

Instrumental colourant formulation

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Abstract: The most successful commercial application of colour science in colour reproduction industries is colour matching or, more accurately, colourant formulation. This means prediction of colourant formulation recipes, which were previously obtained manually by trial and error. A manual, time-consuming, tedious, skilful job is now almost completely replaced by instrumental methods. The absorption and scattering of light by a semi-opaque or translucent object is predicted by the Kubelka-Munk equation, which forms the basis of this technique. Various techniques of instrumental colourant formulation are discussed in detail.

Key words: colour matching, colourant formulation, colour mixing, Kubelka-Munk, principal component analysis (PCA), light absorbance, light scattering, artificial neural networks (ANNs).

4.1 Introduction

Matching of shades, that is, the determination of concentrations of dyes to achieve a certain shade, was an art until the middle of the last century. The secrets of how to apply a particular dye were held closely, and were subject to industrial espionage. They were often controlled by local government. There are few written guides on how to apply dyes until the nineteenth century. Among these are Egyptian papyri and the *Plichto de larte de tentori*, the 1540 Venetian guide to dyeing. Both of these only give formulations on how to dye certain colourants, and do not offer advice on how to match shades. Sample or test dyeing is an old method to match shades, as well as to assess the quality of dyes and chemicals to be used in dyeing. Once sufficient agreement had been reached between the standard and the test dyeing, the dyer proceeded to production dyeing.

The first recording spectrophotometer and the first tristimulus colorimeter were developed by Hardy and Hunter, in 1935 and 1948, respectively. The prediction of recipes was tried in the 1950s by reflectance curve fitting. An analogue computer colour-matching system, Colourant mixture computer (COMIC), was developed in 1958. In 1961 the first recipe prediction

was done on digital computer. The spectrophotometer and digital computer were first interfaced in 1967–68 (Park, 1993). Since then tremendous developments have been done in this field, and now instrumental colour matching is well established commercially.

A long-standing problem for the colour reproduction industries dealing with colourants has been to find the proportions of the colourants required to produce a colour that matches with the colour of the customer's choice. A colour symposium held in the USA in the 1940s was attended by experts and technicians of various fields. After two hours of discussion on various complicated aspects of colour, when the audience was asked to interact, a paint man got to his feet and said, 'What I want is a photoelectric colorimeter that will read the proportions of the pigments required to produce a colour match for a specimen' (Judd and Wyszecki, 1963). The attention of audience focused to this important aspect of colour science and further discussion followed eagerly and intelligently on it. This single incident shows the importance of colour matching to a man engaged in colour reproduction work.

4.2 Defining colour matching

Colour matching is defined (Hunter, 1975) as a procedure for adjusting a colour mixture until all visually apparent differences from a target colour are eliminated.

Colourant mixture formulations are methods for calculating the approximate colourant proportions required to produce or match a given object colour.

The most commonly used method for colour matching in industry is a purely empirical trial and error method, which produces a more or less metameric match, i.e. a match valid for a specific illuminant only.

4.2.1 Obstacles to visual colour matching

Some of the obstacles of visual matching, especially in the case of textile materials, are described below (Thiry, 2004).

Fibre type

The type of fibre can play a large role in the matching process. Natural fibres react very differently from synthetic fibres to dyes, and the process is much harder to control. Each fibre type has a corresponding dye class, and these classes provide different colour gamuts.

Fabric construction

Fabric construction (knit or woven) and surface characteristics (pile or satin) also influence the ability to accurately match colour. Generally, woven

fabrics provide more of a flat colour appearance, while knits and jacquard fabrics add a shadowed, two-tone effect to the colour. Also, higher thread count twill fabrics allow for deeper shades than low weight poplins. The influences of construction and surface characteristics highlight the difference between instrumental and visual colour assessment.

Colour of substrate

Colour and brightness of the substrate itself will often affect the final colour on that substrate. Colours dyed on natural fibres, such as cotton, will always appear flatter than colours on dyed synthetics. This may not be a problem, unless one needs to match colours on both natural and synthetic fabrics.

Inconstancy

Colour inconstancy, or ‘flare’, (the change in colour of a single piece of fabric under different light sources) can be more difficult to control than metamerism.

4.3 Laws of mixing

Laws of mixing vary with the physical properties of the colourants and the medium carrying the colourants.

1. For mixtures of absorbing colourants in transparent materials, the Beer-Lambert relationship accurately predicts the system's transmittance and colour (see Roy Choudhury, 2014, chapter 2, section 2.6.1).
2. For scattering and absorbing colourants in turbid materials, the Kubelka-Munk theory predicts the reflectance or transmittance of a mixture.
3. There are unconventional colourant mixture systems for which no satisfactory theoretical models have been developed. These include systems exhibiting luminescence, metallic reflection, interference and directional scattering. For such systems too, an empirical colourant mixture model relating mixture composition directly to a tristimulus colour response can be developed (Alman and Pfeifer, 1987).

4.4 Kubelka and Munk (K-M) theory

When a light beam is incident on a dyed or pigmented specimen, the radiant energy interacts with colourant particles as well as molecules of the medium carrying those particles, resulting in absorption and scattering of light. In the absorption process, the light energy is absorbed by the colourant, and converted to heat and other forms of energy. In the scattering process, the direction of the light beam is altered. If the light once scattered by the colourant

comes out of the medium, it is said to be single or independent scattering. The mathematical modelling of the single scattering phenomenon is comparatively easy. Raleigh and Mie theory completely accounts for the single scattering phenomenon.

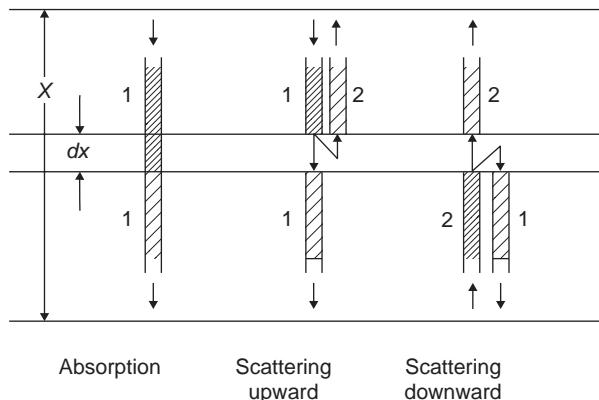
In paint film or dyed textiles, the colourants are closely packed. Therefore, the light scattered by a single particle is re-scattered by many other particles before the light emerges from the turbid media. Such phenomena, called multiple or dependent scattering, are very complex to express mathematically. Multiple scattering refers to scattered light from one particle re-scattered by another particle. But the dependent scattering refers to the perturbation and twisting of the very scattering pattern itself because of the presence of neighbouring particles. This is a more difficult problem, and cannot be solved very satisfactorily. Dependent scattering almost always lowers the scattering efficiency of a pigment. It is seldom observed at the relatively low concentrations utilized in pigmented plastics. In paint films, independent scattering can be observed at pigment volume concentration (PVC) of less than 10% for titanium systems, whereas in dispersions of polystyrene, independent scattering is maintained up to 20% PVC in some cases. This is because the scattering cross-section of titanium particles is several times higher than their geometric cross-section, while in the latter case it is smaller.

Though optical theories for densely packed particulate systems have been developed, they are too complex to be suitable for application to industrial problems. Hence, alternative simpler models are necessary for the purpose. One such simplified approach was employed by Schuster (1905) to explain the propagation of light through stellar atmosphere. Kubelka and Munk (1931) dropped the fluorescence phenomenon to reduce the complexity, and proposed a *two-flux theory*. Considering only absorption and scattering of light inside the media, they assumed that the radiant flux inside the media can be resolved into two fluxes, one going downward and other in the upward direction.

The Kubelka-Munk theory assumes:

1. Diffuse illumination and diffuse viewing without polarization of light.
2. Plane, parallel surface of the object without light losses at the edges.
3. The unit layer is homogeneous and isotropic.
4. Absence of large particles or agglomeration or orientation of the particles.
5. Optical contact between the layers.
6. Scattering particles to be large as compared to the wavelength of light.

Figure 4.1 shows absorption and scattering phenomena that occur in an elementary layer of thickness dx in three stages – absorption of downward flux, upward scattering of downward flux and downward scattering of upward



4.1 Absorption and scattering of two light fluxes as proposed by Kubelka and Munk.

flux. The numbers 1 and 2 represent downward and upward flux of light, respectively.

The thickness dx is small compared to the whole thickness X of the colourant layer, but is large compared to the diameter of the pigment particles, so that the average effect of the particles and not of individual particles is to be taken into account. A layer is assumed to be a solid so extended in two (horizontal) dimensions of space that any light flux lost horizontally through the edges formed in the vertical dimension is too small to worry about, compared to what goes up and down (Kubelka and Munk, 1931). The downward and upward fluxes are designated as i and j , respectively. As the light beam propagates through the media, the light energy of each flux decreases due to absorption and scattering in the opposite direction. The energy scattered from one flux is added to the other flux as the two fluxes are moving in opposite directions. The medium is characterized by empirically introduced optical parameters K and S , commonly known as K-M absorption and scattering coefficients, respectively. The downward flux di is reduced by the amounts $ki \, dx$ due to absorption and $Si \, dx$ due to scattering while passing through the elementary layer dx , but the part $dj \, dx$ reversed in direction by scattering from the upward flux j is added into it. The total change of the downward flux is, thus, as follows (Equation [4.1]):

$$-di = -(S + K)i \, dx + Sj \, dx \quad [4.1]$$

Similarly the total change, dj , of the upward flux is as follows (Equation [4.2]):

$$dj = -(S + K)j \, dx + Si \, dx \quad [4.2]$$

where di and dj have negative and positive signs, respectively, because of the different directions of the two fluxes, and thickness is considered from the unilluminated side of the colourant layer, and hence downward direction means lowering of x and consequently the sign is negative.

Kubelka (1948) further obtained a hyperbolic solution to the above two equations in the following form (Equation [4.3]):

$$R = \frac{1 - R_g (a - b \operatorname{Coth} bSx)}{a - R_g + b \operatorname{Coth} bSx} \quad \text{where } a = 1 + K/S \quad \text{and } b = (a^2 - 1)^{1/2} \quad [4.3]$$

R_g is the reflectance of the background on which a colourant layer is applied or placed. For infinite thickness or in complete hiding, the background reflectance is zero and the above equation reduces to the following form (Equation [4.4]):

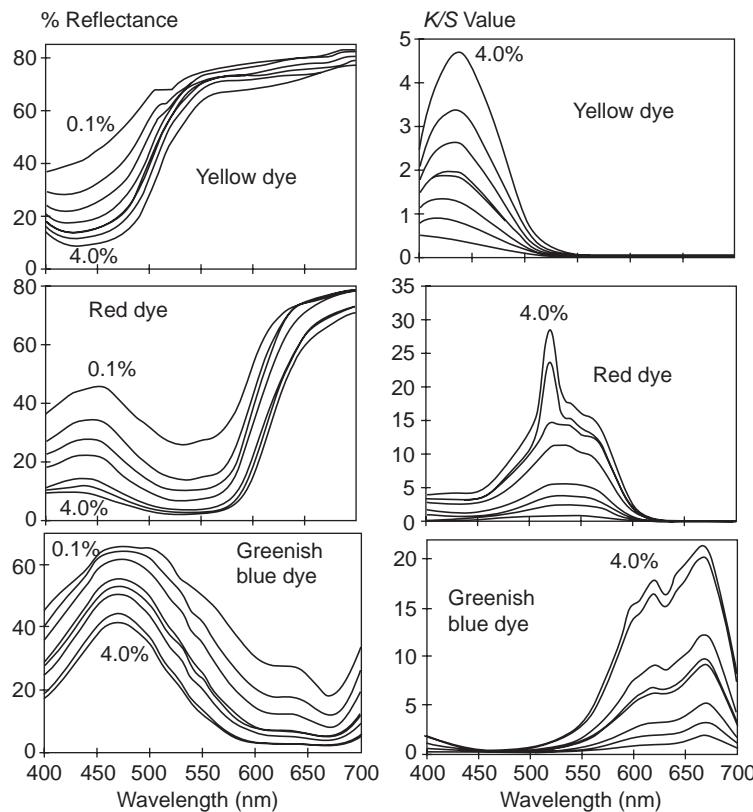
$$R_\infty = 1 + \frac{K}{S} - \left[\left(\frac{K}{S} \right)^2 + 2 \left(\frac{K}{S} \right) \right]^{1/2} \quad [4.4]$$

The inverse of the equation is (Equation [4.5]):

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad [4.5]$$

The function $F(R_\infty)$ is known as Kubelka-Munk function. These equations are valid for a single wavelength or monochromatic light, and calculations are to be made for the whole of visible range. The reflectance, R_∞ , is obtained when the measurement is made at complete opacity. In textiles, the same condition is obtained by repeated folding of the fabric till the reflectance becomes independent of the number of folds. In paints, the same condition may be obtained by thick draw-down on a substrate. For simplicity, R_∞ will be henceforth written as R , but it carries the same meaning.

Figure 4.2 shows %reflectance and K/S values of cotton textile materials dyed with a yellow dye, a red dye and a bright greenish blue (more specifically, turquoise blue) at concentrations 0.1%, 0.25%, 0.5%, 1.0%, 2%, 2.5%, 3.0% and 4.0% of the weight of material. The wavelengths of maximum absorption, λ_{\max} are 430, 540 and 670 nm for the three dyes, respectively. Dyeing in higher depth, i.e. in the presence of higher quantity of the dye, results in lower reflectance and higher K/S values. At the wavelength of



4.2 Reflectance (%) and K/S values cotton textile materials dyed with three dyes at different concentrations.

maximum absorption, maximum changes in reflectance and K/S value occur with change in colourant concentration.

4.5 Limitations of K-M theory

Kubelka-Munk theory has several limitations (Judd and Wyszecki, 1963) as a result of numerous simplified assumptions made in the theory, such as:

1. The scattering and absorption coefficients are assumed to be the same throughout the thickness of colourant layer. The assumption does not hold good for matt and semi-matt paint films, where there is considerable penetration of air in the top elementary layers, or for the paint films exhibiting floating, i.e. accumulation of one pigment, usually the most finely ground one, in the top elementary layer.

2. The theory takes no account of surface reflection. Invariably, there would be some reflection from the surface due to discontinuity of refractive index at the air-object interface. Some correction is, therefore, necessary for reflection from the interface, as follows (Equation [4.6]):

$$\frac{K}{S} = \frac{\left[1 - (R_{\infty} - R_{\infty,0})\right]^2}{2(R_{\infty} - R_{\infty,0})} \quad [4.6]$$

where $R_{\infty,0}$ is the surface reflection factor at complete opacity.

This is determined by dyeing the substrate with increasing concentration of a strongly absorbing dye until the reflectance factor at the wavelength of maximum absorption becomes independent of dye concentration. The limiting value of the reflectance factor is considered as surface reflectance. In computer colourant formulation of textiles, this correction is neglected frequently and the problem is tackled through computation techniques.

3. For paints, the refractive index of the film would be around 1.5, as against 1.0 for air. As a result, a parallel beam of light from a light source striking such a surface perpendicularly will suffer a partial reflection at the boundary, and the portion of the light reflected back will be around 4%. The remaining light enters the film and is diffused by the pigments. The light emerging from the film again suffers partial reflection at the boundary. However, the light is now travelling upwards and strikes the boundary at all possible angles. The reflectivity increases with increase in the angle of incidence and, at an angle equal to the critical angle, all the light reflects back. The light thus reflected back from the boundary is again scattered by the pigment and tries to emerge from the film, and again suffers partial reflection from the boundary. Saunderson (1942) developed a correction formula for both internal and external reflection as in Equation [4.7]:

$$R_t = \frac{R_m - k_1}{1 - k_1 - k_2(1 - R_m)} \quad [4.7]$$

where R_t is the corrected or theoretical reflectance, R_m is the measured reflectance at complete opacity and k_1 is the Fresnel reflectance coefficient representing front-surface reflectance of the film (Equation [4.8]):

$$k_1 = \frac{(n-1)^2}{(n+1)^2} \quad [4.8]$$

k_1 often has a value of approximately 0.04. The value of k_1 depends to some extent on the PVC and wavelength of light. k_2 is the internal reflectance of the film and is difficult to measure. The proposed values are between 0.4 and 0.6. The value depends to some extent on the orientation of the light. For highly glossy samples in specular exclusion mode, the factor k_2 may be omitted.

4. The pigment particles in the colourant layer are assumed to be orientated randomly, so that the light flux is perfectly diffused within the colourant layer. However, in many objects, such as metallic paints, the pigment particles are in the form of flakes and lie mostly horizontally.
5. The incident light is assumed to be perfectly diffused. However, in many instruments, the incident light is collimated and not diffused.
6. The K-M equation is applicable to monochromatic light only. The coefficients are to be determined at numerous wavelengths throughout the visible range. Usually 16 wavelengths at 20 nm intervals from 400 to 700 nm are used for recipe prediction work. Marginal gain in accuracy is reported to be achieved by using 10 nm intervals, while there will be a considerable increase in computation time and data storage requirements.
7. In the case of dark shades, the light is absorbed before it is diffused and reflected. Such low reflectance may give unreliable results for dark shades.
8. Similarly, for thin films, the light may not have a chance to scatter, which makes a significant difference in the results.

In spite of the above restrictions, the K-M function is very popular for colourant formulation work, and many of its restrictions are bypassed by computer iteration and correction programs.

The Kubelka-Munk single-constant/two-constant theories have played an important role in colour science and technology. However, in practice there are some shortcomings. Yang *et al.* (2009) checked the theories with a series of systematic experiments, data processing and analysing, and have revealed several disagreements with the experimental evidence in the case of the additivity colour-mixing law for turbid materials. Taking dyed fabric as an example of coloured turbid material, the K-M light absorption coefficients K , scattering coefficients S and their ratio K/S , were investigated systematically through experiments. The results question the rationality of the additive colour-mixing law for turbid materials from three aspects. First, both the K-M absorption coefficient K and scattering coefficient S are not scalable, and non-linear to dye concentration. Second, the absorption coefficient K and the scattering coefficient S are demonstrated to be highly, yet negatively, correlated, a fact ignored when establishing the theories. Third, in the absorption band, the scattering coefficients decrease with increasing dye concentration, questioning the linearity assumption.

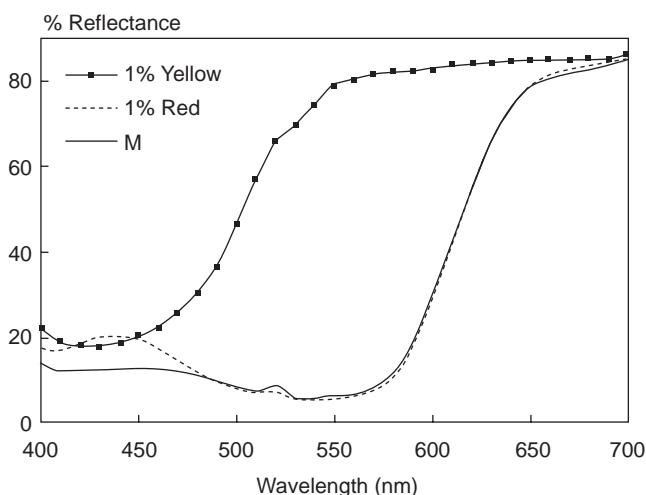
4.6 Additive functions

For colourant formulation, we need a function that is directly related with the concentration of the colourants. Unfortunately, the reflectance or transmittance measured directly by the instrument has no direct relation with the concentration of the colourants. However, the Kubelka-Munk function derived from the reflectance is directly related to colourant concentration.

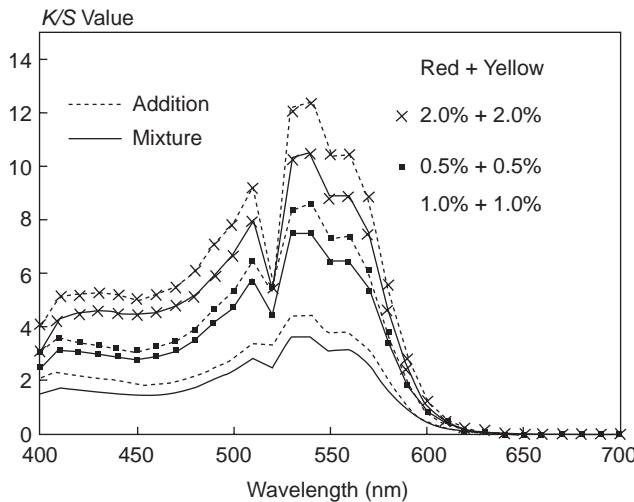
Figure 4.3 shows reflectance curves of the fabrics dyed with 1% yellow dye, 1% red dye and a mixed shade containing 1% of each dye. No direct mathematical relation can be derived between the reflectance values of the mixed shade and those for the components (i.e. self-dyed).

Figure 4.4 shows K/S functions between 400 and 700 nm of three mixed shades (containing 1%, 2% and 3% of both the dyes) as filled lines, and simple mathematical addition of K/S values of the individual self-dyed shades as dashed lines after subtraction of the K/S values of the blank substrate. The sequence of the curves is the same as that shown for the dye mixture composition in the figure. The K/S curves of the mixtures and the respective curves for additions of K/S values of the individual dyes are very close in shape, though not identical. This is because the theory is not very accurate, but only approximate. However, the similarity of the mixture curves and the corresponding addition curves indicate additive nature of the Kubelka-Munk functions.

The theory assumes that the ratio of absorption and scattering coefficients of the colourant is directly proportional to its concentration and is additive in a mixture. If a mixture is made with n colourants with concentrations C_i ,



4.3 Reflectance curves of fabrics dyed with a yellow dye, a red dye and their mixture (M).



4.4 The K/S values at 400–700 nm for mixtures and mathematical additions of K/S values of the respective self-shades.

the coefficients of the resultant mixture, K_M and S_M , can be written as in Equation [4.9]:

$$K_M = \sum_{i=1}^n C_i K_i + K_b, \quad S_M = \sum_{i=1}^n C_i S_i + S_b$$

or $\left(\frac{K}{S}\right)_M = \frac{\sum_{i=1}^n C_i K_i + K_b}{\sum_{i=1}^n C_i S_i + S_b}$ [4.9]

where b stands for the substrate.

Depending on the nature of the colourant and the medium carrying the colourants, the addition function can be written in two ways:

1. Single-constant theory
2. Two-constant theory

4.7 Single-constant theory

In classical Kubelka-Munk analysis, it is assumed that the colourant has both absorbing and scattering power, and this is the case with, for example, pigment embedded in a paint layer. However, textile dyes are considered to be dissolved in the fibre and not to participate in the scattering process. The

fibres are only responsible for the scattering of light. Therefore, the coefficients S_1, S_2, S_3 can be set to zero, as in Equation [4.10]:

$$\begin{aligned} \frac{K}{S} &= \frac{C_1 K_1 + C_2 K_2 + C_3 K_3 + \dots + K_b}{S_b} \\ &= C_1 \left(\frac{K_1}{S_b} \right) + C_2 \left(\frac{K_2}{S_b} \right) + C_3 \left(\frac{K_3}{S_b} \right) + \dots + \frac{K_b}{S_b} \end{aligned} \quad [4.10]$$

Even though K/S_b is a ratio, it amounts to a single constant for each colourant. So in this case, it is possible to characterize a colourant or dye with only one substrate-specific parameter. Thus, the above function is known as *single-constant function*.

The above equations are valid for a single wavelength. Generally, calculations are made at 16 wavelengths at 20 nm intervals from 400 to 700 nm. For a given wavelength, the Equation [4.10] can be rewritten as Equation [4.11]:

$$\begin{aligned} f(R_\lambda) &= \alpha_{\lambda,1} C_1 + \alpha_{\lambda,2} C_2 + \alpha_{\lambda,3} C_3 + \dots + f(R_{\lambda,b}) \\ &= \sum_{i=1}^n \alpha_{\lambda,i} C_i + f(R_{\lambda,b}) \end{aligned} \quad [4.11]$$

For a single dye the equation may be written as in Equation [4.12]:

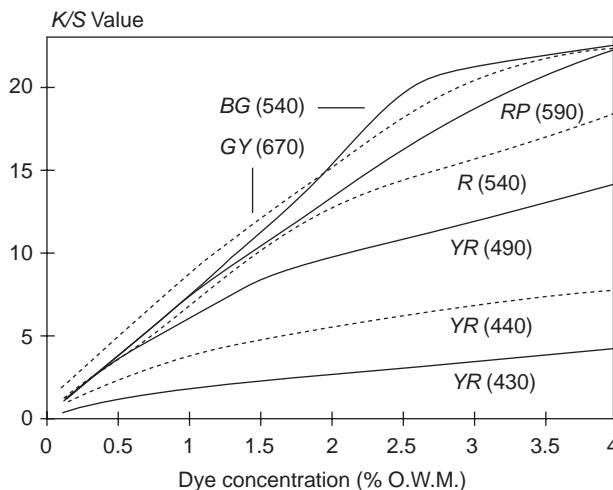
$$\begin{aligned} f(R_\lambda) &= \alpha_\lambda C + f(R_{\lambda,b}) \\ \text{or } \alpha_\lambda &= \frac{f(R_\lambda) - f(R_{\lambda,b})}{C} \end{aligned} \quad [4.12]$$

The absorption coefficient, $\alpha\lambda$, of a dye on a particular substrate can be determined by dyeing the particular substrate with a known concentration of the dye – generally expressed as a percentage of the total weight of material dyed. The coefficients are popularly known as alpha values.

4.7.1 Non-linearity of K-M function

Ideally, the K-M function, $f(R\lambda)$, should have a linear relation with concentration. However, deviations occur much more frequently with the K-M function than with Beer's law for solutions. The linearity may be achieved at low concentration, but deviation from linearity is more common at high concentrations.

Figure 4.5 shows K/S values against dye concentration (percentage of the weight of material) of seven high exhaust (H-E) reactive dyes applied on



4.5 The effect of dye concentration on *K/S* values of cotton fabrics dyed with different reactive dyes.

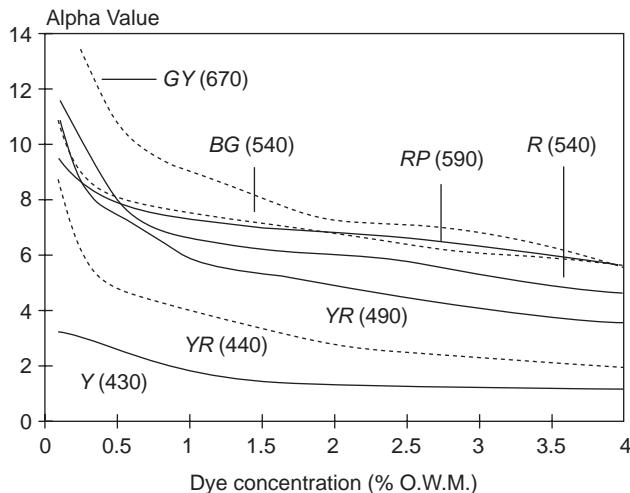
cotton textile materials. The dyes in the figure are identified by Munsell hue name instead of actual dye name. The actual shades of the dyes (Munsell hue name under bracket) were yellow (Y), golden yellow (YR), orange (YR with higher λ_{\max}), red (R), navy-blue (RP), bluish green (BG) and turquoise blue (GY). The values are calculated at the respective wavelengths where maximum absorption occurred for the particular dye, shown under bracket along with Munsell hue name. *K/S* values at different concentrations show non-linear behaviour of varying degrees for all the dyes.

Alpha values for these dyes are calculated using Equation [4.12], and are plotted in Fig. 4.6 against concentration (percentage of the weight of material). The alpha values are not constant at different concentration levels. In fact, the value decreases with increase in concentration for all the dyes. Notably, the alpha values change rapidly with concentration at lower concentrations, instead of being constant as reported earlier.

In addition to the theoretical limitation of K-M theory, there are several other reasons responsible for the non-linearity of the K-M function (Kuehni, 1975), as mentioned below.

For the dyes on textile materials, some of the reasons are:

- Incomplete exhaustion of dye into the fibre, leaving considerable dye in the dye bath.
- Incomplete penetration of dye inside the fibre, resulting in ring dyeing or surface dyeing.
- Interaction between the dyes.



4.6 The effect of dye concentration on alpha values of cotton fabrics dyed with different reactive dyes.

- Scattering by the dyes at higher concentration.

For pigments in paints, printing inks and plastics, some of the reasons are:

- Scattering in preferred direction due to particular shape of the colourants.
- Dissolution of pigment particles in the medium, resulting in reduction in scattering.
- Interaction between pigment particles, particularly at higher PVC.
- The presence of additional interfaces, such as in the case of semi-opaque paint over a layer of white paint.

If the non-linearity is not so great, as in cases where high levels of dye exhaustion can be achieved, e.g. acid dyes on wool, then the simplest approach is to calculate the average absorption coefficient over a range of calibration dye concentrations, typically at six concentrations. Least squares techniques may be used, which minimize the sum of the squares of the differences between the measured values and the predicted values. However, this measure of fit tends to be biased towards the higher dye concentrations, which give larger $f(R)$ values, and hence it is better to use a weighted sum of squares, as follows (Equation [4.13]):

$$\sum \left[\frac{f(R_\lambda) - f(R_{\lambda,b}) - \alpha_\lambda C}{f(R_\lambda)} \right]^2 = \text{minimum} \quad [4.13]$$

Under practical conditions, the influence of dye concentration on the K-M function is handled in various ways in the computer, such as linear or polynomial interpolation method or the empirical linearization method.

In the *linear interpolation method*, an interpolation factor p is calculated as (Equation [4.14]):

$$p = \frac{C_u - C_l}{C_h - C_l} \quad [4.14]$$

where C_u denotes the concentration for which $F(R)$ is wanted, while C_h and C_l denote respectively the concentrations of next higher and next lower level for which data are available. The interpolated K-M function $(K/S)_p$ is then calculated as in Equation [4.15]:

$$\left(\frac{K}{S}\right)_p = \left(\frac{K}{S}\right)_l + p \left[\left(\frac{K}{S}\right)_h - \left(\frac{K}{S}\right)_l \right] \quad [4.15]$$

where the subscripts h and l denote the higher and lower level, respectively as above.

In the *polynomial interpolation method*, the curvature of the K-M function versus concentration frequently obtained with dyes on 33 textiles is expressed as a polynomial regression equation, mathematically represented as (Equation [4.16]):

$$C_r = a_0 + a_1 C + a_2 C^2 \quad [4.16]$$

where C_r stands for true concentration of the dye, C is the concentration computed from a single set of normalized K/S values and a_i are the polynomial coefficients which can be calculated at the wavelength of maximum absorption from calibration data at different concentrations. This will result in savings in computer data storage, but may give erroneous results for dyes showing change in hue with concentration.

In the empirical linearization method, surface-reflectance-factor values are determined to linearize the relationship between K/S value and concentration.

4.8 Two-constant theory

Two-constant theory is applicable for paint, printing ink etc., where the colourants are responsible for both absorption and scattering. In these cases, the absorption and scattering coefficients of the mixture can be built up

from the separate absorption and scattering coefficients of the individual pigments or dyes, as follows (Equation [4.17]):

$$\frac{K}{S} = \frac{C_1 K_1 + C_2 K_2 + C_3 K_3 + \dots + K_b}{C_1 S_1 + C_2 S_2 + C_3 S_3 + \dots + S_b} \quad [4.17]$$

The subscript b refers to the substrate on which the colourants are applied. For each dye, two coefficients or constants (K_i and S_i) are to be determined separately, hence the name *two-constant function*.

4.8.1 Determination of the constants

For the paint and similar systems obeying two-constant theory, K/S ratios are not suffice – K and S coefficients are to be determined separately. Several methods are recommended in the literature for separate determination of K and S values.

In a simple and most commonly used method, the scattering coefficient of white pigment, mostly titanium dioxide, is arbitrarily set to unity ($S_w = 1$) at all wavelengths, and all other K and S values are determined relative to this value.

A draw-down of the white pigment is made and the reflectance, and thereby K/S value, is measured.

$$\text{Since } S_w = 1, K_w = (K/S)_w \quad [4.18]$$

For black pigment (mostly carbon black), two draw-downs are made. One is called *mass-tone*, containing only black pigment and no white pigment. The other is called *reduction*, i.e. a mixture containing both white and black pigments. Generally, one part of black is mixed with ten parts of white. We can write the following Equations [4.19] and [4.20]:

$$\left(\frac{K}{S} \right) = \frac{C_b K_b + C_w K_w}{C_b S_b + C_w S_w} \quad [4.19]$$

$$\left(\frac{K}{S} \right)_m = \frac{C_b K_b}{C_b S_b} \quad [4.20]$$

where subscripts b , r and m refer to black pigment, reduction and mass-tone, respectively.

Only black pigment is present in mass-tone, hence in Equation [4.20], $C_b = 1$ and the equation may be rewritten as Equation [4.21]:

$$K_b = S_b \left(\frac{K}{S} \right)_m \quad [4.21]$$

By solving Equations [4.18]–[4.20], the following Equation [4.22] is obtained:

$$S_b = \frac{C_w \left[(K/S)_r - (K/S)_m \right]}{C_b \left[(K/S)_m - (K/S)_r \right]} \quad [4.22]$$

For coloured pigments, the same method may be used by replacing black pigment with the respective coloured pigment.

However, for high chroma colours, there may be problem, because of the poor separation of the reflectance curves of the white base and mass-tone of bright colours, especially yellow, orange or red pigment at the red end of the spectrum resulting in poorly separated K/S values.

To obtain good separation of the reflectance curves, such pigments are reduced with a little black pigment (say in ratio of 99:1) instead of reduction with white. The K and S values of the mixture of the chromatic pigment and black are determined by the Equations [4.19]–[4.22]. The respective values for the black pigment are determined separately, and the values for the chromatic pigment are determined by subtraction.

Since in this method the assumption that $S_w = 1$ relates to reflectivity only, all the samples should be opaque or the measurement should be at complete opacity. However, with certain pigments, especially yellows, it is difficult to achieve complete opacity in surface coating and in plastic film. In these cases, opacity may be obtained in two ways – either by adding white pigment in mass-tone (e.g. ratio 1:9) or using a mixture of pigment and a small amount of black (e.g. ratio 1:99).

Several alternative methods are also reported in the literature. In the tint-ladder method (Allen, 1978), the coloured pigment to be characterized is mixed with white pigment in different ratios. About five to eight such mixtures, along with a mass-tone, are prepared. The K/S values for each mixture i are determined from the reflectance values, and the following Equation [4.23] may be written:

$$\begin{aligned} \left(\frac{K}{S} \right)_i &= \frac{C_i K_c + (1-C_i) K_w}{C_i S_c + (1-C_i) S_w} \\ \text{or } C_i K_c - C_i \left(\frac{K}{S} \right)_i S_c &= (1-C_i) \left[\left(\frac{K}{S} \right)_i S_w - K_w \right] \end{aligned} \quad [4.23]$$

where subscripts c and w stand for the coloured and white pigments, respectively.

The equation has two unknowns, K_c and S_c , and only two equations suffice for solution. But as five to eight mixtures are prepared, the over-determined system is solved by least squares technique.

The tint-ladder method gives good results except for high chroma colours. In such a situation, three draw-downs are prepared – a mass-tone, a mixture with black and a mixture with white. The mass-tone and the white reduction are used to determine the absorption and scattering coefficients of the coloured pigment in the strongly absorbing regions of the spectrum. The mass-tone and black reduction are used in regions where coloured pigment hardly absorbs any light. In order to make the black reduction method to work, careful selection and standardization of the black pigment is necessary, as it suffers from agglomeration difficulties. In all the above cases, surface reflection correction must be made while measuring K/S values.

4.8.2 New two-constant algorithm

There are two kinds of algorithms for colour matching based on the Kubelka-Munk theory. One algorithm based on the single-constant theory requires the unit k/S_b ratio for each colourant and K_b/S_b for the substrate at each wavelength. It is often applied to colour matching for textile and paper samples. Another algorithm, based on the traditional two-constant theory, requires the unit values of both k and s for each colourant. It is often applied to colour matching for pigment and paint samples. It has been reported that scattering of some disperse dyes cannot be negligible, and computer colour matching based on the traditional two-constant theory has been applied to textile samples (Burlone, 1983; Walowit and others, 1988). However, it is very difficult to determine the unit values of both k and s for each dye as well as for the textile sample which is being matched. Algorithms based on the traditional two-constant theory require the unit values of both k and s for each colourant, but not the values of the k/S_b ratio. Therefore, algorithms based on the traditional two-constant theory cannot be applied to colourants if only the unit k/S_b of each colourant is known, i.e. the algorithms based on the traditional two-constant theory are not suitable for the single-constant theory.

For ' n ' colourants, the Equation [4.17] may be rewritten as Equation [4.24]:

$$\frac{K}{S} = \frac{c_1 k_1 + c_2 k_2 + c_3 k_3 + \dots + c_n k_n + K_b}{c_1 s_1 + c_2 s_2 + c_3 s_3 + \dots + c_n s_n + S_b} = \frac{K_b/S_b + \sum \frac{c_i k_i}{S_b}}{1 + \sum \frac{c_i s_i}{S_b}} \quad [4.24]$$

where c_i , k_i and s_i are concentration, absorption coefficient and scattering coefficient of the ' i 'th colourant, respectively, and K_b and S_b are absorption and scattering coefficients of the substrate ' b ', respectively.

Letting $(K/S)^b = K_b/S_b$, $(k/S_b)^i = k_i/S_b$, $(s/S_b)^i = s_i/S_b$, the mathematically equivalent expression can be written as Equation [4.25]:

$$\frac{K}{S} = \frac{\left(\frac{K}{S}\right)^b + \sum c_i \left(\frac{k}{S_b}\right)^i}{1 + \sum c_i \left(\frac{s}{S_b}\right)^i} \quad [4.25]$$

where both (k/S_b) and (s/S_b) are the new two-constants of each colourant proposed by He and Zhou (2007). They can be determined by measuring the reflectance R_b of substrate without colourant, as well as the reflectance R_∞ of the combination of the substrate and one colourant with various concentrations. If $(K/S)^b$ of the substrate and (k/S_b) and (s/S_b) of each colourant are determined, the K/S values of the mixture for given concentrations of the various colourants can be calculated, and subsequently the spectral reflectivity distribution of the mixture can be calculated by Equation [4.26]:

$$R_\infty = 1 + K/S - [(K/S)^2 + 2K/S]^{1/2} \quad [4.26]$$

where R_∞ is reflectivity of the mixture.

For a single colourant, Equation [4.25] may be rewritten as Equation [4.27]:

$$\frac{K}{S} = \frac{(K/S)^b + c_i(k/S_b)}{1 + c_i(s/S_b)} \quad [4.27]$$

K/S is a non-linear function vs dye concentration c . It can be rearranged as Equation [4.28]:

$$\frac{K/S - (K/S)^b}{c} = - \left(\frac{s}{S_b}\right) \left(\frac{K}{S}\right) + \left(\frac{k}{S_b}\right) \quad [4.28]$$

The value of $[(K/S) - (K/S)^b]/c$ is linearly related to the value of (K/S) , whose slope and intercept are (s/S_b) and (k/S_b) , respectively.

The procedures for measuring both (k/S_b) and (s/S_b) of each colourant are as in Equation [4.5]:

- To measure the reflectance R_b of substrate without colourant as well as the reflectance R_∞ of the combination of the substrate and one colourant with various concentrations,
- To convert R_b into $(K/S)^b$ by Equation [4.5],
- To obtain both (k/S_b) and (s/S_b) of each colourant from Equation [4.28] by using the least squares technique.

The method for measuring the two-constant values of a colourant described by He and Zhou (2007) is advantageous over the traditional two-constant method, as the former method is much easier to use. Algorithms for colourant formulation proposed in their study are suitable for the single-constant theory as well as the new two-constant theory. The recipes predicted by the new two-constant theory are closer to the actual recipes of the standards than the recipes predicted by the single-constant theory. The samples according to the recipe predicted by the new two-constant theory have a smaller colour difference against the standards than the samples according to the recipe predicted by the single-constant theory. Therefore, the scattering of some disperse dyes cannot be negligible. The recipes for those disperse dyes should be better predicted by the new two-constant theory.

4.9 Beyond K-M theory

Kubelka-Munk theory has made several assumptions to reduce the complexity in mathematical derivation. However, this has resulted in several limitations in application of the theory to a variety of problems. A number of modifications have been proposed to overcome some of these limitations.

The theory assumes diffuse illumination and diffuse viewing. Even after a lapse of about half a century since the introduction of K-M theory, not a single instrument has been put forward embodying these assumptions. Atherton (1955) proposed that when the object is represented by a parallel-sided, coloured scattering medium, having a collimated beam of monochromatic light incident normally on one face of the scattering medium, the relation between reflectance and K/S function may be written as Equation [4.29]:

$$R_\infty = \frac{1}{((K/S) + 1)(l - 1)}$$

or $\frac{K}{S} = \left[\frac{1}{R_\infty(l - 1)} - 1 \right]$ [4.29]

where l is the diffusion factor, defined as $d = 1dx$, d being the mean path length of diffused light through the layer of thickness dx .

If the incident light is inclined at an angle $\cos^{-1}(1/n)$ to the normal, the intensity of light incident on the medium is reduced to one- n th and the equation becomes as follows (Equation [4.30]):

$$\frac{K}{S} = \left[\frac{1}{R_\infty (\ln - 1)} - 1 \right] \quad [4.30]$$

The Pineo (1940) function (Equation [4.31]) is similar to the K-M function, but it contains two empirical factors, ρ and n , to give the best fit with experimental results. The function is:

$$\frac{K}{S} = \frac{\left[1 - (R_\infty - \rho)^{1/n} \right]^2}{2(R_\infty - \rho)^{1/n}} \quad [4.31]$$

The values of n do not differ appreciably from unity for most textile fabrics. Hence the function may be considered approximately identical with K-M function except for ρ , which is included to allow for surface reflection of the fabric. Some improvement, particularly for high dye concentration with correspondingly low reflectances, can be achieved.

Preston-Tsien (1982) function may be written as Equation [4.32]:

$$\log \left[\frac{(1/R_\infty)(1-2\rho)+(1/\rho)-4}{(1/\rho)-(1/R_\infty)} \right] = Bc \quad [4.32]$$

where ρ is the coefficient of reflection for the fibre-air interface, and B is a constant involving the absorption coefficient of the dye. The function was derived for dyed viscose rayon filament. The difficulty is to assign a value for ρ , since it is the surface of fabric and not the fibre that is relevant. Thus, wool flannel composed of fibres each having $\rho = 0.04$ (approximately) will have a much smaller surface reflection due to the greater disorientation of the individual fibres. There is no easy method of determination of ρ for a fabric, since it is in the order of 0.01 or less.

Selling (1947) proposed the following empirical Equation [4.33] for the colour analysis of dyed wool:

$$\left[\frac{R_w}{R_\infty} - 1.1 \right]^{1.1} = \alpha C \quad [4.33]$$

in which α is a constant and R_w is the reflectance of the undyed fabric. The significance of the exponent 1.1 is not readily apparent.

To obtain better linearity with dye concentration, a number of additive functions, mostly modified K-M functions, are proposed. A few are mentioned below:

A power function (Equation [4.34]) is as follows:

$$\frac{K}{S} = \left[\frac{(1-R)^2}{2R} \right]^k \quad [4.34]$$

Fink-Jenson (Alderson *et al.*, 1961) proposed the following function (Equation [4.35]):

$$\frac{K}{S} = \frac{(1-R)^2}{(R-R_0)(1+KR)} \quad [4.35]$$

The function (Equation [4.36]) proposed by Love-Oglesby-Gailey (Love *et al.*, 1965) adopts an additional constant to that of Fink-Jenson:

$$\frac{K}{S} = \frac{(k_1 - R)^2}{(R - R_0)(1 + k_2 R)} \quad [4.36]$$

The constants k_1 , k_2 and R_0 are chosen for a particular substrate and for the varying conditions of the sample.

Stearns and Noechel (1944) proposed an additive function for another type of colourant mixture – a mixture of textile fibres. Different textile fibres are dyed with different classes of dyes following different methods. It is customary to dye large batches of fibres to colours surrounding the colour to be matched, and then to make up the final match by mixtures of textile fibres in suitable proportions. These mixtures follow the Kubelka-Munk function, with slight deviation towards additive mixture. The reflectivity function proposed is as follows [Equation 3.37]:

$$F(R_\infty) = \frac{1 - R_\infty}{M(R_\infty - 0.01) + 0.01} = \alpha_1 m_1 + \alpha_2 m_2 + \alpha_3 m_3 + \dots \quad [4.37]$$

where R_∞ is the reflection of the blend and b is a constant to be determined experimentally for each kind of fibre. The value of M is approximately 0.15

for wool mixture. α_i and m_i are the constants and fractional amount of the components, respectively, when $m_1 + m_2 + m_3 + \dots = 1$. The constants, α_i , are calculated from the reflectance of the pure components.

Mélange colour is a colour effect obtained by mixing of fibres in different colours in a blend. One of the biggest problems encountered in the work of mélange colours in textile is that the accurate estimation of fibre colours does not provide a desired colour. In a study (Yeçil and Sabir, 2011), yellow, red and blue colours were used in a mélange yarn made of viscose and polyester fibres. These fibres were blended in different ratios and 165 mélange-coloured bands were obtained. To calculate the model M , in the coefficient, a new approach was developed. A set of M coefficients were calculated for all wavelengths in each mix, in the 400–700 nm (10 nm intervals) range (Equation [4.38]).

$$M = \frac{1}{100}(0.12\lambda + 42.75) \quad [4.38]$$

where λ is the wavelength in nm.

The colour calculations were performed using the new M coefficients. The average colour difference between the measured colour values and the calculated colour values was found as 1.15 CIELAB units. This result suggests that in the fibre blend, estimating the colours of the Steams-Noeichel model might give satisfactory results.

Frielle (1952) proposed a modified additive function (Equation [4.39]) for fibre blends using separate absorption and scattering coefficients as follows:

$$f(R) = \exp \left[\frac{[1-R]^2 S}{2R} \right] \quad [4.39]$$

Reflection measurements of the loose wool before felting gave scattering coefficient, $S \approx 0.30$, and no variation with wavelength.

Minato (1977) compared the performance of various additive functions for dyeing materials and pigment mixtures, and found that a simple modified function performed best for colourant formulation. The function is shown in Equation [4.40]:

$$\frac{K}{S} = \frac{(0.9 - R)^2}{R} \quad [4.40]$$

All the additive functions mentioned above are modified versions of K-M functions. However, K-M theory is a phenomenological theory. The

absorption and scattering coefficients are empirically introduced in the theory. The coefficients determined for one lot of colourant on a particular substrate are not valid for another lot, nor for another substrate, and no conversion formula is available or developed. The theory is highly dependent on calibration. Reliable results will be achieved only if the coefficients are used under the conditions same as those used during calibration. The K-M theory provides no method to evaluate the coefficients from fundamental, optical or morphological aspects such as particle size or refractive index of the colourants. Extensive efforts have been made to correlate K-M function with particle size and refractive index, but without any satisfactory result.

Mie scattering theory (see Roy Choudhury, 2014, chapter 2, section 2.4.1, p. 59) provides a method to calculate the absorption and scattering efficiency of particles from their particle size and refractive index. To use Mie theory, we need to know two ratios – the ratio of diameter of the scattering particle to the wavelength of the incident light, and the ratio of complex refractive indices of the particle and the medium in which the particles are immersed. From Mie theory, we get two quantities, which represent the power of the single particle to absorb light and the power to scatter light. We can also obtain the scattering pattern of the particle, i.e. the relative intensity of scattered light as a function of scattering angle, the mathematical expression of which is known as the phase function of the particle. The scattering pattern calculated by Mie theory is usually very complex and structured.

Mie theory has, however, very definite limitation. It is applicable to the scattering from a single particle isolated in space and speaks nothing about assembly of particles as in case of textiles or paint film. Theory based on successive Mie scattering encounters will lead to enormous complexity. Moreover when the particles are closer to each other by a distance less than about three particle diameter, the very assumptions on which Mie theory is based ceased to hold. Dependent scattering is a great barrier for applicability of Mie theory. Though Mie theory is strictly valid for spherical particles, suitable corrections for the particle shape can be deduced. Allen (1978) commented that Kubelka-Munk theory seems to begin where Mie theory ends. However, plugging the later theory into the former is not possible, because different sets of assumptions are made in the two theories.

Henyey and Greenstein (1941) proposed a phase function with only one adjustable parameter, g , the average cosine of the scattering angle. The said phase function was proposed for astronomical work, and successful use in colourant formulation is yet to be made. As compared to the two parameters in K-M theory, it needs only three parameters to characterize a pigment – absorption and scattering cross-sections, and g .

By multi-flux theory, we acquire the ability to start with fundamental colourant properties such as particle size and refractive index, and using the

information we can calculate, from Mie theory, single particle absorption and scattering phase function.

However, as the theory is based on Mie theory, the results will be valid only if the scattering particles are separated by more than three particle diameters. This is never achievable in paint and textile systems, where the scattering particles are much closer to each other. As Mie theory is not applicable for dependent scattering, it is probably better to work with reflectance value, as in the case of K-M theory. In addition, if the channels are extended to a large number, we expect to get better results than the K-M theory.

The multi-channel technique requires extensive calculation time and would probably be very costly to use for routine colourant formulation at the present stage of computation. At this time, colour measuring instruments employ only K-M theory for colour-matching calculations.

4.10 Instrumental colourant formulation

Instrumental or computerized colourant formulation is inaccurately but widely termed computer colour matching. In fact, the computer does not create any colour sensation matching the standard colour, but merely provide us formulations, or the amounts of colourants which, on application to a substrate, can create a coloured object which will be close in colour with that of standard. Before any formulation is asked for, the computer needs to be provided with spectrophotometric calibration data of the colourants in varying concentration. The colourants, substrate and the procedure of application of the colourant on the substrate should be identical for calibration samples and actual samples prepared by the predicted recipe. Manual colour matching is an art in colour reproduction industries, practised through trial and error for centuries. Computers can reduce both trial and error considerably. A closely related operation, termed *shading* by Allen (1978), is the colour correction of production batches by repeated addition of colourants to match a standard colour.

The first successful instrumental approach was made by Davidson *et al.* (1963) with the help of their analogue match predictor computer, affectionately known as *COMIC*. The numerical values of *K/S* at 16 wavelengths for a known concentration of each dye are represented by the settings of 16 resistances in individual plug-in boxes, up to 5 of which can be inserted into the computer for matching purposes. The *K/S* values of the target shade are similarly represented by resistances whose values are set by the 16 dials at the top of the control panel. On the oscilloscope these values appear as 16 dots, representing an inverse of the reflectance curve. The operator then chooses three suitable dyes and inserts the corresponding plug-in boxes. Adjustment of the first three concentration dials brings the dots down

towards a horizontal reference line. The earlier model was independent of CIE system, and later a tristimulus difference computer was introduced.

In 1955, Atherton of ICI Ltd developed an analogue device based on shadows of wire bent to represent reflectance functions. In the following year, he developed probably the first match prediction program for digital computer (Alderson, 1963). A single prediction took 20–60 s, which was remarkably fast at that time. Park and Stearns (1944) were first to make an adequate theoretical treatment of the problem. Allen published (Allen, 1966) a digital computation algorithm on the basis of single-constant theory, and later (Allen, 1974) a similar algorithm for use with two-constant theory. Because of its simplicity and good formulation predictions, Allen's algorithms have been widely used to date.

A computer match prediction system consists essentially of the following components (Park, 1993):

1. A spectrophotometer for colour measurement (see Roy Choudhury, 2014, chapter 6, section 6.2.2, p. 229), interfaced with
2. A personal computer (PC),
3. Input/output devices, namely visual display unit (VDU) and printer and
4. Software to drive the various devices in the system and to carry out required calculations.

The software is instrument-specific and represents a relatively high proportion of the total system cost. Typical commercial software includes:

1. A match prediction system, including recipe correction and reformulation,
2. A perpetual inventory programme, interfaced with recordable weighing system in dye store,
3. Formulation storage and retrieval, often linked to a colour library and
4. Colour-difference measurement programme, which may be extended to carry out shade sorting of batches.

There may be two types of instrumental matching:

1. Spectrophotometric matching
2. Colorimetric matching

In spectrophotometric matching or *spectral colour match*, the reflectance factor of the standard and the sample will be identical at all wavelengths i.e.

$$R_{\lambda, \text{std}} = R_{\lambda, \text{Sam}} \quad [4.41]$$

where std and Sam stand for standard and sample, respectively.

As the reflectance values of standard and sample match at all wavelengths (generally at 16 wavelengths between 400 and 700 nm), the match will be retained under any illuminant. Such matches are also called invariant or unconditional matches. The reflectance match is difficult to obtain, and mainly feasible, provided the same colourants are being used for both standard and sample. It is also not possible to get a number of alternative recipes, which is a remarkable advantage of computer colourant formulation.

The majority of the computer colourant formulation program relies on equating colorimetric parameters called tristimulus values. Thus, for tristimulus match:

$$(X_{\text{std}}, Y_{\text{std}}, Z_{\text{std}}) = (X_{\text{sam}}, Y_{\text{sam}}, Z_{\text{sam}}) \quad [4.42]$$

This is called a conditional match because the sample matches in colour with the standard under a specific illuminant. When the illuminant is changed, the sample may or may not match with the standard. However, most computer colourant formulation techniques rely on tristimulus match because it is much easier to compute. Several combinations of dyes can give *tristimulus match* to the same standard. Hence, the user can choose one of the suitable alternative combinations on the basis of availability of the dyes, cost and metamerism nature of the match (see Chapter 5).

In the conventional colorimetric approach, the matching occurs only under a particular illuminant and the others are ignored. It seems possible to change the matching criterion to an imperceptible value with non-zero colour difference under the major illuminant, and to benefit from the advantages of reducing the colour-difference values under the other illuminants.

Sluban (1993) offered a strategy of recipe prediction to minimize the metamerism problem colorimetrically. The proposed colour-difference minimization technique leads to more balanced colour-difference values over three different illuminants at the expense of accepting a small colour difference under the illuminant which is selected as a major one in the matching process. The mathematical expression of this matching strategy is shown by Equation [4.43]:

$$W_{D65}^2 (\Delta E_{D65})^2 + W_A^2 (\Delta E_A)^2 + W_{WWF}^2 (\Delta E_{WWF})^2 \rightarrow \min \quad [4.43]$$

where W_{D65} , W_A and W_{WWF} are weightings applied to colour-difference values proportional to the importance of applied illuminants, i.e. daylight (D65), tungsten light (A) and warm white fluorescent (WWF) light, respectively. As the number of primaries in combination is, in practical terms, less than nine, the above equation is minimized by solving an over-determined system in a least squares manner using the iteration procedure.

4.11 Algorithm for single-constant theory

Allen's algorithm proposes computation in two stages. In the first stage, an initial solution, i.e. a rough solution to the problem is obtained by matrix inversion, which may be satisfactory for matches of low metamerism. In the second stage, a final solution is obtained by an iterative method, which starts with the initial solution and improves it using the same inverted matrix. To obtain a tristimulus match, three non-linear simultaneous equations must be solved. The equation in general form may be written as Equation [4.44]:

$$\begin{aligned} A_1(C_1, C_2, C_3) &= X \\ A_2(C_1, C_2, C_3) &= Y \\ A_3(C_1, C_2, C_3) &= Z \end{aligned} \quad [4.44]$$

where X, Y, Z are the tristimulus values of the standard to be matched under a specific illuminant, C_1, C_2 and C_3 are the concentrations of the three dyes required for a match, and A_1, A_2 and A_3 are non-linear functions of concentration of the respective dyes.

4.11.1 Initial solution

There are several ways of finding an initial solution (Kuehni, 1975). In the simplest case, constant values for all the colourants are assumed arbitrarily, or on the basis of Y value of the standard. The reflectance curve of such formula is compared to that of the standard to be matched, and the solution is improved by iteration. The method is rapid, requiring little computational effort. But it is inaccurate, a large number of iterations may be necessary and, in some cases, convergence may not take place.

The vector addition method is based on addition of vector equations in a colour space, not of reflectance, but of an additive function (K-M function) of reflectance as in Equation [4.45]:

$$Vs = C_1V_1 + C_2V_2 + C_3V_3 + V_b \quad [4.45]$$

where V stands for the vector in Kubelka-Munk space, s and b denote standard and substrate, respectively. Three such equations can be set up for the three pseudo-tristimulus values $X_{V,i}$ in Kubelka-Munk space defined as in Equation [4.46]:

$$X_{V,i} = \sum_{\lambda=400}^{700} \left(\overline{x_{i,\lambda}} \cdot E_\lambda \right) \left(\left(\frac{K}{S} \right)_{b,\lambda} + \sum_{j=1}^3 C_j \cdot \alpha_{j,\lambda} \right) \quad [4.46]$$

where i stands for the three pseudo-tristimulus values, \bar{x}_i stands for three colour-matching functions, E stands for the energy distribution of the illuminant, λ stands for the 16 wavelengths between 400 and 700 nm, b stands for the substrate, C_j and α_j stands for concentration and alpha values of the j -th dye.

The only unknowns in Equation [4.38] are the dye concentrations, C_i , of the colourants. The accuracy of the solution of the equation is frequently insufficient, especially for bright colours and metamerич matches, because relatively small differences in K/S values at low absolute K/S values produce large differences in the approximation of the reflectance curve. The accuracy can be improved by using a suitable weighting factor, a derivative of additive function of the standard, $d(R)/dF(R)$, at each wavelength. The vector addition method with derivative weighting provides accurate colour match and the same inverted matrix can be used for iteration.

The vector addition operation is made through matrix operation as it is handled by digital computers very efficiently. The variables for Allen's solution, at 16 wavelengths from 400 to 700 nm at 20 nm interval, are as shown in Fig. 4.7.

As pseudo-tristimulus values in the K-M colour space are considered, which are additive in nature, we may write the following equation for complete tristimulus match:

Pseudo-tristimulus values of the standard = Pseudo-tristimulus values of the match (i.e. substrate + dye)

$$\text{i.e. MES} = \text{MEB} + \text{MEDC}$$

Multiplying weighting function, W on both the sides,

$$\begin{aligned} \text{MEWS} &= \text{MEWB} + \text{MEWDC} \\ \text{or } C &= (\text{MEWD})^{-1} \text{MEW}(S - B) \end{aligned} \quad [4.47]$$

The inverted matrix, $(\text{MEWD})^{-1}$, cannot be calculated beforehand, as W is based on the reflectance factor of the standard or the object colour to be matched, which will change as and when a new match is required. The above vectors are restricted for 3-colourant matches. If 4- or 5-colourant formulations are necessary, we get additional degrees of freedom. Hence, in addition to the pseudo-tristimulus values under daylight (D_{65}), we may consider X values for 4-colourant formulation and X and Y values for 5-colourant formulations under tungsten lamp (illuminant A).

4.11.2 Final solution

The initial solution provides an approximate formulation which allows a good approximation of the reflectance factor of the standard. The accuracy

$$D = \begin{vmatrix} F(R)_{400}^1 & F(R)_{400}^2 & F(R)_{400}^3 \\ F(R)_{420}^1 & F(R)_{420}^2 & F(R)_{420}^3 \\ \dots & \dots & \dots \\ F(R)_{700}^1 & F(R)_{700}^2 & F(R)_{700}^3 \end{vmatrix} \quad 16 \times 3 \text{ matrix for additive functions at unit conc. of 3 dyes}$$

$$S = \begin{vmatrix} F(R)_{400}^{\text{std}} \\ F(R)_{420}^{\text{std}} \\ \dots \\ F(R)_{700}^{\text{std}} \end{vmatrix} \quad 16 \times 1 \text{ matrix for additive functions of the standard colour}$$

$$B = \begin{vmatrix} F(R)_{400}^{\text{sub}} \\ F(R)_{420}^{\text{sub}} \\ \dots \\ F(R)_{700}^{\text{sub}} \end{vmatrix} \quad 16 \times 1 \text{ matrix for additive functions of the substrate}$$

$$M = \begin{vmatrix} \overline{x}_{400} & \overline{x}_{420} & \dots & \overline{x}_{700} \\ \overline{y}_{400} & \overline{y}_{420} & \dots & \overline{y}_{700} \\ \overline{z}_{400} & \overline{z}_{420} & \dots & \overline{z}_{700} \end{vmatrix} \quad 3 \times 16 \text{ diagonal matrix for the colour matching functions}$$

$$E = \begin{vmatrix} E_{400} & 0 & \dots & 0 \\ 0 & E_{420} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & E_{700} \end{vmatrix} \quad 16 \times 16 \text{ diagonal matrix for relative energy distribution of the illuminant generally D}_{65}$$

$$W = \begin{vmatrix} W_{400} & 0 & \dots & 0 \\ 0 & W_{420} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & W_{700} \end{vmatrix} \quad 16 \times 16 \text{ diagonal matrix for weighting function, a derivative of the additive function of the standard}$$

$$C = \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} \quad 3 \times 1 \text{ matrix for three unknown dye concentrations}$$

4.7 The variables for Allen's solution.

of approximation is good if the proposed formulation is non-metameric to the standard. The initial match may not be very satisfactory for several reasons, such as non-linearity of the additive function with concentration, non-linear relation between tristimulus values and concentration, etc. To get a closer match with the standard, correction of the initial solution may be necessary, and this is carried out by computer iteration technique. The principle of the operation is to find the change of tristimulus values with change of concentration of each component dye, and then provide increments of

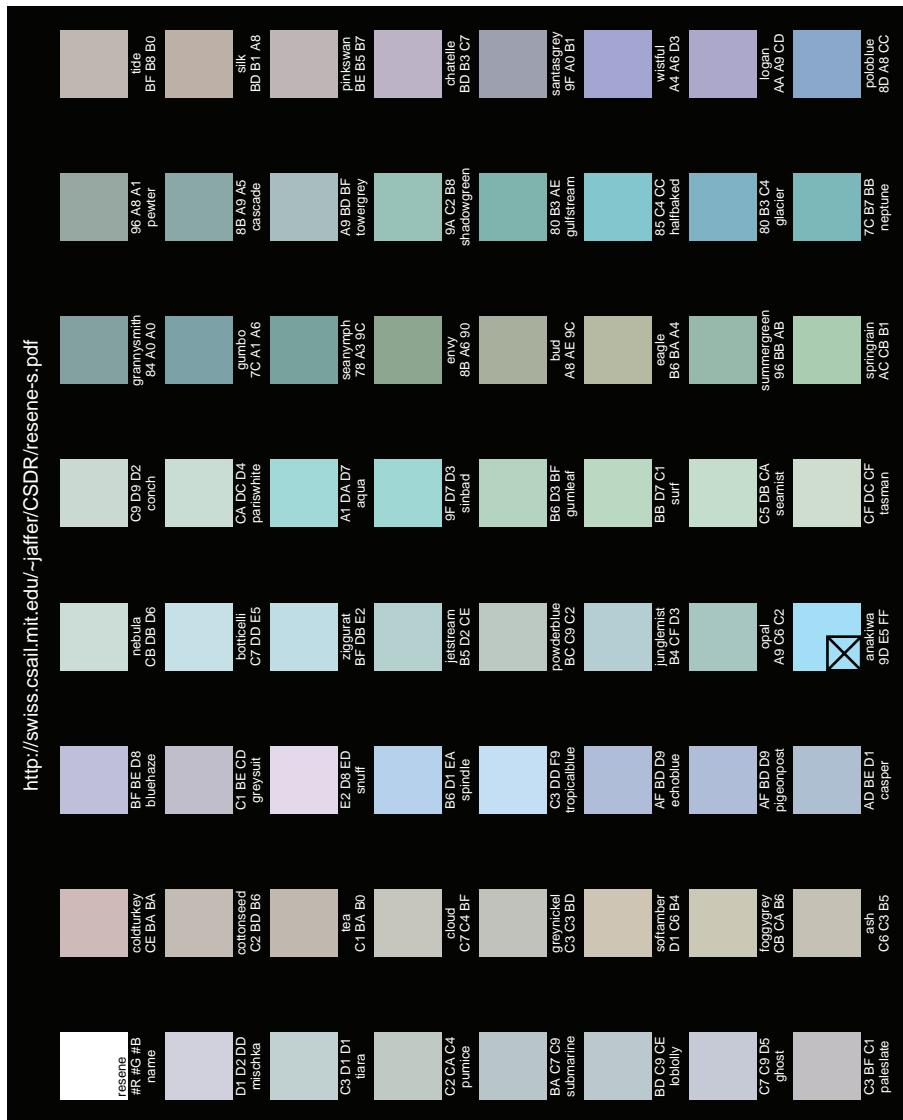


Plate 1 (Chapter 1) A colour chart of idiosyncratic colours by Jaffar available at <http://people.csail.mit.edu/jaffer/Colour/CSDR>

Step 1. Classification of achromatic colours according to lightness



Black, greys, white (in the order of increasing lightness)

Step 2. Classification of chromatic colours according to common names
(principal hues)



Red Yellow Green Blue Purple

Step 3. Further classification of chromatic colours into intermediate hues



Yellow-Green Green Green-Blue

Step 4. Classification of chromatic colours with varying lightness (e.g. same red hue but in the order increasing lightness, very dark red to pink)



Step 5. Classification of chromatic colours with varying saturation or chroma
(e.g. light bluish red with increasing chroma)



Plate II (Chapter 1) Steps for classifying object colours according to colour attributes.



Plate III (Chapter 1) Pantone colour guide.



Plate IV (Chapter 1) Colour harmony manual. (Container Corporation of America.)

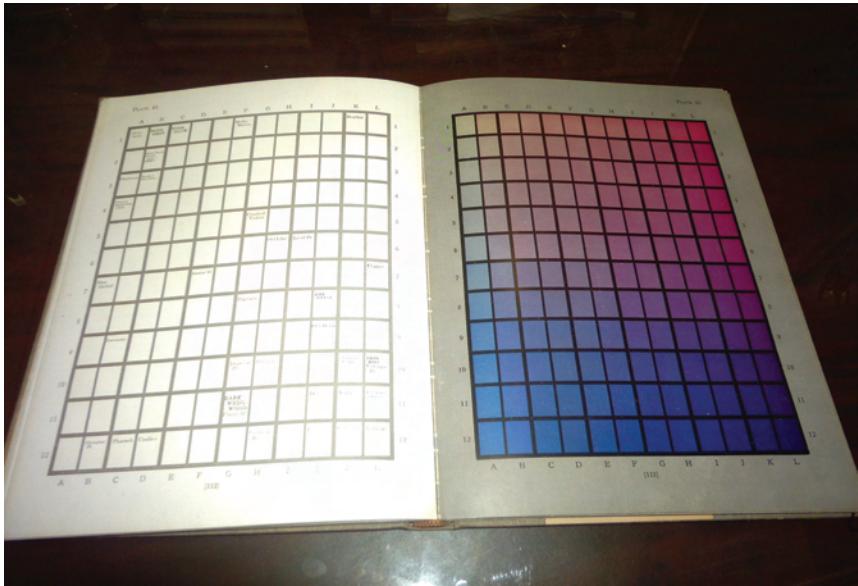


Plate V (Chapter 1) The Dictionary of Colour by Maerz and Paul.

White	-Ish white	Very pale	Very light	Brilliant	
Light gray	Light-ish gray	Pale, light grayish	Light		Vivid
Medium gray	-Ish gray	Grayish	Moderate	Strong	
Dark gray	Dark-ish gray	Dark grayish	Dark	Deep	
Black	-Ish black	Blackish	Very dark	Very deep	

Plate VI (Chapter 1) An example of ISCC-NBS system of colour description (hue name with modifiers).

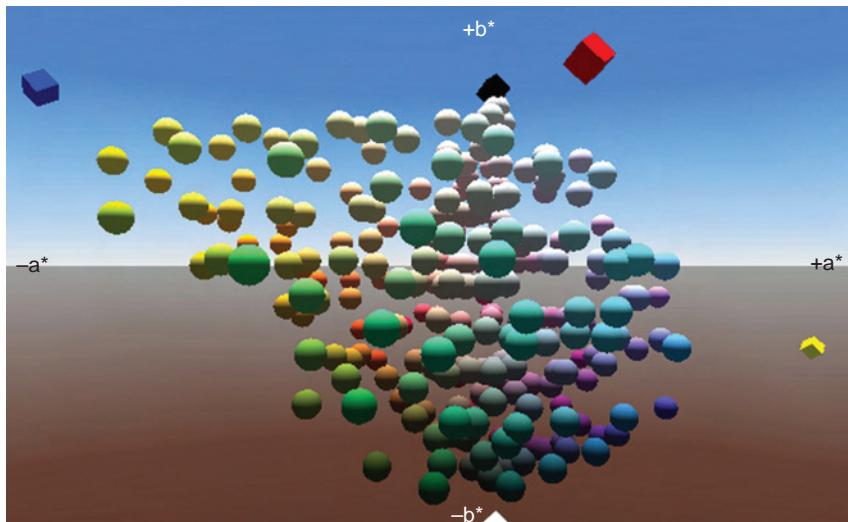


Plate VII (Chapter 1) ISCC-NBS centroid colours shown in CIELAB space (Source: <http://people.csail.mit.edu/jaffer/Color/Dictionaries>, with permission).

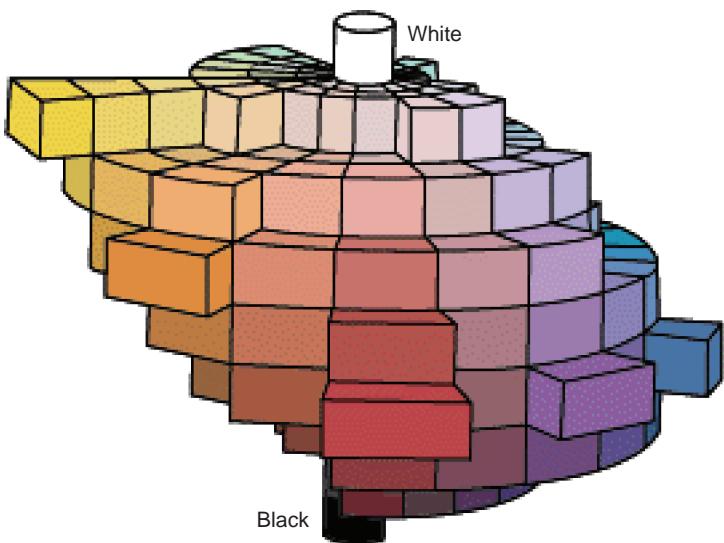


Plate VIII (Chapter 2) Munsell colour solid (© X-Rite).

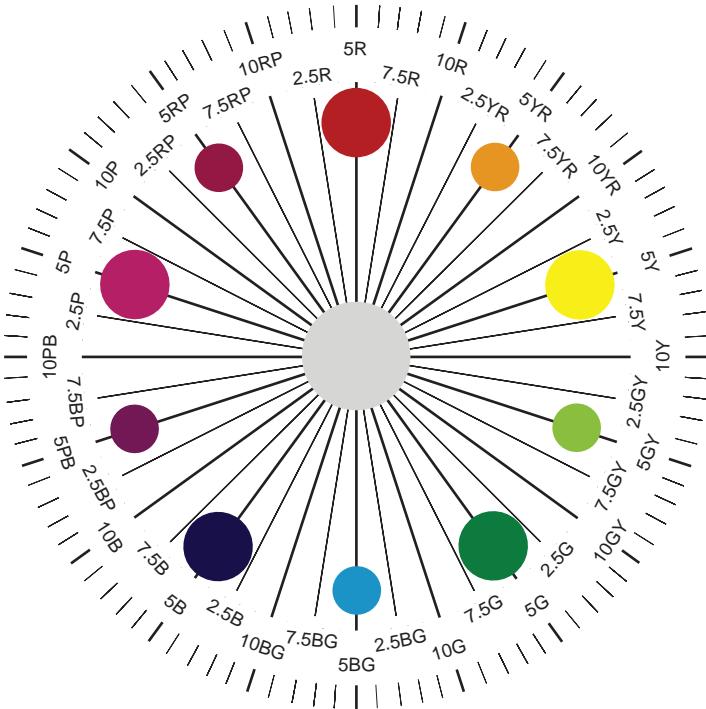


Plate IX (Chapter 2) Munsell Hue circle (© X-Rite).

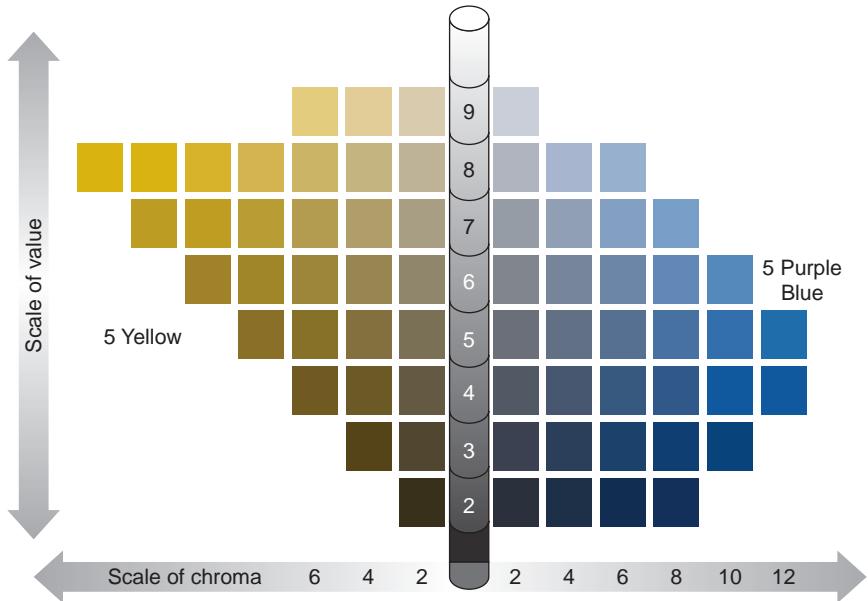


Plate X (Chapter 2) Munsell Value versus Chroma charts for 5Y and 5PB Munsell hues (© X-Rite).

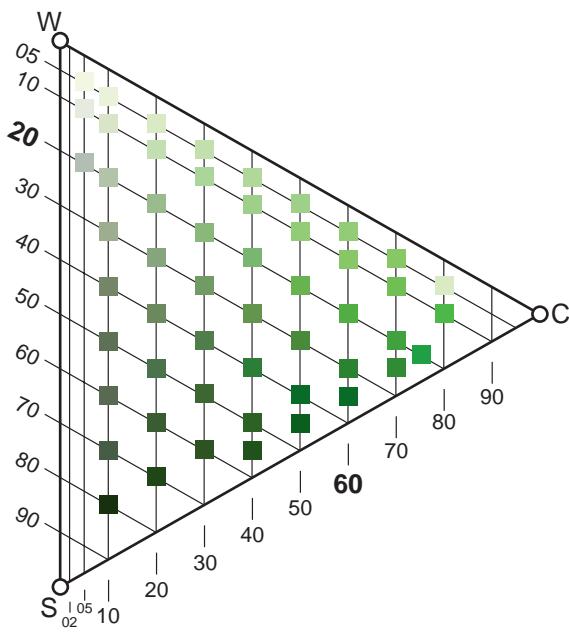


Plate XI (Chapter 2) NCS colour triangle (NCS – Natural Colour System® © property of and used on licence from NCS Colour AB, Stockholm 2014. References to NCS® © in this publication are used with permission from NCS Colour AB.)

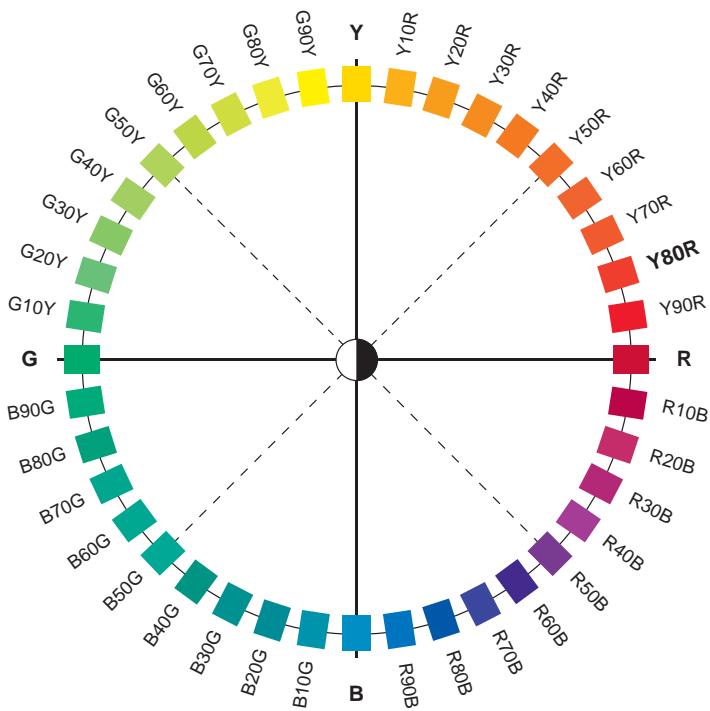


Plate XII (Chapter 2) NCS Colour circle (NCS – Natural Colour System®© property of and used on licence from NCS Colour AB, Stockholm 2014. References to NCS®© in this publication are used with permission from NCS Colour AB.)

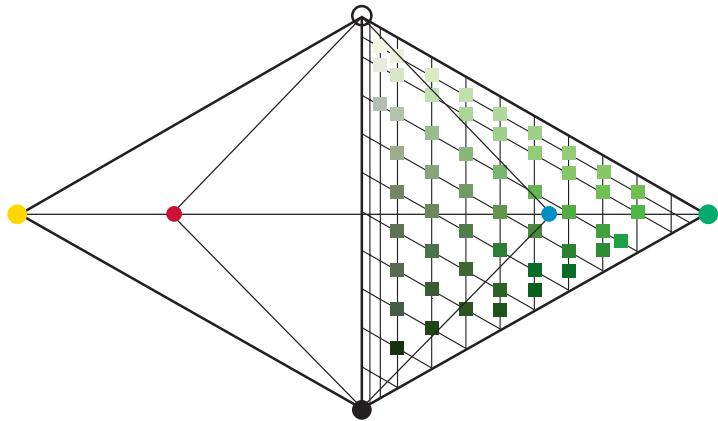


Plate XIII (Chapter 2) NCS colour solid (NCS – Natural Colour System®© property of and used on licence from NCS Colour AB, Stockholm 2014. References to NCS®© in this publication are used with permission from NCS Colour AB.)

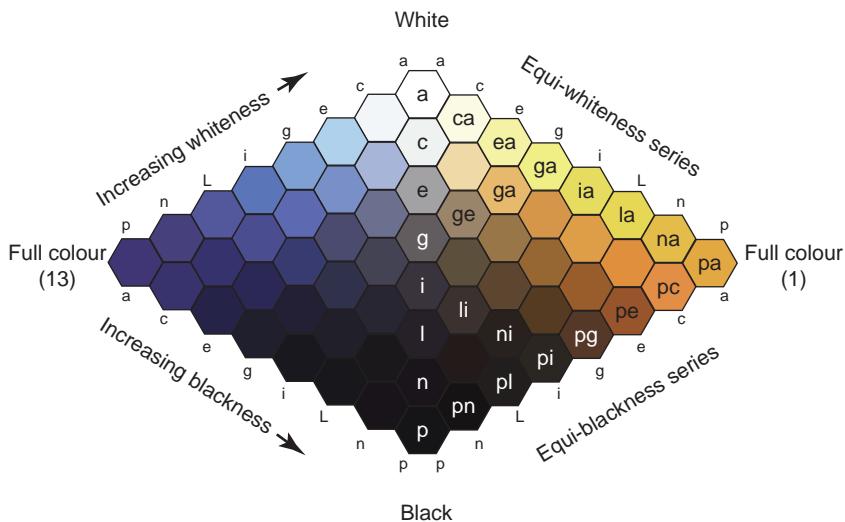


Plate XIV (Chapter 2) A vertical cross-section through Ostwald double-cone colour solid.

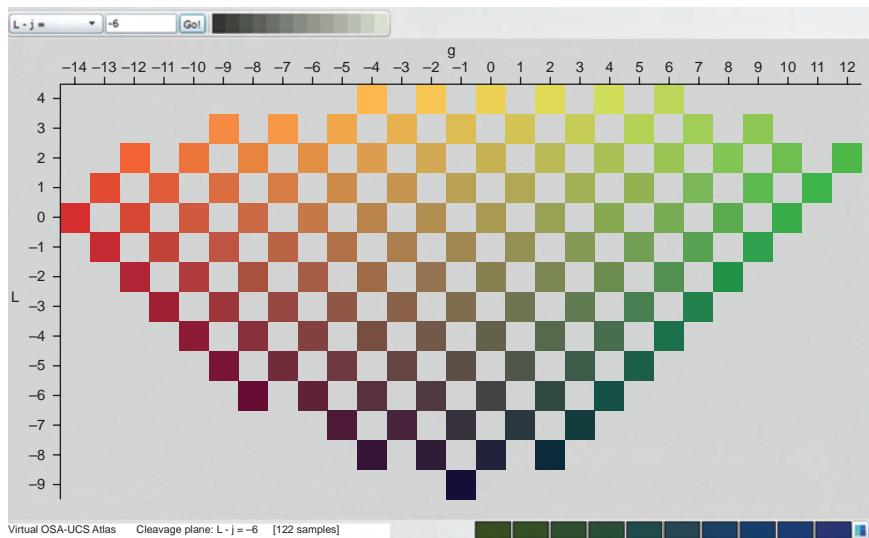


Plate XV (Chapter 2) OSA-UCS colour system at cleavage plane of $L - j = -6$ (Virtual Atlas, Virtual Colour Systems Ltd. <http://www.vcsconsulting.co.uk/Colour/Help/ColourOrderSystems/OSAUCS.html> with permission).

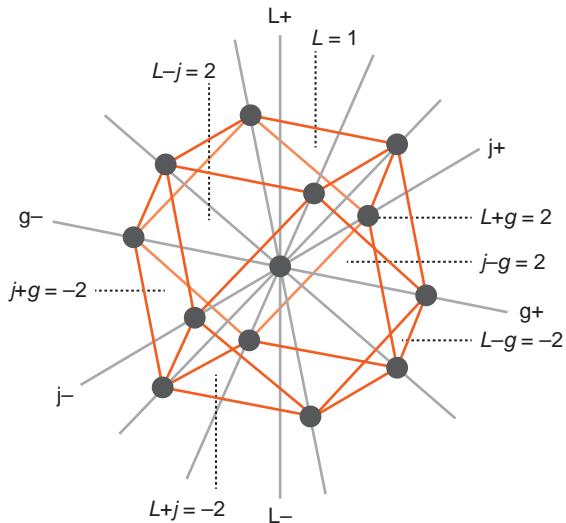


Plate XVI (Chapter 2) OSA-UCS cubo-octahedron colour space (<http://www.handprint.com/HP/WCL/color7.html> last revised 2014 • © 2014 Bruce MacEvoy).

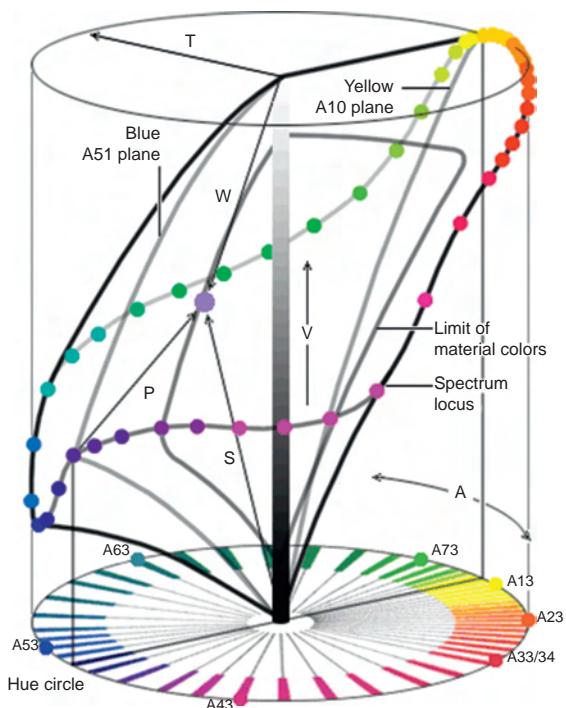


Plate XVII (Chapter 2) Coloroid colour space.

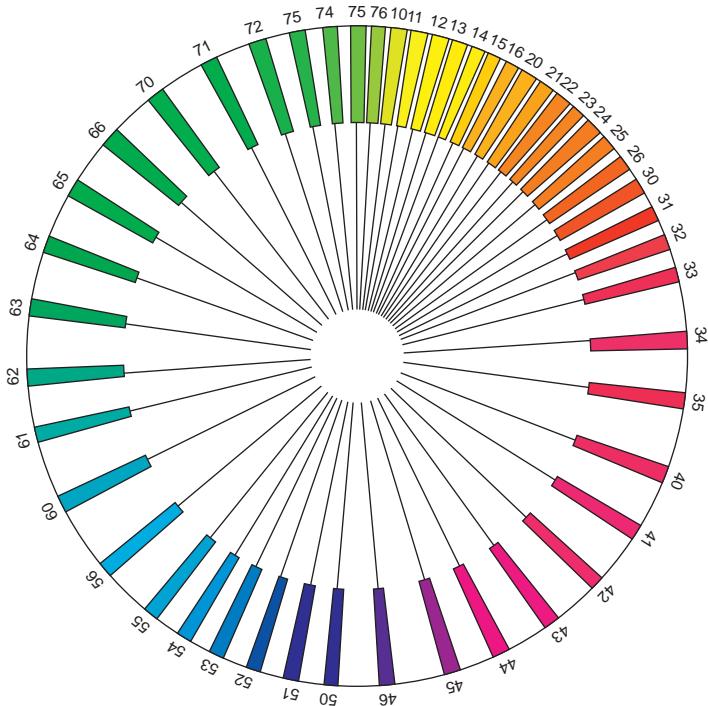


Plate XVIII (Chapter 2) Coloroid hue circle.

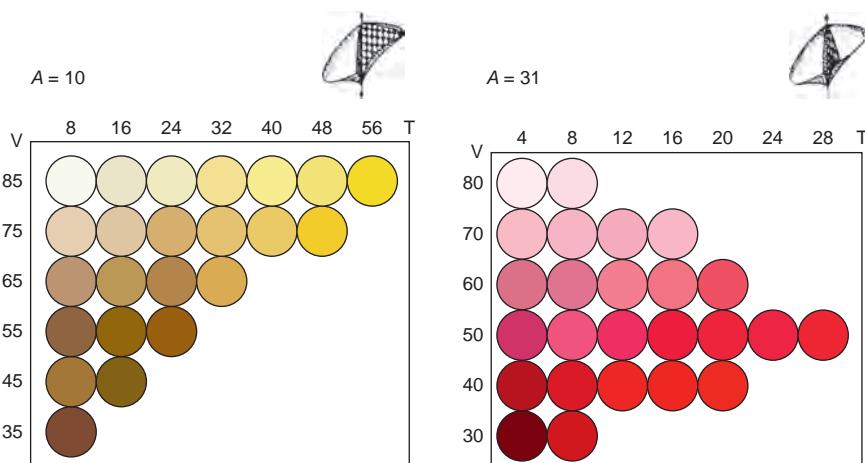


Plate XIX (Chapter 2) Two pages from Coloroid atlas having constant hue (A) of 10 (yellow) and 31 (red).

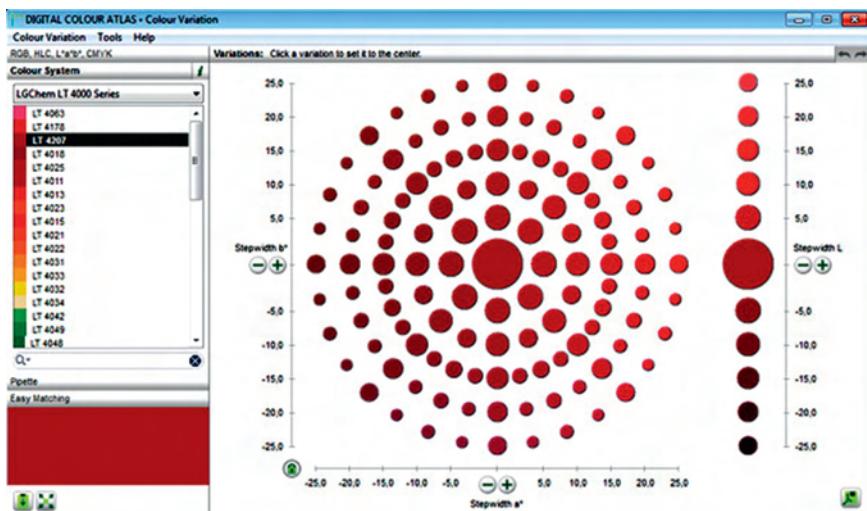


Plate XX (Chapter 2) A colour variation palette of Digital Colour Atlas 5
© dtp studio Oldenburg).

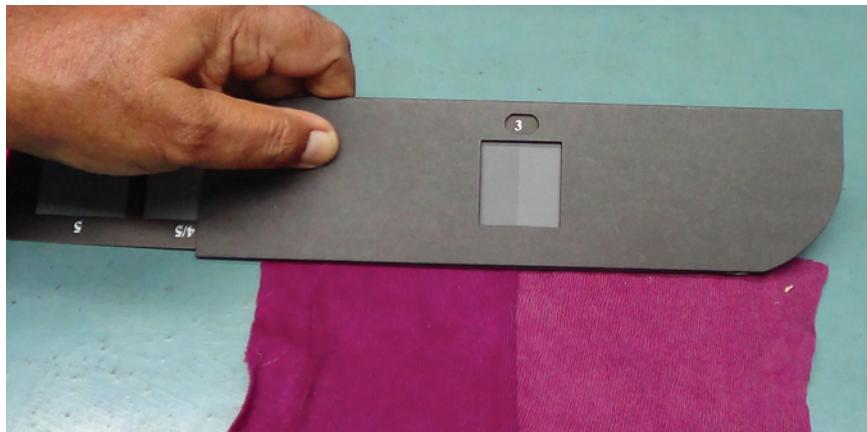


Plate XXI (Chapter 3) Assessment of colour difference using grey scale.

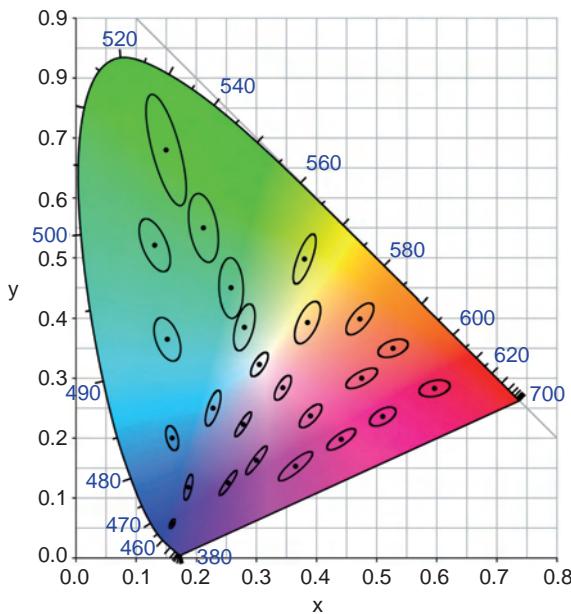


Plate XXII (Chapter 3) Twenty-five Macadam colour discrimination ellipses in CIE 1931 chromaticity diagram at constant lightness, L^* (with permission from Corsoluce www.corsoluce.ru).

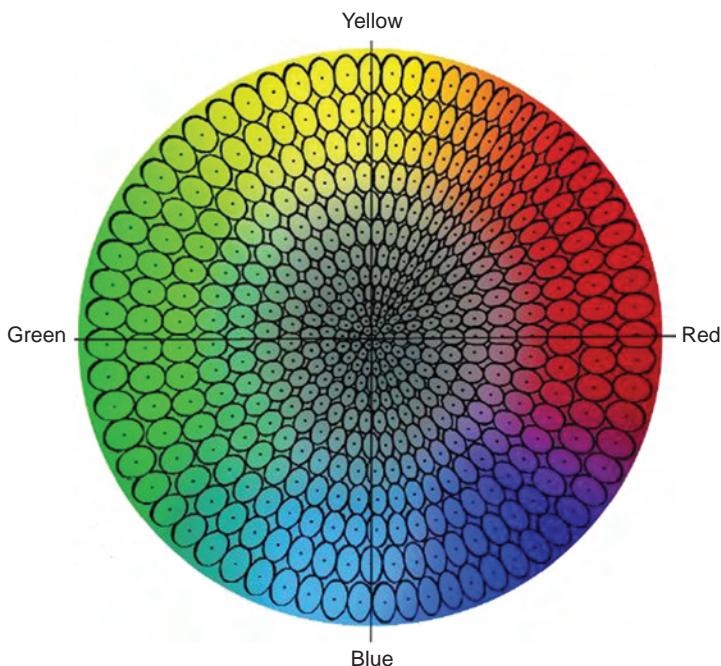


Plate XXIII (Chapter 3) CMC colour tolerance ellipsoids in CIELAB colour space (with permission from SDC).



Plate XXIV (Chapter 5) shows a metameristic fabric set under three illuminants Daylight fluorescent lamp (D65.)



Plate XXV (Chapter 5) Departmental store lamp (TL84.)



Plate XXVI (Chapter 5) The above metameric set under Tungsten lamp (illuminant A).



Plate XXVII (Chapter 7) Original photograph (the original photograph used to create Plates XXVII to XXX, XXXIII to XXXIX, and XLIII-XLIV was kindly supplied by Paritosh Prayagi).



Plate XXVIII (Chapter 7) Red bias.



Plate XXIX (Chapter 7) Green bias.



Plate XXX (Chapter 7) Blue bias.

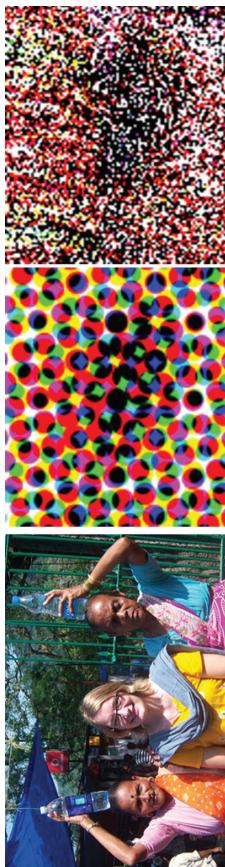


Plate XXXI (Chapter 7) Continuous-tone original, colour print, with AM and FM screening.

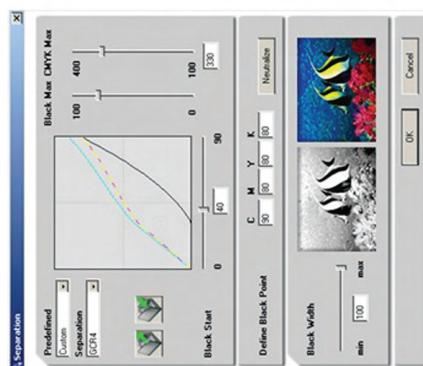
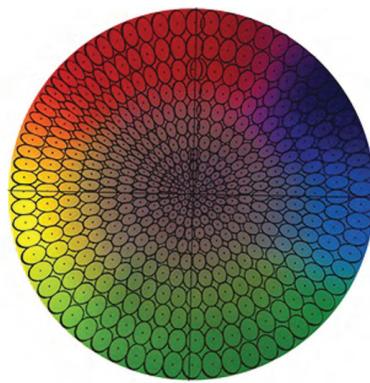


Plate XXXII (Chapter 7) Grey settings in colour management software.

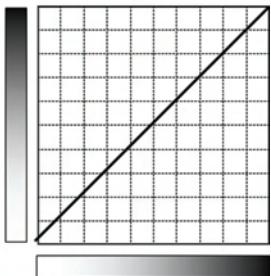


Plate XXXIII (Chapter 7) Facsimile reproduction of original.

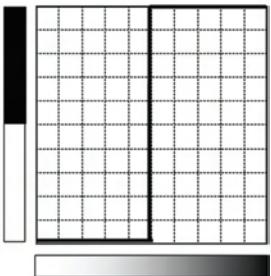


Plate XXXIV (Chapter 7) Very high contrast reproduction, also called posterization.

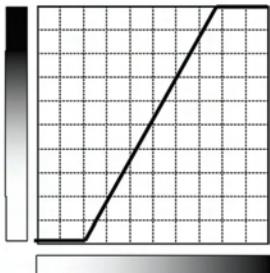


Plate XXXV (Chapter 7) Loss of highlight and shadow details, high contrast mid-tones.

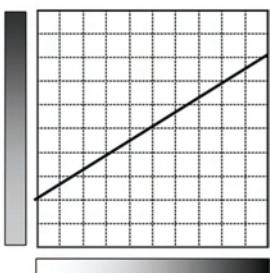


Plate XXXVI (Chapter 7) Dirty highlights and lighter shadows, low contrast mid-tones.



Plate XXXVII (Chapter 7) Cyan tone change giving reddish effect.



Plate XXXVIII (Chapter 7) Magenta tone change giving greenish effect.



Plate XXXIX (Chapter 7) Yellow tone change giving bluish effect.

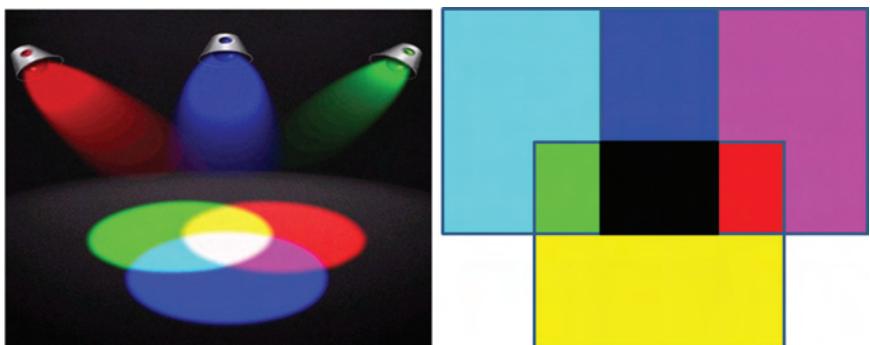


Plate XL (Chapter 7) Additive (left) and subtractive (right) colour reproduction.

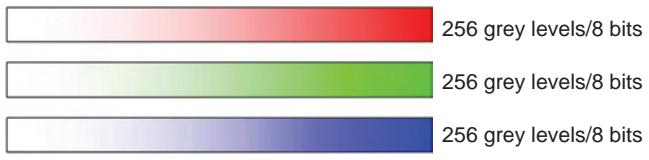
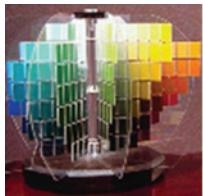


Plate XLI (Chapter 7) RGB bits and grey levels.

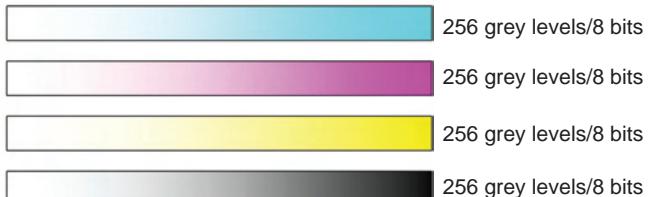
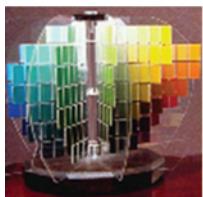


Plate XLII (Chapter 7) CMYK bits and grey levels.



Plate XLIII (Chapter 7) Normal 3-colour and skeleton black.



Plate XLIV (Chapter 7) GCR 3-colour and full scale black.

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	

Plate XLV (Chapter 7) Reproduction colours.

WHITE	RED	GREEN	BLUE	BLACK
3-COLOUR	CYAN	MAGENTA	YELLOW	

Red channel image

WHITE	RED	GREEN	BLUE	BLACK
3-COLOUR	CYAN		YELLOW	

Green channel image

	GREEN	BLUE	BLACK	

Blue channel image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	

Cyan image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	

Magenta image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	

Yellow image

Plate XLVII (Chapter 7) Photographic prints.

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	4-Colour

Cyan image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	4-Colour

Magenta image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	4-Colour

Yellow image

White	Red	Green	Blue	Black
3-Colour	Cyan	Magenta	Yellow	4-Colour

Black image

Plate XLVIII (Chapter 7) Photomechanical printing systems.



Plate XLIX (Chapter 7) Process colours cyan, magenta, yellow with ideal colour characteristics.

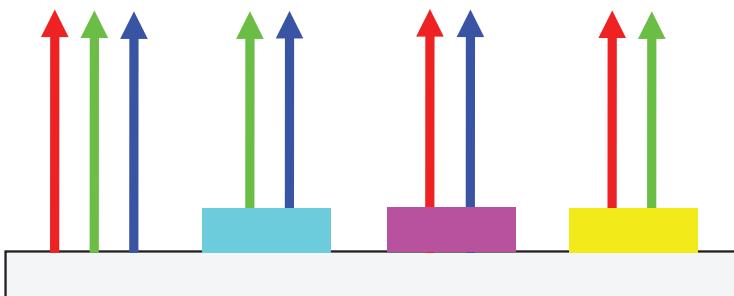


Plate L (Chapter 7) Ideal colour transmissions and reflections.

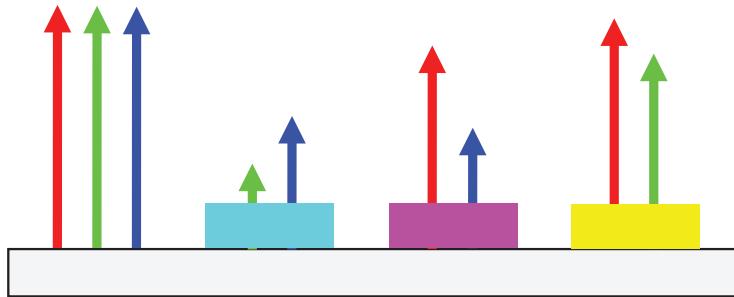


Plate L1 (Chapter 7) Colours deficiencies.

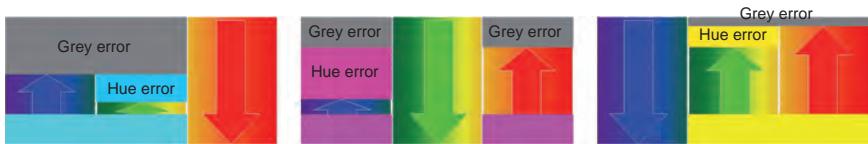


Plate LII (Chapter 7) Colour transmissions and reflections from colourants.

	Substrate			Cyan			Magenta			Yellow		
Reflection Transmission	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
	100	100	100	0	100	100	100	0	100	100	100	0

Plate LIII (Chapter 7) Ideal reflection / transmission of light.

	Substrate			Cyan			Magenta			Yellow		
Reflection Transmission	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
	100	100	100	0	30	55	80	0	45	95	85	0

Plate LIV (Chapter 7) Average actual reflection/transmission of light.

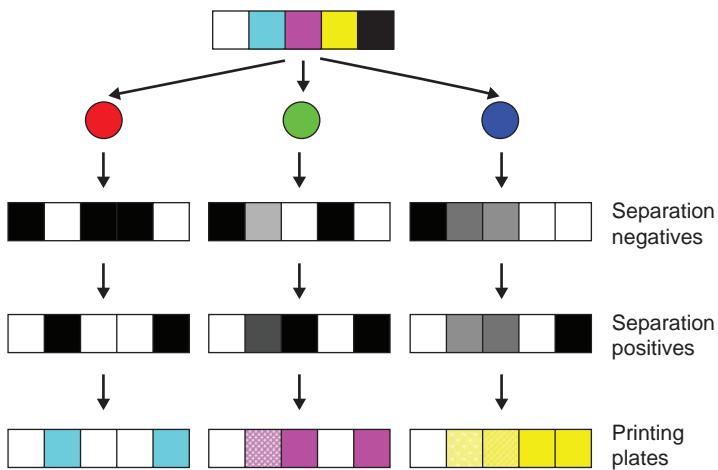


Plate LV (Chapter 7) Uncorrected separations.

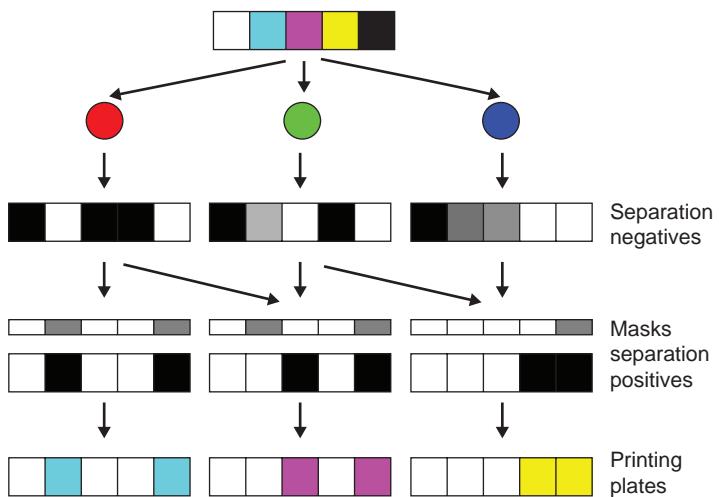


Plate LVI (Chapter 7) Corrected separations.

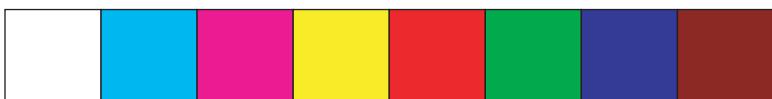


Plate LVII (Chapter 7) Colours present in any three and four colour photomechanical reproduction.

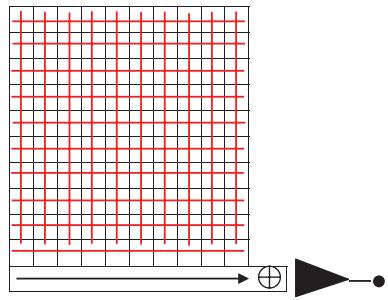
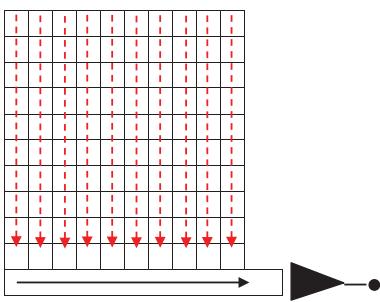


Plate LVIII (Chapter 7) CCD sensor (a) and CMOS sensor (b).

Colour matching functions for 10° -Observer and RGB Sensor Sensitivity

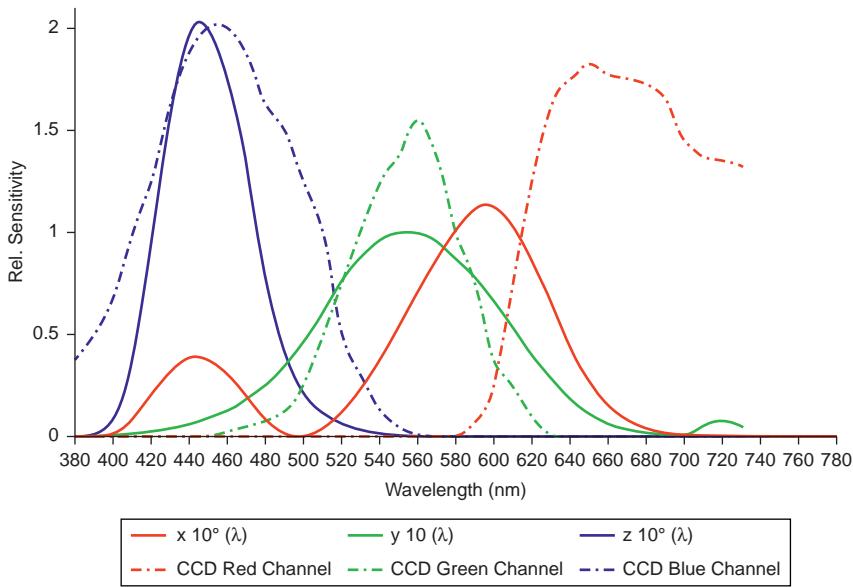


Plate LIX (Chapter 7) RGB sensitivity of CCD sensors vs human eye
(Chromasens GmbH, Konstanz, Germany).

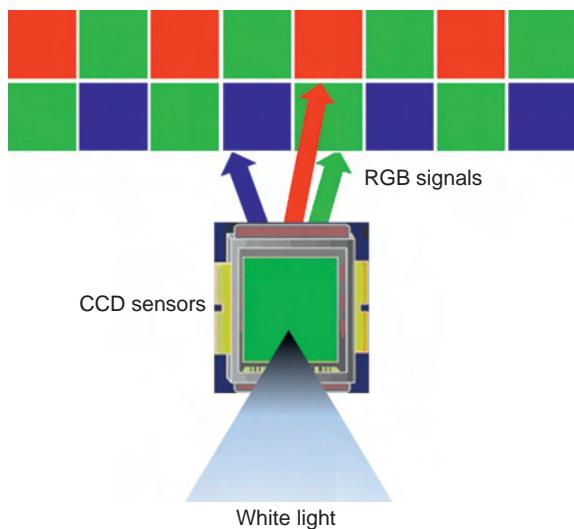


Plate LX (Chapter 7) CCD and CMOS sensor.



Plate LXI (Chapter 7) Digital photography and variety of lighting (a) sunlight (b) yellowish light and (c) bluish light.

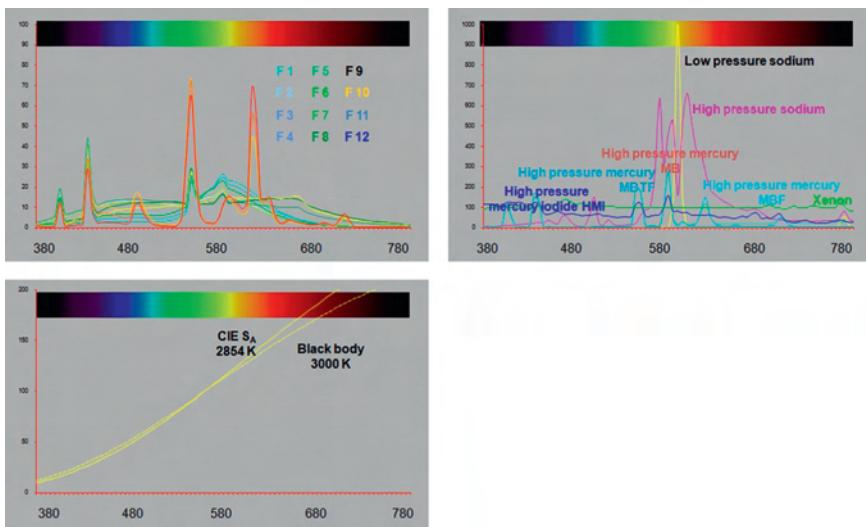


Plate LXII (Chapter 7) Spectrum of various light sources fluorescent (top left), gas discharge (top right), tungsten (left) (based on tables by Hunt and Pointer, 2011, p 356–378, Measuring Colour, John Wiley & Sons, Ltd., England).

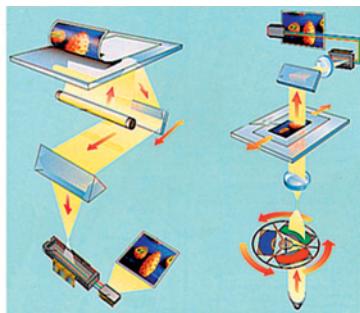


Plate LXIII (Chapter 7) Flatbed scanner. CCD sensor, scanning mechanism (Scitex, Agfa 1997, p 13).



Plate LXIV (Chapter 7) Drum scanner, (Crosfield Electronics, Dainippon Screen) Photomultipliers scanning mechanism (Agfa CD-ROM).

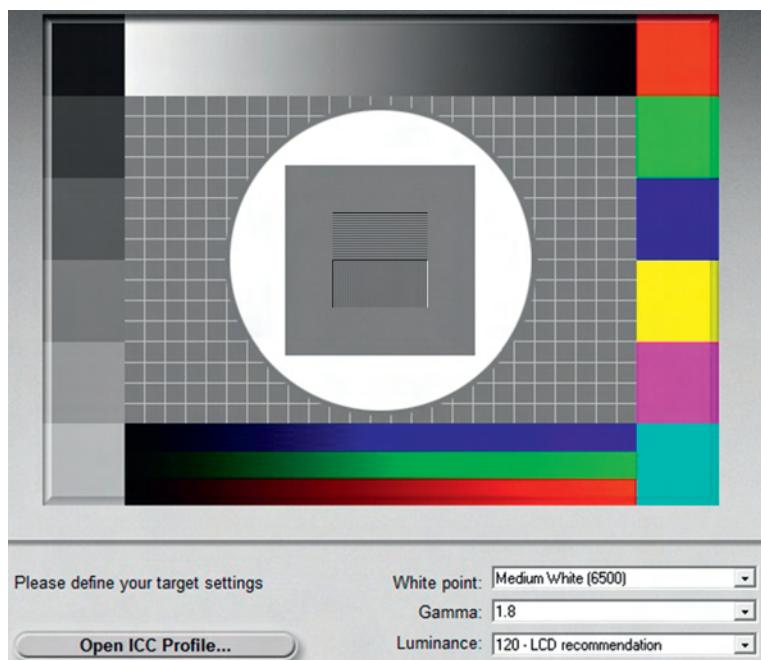


Plate LXV (Chapter 7) Setting monitor white point.

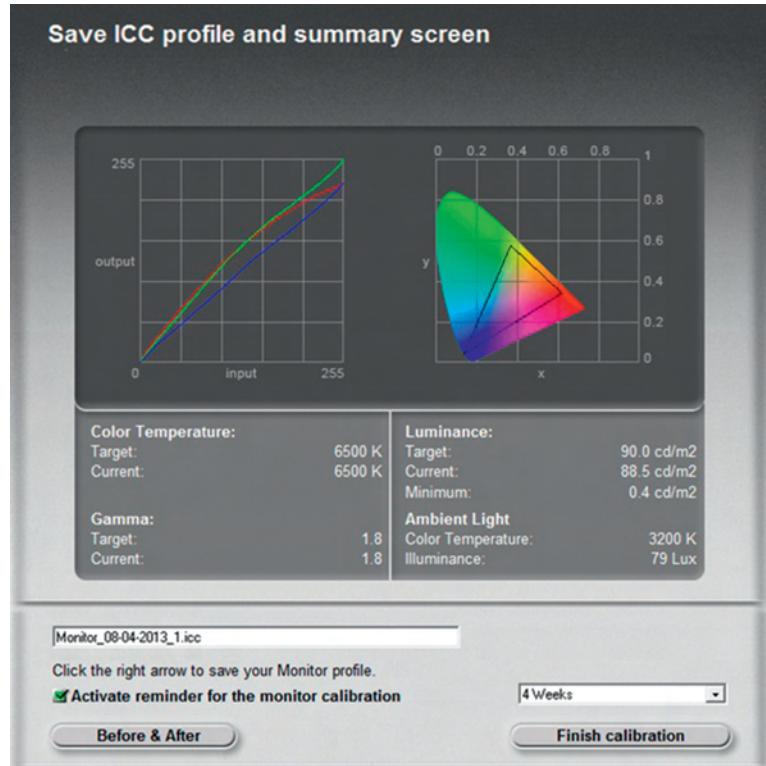


Plate LXVI (Chapter 7) Calibrated monitor settings.



Plate LXVII (Chapter 7) Colour variation across devices from capturing to output (a) capture (b) display and (c) print (Agfa CD-ROM).

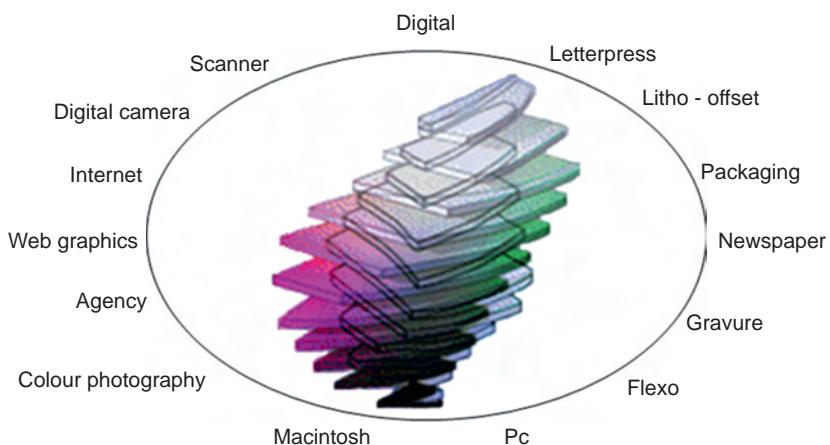


Plate LXVIII CIE colour model central to all device-dependent colour systems.

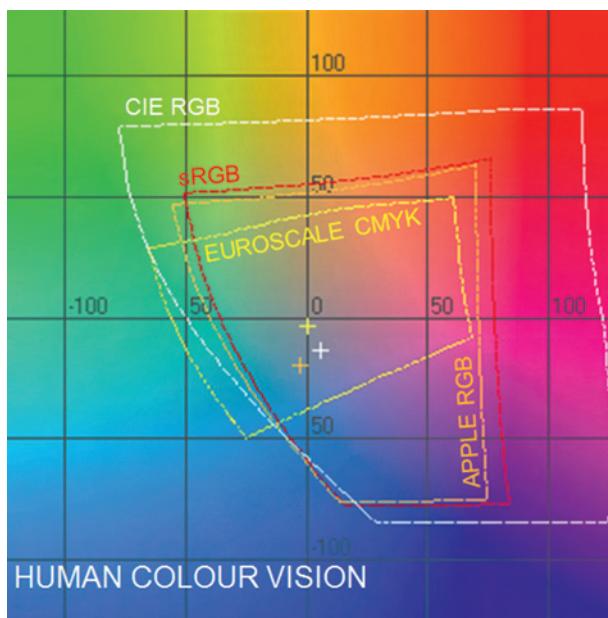


Plate LXIX (Chapter 7) Colour gamut of various reproduction systems.

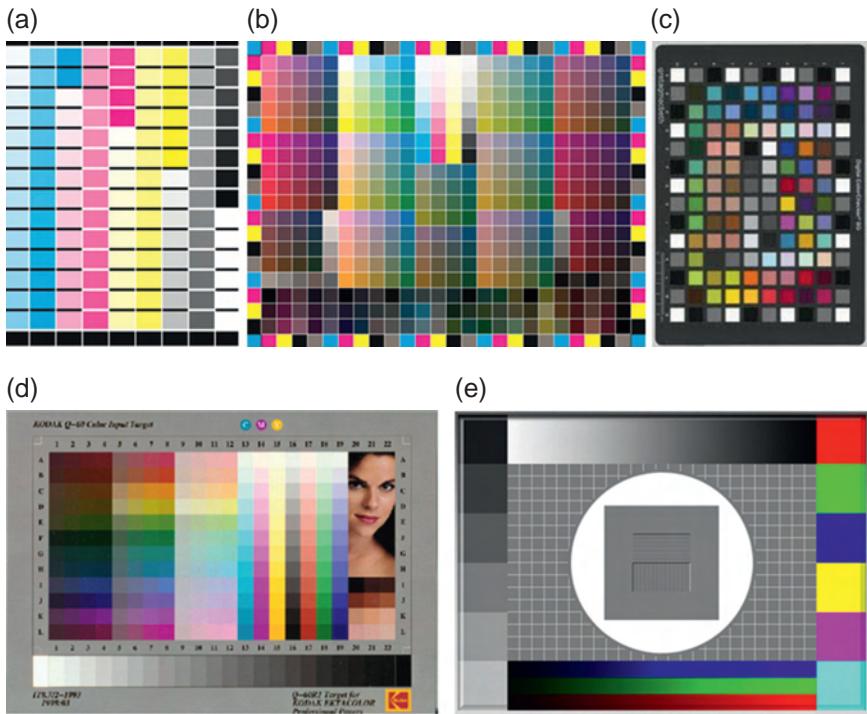


Plate LXX (Chapter 7) Test chards: (a) printer calibration (GretagMacbeth); (b) printer characterization (GretagMacbeth); (c) camera characterization (GretagMacbeth); (d) scanner characterization (Kodak); (e) display monitor characterization.



Plate LXXI (Chapter 7) Colour management through devices.

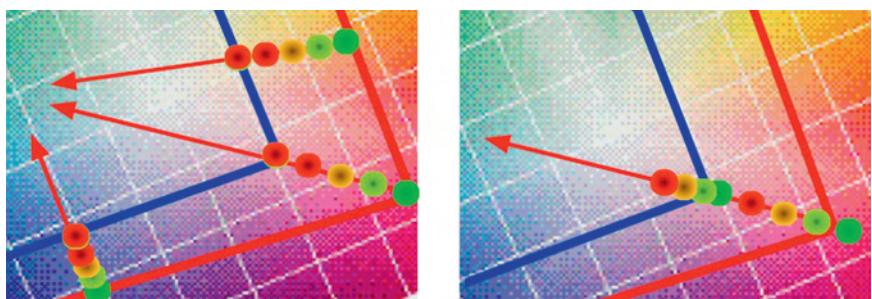
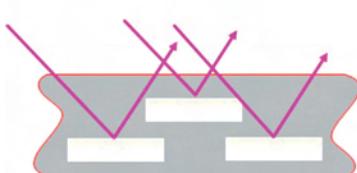


Plate LXXII (Chapter 7) Colour gamut compression.

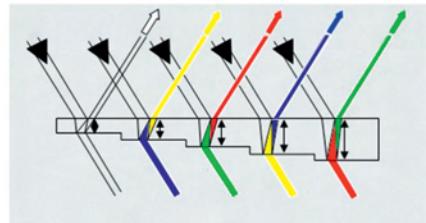
(a)



(b)



(c)



*Plate LXXIII (Chapter 7) (a) Metallic flakes (b) Metallic surface reflection
(c) Perlescent material (Based on information from E. Merck, Germany).*

$$\Delta C = \begin{vmatrix} \Delta C_1 \\ \Delta C_2 \\ \Delta C_3 \end{vmatrix} \quad \text{3 x 1 matrix where } \Delta C_i \text{ is the concentration adjustment of the colourant } i$$

$$T = \begin{vmatrix} \Delta X \\ \Delta Y \\ \Delta Z \end{vmatrix} \quad \text{3 x 1 matrix denotes differences in tristim units values of the standard and calculated formula}$$

4.8 The two additional matrices for correction program.

dye concentration in the initial formulation till the difference of tristimulus value of the standard and proposed formulation reaches an acceptable level.

Allen's algorithm uses the same inverted matrix employed for initial solution for correction program. The two additional matrices are shown in Fig. 4.8.

Allen proposed the following correction matrix as in Equation [4.48]:

$$\Delta C = (\text{MEWD})^{-1} T \quad [4.48]$$

The correction to the initial predicted recipe is then made by the elements of ΔC matrix, and then the pseudo-tristimulus and the consequent value of the T matrix is recalculated. The iteration process is repeated till the solution gives a close match to the standard, i.e. very low values for the elements of matrix T .

4.12 Algorithm for two-constant theory

Allen (1974) proposed another algorithm for the formulation of the colourants obeying two-constant theory, which is a modification of his earlier algorithm (Allen, 1966). He assumed that:

1. The film is opaque to visible light of all wavelengths,
2. Both absorption and scattering coefficients of the film are separate linear functions of concentration,
3. Four colourants are present in the system to have 3 degrees of freedom.

For the initial solution, scattering coefficient of the standard is assumed to be unity, i.e. $S_s = 1$. The fractional concentration of the total colourant in the opaque film is defined as C_T . The concentrations of the three colourants are expressed as similar fractions C_1, C_2 and C_3 . The concentration of the fourth colourant C_4 , usually white pigment, is then calculated as $C_T - C_1 - C_2 - C_3$.

The absorption and scattering coefficient matrices of the three colourants and separately for the fourth colourant are shown in Fig. 4.9.

$$K_i = \begin{vmatrix} K_{400}^1 & K_{400}^2 & K_{400}^3 \\ K_{420}^1 & K_{420}^2 & K_{420}^3 \\ \cdots & \cdots & \cdots \\ K_{700}^1 & K_{700}^2 & K_{700}^3 \end{vmatrix} \quad K_4 = \begin{vmatrix} K_{400}^4 \\ K_{420}^4 \\ \cdots \\ K_{700}^4 \end{vmatrix}$$

$$S_i = \begin{vmatrix} S_{400}^1 & S_{400}^2 & S_{400}^3 \\ S_{420}^1 & S_{420}^2 & S_{420}^3 \\ \cdots & \cdots & \cdots \\ S_{700}^1 & S_{700}^2 & S_{700}^3 \end{vmatrix} \quad S_4 = \begin{vmatrix} S_{400}^4 \\ S_{420}^4 \\ \cdots \\ S_{700}^4 \end{vmatrix}$$

4.9 The absorption and scattering coefficient matrices for four colorants.

$$fK_s = \begin{vmatrix} K_{400}^{\text{std}} \\ K_{420}^{\text{std}} \\ \cdots \\ K_{700}^{\text{std}} \end{vmatrix} \quad S_s = \begin{vmatrix} S_{400}^{\text{std}} \\ S_{420}^{\text{std}} \\ \cdots \\ S_{700}^{\text{std}} \end{vmatrix}$$

$$K_b = \begin{vmatrix} K_{400}^{\text{sub}} \\ K_{420}^{\text{sub}} \\ \cdots \\ K_{700}^{\text{sub}} \end{vmatrix} \quad S_b = \begin{vmatrix} S_{400}^{\text{sub}} \\ S_{420}^{\text{sub}} \\ \cdots \\ S_{700}^{\text{sub}} \end{vmatrix}$$

4.10 The absorption and scattering coefficient matrices for the standard and substrate.

For the standard and substrate 16×1 matrices can be written, separately for absorption and scattering coefficients as shown in Fig. 4.10.

As it is assumed that $S_s = 1$, the following equation may be written as in Equation [4.49]:

$$K_{\text{std},L} = \frac{(1 - R_L^s)^2}{2R_L^s} \quad [4.49]$$

where R_L^s is the reflectance of the standard at the wavelength L .

$$W_s = \begin{vmatrix} W_{s, 400} & 0 & \dots & 0 \\ 0 & W_{s, 420} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & W_{s, 700} \end{vmatrix}$$

$$W_k = \begin{vmatrix} W_{k, 400} & 0 & \dots & 0 \\ 0 & W_{k, 420} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & W_{k, 700} \end{vmatrix}$$

4.11 The 16×16 diagonal matrices for the weighting vectors, W_k and W_s .

The two weighting functions (Equations [4.50] and [4.51]) for absorption and scattering derived from the reflectance factor of the standard are as follows:

$$W_k = +\frac{-2(R_L^s)^2}{1-(R_L^s)^2} \quad [4.50]$$

$$W_s = \frac{R_L^s(1-R_L^s)}{1+R_L^s} \quad [4.51]$$

The weighting vectors, W_k and W_s , are then defined by the 16×16 diagonal matrices as shown in Fig. 4.11. The other two matrices required for initial solution are shown in Fig. 4.12.

We may write an equation similar to Equation [4.47], the solution of which gives the concentration of the colourant.

$$\text{If we write, } W_K(K_i - K_4 U) + W_S(S_i - S_4 U) = P$$

$$\text{and } W_K[K_s - C_T K_4 - (1 - C_T)K_b] + W_S[S_s - C_T S_4 - (1 - C_T)S_b] = Q$$

$$C = (\text{MEP})^{-1} \text{ MEQ} \quad [4.52]$$

where M and E are the matrices for the colour-matching functions and energy distribution of the illuminant, as defined in the case of single-constant theory. Good approximations are generally obtained in spite of the very optimistic assumption $S_s = 1$. For final solution, the same inverted

$$C = \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} \quad \text{and} \quad U = [1 \ 1 \ 1]$$

4.12 The two additional matrices required for initial solution.

matrix, $(MEP)^{-1}$ may be used as in the case of single constant, and the equation for correction is similar to Equation [4.48] and may be written as Equation [4.53]:

$$\Delta C = (MEP)^{-1} T \quad [4.53]$$

4.13 Reformulation program

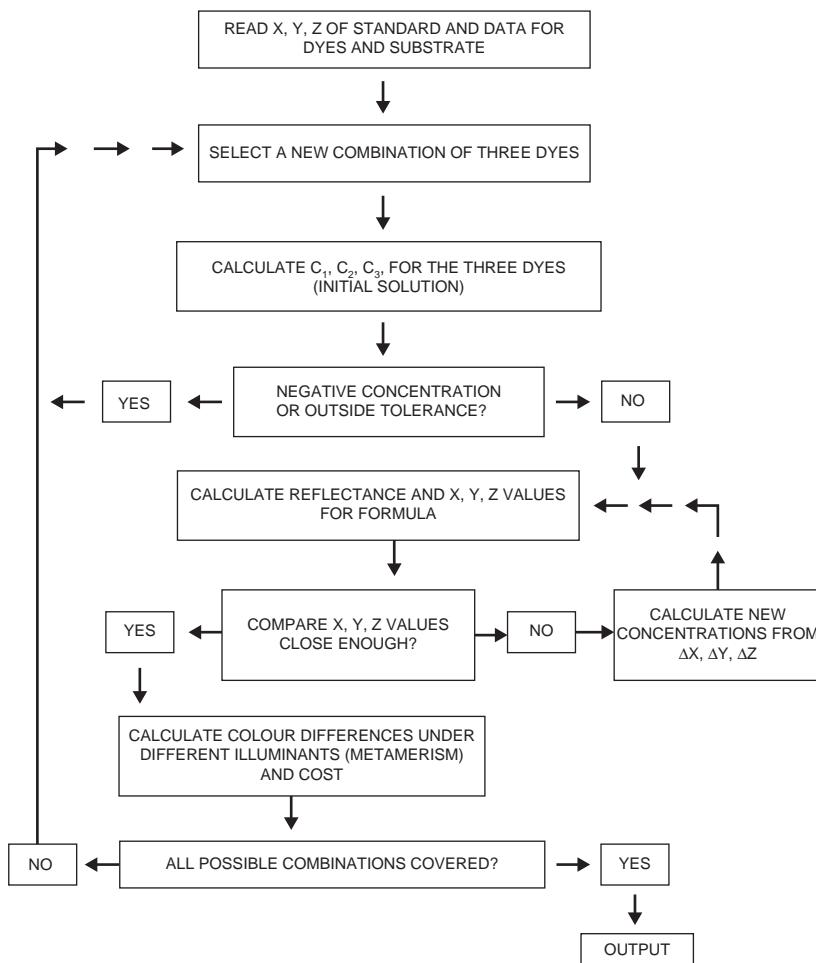
The formulations predicted by the final solution, when applied under practical conditions, may not always give an accurate visual match to the standard due to limitations of the theory and the equations involved, and also due to inaccuracies in calibration data. If the difference between the standard and the batch sample is larger than 3–5 MacAdam units of colour difference (Kuehni, 1975), a computed correction of the batch is useful. Allen (1978) termed the process as *shading*, whereas in the industry it is mostly termed ‘reformulation’. The shading program differs from the formulation program in various respects. In this process, calculations are to be made as to how much of each of the colourants is to be added to the batch sample in order to get a match with the standard. In this respect, it is similar to the correction program followed during final solution. However, in this case we are not concerned with alternate formulations. No metamerism is involved as the standard in this case is not the original customer’s sample, but a production sample set aside as an internal standard.

The mathematics of batch correction is basically similar to that involved during iteration for final solution. The required changes in concentrations are calculated from the differences in the tristimulus values between standard and the batch. The correction matrices are, therefore, similar to Equations [4.48] and [4.53] for single- and two-constant theories, respectively. As the relation between tristimulus values and colourant concentration is non-linear, correction calculation over a large distance in the tristimulus space will be erroneous. The main problem in the reformulation program is to decide about the weighting matrix. Generally, the average of the reflectance factors of the standard and the batch is taken as the weighting factor. In many practical applications, the reformulation program has a more important role than the formulation program. It may be utilized for speeding up production by using an available approximate match as the batch sample, and then

the true formulation is calculated by correction program, as lower number of iterations in this case may give a closer match.

4.14 Computer programming

The computer colourant formulation technique in summarized flow sheet form is shown in Fig. 4.13. There are several types of computer programs available for doing the formulation job. The most popular method is known as *combinatorial program*, as it tries one combination after another until all possible combinations are covered. For the colour to be matched, three tristimulus values under a standard illuminant, mostly D_{65} , are considered.



4.13 The flow chart for computer colourant formulation.

The matching combination of the colourant must have tristimulus values very close to those of the standard, otherwise the combination is rejected. In order to equate three tristimulus values, we must have three equations and three unknowns. For textile dyeing following single-constant theory, three variables are the concentration of three dyes per unit weight of textile material and for paint systems, the concentration of the three colourants plus that of a white pigment provides three degrees of freedom. The total number of possible three combinations, N , depends on the number of dyes in the inventory list and is given by the Equation [4.54] as follows:

$$N = \frac{n!}{r!(n - r)!} \quad [4.54]$$

where n = number of dyes in the inventory list and r = number of dyes per recipe, generally $r = 3$.

The number of possible combinations rapidly increases with the increase of number of dyes considered. For 10 and 20 dyes in the inventory, the number of possible 3-dye combinations will be 120 and 1140, respectively. For four dye combinations, the number of combinations possible is still higher, 210 and 4845, respectively, for the above two cases.

Winey (1978) discussed a visual technique to reduce the number of iterations required by grouping the colourants into a few groups according to the hue and selecting initially one colourant from each group. For producing green colours, if ten pigments are used to make three-colourant combinations and if the pigments are divided into three groups (yellows, greens and blues, and greying colourants), the number of iterations required will be reduced from 120 to 36 only. If none of these combinations is satisfactory, a fourth colourant is to be considered, and an additional 126 combinations are to be tested instead of 210 combinations for four-colourant combinations of ten un-grouped pigments. The ten pigments do not include white pigment, which is to be added for all combinations. If a fourth pigment is to be added, the extra degree of freedom may be utilized to match tristimulus value X_A for illuminant A .

If a fifth pigment is to be used, X_F for a fluorescent lamp may be matched. For a selection of pigments, it may be helpful to calculate the sign of the quantity $\Delta X = X_{\text{formula}} - X_{\text{standard}}$, each time that a formula is calculated by addition of a new pigment, so that a shift of X_A or X_F around the locations of the pigments on the hue circle may be noted. Iteration may be started with an arbitrary combination of pigments and modifying the combination in the direction denoted by the sign of X_A or X_F , the number of combinations to be tested to get low metamerically matches will be substantially less. When a tristimulus match is obtained, we actually determine

the concentrations of the three dyes needed to give a dyeing shade or the concentration of three pigments in a paint system; the final product in both cases will have the same tristimulus values as the standard. The most important feature of computer colourant formulation is that it provides all combinations for which a tristimulus match is possible. A choice of match formulation is, therefore, possible considering availability, cost, fastness, metamerism, etc., of the colourants, the data for which are also provided by the program.

4.15 Spectral colour matching

Tristimulus matching is very fast to compute and provides a number of alternate recipes, from which a choice can be made. Hence, it is very popular for most colour formulation jobs. Even if a pair of object colours have identical tristimulus values under a particular illuminant, it is not necessary that they will match under all possible illuminants. In other words, tristimulus match may calculate colour matches which are metameric in nature, and therefore it is also termed metameric colour matching. Although we can restrict the degree of metamerism tolerable, some degree of metamerism is inevitable with this process.

On the other hand, spectral colour matches are non-metameric in nature and are required for construction of colour filters, quantitative estimation of dyes from spectral absorption curves and many other specialized jobs. The program for spectral match is not combinatorial, as it does not go through all possible combinations. On the contrary, it calculates a formula considering all the colourants at once (instead of three or four at a time) which give the closest possible approximation of the reflectance curve to the standard.

McDonald (1987) proposed a simple method of spectral matching by solving three simultaneous equations similar to Equation [4.11] at three wavelengths where the three dyes have distinctly different absorbing powers, generally at the wavelengths of maximum absorption of the three dyes. In these equations, everything except three concentrations C_1 , C_2 and C_3 are known. The method is very simple and the recipe can be computed with the help of a hand calculator. However, the method is very approximate and valid only for non-metameric matching. McDonald himself had recommended the use of the method only under very restricted circumstances.

The spectral match calculations can be made by linear regression or least squares method, as proposed by McGinnis (1967) or Marquardt (1963). However, the least squares method sometimes gives considerably large errors in a minor range in compensation for the good fit in a major range. Sometimes the method also gives an impractical solution, such as negative concentrations, especially when the number of colourants is large. Ohta and Urabe (1972) proposed a method called the minimax method, in which the

dye concentrations are calculated as the amounts required to minimize the maximum error and claimed that the method gives feasible solutions and good curve fit throughout the range. Assuming the applicability of the Beer-Lambert law, the spectral density distribution $D(\lambda_i)$ of a mixture is written as in Equation [4.55]:

$$D(\lambda_i) = \sum_{j=1}^m c_j d_j(\lambda_i) \quad (i = 1, n) \quad [4.55]$$

where m is the number of dyes in the mixture and n is the number of wavelengths at which measurements are made. C_j and d_j are the amount and spectral density distribution of the j -th dye.

Assuming that the maximum error between $D(\lambda_i)$ and its approximation, $F(\lambda_i)$ is E_{\max} , it may be written as in Equation [4.56]:

$$-E_{\max} \leq F(\lambda_i) - \sum_{j=1}^m c_j d_j(\lambda_i) \leq E_{\max} \quad (i = 1, n) \quad [4.56]$$

The minimax approximation is to minimize the maximum error, E_{\max} , under the above restriction and $C_j \geq 0$ ($j = 1, n$). This problem can be solved by the penalty method of linear programming using slack variables.

4.16 Colour matching of blends

The colour-mixing behaviour of pre-coloured fibres has been widely discussed. According to Burlone (1990) the two-constant Kubelka-Munk theory is sufficiently accurate for colour prediction of blends. He (1983) emphasized the analogy between blending coloured fibres and mixing pigments in the paint industry, both of which can be completely explained by the two-constant Kubelka-Munk theory. A number of papers have been published on the spectrophotometric matching of fibre blends (Burlone, 1983; Walowit *et al.*, 1988). Colorimetric matching achieved by mixing pigments, as an example of the two-constant theory, has been explained by Best (1987). In colorimetric matching of blends of pre-coloured fibres, similar to mixing pigments, sometimes more than four coloured fibres are necessary to provide better matching, lower cost and a lower degree of metamerism. Usually better reflectance curve fitting is obtained with more colourants, which is the result of the higher degree of freedom. For these reasons, the four-colour system cannot always match the blends of pre-coloured fibres.

Sometimes in blending pre-coloured fibres, more than four coloured fibres are necessary for a colorimetric match. Amirshahi and Pailthorpe

(1995) proposed an algorithm with a number of modifications to tristimulus colour matching. Since a spectrophotometric colour match produces a more balanced colour difference between the standard and prediction under different illuminants, they recommended that this method should be used first. This means that instead of assuming unit imaginary scattering values for the first calculation, they considered the reflectance curve and resulting concentrations from the least squares match to the standard curve as a starting recipe. If the match satisfies the ΔE condition, the procedure is stopped and the best colour match has been achieved. Otherwise, the results are considered as an initial recipe.

Second, they did not restrict the number of colourants to four, as proposed by Allen (1974), and they used a fifth coloured fibre when necessary. In a five colourant system, three different possible cases can exist. In the first case, the number of colourants is more than four but the matching condition is still under just one illuminant. This means that the number of colourants is more than the number of equations. This pseudo-inverse algorithm was used by Amirshahi and Pailthorpe (1995). The second possible case is a fifth equation, which can be one of the tristimulus values (mostly X) of samples under any other illuminant, introduced into the system. The technique has been fully described by Best (1987). In the third case, more than five equations can be formed by introducing the tristimulus specifications of samples under other illuminants, as Sluban (1993) suggested for a single-constant Kubelka-Munk theory, to establish a more balanced match under several illuminants. Since the number of equations is more than the number of unknowns, the least squares technique can be applied in this case.

4.17 Principal component analysis (PCA)

Principal component analysis (PCA) is the basis of a new statistical method for data analysis and compression. It is a simple, non-parametric process of extracting appropriate information from confusing datasets. The PCA technique generates a new set of variables, called principal components, which are orthogonal to each other and are a linear combination of the original variables. The fundamental purpose of the PCA is to reduce the extent of the dataset, which consists of a large number of interrelated variables, while maintaining to a workable degree the variation in the dataset. The principal components of a reflectance spectrum are the coefficients of the linear combination of principal component eigenvectors that produce the least squares best fit with that reflectance spectrum.

In colour science, the PCA technique has been used to estimate spectral information from tristimulus values and the recovering spectral information. In this method, the accuracy of estimation mostly depends on the number of principal components which have been used for recovering

reflectance spectra. The number of principal components for an acceptable reconstruction of reflectance spectra or spectral data compression differs from 3 to 9, depending on the type of applied datasets. However, an acceptable estimate is accessible by seven principal components, which are generally considered to be adequate for spectral data compression (Agahian and others, 2008).

Shams-Nateri (2009) proposed an algorithm based on PCA and single-constant spectrophotometric matching methods. Using the normal spectrophotometric matching method, match prediction is carried out at 3 and 16 wavelengths. With the new algorithm, 3, 6, 9, 12 and 16 principal components are used in spectral match prediction. The performance of the new method improves with increasing numbers of principal components. In addition, the recipe prediction accuracy of the new method with three principal components is better than spectrophotometric matching at three wavelengths. The accuracy of PCA–spectrophotometry with 16 principal components is comparable to the normal spectrophotometric matching method at 16 wavelengths. The performance of the PCA method is dependent on the type and size of the database.

Mohtasham *et al.* (2012) employed linear and exponential weighted PCA techniques based on spectral similarity for the prediction of dye concentration in coloured fabrics which had been dyed with three component dye mixtures. The matching strategy was based on the equalization of the first three principal component coordinates of the weighted reflectance curves of the predicted and target sample in a dynamic 3D eigenvector space. The performance of the proposed algorithm was evaluated by the root mean square differences of the reflectance curves and the relative error of the concentration prediction, as well as the metamerism index. The results indicated that the developed exponential weighted PCA method is more accurate than the spectrophotometric method and the simple PCA matching strategy.

In order to control recipe prediction in the instrumental colour matching and to produce more balanced colour differences under multi-illuminants, a method based on tristimulus matching under a virtual illuminant was suggested (Agahian and Amirshahi, 2009). This method takes advantage of the fact that the significance of various lighting conditions could be different in practical colour-matching goals. Consequently, by performing a colour-matching trial under a virtual illuminant consisting of major and minor artificial lights, a more balanced colour difference under multiple lighting conditions could be expected. In order to create such virtual illuminants and control the contribution of each artificial light in the generation of the proposed lights, two well-known statistical methods, the wPCA and wM techniques, were utilized. The performances were evaluated with a collection of 135 woollen samples, which were matched by the use of the

colorimetric colour-matching program under different virtual illuminants. The results showed more balanced colour-difference values under different lighting conditions in comparison with the conventional matching approach under a specific illuminant.

In Adams' zone theory, the initial receptor stage is followed by an intermediate coding stage in which the cone signals are converted to non-linear functions of the X , Y and Z tristimulus values. These functions are assumed to be in the form of the Munsell-value functions VX , VY and VZ (see Roy Choudhury, 2014, chapter 7, section 7.10.4, p. 299). Based on the idea of spectral visual response fitting, the visual difference between the spectral reflectance factor function of the standard and specimen was proposed in this paper. Basic equations used in the recipe formulation as well as recipe correction were derived based on the spectral visual response fitting in matrix form and an algorithm for the least squares match has been developed. The iterative procedure for the recipe correction has been established in this algorithm. Twenty standards were used in numerical experiments conducted by He and Zhou (2009). The experimental results showed that the average colour difference against the standards under the five different illuminants (D65, A, F1, F2 and F3) was smaller than one based on other spectrophotometric fittings, and the colour differences balanced better and produced lower metamerism.

4.18 Advantages and limitations of instrumental colourant formulation

For a decision on the feasibility of computer colourant formulation for a plant, various costs on instrument, computation, personnel, preparation of calibration or primary dyeing, etc., are to be compared with the possible and likely advantages. Sometimes these are difficult to assess. The main points in its favour are:

1. An obvious benefit of the use of instrumental methods is the elimination of the subjective nature of visual assessment and the reduction in the buyer–seller disputes with the consequent improved quality and customer satisfaction.
2. It can provide a number of alternate recipes within a very short time. Therefore, for a colourant reproduction unit dealing with a large number of shades daily, it will assist faster production with less man power than units solely depending on manual shade matching. A wider choice among colourants can be made as a number of alternate recipes are available at a time.
3. The dyestuff costs can be reduced by cost optimization of the formulae.
4. Matches of low metameristic nature can be assured.

5. An important advantage is that dye inventory can be reduced substantially.
6. Processing problems can be investigated by quantitative analysis of production batch samples.
7. The number of trials to get an exact match can be reduced, with resulting savings in dyeing costs and time.

The companies which supply systems incorporating match prediction and measurement of colour-difference claim several benefits. Actual savings by using colour measurement systems vary with the operation being studied. The typical figures for a case study reported by Park (1993) are:

- 25% reduction in total dyeing cost for each addition eliminated,
- 25% reduction in dye cost by use of prediction programmes,
- 10% reduction in dye cost due to use of instrumental quality control,
- 25% reduction in dyes inventory and
- 10% saving of substrate by use of colour sorting programmes.

Though computer colourant formulation is an indispensable tool today for the industries dealing with colourants or coloured goods such as textile, paper, paint, plastics, colourant-producing, graphic art printing, cosmetics, etc., there are several limitations or restrictions of this technique, of which the user should be aware.

The accuracy of the computed formulation should be such that, when applied by a precise method, a match with the standard well within commercial tolerance is obtained. In reality, the accuracy is not good. Typically, industrial tolerance may be approximately 1–2 ANLAB 40 colour-difference unit, the first trial deviates about 2–3 ANLAB 40 units from the standard on average under good conditions. With less favourable conditions, errors of 5 ANLAB 40 units or more occur frequently. The error in concentration may be 5% for an acceptable commercial match, 10–20% for optimal computer results and 30% or more in worst cases (Brockes, 1974).

4.19 Causes of low accuracy in textile dyeing

Some of the reasons for low accuracy in the prediction of textile dyeing formulation are described below (Brockes, 1974; Kuehni, 1975).

4.19.1 Improper dyeing

The low accuracy may be due to improper dyeing, namely:

1. Poor reproducibility
2. Poor levelness.

These defects may be caused by:

1. Variation in dyeing conditions
2. Variation in substrate
3. Variation in dyestuff quality
4. Limitation of the optical theory
5. Incorrect colour measurement due to
 - a. Inaccuracy of the instrument
 - b. Wrong sample presentation

Reproducibility

An important source of error is the non-repeatability of the dyeing process, which may be due to improper dyeing procedure or improper application machinery, errors in weighting of colourants, and auxiliaries and interactions between the dyes.

The important factors on which reproducibility depends are many, and those are different in the laboratory and the works. The most common variables and their effect on colour difference, ΔE (CMC) (under bracket) as reported by Park (1993) are:

- Water supply (≤ 3.0)
- Type of substrate (acrylic – 0.15, wool – 1.5, cotton – 2.0)
- Quality of dyes (≤ 5.0)
- Dye application methods
- Liquor ratio
- pH of dyebath
- Time–temperature profile
- Method for assessing colour (optimized system < 1.0)
- Repeatability in bulk (0.2)
- Laboratory dyeing repeatability (0.12)
- Spectrophotometer repeatability (0.05–0.2).

Computer colour matching is a major dye-house aid in obtaining ‘quick response’, but accuracy of laboratory dyeing can often be a major problem in achieving optimum results. Laboratory dyeing can be repeatable within 0.1–0.2 ΔE (CMC) provided that correct methods and equipment are used in conjunction with suitably qualified and trained staff (Park, 1991).

Matching tolerance is tight, and for most end-users it is found to be around 1 ΔE (CMC) respectively.

Levelness

Unlevel or uneven dyeing may result in concentration differences of 10% or more in the same lot, and may give rise to unpredictable error in colour measurement.

Both these factors can be controlled if standard processes are adopted, making necessary precautions. These errors are controllable, and should not pose serious problems in the accuracy of computer predicted recipes.

4.19.2 Variation in dyeing conditions

For accurate formulation prediction, the dyeing conditions of calibration dyeing and bulk dyeing should be the same. The colour value of a dyed shade depends on the dyeing machinery, temperature, time, pH, dyeing auxiliaries, liquor ratio, washing and soaping, and after-treatments. Incomplete penetration of colour into the fibre may result in variation in colour. *Ring dyeing*, caused by incomplete penetration of dyes, leads to reduced apparent colour strength. Sometimes it may be necessary to change the dyeing conditions and, if new calibration dyeings are not possible to prepare, a concentration correction should be made by calculating strength factors of a yellow, a red and a blue by dyeing in mixture following old and new methods of dyeing, as in Equation [4.57]:

$$f_1 = \frac{C_1}{C'_1} \quad f_2 = \frac{C_2}{C'_2} \quad f_3 = \frac{C_3}{C'_3} \quad [4.57]$$

where C_1 , C_2 and C_3 are the actual concentration of the three dyes and C'_1 , C'_2 and C'_3 are concentrations predicted on the basis of old calibration samples. The correction factors, f_1 , f_2 and f_3 are used to correct the computed formula to produce the dyeing formula.

4.19.3 Substrate variation

Even within the same class of fibres, the chemical nature and morphological structure of the textile fibre and geometric structure of yarn and fabric may vary widely and may produce pronounced differences in the colour of dyed textile material with the same combination of dyestuff. The differences are due to variation of absorption, scattering and, most significantly, of the dye exhaustion properties of the substrate. The light absorption properties of the substrate may change during dyeing. Therefore, a blank bath treatment identical to the dyeing process but without any dye may be carried out before measuring the reflectance of the substrate. The amount of back scattering of light is proportional to the specific surface of the fibre or the surface area per unit mass, which is again inversely proportional to the fibre diameter d , i.e. K/S is directly proportional to d .

The same natural fibre may have different chemical species. For synthetic fibres, the ratio of crystalline, semi-orientated and amorphous regions

influencing the colour of the dyed material depends on the manufacturing processes and treatments before dyeing, mainly on the extent of stretching and heat treatments. Blending of fibres creates further problems of accurate colourant prediction. A number of modifications in the theory have been proposed to deal with fibre blends, but these have not sufficed to solve the problems of prediction of colourant formulations of fibre blends.

4.19.4 Variation in dyestuff quality

Certain dyestuffs interact with each other in the dye bath and may hamper the additivity of the dyes, thereby affecting accuracy of prediction. The dyes can also form small aggregates, thereby creating local concentration variations. The dyestuffs of different batches of the same manufacturer, or of different manufacturers, may vary widely. Such variations will hamper accuracy of formulation predictions significantly. So, for success of computer colourant formulation, the dyestuffs should be highly standardized, with minimum colour variation between successive lots.

But in the case of fluorescent colourants, light energy absorbed in some part of spectrum is used to emit light in another part, and in many cases the absorption and emission bands overlap. To describe fluorescence, an additional quantity, quantum efficiency, is needed, which is difficult to determine. Moreover, quenching or deactivation of fluorescence takes place due to interaction with some other dyes. With the existing approximate method following K-M theory, the computed matches with strongly fluorescent dyes are often significantly worse than those without fluorescence. Several modified methods for colourant formulations with fluorescent dyes are proposed, which will be described separately.

A regularity of the predicted sensitivities to random and proportional dye concentration errors in regard to the position of target colour has been observed with dyeing acrylic with basic dyes (Sluban and Šauperl, 2005). The impact of strength errors on recipe colour is, generally, smallest for recipes for target colours at the ‘lighter’ part of the gamut border. On average, recipes that were the most sensitive to strength errors were those for neutral and less saturated targets of about medium to low lightness. Different recipes for any less saturated mid and low lightness targets had very different sensitivities to strength errors – fortunately, some of these were very low.

4.19.5 Limitation of the optical theory

As discussed earlier, several simplifying assumptions are made in K-M theory. The conditions during measurement may be quite different from those assumed while formulating the theory.

Certain inaccuracies are, therefore, inevitable. Failure of the additivity principle may be caused by dye associations, dye interactions, poor dye penetration, blocking effect near saturation point, etc. The K-M theory does not give satisfactory results with glossy samples and dark colours. A number of complex theories have been proposed, but computations are consequently very complex and lengthy. Significant improvements in accuracy have not been obtained by these theories, as dye-fibre systems are very complex.

4.19.6 Inaccurate colour measurement

Accuracy of the instrument

Colour measurements are done at two stages – once of the calibration dyed samples, and then of the sample to be matched. Generally, the two measurements are done over long intervals of time. The instrument should have, therefore, long term repeatability and, more preferably, good absolute accuracy. The parameters determining the accuracy of the instrument are the 100% line, 0% line and the wavelength scale. If the average colour difference between the measured sample and the calculated match is smaller than 0.3 AN40 units, the instrumental error can be neglected.

Wrong sample presentation

While the instrumental errors of the commercially available spectrophotometer are within tolerable range, the sample presentation to the instrument is a very important factor in deciding the accuracy of the prediction. The sample size generally recommended is of one inch diameter. Various problems, such as bending of the soft sample through the port into the integrating sphere, loss of light at the edges, transparency of thin samples, etc., are enhanced at a smaller sample size, thereby impacting accuracy. However, some instruments give reasonable accuracy even with a smaller sample port of 0.25 inch diameter. The measurement of loose and soft material may be made behind a glass plate. But the mirror reflection and thickness of the plate need to be taken into account. For highly directional materials and materials having large structured elements, multiple measurements may be made by rotating the sample and then averaging the values. Corduroy and velvet cloth pose considerable measuring problems, due to discrepancies between viewing geometries of the instrument and visual observation.

4.20 Causes of low accuracy in paints and plastics

Inaccurate recipe prediction in paints and plastics may be due to poor reproducibility, coefficient variability, limitation of optical theory, human error, etc.

4.20.1 Reproducibility

Variation in subsequent production batches should be strictly controlled, but is more easily controllable in these cases as compared to that in textile dyeing. Time, temperature and other factors during drying, curing, extruding, milling and other operations, need to be strictly controlled. More difficult is the control of the thickness of the applied layer, which is more important for translucent samples. Proper mixing and uniform particle size distributions are very important for both calibration and trial samples.

4.20.2 Constancy of the coefficients

The specific absorption and scattering coefficients are not completely independent of pigment concentration in paints and should be determined at different concentrations, as in the case of textile samples.

4.20.3 Limitation of optical theory

Optical relationships are often less complex in these cases as compared to textile dyeing. Pigment particles are also more separated in the vehicle. The more complex theories, such as multi-flux theory, improve accuracy, especially for pigment formulations that scatter light preferentially in certain directions and for systems showing geometric metamerism.

4.20.4 Human error

For successful application of computer colourant formulations, well-educated and trained personnel are required. At the beginning, considerable thought must be given to integration of the system into the working environment of the plant. The limitations of production depend to a large extent on specific problems in the individual case; these can only be overcome through individual effort.

4.21 Match prediction using fluorescent colourants

Fluorescent dyes contain electrons that are excited by radiation at wavelengths in the region 200–560 nm and emit radiation at higher wavelengths. Fluorescent dyes are important because they considerably extend the gamut of available colours. They can be used to produce attractive colours for baby-wear, and also for high visibility clothing such as climbers' and hunters' dress.

Computation formula involving fluorescent colourant is quite complex – the additional work required for characterizing such colourants, and the

corresponding computation, may not be economical. The main difficulty is that the conventional spectrophotometer used for measuring reflectance of non-fluorescent colourants cannot provide complete description of the fluorescence of a sample. In order to study fluorescence accurately a spectrofluorimeter is required, such as the one designed by NPL (Williams, 1995).

The details of the methods of measuring fluorescence have been described in Roy Choudhury (2014, chapter 8, section 8.4, p. 323). For luminescent (fluorescent) materials the total spectral radiation factor (SRF), β_T across the visible spectrum is the sum of two portions – the spectral reflected radiation factor, $\beta_S(\lambda)$ (S = substrate, generally non-fluorescent) and the spectral fluorescent radiance factor, $\beta_L(\lambda)$ as shown in Equation [8.1] (see Roy Choudhury, 2014, chapter 8, section 8.6, p. 326). $\beta_S(\lambda)$ is due to reflectance only and $\beta_L(\lambda)$ is due to fluorescence only. β_L is not only a function of λ , but also depends on the spectral radiant power distribution, $S(\lambda)$, of the source, σ , irradiating the material. Consequently, the total spectral radiance factor is a function of light source (σ) as well as wavelength (λ). For non-fluorescent materials, the spectral reflected radiation factor, $\beta_S(\lambda)$, is numerically equal to the reflectance factor, R . Hunt (1987) surveyed various methods that had been proposed for separating the contributions of $\beta_S(\lambda)$ and $\beta_L(\lambda)$ to β_T (the ‘two-monochromator’, the ‘two-mode’, the ‘filter reduction’ and the ‘luminescence weakening’ methods), but none proved practicable in this case.

The best method is the dual monochromator system using illuminating as well as viewing monochromators, though such instruments are not available commercially. A commercial spectrophotometer with polychromatic illumination may also be used, but the light source must closely approximate illuminant D65, because the fluorescence depends on the absolute quantity of incident light at the wavelengths of excitation. Moreover, yellowing of the integrated sphere will affect the measured reflectance factor. Reflectance values for non-fluorescent samples are independent of the light source, but fluorescence depends on the relative energy of the light source, not just at the wavelengths being measured, but also at the wavelengths of excitation.

Usually in colourant formulations involving fluorescent samples, the emitted light is neglected. A possible approach is to calculate a weighted least squares match for the true reflectance factor without emitted light and then adjusting the formula on the basis of tristimulus values including the emitted light. It is difficult to calculate the absorption losses of the emitted light. In practice, when a special instrument is not available, the true reflectance curve is approximated by using the absorption portion of the curve and the substrate reflectance data in the emission band; the error is smaller than the error that arises from the neglect of emitted light. Considerable error is, however, encountered while calculating metameric indices. Ganz’s

method (Ganz, 1977) is a simple modification of the K-M theory to allow the equation to be used in cases where the total radiance factor is greater than 100%. The method is claimed to produce good results for the formulations obtained with one fluorescent dye shaded slightly by one or more dyes. With large admixtures, the predictions are poor, as no account is taken for lowering of emitted light through absorption by the other dyes.

4.21.1 Two segments method

Man and Rigg (1985) considered the reflectance curve as two segments.

1. The wavelengths where there is no fluorescence and total radiance factor, R_T , is lower than the reflectance of the substrate, the K-M method, normally used for non-fluorescent dye, can be used.
2. The wavelengths where fluorescence takes place, and the following Equation [4.58] can be used.

$$F = MC_F e^{LC_F^k} \quad [4.58]$$

F is the predicted amount of light emitted by the fluorescent dye in the absence of a non-fluorescent dye and C_F is the percentage shade of the fluorescent dye, M, L, k are constants for a particular dye at the particular wavelength. The predicted amount of fluorescence for the mixture, F_p , is given by Equation [4.59]:

$$F_p = K_1 \left[F \left(\frac{1}{1 + K_2 C_{NF}} \right)^{C_F^{0.2}} \right] \quad [4.59]$$

where K_1 and K_2 are the constants, the values of which at each wavelength are obtained from dyeing of mixtures of the fluorescent dye and non-fluorescent dye, by fitting the predicted reflectance values as closely as possible to the measured values. C_F and C_{NF} are the concentrations of the fluorescent and non-fluorescent dyes, respectively.

For most fluorescent materials, some of the R_T values at particular wavelength ranges are less than those of the substrate where absorption takes place, while for other wavelength ranges, they are higher, indicating emission of fluorescent light.

To measure the absorption by the fluorescent dyes, it is assumed that no fluorescence occurs when maximum concentration of the dye is used. The

measured value at this concentration was used to calculate K-M constant, A_F . The pseudo-reflectance value (R_s) is then calculated as:

$$(K/S)_s = (K/S)_b + A_F C_F \quad [4.60]$$

$$R_s = [100 + (K/S)_s] - \{[100 + (K/S)_s]^2 - 10\,000\}^{1/2} \quad [4.61]$$

where b stands for the substrate.

The predicted reflectance R_P is, therefore, reflectance in the absorption zone, R_s plus fluorescence, F_P , i.e.

$$R_P = R_s + F_P \quad [4.62]$$

Bonham (1986) also used a similar method by giving separate treatments for the fluorescence and non-fluorescence zones. However, many complicated formulae have been proposed for the representation of the emitting zone.

4.21.2 RELEX method

A new spectral quantity, RELEX (Simon *et al.*, 1994), independent of illuminant, has been developed for fluorescent colours. With this quantity, describing the relative excitation of the colourant, when weighted by the SPD of the illuminant and corrected for absorption by other ingredients in a mixture of colourant, the actual fluorescent emission is obtained. This quantity, instead of fluoresced radiance factor $\beta_{L(\lambda)}$, may be added to the reflected radiance factor $\beta_s(\lambda)$ to obtain spectral radiance factor β_T , which can subsequently be used for match prediction by iterative algorithm.

Two assumptions made in this method are:

1. The shape of the emission curve remains unaltered while the total amount of fluorescence varies with excitation energy varying in amount and wavelength.
2. The intensity of the fluorescence is directly proportional to the quantity of excitation energy absorbed by the fluorescing material.

Apparently illuminant-independent fluorescence emission can be calculated by taking a ratio of actual emission and the response of the instrument. But such a measure is incorrect, because several spectrophotometric configurations are required for complete assessment of fluorescent colours namely:

1. A polychromatic instrument to measure spectral radiance factor.
2. A dual monochromator system to obtain $\beta_s(\lambda)$.
3. A method for estimation of illuminant SPD at the sample port.

The amount of fluorescence at the molecular level, β_{Fm} is related to the absorption function (K/S) of the ladder having spectral reflected factor equal to that of the fluorescent colour.

$$\beta_{Fm} = \frac{\beta_L(\lambda)}{f(\beta(\lambda))} \quad [4.63]$$

The total amount of fluorescence, F_T is calculated as in Equation [4.64]:

$$F_T = \sum \beta_{Fm}(\lambda) \Delta\lambda \quad [4.64]$$

Now, the total excitation at a given wavelength, $E_x(\lambda)$, is given as in Equation [4.65]:

$$E_x(\lambda) = E(\lambda)[\beta_U(\lambda) - \beta_D(\lambda)] \quad [4.65]$$

$E(\lambda)$ corresponds to spectral energy distribution irradiating the sample. β_U and β_D are the amounts of excitation energy absorbed by the substrate and the fluorescent dye alone, respectively. The RELEX value, $RE(\lambda)$, is then defined as the ratio of total fluorescence and total excitation, i.e.

$$RE(\lambda) = \frac{F_T}{E_x(\lambda)} \quad [4.66]$$

The RELEX curve is unique for a given fluorescent colourant and the light source used to measure it. Fluorescence is expressed in terms of excitation, which in turn is a function of the concentration of the fluorescent colourant. The excitation for a given level of a fluorescent colourant, $\varepsilon(\lambda)$ is given by:

$$\varepsilon(\lambda) = RE(\lambda) E_x(\lambda) \quad [4.67]$$

Various steps for match prediction by RELEX method are as follows:

1. Prediction of an approximate match for the spectral reflected radiance factor, $\beta_s(\lambda)$, for the fluorescent sample.
2. Calculation of the amount of excitation energy absorbed by the fluorescing components of the mixture.
3. Calculation of the total amount of fluorescent emission absorbed by the mixture, which do not contribute to the total fluorescence.

4. Addition of spectral reflected radiance factor and the resultant fluorescence emission to give spectral radiance factor of the target.

4.21.3 Using artificial neural networks (ANNs)

Traditionally, computer colourant formulation has been implemented using a theory of radiation transfer known as Kubelka-Munk (K-M) theory. The K-M theory allows a mapping between a colourant vector c and a reflectance vector r that defines the colour-prediction problem. One of the main problems with recipe prediction is that the application of exact colour theory is not computationally practical and an approximation to it has to be employed.

Artificial neural networks (ANN) are used for modelling non-linear problems and to predict the output values for given input parameters from their training values. Most of the colouration processes and the related quality assessments are non-linear in nature, and hence neural networks find application in colour science. An ANN is an information processing concept that is inspired by the way biological nervous systems, such as the brain, process information. A class of ANNs known as multi-layer perceptrons (MLP) have been shown to be capable of approximating any continuous function to any degree of accuracy (Funahashi, 1989). An MLP is a layered structure of simple processing units. There may be one or more hidden layers of units between the input and output layer. Most MLPs are fully connected; that is, each unit provides a weighted input to each unit in the next layer. Each unit in the network is also associated with a transfer function that maps the input of the unit to its output and many different transfer functions are available. Information is thus processed from the input layer to the output layer in order to perform a mapping from an input vector. An MLP is a layered structure of simple processing units. The units in the first or input layer take their input from a real-world vector and the output of the units in the last or output layer provide the output of the network. There may be one or more hidden layers of units between the input and output layer. Each unit in the hidden layer receives data from the input vector, with weights being applied to each input. The same process occurs between the hidden layer and the output vector (Skapura, 1996). Most MLPs are fully connected; that is, each unit provides a weighted input to each unit in the next layer. Each unit in the network is also associated with a transfer function that maps the input of the unit to its output and many different transfer functions are available. Information is thus processed from the input layer to the output layer in order to perform a mapping from an input vector \mathbf{i} to an output vector \mathbf{o} .

Before the network can be used to solve a given task it must first be trained using known pairs of input and output vectors. Back-propagation

is a commonly used procedure applied to carry out the training process of an MLP. It works by leading the network to adjust its synaptic weights through a descendent error minimization technique (Skapura, 1996). MLPs can learn to perform an arbitrary mapping if they are presented with sufficient examples of the mapping problem $\mathbf{i} \rightarrow \mathbf{o}$. Learning, in an MLP, is a process of optimization (during which changes are made to the weights in the network) to minimize the RMS error between the desired output vector \mathbf{o}_d and the actual vector \mathbf{o}_a . MLPs thus require a training set of input–output pairs. Once suitably trained, however, the network can perform the mapping $\mathbf{i} \rightarrow \mathbf{o}$ for input vectors \mathbf{i} that were not used during the training of the network – this important property is known as generalization. The attractiveness of ANNs is based on their ability to adapt to new situations and learn the input–output data relationship of a problem, this being done without interference from an external agent.

The application of MLPs to colour match prediction was first demonstrated by Westland *et al.* (1991) and Bishop *et al.* (1991). They concluded that this technique warranted further investigation, and pointed out that it could be applied to colorimetric systems with complex behaviour, i.e. fluorescent dyes and metallic paint, which are difficult to treat using Kubelka–Munk theory.

The method is simple to apply, and requires only a representative database of fluorescent and non-fluorescent colourants, a commercial spectrophotometer adequately calibrated to measure SRF values, and the software to create and train an adequate network able to learn the relationship between the colour parameters and dye concentrations.

Bezerra and Hawkyard (2000) studied four network types to predict dye concentrations and they found that the one using SRF values as the input colour parameters proved to be the most appropriate way to relate a fluorescent coloured sample with the dyes and the concentrations required to reproduce it. When the SRF-C network was used to predict dye concentrations for a sample, the only way to find out the difference in colour between that and the standard sample was to apply the predicted dye concentrations to a substrate and then measure its SRF. The proposed approach of using the reverse topology of the SRF-C network, although not providing the exact SRF curve of the predicted sample, proved to be valuable as an approximation of its SRF curve.

There are limitations in the use of neural networks for colour recipe prediction. An adequate number of samples must be prepared and presented for the network to learn the relationship between fluorescent colour and dye concentrations. In addition, an increase in the number of dyes available will increase the network topology and probably will reduce its performance. A further problem is that the exact colour difference between

standard and predicted samples can only be known by actually dyeing the predicted sample.

The advantages of this system are that no special equipment is required, and is only a means of calibrating the light source to simulate illuminant D65 including the UV content. Employment of the forward SRF-C network and the reverse C-SRF network in an iterative routine should enable a successful match prediction program to be written for fluorescent colours.

Westland and others (2002) showed that although in principle ANNs can learn to map between colourant concentrations and spectral reflectance, in practice the optimization of the various parameters of the network is difficult and consequently it is not easy for the ANN to outperform the K-M model. They demonstrated that the proper use of separate training and test sets is essential in order to correctly assess the generalization performance of trained networks. A hybrid model based upon an ANN but maintaining some key features of the K-M model can outperform both ANN and K-M approaches. Senthilkumar (2010) discussed the application of ANN methods in details and suggested coupling ANNs with fuzzy logic to improve the accuracy.

4.22 Conclusion

Instrumental colourant formulation is one of the most successful commercial applications of colour measurement. It has virtually replaced a tedious manual job for most of the colour reproduction industries, especially textiles and paints. Colour-mixing laws are highly complicated, due to simultaneous occurrence of multiple optical phenomena. Simplified Kuelka-Munk theory is, by and large, most successful for the computation and many of its limitations are overcome by computer iteration technique.

The accuracy also depends on physical state of dyeing, such as uniform distribution of dyes throughout the cross-section, the uniformity of surface characteristics of the fibre, and many other factors. Ring dyeing, dye aggregation, metallic reflection by the colourant, irregular surface reflection from the fibre surface, etc., result in errors in recipe prediction. Fluorescence of the colourants adds further problems. Several newer techniques, such as PCA, ANNs, etc., have recently been adopted to improve the accuracy of the recipe prediction.

4.23 References

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