

Chapter 15

Formulating with Color



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Introduction

Color is of high importance in almost any paint application, and paint producers have developed technologies to satisfy strong consumer demands for an expansive color palette and for the ability to match the color of an existing paint or object. The importance of color to the consumer can be seen in the architectural (décor) paint marketplace. A customer in a paint store expects to see a display with hundreds of colors, and to find, behind the counter, a color reader and tint station that allow the store clerk, who likely has no experience whatsoever in color formulation, to match

virtually any color. Such an operation would not be possible without a comprehensive understanding of the science behind color mixing in systems that simultaneously scatter and absorb visible light.

Color matching is one of the most difficult issues encountered in paint formulation. To color match experimentally typically requires several cycles of mixing colorants at various concentrations into a white paint and measuring the tristimulus values of the resulting paint. The selection of starting point can be aided by the intuition of an experienced color formulator. While this empirical approach can ultimately be successful, the time and material costs are prohibitive for most applications.

As an alternative, we can measure the spectral properties of all the colorants and of the white base paint and, based on theoretical calculations and with the spectrum of the color we wish to match, quickly determine the amounts of different pigments needed to match, or nearly match, the color in question. In most cases, the initial formula is good enough to allow the formulator to skip further rounds of color optimization [1].

As we have seen in prior chapters, additive color mixing is relatively straight forward, and the xy chromaticity diagram can be treated as a road map for color matching. However, although color mixing rules for subtractive color mixing, which is how we create colors in paints, exist, they are more complex, and rely on more simplifying assumptions, which often break down in practice. We will discuss these rules, and their shortcomings, after a brief introduction to light absorption.

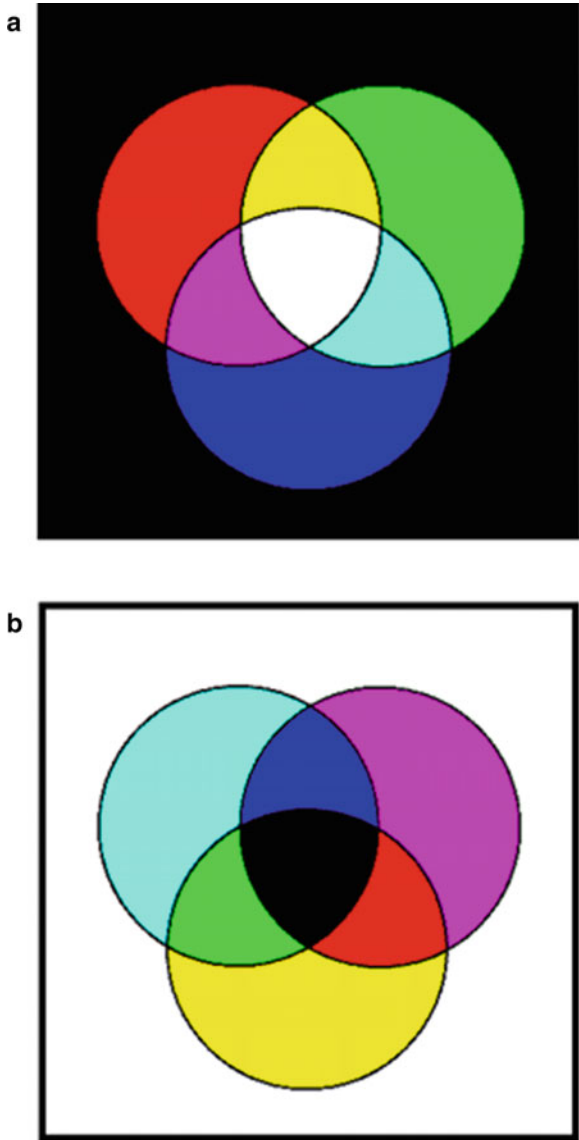
Comparing Additive and Subtractive Mixing

The development of XYZ tristimulus values from color matching experiments relied on mixing lights of different colors to create new colors or match existing ones. Based on the fundamental properties of light mixtures, and the color sensations that we experience from them, we were, in Chap. 6, able to develop a means of measuring and quantifying color sensations—the Standard Observer and the accompanying xy chromaticity diagram.

However, while we perceive and measure color based on additive mixing, this is not how we create it in a paint. When we additively mix light sources of different colors, we begin with a black (unlit) background and add color to it with selective wavelengths of light. When we subtractively make color by mixing paints and colorants, on the other hand, we begin with a white background (the white base paint) and selectively remove certain wavelengths using colored pigment (Fig. 5.2 from Chap. 5, reproduced here as Fig. 15.1). The laws governing the appearance of color mixtures are very different for subtractive mixing than for additive mixing.

An example of this difference is the mixing of red and green. When red and green lights are mixed (such as on an electronic screen), yellow results. When red and green paints are mixed, however, the result is a dark, muddy brown color. This can be seen in Fig. 15.2. This figure shows a screen capture of these two colors being additively combined on an LED monitor, while Fig. 15.2b was created by printing a

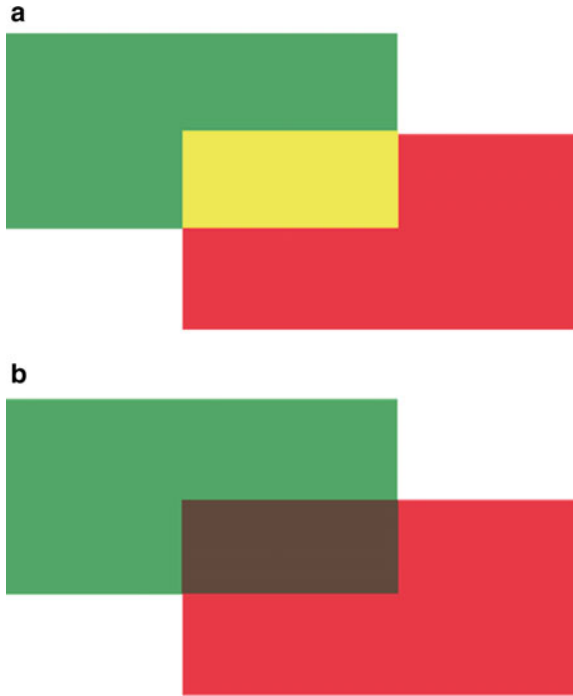
Fig. 15.1 Color mixing. **a** Additive; **b** subtractive



red rectangle on a piece of paper, then returning the paper to the printer and printing the partially overlapping green rectangle. The overlap region is, therefore, covered by a mixture of the inks used to make the red and green rectangles.

One of the most important aspects of additive mixing is that such mixing follows Grassmann's laws. These laws allow us to predict the color sensations of mixtures of different colors by adding their reflectances as a function of wavelength. This, in turn, led to the development of the xy chromaticity diagram (Fig. 6.11 in Chap. 6,

Fig. 15.2 Different ways to mix colors. **a** Additive color mixing. **b** Subtractive color mixing



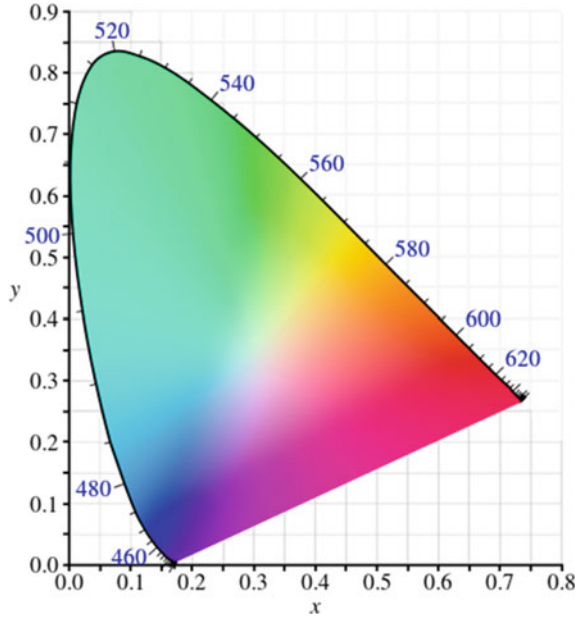
reproduced here as Fig. 15.3). The great usefulness of this diagram is that colors on the line joining any two colors can be created by mixing these two colors. In practice, this result is normally extended to three colors, allowing us to create any color within the gamut defined by the triangle that has the three primary colors as its vertices.

The aspect of Grassmann's laws that allows for this is the additivity principle of color sensations. Of special interest here, a pair of metameric colors, which have different spectra but create the same color sensation, will continue to match when each is combined with a new color, even though the reflectance spectra of the metameric colors (and of their mix with the new color) are different.

Such a mixing law does not exist for subtractive color mixing. For illustration purposes, we have contrived the following example to demonstrate this fact. In Fig. 15.4a, we see the reflectance spectra of two hypothetical metameric paints. Their color is a greenish yellow, as indicated by the inset in this Figure. Although the colors appear the same, they are derived in different ways. Paint A reflects a mix of green and red, while Paint B reflects a single band of wavelengths centered at the yellow/green interface.

Next, we add an identical cyan pigment to both paints. The new pigment gets its color by reflecting all wavelengths except those in the red portion of the visible spectrum (Fig. 15.4b). This is equivalent to saying that this pigment blocks red light and reflects all other colors. The result of adding this pigment to the reflectance spectra of the two paints is shown in Fig. 15.4c.

Fig. 15.3 *xy* chromaticity diagram



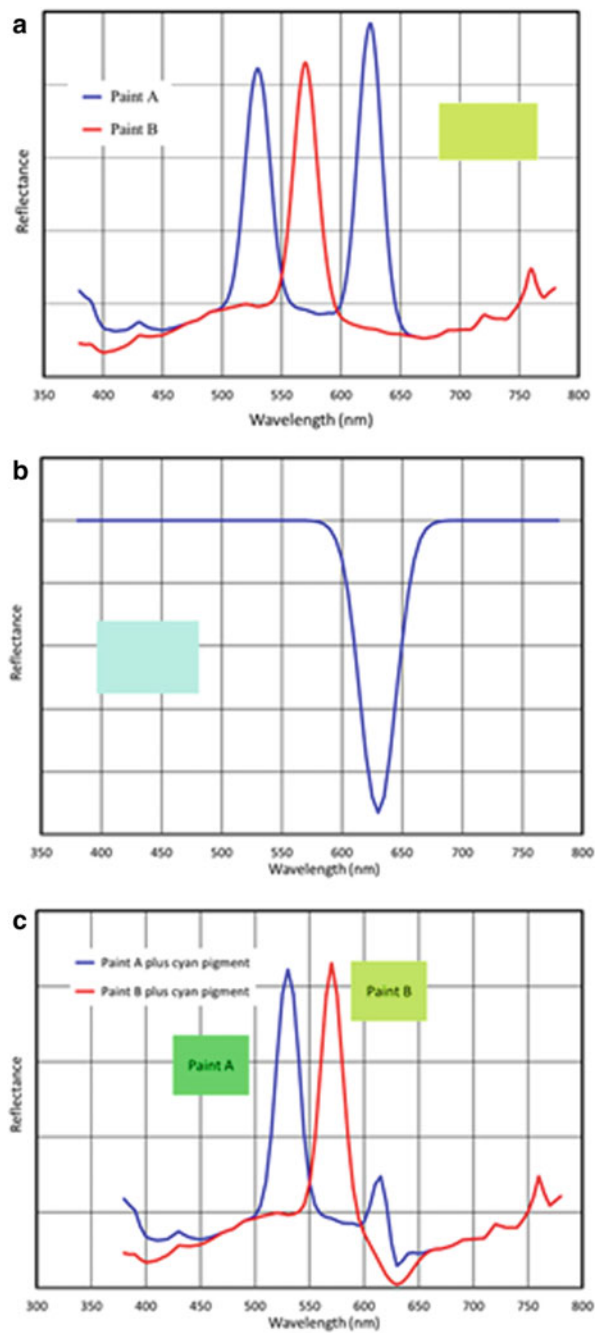
For Paint A, the red portion of the reflectance curve is nearly completely removed, while the green portion remains mostly unchanged. This results in a green appearance for Paint A (see inset in Fig. 15.4c). However, for Paint B, the reflectance spectrum has not shifted greatly, and as a result remains greenish yellow (see inset in Fig. 15.4c). From this example, we can clearly see that Grassmann’s laws do not apply to subtractive color mixing.

The Principles of Simple Light Absorption

Light is both absorbed and scattered by most paints. The ramifications of the simultaneous occurrence of these processes can be quite intricate, and the analysis of paint interactions with light can be very complicated. Understanding these interactions in colored paints begins with understanding light scattering and light absorption separately from one another. In Chap. 3, we discussed light scattering in the absence of absorption. In this section, we will review the principles of light absorption in the absence of light scattering (what we term “simple light absorption”), and then later in this chapter, we will discuss simultaneous scattering and absorption.

The fundamental unit of light is the photon, and all photons have well-defined energies that are determined by their wavelength. When the energy of a photon matches the difference in energy between two energy states of an atom or molecule, that photon can be absorbed by that atom or molecule, a process that moves the

Fig. 15.4 Combination of metameric colors **a** with a second light absorber, **b** to create reflectance spectra of different colors, **c**. Approximate colors are shown in insets



absorbing species to the higher energy state, with the transformation of light energy into another form of energy, as discussed in Chap. 8.

The amount of energy required to change the energy state of a molecule or atom depends on the form of energy into which the photon is transformed. One of the lowest energy state changes transforms light energy into rotational energy in a molecule. The differences in energies between the rotational ground state and rotational excited states match light in the microwave region of the spectrum. Energy levels associated with vibrations between atoms within a molecule are generally matched to infrared light. Ultraviolet light has enough energy to break chemical bonds (the subject of Chap. 14), while X-rays are energetic enough to completely remove electrons from an atom or molecule.

For some molecules, visible light is energetic enough to move an electron from one orbital to another (higher energy) orbital, creating an electronically excited molecule without irreversibly breaking chemical bonds or removing electrons altogether (Chap. 8). This is typically a temporary transition and nearly always the high energy electron will quickly relax into its initial (ground) state, shedding the electronic energy as thermal energy—i.e., the molecule heats up.

The relaxation of electronically excited molecules back to their initial state is of critical importance to color science since it means that the light absorbing molecules are not consumed or in some way permanently altered in this process. As such, this process can be repeated indefinitely. Such is not the case for higher energy absorptions, which irreversibly change the absorbing species.

Quantifying Light Absorption

Even when a photon has the proper energy to change some energy state of an atom or molecule, there is no guarantee that it will in fact be absorbed when it strikes that atom or molecule. Instead, there is a probability that any given interaction will result in absorption. This probability is not the same for all absorbers; those species for which it is high are strong absorbers, while those species for which it is low are weak absorbers.

As discussed in Chap. 8, the total amount of light that is absorbed by a material depends on three factors: the absorption coefficient(s) of the light absorbing material(s) in it, the concentration(s) of these materials, and the distance over which the light travels. The dependence of absorption on these three properties individually is linear, and the total absorption of light passing through a material is summarized by the well-known Beer-Lambert law:

$$A_{\lambda} = \varepsilon_{\lambda}bc$$

where:

A_{λ} is the total amount of light absorbed,

ϵ_λ is the absorption coefficient,

b is the pathlength of the light through the materials, and

c is the concentration of the absorbing specials.

Note that absorption (A) and absorptivity (ϵ) are wavelength dependent, which is reflected in this equation and others by the subscript λ .

The amount of light absorbed by a material can also be quantified by the amount of light transmitted through it or reflected by it. The relationship between the amount of light absorbed and transmitted is given by the following equations:

$$\begin{aligned} \%T_\lambda &= 10^{(2-A)} \\ A_\lambda &= 2 - \log(\%T_\lambda). \end{aligned}$$

If transmittance is expressed as a fraction rather than a percent, the number “2” is removed from these equations. When our interest is in the light reflected, rather than absorbed, we can replace $\%T_\lambda$ with $\%R_\lambda$ in these equations.

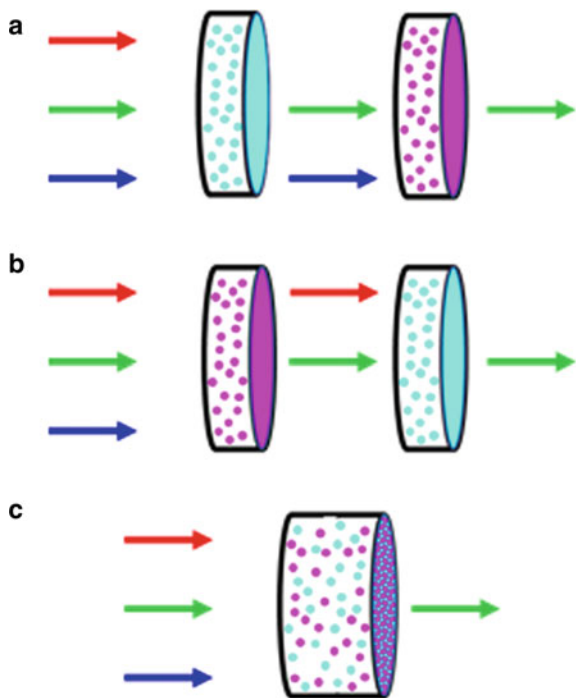
Light Absorption by Non-Scattering Mixtures

Paints are often tinted with more than one light absorbing species (i.e., more than one colorant), and so we must consider the light absorption of mixtures to fully understand color formation and color control in paints. In Fig. 15.5, we shine white light (a combination of red, green, and blue lights) through combinations of two differently colored glass filters, one cyan and the other magenta. As we will see in the next section, these are two of the three subtractive primaries, and these filters selectively absorb red and blue light, respectively. In Fig. 15.5a and b, we see white light passing through these filters sequentially, in each case resulting in the transmittance of green light. In Fig. 15.5c, we have fused the filters together and allowed the colored pigments to diffuse randomly between them.

Intuitively, we might expect the amount of light ultimately transmitted through the filters in Fig. 15.5a and b to be the same, and they are. This is because the light interacts independently with the pigments in the two filters, which is expected since the two pigments are separated from one another. Perhaps less intuitively, the situation in Fig. 15.5c results in the transmittance of the exact same green light as in the other two configurations.¹ We can infer from this that the two pigments interact independently of one another even when they are in close proximity and intimately mixed.

¹ Note that the concentrations of the colorants in the fused filter are half that in each unfused filter, but the thickness of the volume containing each colorant has doubled, resulting in the same total absorption. This is consistent with the facts that the number of absorbing species is the same in the fused filter as in the individual filters, and that the absorption strength of an individual particle does not change with particle concentration or the presence of other types of particles.

Fig. 15.5 White light transmitted through color filters



In Fig. 15.5, each filter absorbed a different region of the visible spectrum and so there was no overlap between them. However, in the vast majority of cases where two (or more) colorants are combined, there is absorption overlap. Of concern to us is how we can calculate the spectra of such combinations. In this case, we cannot simply add or average percent transmittance curves. Instead, the percent transmittance at a particular wavelength is the product of the percent transmittance of the individual colorants at that wavelength. That is, if one colorant transmits 50% of incident light and another transmits 80%, then the total transmission is 80% of 50%, or 40%.

Because of the power relationship between percent transmittance and absorbance, multiplying transmittance values together is the equivalent of adding absorbance values together. In the example above, the absorbance values for the individual components of the mix are 0.301 (for 50% T), 0.097 (for 80% T), which sum to an overall absorbance value of 0.398 (equivalent to 40% T). We will see throughout this chapter the use and usefulness of the additivity of absorbance values.

Finally, by definition, no light is transmitted through an opaque object such as a fully hiding paint film. Our interest here, however, is on the light that is reflected from the film, not light that is transmitted through it. That said, the same rules and equations apply to light reflected from an opaque sample as to light transmitted through a translucent one.

Subtractive Primaries

We can divide the visible spectrum into three broad regions: a long wavelength red region, a mid-wavelength green region and a short wavelength blue region. Roughly speaking, we can say that a representative wavelength from each of these regions can be used as a primary color for additive color mixing (as is the case for RGB color space). Choosing one primary from each region gives us a wide color gamut.

For the subtractive primaries, we begin with a background illuminated by white light, and subtract light from each of the three regions. We can think of these primaries as “white light without red” (that is, blue mixed with green, giving cyan), “white light without green” (that is, blue mixed with red, giving magenta) and “white light without blue” (that is, green mixed with red, giving yellow). We create a wide color gamut when we remove the appropriate amount of color represented by each of these primaries from white. These primaries, and the colors made from them, were shown earlier in Fig. 15.1b.

A significant difference between additive and subtractive color mixing is that for additive mixing we can use a single wavelength for each primary. However, for subtractive mixing, we must use primaries that absorb a range of wavelengths. This is because removing only one wavelength of light has a very small effect on color. Colors span a range of wavelengths, and large regions of this range must be removed to have the desired effect on color.

Metamerism Revisited

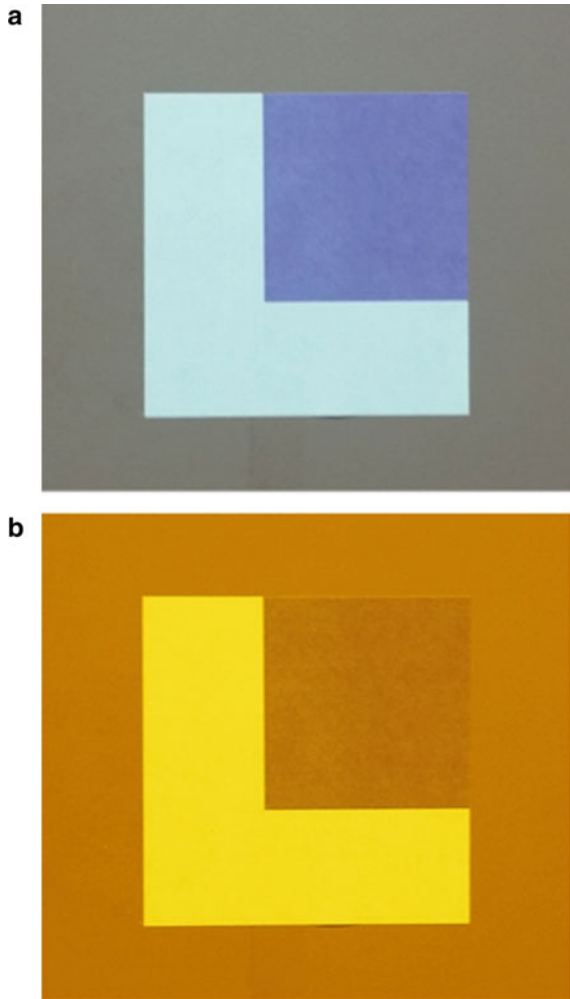
In Chap. 5, we discussed metamerism, which is the phenomenon by which two different stimulus spectra give us the same color sensation. Our discussion was in the context of additive color mixing, where three well-chosen primaries can combine to reproduce most color sensations, even those for which the stimulus spectrum is quite complex. In this context, metamerism is very useful—it is, in fact, the basis by which all color screens and monitors operate, and this form of metamerism makes possible a gamut of millions of colors using only three primary lights.

There are two other forms of metamerism, and these are far less desirable. The first is observer metamerism. In this situation, two different stimulus spectra appear as identical colors to one observer, but different colors to another, even under the same viewing conditions. This comes about because visual perception differs from person to person. Of particular importance are the exact absorption characteristics of the color-sensing chemicals (opsins) in the cone cells, the distribution of these cells on the retina, and age-related yellowing of the lens. All of these vary slightly from one person to another, resulting in color matching functions that vary slightly from one person to another. As an extreme example, a person with color blindness may judge green and red panels to look the same (that is, to be metameric), while someone with more normal vision would see a sharp difference between the two.

The final form of metamerism that we will consider is termed “illuminant metamerism”. This form of metamerism can be a serious issue for the paint maker. Here, we find that two colors match when illuminated by one light source but appear different when illuminated by another. This occurs when the reflectance spectra of the two objects are different, but in such a way that when we multiply them by a certain source spectrum, to give a stimulus spectrum, the resulting color sensations are the same (that is, the stimulus spectra have the same tristimulus values). When illuminated with a different source, the two objects no longer have the same tristimulus values and so their color sensations will be different.

A visual example of this can be seen in Chap. 5, Fig. 5.11, reproduced here as Fig. 15.6. In this figure, a dark blue square was printed on a sheet of white paper, and

Fig. 15.6 Photographic example of metamerism. Both images are of the same composition. **a** Illuminated by white light; **b** Illuminated by yellow light. Note that the color of the light itself is seen in the “L” shaped region



this paper was laid over a mauve background. Figure 15.6a shows the appearance of the paper, the printing, and the background under normal fluorescent lights. Here the difference in color between the blue square and the mauve background is readily apparent. However, in Fig. 15.6b, the same scene is illuminated by a yellow light, the color of which can be seen in the white portion of the paper. Under this light, the blue square and mauve background give nearly identical color sensations.

We can demonstrate this form of metamerism using the reflectance curves from earlier (Fig. 15.4). In that figure, we showed the reflectance curves for two different paints as viewed under Illuminant E. As noted earlier, the tristimulus values for these curves are equal, and so the color sensations of these paints were the same. However, if we change illuminants, we shift these color sensations differently. Figure 15.7 shows the approximate colors of these paints under CIE Illuminants E, D_{65} and FL1. Under Illuminant E the color sensations are equal, as shown in Fig. 15.4a. Under Illuminant D_{65} the color sensations are close, but not quite the same. However, under Illuminant FL1, the color sensations of the two paints are quite noticeably different.

Illuminant metamerism in the coatings industry typically occurs for one of two reasons. The first is when a paint color is matched to a non-paint color. For example, portions of a car exterior are painted while other portions are made of colored plastic

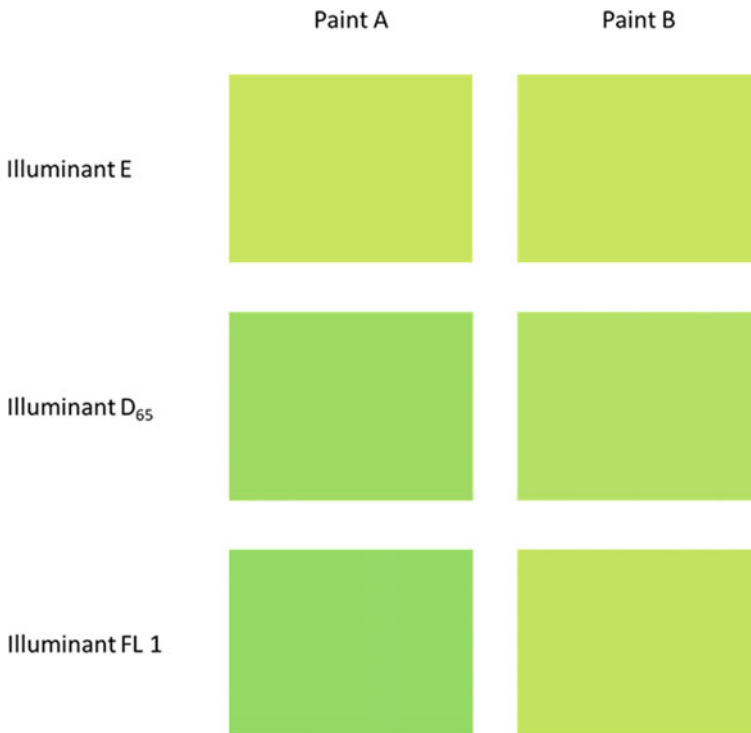


Fig. 15.7 Approximate colors of paints in Fig. 15.4a illuminated by three different light sources

(e.g., the bumper). The colors of the paint and plastic must match one another under any viewing condition. Simply having the same pigments in the same proportions does not guarantee a color match. In addition, different pigments are often used by the plastics and coatings industries. Often the automobile industry will simply paint exterior plastic parts rather than try to attain a so-called “in-mold” color match, in which the polymer is pigmented such that an accurate and non-metameric match can be made.

The second common occurrence of illuminant metamerism occurs when the color of a paint made with one set of pigments is matched to a paint made with a different set of pigments. For example, a paint formulator might wish to duplicate the green color of a certain automotive paint for spot or collision repair but does not have the same green pigment as was used in the original paint. In this case, a match can be successfully made under one type of illumination, only to look different under another illumination. Because different green pigments have different reflectance spectra, it is generally not possible to make a match using two different colored pigments that is not metameric under some lighting condition.

Application to Paints

We discussed light absorption in the absence of scattering above, and light scattering in the absence of absorption in Chap. 3. While some paints interact with light in one of these ways but not the other, most paints—all those that are colored and opaque—scatter and absorb light simultaneously. As might be anticipated, combining these types of light interactions complicates the analysis of color and of color mixing.

The basis for understanding color mixing in paints is a theoretical framework reported by Kubelka and Munk in the early 1930s [2]. They approached the issue of light interactions in paint films by treating a paint film as a homogenous material with certain light scattering and light absorption properties. This ignores the fact that paints are composed of discrete particles that interact with light and that are embedded in a continuous phase of nearly transparent resin. In the Kubelka–Munk model, the mechanisms of light scattering and light absorption are unimportant—what is important is that these processes occur and that they follow certain rules [3].

The Kubelka–Munk approach to light interactions in films containing only scattering particles was discussed in detail in Chap. 13. Here, we will focus on a different aspect this approach—how we can predict color resulting from the mixing of differently colored paints, or when more than one colorant is added to a white base paint. Our goals are to develop a procedure for matching a specific color with a set of colorants and to predict the color of a mixture of colorants or colored paints.

A recurring quantity in the Kubelka–Munk analysis is the ratio K/S , that is, the balance between the amount of light scattered out of an opaque film (S) and the amount of light absorbed by that film (K). In the general case of light interactions with a film, there is a third possible fate of a photon—exiting the bottom surface of the

paint film (where it will interact with the substrate). By definition, films at complete hide have no light crossing their lower surface (the film/substrate interface).

In the analyses of one-constant Kubelka–Munk theory below, we consider only opaque films, and all photons striking such films are either absorbed or reflected back through the film surface. Under these conditions, it is possible to measure the ratio of K/S , but not K and S values separately. The “one constant” in the one-constant Kubelka–Munk analysis is the ratio of K/S . In two-constant Kubelka–Munk theory, also discussed below, we use the individual values of K and S (these are the “two constants”), which are calculated from the optical properties of films that are not thick enough to give complete hide.

S and K are already familiar to us from Chap. 13. The total amount of scattering and absorption in an opaque paint film is simply S times X and K times X , respectively, where “ X ” is the film thickness (analogous to “ b ” in the absorption equation). In colored paints both K and S vary over the wavelength range of visible light, and we typically measure them at wavelengths from 400 to 700 nm, in intervals of 5 nm or 10 nm.

The balance between the total amount of light absorbed by a paint film and the total amount of light scattered by it is KX/SX , which simplifies to K/S . Paints with large K/S ratios are dark and have low reflectance values, whereas those with small K/S ratios are light and have high reflectance values. Kubelka and Munk showed that the equations governing the wavelength-dependent relationship between K/S and reflectance, measured on an opaque film, are²:

$$(K/S)_\lambda = \frac{(1 - R_\lambda)^2}{2R_\lambda} \quad (15.1)$$

$$R_\lambda = 1 + (K/S)_\lambda - \sqrt{(K/S)_\lambda^2 + 2(K/S)_\lambda} \quad (15.2)$$

In these equations and those that follow, reflectance values must be expressed as fractions, from 0 to 1, rather than as percentages, from 0 to 100. That said, reflectance spectra will be shown in various figures in this chapter as percentages, as this conforms to the typical way that absorption is measured and reported.

Equation (15.1) provides us with a simple way to determine the ratio K/S from measured reflectance values at complete hide. This information is sufficient for calculating the color mixing behavior of paints and colorants that contain only one scattering component (typically TiO_2). However, the color mixing behavior of paints

² Note that what we are calling “ R_λ ” here is the reflectance, at each wavelength, of the paint when it is applied thickly enough to give complete opacity. In Chapter 13, we saw similar equations that referenced “ R_∞ ”, which is the total reflectance over the entire visible spectrum (that is, the tristimulus Y value), as determined on a film thick enough for complete hide, rather than the reflectance at specific wavelengths of light. As such, R_∞ is not a function of a particular wavelength of light but is instead a measure of the overall lightness of the paint.

and colorants with more than one light scattering material is controlled by the individual values of K and S. Determining these values separately is more difficult than determining their ratio K/S—the calculations involved are detailed in Chap. 13.

Colored Paints

In our discussion above we showed that light absorption values are additive—that is, we can determine the combined light absorption of a mixture of materials (e.g., different colorants) by adding together their separate absorbances. The contribution to absorbance by a given species is simply its unit absorption coefficient k multiplied by its concentration C .³ We can therefore express mathematically the absorption value of a mixture as:

$$K_{mixture,\lambda} = C_1k_{1,\lambda} + C_2k_{2,\lambda} + C_3k_{3,\lambda} + \dots = \sum C_nk_{n,\lambda} \quad (15.3)$$

As in previous equations, and in those that follow, the symbol “ λ ” indicates values that are wavelength dependent and so must be measured or calculated across the visible light spectrum. The C_n values are the concentrations of each absorbing species, and the $k_{n,\lambda}$ values are the unit absorptivities of each species at each measured wavelength.

Similarly, the scattering value (S) of a mixture is determined by simply adding the individual scattering values for the constituent materials, also adjusted for concentration:

$$S_{mixture,\lambda} = C_1s_{1,\lambda} + C_2s_{2,\lambda} + C_3s_{3,\lambda} + \dots = \sum C_ns_{n,\lambda} \quad (15.4)$$

The K/S ratio for the mixture is simply the sum of K values for the individual components (adjusted for concentration) divided by the sum of S values (also adjusted for concentration) [4]:

$$(K/S)_{mixture,\lambda} = \frac{C_1k_{1,\lambda} + C_2k_{2,\lambda} + C_3k_{3,\lambda} + \dots}{C_1s_{1,\lambda} + C_2s_{2,\lambda} + C_3s_{3,\lambda} + \dots} = \frac{\sum C_nk_{n,\lambda}}{\sum C_ns_{n,\lambda}} \quad (15.5)$$

³ We will follow the established convention of notating the total absorption and scattering of a paint using capital (upper-case) letters K and S while using the lower-case letters k and s to designate unit absorption and scattering coefficients. The latter parameters must be multiplied by concentration to give the total amounts of absorption and scattering. That is,

$$K_{i,\lambda} = Ck_{i,\lambda}$$

$$S_{i,\lambda} = Cs_{i,\lambda}$$

for each component of the paint system.

Color Matching

Matching a paint to a specific color is a multi-step process [5]. It begins with the generation of a library of the spectrum of each available constituent that interacts with light, including all colorants and the white base paint that is to be used for the color match. In addition, the spectrum of the color to be matched is measured.

Next, spectra are calculated for combinations of selected colorants, and these spectra are compared to that of the target color. Colorant selection is chosen based on the target color, either by prior experience or through an automated selection process. A least-squares analysis is used to quantify the degree to which the spectrum of particular combinations matches the target spectra [6]. This program can optimize color in one of two ways: either to get the least deviation between the target and calculated spectra (for example, minimizing the area of a graph of the difference between the two spectra), or to get the closest color match based on the CIE X, Y and Z tristimulus values calculated for the spectra [1, 5].

Unless the exact same colorants are used in the test paint and target paint, it is likely that there will be some degree of metamerism between the two (if the same colorants are used, then an exact match can be made, resulting in no metamerism). Optimizing for the least deviation between the two spectra typically results in less severe metamerism, while optimizing on tristimulus values typically results in a better match under a single lighting condition but is more prone to the generation of metameric colors. In addition, minimizing the number of colorants used to match the spectra decreases the likelihood and severity of metamerism.

One-Constant Kubelka–Munk Theory and Practice

Equation (15.5) simplifies considerably when only one of the mixture components contributes to scattering. This situation describes the coating formulations for which TiO_2 is the only light scattering material (that is, scattering from extenders and colorants is insignificant due to their much lower indices of refraction). This leads us to the so-called one-constant equation Kubelka–Munk equation [7]:

$$\begin{aligned} (K/S)_{mixture,\lambda} &= \frac{C_w k_{w,\lambda} + C_1 k_{1,\lambda} + C_2 k_{2,\lambda} + \dots}{C_w S_w} \\ &= (k_w/S_w)_\lambda + \frac{C_1}{C_w} (k_1/S_w)_\lambda + \frac{C_2}{C_w} (k_2/S_w)_\lambda + \dots \end{aligned} \quad (15.6)$$

where the subscript “w” refers to the white pigment. The term “one constant” refers to the fact that in this procedure we use the ratio K/S for each component and do not calculate K and S separately. We can measure this ratio for a given paint by measuring the reflectance of that paint at complete hide (Eq. 15.1). To measure K

and S separately, as is done in the two-constant approach, we must measure the reflectances of paint films that are not at complete hide.

In many paints, the white pigment is incorporated into a base paint to which colorant is added. Assuming that the volume of colorant added is small compared to the volume of white base, the concentration of the white pigment will not change when tinted. We will therefore define the unit concentration of the white pigment as its concentration in the base ($C_w = 1$). This simplifies the above equation to:

$$(K/S)_{mixture,\lambda} = (K/S)_{w,\lambda} + C_1(k_1/S_w)_\lambda + C_2(k_2/S_w)_\lambda + \dots \quad (15.7)$$

Calculating the Colors of Paint Mixtures

When mixing colorants into a white base paint, we can use Eq. (15.7) above to model and predict the color resulting from a colorant mixture, if we know the reflectance spectrum of each colorant when incorporated individually into the base paint. To demonstrate this, we will consider three color mixing examples that are representative of this practice.

For these examples, we will use the same white base paint. We will make the assumptions that all scattering comes from the white base, that the white base may absorb some light (that is, it may not be a true white), that the volume of colorant added to the base paint is insignificant compared to the volume of the base paint itself, that the drawdowns we analyze are made at sufficient thickness to give us complete hide at all visible light wavelengths, and that there are no interactions between pigments that would alter either the s or the k of any species. Finally, we will assume that the unit absorptivity k for each colorant is constant over all concentrations considered. Of these assumptions, this final one is the most likely to be violated in practice, resulting in computational inaccuracies for dark paints. In those cases, an equation should be developed relating k to concentration, and this equation used in place of a constant k value in any calculations.

The Saunderson Correction

In addition to these assumptions, there is an implicit assumption in most reflectance measurements that there is no loss of light intensity due to reflection at the surface of the film when light passes between air and the film, or when light travels from the film into the substrate. Since our concern is with the reflectance events that occur within the paint film (“internal reflectance”), we may wish to correct the measured R values so as to remove the effects of any reflectances that occur at the air/film or film/substrate interfaces and avoid this implicit assumption. While this is an important

consideration in some situations and studies, for others the measured reflectances are sufficient for analysis [8].

The factor controlling whether or not corrected reflectances are needed is the type of analyses under consideration. When analyzing the reflectances of paints of different colors, but otherwise similar compositions and properties (i.e., same gloss, same TiO₂ content, same resin, etc.), the effects of surface reflectance nearly cancel, and we can safely use the measured reflectance values rather than corrected ones. We will test this assumption in one of our worked examples by comparing R_λ values calculated on both a corrected and uncorrected basis. On the other hand, if the motivation of the work is to match measured reflectance data to theoretical data, to measure reflectance with high accuracy, or to derive new insights in light interactions in a paint film, then the measured data must be corrected for surface reflectance.

Reflection at surfaces was first studied by Fresnel. Surface reflection occurs whenever there is a discontinuity in refractive index—that is, whenever light passes from a material with one refractive index into a material with a different refractive index. The magnitude of Fresnel reflectance is determined by the degree of difference between the refractive indices (see also Chap. 3, Eq. 3.2)⁴:

$$\text{Reflected intensity} = \left[\frac{n_1 - n_2}{n_1 + n_2} \right]^2. \quad (15.8)$$

For our purposes, n_1 is the refractive index of air (1.0) and n_2 is the refractive index of the film, which is typically assumed to be 1.5 for most paints.

There are some situations where the effects due to reflection when comparing two films do not adequately cancel. In these situations, a correction can be made to the measured reflectance values that remove from them the contribution of surface reflectance. This correction was developed by Saunderson [9], and takes into account the surface reflection that occurs both when the light enters the film and when internally reflected light leaves through the top surface of the film (since we are only considering films with complete hide, none of the light will leave through the bottom surface, or back, of the film). This correction is:

$$R_{\lambda,i} = \frac{R_{\lambda,m} - K_1}{1 - K_1 - K_2 + K_2 \cdot R_{\lambda,m}} \quad (15.9)$$

where $R_{\lambda,i}$ is the internal reflectance within the film (which is the reflectance value used in the Kubelka–Munk equations), $R_{\lambda,m}$ is the measured reflectance, K_1 is the Fresnel reflectance (Eq. 15.8), which corrects for light reflecting when traveling from air to the film, and K_2 is a correction for the reflection of light that occurs at the film/air interface when the light exits through the top surface of the film. Note that

⁴ This equation applies only to light that is incident normal to the surface. The relationship between the fraction of light reflected and the angle of incidence is complex.

the symbol “K” here is used much differently than in the Kubelka–Munk equations, where “K” is the absorption coefficient.

Assuming the light within the film is completely diffuse (that is, its direction is completely randomized), K_2 can be calculated by integrating the Fresnel equations from 0 to 90 degrees. The value for K_2 generally falls between 0.4 and 0.6. A K_2 value of 0.40 has been reported to give good results [10], although some workers prefer to use K_2 as an adjustable parameter to optimize the fit between a calculated reflectance spectrum and its measured counterpart [7, 11]. In any event, the actual value used for K_2 is less important than is using the same value in all calculations [12].

The Saunderson correction is applied as follows [5]: The measured reflectance values are transformed into internal reflectance values ($R_{\lambda,i}$) using Eq. (15.9). These reflectances are used to determine the $(K/S)_\lambda$ values for the film, using Eq. (15.1). The $(K/S)_\lambda$ values are then processed (by the procedure shown in the worked examples) to give the internal reflectance spectra of mixed color paints. These calculated internal reflectance values are then be back-transformed into corrected measured reflectance values ($R_{\lambda,corrected}$), using this equation [9]:

$$R_{\lambda,corrected} = K_1 + \frac{(1 - K_1) \cdot (1 - K_2) \cdot R_{\lambda,i}}{1 - K_2 \cdot R_{\lambda,i}} \quad (15.10)$$

Worked Examples

There are several different situations where we would like to accurately predict the reflectance spectrum of a colored paint. The two most common are matching a specific color using a limited number of colorants with known reflectances, and predicting the color formed when two or more colorants or paints with known reflectance spectra are mixed.

This process begins by measuring the optical properties of the colorants or colored paints containing the colorants. These measurements are then combined mathematically to determine the expected spectra of paint mixtures.

The steps for this process are:

1. Measure the reflectance spectrum of the paints that will be the basis of our mixtures.
2. If desired, apply the Saunderson correction to the measured reflectance values using Eq. (15.9).
3. Convert the reflectance values into K/S values using Eq. (15.1).
4. Combine the K/S values measured for the basis paints for the mixture of interest using Eq. (15.6).
5. Convert the K/S values for the mixture to reflectance values using Eq. (15.2).

6. If the Saunderson correction was used (step 2), back-transform the reflectance values using Eq. (15.10).
7. The calculated reflectance spectrum for the mixture can be compared to the measured reflectance spectrum if desired. The color sensations of each can be converted to $L^*a^*b^*$ values by applying the procedure described in Chap. 6. The difference in calculated and measured colors can be quantified as ΔE and used to determine the validity of the calculated spectrum.

In the examples below, we will apply Saunderson correction to the measured reflectance values using 0.04 for the K_1 value and 0.40 for the K_2 value. In these examples, we will evaluate four situations that are commonly encountered in color mixing—mixing two paints of different color, diluting a colored paint with its white base paint, adding more colorant to a paint that already has that same colorant (i.e., increasing the concentration of that colorant), and adding a colorant to a paint that already has a different colorant (that is, to a paint of a different color). Because the same base paint is used in all of these examples, the TiO_2 content will be the same for all mixtures of paints, making the scattering (S_w) and absorption (K_w) contributions of the white base paint the same in all colored paints. Note that this would not be true if we were mixing paints with different TiO_2 concentrations.

Our examples will make use of two colorants—one purple, the other yellow—and four paints—a white base paint, and a purple paint, a yellow paint and a gold paint (the latter made by doubling the yellow colorant amount in the yellow paint). The visible light reflectance curves for the four paints, measured in 10 nm intervals, are shown in Fig. 15.8. We see that the white paint reflects only ca. 90% of the incident light, rather than 100%, which technically makes this paint a very light gray color,

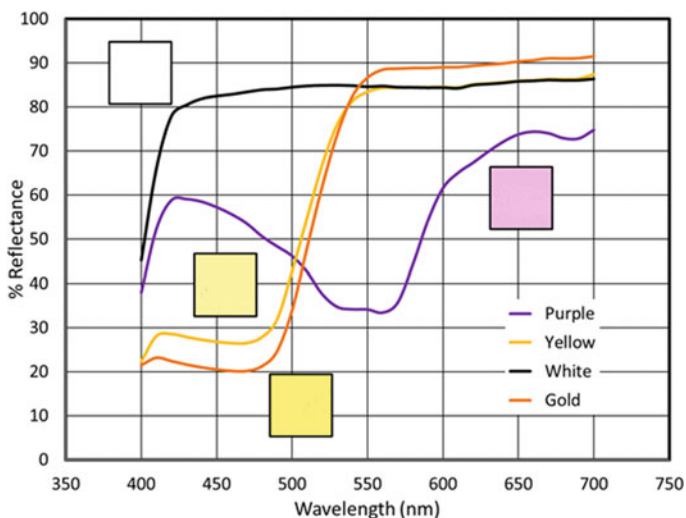


Fig. 15.8 Reflectance spectra of the four paints used in the color mixing studies. Insets show paint color

rather than true white. This is not uncommon for “white” paints, and most people would consider this level of brightness to signify white, rather than gray.

In our first example, we will mix the yellow paint with the purple paint. We will not initially choose specific amounts of the two paints for this mixture, but instead solve the problem more generally. We begin by defining the K/S values for the initial paints, starting with the yellow paint. This paint is a mixture of yellow colorant (y_c) and white paint (w). Since we are deriving a general solution to such mixing, we will leave these concentrations as parameters rather than numeric values.

Substituting into Eqs. (15.3) and (15.4), we get:

$$K_{yellow\ paint,\lambda} = C_{y_c}k_{y_c,\lambda} + C_wk_{w,\lambda} \quad (15.11)$$

$$S_{yellow\ paint,\lambda} = C_{y_c}s_{y_c,\lambda} + C_ws_{w,\lambda} = C_ws_{w,\lambda} \quad (15.12)$$

Note that we have removed the term $C_{y_c}s_{y_c,\lambda}$ from the scattering component (Eq. 15.12) because we are assuming that the colorant does not scatter light (if the colorant scatters light, then the two-constant Kubelka–Munk approach must be used, as outlined below). Although the ideal white paint would not absorb any light, as mentioned above and clearly seen in Fig. 15.8, the white base paint in our case does absorb some light and so we must include the contribution $C_wk_{w,\lambda}$ in the absorbance component of this paint.

From Eqs. (15.5) and (15.11) we define the K/S value for the yellow paint as:

$$(K/S)_{yellow,\lambda} = (K_{yellow\ paint,\lambda}/S_{yellow\ paint,\lambda}) = (K_{yellow\ paint,\lambda}/C_ws_{w,\lambda}) \quad (15.13)$$

Similarly, for the purple paint:

$$(K/S)_{purple,\lambda} = (K_{purple\ paint,\lambda}/C_ws_{w,\lambda}) \quad (15.14)$$

We next consider the mixture of A parts yellow paint and B parts purple paint. Substituting Eqs. (15.11) and (15.12), and their purple counter-parts, into Eq. (15.5) gives, for the mixture,

$$\begin{aligned} (K/S)_{mixture,\lambda} &= \frac{\sum C_n k_{n,\lambda}}{\sum C_n s_{n,\lambda}} = \frac{A \cdot K_{yellow\ paint,\lambda} + B \cdot K_{purple\ paint,\lambda}}{A \cdot C_w s_{w,\lambda} + B \cdot C_w s_{w,\lambda}} \\ &= \frac{A \cdot K_{yellow\ paint,\lambda} + B \cdot K_{purple\ paint,\lambda}}{(A + B) \cdot C_w s_{w,\lambda}} \\ &= \left(\frac{A}{(A + B)} \right) \cdot \frac{K_{yellow\ paint,\lambda}}{C_w s_{w,\lambda}} + \left(\frac{B}{(A + B)} \right) \cdot \frac{K_{purple\ paint,\lambda}}{C_w s_{w,\lambda}} \end{aligned} \quad (15.15)$$

Substituting Eqs. (15.13) and (15.14) into Eq. (15.15) gives:

$$(K/S)_{mixture,\lambda} = \left(\frac{A}{(A+B)} \right) \cdot (K/S)_{yellow,\lambda} + \left(\frac{B}{(A+B)} \right) \cdot (K/S)_{purple,\lambda}$$

or

$$(K/S)_{mixture,\lambda} = C'_y \cdot (K/S)_{yellow,\lambda} + C'_p \cdot (K/S)_{purple,\lambda} \quad (15.16)$$

where C'_y is the fractional concentration of the yellow paint and C'_p is the fractional concentration of the purple paint. Note that, since C'_y and C'_p add up to 1.0, the scattering component of all mixtures, regardless of the values of A and B, are the same and identical to the scattering component of the white base paint.

Equation (15.16) can be worded as “the K/S for the mixture is the weighted sums of the (K/S) values of the components”. This is something we may have expected intuitively based on the additive natures of the absorption and of scattering.

A comparison of the calculated reflectance values of a 3:1 mix of the purple and yellow paints to the measured values for a physical mix of these paints is shown in Fig. 15.9. As can be seen, there is excellent agreement between the calculated and measured reflectance values. Such agreement confirms the validity of this type of analysis as well as the complete compatibility between the different color pigments.

We next look at the dilution of a colored paint with its white base paint. Here, we will consider a series of three dilutions of the gold paint with the white base paint, as well as the gold and white base paints themselves. Such a series of paints is called a “tint ladder” and is very useful in determining whether the k and s values

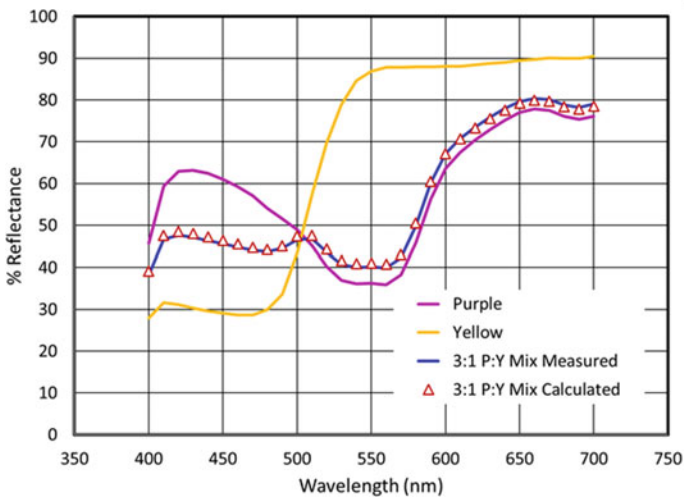


Fig. 15.9 Reflectance spectra for purple and yellow paint mixture (3:1 by volume)

(that is, the unit absorptivity and unit scattering constants) for the colored components of the paint are constant over the range of concentrations that they bracket. This is a basic assumption in paint color mixing but is often violated, especially at high colorant concentrations. If this assumption is found to be violated, then a mathematical expression of the k or s values as a function of concentration must be determined, and this expression is used in place of the constants k and s in the color mixing equations. Obviously, this adds much complexity to these calculations.

The following five paints are used in this example:

- undiluted gold paint
- 75% gold paint, 25% white base
- 50% gold paint, 50% white base
- 25% gold paint, 75% white base
- white base.

Note that the third paint is identical to the yellow paint used in the previous example (i.e., it is the paint with the $2 \times$ concentration of yellow pigment that is then diluted by one half). In this example, we will calculate the predicted spectra both with and without the Saunderson correction. We can then compare the calculated results to the measured results to determine the magnitude of this correction for these paints.

To calculate the predicted reflectance spectra of the different dilutions, we will use Eq. (15.16), but with the yellow and purple paints being replaced by the gold and white paints (Eq. 15.17). Importantly, to calculate the optics of, for example, the gold paint diluted to 75% with the white base paint, we do not simply take three quarters of the K/S value of the gold paint. Doing so would ignore the contribution that the added white base makes to the absorption of the mixture.

$$(K/S)_{mixture} = C'_y \cdot (K/S)_{gold,\lambda} + C'_p \cdot (K/S)_{white,\lambda} \quad (15.17)$$

The measured reflectance values of the five paints are shown as solid lines in Fig. 15.10. In this figure, the reflectance values predicted for the three mixtures are shown as symbols and the measured reflectance values are given as lines. Figure 15.10a shows the results when the Saunderson correction is omitted and Fig. 15.10b shows the results with the Saunderson correction included. In this case, the fit of predicted and measured reflectances improves with inclusion of this correction, although even the uncorrected values are close to those measured.

We next consider the addition of colorant into a paint already colored by this same colorant. In this case, we will calculate the reflectance spectrum of the yellow paint to which a second, identical dose of yellow colorant was added (that is, we will calculate a predicted spectrum for the gold paint, based on the addition of more yellow colorant to the yellow paint).

Our first inclination may be to simply double the K/S value for the initial yellow paint (that is, we double K and leave S unchanged). Doing so, however, will also double the contribution of the white base paint to the total absorption, which is incorrect since the concentration of the white pigment in the double dosed paint is the same as in the single dosed paint.

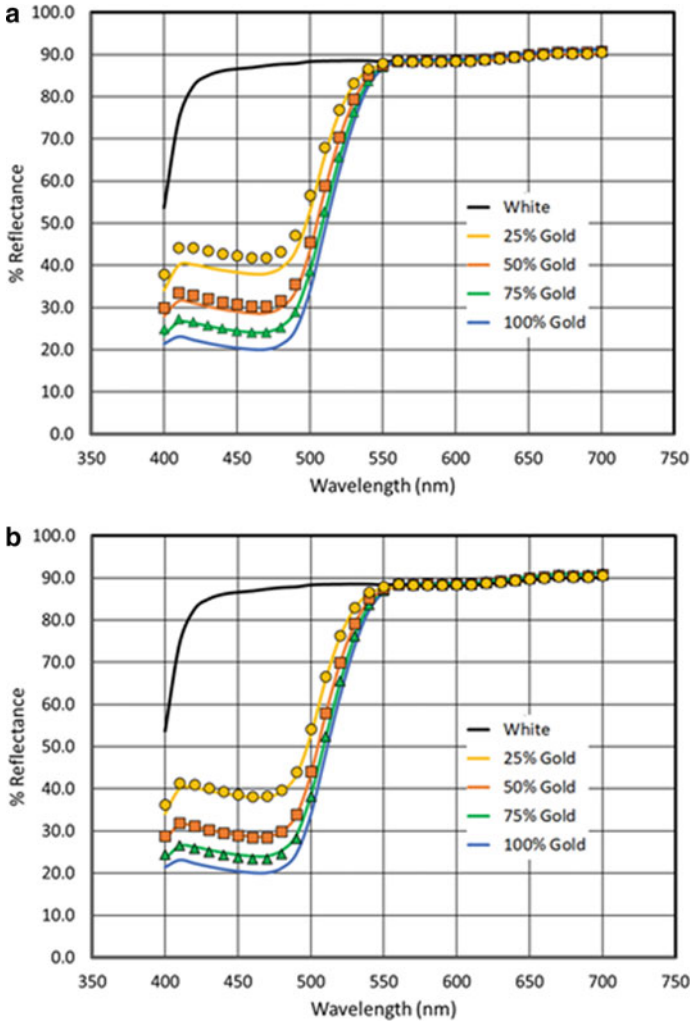


Fig. 15.10 Reflectance spectra of diluted gold paints. **a** Uncorrected. **b** With Saunderson correction

Instead we begin with Eqs. (15.3)–(15.5) and define the individual absorption and scattering contributions of the components of the double dosed paint, which gives us:

$$K_{double\ dose,\lambda} = (C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda}) + C_{yc}k_{yc,\lambda} \tag{15.18}$$

$$S_{double\ dose,\lambda} = C_wS_{w,\lambda} \tag{15.19}$$

$$\begin{aligned}
 (K/S)_{double\ dose,\lambda} &= \frac{(C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda}) + C_{yc}k_{yc,\lambda}}{C_wS_{w,\lambda}} \\
 &= \frac{(C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda})}{C_wS_{w,\lambda}} + \frac{C_{yc}k_{yc,\lambda}}{C_wS_{w,\lambda}}
 \end{aligned} \tag{15.20}$$

The terms in parentheses in Eqs. (15.18) and (15.20) are the K contribution of the original paint, and the $C_{yc}k_{yc,\lambda}$ term is the contribution from the added colorant.

Equation (15.20) is partially solvable with the information we have on hand because we know, from

Equations (15.11) and (15.12), that $(K/S)_{yellow\ paint}$ is:

$$(K/S)_{Yellow,\lambda} = \frac{C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda}}{C_wS_{w,\lambda}} \tag{15.21}$$

We can combine Eqs. (15.20) and (15.21) to give:

$$(K/S)_{double\ dose,\lambda} = (K/S)_{Yellow,\lambda} + \frac{C_{yc}k_{yc,\lambda}}{C_wS_{w,\lambda}} \tag{15.22}$$

We have the measured reflectance curve of $(K/S)_{yellow\ paint}$ (Fig. 15.8), but we do not have the absorption values for the yellow colorant. We can measure this separately on the colorant alone—this is referred to as a masstone—but in the present case, we can calculate the absorption spectrum of the colorant based on the absorption spectra of the white paint and yellow paint. To do this, we modify the right side of Eq. (15.20) by adding and subtracting $C_wk_{w,\lambda}/C_wS_{w,\lambda}$ to it:

$$(K/S)_{double\ dose,\lambda} = \frac{(C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda}) + C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda}}{C_wS_{w,\lambda}} - \frac{C_wk_{w,\lambda}}{C_wS_{w,\lambda}} \tag{15.23}$$

This simplifies to:

$$(K/S)_{double\ dose,\lambda} = \frac{2 \cdot (C_{yc}k_{yc,\lambda} + C_wk_{w,\lambda})}{C_wS_{w,\lambda}} - \frac{C_wk_{w,\lambda}}{C_wS_{w,\lambda}} \tag{15.24}$$

The first term on the right-hand side of Eq. (15.24) is simply double the K/S value of the yellow paint (refer to Eq. 15.21). The other term in Eq. (15.24), $C_wk_{w,\lambda}/C_wS_{w,\lambda}$, is simply the (K/S) value of the white base paint. Based on these observations, we can restate Eq. (15.24) as:

$$(K/S)_{double\ dose,\lambda} = 2 \cdot (K/S)_{Yellow,\lambda} - (K/S)_{w,\lambda} \tag{15.25}$$

In Fig. 15.11, we see a comparison of the spectrum calculated from Eq. (15.25)

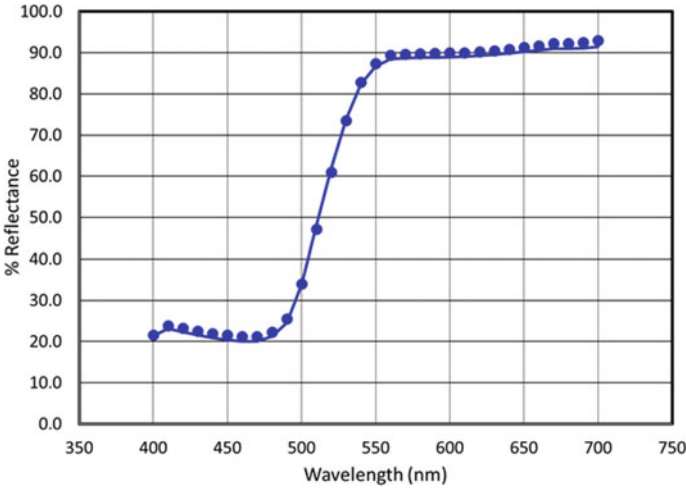


Fig. 15.11 Comparison between measured (line) and calculated (circles) reflectance values for a yellow paint with additional yellow colorant (i.e., the measured results are for the gold paint)

and the spectrum measured for the gold sample. In this case, the two spectra match nearly perfectly.

Our final example is for the addition of the yellow colorant into the purple paint. Here we will add the same amount of yellow colorant as used to make the yellow paint. This example is similar to that above, where yellow colorant was added to a yellow paint, but here with the complication that there are two colorants involved, rather than one.

Again we begin with Eqs. (15.3)–(15.5):

$$K_{yellow\ dose\ into\ purple, \lambda} = (C_{pc}k_{pc,\lambda} + C_wk_{w,\lambda}) + C_{yc}k_{yc,\lambda}$$

$$S_{yellow\ dose\ into\ purple, \lambda} = C_wS_{w,\lambda}$$

$$(K/S)_{yellow\ dose\ into\ purple, \lambda} = \frac{(C_{pc}k_{pc,\lambda} + C_wk_{w,\lambda}) + C_{yc}k_{yc,\lambda}}{C_wS_{w,\lambda}} \tag{15.26}$$

We can rewrite Eq. (15.26) as:

$$(K/S)_{yellow\ dose\ into\ purple, \lambda} = (K/S)_{purple,\lambda} + \frac{C_{yc}k_{yc,\lambda}}{C_wS_{w,\lambda}} \tag{15.27}$$

As was done with in the double dose of yellow colorant, we add and subtract $C_wk_{w,\lambda}/C_wS_{w,\lambda}$ to the right-hand side of Eq. (15.27):

$$(K/S)_{yellow\ dose\ into\ purple, \lambda} = (K/S)_{purple, \lambda} + \frac{C_{yc}k_{yc, \lambda} + C_wk_{w, \lambda}}{C_wS_{w, \lambda}} - \frac{C_wk_{w, \lambda}}{C_wS_{w, \lambda}} \tag{15.28}$$

We can substitute terms on the right side of Eq. (15.28) with Eq. (15.21) and with the definition of the K/S for the white paint ($C_wk_{w, \lambda}/C_wS_{w, \lambda}$):

$$(K/S)_{yellow\ dose\ into\ purple, \lambda} = (K/S)_{purple, \lambda} + (K/S)_{yellow, \lambda} - (K/S)_{white, \lambda} \tag{15.29}$$

Notice that we arrive at the exact same Equation if we were to dose the purple colorant into the yellow paint, as expected since these paints would have identical compositions.

The results of this calculation are shown in Fig. 15.12, along with the measured values for this paint and the measured spectra for a mix of the yellow and purple paints together in equal proportions, for reference. As can be seen, mixing the yellow and purple paints together gives a different reflectance spectrum than adding yellow colorant to the purple paint. This is because we are diluting the purple colorant when we mix the yellow and purple paints but not when we add the yellow colorant into the purple paint.

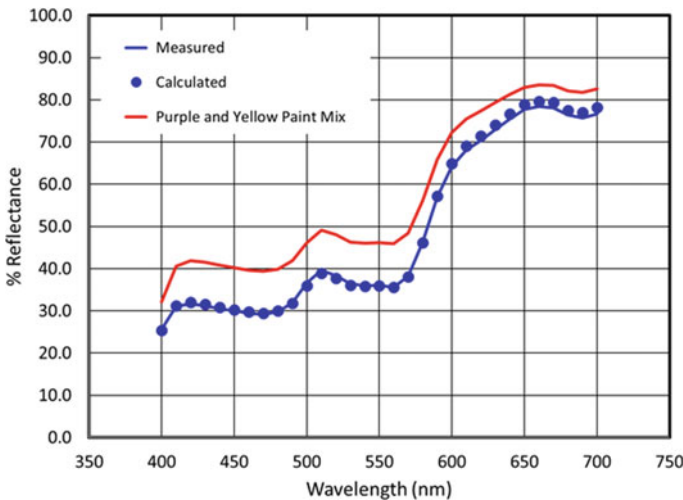


Fig. 15.12 Comparison between measured (blue line) reflectance values for a yellow paint with additional colorant, the calculated values for this paint (blue circles) and the measured values for a mix of the purple and yellow paints (red line)

Two-Constant Kubelka–Munk Theory

In the analyses outlined above, we assumed that the only significant light scattering came from the TiO_2 pigment. However, some colorants provide a non-insignificant amount of scattering in addition to their light absorption properties. When this is the case, we can no longer use Eq. (15.6) and those equations derived from it. Instead, we must use Eq. (15.5). This situation is referred to as the two-constant Kubelka–Munk analysis. A detailed study of this approach, as well as approaches that are hybrids of the one-constant and two-constant approaches, is beyond the scope of this book, but such studies are detailed elsewhere [13–18].

Limitations of the Kubelka–Munk Analysis of Color Matching

The equations and procedures that follow from the Kubelka–Munk analysis of colored paints are based on a number of assumptions, many of which were mentioned in the text. As such the values computed using these equations are only as good as the assumptions supporting them. It is important that, when using these equations to predict the colors of paint mixtures, the calculated values are confirmed by experimental values at the extremes of colorant concentrations.

Finally, in our examples of calculating the predicted reflectance spectra of paint mixtures, we included mixtures with different concentrations of colorants (e.g., the dilution of the gold paint with white base paint) but did not include examples of mixtures with different concentrations of TiO_2 . This was intentional. As discussed in Chap. 4, the scattering strength of TiO_2 particles changes significantly with TiO_2 concentration in paint films. If we were to add TiO_2 pigment to either the base paint or to a mixture of paints, or if we were to mix two paints with different TiO_2 content, the S_λ value would not simply change proportionally, as is the case for adding colorant to the base paint. We, therefore, see that we must limit all mixtures of paints to those having the same white base paint.

Inks

While inks and coatings share a number of related properties, there are some important differences between them. Inks are typically applied at a much lower thickness than paints, are typically applied only to white substrates (uncolored paper) and are not applied at complete hiding (in fact, many inks have minimal S values, making complete hide impossible except for black). Because inks are not applied at complete hide, some of the optical properties of the substrate (paper) show through the ink and so contribute to appearance. This is intentional as it can lead to brighter colors than if the ink was opaque.

Printer inks normally consist of four different colorants—the three subtractive primaries (cyan, magenta, and yellow) and black. These are collectively referred to as the CMYK colorants.⁵ Black ink is included for two reasons—it provides a truer black than a mix of the three colorants gives, and the colored pigments are generally more expensive than the black pigment, resulting in a higher cost for creating black by combining the three subtractive primaries.

Bright shades of colors are often needed in printing. In paints we create brightness by increasing the white pigment concentration, which increases the scattering of the film and so decreases the amount of light absorbed by it. In inks a different approach is used. Rather than mixing white pigment into the inks, the inks are applied thinly enough that the brightness of the underlying paper shows through [5]. As a general rule, the laws of optics are such that a higher brightness can be made by applying a thin coating of a non-light scattering colorant over a white background than can be made by combining the colorant with white. This rule is commonly used to increase brightness in ink applications but is seldom used for paints. The distinguishing factor being the color of the substrate—in inks the substrate is almost always white, whereas in paints it can be of any color. Paints are, of course, specifically designed to completely hide the substrate, whatever its color may be, and so cannot benefit from the substrate brightness.

Inks also differ from coatings in another fundamental way, and that is in how colors are mixed. In some printing processes, inks are applied as dots that are too small to be resolved by the human eye. When dots of different colors are placed one on top of the other, the colors subtractively mix, but when dots are placed separately but so close to one another that they cannot be resolved, the colors mix additively. This latter situation is quite analogous to the creation of color on an electronic screen by the activation of different colored dots that are too close together to be resolved.

There is a style of artistic painting that, like inks, exhibits both subtractive and additive color mixing. This style is called “pointillism” and entails placing small drops of color—too small to resolve by eye—next to one another. As in inks, this gives a different color sensation than if the colored paints were mixed prior to application.

The recognition that closely juxtaposed dots could create colors additively was first made by Chevreul in the mid-nineteenth century and was later popularized by the artist Georges Seurat at the end of that century. Seurat’s most famous painting, “A Sunday Afternoon on the Island of La Grande Jatte”, was created in this style (Fig. 15.13). This painting is quite large and meant viewed from a distance, which causes the colors of neighboring dots to blend with one another rather than to be seen discretely. On close inspection, the dots of paint are quite distinctive Fig. 15.13 inset. Seurat did not simply happen to paint in this manner—he was instead quite deliberate in its style, which at the time represented an innovation in the way that colors could be created with paints.

⁵ Here, “K” refers to the black colorant; “B” is not used as there is an opportunity to misinterpret this abbreviation as blue.



Fig. 15.13 “A Sunday Afternoon on the Island of La Grande Jatte”, G. Seurat (Art Institute of Chicago)

Summary

An object can interact with light by absorbing it, scattering it, or both. The laws of light absorption follow from the conjecture that light encountering a given absorption center has a specific chance of being absorbed by it, and that this chance does not change with concentration of the absorption centers. Light absorption can be characterized on either a percentage basis (percent reflectance) or a logarithmic basis (absorbance). For the color properties of paints, absorption is typically used because the absorbance of a mix of materials is simply the concentration weighted sum of the individual absorbances.

Most paints interact with light through both absorption and scattering. Predicting the color of a paint or colorant mixture, or matching a specific color, can be done using the Kubelka–Munk framework. In this framework, a unit volume of paint film is characterized as having certain scattering (S) and absorption (K) strengths without regard to the physical processes that give rise to these interactions. Many optical properties of the film are controlled by the relative strengths of absorption

and scattering (S and K), and so their ratio (K/S) is of high importance in the various Kubelka–Munk equations.

Because both S and K are additive, the S and K values for mixtures of colors are simply the weighted average values for the component colors. This provides a means of predicting the reflectance spectrum of a color mix based on the reflectance spectra of the component colors. The reflectance values of the component spectra, at each wavelength of interest, are converted into K/S values, and then the K/S values of the components are weighted according to concentration, then added together. This gives the K/S of the mixture at that wavelength. The K/S values for each wavelength are then converted to reflectance values, resulting in the predicted reflectance spectrum for the color mixture.

The Kubelka–Munk equations are based on reflectances within the paint film, and these differ from the measured reflectance values due to light reflecting at the air/film interface. When comparing paints that differ in color but are otherwise similar (i.e., the same TiO₂ content, gloss, etc.), surface reflectance can be ignored without great loss of accuracy. However, in cases where the paints differ significantly, or when the goal is to compare measured reflectance values to a theory, then corrections to the reflectance values should be made.

References

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