Experiments on subtractive color mixing with a spectrophotometer

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We describe experiments on color mixing suitable for undergraduate nonscience majors. A commercial spectrophotometer is used to study the spectra of light sources, combinations of color filters, and mixtures of acrylic paints. Special emphasis is placed on teaching the fundamentals of subtractive color mixing and the complex processes that occur in mixing pigments.

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I. INTRODUCTION

The experiments described in this paper were developed as part of a laboratory for a "Physics in the Arts" course for undergraduate nonscience majors. In a prior experiment the students studied additive color mixing using three projectors, with red, green, and blue filters (RGB), respectively, each with variable intensity. The intensity of these RGB lights is measured to determine the RGB components of various colored papers (or of colored plastic filters) illuminated by white light. The goal of that experiment is to analyze how an arbitrary color can be represented by addition of RGB.

In daily life the most common experience of additive color mixing is in the display of colors on TV or computer displays. Irrespective of the display technology (for example, color LCD, plasma screens, digital light processing), these displays are based on closely spaced arrays of RGB colored pixels, sufficiently close that the additive perception of the retina corresponds to the sum of multiple RGB pixels. Subtractive color mixing is encountered primarily in connection with mixing of paints or pigments, be it in the artist's studio or in magazine or computer printing. The other use of subtractive color mixing is in color photography, where the gamut of colors in slides or motion picture film is produced by three layers of color-absorbing chemicals, dyed respectively with the subtractive primaries cyan (blue-green), magenta, and yellow.

To analyze the spectral intensity distribution of different colored filters and of paints mixed in different proportions, we use a spectrophotometer connected to a computer, which displays the intensity of diffusely reflected (or scattered) light at each wavelength relative to a predefined white surface. In practice, there is a wide latitude in what people consider a "white surface." This experiment is possible in an undergraduate teaching lab because miniature-grating spectrophotometers are now commercially available at reasonable cost.

The understanding of color perception and the physical behavior of pigments is complex. For instance, the assumption that yellow paint diffusely reflects primarily yellow wavelengths is incorrect. Rather, the experiments discussed in the following show that yellow reflects a wide range of red and green wavelengths, that is, a significant fraction of the visible spectrum. Similarly, cyan reflects almost all wavelengths in the blue and green spectral regions, and magenta reflects a wide range of blues and reds.

The color (hue[1]) of mixed pigments is governed by a subtractive process: any wavelength strongly absorbed by either pigment will be absent from the light reflected by the mixture. Therefore, the hue is determined by the wavelengths that neither pigment absorbs. In this sense pigment mixing is a subtractive process.

The quantitative description of pigment mixing in terms of multiple interactions is described in Refs. 2–4. The experiments described here aim to give a qualitative understanding of color mixing mechanisms. In addition, these experiments may impart an appreciation of the complex nature of mixing pigments, and an appreciation for the experience and intuition of the artists who mix pigments without a quantitative analysis of the physical phenomena and components at play.

In Sec. II we describe the experimental setup and discuss some design considerations. As the first example of spectra, we present in Sec. III the emission spectra of different common light sources, such as incandescent and fluorescent lights. The experiments described in Sec. IV introduce the concept of subtractive color mixing by means of filters placed between a lamp and a white piece of paper. For clarity, we first present and discuss spectra from filters that transmit sharply defined wavelength bands (interference filters). We then present experiments on colored plastic filters, which exhibit broad spectra similar to those of pigments. One surprising but easily understood effect is that stacking identical filters can lead not just to a decrease in brightness, but to a significant change in hue.

As discussed in Sec. V, a major message to be learned from mixing highly saturated paints is that mixed pigments are less bright than either component at all wavelengths because paint of a specific color derives its hue by removing some wavelengths. Mixing paints, therefore, removes yet more light. Another major message is that there is also an additive component to the mixing of paints, when the subtractive spectra of two mixed components should yield black. Section VI summarizes our experience with the use of the spectrophotometer and suggests possible improvements.

II. EXPERIMENTAL ARRANGEMENT

The experimental arrangement using a commercial spectrophotometer[5] is shown in Fig. 1. A fiber optic probe transmits light reflected from an illuminated sample to a miniature grating spectrometer, which contains a 2048 element linear silicon CCD array in the image plane. The spectrometer is connected to the USB port of a computer, which displays either the spectral distribution of intensity or the reflectance of the surface (percentage reflected relative to a white reference surface) versus wavelength.

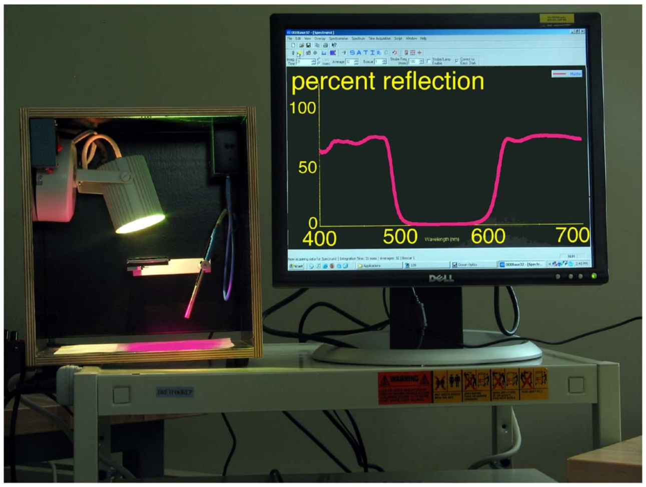


Fig. 1. The experimental equipment is encased in a plywood box (left). The box contains and supports a halogen lamp illuminating a large area of the sample at the bottom, while the fiber-optic probe collects light reflected by a small spot on the sample. The probe is connected to the spectrophotometer (mounted on the upper right inside the box), which in turn is connected to a computer that displays the spectral distribution of light reflected from the sample. The spectrum is a transmittance curve if the sample at the bottom is white paper, and a filter is mounted between the lamp and the paper (a magenta filter in this photograph). Alternatively, the spectral distribution can be the reflectance curve if a painted surface illuminated by white light is used as a sample. The spectra are acquired in real time and displayed on the computer display. The spectrum and lettering on the monitor were edited for clarity.

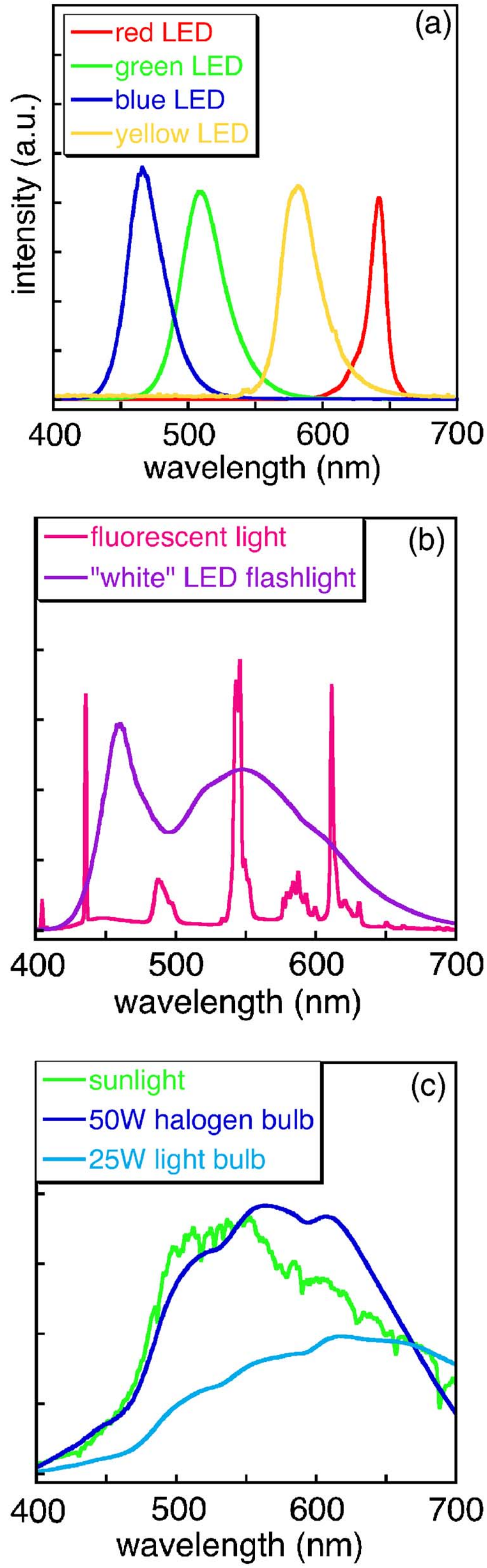


Fig. 2. (a) Emission spectra from blue, green, yellow, and red light emitting diodes (LED). (b) The emission spectrum from a white LED flashlight and a fluorescent ceiling light. (c) Emission spectra from sunlight, an incandescent 25 W light bulb, and a 50 W halogen bulb.

The standard reflection/backscattering probe available from the manufacturer contains a bundle of seven closely packed optical fibers: six fibers are coupled to a tungsten light source to illuminate a small area of the sample, while the center fiber transmits the light reflected by the sample to the spectrometer. Our arrangement is different from the commercial one, in that we use an external 20 W halogen lamp[6] to illuminate the sample surface. Furthermore, the fiber bundle is replaced by a single-fiber probe, the probe end of which is protected by a 6 mm diameter stainless steel ferrule. This arrangement has several advantages for student use. The much higher illumination of the sample due to the halogen lamp permits real-time data acquisition free of statistical fluctuations in less than 1 s. Typically we set the acquisition time to 30 ms and average ten spectra. Another advantage of the larger illuminated area is that the surface is readily visible to two or three students in a group.

To study the spectrum of colored filters we provide a simple filter holder, positioned approximately halfway between the lamp and the white surface at the bottom of the box. The only drawback is that even a 20 W halogen bulb is slightly too bright and too hot for our purposes. A heat-absorbing filter[7] was recently added to the filter holder in the lamp to reduce the heat load on the plastic filters.

The box shown in Fig. 1 serves as a mounting surface for the various components and also shields the sample from extraneous room light. The enclosure is made of plywood with interior width of 26 cm, height 28 cm, and depth 17 cm. The inside surfaces are coated with matte black paint. The orientation of the probe is adjustable. The filter holder swings out of the way when not in use. A slot at the bottom of the rear wall of the box is provided to admit long pieces of paper.

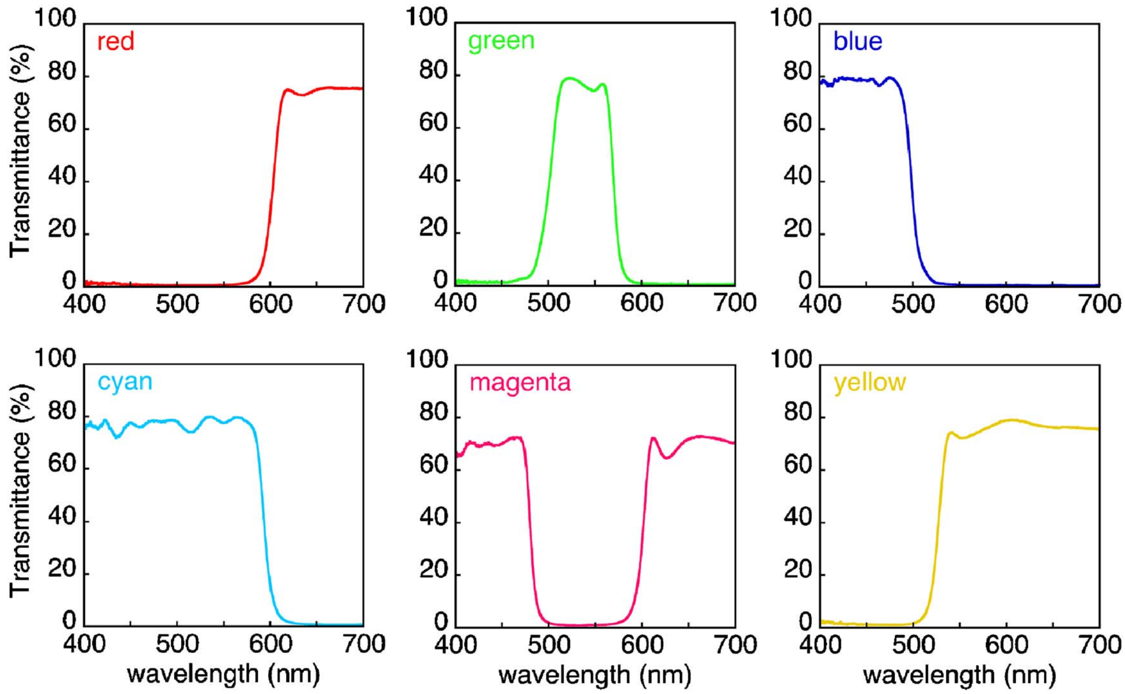


Fig. 3. Transmittance curves of R, G, B interference filters (top) and of C, M, Y interference filters (bottom). The filters used are commercial dichroic filters (Ref. 8).

III. SPECTRA OF DIFFERENT LIGHT SOURCES

Students are first asked to record the spectra of different light sources. They place a white sheet of paper underneath the probe and adjust the range of the spectrograph to 400–700 nm. Because LEDs have become common light sources, we have the students inspect the spectra of various LEDs [see Fig. 2(a)]. An ulterior motive of this exercise is to reinforce the association of colors (B, G, Y, R) with wavelength regions.

The spectra from other common light sources based on fluorescence and incandescence (thermal emission) are presented in Figs. 2(b) and 2(c). These sources include incandescent and halogen light bulbs, sunlight, and fluorescent light. A comparison of all these spectra with that of an LED white flashlight [Fig. 2(b)] reveals the striking qualitative difference between incandescence [Fig. 2(c)], fluorescence [Fig. 2(b)], and band gap emission in semiconductors [Fig. 2(a)]. In our laboratory the fluorescent light spectrum is easily observed by tilting the box so that the overhead lights illuminate the white paper. If the lab is conducted during daylight hours, observation of natural daylight is also of interest. We either position the box so that sunlight falls on the paper, or we remove the entire stem that holds the probe and point the probe toward the sky.

The spectra in Fig. 2(c) illustrate that the spectrum of sunlight is shifted toward blue compared to that of light bulbs, that is, the sun is hotter than the filaments. Some students will be excited to learn that the dips in the spectrum of the sun give a fingerprint of the elements present on the surface of the sun. Absorption by hydrogen, for example, causes the dips at 657 and 487 nm (H-α H-β Balmer lines), and the dips near 628 and 686 nm reveal the presence of molecular oxygen Fraunhofer lines.

IV. SUBTRACTIVE COLOR WITH FILTERS

The spectrophotometer can be set up to display the percentage of light reflected from a surface relative to a white surface.

Neutral density gray filters. Students find, as expected, that a gray filter of 50% transmission shows nearly uniform attenuation across the visible spectrum. Observing the spectrum with two such filters leads students to realize that in the subtractive process the transmission is the product of the transmission of the filters: $0.5\times0.5=0.25$, rather than the sum of the percentages absorbed.

Sharp-spectrum interference filters. We make use of six filters, three additive primaries, red, green, and blue, and three subtractive primaries, cyan, magenta, and yellow. The corresponding spectra are shown in Fig. 3. In this case, when we add for instance R to B we find zero transmission, that is, black. Similarly, G+R is nearly black. In contrast, combining the subtractive primary filters in pairs yields C+Y=G, C+M=B, and M+Y=*R*. It thus becomes plausible for students that if we use three subtractive primary filters (or pigments) of different densities, we can produce hues all the way from blue to blue-green to green-yellow, orange, and red.

Colored plastic filters. The filters used in Fig. 3 represent ideal cases. Painted surfaces do not have sharply delineated spectra. Rather, the spectra of reflected light are similar to those of colored semi-transparent plastic film filters. Examples of such filters are presented in Fig. 4. The black curves are the transmittance curves calculated by multiplying the transmittances of the two subtractive-primary filters.

As the density of a filter is increased, the transmittance decreases, making the transmitted light less bright. What is less obvious is that in addition to the change in brightness,

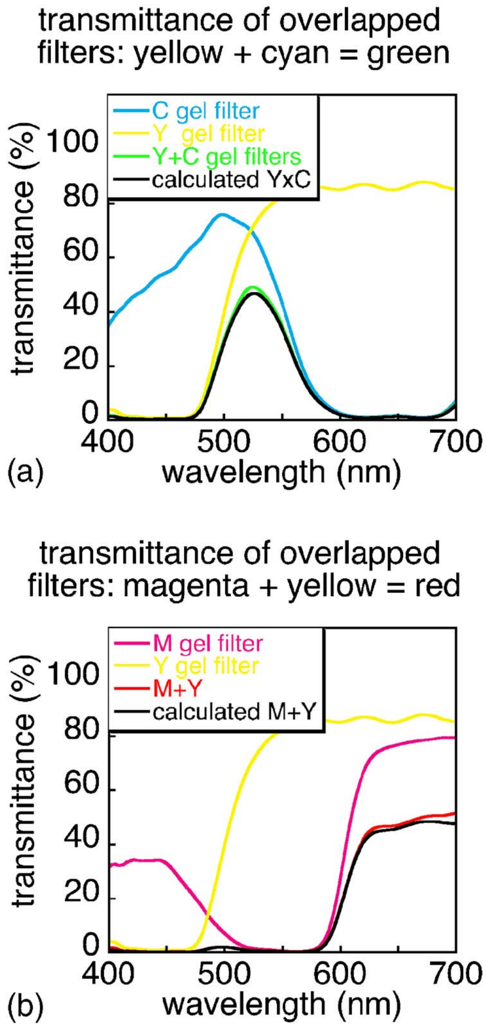


Fig. 4. The transmittance curves of (a) yellow + cyan and (b) magenta + yellow filters. The filters were commercial colored plastic film filters (Ref. 9). Notice the good agreement of the calculated and measured resulting spectra: green and red, respectively.

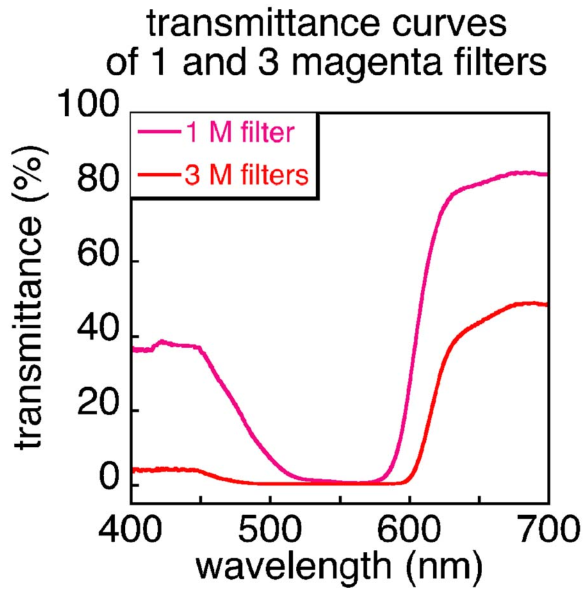


Fig. 5. Transmittance curve of a magenta plastic-dye filter and of three layers of the same filter (Ref. 9). Note the shift in hue toward red when three filters are used.

the hue changes, as is illustrated in Fig. 5, which shows the transmittance curve of three identical magenta filters compared to a single filter. Inspection of the light either by eye or by the spectrophotometer immediately shows a striking shift toward red when three filters are used. The explanation is that this particular magenta has a larger transmittance in the red (0.8) than in the blue (0.37), so that after three filters, almost no blue is left ($0.37^3=0.05$). This observation is relevant to photographic color film, in which the color shift caused by incorrect exposure does not simply lighten or darken the image, but changes hues.

V. PIGMENTS

When two paints of different colors are mixed, a third color is obtained, which is different from each of the two components. Can we anticipate what color will result? Artists do so regularly, using their experience; that is, after preparing and seeing many mixtures of different colors, they can remember the resulting colors. We analyze two paints separately and then in a mixture containing both paints. In each case the analysis consists of acquiring the reflectance curve of each color, which is the intensity of light diffusely reflected by the color at each wavelength relative to a white surface.

Mixing of subtractive primaries. In Fig. 6 we present (a) cyan and yellow, which mixed in equal amounts give green, (b) cyan and magenta (give blue), and (c) magenta and yellow (give red). In all these cases there is a change in hue, saturation, and brightness. Also notice that the brightness always decreases in the mixed color, compared with either of the separate colors (with the exception of white, as we will discuss). As seen for overlapping filters, a good approximation of the resulting color can be calculated by multiplying the relative reflectance of the two component colors and rescaling the resulting reflectance curve. (The calculated spectra of Fig. 6 were multiplied by 1.3, 1.3, and 0.9, respectively, to match the experimentally measured spectral intensity.)

Although the measured and calculated spectra of the mixed blue are very similar [Fig. 6(b)], the mixed green and red is less satisfactory [Figs. 6(a) and 6(c)]. The calculated spectrum is shifted by 10 nm compared to the measured one. This shift takes place in opposite directions: toward red for the mixed green and toward blue for the mixed red. The origin of this shift is not understood, but must depend on pigment multiple back scattering and not on pigment transmission, because it does not take place when overlapping filters are used, as shown in Fig. 4.

Adding white. A white pigment does not absorb light: it scatters light of all wavelengths. Thus, mixing white with any other color adds intensity over the entire spectrum so that the resulting color is lighter, and correspondingly the resulting spectrum is higher in intensity, as shown in the spectra of Fig. 7. For this reason artists often add white to their color mixtures to counteract the loss in brightness due to subtractive color mixing.

Adding white to a paint corresponds to shifting up the off-peak portion of the spectrum (400–550 nm in Fig. 7). Light of wavelengths between 420 and 550 nm is mostly absorbed by red paint. When we add white, part of that light

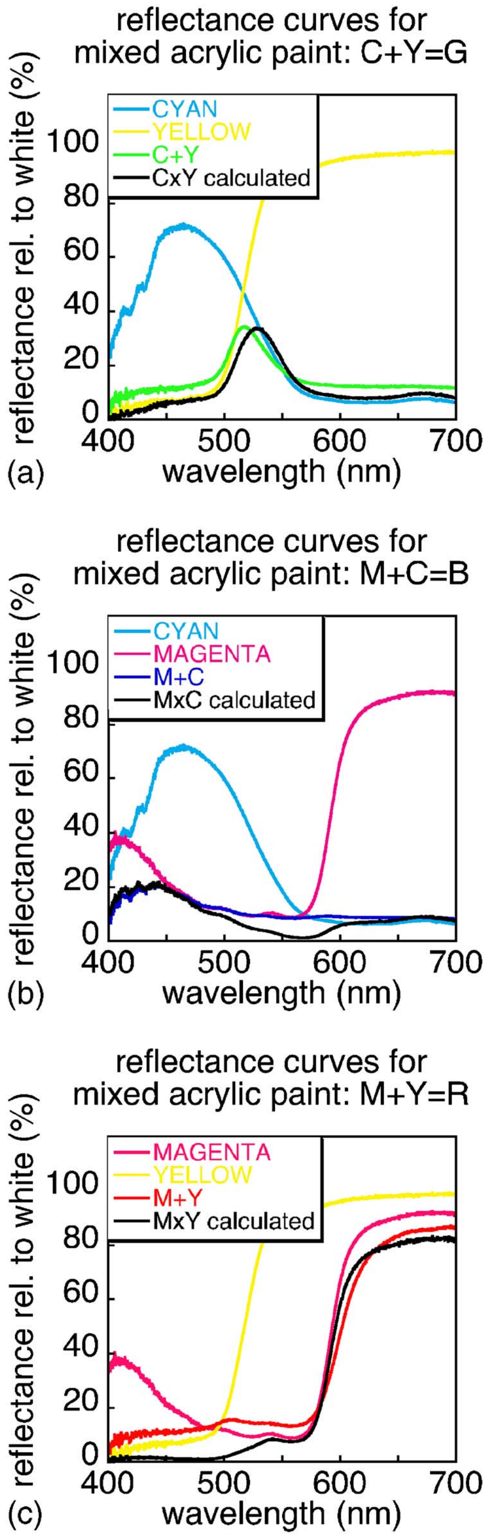


Fig. 6. Mixing of (a) equal amounts of cyan and yellow, (b) cyan and magenta, and (c) magenta and yellow give green, blue, and red, respectively. The solid black curves represent the calculated spectra, obtained by multiplying the two component spectra, and rescaling the intensities (Ref. 10).

is diffusely reflected, and correspondingly that portion of the spectrum is raised to a higher intensity (from approximately 15% to approximately 40% in Fig. 7).

Adding black. A vivid demonstration of multiple scattering is provided by the addition of a small fraction (for example, 1%) of black to a colored paint: the result is a much darker color. For example, a small number of black pigments in an orange paint will have multiple chances to absorb light multiply scattered from orange pigments. Each time this orange light meets a black pigment it is absorbed. A small number of black pigments, therefore, have a large effect on the final color of the mixture. In Fig. 8 we show the effect of mixing 1%, 10%, and 50% black to orange acrylic paint. The reflectance curves show that as little as 1% black decreases the brightness by more than 60%.

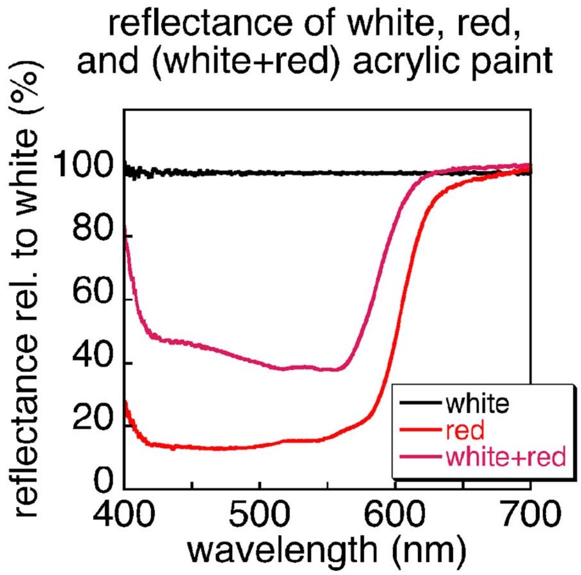


Fig. 7. The reflectance spectra from white and red paints are shown as black and red lines, respectively. When these two paints are mixed in equal proportions the resulting color is low saturation red, that is, pink (Ref. 11).

Additive contribution in mixed paints. Another fundamental mechanism must be taken into account when analyzing the mixing of pigments in paints. There is a small additive mixing component, which is always present, but becomes

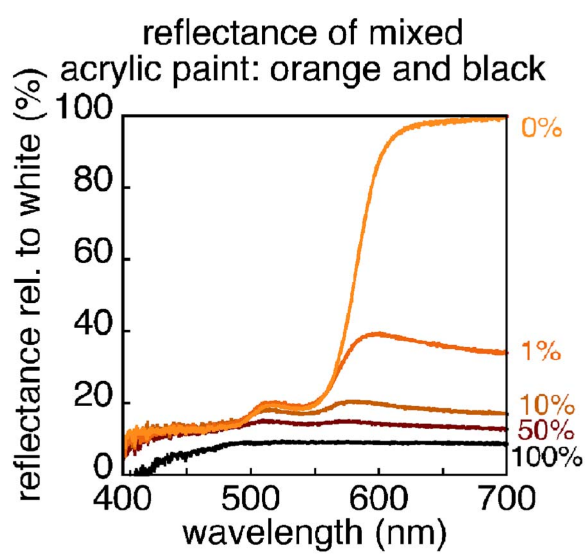
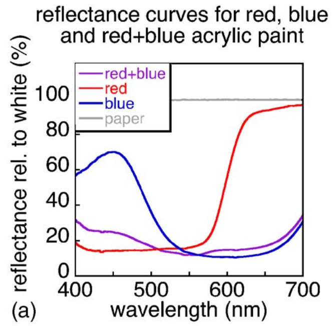


Fig. 8. The reflectance curves of orange acrylic paint, black acrylic paint, and mixtures of the two in different proportions (Ref. 12). The mixed volumes were measured using Gilson pipettes and the percentage of black paint is reported for each curve by the right axis.



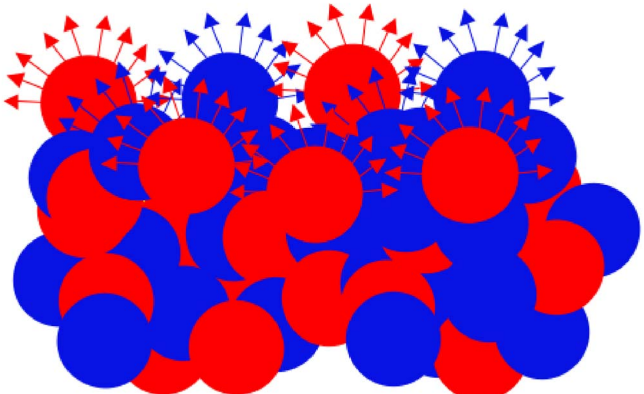


Fig. 9. The reflectance curves for (a) red, blue, and red + blue paints. The resulting color is not black but a dark purple, which is red light + blue light (Ref. 13). (b) Idealized pigments in a paint mixture: red pigments absorb green and blue while scattering red light in all directions, so do blue pigments, only scattering blue light. Near the surface, blue and red lights escape after only one scattering interaction with one blue or red pigment.

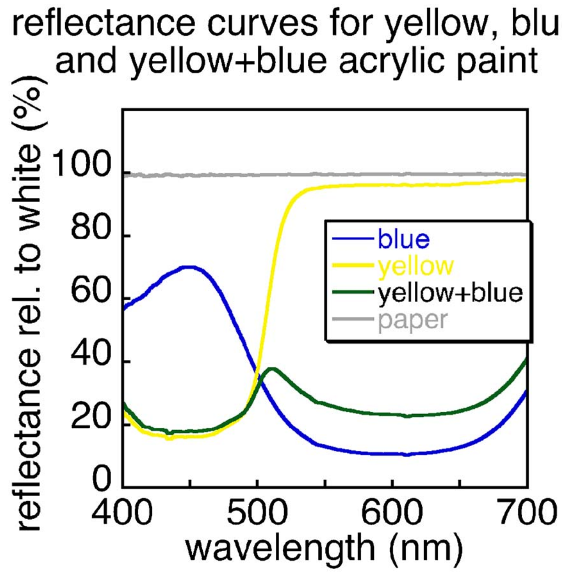


Fig. 10. The reflectance curves for yellow, blue, and yellow + blue paints. Note that, because yellow and blue are complementary colors, the resulting mixed color should be black, while in reality it is a dark green, with a maximum in the only region in which both spectra have significant reflectance, that is, green (Ref. 14).

dominant only when the mixed color is very dark, because the two separate color spectra are far apart, for instance red and blue, as shown in Fig. 9. When mixing these two colors, the resulting color should in principle be black, but instead it is a low intensity purple, with some red light and some blue light additively combined. Red pigments absorb all blue and green from the illuminating white light and diffusely reflect only red light. The reflected red light is in turn almost completely absorbed by nearby blue pigments. Conversely, blue pigments absorb red and diffusely reflect blue. Red and blue pigments, therefore, absorb each other's reflected light. Near the surface, however, some red and some blue lights escape absorption and are reflected back toward the eye and the spectrophotometer after single scattering by one pigment only, making the mixed color appear purple: the result of red light + blue light in additive color mixing.

Note that in Fig. 9(a) neither the red nor blue paints are saturated, that is, their spectra do not go down to zero intensity in the off-peak region. Consequently, the resulting purple is unsaturated. Similar phenomena are observed in almost all the commercially available paints. In Fig. 8, for instance, the mixtures containing orange paint are unsaturated.

Another phenomenon is illustrated by the data of Fig. 10. Yellow and blue are complementary colors, their spectra should not overlap at all, and their mixture should be black. The Y and B spectra of real pigments, however, have a small region of overlap, in which neither reflectance is zero. The product of the two spectra, therefore, is not black, but has a peak in the green region.

VI. CONCLUSIONS

Our experience is that nonscience students have no difficulty with the use of the spectrophotometer and the associated computer display programs. Students complete most of the experiments presented here in a two-hour laboratory session. Acceptance by the students is uniformly high. These experiments deepen their understanding of subtractive color mixing and lead to an appreciation of the complexity of the phenomena encountered in mixing paints.

The software associated with the commercial spectrophotometer allows the students to display the spectral distribution and, if desired, to overlap a number of spectra for comparison. It is left to students to associate the wavelength scale with the sequence of spectral colors. We have not done so here, but it should be possible to add a band of spectral colors on the computer screen to remind the student to which colors the wavelengths marked on the abscissa correspond.

Hues may be represented in a color triangle such as Maxwell's color triangle or, more quantitatively, the CIE (Commision Internationale de L'Eclairage) chromaticity diagram.[15–17] Software is available to display the spectral content acquired by the spectrophotometer as a point in the CIE diagram. Alternatively, the spectral distribution can also be represented as RGB components.

With or without these further refinements, students learn the fundamentals of color and color mixing doing this simple and relatively inexpensive laboratory session. We have tested these experiments on a total of 520 non-science-major students, who invariably enjoyed the lab and described it as a lot of fun. We look forward to hearing from other professors using our experience to implement similar labs at their colleges.

Some additional references to relevant background literature may be useful to the reader less familiar with the subject.[18–20]

[a]Previously published as Gelsomina De Stasio. Electronic mail: pupa@physics.wisc.edu
[b]Electronic mail: haeberli@wisc.edu
[1]Definitions: Given any color, a matching color that appears to the normal retina identical to the color in question, can always be obtained by combining light of a single wavelength with white light (except for magentas and purples, which are specified by the complementary wavelength). The wavelength of the matching color is called the dominant wavelength. The corresponding attribute of visual sensation is called the *hue*. The fraction of white light is called *saturation*. Saturation is also known as *purity*. High saturation colors require a small percentage of white in the matching color, low saturation colors require a large percentage of white. These are pale pink, sky blue, pale yellow, beige, and all colors commonly called pastels. The adjectives saturated and pale are therefore antonyms. To match those colors, the matching color requires a large fraction of white. Some authors define saturation in paints and pigments to be the parameter related to the amount of black, but we do not see a reason for such distinction. *Brightness* (also known as *lightness*) is the parameter of a color according to which an area appears to emit more or less light. The adjectives bright and dark (or light and dark) are therefore antonyms. In the literature there is a preference to use the term brightness for luminant sources, and lightness for illuminated surfaces. Different color systems (Munsell, Oswald, and DIN) use other terms (for example, value, chroma), but for simplicity we use terminology familiar from everyday English.
[2]P. Kubelka and F. Munk, “Ein Beitrag zur Optik der Farbanstriche,” Z. Tech. Phys. (Leipzig) **12**, 593–601 (1931).
[3]Chet S. Haase and Gary W. Meyer, “Modeling pigmented materials for realistic image synthesis,” ACM Trans. Graphics **14**, 305–335 (1992).
[4]The Kubelka-Munk theory is presented in accessible form in Mahnaz Mohammadi and Roy S. Berns, “Verification of the Kubelka-Munk turbid media theory for artist acrylic paint,” MCSL technical report summer 2004, ⟨www.art-si.org/publications.htm⟩.
[5]Ocean Optics CHEM2-VIS-FIBER USB2000-VIS-NIR fiber optic spectrometer, ⟨oceanoptics.com⟩. The price (including a light source and cuvette holder for absorption experiments, which are not used here) is $1499 with trade in. The cost of an Ocean Optics spectrometer with a 650 channel CCD (Red Tide USB650) is $999 (without optical fiber or software) and is available at ⟨oceanoptics.com⟩, ⟨vernier.com⟩, and ⟨pasco.com⟩.
[6]The lamp is a W.A.C. lighting model 900P with a built-in transformer. The light bulb is an MR16 20W narrow beam bulb (color temperature 2050 K). Lower wattage bulbs (MR11 or MR8) may be more suitable but did not fit our lamp.
[7]Edmund Optics NT45-648, ⟨www.edmundoptics.com⟩.
[8]50 mm × 50 mm additive and subtractive dichroic filters set, NT-46-140 and NT-46-141, Edmund Optics.
[9]Color Film Gel Sheets #10026, Rainbow Symphony, ⟨store.rainbowsymphonystore.com/cofige.html⟩.
[10]Winsor & Newton Galeria acrylic paints: process yellow (pigment PY74), process magenta (PV19), and process cyan (PB 15:3).
[11]Dahler Rowney acrylic paints: titanium white 009 and chromium red 503.
[12]Van Gogh acrylic paints Azo orange 276 and black.
[13]Van Gough acrylic paints: blue #504 and red #396.
[14]Paints used for these experiments were Van Gogh acrylic paints (ultramarine blue #504 and primary yellow #275).
[15]⟨www.cs.bham.ac.uk/~mer/colour/cie.html⟩.
[16]Kurt Nassau, *The Physics and Chemistry of Color*, 2nd ed. (Wiley, New York, 2001), Chap. 1.
[17]G. Waldman, *Introduction to Light: The Physics of Light, Vision and Color* (Dover, Mineola, NY, 2002), Chap. 11.
[18]T. N. Cornsweet, *Visual Perception* (Academic, New York, 1974).
[19]A. Byrne and D. Hilbert, *Readings on Color: The Science of Color* (MIT, Cambridge, MA, 1997).
[20]P. U. P. A. Gilbert and W. Haeberli, *Physics in the Arts* (Elsevier, Amsterdam, 2007).

THE ARGUMENT FROM PERSONAL INCREDULITY

“The human journey to cosmic space and time was bedeviled at every step of the way by what the biologist Richard Dawkins calls the Argument from Personal Incredulity: If it seems impossible to believe, it must be wrong. Aristarchus confronted the incredulity of his contemporaries, as did Copernicus, Bruno, Galileo, and Darwin. The universe invariably turned out to be bigger and older than we had previously thought possible. The light-years and the eons are a tribute to the power of the boldest, most daring human thinkers to transcend ‘common sense.’”

Raymo, Chet, *Walking Zero: Discovering Cosmic Space and Time Along the Prime Meridian* (Walker and Company, New York, NY, 2006), p. 179.