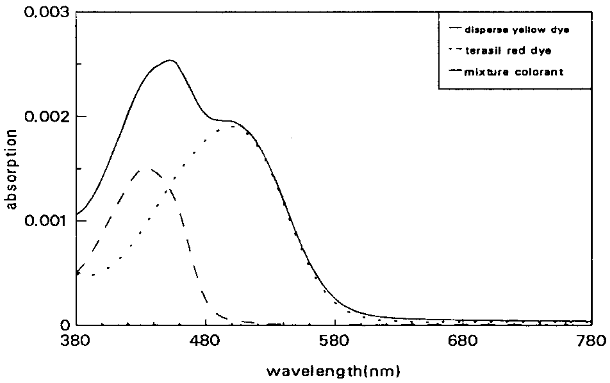


Fig.(4-a)

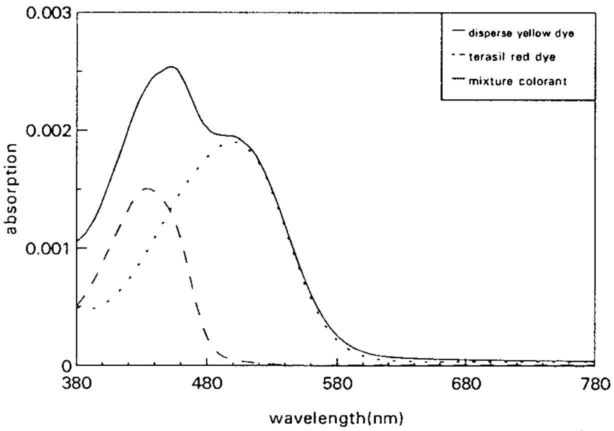


Fig.(4-a)

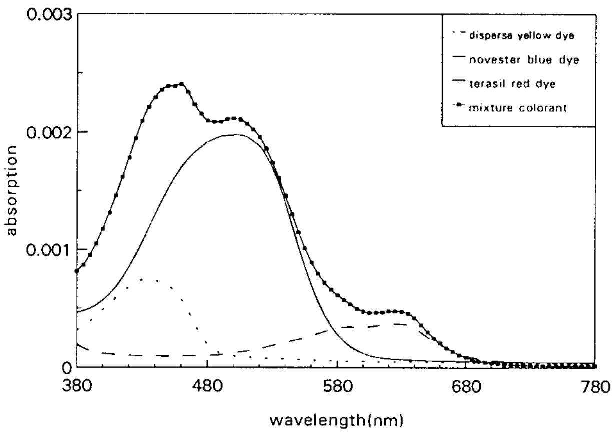


Fig.(4-c)

Figure 4 (a) Absorbance of the Terasil red and Disperse yellow dyes and of their mixture. (b) Absorbance of the Terasil red and Novester blue dyes and of their mixture. (c) Absorbance of the Terasil red and Disperse yellow and Novester blue and of their mixture.

blue CB2. Figure 4(c) shows the spectral absorbance of a recipe of a mixture of three colorants (Terasil red R, Disperse yellow C-3G, and Novester blue CB2) and of their individual absorbances.

To verify the validity of the model, the spectral reflectances of three logical fiber samples dyed with the three mixture colorants stated (mixtures 1, 2, and 3 in Table I) are predicted using two different treatments.

Firstly, using the measured spectral absorbances of the individual dyestuffs, the spectral reflectance of each of these logical dyed samples of polyester fibers is calculated from the treatment suggested by Sokkar et al.[6] (Fig. 5). The Cauchy's constants used in the model for these dyed fibers are given in Table II. The Kubelka–Munk functions $F(R)$, for each of these individual dyed fibers is calculated using the following relation:

$$F(R) = K/S = (1 - R_\lambda)^2/2R_\lambda$$

Assuming the additivity of this function, the function $F(R)$ of the samples dyed with mixtures of these dyes can be determined from the sum of the functions of their mixture components

$$F_m(R_\lambda) = \sum_i F_i(R_\lambda) \quad i = 1, 2, 3$$

The reflectance of these logical samples dyed with these mixtures are then deduced using the inverted form of Kubelka–Munk function, as follows:

$$R_m = F(R_\lambda) + 1 - [F(R_\lambda)^2 + 2F(R_\lambda)]^{1/2}$$

They are represented in Figure 6 by the dashed curves.

Secondly, we applied the model directly on the mixture colorants. The spectral reflectances of the logical dyed samples were predicted from the ab-

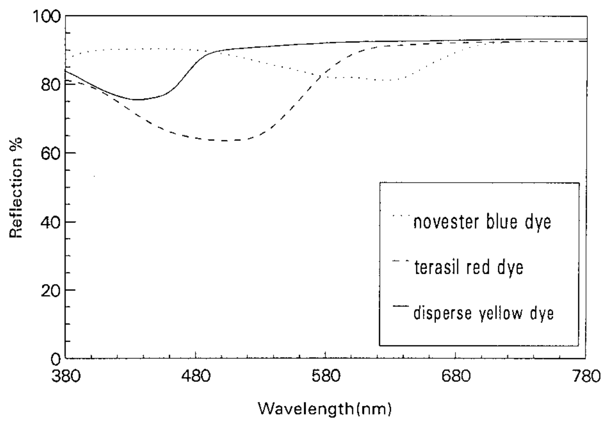


Figure 5 Reflectance of polyester fibers dyed with Terasil red, Disperse yellow, and Novester blue dyes.

sorbances of the mixture colorants and are represented in Figure 6 by the solid curves.

In order to assess the model, the color differences ΔE between the calculated reflectances with the help of Kubelka–Munk analysis and those predicted by the model were calculated using the CIE 1976 ($L^*a^*b^*$) formula,[11] as follows:

$$\Delta E(L^*, a^*, b^*) = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2}$$

where

$$L^* = 116[Y/Y_o]^{1/3} - 16$$
$$a^* = 500[(X/X_o)^{1/3} - (Y/Y_o)^{1/3}]$$
$$b^* = 200[(Y/Y_o)^{1/3} - (Z/Z_o)^{1/3}]$$

with $Y/Y_o \leq 0.008856$ and similar conditions for X/X_o and Z/Z_o. The tristimulus values X_o, Y_o, Z_o define the tristimulus values of the reference white object in the C. I. E. (Commission Internationale de l'Eclairage) system. The color difference ΔE between each of the couples of the reflectances curves is indicated in the figures. As can be shown in these figures, the calculated spectral reflectances using the model fit well those calculated through the Kubelka–Munk function. The differences between the two reflectances is evaluated in units of color difference of the C.I.E. The value of ΔE does not exceed 1.3 units in most cases.

The model is also applied to physical samples of fibers (in which, for the purpose of comparison, reflectances could be measured experimentally) dyed with colorant mixtures predescribed in Table I (mixtures 4, 5, and 6). The predicted spectral reflectances of these samples (dashed curves in Fig. 7) were compared to those measured experimentally (solid curves). The spectral absorbance of each of these colorant mixtures on which the prediction is based is also given in the figure. The color difference between each of the two reflectances are also calculated and are noted on the figure. It can be shown that the experimental reflectance curves and the corresponding calculated ones using the model are nearly coincident.

CONCLUSION

The Allen and Goldfinger model for the prediction of reflectance of dyed fabrics is extended success-

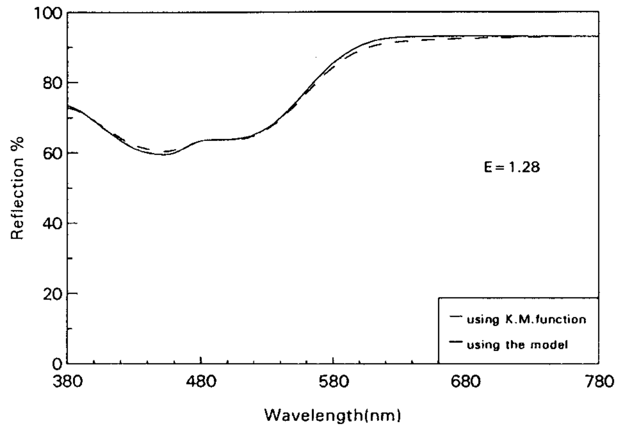
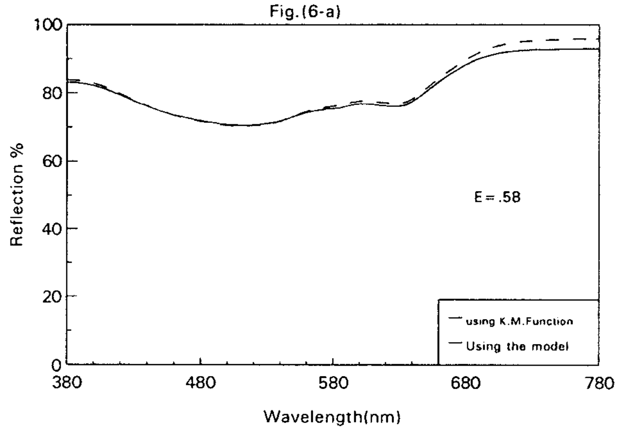


Fig.(6-a)



Fig(6-b)

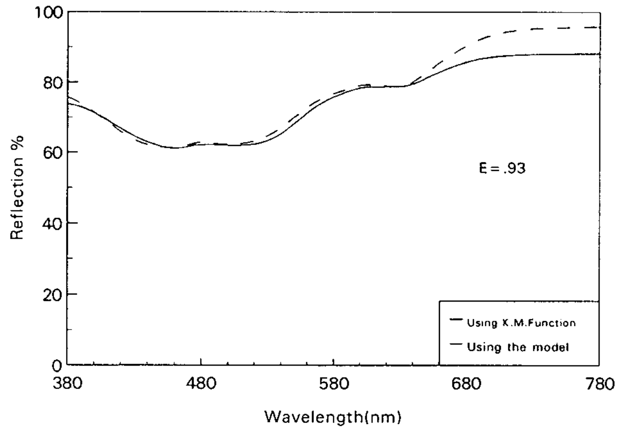


Fig.(6-c)

Figure 6 (a) Calculated reflectance of dyed fibers with a mixture of Terasil red and Disperse yellow using the model (solid curve) and using Kubelka–Munk analysis (dashed curve). (b) Calculated reflectance of dyed fibers with a mixture of Terasil red and Novester Blue using the model (solid curve) and using Kubelka–Munk analysis (dashed curve). (c) Calculated reflectance of dyed fibers with a mixture of Terasil red, Disperse yellow, and Novester Blue using the model (solid curve) and using Kubelka–Munk analysis (dashed curve).

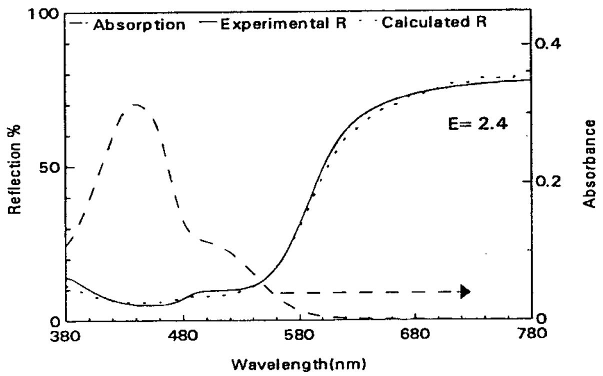


Fig. (7-a)

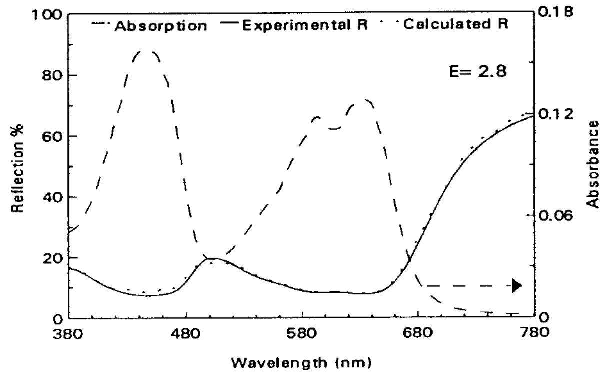


Fig. (7-b)

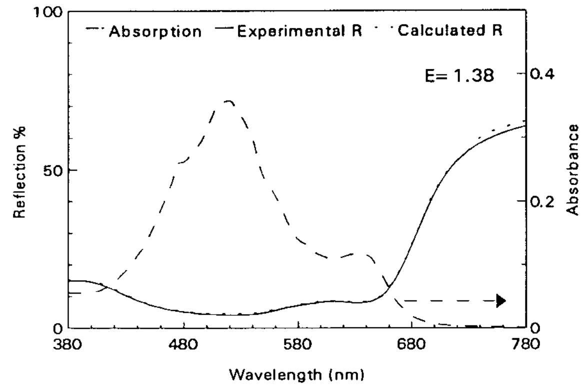


Fig. (7-c)

Figure 7 Measured and calculated reflectance of fibers dyed with a mixture of colorants of (a) Terasil red and Disperse yellow, (b) Novester blue and Terasil red, and (c) Novester blue and Disperse yellow. Their absorbance is represented on the right y-axis.

fully to colorant–mixture-dyed fibers. In this extension, the effect of optical anisotropy of the dyed fibers and the dispersion in the visible range are taken into consideration. The model is verified on a number of colorant mixtures and showed good accordance with the treatment based on the Kubelka–Munk analysis.

The model is applied on fibers dyed with a colorant mixtures of two and three dyes. The results are quite satisfactorily. The difference between the calculated reflectances by the model and those measured experimentally is a few units of the C. I. E. color difference.

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